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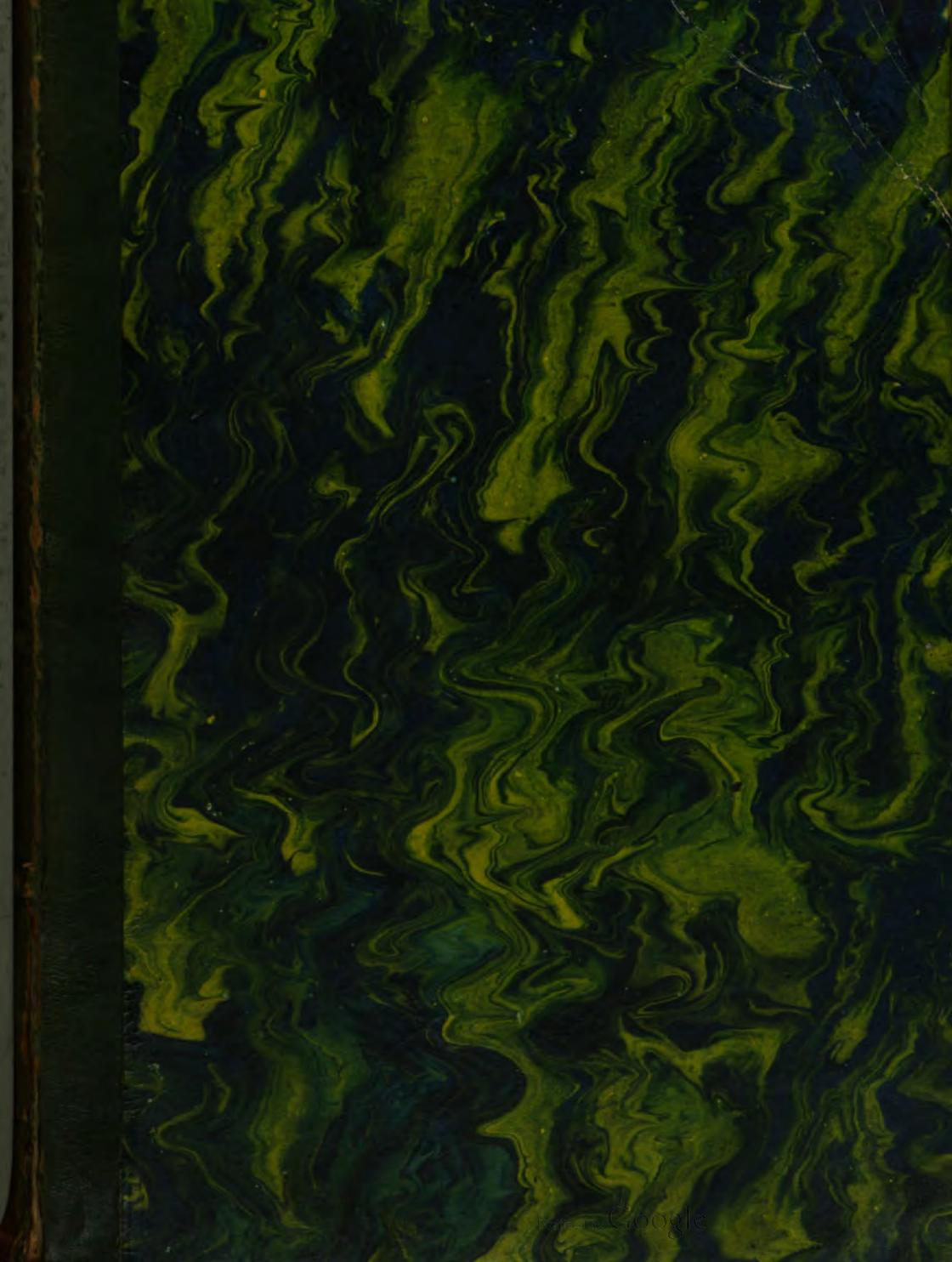
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THE  
ELEMENTS  
OF  
EXPERIMENTAL CHEMISTRY,

BY  
WILLIAM HENRY, MD. FRs.

Vice-President of the Literary and Philosophical, and Natural History Societies of Manchester; Member of the Royal Medical and Wernerian Societies of Edinburgh; the Medico-Chirurgical and Geological Societies of London; the Physical Society of Jena; the Natural History Society of Moscow; the Literary and Philosophical Society of New York, &c. &c.

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THE NINTH EDITION,

COMPREHENDING ALL THE RECENT DISCOVERIES; AND ILLUSTRATED WITH TEN  
PLATES BY LOWRY, AND SEVERAL ENGRAVINGS ON WOOD.

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IN TWO VOLUMES.

VOL. I.

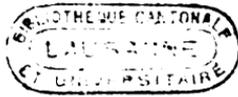
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1823.

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**C. Baldwin, Printer,  
New Bridge-street, London**



TO  
**JOHN DALTON, FRS.**

President of the Literary and Philosophical Society of Manchester; Member  
of the Academy of Sciences of the Royal Institute of France; &c.

AS A  
TESTIMONY OF RESPECT  
FOR THE  
ZEAL, DISINTERESTEDNESS, AND SUCCESS,  
WITH WHICH  
HE HAS DEVOTED HIMSELF TO THE ADVANCEMENT OF  
CHEMICAL PHILOSOPHY,  
THIS WORK IS INSCRIBED,  
BY HIS FRIEND,  
***THE AUTHOR.***

*Manchester, April, 1823.*

## CORRIGENDA.

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- VOL. I.** page 43, l. 9 from bottom, for  $11\frac{1}{2}$  of the former to  $88\frac{1}{2}$  of the latter, or 1 to  $7\frac{1}{2}$ , read 11.1 to 88.9, or 1 to 8.
- p. 51, l. 5 and 7, for  $7\frac{1}{2}$ , read 8.
- p. 84, l. 9. This, so far as it respects Petit and Dulong, is incorrect, for they assume that radiation is the same in air and other gases as in vacuo, the different velocities of cooling being due to the conducting powers of elastic media.
- p. 102, l. 13 from bottom, for precisely read nearly.
- p. 111, l. 21, for  $(202^{\circ})$  read  $(102^{\circ})$ .
- p. 126, l. 3, after end, insert containing mercury.
- p. 141 in the Table. The specific gravity of nitric oxide, though copied exactly from Berzelius and Dulong, is incorrect.
- p. 128, l. 14, for condensing into one volume, read into two volumes.
- p. 160, l. 19, for from  $32^{\circ}$  to  $212^{\circ}$ , read from  $-40^{\circ}$  to  $+212^{\circ}$
- p. 229, l. 9 from bottom, after oxygen, insert chlorine.
- Passim*, except when it is applied to potash of commerce, for potash read potassa.
- VOL. II.** p. 166, l. 11, for protoxide read peroxide.

# PREFACE

TO THE

NINTH EDITION.

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CHEMISTRY is, of all the sciences, that which is most eminently progressive, scarcely a year elapsing during which it is not enriched by a great variety of new facts,—by the resolution of compounds into more simple elements,—by combinations before unknown,—and sometimes by general laws of extensive application and influence. Every new edition of a chemical book must necessarily, therefore, if it keep pace with the progress of discovery, differ essentially from the one which preceded it; for while it embraces every thing that is new and important, it must reject whatever recent experience has proved to be erroneous. It is by freely effecting the latter purpose, that I have been enabled to accommodate this work to the state of the science, without materially enlarging the size of the volumes. They will be found, however, by those who may be at the pains of comparing this edition with the last, to comprise a large proportion of new matter. I have been induced also, by mature consideration of those analogies which have of late years been unfolded among chemical substances, to adopt an entirely different arrangement, the principle of which is fully explained in the concluding pages of the INTRODUCTION. It is founded, as to its leading outline, on those relations of bodies to Electricity, which have been

developed by the genius of Sir Humphry Davy, and, though the classification is far from being unobjectionable, it seems to me the best that can be followed in the present state of the science.

To this edition, a tenth copper plate is annexed; and a number of wood cuts, from accurate drawings by Mr. Joseph Farey, are, for the first time, interspersed through the work, wherever it appeared to me that the subject required such illustration. Among the Tables, in the Appendix to the Second Volume, is inserted one of *Chemical Equivalents*, the numbers of which, whenever they differ from those in the body of the work, are to be regarded as most worthy of confidence. In the **ADDENDA**, too, will be found notices of recent discoveries, to the latest period which the publication would permit.

Although no pains have been spared to render these volumes a faithful abstract of the present state of Chemistry, yet it is more than probable that errors and omissions will still be detected in them. In rectifying these, I hope to be assisted by a continuance of those candid criticisms, both through public and private channels of communication, by which I have already greatly benefited.

*Manchester, April, 1823.*

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# INTRODUCTION.

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**NATURAL PHILOSOPHY**, in its most extensive sense, is a term comprehending every science, that has for its objects the properties and affections of matter. But it has attained, by the sanction of common language, a more limited signification; and chemistry, though strictly a branch of natural philosophy, is generally regarded as a distinct science. Between the two it may, perhaps, be difficult to mark out precisely the line of separation: but, an obvious character of the facts of natural philosophy is, that they are always attended with sensible motion; and the determination of the laws of motion is peculiarly the office of its cultivators. Chemical changes, on the other hand, of the most important kind, often take place without any apparent motion, either of the mass, or of its minute parts; and where the eye is unable to perceive that any change has occurred. The laws of gravitation, of central forces, and all the other powers that fall under the cognizance of the natural philosopher, produce, at most, only a change of place in the bodies that obey their influence. But, in chemical changes, we may always observe an important difference in the properties of things: their appearances and qualities are completely altered, and their individuality destroyed. Thus, two highly corrosive and deleterious substances, by uniting chemically together, may become mild and harmless; the combination of two colourless substances may present us with a compound of brilliant complexion; and the union of two fluids, with a compact and solid mass.

Chemistry, therefore, may be defined, that science, the object of which is to discover and explain the changes of composition that occur among the integrant and constituent parts of different bodies.\*

From this definition, it may readily be conceived, how wide is the range of chemical inquiry; and, by applying it to the various events that daily occur in the order of nature, we shall be enabled to separate them with accuracy, and to allot, to the sciences of natural philosophy and chemistry, the proper objects of the cultivation of each. Whenever a change of place is a necessary part of any event, we shall call in the aid of the former. When this condition may be dispensed with, we shall resort to chemistry for the light of its principles. But it will be often found, that the concurrence of the two sciences is essential to the full explanation of phenomena. The water of the ocean, for example, is raised into the atmosphere by its chemical combination with the matter of heat; but the clouds, that are thus formed, maintain their elevated situation by virtue of a specific gravity inferior to that of the lower regions of the air,—a law, the discovery and application of which are due to the natural philosopher, strictly so called.

It has not been unusual to consider chemistry, under the twofold view of a science and of an art. This arrangement, however, appears to have had its origin in an imperfect discrimination between two objects, that are essentially distinct. Science consists of assemblages of facts, associated together in classes, according to circumstances of resemblance or analogy. The business of its cultivators is, first, to investigate and

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\* The reader, who wishes to examine other definitions of chemistry, will find a variety of them, collected by Dr. Black, in the first volume of his "Lectures," published, since his death, by Professor Robison.

establish individual truths, either by the careful observation of natural appearances, or of new and artificial combinations of phenomena produced by the instruments of experiment. The next step is the induction, from well ascertained facts, of general principles or laws, more or less comprehensive in their extent, and serving, like the classes and orders of natural history, the purposes of an artificial arrangement. Of such a body of facts and doctrines, the SCIENCE OF CHEMISTRY is composed. But the employment of the artist consists merely in producing a given effect, for the most part by the sole guidance of practice or experience. In the repetition of processes, he has only to follow an established rule; and, in the improvement of his art, he is benefited generally by fortuitous combinations, to which he has not been directed by any general axiom. An artist, indeed, of enlarged and enlightened mind, may avail himself of general principles, and may employ them in perfecting established operations: but the art and the science are still marked by a distinct boundary. In such hands, they are auxiliaries to each other; the one contributing a valuable accession of facts; and the other, in return, imparting fixed and comprehensive principles, which simplify the processes of art, and direct to new and important practices.

The possession of the general principles of chemistry enables us to understand the mutual relation of a great variety of events, that form a part of the established course of nature. It unfolds the most sublime views of the beauty and harmony of the universe; and develops a plan of vast extent, and of uninterrupted order, which could have been conceived only by perfect wisdom, and executed by unbounded power. By withdrawing the mind, also, from pursuits and amusements

that excite the imagination, its investigations may tend, in common with the rest of the physical sciences, to the improvement of our intellectual and moral habits; to strengthen the faculty of patient and accurate thinking; and to substitute placid trains of feeling, for those which are too apt to be awakened by the contending interests of men in society, or the imperfect government of our own passions.

The class of natural events that call for the explanation of chemical science, is of very considerable extent; and the natural philosopher (using this term in its common acceptation) is wholly incompetent to unfold their connexion. He may explain, for example, on the principles of his own science, the annual and diurnal revolutions of the Earth, and part of the train of consequences depending on these rotations. But here he must stop: and the chemist must trace the effects, on the Earth's surface, of the caloric and light derived from the sun; the absorption of caloric by the various bodies on which it falls; the consequent fluidity of some, and volatilization of others; the production of clouds, and their condensation in the form of rain; and the effects of this rain, as well as of the sun's heat, on the animal, vegetable, and mineral kingdoms. In these minuter changes, we shall find, there is not less excellence of contrivance, than in the stupendous movements of the planetary system. And they interest us even more nearly; because, though not more connected with our existence or comfort, yet they are more within our sphere of observation; and an acquaintance with their laws admits of a more direct application to human affairs.

There is another branch of knowledge (that of natural history), which is materially advanced by the application of chemical science. The classifications of the naturalist are derived

from an examination and comparison of the external forms, both of animate and inanimate bodies. He distributes the whole range of nature into three great and comprehensive kingdoms,—the animal, the vegetable, and the mineral. Each of these, again, is subdivided into several less extensive classes; and individual objects are referred to their place in the system, by the agreement of their characters, with those assigned to the class, order, and genus. In the different departments of natural history, these resemblances vary in distinctness, in facility of observation, and in certainty of description. Thus, the number and disposition of the parts of fructification in vegetables afford marks of discrimination, which are well defined, and easily ascertained. But minerals, that are not possessed of a regularly crystallized form, are distinguished by outward qualities that scarcely admit of being accurately conveyed by language; such as minute shades of colour; or trifling differences of hardness, transparency, &c. To the evidence of these loose and varying characters, that of the chemical composition of minerals has within the few past years been added; and mineralogy has been advanced, from a confused assemblage of its objects, to the dignity of a well methodized and scientific system. In the example of crystallized bodies, the correspondence between external form and chemical composition, has been most successfully traced by the genius of Haüy; whose method of investigation has enabled him, in numerous instances, to anticipate, from physical characters, the results of the most skilful and laborious analysis.

It is unnecessary to pursue this part of the subject to a greater extent; because, to all who have been in the habit of philosophical investigation, the connexion between the sciences must be sufficiently apparent; and because there is another

ground, on which chemistry is more likely to claim, with success, the respect and attention of the great mass of mankind. This is, its capacity of ministering to our wants and our luxuries, and of instructing us to convert to the ordinary purposes of life, many substances which nature presents to us in a rude and useless form. The extraction of metals from their ores; the conversion of the rudest materials into the beautiful fabrics of glass and porcelain; the production of wine, ardent spirits, and vinegar; and the dyeing of linen, cotton, and woollen manufactures,—are only a few of the arts that are dependent on chemistry for their improvement, and even for their successful practice.

It cannot, however, be denied, that all the arts, which have been mentioned, were practised in times when the rank of chemistry, as a science, was extremely degraded; and that they are the daily employment of unlettered and ignorant men. But to what does this confession amount; and how far does it prove the independence of the above arts on the science of chemistry?

The skill of an artist is compounded of knowledge and of manual dexterity. The latter, it is obvious, no science can teach. But the acquirement of experience, in other words, a talent for the accurate observation of facts, and the habit of arranging facts in the best manner, may be greatly facilitated by the possession of scientific principles. Indeed, it is hardly possible for any one to frame rules for the practice of a chemical art, or to profit by the rules of others, who is unacquainted with the general doctrines of the science. For, in all rules, it is implied, that the promised effect will only take place, when circumstances are precisely the same as in the case under which the rule was formed. To ensure an uner-

ring uniformity of result, the substances, employed in chemical processes, must be of uniform composition and excellence; or, when it is not possible to obtain them thus unvaried, the artist should be able to judge precisely of the defect, that he may proportion his agents according to their qualities. Were chemical knowledge more generally possessed, we should hear less of failures and disappointments in chemical operations; and the artist would commence his proceedings, not, as at present, with distrust and uncertainty, but with a confident and well grounded expectation of success.

It will scarcely be contended, that any one of the arts has hitherto attained the extent of its possible perfection. In all, there is yet a wide scope for improvement, and an extensive range for ingenuity and invention. But from what class of men are we to expect useful discoveries? Are we to trust, as hitherto, to the favour of chance and accident: to the fortuitous success of those who are not guided in their experiments by any general principles? Or shall we not rather endeavour to inform the artist, and induce him to substitute, for vague and random conjecture, the torch of induction and of rational analogy? In the present imperfect state of his knowledge, the artist is even unable fully to avail himself of those fortunate accidents, by which improvements sometimes occur in his processes; because, to the eye of common observation, he may have acted agreeably to established rules, and have varied in circumstances which he can neither perceive nor appreciate. The man of science, in these instances, sees more deeply, and, by availing himself of a minute and accidental difference, contributes at once to the promotion of his own interest, and to the advancement of his art.

But it is the union of theory with practice that is now recommended. And "when theoretical knowledge and practical skill are happily combined in the same person, the intellectual power of man appears in its full perfection, and equally fits him to conduct, with a masterly hand, the details of ordinary business, and to contend successfully with the untried difficulties of new and perplexing situations. In conducting the former, mere experience may frequently be a sufficient guide; but experience and speculation must be combined to prepare us for the latter." \* "Expert men," says Lord Bacon, "can execute and judge of particulars one by one; but the general counsels, and the plots, and the marshalling of affairs, come best from those that are learned."

This recommendation to artists, of the acquirement of scientific knowledge, is happily sanctioned by the illustrious success, in our own days, of the application of theory to the practice of certain arts. Few persons are ignorant of the benefits, that have resulted to the manufactures of this country, from the inventions of Mr. Watt and Mr. Wedgwood; both of whom have been not less benefactors of philosophy than eminent for practical skill. The former, by a clear insight into the doctrine of latent heat, resulting, in a great measure, from his own acuteness and patience of investigation, and seconded by an unusual share of mechanical skill, has perhaps brought the steam-engine to its acme of perfection. Mr. Wedgwood, aided by the possession of extensive chemical knowledge, made rapid advances in the improvement of the art of manufacturing porcelain; and, besides raising himself to great opulence and distinction, has created for his country

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\* Stewart's Elements of the Philosophy of the Human Mind, chap. iv. sect. 7.



a source of most profitable and extensive industry. In an art, also, which is nearly connected with the manufactures of our own town,\* and the improvement of which must, therefore, “come home to our business and bosoms,” we owe unspeakable obligations to two speculative chemists,—to Scheele, who first discovered chlorine; and to Berthollet, who first instructed us in its application to the art of bleaching.

Examples, however, may be urged against indulgence in theory; and instances are not wanting, in which the love of speculative refinement has withdrawn men entirely from the straight path of useful industry, and led them on gradually to the ruin of their fortunes. But from such instances, it would be unfair to deduce a general condemnation of theoretical knowledge. It would be the common error of arguing against things that are useful, from their occasional abuse.—In truth, projects which have, for their foundation, a dependence on chemical principles, may be undertaken with a more rational confidence, than such as have in view the accomplishment of mechanical purposes; because, in chemistry, we are better able, than in mechanics, to predict, from an experiment on a small scale, the probable issue of more extensive attempts. No one, from the successful trial of a small machine, can affirm, with unerring certainty, that the same success will attend one on a greatly enlarged plan; because the amount of the resistances, that are opposed to motion, increases often in a *ratio* greater than, from theory, could ever have been foreseen. But the same law, by which the mineral alkali is extracted from a pound of common salt, must equally operate on a thousand times the quantity; and, even when we

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\* Manchester; where the substance of this discourse was originally delivered as an introductory lecture.

augment our quantities in this immense degree, the chemical affinities, by which so large a mass is decomposed, are exerted only between very small particles. The failures of the mechanic, therefore, arise from the nature of things; they occur, because he has not in his power the means of foreseeing and calculating the causes that produce them. But, if the chemist fail in perfecting an economical scheme on a large scale, it is either because he has not sufficiently ascertained his facts on a small one, or has rashly embarked in extensive speculations, without having previously ensured the accuracy of his estimates.

The benefits which we are entitled to expect from the efforts of the artist and the man of science, united in one person, and at the same time tempered and directed by prudential wisdom, affect not only individual but national prosperity. To the support of its distinction, as a commercial nation, this country is to look for the permanency of its riches, its power, and, perhaps, even of its liberties; and this pre-eminence is to be maintained, not only by local advantages, but on the more certain ground of superiority in the productions of its arts. Impressed with a full conviction of this influence of the sciences, a neighbouring and rival people have offered the most public and respectful incitements to the application of theory in the improvement of the chemical arts; and, with the view of promoting this object, national institutions have been formed among them, which have been already, in several instances, attended with the most encouraging success. It may be sufficient, at present, to mention, as an example, that France, during a long war, supplied, from her own native resources, her enormous, and, perhaps, unequalled consumption of nitre.

The general uses of chemistry have been thus fully enlarged upon, because it is a conviction of the utility of the science, that can alone recommend it to attentive and persevering study. It may now be proper to point out, in detail, a few of its more striking applications.

I. The art which is, of all others, the most interesting, from its subserviency to wants that are interwoven with our nature, is **AGRICULTURE**, or the art of obtaining, from the earth, the largest crops of useful vegetables at the smallest expense.

The vegetable kingdom agrees with the animal one, in the possession of a living principle. Every individual of this kingdom is regularly organised, and requires for its support an unceasing supply of food, which is converted, as in the animal body, into substances of various forms and qualities. Each plant has its periods of growth, health, disease, decay, and death; and is affected, in most of these particulars, by the varying condition of external circumstances. A perfect state of agricultural knowledge would require, therefore, not only a minute acquaintance with the structure and economy of vegetables, but with the nature and effects of the great variety of external agents, that contribute to their nutriment, or influence their state of health and vigour. It can hardly be expected, that the former attainment will ever be generally made by practical farmers; and it is in bringing the agriculturist acquainted with the precise composition of soils and manures, that chemistry promises the most solid advantages. Indeed, any knowledge that can be acquired on this subject, without the aid of chemistry, must be vague and indistinct, and can neither enable its possessor to produce an intended effect with certainty, nor be communicated to others in language sufficiently intelligible. Thus we are told, by Mr.

Arthur Young, that, in some parts of England, any loose clay is called marl, in others marl is called chalk, and in others clay is called loam. From so confused an application of terms, all general benefits of experience in agriculture must be greatly limited.

Chemistry may, to agriculturists, become a universal language, in which the facts, that are observed in this art, may be so clothed, as to be intelligible to all ages and nations. It would be desirable, for example, when a writer speaks of clay, loam, or marl, that he should explain his conception of these terms, by stating the chemical composition of each substance expressed by them. For, all the variety of soils and manures, and all the diversified productions of the vegetable kingdom, are capable of being resolved, by chemical analysis, into a small number of elementary ingredients. The formation of a well defined language, expressing the proportion of these elements in the various soils and manures, now so vaguely characterized, would give an accuracy and precision, hitherto unknown, to the experience of the tillers of the earth.

It has been said, by those who contend for pure empiricism in the art of agriculture, that it has remained stationary, notwithstanding all improvements in the sciences, for more than two thousand years. "To refute this assertion," says Mr. Kirwan, "we need only compare the writings of Cato, Columella, or Pliny, with many modern tracts, or still better, with the modern practice of our best farmers."—"If the exact connexion of effects with their causes," he adds, "has not been so fully and extensively traced in this as in other subjects, we must attribute it to the peculiar difficulty of the investigation. In other subjects, exposed to the joint opera-

tion of many causes, the effect of each, singly and exclusively taken, may be particularly examined, and the experimenter may work in his laboratory, with the object always in his view. But the secret processes of vegetation take place in the dark, exposed to the various and indeterminable influences of the atmosphere, and require, at least, half a year for their completion. Hence the difficulty of determining on what peculiar circumstance success or failure depends; for, the diversified experience of many years can alone afford a rational foundation for solid, specific conclusions."\*

II. To those who study **MEDICINE** as a branch of general science, or with the more important view of practical utility, chemistry may be recommended with peculiar force and propriety.—The animal body may be regarded as a living machine, obeying the same laws of motion as are daily exemplified in the productions of human art. The arteries are long, flexible, and elastic canals, admitting, in some measure, the application of the doctrine of hydraulics; and the muscles are so many levers, of precisely the same effect with those which are employed to gain power in mechanical contrivances. But there is another view, in which, with equal justice, the living body may be contemplated. It is a laboratory, in which are constantly going forward processes of various kinds, dependant on the operation of chemical affinities. The conversion of the various kinds of food into blood, a fluid of comparatively uniform composition and qualities; the production of animal heat by the action of the air on that fluid, as it passes through the lungs; and the changes, which the blood

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\* See Kirwan on Manures.

afterwards undergoes in its course through the body,—are all, exclusively, subjects of chemical inquiry. To these, and many other questions of physiology, chemistry has of late years been applied with the most encouraging success; and it is to a long continued prosecution of the same plan, that we are to look for a system of physiological science, which shall derive new vigour and lustre from the passing series of years.

It must be acknowledged, however, as has been observed by Sir H. Davy,\* that “the connexion of chemistry with physiology has given rise to some visionary and seductive theories; yet even this circumstance has been useful to the public mind, in exciting it by doubt, and in leading it to new investigations. A reproach, to a certain degree just, has been thrown upon those doctrines known by the name of chemical physiology; for, in the applications of them, speculative philosophers have been guided rather by the analogies of words than of facts. Instead of endeavouring slowly to lift up the veil, which conceals the wonderful phenomena of living nature; full of ardent imaginations, they have vainly and presumptuously attempted to tear it asunder.”

III. There is an extensive class of arts, forming, when viewed collectively, a great part of the objects of human industry, which do not, on a loose and hasty observation, present any general principle of dependency or connexion. But they appear thus disunited, because we have been accustomed to attend only to the productions of these arts, which are, in truth, subservient to widely different purposes. Who

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\* In his eloquent “Discourse, Introductory to a Course of Lectures,” &c. London. Johnson. 1802.

would conceive, for instance, that iron and common salt; the one a metal, the use of which results from its hardness, ductility, and malleability; the other a substance, chiefly valuable from its acting as a preservative and seasoner of food,—are furnished by arts alike dependent on the general principles of chemistry? The application of science, in discovering the principles of these arts, constitutes what has been termed **ECONOMICAL CHEMISTRY**; amongst the numerous objects of which, the following stand most distinguished:

1st. *Metallurgy*, or the art of extracting metals from their ores, comprehending that of *Assaying*, by which we are enabled to judge, from the composition of a small portion, of the propriety of working large and extensive strata. To the metallurgist, also, belong the various modifications of the metals when obtained, and the union of them together, in different proportions, so as to afford compounds adapted to particular uses.—Throughout the whole of this art, much practical improvement may be suggested by attention to the general doctrines of chemistry. The artist may receive useful hints respecting the construction of furnaces for the fusion of ores and metals; the employment of the proper fluxes; the utility of the admission or exclusion of air; and the conversion of the refuse of his several operations to useful purposes. When the metals have been separated from their ores, they are to be again subjected to various chemical processes. Cast or pig iron is to be changed into the forms of wrought or malleable iron and of steel. Copper, by combination with zinc or tin, affords the various compounds of brass, pinchbeck, bell-metal, gun-metal, &c. Even the art of printing owes something of its present unexampled perfection to the improvement of the metal of types.

2d. Chemistry is the foundation of those arts that furnish us with *saline substances*, an order of bodies highly useful in the business of common life. Among these, the most conspicuous are, sugar in all its various forms; the vegetable and mineral alkalis, known in commerce by the names of potash, pearlash, and barilla; common salt; green and blue vitriol, and alum; nitre or saltpetre; sugar of lead; borax; and a long catalogue, which it is needless to extend farther.

3d. The manufacturer of *glass*, and of various kinds of *pottery* and *porcelain*, should be thoroughly acquainted with the nature of the substances he employs; with their fusibility, as affected by difference of proportion, or by the admixture of foreign ingredients; with the means of regulating and measuring high degrees of heat; with the principles on which depend the hardness of his products, and their fitness for bearing sudden vicissitudes of heat and cold; and with the chemical properties of the best adapted colours and glazings.— Even the humble art of making bricks and tiles has received, from the chemical knowledge of Bergman, the addition of several interesting facts.

4th. The preparation of various kinds of *fermented liquors*, of wine, and ardent spirits, is intimately connected with chemical principles. Malting, the first step in the production of some of these liquors, consists in the conversion of part of the grain into saccharine matter, essential in most instances to the success of the fermentative change. To acquire a precise acquaintance with the circumstances, that favour or retard the process of fermentation, no small share of chemical knowledge is required. The brewer should be able to ascertain, and to regulate exactly, the strength of his infusions, which will vary greatly when he has seemingly followed the same



routine. He should be aware of the influence of minute changes of temperature in retarding or advancing fermentation; of the means of promoting it by proper ferments; and of the influence of the presence or exclusion of atmospherical air. A complete acquaintance with the chemical principles of his art, can hardly fail to afford him essential aid in its practice.

The production of ardent spirits is only a sequel of the vinous fermentation, and is, therefore, alike dependent on the doctrines of chemistry.

5th. The arts of *bleaching*, *dyeing*, and *printing*, are, throughout, a tissue of chemical operations. It is not unusual to bear the new mode of bleaching distinguished by the appellation of the chemical method; but it is, in truth, not more dependent on the principles of this science, than the one which it has superseded, nor than the kindred arts of dyeing and printing. In the instance of bleaching, the obligation due to the speculative chemist is universally felt and acknowledged. But the dyer and the calico-printer have yet to receive from the philosopher some splendid invention, which shall command their respect, and excite their attention to chemical science. From purely speculative men, however, much less is to be expected, than from men of enlightened experience, who endeavour to discover the design and reason of each step in the processes of their arts, and fit themselves for more effectual observation of particular facts, by diligently possessing themselves of general truths.

The objects of inquiry that present themselves to the dyer and calico-printer, are of considerable number and importance. The preparation of goods for the reception of colouring matter; the application of the best bases, or means of fixing fugitive colours; the improvement of colouring ingredients

themselves; and the means of rendering them permanent, so that they shall not be affected by soap, or by the accidental contact of acids or other corrosive bodies; are among the subjects of chemical investigation. It is the business of the dyer, therefore, to become a chemist; and he may be assured that, even if no brilliant discovery should be the reward of the acquisition, he will yet be better fitted by it for conducting common operations, with certain and unvaried success.

6th. The *tanning and preparation of leather* are processes strictly chemical, which were involved in mystery, till they were reduced to well established principles by the researches of Seguin, and by the subsequent experiments of Davy. In this, as in most other examples, the application of science to the practical improvement of an art, has to encounter the obstacles of ignorance and prejudice. But the interests of men are sure finally to prevail; and the most bigotted attachment to established forms must give place to the clearly demonstrated utility of new practices. Such a demonstration is generally furnished by some artist of more enlightened views than his neighbours, who has the spirit to deviate from ordinary rules; and thus becomes (not unfrequently with some personal sacrifice) a model for the imitation of others, and an important benefactor of mankind.

Many other chemical arts might be enumerated; but enough, I trust, has been said, to evince the connexion between practical skill and the possession of scientific knowledge. I shall now, therefore, proceed to explain the principle of the arrangement which I have selected for the following work.

The order, which I have adopted as most eligible, is to commence with those facts, which conduct directly to the establishment of general principles. Attraction or affinity, as the great cause of all chemical changes, and as admitting of

illustration by phenomena that are sufficiently familiar, has a primary claim to consideration. The development of its laws will lead too to the explanation of a number of terms, without which it is scarcely possible to describe the most common chemical appearances. Next to that of attraction, the influence of Heat, over the forms and properties of bodies, is the most generally observed fact; and as heat is a power, which is constantly opposed to that of affinity, there is the more propriety in contrasting their operation. With heat, Light, as a repulsive agent, is frequently associated. Electricity, also, belongs to the same class of powers; and has, indeed, such an extensive control over the phenomena of Chemistry, as to have supplied the basis of a division of bodies into two great and comprehensive classes, according to their electrical habitudes. When, for example, a body composed of two elements is placed between surfaces oppositely electrified, the one element is uniformly attracted to the positive, and the other to the negative surface. And as like electricities repel, and unlike attract, each other, it is inferred that the element, which arranges itself at the *positive* pole, is naturally in a state of *negative* electricity, and the reverse with respect to the other. Hence the distribution of all bodies into the two great classes of **ELECTRO-NEGATIVE** and **ELECTRO-POSITIVE**.

To this arrangement, it may be objected that bodies, which are properly ranked in the electro-positive division, when considered in their relations to substances of an opposite class, nevertheless exert a contrary energy towards bodies of the same class with themselves. This is distinctly the case with the metals, which, though all electro-positive towards oxygen, are, in many cases, electro-negative towards each other; and the same exception may be extended to a variety of other

cases. It must be considered, however, that classifications have no foundation in nature, and are entirely the work of human reason; that they are merely artificial contrivances for the purpose of assisting us in the acquirement and retention of knowledge; and must partake of the imperfections of all human inventions. It is under a full sense then of its defects, that I adopt the arrangement followed in this work; and I consider it only as a provisional one, till the progress of science shall have unfolded still more striking and consistent analogies.

The **ELECTRO-NEGATIVE BODIES**, at present known, are at most only four; namely, **OXYGEN, CHLORINE, IODINE, and FLUORINE**. They require, therefore, no sub-division into orders, or genera. But the **ELECTRO-POSITIVE CLASS** includes so great a number of individuals, that it becomes quite necessary to aid the memory by selecting, from among them, resemblances which may be the foundation of less comprehensive divisions. On investigating their properties and combinations, it will be found that several of them, not possessing the qualities of metals (which also belong to the electro-positive class), are capable of forming acids by combination with oxygen, chlorine, or hydrogen. These may, therefore, be set apart under the general name of **SIMPLE ACIDIFIABLE BODIES**, to which, as a few of the metals are also acidifiable, may be added, for greater precision, the epithet **NON-METALLIC**. They are, **HYDROGEN, NITROGEN, CARBON, BORON, PHOSPHORUS, SULPHUR, and SELENIUM**. In describing the properties of each individual of this genus, I shall first examine its relations to each of the four electro-negative elements. This will lead to an early exposition of the nature and effects of **ACIDS**, a kind of compounds, which are concerned in al-

most all the operations of Chemistry, and a knowledge of which will be found greatly to assist in developing the properties of the Metals. Before proceeding, however, to the Metals, I shall describe, for the sake of convenience, though it may be less conformable to strictly philosophical order, the COMPOUNDS OF SIMPLE ACIDIFIABLE BODIES WITH EACH OTHER. This will enable me to introduce, at an early period, the history of ammonia; of the compounds of hydrogen with sulphur; of cyanogen; and of a few acids with compound bases; and thus to render still more complete the history of the Metals, and of their Oxides; for most of these have important relations, not only to the acids, but to the compounds of acidifiable bodies with each other.

The METALS themselves constitute the remaining division of electro-positive bodies, and I shall trace the connections of each of them and of its oxides with the four electro-negative bodies,—with the acids,—with simple and compound acidifiable bodies,—and finally, with other metals. It is, therefore, in the section devoted to each individual metal, that the reader, who may occasionally consult these volumes, is to look for the history of the salifiable bases, whether alkalis, earths, or merely oxides; for that of the salts formed by the union of the different bases with acids; and for the action of those salts on all bodies, the properties of which may have been described in antecedent chapters. Of the metals, I have adopted sub-divisions, which appear to me sufficiently to classify them by their most striking resemblances, without the inconvenience of those multifarious distinctions, which serve rather to oppress than to assist the memory.

So far, the bodies, which will have been introduced to the reader's notice, belong neither to the animal nor the vege-

table kingdoms, the subjects of which will next demand our attention. The confines between these kingdoms, it is well known, have, in many instances, been traced by the hand of nature so indistinctly, that it is difficult to pronounce to which of them particular individuals ought to be referred. Nor are we always relieved from the difficulty, by appealing to chemical properties; for it frequently happens that azote, which was formerly supposed to belong exclusively, or nearly so, to animal matters, is evolved in the form of ammonia, by the destructive decomposition of vegetables. The distinction, however, between animals and vegetables, understood in its popular sense, is sufficient to serve as the basis of a subordinate division of bodies, till improved processes of analysis, and more refined and extended results, shall enable us to take a wider survey of nature, and to found our classifications on the true constitution of bodies, by which are implied, not only the kind and number of their elementary atoms, but the manner in which they are grouped.

Having concluded the history, both of inorganic and organic bodies, it will only remain to lay down practical rules, deduced from facts and principles that have been explained in the course of the work, for solving a few of the most interesting problems in **CHEMICAL ANALYSIS**; and to present, in a series of **TABLES**, synoptical views of such facts, as are best exhibited under that form.

which continues rising till it is full, when it is stopped by the cross bar to which the pullies are attached.

To transfer the gas, or to apply it to any purpose, the cock *b* is to be shut, and an empty bladder, or bottle of elastic gum, furnished with a stop cock, to be screwed on *a*. When the vessel *c* is pressed down by the hand, the gas passes down the central pipe, which it had before ascended, and its escape at *b* being prevented, it finds its way up a vertical pipe which is fixed to the outer surface of the vessel, and which is terminated by the cock *a*. By means of an ivory mouth-piece screwed upon this cock, the gas, included in the instrument, may be respired; the nostrils being closed by the fingers. When it is required to transfer the gas into glass jars standing inverted in water, a crooked tube may be employed, one end of which is screwed upon the cock *b*; while the other aperture is brought under the inverted funnel, fixed into the shelf of the pneumatic trough. (See fig. 41, *c*.)

Several alterations have been made in the form of this apparatus; but they are principally such as add merely to its neatness and beauty, and not to its utility; and they render it less easy of explanation. The counterpoises *ee* are now, for example, generally concealed in the framing, and the moveable vessel *c* is frequently made of glass.

When large quantities of gas are required (as at a public lecture), the gas-holder (plate iv. fig. 36), will be found extremely useful. It is made of tinned iron plate, japanned both within and without. Two short pipes, *a* and *c*, terminated by cocks, proceed from its sides, and another, *b*, passes through the middle of the top or cover, to which it is soldered, and reaches within half an inch of the bottom. It will be found convenient also to have an air-cock, with a very wide bore, fixed to the funnel at *b*. When gas is to be transferred into this vessel from the gazometer, the vessel is first completely filled with water through the funnel, the cock *a* being left open, and *c* shut. By means of a horizontal pipe, the aperture *a* is connected with *a* of the gazometer. The cock *b* being shut, *a* and *c* are opened, and the vessel *c* of the gazometer (fig. 35), gently pressed downwards with the hand. The gas then descends from the gazometer till the air-holder

is full, which may be known by the water ceasing to escape, through the cock *c*. All the cocks are then to be shut, and the vessels disunited. To apply this gas to any purpose, an empty bladder may be screwed on *a*; and water being poured through the funnel *b*, a corresponding quantity of gas is forced into the bladder. By lengthening the pipe *b*, the pressure of a column of water may be added: and the gas being forced through *a* with considerable velocity, may be applied to the purpose of a blow-pipe, &c. &c. The apparatus admits of a variety of modifications. The most useful one appears to me to be that contrived by Mr. Pepys, consisting chiefly in the addition of a shallow cistern (*e*, plate ix. fig. 85) to the top of the air-holder, and of a glass register tube *f*, which shows the height of the water, and consequently the quantity of gas, in the vessel. A more minute account of it will be given in the description of the ninth plate.\*

The gazometer, already described, is fitted only for the reception of gases that are confinable by water; because quicksilver would act on the tinning and solder of the vessel, and would not only be spoiled itself, but would destroy the apparatus. Yet an instrument of this kind, in which mercury can be employed, is peculiarly desirable, on account of the great weight of that fluid; and two varieties of the mercurial gazometer have therefore been invented. The one, of glass, is the contrivance of Mr. Clayfield, and may be seen represented in the plate prefixed to Sir H. Davy's 8vo. vol. of *Researches*, published in 1800. In the other, invented by Mr. Pepys, the cistern for the mercury is of cast-iron. A drawing and description of it may be found in the 5th vol. of the *Philosophical Magazine*; but as neither of these instruments are essential to the chemical student, and as they are required only in experiments of research, I deem it sufficient to refer to the minute descriptions of their respective inventors. Mr. Newman has lately joined a gazometer of this kind to an improved mercurial trough, by means of which the advantages of both are obtained with only 60 or 70

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\* Descriptions and figures of improved gas-holders may be seen also in the 13th, 24th, 27th, and 44th vols. of the *Philosophical Magazine*.



pounds of quicksilver. A description and drawing of this apparatus is given in the *Journal of Science and the Arts*, i. 186. (See also pl. x. at the end of this volume.)

For those gases that are absorbed by water, a mercurial trough is necessary. For the mere exhibition of a few experiments on these condensible gases, a small wooden trough, 11 inches long, two wide, and two deep, cut out of a solid block of mahogany, is sufficient; but for experiments of research, one of considerable size is required. (See plate iii. fig. 31, *f. f.*)

The apparatus, required for *submitting gases to the action of electricity*, is shown in plate ix. fig. 84; where *a* represents the knob of the prime conductor of an electrical machine; *b* a Leyden jar, the ball of which is in contact with it, as when in the act of charging; and *c* the tube standing inverted in mercury, and partly filled with gas. The mercury is contained in a strong wooden box *d*, to which is screwed the upright iron pillar *e*, with a sliding collar for securing the tube *c* in a perpendicular position. When the jar *b* is charged to a certain intensity, it discharges itself between the knob *a* and the small ball *i*, which, with the wire connected with it, may be occasionally fitted on the top of the tube *c*. The strength of the shocks is regulated by the distance between *a* and *i*.

By the same apparatus, inflammable mixtures of gases may be exploded by electricity. In this case, however, the jar *b* is unnecessary, a spark received by *i* from *a* being sufficient to kindle the mixture.

The method of *weighing gases* is very simple, and easily practised. For this purpose, however, it is necessary to be provided with a good air-pump; and with a globe or flask, furnished with a brass cap and air-cock, as shown fig. 22, *b*. A graduated receiver is also required, to which an air-cock is adapted, as shown at fig. 22, *a*.

Supposing the receiver *a* to be filled with any gas, the weight of which is to be ascertained, we screw the cock of the vessel *b* on the transfer plate of an air-pump, and exhaust it as completely as possible. The weight of the exhausted

vessel is then very accurately taken, even to a small fraction of a grain; and it is screwed upon the air-cock of the receiver *a*. On opening both cocks, the last of which should be turned very gradually, the gas ascends from the vessel *a*; and the quantity, which enters into the flask, is known by the graduated scale on *a*. On weighing the vessel a second time, we ascertain how many grains have been admitted. If we have operated on common air, we shall find its weight to be at the rate of about 30.5 grains to 100 cubical inches. The same quantity of oxygen gas will weigh about 34 grains, and of carbonic acid gas upwards of 47 grains.

In experiments of this kind it is necessary either to operate with the barometer at 30 inches, and the thermometer at 60° Fahrenheit, or to reduce the volume of gas employed to that pressure and temperature, by rules which will presently be given. Great care is to be taken, also, not to warm any of the vessels by contact with the hands, from which they should be defended by a glove. On opening the communication between the receiver and the exhausted globe, if any water be lodged in the air-cock attached to the former, it will be forcibly driven into the globe, and the experiment will be frustrated. This may be avoided by using great care in filling the receiver with water, before passing into it the gas under examination.

The specific gravity of any gas compared with common air is readily known, when we have once determined its absolute weight. Thus if 100 cubic inches of air weigh 30.5 grains, and the same quantity of oxygen gas weighs 34 grains, we say,  
 $30.5 : 34 :: 1.000 : 1.1147.$

The specific gravity of oxygen gas will therefore be as 1.1147 to 1.000. We may determine, also, the specific gravity of gases, more simply, by weighing the flask, first when full of common air, and again when exhausted; and afterwards by admitting into it as much of the gas under examination as it will receive; and weighing it a third time. Now as the loss between the first and second weighing is to the gain of weight on admitting the gas, so is common air to the gas whose specific gravity we are estimating. Supposing, for example,

that by exhausting the flask it loses 30.5 grains, and that by admitting carbonic acid it gains 47; then

$$30.5 : 47 :: 1.000 : 1.5409.$$

The specific gravity of carbonic acid is therefore 1.5409, air being taken at 1.000. And knowing its specific gravity, we can, without any farther experiment, determine the weight of 100 cubic inches of carbonic acid; for as the specific gravity of air is to that of carbonic acid, so is 30.5 to the number required; or

$$1.000 : 1.5409 :: 30.5 : 47.$$

One hundred inches of carbonic acid, therefore, will weigh 47 grains.

Previously to undertaking experiments on other gases, it may be well for an unpractised experimentalist to acquire manual dexterity by transferring common air from one vessel to others of different sizes, in the following manner.

1. When a glass jar, closed at one end, is filled with water, and held with its mouth downwards, in however small a quantity of water, the fluid is retained in its place by the pressure of the atmosphere on the surface of the exterior water. Fill in this manner, and invert, on the shelf of the pneumatic trough, one of the jars, which is furnished with a stopper (fig. 23). The water will remain in the jar so long as the stopper is closed; but immediately on removing it, the water will descend to the same level within as without; for it is now pressed, equally upwards and downwards, by the atmosphere, and falls therefore in consequence of its own gravity.

2. Place the jar filled with water and inverted, over one of the funnels of the shelf of the pneumatic trough. Then take another jar, filled (as it will be of course) with atmospheric air. Place the latter with its mouth on the surface of the water; and on pressing it in the same position below the surface, the included air will remain in its situation. Bring the mouth of the jar beneath the funnel in the shelf, and incline it gradually. The air will now rise in bubbles, through the funnel, into the upper jar, and will expel the water from it into the trough.

3. Let one of the jars, provided with a stop-cock at the top, be placed full of air on the shelf of the trough. Screw

upon it an empty bladder; open the communication between the jar and the bladder, and press the former into the water. The air will then pass into the bladder, till it is filled; and when the bladder is removed from the jar, and a pipe screwed upon it, the air may be again transferred into a jar inverted in water.

For the purpose of transferring gases from a wide vessel standing over water, into a small tube filled with and inverted over mercury, I have long used the following simple contrivance of Mr. Cavendish. A tube, eight or ten inches long, and of very small diameter, is drawn out to a fine bore, and bent at this end, so as to resemble the italic letter *l*. The point is then immersed in quicksilver, which is drawn into the tube till it is filled, by the action of the mouth. Placing the finger over the aperture at the straight end, the tube filled with quicksilver is next conveyed through the water, with the bent end uppermost, into an inverted jar of gas. When the finger is removed, the quicksilver falls from the tube into the trough, or into a cup placed to receive it, and the tube is filled with the gas. The whole of the quicksilver, however, must not be allowed to escape; but a column must be left, a few inches long, and must be kept in its place by the finger. Remove the tube from the water; let an assistant dry it with a towel or with blotting paper; and introduce the point of the bent end into the aperture of the tube standing over quicksilver. On withdrawing the finger from that aperture which is now uppermost, the pressure of the column of quicksilver, added to the weight of the atmosphere, will force the gas from the bent tube into the one standing in the mercurial trough.

On every occasion, when it is necessary to observe the precise quantity of gas, at the commencement and close of an experiment, it is essential that the barometer and thermometer should exactly correspond at both periods. An increased temperature, or a fall of the barometer, augments the apparent quantity of gas; and a reduced temperature or a higher barometer diminishes its bulk. Another circumstance, an attention to which is indispensable in all accurate experiments, is that the surface of the fluid, by which the gas is confined,

should be precisely at the same level within and without the jar. If the fluid be higher within the jar, the contained gas will be under a less pressure than that of the atmosphere, the weight of which is counterpoised by that of the column of fluid within. In mercury, this source of error is of very considerable amount; as any person may be satisfied by raising above the surface of the quicksilver of a trough, a tube partly filled with that fluid, and partly with air, for the volume of the air will enlarge as the surface of the mercury within the tube is elevated above the outer surface.

In experiments on gases, it is not always possible to begin and conclude an experiment at precisely the same temperature, or with the same height of the barometer; or even to bring the mercury within and without the receiver to the same level. In these cases, therefore, calculation becomes necessary; and with the view of comparing results more readily and accurately, it is usual to reduce quantities of gas to the bulk they would occupy under a given pressure, and at a given temperature. In this country, it is now customary to assume as a standard 30 inches of the barometer, and 60° of Fahrenheit's thermometer; and to bring to these standards observations made under other degrees of atmospheric pressure and temperature. The rules for these corrections, which are sufficiently simple, are the following:

*Rules for reducing the Volume of Gases to a mean Height of the Barometer, and mean Temperature.*

1. *From the space occupied by any quantity of gas under an observed degree of pressure, to infer what its volume would be under the mean height of the barometer, taking this at 30 inches, as is now most usual.*

This is done by the rule of proportion; for, as the mean height is to the observed height, so is the observed volume to the volume required. For example, if we wish to know what space would be filled, under a pressure of 30 inches of mercury, by a quantity of gas, which fills 100 inches, when the barometer is at 29 inches,

$$30 : 29 :: 100 : 96.66.$$

The 100 inches would, therefore, be reduced to 96.66.

2. *To estimate what would be the volume of a portion of gas, if brought to the temperature of 60° Fahrenheit.*

Divide the whole quantity of gas by 480: the quotient will show the amount of its expansion or contraction by each degree of Fahrenheit's thermometer. Multiply this by the number of degrees, which the gas exceeds, or falls below, 60°. If the temperature of the gas be above 60°, subtract, or if below 60°, add, the product to the absolute quantity of gas; and the remainder in the first case, or sum in the second, will be the answer. Thus, to find what space 100 cubic inches of gas at 50° would occupy if raised to 60°, divide 100 by 480; the quotient 0.208 multiplied by 10 gives 2.08, which added to 100 gives 102.08 the answer required. If the temperature had been 70°, and we had wished to know the volume which the gas would have occupied at 60°, the same number 2.08 must have been subtracted from 100, and 97.92 would have been the answer.

3. In some cases, it is necessary to make a double correction, or to bring the gas to a mean both of the barometer and thermometer. We must then first correct the temperature, and afterwards the pressure. Thus to know what space 100 inches of gas at 70° Fahrenheit, and 29 inches barometer, would fill at 60° Fahrenheit and 30 inches barometer, we first reduce the 100 inches, by the second process, to 97.92. Then by the first

$$30 : 29 :: 97.92 : 94.63.$$

Or 100 inches thus corrected, would be only 94.63.

4. *To ascertain what would be the absolute weight of a given volume of gas at a mean temperature, from the known weight of an equal volume at any other temperature; first, find by the second process what would be its bulk at a mean temperature; and then say, as the corrected bulk is to the actual weight, so is the observed bulk to the number required. Thus if we have 100 cubic inches of gas weighing 50 grains at 50° Fahrenheit, if the temperature were raised to 60° they would expand to 102.08. And*

$$102.08 : 50 :: 100 : 49.$$

Therefore 100 inches of the same gas at 60° would weigh 49 grains.

5. To learn the absolute weight of a given volume of gas under a mean pressure, from its known weight under an observed pressure, say, as the observed pressure is to the mean pressure, so is the observed weight to the corrected weight. For example, having 100 inches of gas which weigh 50 grains under a pressure of 29 inches, to know what 100 inches of the same gas would weigh, the barometer being 30 inches,

$$29 : 30 :: 50 : 51.72.$$

Then 100 inches of the same gas, under 30 inches pressure, would weigh 51.72 grains.

6. In some cases it is necessary to combine the two last calculations. Thus, if 100 inches of gas at 50° Fahrenheit, and under 29 inches pressure, weigh 50 grains, to find what would be the weight of 100 inches at 60° Fahrenheit, and under 30 inches of the barometer, first correct the temperature, which reduces the weight to 49 grains. Then,

$$29 : 30 :: 49 : 50.7.$$

One hundred inches, therefore, would weigh 50.7 grains.

#### *Corrections for Moisture in Gases.*

Another correction, which it is often necessary to make in taking the weight of gases, is for the quantity of aqueous vapour diffused through them. It is obvious that all gases, which are specifically heavier than aqueous vapour, must have their specific gravity diminished by admixture with steam; and, on the contrary, all gases that are specifically lighter than steam must have their specific gravity increased by that admixture. For the following formulæ, I am indebted to Mr. Dalton, who has obligingly stated them at my request.

“At ordinary temperatures, the tension or elasticity of aqueous vapour varies from  $\frac{1}{100}$  to  $\frac{1}{40}$  of the whole atmospheric pressure; in the present case, it is supposed to be a given quantity. The specific gravity of pure steam compared with that of common air, under like circumstances of temperature and pressure, is, according to Gay Lussac, as 0.620 to 1.

Let  $a$  = weight of 100 cubic inches of dry common air, at the pressure 30 inches and temperature 60° Fahr.;  $p$  = any

variable pressure of atmospheric air; and  $f$  = pressure or tension of vapour in any moist gas. Then the following formulæ will be found useful in calculating the volumes, weights, and specific gravities of dry and moist gases; putting  $M$  for the volume of moist gas;  $D$  for that of dry gas; and  $V$  for that of vapour, all of the same pressure and temperature.

$$1. M = D + V.$$

$$2. \frac{p-f}{p} M = D.$$

$$3. \frac{f}{p} M = V.$$

$$4. M = \frac{p D}{p-f} = \frac{p V}{f}$$

If we wish to infer the specific gravity of any dry gas from the observed specific gravity or weight of the same mixed with vapour, it will be convenient to expound  $p$  by that particular value which corresponds with  $a$ , namely 30 inches of mercury; and let  $s$  = the specific gravity of the dry gas, and  $w$  = the observed weight of 100 cubic inches of the moist gas.

Then we shall have the following, viz.:

$$5. \frac{30-f}{30} \cdot s a + \frac{f}{p} \times .620 a = w.$$

$$6. s = \frac{30}{30-f} \left( w - \frac{f}{p} \times .620 a. \right)$$

#### *Exemplifications.*

1. 98 vol. dry air + 2 vol. vapour = 100 vol. of moist air.

2. Given  $p = 30$ ,  $f = .5$ , and  $M = 100$ .

Then  $\frac{p-f}{p} \cdot M = D$ , the dry air, =  $98\frac{1}{2}$ .

3. And  $\frac{f}{p} M = V$ , the vapour, =  $1\frac{1}{2}$ .

4. Given  $D = 100$ ,  $p = 30$ ,  $f = .4$ .

Then  $\frac{30 \times 100}{29.6} = 101.35$ , the moist air.

Given  $V^* = 2$ ,  $p = 30$ ,  $f = .3$ .

Then  $\frac{30 \times 2}{.3} = 200$ , the moist air.

\* It is easy to see that  $V$ , in this and the other cases, mostly will denote a virtual volume only; or such as would result, if the vapour were condensable like a gas, without being convertible into a liquid.



5. Let  $f = .5$ ,  $s = 1.111$ ,  $a = 30.5$ ,  $p = 29.5$ ,

Then  $\frac{30-.5}{30} 1.111 \times 30.5 + \frac{.5}{29.5} \times .62 \times 30.5 = 33.64 = u$ , which gives the specific gravity 1.103.

6. Let  $f$ ,  $a$ , and  $p$  as above, and  $w = 2.5$ , corresponding to sp. gr. 0.8197.

Then  $s = \frac{30}{29.5 \times 30.5} \left( 2.5 - \frac{.5}{29.5} \times .62 \times 30.5 \right) = .07266$ .

The above formulæ apply equally well if V be a permanent gas, or any other vapour beside that of water, the specific gravity of the gas or vapour being substituted instead of .620 that of steam."

## CHAPTER II.

## OF CHEMICAL AFFINITY.

ALL bodies, composing the material system of the universe, have a mutual tendency to approach each other, whatsoever may be the distances at which they are placed. The operation of this force extends to the remotest parts of the planetary system, and is one of the causes that preserve the regularity of their orbits. The smaller bodies, also, that are under our more immediate observation, are influenced by the same power, and fall to the Earth's surface, when not prevented by the interference of other forces. From these facts, the existence of a property has been inferred, which has been called *attraction*, or more specifically, the *attraction of gravitation*. Its nature is entirely unknown to us; but some of its laws have been investigated, and successfully applied to the explanation of phenomena. Of these, the most important are, that the force of gravity acts on bodies directly in proportion to the quantity of matter in each; and that it decreases in the reciprocal proportion of the squares of the distances.

From viewing bodies in the aggregate, we may next proceed to contemplate them as composed of minute particles. Of the nature of these particles, we have no satisfactory evidence. It is probable that they consist of solids, which are incapable of mechanical division, but are still possessed of the dimensions of length, breadth, and thickness. In simple bodies, the particles must be all of the same nature, or *homogeneous*. In compound bodies, we are to understand, by the term *particles*, the smallest parts into which bodies can be resolved without decomposition. The word *atom* has of late been revived, to denote both these kinds of particles; and we may, therefore, speak with propriety of *simple atoms* and of *compound atoms*. When two atoms of different kinds unite to form a third or compound atom, we may term the two first *component atoms*; and if these have not been decomposed, they may be called *elementary or primary atoms*.

The atoms or particles of bodies are also influenced by the force of attraction, but not unless when placed in apparent contact. Hence a distinction has been made between gravitation, and that kind of attraction which is effective only at insensible distances. The latter has been called *contiguous attraction* or *affinity*; and it has been distinguished, as it is exerted between particles of matter of the *same* kind, or between particles of a *different* kind.

By the *affinity of aggregation*, the *cohesive affinity*, or, more simply *cohesion*, is to be understood that force or power, by which particles or atoms of matter of *the same kind* attract each other, the only effect of this affinity being an aggregate or mass. Thus a lump of copper may be considered as composed of an infinite number of minute particles or integrant parts, each of which has precisely the same properties, as those that belong to the whole mass. These are united by the force of cohesion. But if the copper be combined with another metal (such as zinc), we obtain a compound (brass), the constituent parts of which, copper and zinc, are combined by the power of chemical affinity. In simple bodies, therefore, cohesion is the only force exerted between their particles. But in compound bodies, we may distinguish the force, with which the *primary* or *component* atoms are united, from that which the *compound* atoms exert towards each other; the former being united by chemical affinity, and the latter by the cohesive attraction.



## SECTION I.

### *Of Cohesion, Solution, and Crystallization.*

THE cohesive affinity is a property, which is common to a great variety of bodies. It is most strongly exerted in solids; and in these it is proportionate to the mechanical force required for effecting their disunion. In liquids, it acts with considerably less energy; and in aëriform bodies we have no evidence that it exists at all; for their particles, as will afterwards be shown, are mutually repulsive, and, if not held to-

gether by pressure, would probably separate to immeasurable distances. The force of this attraction is not only different among different bodies, but in various states of the same body. Thus in the cohesion of certain metals (steel for instance), important changes are produced by the rate of cooling, by hammering, and by other mechanical operations. Water, also, in a solid state, has considerable cohesion, which is much diminished when it becomes liquid, and is entirely destroyed when it is changed into vapour.

The most important view, in which the chemist has to consider cohesion, is that of a force either counteracting or modifying chemical affinity; for the more strongly the particles of any body are united by this power, the less are they disposed to enter into combination with other bodies. In many cases, a very powerful affinity existing between two substances may be rendered wholly inefficient, by the strong cohesion of one or both of them. Hence it has been received as an axiom, that *the affinity of composition is inversely proportionate to the cohesive affinity*. To the language, however, in which this axiom is expressed, it has been justly objected, that it implies an accuracy of proportion between the forces of cohesion and of chemical affinity, which cannot be proved to exist; since all that can truly be affirmed is, in general terms, that the affinity of composition is less effective, as the attraction of cohesion is stronger.

The cohesion of bodies may be overcome, 1st, by mechanical operations, as by rasping, grinding, pulverising, and other modes of division, which are generally employed as preliminary steps to chemical processes. In some instances, even a minuter division of bodies is necessary, than can be accomplished by mechanical means; and recourse is then had to precipitation. Silica, for example, in the state of rock crystal, may be boiled for a long time in liquid potash, without any appearance of chemical action. It may even be bruised to the finest powder, without being rendered sensibly soluble. But when first precipitated from a state of chemical solution, it is readily dissolved by that menstruum, and even by some acids.

2dly. Cohesion may be counteracted by heat, applied so as to melt one or both of the bodies, if fusible; or to raise them

into vapour, if volatile. Lead and sulphur contract no union, till one or both of them is melted by heat. Arsenic and sulphur are united most effectually, by bringing them into contact, when both are in a state of vapour.

3dly. Cohesion may be counteracted by *solution*; and this is so general a condition of chemical union, that it was formerly received as an axiom, that *bodies do not act on each other, unless one or both are in a state of solution*; a principle, to which the progress of chemical science has since discovered many exceptions.

The term *solution* is applied to a very extensive class of phenomena. When a solid disappears in a liquid, if the compound exhibit perfect transparency, we have an example of solution. The expression is applied, both to the *act* of combination, and to the *result* of the process. When common salt, such as is used in cookery, is agitated with water, it disappears; in other words, its solution takes place; and we also term the liquid which is obtained, *a solution of salt in water*. This is one of the simplest cases that can be adduced, of the efficiency of chemical affinity; for solution is always the result of an affinity between the fluid and the solid which is acted upon, feeble it is true, yet sufficient in force to overcome the cohesion of the solid. This affinity continues to act, until, at length, a certain point is attained, where the affinity of the solid and fluid for each other is overbalanced by the cohesion of the solid, and the solution cannot be carried farther. This point is called *saturation*, and the fluid obtained is termed a *saturated solution*.

With respect to common salt, water acquires no increase of its solvent power by the application of heat. But there are various salts with which water may be saturated at the common temperature of the atmosphere, and will yet be capable of dissolving a still farther quantity by an increase of its temperature. When a solution, thus charged with an additional quantity of salt, is allowed to cool, the second portion of salt is deposited in a form resembling its original one.

To recover a salt from its solution, if its solubility does not vary with the temperature of the solvent, as in the instance

of common salt, it is necessary to expel a portion of the fluid by heat. This constitutes the process of *evaporation*. If the evaporation be carried on very slowly, so that the particles of the solid may approach each other in the way best adapted to them, we obtain solid figures, of a regular shape, called *crystals*. The crystallization of a solid may also take place from that state of fluidity which is produced by heat. Thus several of the metals crystallize on cooling from a melted state; and some volatile bodies, as arsenic, assume, when condensed from the state of vapour, the shape of regular crystals.

In the act of separating from the water in which they were dissolved, the crystals of almost all salts carry with them a quantity of water, which is essential to the regularity of their form, and cannot be expelled without reducing them to shapeless masses. It is termed their *water of crystallization*. Its proportion varies in different salts; in some it is extremely small; in others it constitutes the principal part of the salt, and is even so abundant, as to liquefy them on the application of heat, producing what is called the *watery fusion*. In every salt it exists, not in an uncertain but in a definite proportion, bearing in the same salt the same ratio to the solid saline matter, but differing for different salts. The water of crystallization is retained also in different salts with very different degrees of force. Some crystals, which lose their watery ingredient by mere exposure to the atmosphere, are said to *effloresce*. Others, on the contrary, not only hold their water of crystallization very strongly, but even attract more; and, on exposure to the atmosphere, become liquid, or *deliquiate*. The property itself is called *deliquescence*.

When two salts are contained in the same solution, which vary in their degree of solubility, and which have no remarkable attraction for each other, they may be obtained separate. For by carefully reducing the quantity of the solvent by evaporation, the salt whose particles have the greatest cohesion, will crystallize first. If both salts are more soluble in hot than in cold water, the crystals will not appear till the liquid cools. But if one of them, like common salt, is equally soluble in hot and in cold water, crystals will appear, even during

# ELEMENTS

OF

## EXPERIMENTAL CHEMISTRY.

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### PART I.

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#### CHAPTER I.

##### OF A CHEMICAL LABORATORY AND APPARATUS.

A CHEMICAL laboratory, though extremely useful, and even essential, to all who embark extensively in the practice of chemistry, either as an art, or as a branch of liberal knowledge, is by no means required for the performance of those simple experiments, which furnish the evidence of the fundamental truths of the science. A room that is well lighted, easily ventilated, and destitute of any valuable furniture, is all that is absolutely necessary for the purpose. It is even adviseable, that the construction of a regular laboratory should be deferred, till the student has made some progress in the science; for he will then be better qualified to accommodate its plan to his own peculiar views and convenience.

It is scarcely possible to offer the plan of a laboratory, which will be suitable to every person, and to all situations; or to suggest any thing more than a few rules that should be generally observed. Different apartments are required for the various classes of chemical operations. The principal one may be on the ground floor; twenty-five feet long, sixteen or eighteen wide, and open to the roof, in which there should be contrivances for allowing the occasional escape of suffocating vapours. This will be destined chiefly for containing furnaces, both fixed and portable. It should be amply furnished with shelves and drawers, and with a large table in the

centre, the best form of which is that of a double cross. Another apartment may be appropriated to the minuter operations of chemistry; such as those of precipitation on a small scale, the processes that require merely the heat of a lamp, and experiments on the gases. In a third of smaller size, may be deposited accurate balances, and other instruments of considerable nicety, which would be injured by the acid fumes that are constantly spread through a laboratory.

The following are the principal instruments that are required in chemical investigations; but it is impossible, without entering into very tedious details, to enumerate all the apparatus that should be in the possession of a practical chemist.

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## SECTION I.

### *Of Apparatus for General Purposes.*

**I. FURNACES.** These may be formed either of solid brick-work, or of such materials as admit of their removal from place to place.

The directions generally laid down in elementary books of chemistry for the construction of **FIXED FURNACES** appear to me deficient in precision, and such as a workman would find it difficult to put in practice. I have, therefore, given plans and sections, in the last two plates, of the various kinds of furnaces; and, in the Appendix, minute instructions will be found for erecting them.\*

The furnaces of most general utility are, 1st, the *Wind Furnace*, in which an intense heat is capable of being excited for the fusion of metals, &c. In this furnace, the body submitted to the action of heat, or the vessel containing it, is placed in contact with the burning fuel. Fig. 60 exhibits one of the most common construction. Fig. 61 is the section of a wind furnace; the plan of which was obligingly communicated to me by Mr Knight, of Foster-lane, London, to whom, also, I am indebted for that represented, fig. 62. The

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\* See the Description of the 7th and 8th plates in the Appendix.



wind furnace of Mr. Chevenix is shown by fig. 74. 2dly, The *Evaporating Furnace* is formed of iron plates, joined together by rabbeting, and placed over horizontal returning flues of brick. Figs. 64 and 65, are two views of this furnace as recommended by Mr. Knight. When evaporation is performed by the naked fire, the vessel may be placed on the top of the furnace, fig. 60 or 61; and when effected through the intervention of a water bath, a shallow kettle of water, in which is placed the evaporating dish and its contents, may be set in the same situation. For the purposes of evaporating liquids, and drying precipitates on a small scale, at a temperature not exceeding  $212^{\circ}$  Fahr. a convenient apparatus is represented by fig. 27. 3dly, The plan of a *Reverberatory furnace* is exhibited by figs. 66, 67, and 68. 4thly, The *Furnace for distilling by a Sand Heat* is constructed by setting upon the top of the brick-work, fig. 60, the iron pot, fig. 71; a door being made in the side of the furnace for introducing fuel. Distillation by the naked fire is performed with the wind furnace, figs. 62, 63. 5thly, The *Cupelling or Enamelling Furnace*, is shown by figs. 69, 70.

Portable furnaces, however, are amply sufficient for all the purposes of the chemical student, at the outset of his pursuit. The one which I prefer is that shown by figs. 58 and 59. It was originally contrived, I believe, by Mr. Schmeisser;\* and is made with considerable improvements, and sold by the dealers in chemical apparatus. Its size is so small, that it may be set on a table, and the smoke may be conveyed by an iron pipe, into the chimney of the apartment. In the furnace, as it is usually sold, the chimney, adapted for distillation with a sand heat, passes directly through the sand-bath, the form of which is necessarily, when thus constructed, a very inconvenient one. I have found it a great improvement to make the aperture for the chimney at *k*. This allows us to have a sand-bath of the usual shape, as shown by fig. 59; or even to place evaporating dishes, or a small boiler, on the top of the furnace. The aperture of the side flue may be

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\* See his Mineralogy, Tab. iii. and iv.

closed by a stopper, when we dispose the furnace as shown by fig. 58. Dr. Black's furnace is generally made of a larger size, and is adapted to operations on a more considerable scale. (See figs. 72 and 73.) Both these furnaces are constructed of thin iron plates, and are lined with fire-clay. They will be minutely described in the references to the plates.

For the purpose of exciting a sudden heat, and of raising it to great intensity, nothing can be better adapted than a very simple, cheap, and ingenious furnace, contrived by Mr. Charles Aikin, fig. 55. It is formed out of pieces of black-lead melting pots, in a manner to be described in the Appendix, and is supplied with air by a pair of double bellows, *d*. By a slight alteration, this furnace may occasionally be employed for the operation of cupelling. (See fig. 57.)

II. For containing the materials, which are to be submitted to the action of heat in a wind furnace, vessels called **CRUCIBLES** are employed. They are most commonly made of a mixture of fire-clay and sand, occasionally with the addition of plumbago, or black lead. The Hessian crucibles are best adapted for supporting an intense heat without melting; but they are liable to crack when suddenly heated or cooled. The porcelain ones, made by Messrs. Wedgwood, are of much purer materials, but are still more apt to crack on sudden changes of temperature; and, when used, they should, therefore, be placed in a common crucible of larger size, the interval being filled with sand. The black-lead crucibles resist very sudden changes of temperature, and may be repeatedly used; but they are destroyed when some saline substances (such as nitre) are melted in them, and are consumed by a current of air. For certain purposes, crucibles are formed of pure silver or platina. Their form varies considerably, as will appear from inspecting plate vi. figs, 49, 50, 51, and 54. It is necessary in all cases, to raise them from the bars of the grate, by a stand, fig. 53, *a* or *b*. For the purpose of submitting substances to the continued action of a red heat, and with a considerable surface exposed to the air,

the hollow arched vessel, with a flat bottom, fig. 52, termed a *muffle*, is commonly used. In fig. 69, *d*, *e*, the muffle is shown, placed in a furnace for use.

III. EVAPORATING VESSELS should always be of a flat shape, so as to expose them extensively to the action of heat. (See a section of one, fig. 12.) They are formed of glass, of earthen ware, and of various metals. Those of glass are with difficulty made sufficiently thin, and are often broken by change of temperature; but they have a great advantage in the smoothness of their surface, and in resisting the action of most acid and corrosive substances. Evaporating vessels of porcelain, or Wedgwood's ware, are next in utility, are less costly, and less liable to be cracked. They are made both of glazed and unglazed ware. For ordinary purposes the former are to be preferred; but the unglazed should be employed when great accuracy is required, since the glazing is acted on by several chemical substances. Evaporating vessels of glass or porcelain are generally bedded, up to their edge, in sand (see fig. 65); but those of various metals are placed immediately over the naked fire. When the glass or porcelain vessel is very thin, and of small size, as a watch glass for example, it may be held by means of a small prong, represented under fig. 12; or it may be safely placed on the ring of the brass stand, plate i. fig. 13, and the flame of an Argand's lamp, cautiously regulated, may be applied beneath it. A lamp thus supported, so as to be raised or lowered, at pleasure, on an upright pillar, to which rings, of various diameters, are adapted, will be found extremely useful; and, when a strong heat is required, it is advisable to employ a lamp, furnished with double concentric wicks. A lamp for burning spirit of wine will, also, be found very convenient, especially if provided (as they now generally are) with a glass cap to cover the wick when not in use, which being fitted by grinding, prevents the waste of the spirit by evaporation.

IV. In the process of evaporation, the vapour for the most part is allowed to escape; but of certain chemical processes, the collection of the volatile portion is the principal object.

This process is termed **DISTILLATION**. It is performed in vessels of various forms and materials. The common still is so generally known, that a representation of it in the plates was deemed unnecessary.\* It consists of a vessel, generally of copper, shaped like a tea-kettle, but without its spout and handle. Into the opening of this vessel, instead of a common lid, a hollow moveable head is affixed, which ends in a narrow, open pipe. This pipe is received into another tube of lead, which is twisted spirally, and fixed in a wooden tub, so that it may be surrounded by cold water. (Fig. 40, *dd*.) When the apparatus is to be used, the liquid intended to be distilled is poured into the body of the still, and the head is fixed in its place, the pipe, which terminates it, being received into the leaden worm. The liquid is raised into vapour, which passes into the worm, is there condensed by the surrounding cold water, and flows out at the lower extremity.

The common still, however, can only be employed for volatilizing substances that do not act on copper, or other metals, and is, therefore, limited to very few operations. The vessel, fig. 2, is of glass, or earthen ware, and is also intended for distillation. It is termed an *alembic*, and consists of two parts; the body *a* for containing the materials, and the head *b* by which the vapour is condensed; the pipe *c* conveying it to a receiver. Vessels, termed *retorts*, however, are more generally used. Fig. 1, *a*, shows the common form, and fig. 13, *a*, represents a stoppered, or tubulated retort. Retorts are made of glass, of earthen ware, or of metal. When a liquid is to be added at distant intervals during the process, the best contrivance is that shown fig. 26, *a*, consisting of a bent tube, with a funnel at the upper end. When the whole is introduced at first, it is done either through the tubulure, or, if into a plain retort, through the funnel, fig. 10, by means of which the liquid may be poured in, without touching the inside of the retort neck.

To the retort, a *receiver* is a necessary appendage: and this may either be plain, fig. 1, *b*, or tubulated, as shown by the dotted lines at *c*. To some receivers a pipe is added (fig. 13, *b*),

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\* See Aikin's Chem. Dict. pl. ii. fig. 21.

which may enter partly into a bottle beneath. This vessel, which is principally useful for enabling us to remove the distilled liquid, at different periods of the process, is termed a *quilled receiver*. For some purposes, it is expedient to have the quilled part accurately ground to the neck of the bottle, *c*, which should then be furnished with a tubulure, or second neck, having a ground stopper, and should be provided, also, with a bent tube, to be occasionally applied, for conveying away any gases that may be produced. The condensation of the vapour is much facilitated, by lengthening the neck of the retort with an *adopter* (fig. 11), the wider end of which slips over the retort neck, while its narrow extremity is admitted into the mouth of the receiver. (See fig. 63.)

Heat may be applied to the retort in several modes. When the vessel is of earthen ware, and when the distilled substance requires a strong heat to raise it into vapour, the naked fire is applied, as shown fig. 63. Glass retorts are generally placed in heated sand (fig. 59); and, when of a small size, the flame of an Argand's lamp, cautiously regulated, may be conveniently used (fig. 13).

In several instances, the substance raised by distillation is partly a condensable liquid, and partly a gas, which is not condensed till it is brought into contact with water. To effect this double purpose, a series of receivers, termed *Woulfe's Apparatus*, is employed. The first receiver (*b*. fig. 30) has a right-angled glass tube, open at both ends, fixed into its tubulure; and the other extremity of the tube is made to terminate beneath the surface of distilled water, contained, as high as the horizontal dotted line, in the three-necked bottle *c*. From another neck of this bottle, a second pipe proceeds, which ends, like the first, under water, contained in a second bottle *d*. To the central neck a straight tube, open at both ends, is fixed, so that its lower end may be a little beneath the surface of the liquid. Of these bottles any number may be employed that is thought necessary.

The materials being introduced into the retort, the arrangement completed, and the joints secured in the manner to be presently described, the distillation is begun. The condensable vapour collects in a liquid form in the balloon *d*, while

the evolved gas passes through the bent pipe, beneath the surface of the water in *c*, which continues to absorb it till saturated. When the water of the first bottle can absorb no more, the gas passes, uncondensed, through the second right-angled tube, into the water of the second bottle, which, in its turn, becomes saturated. Any gas that may be produced, which is not absorbable by water, escapes through the bent tube *e*, and may be collected, if necessary.

Supposing the bottles to be destitute of the middle necks, and, consequently, without the perpendicular tubes, the process would be liable to be interrupted by an accident: for if, in consequence of a diminished temperature, an absorption or condensation of gas should take place, in the retort *a*, and, of course, in the balloon *b*, it must necessarily ensue that the water of the bottles *c* and *d* would be forced, by the pressure of the atmosphere, into the balloon, and possibly into the retort, which might cause a dangerous explosion; but, with the addition of the central tubes, a sufficient quantity of air rushes through them to supply any accidental vacuum. This inconvenience, however, is still more conveniently obviated by Wether's tube of safety (fig. 31, *b*), which supersedes the expediency of three-necked bottles. The apparatus being adjusted, as shown by the figure, a small quantity of water is poured into the funnel, so as to about half fill the ball *b*. When any absorption happens, the fluid rises in the ball, till none remains in the tube, when a quantity of air immediately rushes in and supplies the partial vacuum in *a*. On the other hand, no gas can escape, under ordinary circumstances; because any pressure from within is instantly followed by the formation of a high column of liquid in the perpendicular part, which resists the egress of gas. This ingenious invention I can recommend, from ample experience of its utility.

Very useful alterations in the construction of Woulfe's apparatus have been contrived also by Mr. Pepys and Mr. Knight. That of the former is shown (fig. 32), where the balloon *b* is surmounted by a vessel *c* accurately ground to it, and furnished with a glass valve, resembling that affixed to Nooth's apparatus for impregnating water with carbonic acid, commonly sold under that name in the glass shops. This

valve allows gas to pass freely into the vessel *c*, but prevents the water which *c* contains from falling into the balloon. Mr. Knight's improvement is described, and represented in a plate, in the *Philosophical Magazine*, vol. xx.\*

When a volatile substance is submitted to distillation, it is necessary to prevent the escape of the vapour through the junctures of the vessels; and this is accomplished by the application of LUTES. The most simple method of confining the vapour, it is obvious, would be to connect the places of juncture accurately together by grinding; and accordingly the neck of the retort is sometimes ground to the mouth of the receiver. This, however, adds too much to the expense of apparatus to be generally practised.

When the distilled liquor has no corrosive property (such as water, alcohol, ether, &c.), slips of moistened bladder, or of paper, or linen, spread with flour paste, white of egg, or mucilage of gum arabic, sufficiently answer the purpose. The substance which remains, after expressing the oil from bitter almonds, and which is sold under the name of almond-meal, or almond powder, forms a useful lute, when mixed, to the consistency of glaziers' putty, with water or mucilage. For confining the vapour of acid, or highly corrosive substances, the fat lute is well adapted. It is formed by beating perfectly dry and finely sifted tobacco pipe-clay, with painters' drying oil, to such a consistence that it may be moulded by the hand. The same clay, beat up with as much sand as it will bear, without losing its tenacity, with the addition of cut fibres of tow, or of a little horse-dung, and a proper quantity of water, furnishes a good lute, which has the advantage of resisting a considerable heat, and is applicable in cases where the fat lute would be melted or destroyed. Various other lutes are re-

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\* Another modification of this apparatus, by Dr. Murray, is represented in *Nich. Journ.* 8vo. vol. iii. or in *Murray's System of Chemistry*, vol. i. pl. v. fig. 40. Fig. 41 of the same plate exhibits a cheap and simple form of this apparatus, contrived by the late Dr. Hamilton, and depicted originally in his translation of *Berthollet on Dyeing*. Mr. Burkitt's improvement of this apparatus may be seen in *Nicholson's Journal*, 4to. vol. v. 349; and an American invention for the same purpose is represented in the *Quarterly Journal*, viii. 384.

commended by chemical writers ; but the few that have been enumerated I find to be amply sufficient for every purpose.

On some occasions, it is necessary to protect the retort from too sudden changes of temperature, by a proper coating. For glass retorts, a mixture of moist common clay, or loam, with sand, and cut shreds of tow or flax, may be employed. If the distillation be performed by a sand heat, the coating needs not to be applied higher than that part of the retort which is bedded in sand ; but if the process be performed in a wind furnace (fig. 63), the whole body of the retort, and that part of the neck also which is exposed to the fire, must be carefully coated. To this kind of distillation, however, earthen retorts are better adapted ; and they may be covered with a composition originally recommended by Mr. Willis. Two ounces of borax are to be dissolved in a pint of boiling water, and a sufficient quantity of slaked lime added, to give it the thickness of cream. This is to be applied by a painter's brush, and allowed to dry. Over this a thin paste is afterwards to be applied, formed of slaked lime and common linseed-oil, well mixed and perfectly plastic. In a day or two, the coating will be sufficiently dry to allow the use of the retort.

For joining together the parts of iron vessels, used in distillation, a mixture of the finest China clay, with a solution of borax, is well adapted. In all cases, the different parts of any apparatus made of iron should be accurately fitted by boring and grinding, and the above lute is to be applied to the part which is received into an aperture. This will generally be sufficient without any exterior luting ; otherwise the lute of clay, sand, and flax, already described, may be applied over the joint.

In every instance, where a lute or coating is applied, it is advisable to allow it to dry before the distillation is begun ; and even the fat lute, by exposure to the air during one or two days after its application, is much improved in firmness. The clay and sand lute is perfectly useless, except it be previously quite dry. In applying a lute, the part immediately over the juncture should swell outwards, and its diameter should be gradually diminished on each side. (See fig. 13, where the luting is shown, applied to the joining of the retort and receiver.)



Beside the apparatus already described, a variety of vessels and instruments are necessary, having little resemblance to each other, in the purposes to which they are adapted. Glass vessels are required for effecting *solution*, which often requires the application of heat, and sometimes for a considerable duration. In the latter case, it is termed digestion, and the vessel, fig. 4, called a *matrass*, is the most proper for performing it. When solution is required to be quickly effected, the bottle, fig. 5, with a rounded bottom, may be used; or a common Florence oil flask serves the same purpose extremely well, and bears, without cracking, sudden changes of temperature. For *precipitations*, and separating liquids from precipitates, either form of the decanting-jar (fig. 14), will be found useful; or, if preferred, it may be shaped as in fig. 26, *f*. Liquids, of different specific gravities, are separated by the vessel, fig. 3; the heavier fluid being drawn off through the cock *b*, and air being admitted by the removal of the stopper *a*, to supply its place. Glass rods, of various lengths, and spoons of the same material, or of porcelain, are useful for stirring acid and corrosive liquids; and a stock of cylindrical tubes, of various sizes, is required for occasional purposes. It is necessary also to be provided with a series of glass measures, graduated into drachms, ounces, and pints. The small tube, fig. 15, called a *dropping tube*, which is open at each end and blown in the middle into a ball, will be found useful in directing a fine stream of water upon the edges of a filtre, or any small object. The same purpose may, also, be very conveniently effected by fixing a piece of glass tube of small bore, two or three inches long, and bent at one end to an obtuse angle, into a hole bored in a cork, which may be used as the stopple of an eight ounce vial filled with water, fig. 25, *a*. On inverting the vial, and grasping the bottom part of it, the warmth of the hand expels either a few drops or a small stream of water, which may be directed upon any minute object. When the flow ceases, it may be renewed, if required, by setting the bottle, for a moment, with its mouth upwards (which admits a fresh supply of cool air), and then proceeding as before.

For the drying of precipitates, and other substances, by a

heat not exceeding  $212^{\circ}$ , a very useful apparatus is sold in London, by the makers of chemical implements. It is represented, supported by the ring of a lamp-stand, by fig. 27. The vessel *a* is of sheet-iron or copper japanned and hard-soldered; *c* is a conical vessel of very thin glass, having a rim, which prevents it, when in its place, from entirely slipping into *a*; and *d* is a moveable ring, which keeps the vessel *c* in its place. When the apparatus is in use, water is poured into *a* about as high as the dotted line; the vessel *c*, containing the substance to be tried, is immersed in the water, and secured by the ring *d*; and the whole apparatus set over an Argand's lamp. The steam escapes by means of the chimney *b*, through which a little hot water may be occasionally poured, to supply the waste by evaporation. By changing the shape of *c* to the segment of a sphere, still retaining the rim, I have found it a most convenient vessel for evaporating fluids. For the purpose of depriving organic substances of water without decomposing them, they may be exposed to a temperature of  $212^{\circ}$  Fahr. in a vacuum with sulphuric acid. An ingenious apparatus for this purpose, invented by Dr. Prout, is described in the *Annals of Philosophy*, vol. vi. p. 272.

Accurate beams and scales, of various sizes, with corresponding weights, some of which are capable of weighing several pounds, while the smaller size ascertains a minute fraction of a grain, are essential instruments in the chemical laboratory. A balance of great accuracy and sensibility, and at the same time attainable at a moderate expence, has been invented by Capt. Kater. It is described in the *Quarterly Journal*, xi. 280, and xii. 40. Mortars, also, should be at hand of various materials, such as glass, porcelain, agate, and metal. Wooden stands, too, of various kinds, for supporting receivers, should be provided.\* For purposes of this sort, and for occasionally raising to a proper height any article of apparatus, a series of blocks, made of well seasoned wood, eight inches (or any other number) square, and respectively eight, four, two, one, and half an inch in thickness, will be found extremely useful; since, by combining them in different ways, thirty-one different heights may be obtained.

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\* See Aikin's Chem. Dict. pl. iv. fig. 59, e.

The blow-pipe is an instrument of much utility in chemical researches. A small one, invented by Mr. Pepys, with a flat cylindrical box for condensing the vapour of the breath, and for containing caps, to be occasionally applied with apertures of various sizes, is perhaps the most commodious form.\* One of a much smaller size, for carrying in a pocket-book, has been contrived by Dr. Wollaston.† A blow-pipe, which is supplied with air from a pair of double bellows, worked by the foot, ‡ may be applied to purposes that require both hands to be left at liberty, and will be found useful in blowing glass, and in bending tubes. The latter purpose, however, may be accomplished by holding them over an Argand's lamp with double wicks. A simple and ingenious apparatus, in which atmospheric air is expelled from a jet by the pressure of a column of water, is described by Mr. Tilley in the 43d vol. of the Philosophical Magazine. Another contrivance of a similar kind, recommended by Dr. Clarke in the Annals of Philosophy, N. S. i. 428, is sold in London under the name of Toft's Blow-pipe, but it appears to me objectionable on account of the room which it occupies. Occasionally, when an intense heat is required, the flame of the blow-pipe, instead of being supported by the mouth or by common air, may be kept up by a stream of oxygen gas, expelled from a bladder or from a gas-holder.§ The blow-pipe invented by Mr. Brooke consists of a small square box of copper or iron, into which air is forced by a condensing syringe, and from which it is suffered to rush, through a tube of very small aperture, regulated by a stop-cock, against the flame of a lamp or candle.|| By means of a screw added to the syringe, the receiver may be filled with oxygen gas, or, as will be described hereafter, with a mixture of hydrogen and oxygen gases. Blow-pipes on this construction may be had of Mr. Newman, and of most of the other makers of philosophical instruments. The application

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\* See Aikin's Chem. Dict. pl. vii. fig. 71, 72, 73.

† It is described in Nich. Journ. xv. 284. See also pl. x. at the end of this volume.

‡ Phil. Mag. xliiii. 280.

§ See a representation of the apparatus for this purpose, in the Chemical Conversations, pl. ix.

Thomson's Annals, vii. 367 ; or Quarterly Journal, i. 65.

of the blow-pipe to chemical analysis, and especially to the examination of minerals, may be best learned from the ample and perspicuous directions contained in Berzelius's *Treatise on the Use of the Blow-pipe*, in one vol. 8vo. lately translated by Mr. Children.

In the course of this work, various other articles of apparatus will be enumerated, in detailing the purposes to which they are adapted, and the principles on which they are constructed. It must be remembered, however, that it is no part of my object to describe every ingenious and complicated invention, which has been employed in the investigation of chemical science: but merely to assist the student in attaining apparatus for general and ordinary purposes. For such purposes, and even for the prosecution of new and important inquiries, very simple means are sufficient; and some of the most interesting chemical facts may be exhibited and even ascertained, with the aid merely of Florence flasks, of common vials, and of wine glasses. In converting these to the purposes of apparatus, a considerable saving of expense will accrue to the experimentalist; and he will avoid the encumbrance of various instruments, the value of which consists in show, rather than in real utility.

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## SECTION II.

### *Of the Apparatus for Experiments on the Gases.*

FOR performing the necessary experiments on gases, many articles of apparatus are essential, that have not hitherto been described. It may assist the student in obtaining the necessary instruments, if a few of the most essential be here enumerated. In this place, however, I shall mention such only, as are necessary in making a few general experiments on that interesting class of bodies.

The apparatus, required for experiments on gases, consists partly of vessels fitted for containing the materials that afford them, and partly of vessels adapted for the reception of gases, and for submitting them to experiment.

1. For procuring such gases as are producible without a very strong heat, glass bottles, furnished with ground stoppers and bent tubes, are sufficient (plate ii. fig. 18). Of these several will be required, of different sizes and shapes, adapted to different purposes. If these cannot be procured, a Florence flask, with a cork perforated by a bent glass tube, or even by a tin pipe, will serve for obtaining some of the gases.

Those gases that require, for their liberation, a red heat, may be procured, by exposing to heat the substance capable of affording them, in earthen retorts or tubes; or in a gun barrel, the touch-hole of which has been accurately plugged by an iron pin. To the mouth of the barrel must be affixed a glass tube, bent so as to convey the gases where it may be requisite.

A very convenient apparatus, for obtaining such gases as cannot be disengaged without a red heat, is sold at the shops for philosophical apparatus in London. It consists of a cast-iron retort, having a jointed metallic conducting tube fitted to it by grinding; by means of which the gas may be conveyed in any direction, and to any moderate distance. It is represented as placed, when in actual use, between the bars of a common fire-grate (plate ix. fig. 85, *a*, *b*.)

2. For receiving the gases, glass jars, of various sizes (figs. 22, 23), are required, some of which should be furnished with necks at the top, fitted with ground stoppers. Others should be provided with brass caps, and screws, for the reception of air-cocks (fig. 22). Of these last (the air-cocks), several will be found necessary; and, to some of them, bladders, or elastic bottles, should be firmly tied, for the purpose of transferring gases. These jars will also be found extremely useful in experiments on the properties and effects of the gases. Some of them should be graduated into cubical inches.

To contain these jars, when in use, a vessel will be necessary, capable of holding a few gallons of water. This may either be of wood, if of considerable size; or, if small, of tin, japanned or painted. Plate iv. fig. 41, *ff*, exhibits a section of this apparatus, which has been termed the pneumato-chemical trough, or pneumatic cistern. Its size may vary with that of the jars employed; and, about two or three

inches from the top, it should have a shelf, on which the jars may be placed, when filled with air, without the risk of being upset. In this shelf should be a few small holes, to which inverted funnels may be soldered.

A glass tube, about 18 inches long, and three quarters of an inch diameter (fig. 24,) closed at one end, and divided into cubic inches, and tenths of inches, will be required for ascertaining the purity of air by nitrous gas. It should be accompanied also with a small measure, containing about two cubic inches, and similarly graduated. For employing the solution of nitrous gas in liquid sulphate of iron, glass tubes, about five inches long, and half an inch wide, divided decimally, are also necessary. Besides these, the experimentalist should be furnished with air funnels (fig. 19), for transferring gases from wide to narrow vessels.

An apparatus, almost indispensable in experiments on this class of bodies, is a GAZOMETER, which enables the chemist to collect and to preserve large quantities of gas, with the aid of only a few pounds of water. In the form of this apparatus there is considerable variety; but, at present, I have no other view than that of explaining its general construction and use. It consists of an outer fixed vessel *d* (plate iv. fig. 35), and an inner moveable one, *c*, both of japanned iron. The latter slides easily up and down within the other, and is suspended by cords passing over pulleys, to which are attached the counterpoises, *ee*. To avoid the encumbrance of a great weight of water, the outer vessel *d* is made double, or is composed of two cylinders, the inner one of which is closed at the top and at the bottom. The space of only about half an inch is left between the two cylinders, as shown by the dotted lines. In this space the hollow vessel *c* may move freely up and down. The interval is filled with water as high as the top of the inner cylinder. The cup, or rim, at the top of the outer vessel, is to prevent the water from overflowing, when the vessel *c* is forcibly pressed down, in which situation it is placed whenever gas is about to be collected. The gas enters from the vessel in which it is produced, by the communicating pipe *b*, and passes along the perpendicular pipe marked by dotted lines in the centre, into the cavity of the vessel *c*,

the act of evaporation. In this way we may completely separate nitre from common salt, the crystals of the latter being formed during evaporation; while those of nitre do not appear till some time after the fluid has cooled.

Salts, which are thus deposited in regular shapes, generally adhere to the surface of the vessel containing the solution, or to any substance, such as pieces of thread or of wood, introduced for the purpose of collecting them. But a still more effectual way of inducing crystallization is to immerse, in the solution, a crystal of the same kind with that which we expect to be formed. The crystal, thus exposed, receives successive additions to its several surfaces, and preserves its form, with a considerable addition to its magnitude. This curious fact was originally noticed by Le Blanc, who has founded on it a method of obtaining large and perfect crystals..

In some instances, the affinity of a salt for its solvent is so powerful, that it will not separate from it in the form of crystals; but will yet crystallize from another fluid, which is capable of dissolving it, and for which it has a weaker affinity. Potassa, for instance, cannot be made to crystallize from its watery solution, but will yet separate, in a regular form, from its solution in alcohol.

Every solid, that is susceptible of crystallization, has a tendency to assume a peculiar shape. Thus common salt, when most perfectly crystallized, forms regular cubes; nitre has the shape of a six-sided prism; and alum that of an octahedron. It has, indeed, been alleged, as an objection to the modern theory of crystallization, that minerals, differing essentially in their composition, have precisely the same primitive form. For example, the primitive form of carbonate of lime, and of the compound carbonate of lime and magnesia, is, in both, a regular rhomboid, so nearly resembling each other, as to have been supposed to be precisely the same. In this case, however, Dr. Wollaston has shown, that though the figures are similar, yet their angles, on admeasurement by a nice instrument, differ very appreciably.\* But other instances have been since brought forward by M. Beudant, in which

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\* Phil. Trans. 1812.

artificial salts, composed of *dissimilar* ingredients, have *the same* crystalline form; and Dr. Wollaston has satisfied himself of the accuracy of M. Beudant's remark, that the mixed sulphates of copper and iron, of zinc and iron, and of copper, zinc, and iron, assume forms, in which no difference has yet been discovered from that of simple sulphate of iron alone.\* He apprehends, indeed, that on minute investigation, some difference will be found, either in the angles or linear measures of those different salts; but till this has been established, the facts, as they stand, must be acknowledged to be exceptions to the principle, that *identity of crystalline form is necessarily connected with identity of chemical composition*. In the instances which have been given, the perfect transparency of the crystals forbids our considering them as an intermixture of foreign matter grouped together by sulphate of iron; and this explanation is, also, irreconcilable with the fact, discovered by Dr. Wollaston, that a mixed solution of sulphates of zinc and copper, in certain proportions, affords crystals which, though containing no iron, still agree so nearly in form with those of sulphate of iron, that he could not undertake to point out any difference between them.

It has been long known that the same solid admits of great varieties of crystalline figure, without any variation of its chemical composition. Calcareous spar, for example, appears in six-sided prisms, in three or six-sided pyramids, and in many other shapes. These varieties are occasioned by accidental circumstances, which modify the operation of the force of cohesion. The diversities of shape are, on first view, extremely numerous; and yet, upon a careful examination and comparison, they are found to be reducible to a small number of simple figures, which, for each individual species, is always the same.

The attempt to trace all the observed forms of crystals to a few simple or primary ones, seems to have originated with Bergman †. In the instance of calcareous spar, this distinguished chemist demonstrated that its numerous modifications

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\* Thomson's Annals, xi. 268, 283. xiii. 126, and Mitscherlich Ann. de Chim. et Phys. xiv. 172, 326.

† Bergman's Essays, ii.



may possibly result from one simple figure, the rhomb, by the accumulation of which, in various ways, crystals of the most opposite forms may be generated. This theory he extended to crystals of every kind; and he accounted for the differences of their external figures, by varieties of their mechanical elements or minute molecules.

About the same period with Bergman, or immediately afterwards, M. Romé de l'Isle pursued still farther the theory of the structure of crystals. He reduced the study of crystallography to principles more exact, and more consistent with observation. He classed together, as much as he was able, crystals of the same nature. From among the different forms belonging to the same species, he selected, for the primitive form, one which appeared to him to be the most proper, on account of its simplicity. Supposing this to be truncated in different manners, he deduced the other forms, and established a certain gradation, or series of passages, from the primitive form to complicated figures, which on first view would scarcely appear to have any connexion with it. To the descriptions and figures of the primitive forms, he added the mechanical measurement of the principal angles, and showed that these angles are constantly the same in each variety. It must be acknowledged, however, that the primitive forms, assumed by this philosopher, were entirely imaginary, and not the result of any experimental analysis. His method was to frame an hypothesis; and then to examine its coincidence with actual appearances. On his principles any form might have been the primitive one, and any other have been deduced from it.

It was reserved for the sagacity of the Abbé Haüy to unfold the true theory of the structure of crystals, and to support it both by experimental and mathematical evidence. By the mechanical division of a complicated crystal, he first obtains the simple form, and afterwards constructs, by the varied accumulation of the primitive figure, according to mathematical synthesis, all the observed varieties of that species.

Every crystal may be divided by means of proper instruments; and, if split in certain directions, presents plane and smooth surfaces. If split in other directions, the fracture is rugged, is the mere effect of violence, and is not guided by

the natural joining of the crystal. This fact had been long known to jewellers and lapidaries; and an accidental observation of it proved, to the Abbé Haiüy, the key of the whole theory of crystallization. By the skilful division of a six-sided prism of calcareous spar, he reduced it to a rhomb, precisely resembling that which is known under the name of Iceland crystal. Other forms of calcareous spar were subjected to the same operation; and, however different at the outset, finally agreed in yielding, as the last product, a rhomboidal solid. It was discovered also by Haiüy, that if we take a crystal of another kind (the cubic fluor spar for instance), the nucleus, obtained by its mechanical division, will have a different figure, *viz.* an octahedron. Other crystallized bodies produce still different forms; which are not, however, very numerous. Those which have hitherto been discovered, are reducible to six; the parallelepipedon, which includes the cube, the rhomb, and all the solids which are terminated by six faces, parallel two and two; the tetrahedron; the octahedron; the regular hexahedral prism; the dodecahedron with equal and similar rhomboidal planes; and the dodecahedron with triangular planes.

The solid of the primitive form, or nucleus of a crystal obtained by mechanical division, may be subdivided in a direction parallel to its different faces. All the sections thus produced being similar, the resulting solids are precisely similar in shape to the nucleus, and differ from it only in size, which continues to decrease as the division is carried farther. To this division, however, there must be a limit, beyond which we should come to particles so small, that they could no longer be divided. At this term, therefore, we must stop: and to these last particles, the result of an analysis of the primitive nucleus, and similar to it in shape, Haiüy has given the name of the *integral molecule*. If the division of the nucleus can be carried on in other directions than parallel to its faces, the integral molecule may then have a figure different from that of the nucleus. The forms, however, of the integral molecule, which have hitherto been discovered, are only three; the tetrahedron, the simplest of pyramids; the triangular prism, the simplest of prisms; and the parallelepipedon, including

the cube and rhomboid, the simplest of solids which have their faces parallel two and two. With respect to octahedral crystals, there is a difficulty, whether the octahedron, or tetrahedron, is to be adopted as the primitive form; and, whichever be chosen, since neither of them can fill space without leaving vacuities, it is not easy to conceive any arrangement, by which the particles will remain at rest. To obviate this difficulty, Dr. Wollaston has suggested that, in such instances, the elementary particles may be perfect spheres; and by the due application of spheres to each other, he has shown, that a variety of crystalline forms may be produced; \* *viz.* the octahedron, the tetrahedron, and the acute rhomboid. If other particles, having the same relative arrangement, be supposed to have the shape of oblate spheroids, the regular rhomboid will be the resulting figure; and if the spheroids be oblong instead of oblate, they will generate prisms of three or six sides. The cube, also, Dr. Wollaston has shown, may be explained by the aggregation of spheroidal particles.

A method of developing the structure of crystals, by a new process, which appears greatly superior to that of mechanical division, has been described by Mr. Daniel.† It consists in exposing any moderately soluble salt to the slow and regulated action of a solvent. A shapeless mass of alum, for instance, weighing about 1500 grains, being immersed in 15 ounce measures of water, and set by, in a quiet place, for a period of three or four weeks, will be found to have been more dissolved toward the upper than the lower part, and to have assumed a pyramidal form. On further examination, the lower end of the mass will present the form of octahedrons and sections of octahedrons, in high relief and of various dimensions. They will be most distinct at its lower extremity, becoming less so as they ascend. This new process of dissection admits of extensive application. Borax in the course of six weeks, exhibits eight sided prisms with various terminations; and other salts may be made to unfold their external structure by the slow agency of water. Car-

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\* Phil. Trans. 1813, p. 51.

† Jour. of Science and the Arts, i. 24.

bonate of lime, carbonate of strontites, and carbonate of barytes, give also distinct results, when acted upon by weak acids; and even amorphous masses of those metals, which have a tendency to assume a crystalline form, such as bisinuth, antimony, and nickel, when exposed to very dilute nitric acid, presented at the end of a few days distinct crystalline forms. Large crystals of sulphuret of antimony, Mr. Faraday has also found, admirably illustrate Mr. Daniel's mode of displaying crystalline texture. When such a crystal is introduced into a portion of fused sulphuret, it begins to melt down, but not uniformly, for crystals are left more than half an inch long projecting from it.\* The results of these experiments, when minutely traced and investigated; afford strong confirmation to the theory, that the spheroidal is the true form of the ultimate particles of crystallized bodies.

The primitive form, and that of the integral molecule having been experimentally determined by the dissection of a crystal, the next step is to discover the law, according to which these molecules are arranged, in order to produce, by their accumulation around the primitive figure, the great variety of secondary forms. What is most important in the discoveries of Haüy, and what constitutes in fact the essence of his theory, is the determination of these laws, and the precise measurement of their action. He has shown that all the parts of a secondary crystal, superadded to the primitive nucleus, consist of laminae, which decrease gradually by the subtraction of one or more layers of integrant molecules; so that theory is capable of determining the number of these ranges, and, by a necessary consequence, the exact form of the secondary crystal.

By the development of these laws of decrement, Haüy has shown how, from variations of the arrangement of the integrant molecules, a great variety of secondary figures may be produced. Their explanation, however, would involve a minuteness of detail, altogether unsuitable to the purpose of this work: and I refer, therefore, for a very perspicuous statement of them, to the first and ninth volumes of the *Philosophical Magazine*.

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\* *Jour. of Science and the Arts*, xi. 202.

A popular view of the subject of crystallography may be found also in Mr. Larkin's "Introduction to Solid Geometry," London, 1820; and models of crystals, very neatly and accurately cut in wood, may be procured from the author of that work, which will essentially facilitate the student's progress. The use of the *goniometer* is quite necessary to the accurate determination and description of the forms of crystals. When great precision is not required, and the crystal is of considerable size, the *common goniometer* will sufficiently answer the purpose; but to obtain very correct admeasurements, the *reflecting goniometer* of Dr. Wollaston is alone worthy of dependence. Both these instruments are described, and perspicuous directions given for their use, in a very useful little volume published by Mr. William Phillips, under the title of "An Elementary Introduction to the Knowledge of Mineralogy," and also in the first volume of "Conversations of Mineralogy," where distinct and excellent engravings are given of both instruments.



## SECTION II.

### *Of Chemical Affinity, and the General Phenomena of Chemical Action.*

CHEMICAL affinity, like the cohesive attraction, is effective only at insensible distances: but it is distinguished from the latter force, in being exerted between the particles or atoms of bodies of *different kinds*. The result of its action is not a mere aggregate, having the same properties as the separate parts, and differing only by its greater quantity or mass, but a new compound, in which the properties of the components have either entirely or partly disappeared, and in which new qualities are also apparent. The combinations effected by chemical affinity are permanent, and are destroyed only by the interference of a more powerful force, either of the same or of a different kind.

As a general exemplification of chemical action, we may examine that which takes place between potash and sulphuric

acid. In their separate state, each of these bodies is distinguished by striking peculiarities of taste, and by other qualities. The alkali, on being added to blue vegetable infusions, changes their colour to green; and the acid turns them red. But if we add the one substance to the other, very cautiously and in small quantities, examining the effect of each addition, we shall at length attain a certain point, at which the liquid will possess neither acid nor alkaline qualities; the taste will be converted into a bitter one; and the mixture will produce no effect on blue vegetable colours. Here then, the qualities of the constituent parts, or at least some of their most important ones, are destroyed by combination. When opposing properties thus disappear, the bodies combined have been said to *saturate* each other; and the precise term, at which this takes place, has been called the *point of saturation*. It is advisable, however, to restrict this expression to weaker combinations, where there is no remarkable alteration of qualities, as in cases of solution; and to apply to those results of more energetic affinities, which are attended with loss of properties, the term *neutralization*.

At the same time that the properties of bodies disappear on combination, other new qualities, both sensible and chemical, are acquired; and the affinities of the components for other substances become in some cases increased, in others diminished in energy. Sulphur, for example, is destitute of taste, smell, or action on vegetable colours; and oxygen gas is, in these respects, equally inefficient. But the compound of sulphur and oxygen is intensely acid; the minutest portion instantly reddens blue vegetable infusions; and the acid is disposed to enter into combination with a variety of bodies, for which its components evinced no affinity. Facts of this kind sufficiently refute the opinion of the older chemists, that the properties of compounds are *intermediate* between those of their component parts; for, in instances like the foregoing, the compound has qualities, not a vestige of which can be traced to either of its elements.

It is not, however, in all cases, that the change of properties is so distinct and appreciable by the senses, as in the instances which have been just now described. In some examples of

chemical union, the change is scarcely perceptible to the eye or the taste, when the chemist is nevertheless certain that combination must have taken place. This occurs chiefly in the mixture of saline solutions with each other, where a complete exchange of principles ensues, without any evident change of properties. Examples of this kind, cannot, however, be understood, till the subject of complex affinity has been first elucidated.

The existence of chemical affinity between any two bodies is inferred, therefore, from their entering into chemical combination; and that this has happened, a change of properties may be considered as a sufficient proof, even though the change may not be very obvious, and may require accurate examination to be perceived at all.

The proof, which establishes the nature of chemical compounds, is of two kinds, *synthesis* and *analysis*. Synthesis consists in effecting the chemical union of two or more bodies; and analysis in separating them from each other, and exhibiting them in a separate state. When we have a compound of two or more ingredients, which are themselves compounded also, the separation of the compounds from each other may be called the *proximate analysis* of the body; and the farther separation of these compounds into their most simple principles, its *ultimate analysis*. Thus the proximate analysis of sulphate of potash consists in resolving it into potash and sulphuric acid; and its ultimate analysis is effected by decomposing the potash into potassium and oxygen, and the sulphuric acid into oxygen and sulphur.

When the analysis of any substance has been carried as far as possible, we arrive at its most simple principles, or *elements*, by which expression we are to understand, not a body that is *incapable* of further decomposition, but only one which *has not yet been decomposed*. The progress of chemical science, for several centuries past, has consisted in carrying still farther the analysis of bodies, and in proving those to be compounded, which had before been considered as elementary.

Beside the alteration of properties, which usually accompanies chemical action, there are certain other phenomena, which are generally observed to attend it.

1st. In almost every instance of chemical union, the *specific gravity* of the compound is greater than might have been inferred from that of its components; and this is true both of weaker and more energetic combinations. When equal weights of water and sulphuric acid are made to combine, the specific gravity of the resulting liquid is not the mean, but considerably greater than the mean. The law extends also to solids. But though general, it is not universal; for in a very few instances, chiefly of aëriform fluids, condensation does not attend chemical union. And in the combination of metals with each other the reverse even takes place, the compound being, in some cases, specifically lighter than might have been expected, from the specific gravity of its elements, and their proportion to each other.

2dly. When bodies combine chemically, it may be received as a general fact, that their *temperature* changes. Equal weights of oil of vitriol and water, both at the temperature of 50° of Fahr. are heated, by sudden mixture, to considerably above 212°. In other examples, a contrary effect takes place, and a diminished temperature, or, in other words, a production of cold, is observed. This is all that it is at present necessary to state on the subject, which will be more fully considered when we come to treat of caloric.

3dly. The *forms of bodies* are often materially changed by chemical combination. Two solids may, by their union, become fluid; or two fluids may become solid. Solids are also often changed into aëriform fluids; and, in many instances, the union of two airs, or gases, is attended with their sudden conversion into the solid state. By long exposure of quicksilver to a moderate heat, we change it from a brilliant liquid into a reddish scaly solid; and by heating this solid in a retort, we obtain an aëriform fluid, or gas, in considerable quantity, and recover the quicksilver in its original form.

4thly. Change of *colour* is a frequent, but not universal concomitant of chemical action. In some cases, brilliant colours are destroyed, as when chlorine is made to act on solution of indigo. In other instances, two substances, which are nearly colourless, form, by their union, a compound distinguished by beauty of colour, as when liquid potash is added



to very dilute syrup of violets. Certain colours appear also to belong essentially to chemical compounds, and to be characteristic of them. Thus 100 parts of quicksilver, and 4 of oxygen, invariably give a black compound; and the same quantity, with 8 parts of oxygen, a red compound.

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### SECTION III.

#### *Of the Proportions in which bodies combine; and of the Atomic Theory.*

In the chemical combination of bodies with each other, a few leading circumstances deserve to be remarked.

1st. Some bodies unite in all proportions; for example, water and sulphuric acid, or water and alcohol.

2dly. Other bodies combine in all proportions, as far as a certain point, beyond which combination no longer takes place. Thus water will take up successive portions of common salt, until at length it becomes incapable of dissolving any more. In cases of this sort, as well as in those included under the first head, combination is weak and easily destroyed, and the qualities which belonged to the components in their separate state continue to be apparent in the compound.

3dly. There are many examples in which bodies unite in one proportion only; and in all such cases the proportion of the elements of a compound must be uniform for the species. Thus hydrogen and oxygen unite in no other proportions, than those constituting water, which, by weight, are very nearly  $11\frac{1}{2}$  of the former to  $88\frac{1}{2}$  of the latter, or 1 to  $7\frac{1}{2}$ . In cases of this sort, the combination is generally energetic; and the characteristic qualities of the components are no longer observable in the compound.

4thly. Other bodies unite in several proportions: but these proportions are definite, and, in the intermediate ones, no combination ensues. Thus 100 parts by weight of charcoal combine with  $132\frac{1}{2}$  of oxygen, or with 265, but with no intermediate quantity; 100 parts of manganese combine with 14

of oxygen, or with 28, or with 42, or with 56, and with those proportions only.

Now it is remarkable, that when one body enters into combination with another, in several different proportions, the numbers indicating the greater proportions are exact simple multiples of that denoting the smallest proportion. In other words, if the smallest proportion in which B combines with A, be denoted by 10, A may combine with twice 10 of B, or with three times 10, and so on; but with no intermediate quantities. There cannot be a more striking instance of this law than that above mentioned, of the compounds of manganese with oxygen; in which the oxygen of the three last compounds may be observed to be a multiplication of that of the first (14) by the numbers 2, 3, and 4. Examples, indeed, of this kind have, of late, so much increased in number, that the law of simple multiples bids fair to become universal, with respect at least to chemical compounds, the proportions of which are definite.

Facts of this kind are not only important in themselves, but also on account of the generalizations that have been deduced from them; for on them Mr. Dalton has founded what may be termed the *Atomic Theory of the chemical Constitution of Bodies*. Till this theory was proposed, we had no adequate explanation of the uniformity of the proportions of chemical compounds; or of the nature of the cause which renders combination, in other proportions, impossible. In this place I shall offer only a brief illustration of the theory; for in the course of the work I shall have occasion to apply it to the explanation of a variety of phenomena.

Though we appear, when we effect the chemical union of bodies, to operate on *masses*, yet it is consistent with the most rational view of the constitution of bodies to believe, that it is only between their *ultimate particles*, or *atoms*, that combination takes place. By the term *atoms*, it has been already stated, we are to understand the smallest parts of which bodies are composed. An atom, therefore, must be mechanically indivisible, and of course a fraction of an atom cannot exist, and is a contradiction in terms. Whether the atoms of dif-

rent bodies be of the same size, or of different sizes, we have no sufficient evidence. The probability is, that the atoms of different bodies are of unequal sizes; but it cannot be determined whether their sizes bear any regular proportion to their relative weights. We are equally ignorant of their shape; but it is probable, though not essential to the theory, that they are spherical. This, however, requires a little qualification. The atoms of all bodies probably consist of a solid corpuscle, forming a nucleus, and of an atmosphere of heat, by which that corpuscle is surrounded; for absolute contact is never supposed to take place between the atoms of bodies. The figure of a simple atom may readily, therefore, be conceived to be spherical. But in compound atoms, consisting of a single central atom, surrounded by other atoms of a different kind, it is obvious that the figure (contemplating the solid corpuscles only) cannot be spherical; yet if we include the atmosphere of heat, the figure of a compound atom may be spherical, or some shape approaching to a sphere.

Taking for granted that combination takes place between the atoms of bodies only, Mr. Dalton has deduced, from the relative weights in which bodies unite, the relative weights of their ultimate particles, or atoms. When only one combination of any two elementary bodies exists, he assumes, unless the contrary can be proved, that its elements are united atom to atom singly. Combinations of this sort he calls *binary*. But if several compounds can be obtained from the same elements, they combine, he supposes, in proportions expressed by some simple multiple of the number of atoms. The following table exhibits a view of some of these combinations:

- 1 atom of A + 1 atom of B = 1 atom of C, binary.
- 1 atom of A + 2 atoms of B = 1 atom of D, ternary.
- 2 atoms of A + 1 atom of B = 1 atom of E, ternary.
- 1 atom of A + 3 atoms of B = 1 atom of F, quaternary.
- 3 atoms of A + 1 atom of B = 1 atom of G, quaternary.

A different classification of atoms has been proposed by Berzelius, viz. into, 1stly, *elementary* atoms; 2dly, *compound* atoms. The compound atoms he divides again into three

different species, namely, 1st, atoms formed of only two elementary substances united, or *compound atoms of the first order*: 2dly, atoms composed of more than two elementary substances; and these, as they are only found in organic bodies, or bodies obtained by the destruction of organic matter, he calls *organic atoms*: 3dly, atoms formed by the union of two or more compound atoms; as for example, the salts. These he calls *compound atoms of the second order*.

If elementary atoms of different kinds were of the same size, the greatest number of the atoms of A that could be combined with an atom of B would be 12; for this is the greatest number of spherical bodies that can be arranged in contact with a sphere of the same diameter. But this equality of size, though adopted by Berzelius, is not necessary to the hypothesis of Mr. Dalton; and is, indeed, supposed by him not to exist.

As an illustration of the mode in which the weight of the atoms of bodies is determined, let us suppose that any two elementary substances, A and B, form a binary compound; and that they have been proved experimentally to unite in the proportion, by weight, of 5 of the former to 4 of the latter; then, since, according to the hypothesis, they unite particle to particle, those numbers will express the relative weights of their atoms. But besides combining atom to atom singly, 1 atom of A may combine with 2 of B, or with 3, 4, &c. Or 1 atom of B may unite with 2 of A, or with 3, 4, &c. When such a series of compounds exists, the relative proportion of their elements ought necessarily, on analysis, to be proved to be 5 of A to 4 of B; or 5 to  $(4 + 4 =) 8$ ; or 5 to  $(4 + 4 + 4 =) 12$ , &c.; or, contrariwise, 4 of B to 5 of A; or 4 to  $(5 + 5 =) 10$ ; or 4 to  $(5 + 5 + 5 =) 15$ . Between these there ought to be no intermediate compounds: and the existence of any such (as 5 of A to 6 of B, or 4 of B to  $7\frac{1}{2}$  of A) would, if clearly established, militate against the hypothesis.

To verify these numbers, it may be proper to examine the combinations of A and B with some third substance, for example with C. Let us suppose that A and C form a binary compound, in which analysis discovers 5 parts of A and 3 of C. Then, if C and B are, also, capable of forming a binary com-

pound, the relative proportion of its elements ought to be 4 of B to 3 of C; for these numbers denote the relative weights of their atoms. Now this is precisely the method, by which Mr. Dalton has deduced the relative weights of oxygen, hydrogen, and nitrogen; the two first from the known composition of water, and the two last from the proportion of the elements of ammonia. Extending the comparison to a variety of other bodies, he has obtained a scale of the relative weights of their atoms.

In several instances, additional evidence is acquired of the accuracy of the weight, assigned to an element, by our obtaining the same number from the investigation of several of its compounds. For example:

1. In *water*, the hydrogen is to the oxygen as 1 to 8.
2. In *olefiant gas*, the hydrogen is to the carbon as 1 to 6.
3. In *carbonic oxide* the oxygen is to the carbon as 8 to 6.

Whether, therefore, we determine the weight of the atom of carbon, from the proportion in which it combines with hydrogen, or with oxygen, we arrive at the same number 6; an agreement which, as it occurs in various other instances, can scarcely be an accidental coincidence. In a similar manner, 8 is deducible, as representing the atom of oxygen, both from the combination of that base with hydrogen and with carbon; and 1 is inferred to be the relative weight of the atom of hydrogen from the two principal compounds into which it enters.

In selecting the body, which should be assumed as unity, Mr. Dalton has been induced to fix on hydrogen, because it is that body which unites with others in the smallest proportion. Thus, in *water*, we have 1 of hydrogen by weight to 8 of oxygen; in *ammonia*, 1 of hydrogen to 14 of nitrogen; in *carbureted hydrogen*, 1 of hydrogen to 6 of carbon; and in *sulphureted hydrogen*, 1 of hydrogen to 16 of sulphur. Taking for granted that all these bodies are binary compounds, we have the following scale of numbers, expressive of the relative weights of the atoms of their elements:

Hydrogen .....	1
Oxygen .....	8
Nitrogen .....	14
Carbon .....	6
Sulphur .....	16

Drs. Wollaston and Thomson, and Professor Berzelius, on the other hand, have assumed oxygen as the decimal unit, (the first making it 10, the second 1, and the third 100,) chiefly with a view to facilitate the estimation of its numerous compounds with other bodies. This, perhaps, is to be regretted, even though the change may be in some respects eligible, because it is extremely desirable that chemical writers should employ an universal standard of comparison for the weights of the atoms of bodies. It is easy, however, to reduce their numbers to Mr. Dalton's by the rule of proportion. Thus as 8 (Mr. Dalton's number for oxygen, corrected by the latest experiments) is to 1 (his number for hydrogen), so is 10 (Dr. Wollaston's number for oxygen) to 1.25 the number for hydrogen.

Sir H. Davy has assumed, with Mr. Dalton, the atom of hydrogen as unity; but that philosopher, and Berzelius also, have modified the theory, by taking for granted that water is a compound of one proportion (atom) of oxygen, and two proportions (atoms) of hydrogen. This is founded on the fact, that two measures of hydrogen gas and one of oxygen gas, are necessary to form water; and on the supposition, that equal measures of different gases contain equal numbers of atoms. And as, in water, the hydrogen is to the oxygen by weight as 1 to 8, two atoms or volumes of hydrogen must, on this hypothesis, weigh 1, and one atom or volume of oxygen 8, or if we denote a single atom of hydrogen by 1, we must express an atom of oxygen by 16. It is objectionable, however, to this modification of the atomic theory, that it contradicts a fundamental proposition of Mr. Dalton, the consistency of which with mechanical principles he has fully shown; namely, that *that* compound of any two elements, which is with most difficulty decomposed, must be presumed, unless the contrary can be proved, to be a binary one.

It is easy to determine, in the manner already explained, the relative weights of the atoms of two elementary bodies, which unite only in one proportion. But when one body unites, in different proportions, with another, it is necessary, in order to ascertain the weight of its atom, that we should know the smallest proportion in which the former combines with the latter. Thus, if we have a body A; 100 parts of which by weight combine with not less than 32 of oxygen, the relative weight of its atom will be to that of oxygen as 100 to 32; or, reducing these numbers to their lowest terms, as 25 to 8; and the number 25 will, therefore, express the relative weight of the atom of A. But if, in the progress of science, it should be found, that 100 parts of A are capable of uniting with 16 parts of oxygen, then the relative weight of the atom of A must be doubled, for as 100 is to 16, so is 50 to 8. This example will serve to explain the changes, that have been sometimes made, in assigning the weights of the atoms of certain bodies; changes, which, it may be observed, always consist either in a multiplication, or division, of the original weight, by some simple number.

There are (it must be acknowledged) a few cases, in which one body combines with another in different proportions; and yet the greater proportions are not multiples of the less, by any entire number. For example, we have two oxides of iron, the first of which consists of 100 iron and about 30 oxygen; the second of 100 iron and about 45 oxygen. But the numbers 30 and 45 are to each other as 1 to  $1\frac{1}{2}$ . It will, however, render these numbers (1 and  $1\frac{1}{2}$ ) consistent with the law of simple multiples, if we multiply each of them by 2, which will change them to 2 and 3; and if we suppose that there is an oxide of iron (though it has not yet been obtained experimentally), consisting of 100 iron and 15 oxygen; for the multiplication of this last number by 2 and 3, will then give us the known oxides of iron.

In some cases, where we have the apparent anomaly of 1 atom of one substance, united with  $1\frac{1}{2}$  of another, it has been proposed, by Dr. Thomson,\* to remove the difficulty, by multiplying both numbers by 2; and by assuming that, in such compounds, we have 2 atoms of the one combined with

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\* Thomson's Annals, v. 187.

3 atoms of the other. Such combinations, it is true, are exceptions to a law deduced by Berzelius; *that, in all inorganic compounds, one of the constituents is in the state of a single atom.* But they are in no respect inconsistent with the views of Mr. Dalton; and are, indeed, expressly admitted by him to be compatible with this hypothesis, as well as confirmed by experience.\* Thus it will appear, in the sequel, that some of the compounds of nitrogen with oxygen are constituted in this way.

Several objections have been proposed to the theory of Mr. Dalton; but, of these, I shall notice only the most important.

1. It has been contended, that we have no evidence, when one combination only of two elements exists, that it must be a binary one; and that we might equally well suppose it to be a compound of two atoms of the one body, with one atom of the other. In answer to this objection, we may urge the probability that when two elementary bodies A and B unite, the most energetic combination will be that in which one atom of A is combined with one atom of B; for an additional atom of B will introduce a new force, diminishing the attraction of those elements for each other, namely, the mutual repulsion of the atoms of B; and this repulsion will be the greater, in proportion as we increase the number of the atoms of B.

2dly. It has been said, that, when more than one compound of two elements exist, we have no proof which of them is the binary compound, and which the ternary; for example, that we might suppose carbonic acid to be a compound of an atom of charcoal and an atom of oxygen, and carbonic oxide to be a compound of an atom of oxygen with two atoms of charcoal. To this objection, however, it is a satisfactory answer, that such a constitution of carbonic acid and carbonic oxide would be directly contradictory of a law of chemical combination, namely, that it is attended, in most cases, with an increase of specific gravity. It would be absurd, therefore, to suppose carbonic acid, which is the heavier body, to be only once compounded, and carbonic oxide, which is the lighter, to be twice compounded. Moreover, it is universally observed, that of chemical compounds, the most simple are the most difficult to be decomposed; and this being the case with carbonic oxide,

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\* Thomson's Annals, iii. 174.



we may naturally suppose it to be more simple than carbonic acid.

3dly. It has been remarked, that instead of supposing water to consist of an atom of oxygen united with an atom of hydrogen, and that the atom of the former is  $7\frac{1}{2}$  times heavier than that of the latter, we might, with equal probability, conclude that, in water, we have  $7\frac{1}{2}$  times more atoms *in number* of oxygen than of hydrogen. But this, if admitted, would involve the absurdity, that in a mixture of hydrogen and oxygen gases, so contrived that the ultimate atoms of each should be in equal number, seven atoms of oxygen should desert all the proximate atoms of hydrogen, in order to unite with one at a distance, for which they must necessarily have a less affinity. In this case, a less force must overcome a greater; and, finally, only a small number of the atoms of hydrogen would be engaged by the atoms of oxygen, the rest remaining in a state of freedom.

It would be claiming too much, however, for the theory of Mr. Dalton to assert that, in its present state, it is to be considered as fully established in all its details. In a variety of cases, as will appear in the progress of this work, we stand in need of analyses sufficiently exact to enable us to assign, with any confidence, the relative weights in which bodies combine. It is probable also, that many of these, now considered as well determined, will hereafter be essentially changed. The instances, in which the theory agrees with the results of analysis, are already too numerous to allow them to be considered as accidental coincidences; and no phenomena have hitherto been shown to be irreconcilable with the hypothesis. Its value and importance, if confirmed by the accession of new facts, will be scarcely less felt as a guide to further investigations into the constitution of bodies, than as a test of the accuracy of our present knowledge; and the universality of its application to chemical phenomena will be scarcely inferior to that of the law of gravitation in explaining the facts of natural philosophy.\*

\* A perspicuous and able statement of the atomic theory, published by Mr. Ewart, in the sixth volume of Thomson's Annals, deserves the reader's perusal. See also Dr. Mc'Nevin's paper on the Atomic Theory, xvi. 195—289.

A modification of the law of definite proportions, so far as respects aëriiform bodies, has been proposed by Gay Lussac, namely, that they combine in proportions determinable not by weight but by *volume*, the ratios being 1 *measure* of A to 1 of B, or 1 to 2, or 1 to 3, &c. Water, for example, results from the union of 2 volumes of hydrogen with 1 volume of oxygen; muriate of ammonia from 1 volume of muriatic acid gas + 1 of ammonia; nitrous gas from 1 measure of oxygen + 1 of nitrogen; nitrous oxide from 1 oxygen + 2 nitrogen; nitrous acid from 2 oxygen + 1 nitrogen. In some instances, as in that of water, this law is not inconsistent with the atomic theory; but in other instances it cannot be reconciled with the relative weights assigned to the atoms of certain elementary bodies. In nitrous gas, for example, which Mr. Dalton conceives to be formed by the union of 1 atom of oxygen with 1 atom of nitrogen, equal volumes of those gases would give for the relative weights of oxygen and nitrogen, numbers differing widely from those derived by other methods. The two hypotheses of atoms and of volumes cannot, therefore, both be true; and from some well ascertained exceptions to the latter, it appears to me that the theory of volumes will scarcely be found tenable.

Before dismissing the consideration of the proportions in which bodies combine, it will be proper to notice a few general principles, which, though they are connected with the atomic theory, have been derived from experience.

1. When we have ascertained the proportion in which any two or more bodies A B C, &c. of one class neutralize another body X of a different class, it will be found that the same relative proportions of A B C, &c. will be required to neutralize any other body of the same class as X. Thus, since 100 parts of real sulphuric acid, and 68 (omitting fractions) of muriatic acid neutralize 118 of potash, and since 100 of sulphuric acid neutralize 71 of lime, we may infer that 68 of muriatic acid will neutralize the same quantity (71) of lime. The great importance of this law will readily be perceived, not only as it enables us to anticipate, but also to correct, the results of analysis.

2dly. If the quantities of two bodies, A and B, that are ne-

cessary to saturate a given weight of a third body X, be represented by  $q$  and  $r$ , these quantities may be called *equivalents*. Thus, in the example above cited, 100 parts of sulphuric acid and 68 of muriatic acid, are equivalents of each other. A *Table of Equivalents*, which will be found extremely useful in various calculations, will be given in the Appendix. By adapting a table of this sort to a moveable scale, on the principle of Gunter's sliding rule, Dr. Wollaston has lately constructed an instrument, called the *Logometric Scale of Chemical Equivalents*, which is capable of solving, with great facility, a number of problems, interesting both to the scientific and practical chemist.\* Some applications of this instrument, to researches into the constitution of organic bodies, have been pointed out by Dr. Prout. (Ann. of Phil. vi. 270.)



#### SECTION IV.

##### *Of Elective Affinity.*

AN important law of affinity, which is the basis of almost all chemical theory, is, that one body has not the same force of affinity towards a number of others, but attracts them unequally. Thus A will combine with B in preference to C, even when these two bodies are presented to it under equally favourable circumstances. Or, when A is united with C, the application of B will detach A from C, and we shall have a new compound consisting of A and B, C being set at liberty. Such cases are examples of what is termed in chemistry *simple decomposition*, by which it is to be understood that a body acts upon a compound of two ingredients, and unites with one of

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\* This instrument may be had, with printed instructions for its use, of Mr. Cary, Optician, London; and its cost is so trifling, that I consider a plate of it to be quite unnecessary. A common sliding rule will be found a most useful accompaniment to it. This also, with a book of instructions for its use, by Mr. Bevan, may be had of Mr. Cary. Facility in the use of the common sliding rule will be found extremely useful to the chemist, especially in all operations of arithmetic, in which proportion is concerned.

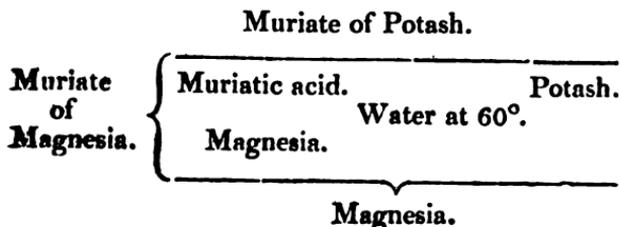
its constituents, leaving the other at liberty. And as the forces of affinity of one body to a number of others vary, this body has been metaphorically represented as making an election; and the affinity has been called *single elective affinity*. Thus if to the muriate of lime, consisting of lime and muriatic acid, we add potash, the muriatic acid exerts a stronger elective affinity for the potash than for the lime; and the lime falls down in the state of a powder, or is *precipitated*. Of facts of this kind a great variety have been comprehended in the form of tables, the first idea of which seems to have occurred nearly a century ago, to Geoffroy, a French chemist. The substance, whose affinities are to be expressed, is placed at the head of a column, and is separated from the rest by a horizontal line. Beneath this line are arranged the bodies, with which it is capable of combining, in the order of their respective forces of affinity; the substance which it attracts most strongly being placed nearest to it, and that, for which it has the least affinity, at the bottom of the column. The affinities of muriatic acid, for example, are exhibited by the following series:—

MURIATIC ACID.

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Barytes,  
Potash,  
Soda,  
Lime,  
Ammonia,  
Magnesia,  
&c. &c.

Simple decompositions may be expressed also by another form, contrived by Bergman. Thus the following scheme illustrates the decomposition of muriate of magnesia by potash:—



The original compound (muriate of magnesia) is placed on the outside and to the left of the verticle bracket. The included space contains the original principles of the compound, and also the body which is added to produce decomposition. Above and below the horizontal lines are placed the new results of their action. The point of the lower horizontal line being turned downwards, denotes that the magnesia falls down or is precipitated; and the upper line, being perfectly straight, shows, that the muriate of potash remains in solution. If both the bodies had remained in solution, they would both have been placed above the upper line; or, if both had been precipitated, beneath the lower one. If either one or both had escaped in a volatile form, this would have been expressed by placing the volatilized substance above the diagram, and turning upwards the middle of the upper horizontal line. But since decompositions vary under different circumstances, it is necessary to denote, by the proper addition to the scheme, that the bodies are dissolved in water of the temperature of 60°.

No chemical facts can appear, on first view, more simple or intelligible, than those which are explained by the operation of single elective affinity. It will be found, however, on a more minute examination, that this force, abstractedly considered, is only one of several causes which are concerned in chemical decompositions, and that its action is modified, and sometimes even subverted, by counteracting forces.

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## SECTION V.

### *Of the Causes which modify the Action of Chemical Affinity.*

THE order of decomposition is not, as might be inferred from the law of elective affinity, invariable; but, in certain cases, may even be reversed. Thus though A may attract B more strongly than either A or B is attracted by C, yet, under some circumstances, C may be employed to decompose partially the compound A B. Again, if we mix together A B and

C, using the two first in the proportions required to neutralize each other, it will be found that A and B have not combined to the exclusion of C, but that we have a compound of B with A, and another of B with C, in proportions regulated by the quantities of A and C, which have been employed. Facts of this kind have been long known to chemists. It had been ascertained, for example, before the time of Bergman, that sulphate of potash, a salt composed of sulphuric acid and potash, is partly decomposed by nitric acid, although the nitric has a weaker affinity than the sulphuric acid for that alkali. Examples of the same kind have since been multiplied by Berthollet, who has asserted that in the following, as well as in other cases, a substance possessing a weaker attraction, displaces another having a stronger, for a third body :\*

1. Potash separates sulphuric acid from barytes.
2. Lime separates sulphuric acid from potash.
3. Potash separates oxalic acid from lime.
4. Nitric acid separates lime from oxalic acid.
5. Potash separates phosphoric acid from lime.
6. Potash separates carbonic acid from lime.
7. Soda separates sulphuric acid from potash.

These facts, and a variety of similar ones, are to be explained, according to the views of Berthollet, on the following principles :

1. When two substances are opposed to each other with respect to a third, as in the foregoing examples, they may be considered as antagonist forces ; and they share the third body between them in proportion to the intensity of their action. But this intensity, according to Berthollet, depends not only on the *energy of the affinities*, but on the *quantities* of the two bodies opposed to each other. Hence a larger quantity of one of the substances may compensate a weaker affinity, and the reverse. To the absolute weight of a body, multiplied by the degree of its affinity, he has given the name of *mass*, a

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\* In each of the examples given in the Table, the body, first mentioned, decomposes a compound of the second and third, although its attraction for the second is inferior to that of the third.

term in some degree objectionable from the different meaning which is affixed to it in mechanical philosophy. As an illustration, let us suppose (what is not strictly accurate in point of fact) that the affinity of barytes for muriatic acid is twice as strong as that of potash, or that these affinities are respectively denoted by the numbers 4 and 2. In this case the same *mass* will result from 4 parts of barytes as from 8 of potash; because the same product (16) is obtained in each instance, by multiplying the number indicating the affinity into that denoting the quantity; for 4 (the affinity of barytes) multiplied by 4, (the quantity assumed in this example) is equal to 16; and 2 (the affinity of potash) multiplied by 8 (its quantity) is also equal to 16. In this case, therefore, to divide equally a portion of muriatic acid between barytes and potash, these bodies should be employed in the proportion of 2 of the former to 4 of the latter.

The influence of quantity explains also the difficulty which is observed in effecting, in any instance, the total decomposition of a compound of two principles by means of a third. The immediate effect of a third body C, when added to a compound A B, is to abstract from B a portion of the substance A; and consequently a portion of B is set at liberty, the attraction of which for A is opposed to that of the uncombined part of C. The farther this decomposition is carried, the greater will be the proportion of B, which is brought into an uncombined state; and the more powerfully will it oppose any farther tendency of C to detach the substance A. At a certain point, the affinities of B and C for A will be exactly balanced, and the decomposition will proceed no farther. In a few cases, it is acknowledged by Berthollet, a third body separates the whole of one of the principles of a compound; but this he supposes to happen in consequence of the agency of other extraneous forces, the nature of which remains to be pointed out.

2dly. *Cohesion* is a force, the influence of which over the chemical union of bodies, has already been explained in a former section; and other illustrations of its interference will be given, when we consider the subject of the limitations to chemical combination.

3dly. *Insolubility* is another force, which essentially modifies the exertion of affinity. It is to be considered, indeed, merely

as the result of cohesion, with respect to the liquid in which the effect takes place.

When a soluble substance and an insoluble one are presented, at the same time, to a third, for which they have nearly an equal affinity, the soluble body is brought into the sphere of action with great advantages over its antagonist. Its cohesion at the outset is but little, and by solution is reduced almost to nothing; while that of the insoluble body remains the same. The whole of the soluble substance also exerts its affinity at once; while a part only of the insoluble one can oppose its force. Hence the soluble substance may prevail, and may attach to itself the greatest proportion of the third body, even though it has a weaker affinity than the insoluble one to the subject of combination.

Insolubility, however, under certain circumstances, is a force which turns the balance in favour of the affinity of one body when opposed to the affinity of another. For example, if to the soluble compound, sulphate of soda, we add barytes, the new compound, sulphate of barytes, is precipitated the instant it is formed: and being removed from the sphere of action, the soda can exert no effect upon it by its greater quantity or mass. For the same reason, when soda is added to sulphate of barytes, the sulphate is protected from decomposition both by its insolubility and by its cohesion.

These facts sufficiently prove that the order of precipitation, which was formerly assumed as the basis of tables of elective affinity, can no longer be considered as an accurate measure of that force; and that the body, which is precipitated, may, in some cases, be superior in affinity to the one which has caused precipitation. In these cases, a trifling superiority in affinity may be more than counterbalanced by the cohesive force, which causes insolubility.

4thly. *Great specific gravity* is a force, which must concur with insolubility or cohesion in originally impeding combination; and when chemical union has taken place, it must come in aid of affinity, by removing the new compound from the sphere of action. It is scarcely necessary to enlarge on the operation of a force, the nature of which must be so obvious.

5thly. *Elasticity*. Cohesion, it has already been stated, may prove an impediment to combination; and on the other



hand, it is possible that the particles of bodies may be separated so widely, as to be removed out of the sphere of their mutual attraction. Such appears to be the fact with regard to a class of bodies called airs or gases. The bases of several of these have powerful attractions for the bases of others, and for various liquids, and yet they do not combine on simple admixture, but strong mechanical pressure brings their particles sufficiently near, to be within the influence of their mutual attraction, and combination immediately ensues.

Again if two bodies, one of which has an elastic and the other a liquid form, be presented at the same time to a solid, for which they have both an affinity, the solid will unite with the liquid in preference to the gas. Or if we add to the compound of an elastic substance with an inelastic one, a third body also inelastic, the two latter combine to the exclusion of the elastic body. For example, if to the compound of potash and carbonic acid we add sulphuric acid, the latter acid, acting both by its affinity and its quantity, disengages a portion of carbonic acid. This, by its elasticity, is removed from the sphere of action, and presents no obstacle to the farther operation of the sulphuric acid. Hence elastic bodies act only by their affinity; whereas liquids act both by their affinity and quantity conjoined. And though the affinity of the liquid, abstractedly considered, may be inferior to the affinity of the elastic body, yet, united with quantity, it prevails. In the above instances, the whole of the elastic acid may be expelled by the fixed acid: whereas, as it has already been observed, decomposition is incomplete, if the substance which is liberated remain within the sphere of action.

6thly. *Efflorescence* is a circumstance which occasionally influences the exertion of affinity; but this is only of very rare occurrence. The simplest example of it is that of lime, and muriate of soda. When a paste composed of these two substances with a great excess of lime, is exposed, in a moist state, to the air, the lime, acting by its quantity, disengages soda from the common salt, which appears in a dry form, on the outer surface of the paste, united with carbonic acid absorbed from the atmosphere. In this case the soda, which is separated, being removed from contiguity with the interior

part of the mass, presents no obstacle to the farther action of the lime, and the decomposition is carried farther than it would have been, had no such removal happened.

7thly. The influence of *temperature* over chemical affinity is extremely extensive and important; but at present a very general statement only of its effects is required. In some cases an increased temperature acts in promoting, and at others in impeding, chemical combination: and it materially affects also the order of decompositions.

An increased temperature promotes chemical union by diminishing or overcoming cohesion. Thus metals unite by fusion, and several salts are more soluble in hot than in cold water. Whenever heat is an obstacle to combination, it produces its effect by increasing elasticity. Hence water absorbs a less proportion of ammonia at a high than at a low temperature. A reduction of the temperature of elastic bodies, by lessening their elasticity, facilitates their union with other substances. In certain cases, an increased temperature has the combined effects of diminishing cohesion and increasing elasticity. When sulphur is exposed to oxygen gas, no combination ensues, until the sulphur is heated; and though the elasticity of the gas is thus increased, yet the diminution of cohesion of the solid is more than proportionate, and chemical union ensues between the two bodies.

8thly. The *electrical state* of bodies has a most important influence over their chemical union. This, however, is a subject, of which it would be difficult to offer a general view, and for its full development I refer to a subsequent chapter on *Electro-chemistry*.

9thly. *Mechanical pressure* is another force, which has considerable influence over chemical affinity. With respect to solid bodies, its agency is not frequent; but we have unequivocal examples of its operation in cases, where detonation is produced by concussion. The effects of pressure are chiefly manifested, in producing the combination of æriform bodies either with solids, with liquids, or with each other; and in preserving combinations, which have been already formed, under circumstances tending to disunite them. Chalk, for example, is a compound of lime and carbonic acid; and

these bodies, by the simple application of an intense heat, are separable from each other; but under strong pressure, a heat may be applied sufficient to melt the chalk, without expelling the carbonic acid. It is this principle (of the influence of pressure in opposing chemical decomposition) that is the foundation of Dr. Hutton's ingenious Theory of the Earth.

Such are the most important circumstances, that modify the exertion of chemical affinity. Of their influence, sufficient illustrations have been given to prove, that in every case of combination and decomposition, we are not to consider the force of affinity abstractedly; but are to take into account the agency of other powers, as cohesion, quantity, insolubility, elasticity, efflorescence, and temperature. By the action of these extraneous powers, Berthollet has endeavoured to explain certain facts which are not easily understood on any other principle. Of these the most important are, 1stly, the establishment of proportions in chemical compounds; and 2dly, the modification produced in the affinities of bodies by chemical union.

1. Independently of these extraneous forces, Berthollet imagines that there are no limits to combination, or that two bodies, which are now susceptible of union only in one or in few proportions, might, if these forces were annihilated, be united in every proportion. The causes which he has assigned, as chiefly regulating proportion, are cohesion and elasticity. To take one of the simplest cases, the proportion, in which a salt can be combined with water, depends on the balance between the chemical affinity of the bodies for each other, and the cohesive attraction of the salt. In this case, then, cohesion is the limiting power. As an example of the influence of this force when more energetic affinities are exerted, if we add to diluted sulphuric acid a solution of barytes, a compound is formed, consisting of sulphuric acid and barytes, which, in consequence of its great insolubility or cohesion, is instantly removed from contact with the redundant acid, and with established proportions.

The agency of elasticity in limiting proportion, may be exemplified by the combination of hydrogen and oxygen. If

a mixture of the two gases be inflamed, the new compound, water, is immediately separated from what is superfluous of both ingredients, by its superior density. In other instances, the bases of aëriiform substances are combined in various proportions, and in such examples, there are several terms of greatest condensation, as in the case of oxygen and nitrogen.

2. Another important part of the theory of Berthollet is, that the affinities of a compound are not newly acquired; but are merely the modified affinities of its constituents, the action of which, in their separate state, was counteracted by the prevalence of opposing forces. By combination, these forces are so far overcome, that the affinities of the constituents are enabled to exert themselves.

The action of different affinities existing in one compound, Berthollet terms *resulting affinities*, while the individual affinities of the constituents he calls *elementary affinities*. Thus nitric acid acts on potash by an affinity, which results from those of oxygen and azote for potash. And as all affinity is mutual, the term *resulting affinity* is applied, also, to that force, with which a simple body acts on a compound: to the affinity, for example, which any simple body may exert on nitric acid. A simple body, indeed, may exert towards a compound both an elementary and resulting affinity. If the elementary affinity prevails, it will unite only with one of the principles of the compound, as when a simple body, by its affinity for oxygen, decomposes nitric acid, and liberates its nitrogen in a separate form. If the resulting affinity be predominant, the simple body will unite with the whole compound without effecting any disunion of its elements.

From these views it may be inferred, that we are not, in any case, to deny the existence of an affinity between two bodies, merely because they do not combine when presented to each other; for an affinity may exist, but may be suppressed by the prevalence of opposing forces. According to the doctrine of Berthollet, affinity is a force exerted by every body towards every other; even though not made apparent by any effect. On this principle, we are able to explain certain phenomena, which are wholly unintelligible on any other, and especially those which have been referred to *disposing affinity*. The

action of sulphuret of potash, for example, on oxygen gas, has been ascribed to the disposing affinity of potash for sulphuric acid. This, however, is ascribing an affinity to a compound, before that compound has existence. It is much more probable, that besides the diminished cohesion of the sulphur, the affinity of potash for oxygen has some share in producing the combination. On this principle the united affinities of the potash and sulphur for oxygen (in other words the *resulting affinities* of the sulphuret of potash) are the efficient causes of chemical union. This explanation, at least, does not, like the theory of disposing affinities, involve an absurdity.

The theory of Berthollet, however, which promised, on its first development, to form a new era in chemical philosophy, has lost much of its probability, by the subsequent progress of the science. It is directly, indeed, at variance with the doctrine of definite proportions, which every day gathers strength by the accumulation of new and well-established facts. It is liable, moreover, to the following objections.

1st. It has been shown by Professor Pfaff, of Kiell,\* that, in various cases, where two acids are brought into contact with one base, the base unites with one acid, to the entire exclusion of the other. When, for example, to a given weight of lime, quantities of sulphuric and tartaric acids are put, either of which would exactly neutralize the lime, the sulphuric acid unites with the lime, to the entire exclusion of the tartaric. The same evidence of a superior affinity of the sulphuric acid over that of the oxalic is obtained, by placing those acids in contact with as much oxide of lead, as would exactly saturate either of them. Again, comparing the action of two bases on one acid, the same law is found to hold good: for when potash and magnesia are mixed with just as much sulphuric acid, as is required to neutralize either of them, the potash seizes the whole of the acid, and no part of it unites with the magnesia. Nor can these effects be explained by any of those extraneous forces, which Berthollet supposes, in all cases, to regulate chemical combination; or by any principle, but a stronger affinity of sulphuric acid, than of tartaric or

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\* 77 Ann. de Chim. p. 259.

oxalic acid, for the different bases; and of potash, than of magnesia, for the same acid.

2dly. Some of the cases, before quoted from Berthollet, to show the reciprocal displacement of two bodies by each other from a third (it has been justly observed), are examples, not of *single* elective affinity, in which three bodies only are concerned; but of *complex* affinity, in which the attractions of four bodies are brought into action. In the first case, for example, there is reason to believe, that sulphuric acid is displaced from barytes, not by pure potash, but by potash which has absorbed carbonic acid from the atmosphere.

3dly. In other cases, the consideration of the affinities of two bodies A and B, for a third C, is complicated with this circumstance, that the neutral compound of A and B has an affinity for a farther portion of one of its ingredients. If then C be brought into contact with the compound A B, we may have, acting at the same moment, the affinity of C for A, which partly decomposes the compound A B; and the affinity of the undecomposed part of A B, for that portion of B which is set at liberty. For instance, when nitric acid acts on sulphate of potash, some nitrate of potash is formed; and the sulphuric acid, which is set at liberty, uniting with the undecomposed sulphate of potash, composes a new salt, consisting of sulphate of potash with an excess of sulphuric acid.

4thly. It is a strong objection to the theory of Berthollet that, in some cases, decompositions happen, which, according to his views, ought not to take place; and that in others, decompositions do not ensue, which the theory would have led us to have anticipated.

5thly. The theory is objectionable, inasmuch as, in several instances, properties are supposed to operate, before the bodies exist, to which those properties are attributed. It is inconceivable, for instance, that the cohesion, or insolubility, of sulphate of barytes, can have any share in producing the decomposition of sulphate of potash by that earth; for the insolubility of sulphate of barytes can have no agency, till that compound is formed; which is the very effect to be explained.

Notwithstanding these objections to the theory of Berthollet, when carried so far as has been done by its author, in the

explanation of chemical phenomena, it must still be admitted that the extraneous forces, pointed out by that acute philosopher, have great influence in modifying the effects of chemical affinity. But these forces are entitled only to be considered as secondary causes; and not as determining combinations or decompositions, nor as regulating the proportions in which bodies unite, independently of the superior force of chemical affinity.

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## SECTION VI.

### *Of the Estimation of the Forces of Affinity.*

THE affinities of one body for a number of others are not all of the same degree of force. This is all that the present state of our knowledge authorizes us to affirm; for we are ignorant *how much* the affinity of one body for another is superior to that of a third. The determination of the precise forces of affinity would be an important step in chemical philosophy: for its phenomena would then be reduced to calculation; and we should be enabled to anticipate the results of experiment. That the force of chemical affinity must be prodigiously great, is evident from its effect in preserving the combination of water with some bodies (the alkalies for instance) when exposed to a violent heat notwithstanding its great expansive force, and though water is not essential to the constitution of those bodies.

The observed order of decomposition, it has already been stated, does not enable us to assign the order of the forces of affinity; because, in all decompositions, other forces are concerned. We are, therefore, obliged to seek some other method of determining the problem. Of these several have been proposed.

When the surface of one body is brought into contact with another surface of the same kind, as when the smooth surfaces of a divided leaden bullet are pressed together, they adhere by the force of cohesion, their particles being all of *the same kind*. But when the surfaces of different bodies are thus brought into apparent contact, it is reasonable to suppose

that their adhesion arises from chemical affinity, because their particles are of *different kinds*. Guyton proposed, therefore, the comparative force, with which different surfaces adhere, as a competent measure of chemical affinity. His experiments were made on plates of different metals, of precisely the same size and form, suspended by their centres from the arm of a sensible balance. The lower surfaces of these plates were successively brought into contact with mercury, which was changed for each experiment, and the weight was observed, which it was necessary to add to the opposite scale, in order to detach the several metals. Those which required the largest weight were inferred to have the greatest affinity; and it is remarkable, that the order of affinities, as determined in this way, correspond with the affinities as ascertained by other methods. The following were the results :

Gold adhered to mercury with a force of . . . .	416 grains.
Silver . . . . .	429
Tin . . . . .	418
Lead . . . . .	397
Bismuth . . . . .	372
Zinc . . . . .	204
Copper . . . . .	142
Antimony . . . . .	126
Iron . . . . .	115
Cobalt . . . . .	8

This method, it must be obvious, is of too limited application to be of much utility; for few bodies have the mechanical conditions, which can enable us to subject them to such a test. How, for example, could the affinities of acids for alkalis be examined on this principle? It may be doubted, also, whether in the cases to which it may be applied, it does not measure the facility of combination, rather than the actual force of affinity.

To determine the absolute forces of affinity, which one body exerts towards a number of others, Mr. Kirwan has proposed the quantity of each which is required to produce neutralization, in other words, its *equivalent*. This he has ascertained by experiment in a great variety of instances, a few of which



are contained in the following tables; the numbers being altered, to accommodate them to recent discoveries.

100 Parts of SULPHURIC ACID require for Neutralization	100 Parts of POTASH require
194 parts of barytes.	115 of nitric acid.
138 .... of strontites.	93 of carbonic acid.
118 .... of potash.	84.5 of sulphuric.
78.2 .... of soda.	58 of muriatic.
71 .... of lime.	
49.2 .... of magnesia.	
49 .... of ammonia.	

In judging of the affinities of the same acid for different bases, Mr. Kirwan assumed that they are represented by the numbers indicating the quantities of each base required for neutralization. Thus, because 100 parts of sulphuric acid neutralize 194 of barytes, and 118 of potash, the affinity of the former is superior to that of the latter in the proportion of 194 to 118. So far the inference corresponds with the order of decomposition; for barytes takes sulphuric acid from potash. But if we examine the affinities of potash, as represented in the second table, we shall find that, on this principle, they are directly contradictory to fact. Thus the affinity of sulphuric acid should be inferior to that of the carbonic; whereas it is well known that the former displaces the latter from all its combinations. Mr. Kirwan was, therefore, driven to the necessity of establishing a precisely opposite rule in determining the affinities of different acids for the same base, and of assuming that they are *inversely* proportionate to the affinity of the saturating acid. Thus the affinity of carbonic acid for potash would be represented by 84.5, and that of sulphuric acid by 93. This, however, involves a contradiction; since it is implied that a stronger affinity, in one instance, requires a greater quantity of the saturating principle, as in the relation of barytes and potash to sulphuric acid; and that, in the other, it requires a less quantity, as in the instance of the sulphuric and carbonic acids with respect to potash.

Since neutralization is an effect of chemical affinity, which must in all cases bear a proportion to its cause, it has been

assumed by Berthollet, that the substance which, in the *smallest quantity*, neutralizes another, is the one possessing the strongest affinity. On this principle the affinities of sulphuric acid for different bases will be exactly the reverse of the order established by Mr. Kirwan; and to that order, which would have been assigned from observed decompositions. Thus ammonia will have a stronger affinity for sulphuric acid than any of the substances which are placed above it in the table; though it is separated, by each of these, from its union with that acid.

It is in the extraneous forces, which have been enumerated as influencing chemical affinity, that we are to seek, according to Berthollet, for the explanation of this apparent anomaly, and especially in the forces of cohesion and elasticity. The elasticity of ammonia, for example, turns the balance in favour of magnesia, lime, &c. There is an obvious difficulty, however, in the application of the theory. For as the elasticity of ammonia is suppressed by its combination with sulphuric acid, what, it may be asked, but a superior affinity for sulphuric acid, existing in the substances which stand above ammonia in the table, can occasion the first commencement of decomposition? The problem, therefore, of determining the absolute forces of affinity can scarcely be admitted to be solved. Even if it were, we should not be able to predict the order of decomposition, unless the modifying forces of cohesion, elasticity, &c. could be at the same time subjected to precise admeasurement. Until both these objects are accomplished, the results of chemistry can in no case be obtained by calculation, but the science must remain a collection of general principles, derived from experiment and induction.

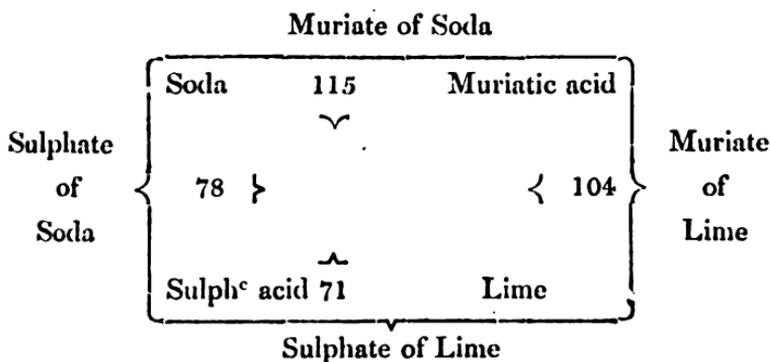
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## SECTION VII.

### *Of Complex Affinity.*

UNDER the more general name of *complex affinity*, Berthollet includes that which has hitherto been considered as produced by the action of four affinities, and which has com-

monly been denominated *double elective affinity*. It frequently happens that the compound of two principles cannot be destroyed either by a third or a fourth separately applied; but if the third and fourth be combined, and placed in contact with the former compound, a decomposition, or a change of principles will ensue. Thus when lime water is added to a solution of the sulphate of soda, no decomposition happens, because the sulphuric acid attracts soda more strongly than it attracts lime. If the muriatic acid be applied to the same compound, still its principles remain undisturbed, because the sulphuric acid attracts soda more strongly than the muriatic. But if the lime and muriatic acid, previously combined, be mixed with the sulphate of soda, a double decomposition is effected. The lime, quitting the muriatic acid, unites with the sulphuric; and the soda, being separated from the sulphuric acid, combines with the muriatic. These decompositions are rendered more intelligible by the following diagram, contrived by Bergman.



On the outside of the vertical brackets are placed the original compounds; and above and below the diagram, the new compounds. The upper line, being straight, indicates that the muriate of soda remains in solution; and the middle of the lower line, being directed downwards, that the sulphate of lime is precipitated.

In all cases similar to the foregoing, Mr. Kirwan conceives that we may trace the operation of two distinct series of affinities. The affinities tending to preserve the original compounds (which in the above example are those between sulphuric acid

and soda, and between muriatic acid and lime), he terms the *quiescent affinities*; because they resist any change of composition. On the other hand the affinities, which tend to disunite the original compounds and to produce new ones (such as those between muriatic acid and soda, and between sulphuric acid and lime), he terms *divellent affinities*. In order that an effect may be produced, the divellent affinities must necessarily be superior to the quiescent. Now, assuming the numbers in Mr. Kirwan's tables to express accurately the forces of affinities, the double exchange of principles, which happens in the preceding instance, is readily explained. Thus the quiescent affinities are

$$\begin{array}{r} \text{Those of lime to muriatic acid} = 104 \\ \text{of soda to sulphuric acid} = 78 \\ \hline 182 \end{array}$$

The divellent affinities, opposed to these, consist of

$$\begin{array}{r} \text{The affinity of soda to muriatic acid} = 115 \\ \text{lime to sulphuric acid} = 71 \\ \hline 186 \end{array}$$

The original compound, therefore, is preserved by a force equivalent to 182, and the tendencies to produce new compounds are represented by the number 186. The divellent affinities are, therefore, predominant.

The theory of quiescent and divellent affinities, however, though highly attractive from its simplicity, and from the facility with which it solves certain phenomena, is completely defective in the explanation of others. For example, sulphate of potash is decomposed by muriate of barytes. Yet, estimating in the above manner the quiescent and divellent affinities, an exchange of principles ought not to ensue. The affinities tending to preserve the original compound, are those of sulphuric acid for potash = 118, and of muriatic acid for barytes = 285. The divellent affinities are that of muriatic acid for potash = 174 + that of sulphuric acid for barytes = 194. The quiescent affinities then are 118 + 285 = 403,

and the divellent  $174 + 194 = 368$ . This leaves a balance of 35 in favour of the quiescent affinities; and yet decomposition ensues, when the two compounds are brought into contact.

It must be acknowledged that the numbers, assumed by Mr. Kirwan do not correspond with the actual forces of affinity. But even if they are taken according to the principle assumed by Berthollet, they will not be found universally applicable. The reason of this is, that the phenomena produced by complex affinity, like those occasioned by simple affinity, are materially influenced by the extraneous forces of cohesion, quantity, elasticity, temperature, &c. The effect of quantity is shown by the fact, that if two salts be mixed together in certain proportions, decomposition will ensue, but not if mixed in other proportions. Thus from the mingled solutions of two parts of muriate of lime and one of nitrate of potash, we obtain muriate of potash; but not from equal weights of the two salts. Insolubility, or precipitation, has also a considerable influence on the result. When this occurs, the influence of quantity is destroyed, as in the case of sulphate of potash and muriate of barytes. Elasticity, and an increased temperature (which operates by increasing elasticity), and the reverse of this, or a greatly *diminished* temperature, have also a powerful influence in promoting the action of complex affinities. Thus of four principles, two of which are volatile and two fixed, the two which are volatile will be most disposed to unite together at a high temperature. The nature of the fluid, in which salts are dissolved, has also an important influence on their tendency to mutual decomposition.\* Thus changes take place in the midst of an alcoholic medium, which do not happen to the same bodies dissolved in water.† We have even instances, in which though a compound A B decomposes another compound C D, A uniting with C, and B with D, yet (which could not have been expected *à priori*) the compound A C is reciprocally decomposed by D B, and the original compounds A B and C D are regenerated.‡ Hence the phenomena of complex decomposition concur with

\* Ann. de Chim. et Phys. iv. 366. † Dr. Murray on Sea Water.

‡ See the sect. on Sulphate of Barytes.

those of a more simple kind, in proving that affinity is not an uniform force, but is materially influenced by various modifying circumstances; and that we cannot confidently anticipate results, from comparing the numerical expressions of quiescent and divellent affinities.

One great obstacle to the construction of tables, capable of representing the forces of affinity, is the difficulty of ascertaining, with precision, the quantities of bodies required for neutralization. Notwithstanding all the care employed by Mr. Kirwan, considerable errors appear to have crept into the results of his experiments. This will sufficiently appear, when they are examined by a test, originally proposed by Guyton. It must be obvious that if between two salts, which are mixed together in solution, decomposition should ensue, and the mixture should afterwards be found neutral, the quantity of acid, which has quitted one of the bases, must have been exactly equivalent to the saturation of the other base, also deserted by its acid. If, for example, we mingle the muriate of magnesia and sulphate of soda, the mixture continues neutral; and hence it follows that the muriatic acid, which has quitted the magnesia, must have been exactly equal to the neutralization of the soda, deserted by the sulphuric acid. But from a calculation, founded on the proportion of the ingredients of these salts, as established by Mr. Kirwan, it appears that the soda, detached from the sulphuric acid, is not adequate to the saturation of the muriatic acid. The mixture, therefore, ought to be acid; and since this is contrary to fact, we may safely infer that there is an error in his estimation of the ingredients composing these salts. No tables, indeed, can be correct, unless they stand the test of this mode of verification. Such a table has been calculated by Fischer from the experiments of Richter; but even this table seems in several respects to be of questionable accuracy. I have thought it, however, entitled to a place among the tables in the Appendix; and I shall annex, also, a more correct one, the data of which are chiefly supplied by Dr. Wollaston's paper on Chemical Equivalents.\*

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\* Phil. Trans. 1814.

## SECTION VIII.

*Experimental Illustrations of Chemical Affinity, Solution, &c.*

FOR these experiments, a few wine glasses, or, in preference, deep ale glasses, will be required; and a Florence flask for performing the solutions.

I. *Some bodies have no affinity for each other.*—Oil and water, mercury and water, or powdered chalk and water, when shaken together in a vial, do not combine, the oil or water always rising to the surface, and the mercury or chalk sinking to the bottom.

II. *Examples of chemical affinity, and its most simple effect, viz. solution.*—Sugar or common salt disappears or dissolves in water; chalk in dilute muriatic acid.\* Sugar and salt are, therefore, said to be *soluble* in water, and chalk in muriatic acid. The liquid, in which the solid disappears, is termed a *solvent* or *menstruum*. Chalk or sand, on the contrary, when mixed with water by agitation, always subsides again. Hence they are said to be *insoluble*.

III. *Influence of mechanical division in promoting the action of chemical affinity, or in favouring solution.*—Lumps of chalk or marble dissolve much more slowly in dilute muriatic acid, than equal weights of the same bodies in powder. Muriate of lime, or nitrate of ammonia, cast, after liquefaction by heat, into the shape of a solid sphere, is very slowly dissolved; but with great rapidity when in the state of a powder or of crystals. When a lump of the Derbyshire fluuate of lime is immersed in concentrated sulphuric acid, scarcely any action of the two substances on each other takes place; but if the stone be finely pulverized, and then mingled with the acid, a violent action is manifested, by the copious escape of vapours of fluoric acid. In the common arts of life, the rasping and grinding of wood and other substances are familiar examples.

IV. *Hot liquids, generally speaking, are more powerful solvents than cold ones.*—To four ounce-measures of water, at the temperature of the atmosphere, add three ounces of sulphate

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\* I omit, purposely, the distinction between the solution and dissolution.

of soda in powder. Only part of the salt will be dissolved, even after being agitated some time. Apply heat, and the whole of the salt will disappear. When the liquor cools, a portion of salt will separate again in a regular form or in *crystals*. This last appearance affords an instance of *crystallization*.

To this law, however, there are several exceptions; for many salts, among which is muriate of soda, or common salt, are equally, or nearly equally, soluble in cold as in hot water. (See the table of solubility of salts in water, in the Appendix.) Hence, a hot, and saturated solution of muriate of soda does not, like the sulphate, deposit crystals on cooling. To obtain crystals of the muriate, and of other salts which observe a similar law as to solubility, it is necessary to evaporate a portion of the water; and the salt will then be deposited, even while the liquor remains hot. In general, the more slow the cooling, or evaporation, of saline solutions, the larger and more regular are the crystals.

V. *A very minute division of bodies is effected by solution.*—Dissolve two grains of sulphate of iron in a quart of water, and add a few drops of this solution to a wine-glassful of water, into which a few drops of tincture of galls have been stirred. The dilute infusion of galls will speedily assume a purplish hue. This shows that every drop of the quart of water, in which the sulphate of iron was dissolved, contains a notable portion of the salt.

VI. *Some bodies dissolve much more readily and copiously than others.*—Thus, an ounce measure of distilled water will dissolve half its weight of sulphate of ammonia, one third its weight of sulphate of soda, one sixteenth of sulphate of potash, and only one five-hundredth its weight of sulphate of lime.

VII. *Mechanical agitation facilitates solution.*—Into a wine-glassful of water, tinged blue with the infusion of litmus, let fall a small lump of solid tartaric acid. The acid, if left at rest, even during some hours, will only change to red that portion of the infusion which is in immediate contact with it. Stir the liquor, and the whole will immediately become red.

VIII. *Bodies do not act on each other, unless either one or both be in a state of solution, or at least contain water.*—1. Mix some



dry tartaric acid with dry bi-carbonate of soda, and grind them together in a mortar. No combination will ensue till water is added, which, acting the part of a solvent, promotes the union of the acid and alkali, as appears from a violent effervescence. It has been shown by Link,\* that the water of crystallization, existing in certain salts, acts as free water in occasioning chemical action. For example, acetate of lead and sulphate of copper, both in crystals, become green when triturated together, a proof of the mutual decomposition of those two salts.

2. Spread thinly, on a piece of tinfoil, three or four inches square, some dry nitrate of copper,† and wrap it up. No effect will follow. Unfold the tinfoil, and having sprinkled the nitrate of copper with the smallest possible quantity of water, wrap the tinfoil up again as quickly as possible, pressing down the edges closely. Considerable heat, attended with fumes, will now be excited; and, if the experiment has been dexterously managed, even light will be evolved. This shows that nitrate of copper has no action on tin, unless in a state of solution.

IX. *Bodies, even when in a state of solution, do not act on each other at perceptible distances; in other words, contiguity is essential to the action of chemical affinity.*—Thus, when two fluids of different specific gravities, and which have a strong affinity for each other, are separated by a thin stratum of a third, which exerts no remarkable action on either, no combination ensues between the uppermost and lowest stratum. Into a glass jar, or deep ale glass, pour two ounce-measures of a solution of subcarbonate of potash, containing, in that quantity, two drachms of common salt of tartar. Under this introduce, very carefully, half an ounce-measure of water, holding in solution a drachm of common salt; and again, under both these, two ounce-measures of sulphuric acid, which has been diluted with an equal weight of water, and allowed

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\* Thomson's Annals, vii. 426.

† To prepare nitrate of copper, dissolve the filings or turnings of that metal in a mixture of one part nitrous acid and three parts water; decant the liquor when it has ceased to emit fumes: and evaporate it to dryness, in a copper or earthen dish. The dry mass must be kept in a bottle.

to become cool. The introduction of a second and third liquid beneath the first, is best effected, by filling, with the liquid to be introduced, the dropping tube, fig. 15. pl. i. which may be done by the action of the mouth. The finger is then pressed on the upper orifice of the tube; and the lower orifice, being brought to the bottom of the vessel containing the liquid, the finger is withdrawn, and the liquid descends from the tube, without mingling with the upper stratum. When a solution of carbonate of potash is thus separated from diluted sulphuric acid, for which it has a powerful affinity, by the intervention of a thin stratum of brine, the two fluids will remain distinct and inefficient on each other; but, on stirring the mixture, a violent effervescence ensues, in consequence of the action of the sulphuric acid on the potash.

X. *Two bodies, having no affinity for each other, unite by the intervention of a third.*—Thus, the oil and water which, in Experiment I., could not, by agitation, be brought into union, unite immediately on adding a solution of caustic potash. The alkali, in this case, acts as an intermedium. The fact, indeed, admits of being explained by the supposition, that the oil and alkali form, in the first instance, a compound which is soluble in water.

XI. *Saturation and neutralization illustrated.*—Water, after having taken up as much common salt as it can dissolve, is said to be *saturated* with salt. Muriatic acid, when it has ceased to act any longer on lime, is said to be *neutralized*, as is also the lime.

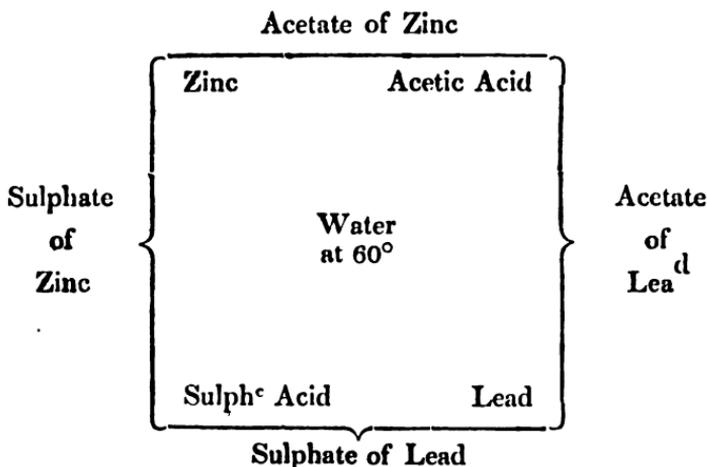
XII. *The properties characterizing bodies, when separate, are destroyed by chemical combination, and new properties appear in the compound.*—Thus, muriatic acid and lime, which, in a separate state, have each a most corrosive taste, lose this entirely when mutually saturated; the compound is extremely soluble, though lime itself is very difficult of solution; the acid no longer reddens syrup of violets; nor does the lime change it, as before, to green. The resulting compound, also, muriate of lime, exhibits new properties. It has an intensely bitter taste; is susceptible of a crystallized form; and the crystals, when mixed with snow or ice, generate a degree of cold sufficient to freeze quicksilver.

XIII. *Single elective affinity illustrated.*—1. Add to the combination of oil with alkali, formed in Experiment X., a little diluted sulphuric acid. The acid will seize the alkali, and set the oil at liberty, which will rise to the top. In this instance, the affinity of alkali for acid is greater than that of alkali for oil. 2. To a dilute solution of muriate of lime (prepared in Experiment II.), add a little of the solution of pure potash. The potash will seize the muriatic acid, and the lime will fall down, or be *precipitated*.

XIV. *In every instance, in comparing the affinities of two bodies for a third, a weaker affinity, in one of the two compared, will be found to be compensated by increasing its quantity.*—It is not easy to offer clear and unequivocal examples of this law, and such as the student may submit to the test of experiment. The following, however, may illustrate the proposition sufficiently: Mingle together, in a mortar, one part of muriate of soda (common salt) with half a part of red oxide of lead (litharge, or red lead), and add sufficient water to form a thin paste. The oxide of lead, on examining the mixture after twenty-four hours, will be found not to have detached the muriatic acid from the soda; for the strong taste of that alkali will not be apparent. Increase the weight of the oxide of lead to three or four times that of the salt; and, after the same interval, the mixture will exhibit, by its taste, marks of uncombined soda. This proves, that the larger quantity of the oxide must have detached a considerable portion of muriatic acid from the soda, though the oxide has a weaker affinity for that acid than the soda possesses.

Another illustration of the same general principle has been suggested by Berzelius. It is necessary to premise, that the colour of the compound of sulphuric acid with oxide of copper is blue, and that of muriatic acid with the same oxide, green. To a saturated solution of sulphate of copper in water, add by degrees concentrated muriatic acid. Every addition will render the colour of the liquid more distinctly green, showing an increased production of muriate of copper; the oxide of copper being divided between the sulphuric and muriatic acids, in proportion to the quantity of each acid that is present.

XV. *Double elective affinity exemplified.*—In a watery solution of sulphate of zinc, immerse a thin sheet of lead: the lead will remain unaltered, as also will the sulphate of zinc, because zinc attracts sulphuric acid more strongly than lead. But let a solution of acetate of lead be mixed with one of sulphate of zinc; the lead will then go over to the sulphuric acid, while the zinc passes to the acetic. The sulphate of lead being insoluble, will fall down in the state of a white powder; but the acetate of zinc will remain in solution. The changes that occur in this experiment will be better understood from the following scheme:



The vertical brackets include the original compounds, *viz.* sulphate of zinc, and acetate of lead; and the horizontal line and bracket point out the new ones, *viz.* acetate of zinc and sulphate of lead. By the upper horizontal line, it is denoted, that the acetate of zinc remains in solution; and, by the point of the lower bracket being directed downwards, it is meant to express, that the sulphate of lead falls down, or is precipitated.

## CHAPTER III.

## OF HEAT OR CALORIC.



## SECT. I.

*General Observations on Heat.*

WHEN we apply the hand to a body which is hotter than itself, we are sensible of a peculiar feeling, which we agree to call the *sensation of heat*. At the same time we observe, in almost all bodies that are placed in the same situation with the hand, certain effects, the most remarkable of which is an enlargement of their dimensions. These circumstances, with very few exceptions, so constantly accompany each other, that we can have little or no hesitation in referring them to one and the same cause. Of the nature of this cause we have no satisfactory evidence; and we are unable to demonstrate either that it consists in any general quality of bodies, or that it resides in a distinct and peculiar kind of matter. The opinion, however, which best explains the phenomena, is that which ascribes them to an extremely subtile fluid, of so refined a nature, as to be capable of insinuating itself between the particles of the most dense and solid bodies. To this fluid, as well as to the sensation which it excites, the term *heat* was formerly applied. But there was an obvious impropriety in confounding, under one appellation, two things so distinct as a sensation and its cause; and the term *caloric*, first proposed by Lavoisier, is now, therefore, generally adopted to denote the cause of heat. Occasionally, however, in order to avoid too frequent a repetition of the same word, the term *heat* is still employed in a more extensive sense, to express not only the sensation which it usually denotes, but also some of the modifications of caloric.

Caloric, so far as its chemical agencies are concerned, may be chiefly considered under two views—as an antagonist to the cohesive attraction of bodies—and as concurring with, and increasing elasticity. By removing the particles of any solid

to a greater distance from each other, their cohesive attraction is diminished; and one of the principal impediments to their union with other bodies is overcome. On the other hand, caloric may be infused into bodies in such quantity, as not only to overcome cohesion, but to place their particles beyond the sphere of chemical affinity. Thus, in the class of substances called gases, the base or ponderable ingredient, whether solid or liquid, is dissolved in so much caloric, that, with few exceptions, the bases of different gaseous bodies do not unite by simple mixture of the gases themselves. But if, of two gases, we employ either one or both in a state of great condensation, or compress their particles near enough to each other by any means, the gravitating matter of both unites, and forms a new compound. Thus hydrogen and oxygen gases remain together in a state of mixture, for any length of time, without combining; but if we force their particles into a state of contiguity, by sudden and violent mechanical pressure, their bases unite and compose water. In many cases, also, when two bodies are combined together, one of which is fixed, and the other becomes elastic by union with caloric, we are able, by its interposition alone, to effect their disunion. Thus carbonate of lime gives up its carbonic acid by the mere application of heat.

We may consider, then, all bodies in nature as subject to the action of two opposite forces, the mutual attraction of their particles on the one hand, and the repulsive power of caloric on the other; and bodies exist in the solid, liquid, or elastic state, as one or the other of these forces prevails. Water, by losing caloric, has its cohesion so much increased, that it assumes the solid form of ice; adding caloric, we diminish again its cohesion, and render it fluid; and, finally, by a still farther addition of caloric, we change it into vapour, and give it so much elasticity, that it may be rendered capable of bursting the strongest vessels. In many liquids, the tendency to elasticity is even so great, that they pass at common temperatures, to the gaseous form, by the mere removal of the weight of the atmosphere.

Caloric, like all other bodies, may exist in two different states, in a state of freedom, and in a state, either of combination or of something nearly resembling it. In the former

state, it is capable of exciting the sensation of heat, and of producing expansion in other bodies. To this modification the terms *free* or *uncombined caloric*, or *caloric of temperature*, have been applied. By the term temperature we are to understand the state of a body relatively to its power of exciting the sensation of heat, and occasioning expansion; effects which, in all probability, bear a proportion to the quantity of free caloric in a given space, or in a given quantity of matter. Thus what we call a high temperature may be ascribed to the presence of a large quantity of free caloric; and a low temperature to that of a small quantity. We are unacquainted, however, with the extremes of temperature; and may compare it to a chain, of which a few of the middle links only are exposed to our observation, while its extremities are far removed from our view.

The degree of expansion produced by caloric, it will afterwards appear, bears a sufficient proportion to its quantity, to afford us a means of ascertaining the latter with tolerable accuracy. In estimating temperature, indeed, our senses are extremely imperfect; for we compare our sensations of heat, not with any fixed or uniform standard, but with those sensations, of which we have had immediately previous experience. The same portion of water will feel warm to a hand removed from contact with snow, and cold to another hand which has been heated before the fire. To convey, therefore, any precise notion of temperature, we are obliged to describe the degree of expansion produced in some one body, which has been previously agreed upon as a standard of comparison. The standard most commonly employed is a quantity of quicksilver, contained in a glass ball, which terminates in a long narrow tube. This instrument, called a *thermometer*, is of the most important use in acquiring and recording our knowledge of the properties and laws of caloric. The thermometer, however, it must be obvious, is no otherwise a measure of the quantity of caloric, than as it ascertains the amount of one of its principal effects. In this respect, it stands in much the same predicament as the hygrometers of Saussure or Deluc, when considered as means of determining the moisture of the atmosphere. These last instruments, it may be remembered, are composed of some substance (such as a human hair, or a

slip of whalebone) which is lengthened by a moist atmosphere and contracted by a dry one; and in a degree proportionate to the moisture or dryness. But all the information, which hygrometers of this sort give us, is the degree of moisture between certain points that form the extremities of their scales; and they are quite incompetent to measure the absolute quantity of watery vapour in the air.

In explaining those properties and laws of caloric, which have become known to us by means of the thermometer, it appears a sufficiently natural division of the subject to describe, 1stly, those effects which caloric produces, without losing its properties of exciting the sensation of heat and occasioning expansion: and, 2dly, those agencies, in which its characteristic properties are destroyed, and in which it ceases to be cognizable by our senses or by the thermometer.

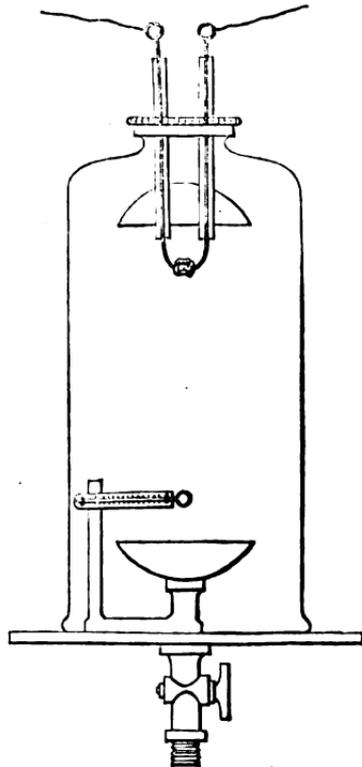
The EXPANSION or DILATATION of bodies, it will appear, is an almost universal effect of an increase of temperature. Its amount, however, is not the same in all bodies, but differs very essentially. By the same increase of temperature, liquids expand more than solids, and æriform bodies much more than either. Nor is the same quantity of expansion effected in the *same* solid or liquid, at all temperatures, by adding similar quantities of heat; for, generally speaking, bodies expand by equal increments of caloric, more in high than in low temperatures. The explanation of this fact is, that the force opposing expansion (*viz.* cohesion) is diminished by the interposition of caloric between the particles of bodies: and, therefore, when equal quantities of caloric are added in succession, the last portions meet with less resistance to their expansive force than the first. In gases, which are destitute of cohesion, equal increments of heat appear, on the contrary, to be attended with precisely equal augmentations of bulk.

An important property of free caloric, the knowledge of which has been acquired by means of the thermometer, is its *tendency to an equilibrium*. Twenty or thirty different bodies, for instance, all unequally heated, soon arrive, when exposed in a still atmosphere, at an equality of temperature. When a heated ball of iron is exposed to the open air, the caloric, which is accumulated in it, flows out; and its temperature is gradually reduced to that of the surrounding medium. This



is owing to two distinct causes: the air, immediately surrounding the ball, acquires part of the caloric which escapes; and, having its bulk increased, is rendered specifically lighter, and ascends. This is succeeded by a cooler and heavier portion of air from above, which in its turn is expanded and carries off a second quantity of caloric. Hence a considerable part of the caloric, which is lost by a heated body, is conveyed away by the ambient air; a property, of which advantage is taken in the warming and ventilating of apartments. But the refrigeration cannot be wholly explained on this principle; for it has been long known that heated bodies cool, though with less celerity, under the exhausted receiver of an air pump, and even in a Torricellian vacuum.

When the phenomena accompanying the cooling of bodies are accurately examined, it is found that a part of the caloric, which escapes, moves through the atmosphere with immeasurable velocity. In an experiment of M. Pictet, no perceptible interval took place between the time at which caloric quitted a heated body, and its reception by a thermometer at the distance of sixty-nine feet. It appears also, from the experiments of the same philosopher, to move with equal ease in all directions, and not to be at all impeded by a strong current of air meeting it transversely. Hence it follows that the propagation of caloric, in this state of rapid movement, does not depend on any agency of the medium through which it passes. This was satisfactorily proved, too, by Sir. H. Davy, who contrived by means of the apparatus, represented in the annexed sketch, to effect the radiation of heat *in vacuo*. Between the points of two wires, inclosed in glass tubes which passed through



a brass plate, was placed a piece of charcoal, which was intensely ignited by voltaic electricity, and the effect of radiation in the focus of the lower concave mirror was ascertained by a delicate thermometer, first when the receiver was full of air, and next when it was exhausted to  $\frac{1}{10}$ . In the latter case, the effect of radiation was found to be three times greater than in an atmosphere of common density. The same conclusions flow, also, from the experiments of Petit and Dulong on the rate of cooling of bodies *in vacuo*.

Like light, heat appears to be transmitted in parallel rays, and it has, therefore, been called **RADIANT CALORIC**. The comparative quantities of caloric lost by radiation and by conduction may be approximated by observing what time it takes to cool, through the same number of degrees, in air and in *vacuo*. By experiments of this kind, Dr. Franklin thought he had ascertained that a body, which requires five minutes in *vacuo*, will cool in air, through the same number of degrees, in two minutes. Count Rumford's experiments with a Torricellian vacuum give the proportions of 5 to 3. It will, perhaps, not be very remote from the truth, if it be stated, in general terms, that one half of the caloric, lost by a heated body, escapes by radiation, and that the rest is carried off by the ambient atmosphere.

The rate of cooling appears to bear a proportion to the elevation of temperature of a body above that of the surrounding medium. Hence in part it is, that a heated body, during refrigeration, loses unequal quantities of caloric in equal times. The series appears to be pretty nearly a geometrical one. Thus, supposing the temperature of a body to be 1000 degrees above the surrounding medium,

In the first minute it will lose	$\frac{1}{10}$	of its heat or	900°
In the second .....	$\frac{1}{10}$	of the remainder =	90
In the third .....	$\frac{1}{10}$	of 10 .....	= 9

This law of refrigeration, originally laid down by Newton, it is asserted by Dr. Delaroché, though nearly accurate at low temperatures, is far from being so at high ones; and his objections have been fully confirmed by Petit and Dulong, who have shown that the error increases as the temperature aug-

ments, and at length becomes enormously great. (Annals of Philosophy, vol. xiii.)

The movement of caloric by radiation occurs only in free space, or through transparent media. It appears to be the same through all the different varieties of aëriform bodies; though, as will afterwards appear, the gases differ materially from each other in their *conducting power*. Caloric, also, radiates from bodies at all temperatures, but the quantity radiated bears some proportion to the excess of the temperature of the hot body above that of the surrounding medium. Hence if we have any number of bodies at different temperatures in the vicinity of each other, they may all, agreeably to the ingenious theory of M. Prévost, be considered both as radiating and receiving caloric; but the hot ones will radiate more than they receive, while the cold ones will receive more than they radiate.

The process of radiation appears to be constantly going on from the surface of the earth, and it is partly on this principle that we are to explain why the heat which our planet is incessantly receiving from the sun, does not accumulate to such a degree as to render it a less fit habitation for man. The period, when radiation from the surface of the globe is most discoverable by its effects, seems to be during the night, especially when the sky is perfectly unclouded, for a covering of clouds serves as a mantle to the earth, and prevents the free escape of radiant heat. Under favourable circumstances, it has been shown by Dr. Wells, that the temperature of the ground, especially when its covering is formed of some substance that radiates freely, is several degrees below that of the atmospheric stratum, a few feet above it. It is this diminished temperature of the earth's surface, that occasions the deposition of dew and hoar frost, which are always observed to be most abundantly formed under a clear unclouded sky.

Caloric, besides radiating through transparent media, is capable, also, of passing through dense and opaque bodies, though with prodigiously impaired velocity. Thus a long bar of iron, heated at one end, requires considerable time to become hot at the other. This property in bodies has been called their *CONDUCTING POWER*, and it exists, in different bodies, in very different degrees. It is not, however, found

to bear a proportion to any other quality of bodies, such as their densities, &c.

All the properties of caloric, which have been hitherto described, belong to it when supposed to be in a free or uncombined form; for it continues to produce the sensation of heat and to expand the mercury of the thermometer. In the instances of its agency, also, that have been mentioned, no permanent change of form or of properties is effected in the bodies which have imbibed caloric. A bar of iron, after being expanded by heat, returns on cooling to the same state as before, and exhibits all its former qualities. In certain cases, however, caloric is absorbed by bodies, with the loss of its distinguishing properties. It can then be no longer discovered by our senses or by the thermometer: and it produces important and sometimes permanent changes in the bodies into which it enters.

Those effects of caloric, in the production of which it loses its distinguishing properties, may be classed under two general heads.

I. *Bodies, in passing from a denser to a rarer state, generally absorb caloric.*—Thus solids, during liquefaction, imbibe a quantity of caloric, which ceases to be apparent to our senses or to the thermometer; or, as it has been termed, *becomes latent*. In a similar manner, solids and liquids, during their conversion into vapours or gases, render latent a quantity of caloric, which is essential to the elasticity of the new product. In common language cold is, in such cases, said to be produced; but by the production of cold we are to understand, in philosophical language, nothing more than the passage of caloric from a free to a latent form.

II. *Bodies, by an increase of density, mostly evolve or give out caloric, which passes from a latent to a free state.*—The simplest illustration of this law is in the effect of hammering a piece of metal, which may thus be intensely heated, while all that is permanently effected is an augmentation of its density. Liquids by becoming solids, or gases by conversion into liquids, also, evolve caloric, or produce an increase of temperature. A pound of water condensed from steam, will render 100 pounds of water at 50° warmer by 11°; whereas a pound of boiling water will produce the same rise of temperature in no more than

about  $18\frac{1}{7}$  pounds. This is owing to the much greater quantity of caloric, existing in a pound of steam, than in a pound of boiling water, though steam and boiling water affect the thermometer in precisely the same degree.

It is a question which has excited considerable interest among philosophers, whether caloric, when thus absorbed and rendered latent, enters into chemical combination, or is merely united by the same kind of ties as that portion of caloric that produces the temperature of bodies. Does ice, for example, when changed into water, form a chemical union with caloric, similar to that which exists between potash and sulphuric acid? Such appears to have been the opinion of Dr. Black, who, by the powers of an original and well-directed genius, discovered, about the year 1760, the greater number of those facts that formed the groundwork of the theory of latent heat. The resemblance, however, between chemical union and the disappearance of caloric, which, on first view, appears extremely striking, will be found, it must be confessed, less close on a nearer examination. For caloric may be made to quit those bodies, into which it has entered with a loss of its peculiar properties, merely by reducing their temperature; whereas chemical combinations in general cannot be destroyed, except by the interference of more energetic affinities. In opposition to the foregoing theory, it has been contended that the absorption of caloric by bodies is a consequence of what has been called a change of their *capacity*. Thus ice, it is supposed, in becoming water, has its capacity for caloric increased, and the absorption of caloric is a consequence of this increased capacity. This theory, however, is deficient, inasmuch as it fails to explain what is the cause of that change of form, which is assumed to account for the increase of capacity. Notwithstanding this obvious objection, I have retained the term *capacity* to express, in the abstract, that power by which bodies absorb and render latent different quantities of caloric; or the property of requiring more or less caloric for raising their temperature an equal number of degrees. The absorption of caloric, then, will always be owing to an increase, and its evolution to a decrease, of capacity. The use of these terms may be exemplified by a slight change of the perspicuous language of Dr. Crawford. "The capacity for

containing caloric,"\* he observes, "and the absolute caloric contained, are distinguished as a force from the subject upon which it operates. When we speak of the *capacity*, we mean a power inherent in the heated body; when we speak of the *absolute caloric*, we mean an unknown principle, which is retained in the body by the possession of this power; and when we speak of the *temperature*, we consider the unknown principle as producing certain effects upon the thermometer."

As the capacities of bodies determine their relative quantities of caloric, it seems reasonable to conclude, that if we can ascertain how much caloric a body absorbs or gives out in changing its form, and in what proportion its capacity is at the same time altered, we may deduce the *absolute quantity of heat* which it contains. Now it will be afterwards shown that the heat, evolved by water in freezing, is equal to  $140^{\circ}$ ; and the capacity of water has been stated to bear to that of ice the proportion of 10 to 9. Water, then, in becoming ice, must give out  $\frac{1}{10}$ th of its whole caloric, and as this amounts to  $140^{\circ}$ , ten times  $140$  (or  $1400^{\circ}$ ) is the whole quantity of caloric in water at the temperature of  $32^{\circ}$ ; and deducting  $140$  from  $1400$ , we have  $1260^{\circ}$  for the caloric contained in the ice itself. This method of determining the problem seems, however, to me, to be liable to several objections, which it would take up too much room to state in this place, and which I have elsewhere urged at considerable length.† Nor does it appear that any other mode of investigation, yet proposed, is capable of giving us approximations to the truth that are more to be relied on; for enormous differences as to the *absolute zero*, or point of total privation of heat on the thermometric scale, have resulted from the inquiries of different philosophers, showing that we still want the data essential to such an investigation.

These general observations I have deemed it necessary to make, with a view of connecting together the propositions respecting caloric, and the experiments illustrating them, that form the subject of the following sections. The inquiry respecting heat is one which presents a boundless field for in-

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\* Dr. Crawford on Heat, p. 8.

† Manchester Memoirs, v. ; or Phil. Mag.

teresting speculation ; and it would have been easy to have extended very considerably the discussion of its nature and properties. But in this work, I have no farther object than to lead the student, by easy steps, to a knowledge of what has been actually determined by experiment, or strictly and legitimately deduced from it.



## SECTION II.

### *Illustrations of the Effects of Free Caloric.*

I. *Caloric expands all bodies.*—The expansion of *liquids* is shown by that of the mercury of a thermometer, or by immersing in hot water a glass matrass (pl. i. fig. 4), filled, up to a mark in the neck, with spirit of wine, tinged with any colouring substance. The spirit expands immediately when heated, and would overflow if not placed in a cooler situation. The degree of expansion produced in different liquids, by similar elevations of temperature, varies very considerably. Thus, water expands much more than mercury, and alcohol more than water. This difference of expansibility is even sufficiently striking to appear in a remarkable degree, when we immerse, in water heated to  $150^{\circ}$ , three equal glass vessels of the shape of thermometer tubes, containing the one mercury, the other water, and the third spirit of wine. The spirit will begin to escape from the aperture of the vessel, before the mercury has ascended far in the stem.\* The expansion of *aëriform bodies* is shown, by holding, near the fire, a bladder half filled with air, the neck of which is closely tied, so as to prevent the enclosed air from escaping. The bladder will soon be fully distended, and may even be burst by continuing and increasing the heat. All aëriform bodies when deprived of moisture, and even condensable vapours, when not in contact with the liquids from which they have been produced, undergo the same expansion or contraction, at all temperatures hitherto tried, by similar additions or subtractions of

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\* See a table of the expansion of liquids in the Appendix.

heat. This, for a single degree of Fahrenheit's thermometer, is  $\frac{1}{483}$  part of their bulk, between  $32^{\circ}$  and  $212^{\circ}$ , as first determined by Mr. Dalton, and afterwards confirmed by Gay Lussac. At a cherry red heat (= about  $1095^{\circ}$  Fahr.) Sir H. Davy found that a volume of air = 1 at  $212^{\circ}$  Fahr., became 2.5 volumes. (On Flame, p. 68).

The expansion of solids may be made apparent by heating a rod of iron, of such a length as to be included, when cold, between two points, and the diameter of which is such, as barely to allow it to pass through an iron ring. When heated, it will have become sensibly longer; and it will be found incapable of passing through the ring. This property of metals has been applied to the construction of an instrument for measuring temperature, called a *pyrometer*, a neat and distinct representation of which is given in the first volume of "Chemical Conversations." On the same principle, M. Bréguet has constructed a very sensible metallic thermometer. (Ann. de Chim. et Phys. v. 312). It consists of a slip of silver and another of platina coiled into a spiral, one end of which is fixed, while the other is connected with an index which traverses a circular graduated plate. This instrument is capable not only of measuring, distinctly, variations of temperature too slight to be shown by a common thermometer, but also of being affected by changes too transient to be perceived even by an air thermometer. Mr. Daniell has, also, availed himself of the same property of expansion, in constructing a thermometer for measuring high degrees of heat. A bar of platina is inclosed in a case made of the same ware as black lead crucibles, and is fixed to it at one end, while the other is left free to move an index, by which means degrees of heat above ignition admit of being accurately measured. (Jour. of Science, xi. 309).

The degree of expansion is not the same for all solids, and even differs materially in substances of the same class. Thus, the metals expand in the following order, the most expansible being placed first; zinc, lead, tin, copper, bismuth, iron, steel, antimony, palladium, platina.\* The experiments of Dr. Ure (Phil. Trans. 1818), tend to show that equal degrees of expan-

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\* See the table in the Appendix.



sion are produced in a bar of metal, by a succession of similar increments of heat. Thus if the absolute elongation of a metallic rod heated from  $32^{\circ}$  to  $122^{\circ}$ , be called 10, then its elongation, by each of four successive intervals of  $90^{\circ}$  Fahr, was, as nearly as possible, 10 also.

All bodies, after being heated, return again, on cooling, precisely to their former dimensions.

The expansion of metals produces important effects in various mechanical instruments, especially in clocks; for a pendulum vibrating seconds will, by a change of temperature equal to  $30^{\circ}$  Fahr. alter its length about  $\frac{1}{5000}$  part, which is sufficient to change its rate of going eight seconds of time per day. To obviate this inconvenience, various contrivances have been resorted to, which are described in works on practical horology.

To the general law of the expansion of bodies by heat and their contraction by cold, there are, however, several exceptions. Water by freezing is considerably increased in bulk; salts in the act of crystallizing expand; and some of the metals, as cast iron, bismuth, and antimony, have their dimensions enlarged by congealing; but mercury and other metals follow the general law, and occupy less bulk when solid than when fluid.

II. *Construction of the thermometer founded on the principle of expansion.*—The thermometer is an instrument of so much importance, that it may be expedient to explain the construction of the different kinds which are required in chemical researches.

The instrument employed by Sanctorio, to whom the invention of the thermometer is generally ascribed, was of a very simple kind, and measured variations of temperature by the variable expansion of a confined portion of air. To prepare this instrument, a glass tube (pl. i. fig. 9) is to be provided, eighteen inches long, open at one end, and blown into a ball at the other. On applying a warm hand to the ball, the included air expands, and a portion is expelled through the open end of the tube. In this state, the aperture is quickly immersed in a cup filled with any coloured liquid, which ascends into the tube, as the air in the ball contracts by cooling. The instrument is now prepared. An increase of temperature forces the liquor down the tube; and, on the contrary, the

application of cold causes its ascent. These effects may be exhibited alternately by applying the hand to the ball, and then blowing on it with a pair of bellows. By the application of a graduated scale, the amount of the expansion may be measured.

The ball of the above instrument, it must be obvious, cannot be conveniently applied to measure the temperature of liquids. For adapting it to this purpose, a slight variation may be made in its construction, as represented fig. 8, *a*. To prepare this instrument, a small spherical glass vessel is to be about one 6th or one 4th filled with any coloured liquid. The tube, open at both ends, is then to be cemented into the neck, with its lower aperture beneath the surface of the fluid. The expansion of the included air drives the liquid up the stem, to which we may affix a graduated scale, corresponding with that of a common mercurial thermometer. Other modifications have also been made by different philosophers. One of the most useful and simple forms is represented fig. 8, *b*. It consists merely of a tube of very small bore, from 9 to 12 inches long, at one end of which is blown a ball, from half an inch to an inch in diameter, which is afterwards blackened by paint, or by the smoke of a candle. A small column of coloured liquid, about an inch in length, is then introduced, by a manipulation similar to that already described. To fit the instrument for use, this column ought to be stationary, about the middle of the tube, at the common temperature of the atmosphere. The slightest variation of temperature occasions the movement of the coloured liquid; and a scale of equal parts measures the amount of the effect.

An insuperable objection, however, to the air thermometer, *as thus constructed*, is, that it is affected, not only by changes of temperature, but by variations of atmospheric pressure. Its utility consists in the great amount of the expansion of air, which, by a given elevation of temperature, is increased in bulk above twenty times more than mercury. Hence it is adapted to detect minute changes, which the mercurial thermometer would scarcely discover; and its expansions being uniform for equal additions of heat, it is better adapted than any liquid for becoming, when properly applied, an accurate measure of temperature.

An important modification of the air thermometer has been invented by Mr. Leslie, and employed by him, with great advantage, in his interesting researches respecting heat. To this instrument he has given the name of the Differential Thermometer. Its construction is as follows: "Two glass tubes of unequal length, each terminating in a hollow ball, and having their bores somewhat widened at the other ends (a small portion of sulphuric acid, tinged with carmine, being introduced into the ball of the longer tube), are joined together by the flame of a blow-pipe, and afterwards bent nearly into the shape of the letter U (see fig. 7), the one flexure being made just below the joining, where the small cavity facilitates the adjustment of the instrument. This, by a little dexterity, is performed, by forcing, with the heat of the hand, a few minute globules of air from the one cavity into the other. The balls are blown as equal as the eye can judge, and from four 10ths to seven 10ths of an inch diameter. The tubes are such as are drawn for thermometers, only with wider bores; that of the short one, to which the scale is affixed, must have an exact calibre of a 50th, or a 60th, of an inch. The bore of the long tube need not be so regular, but should be visibly larger, as the coloured liquid will then move quicker under any impression. Each leg of the instrument is from three to six inches in height, and the balls are from two to four inches apart.

"A moment's attention to the construction of this instrument will satisfy us, that it is affected only by the *difference* of heat in the corresponding balls; and is calculated to measure such difference with peculiar nicety. As long as both balls are of the same temperature, whatever this may be, the air contained in both will have the same elasticity, and, consequently, the intercluded coloured liquor, being pressed equally in opposite directions, must remain stationary. But if, for instance, the ball which holds a portion of the liquor be warmer than the other, the superior elasticity of the confined air will drive the liquid forwards, and make it rise, in the opposite branch, above the zero, to an elevation proportional to the excess of elasticity, or of heat." The amount of the effect is ascertained by a graduated scale, the interval between

freezing and boiling being distinguished into 100 equal degrees. This instrument, it must be obvious, cannot be applied to measure variations in the temperature of the surrounding atmosphere, for the reason already assigned. It is peculiarly adapted to ascertain the difference of the temperatures of two contiguous spots in the same atmosphere; for example, to determine the heat in the focus of a reflector.

A differential thermometer has been contrived by Dr. Howard, resembling that of Mr. Leslie in its general form, but in which the degree of heat is measured by the expansive force of the vapour of ether or spirit of wine *in vacuo*. Directions for constructing it are given in the 8th volume of the Quarterly Journal of Science, p. 219. It is intended to be applied to the same purposes as that of Mr. Leslie, but is more sensible to changes of temperature, and the movement of the fluid (ether tinged by a drop of tincture of cochineal), follows instantaneously the application of the heating cause, whereas in the air thermometer some time is required before the effect takes place.

Thermometers, filled with spirit of wine (a liquid which has not been congealed by any degree of cold hitherto produced), are best adapted to the measurement of very low temperatures, at which mercury would freeze. The amount of the expansion of alcohol, also, which exceeds that of mercury above eight times, fits it for ascertaining very slight variations of temperature. But it cannot be applied to measure high degrees of heat; because the conversion of the spirit into vapour would burst the instrument.

The fluid, best adapted for filling thermometers, is mercury, which, though it expands less in amount than air, or alcohol, still undergoes this change to a sufficient degree; and, in consequence of its difficult conversion into vapour, may be applied to the admeasurement of more elevated temperatures. As a considerable saving of expense will accrue to the experimentalist, who is able to construct mercurial thermometers, I shall offer some rules for this purpose. In general, however, I should deem it preferable merely to superintend their construction, and to be satisfied, by actual inspection, that the necessary accuracy is observed; because much time must be

unavoidably lost, in acquiring the manual skill which is essential to construct them neatly.

Thermometer tubes may be had at the glass-house, and of various philosophical instrument makers. In purchasing them, those should be rejected that are not hermetically sealed at both ends; because the smallest condensation of moisture, which must take place when air is freely admitted within the tube, is injurious to the accuracy of the instrument. A small bottle of elastic gum should be provided, in the side of which a brass valve is fixed, or a piece of brass perforated by a small hole, to be occasionally stopped by the finger. A blow-pipe is also an essential part of the apparatus; and, in addition to one of the ordinary kind, it will be found useful to have one which is supplied with air by a pair of double bellows, worked by the foot.

Before proceeding to the construction of the thermometer, it is necessary to ascertain, that the tube is of equal diameter in different parts. This is done by breaking off both of the sealed ends, immersing one of them an inch or two deep in clean and dry mercury, and then closing the other end with the finger. On withdrawing the tube from the mercury, a small column of that fluid remains in it, the length of which is to be examined, by laying the tube horizontally on a graduated ruler.\* By inclining the tube, this column may be gradually moved through its whole length; and if the tube be of uniform bore, it will measure the same in every part. Such a degree of perfection, however, is scarcely ever to be observed throughout tubes of considerable length; but, in general, a portion of the tube will be found perfect, of sufficient length for a thermometer, and this part is to be broken off.

On one end of the tube let the neck of the elastic bottle be firmly tied; and let the other end be heated by the flame of the blow-pipe, till the glass softens. The softened part must then be pressed, by a clean piece of metal, into the form of a

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\* If the tube be of an extremely small bore, the mercury will not enter, and must be drawn in by the action of the elastic bottle, and not by the mouth.

rounded button; and to this the flame of the lamp must be steadily applied, till it acquires a white heat, and seems about to enter into fusion. To prevent its falling on one side, the tube, during this time, must be constantly turned round by the hand. When the heated part appears perfectly soft, remove it quickly from the lamp, and, holding the tube vertically, with the elastic bottle uppermost, press this last gently with the hand. The glass will be blown into a small ball, but not into one sufficiently thin for the purpose. To this the flame of the lamp must again be applied, turning it quickly round; and, on a second or third repetition of the process of blowing, the ball will be completely formed. The proportion of the size of the ball to the bore of the tube can only be learned by some experience.

To fill the ball, which has been thus formed, with mercury, the air must first be expelled by holding it over the flame of an Argand's lamp, and then quickly immersing the open end of the tube in very clean and dry quicksilver. As the ball cools, the mercury will ascend, and will partly fill it. Let a paper funnel be tied firmly over the open end of the tube; into this pour a small portion of quicksilver, and apply the heat of the lamp to the ball. Any remaining portion of air will thus be expelled; and if the heat be raised so as to boil the mercury, the ball and stem will be filled with mercurial vapour, the condensation of which, on removing the ball from the lamp, will occasion a pretty complete vacuum. Into this vacuum, quicksilver will descend from the paper cone; and the instrument will be completely filled. But for the purpose of a thermometer, it is necessary that the mercury should rise only to a certain height of the stem; and a few drops may, therefore, be expelled by cautiously applying the heat of the lamp. To estimate whether the proper quantity of quicksilver has been left in the instrument, immerse the ball first in ice-cold water, and then in the mouth. The space between these two points will comprise about  $64^{\circ}$ , or rather more than one third of the whole space between the freezing and boiling points of water. If the empty part of the tube exceeds, in length, about three times the portion thus filled by the expanded quicksilver, we may proceed (when an instru-

ment is wanted with a scale including only from  $32^{\circ}$  to  $212^{\circ}$ ) to seal it hermetically, which is done as follows: The part to be sealed is first heated with the blow-pipe, and drawn out to a fine capillary tube; the bulb is then heated, till a few particles of quicksilver have fallen from the top of the tube: at this moment, the flame of another candle is directed, by the blow-pipe, on the capillary part of the tube, the candle is withdrawn from the ball, and the tube is sealed, at the instant when the mercury begins to descend. If this operation has been skilfully performed, so as to leave no air in the tube, the whole of the tube should be filled with quicksilver on holding the instrument with the ball uppermost.

To have very large degrees, the ball must bear a considerable proportion to the tube; but this extent of scale cannot be obtained without sacrificing, in some measure, the sensibility of the instrument.\* The whole of the process of constructing thermometers neatly and accurately is connected with the possession of manual skill, which practice only can confer; and it is scarcely possible, without the most tedious minuteness, to describe all the necessary precautions and manipulations. These will readily suggest themselves to a person who carries the above instructions into effect.

In graduating thermometers, the first step consists in taking the two fixed points. The freezing point is ascertained, by immersing, in thawing snow or ice, the ball and part of the stem; so that the mercury, when stationary, shall barely appear above the surface. At this place let a mark be made with a file. In taking the boiling point, considerable caution is required; and, for reasons which will afterwards be stated, attention must be paid to the state of the barometer, the height of which, at the time, should be precisely 29.8. A tin vessel is to be provided, (for, according to Gay Lussac,† one of glass leads to erroneous results,) four or five inches longer than the thermometer, and furnished with a cover, in

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\* Directions for constructing thermometers of great sensibility are given by the Chevalier Landriani, in the 7th volume of the *Journal of Science*, p. 183.

† 82 *An. de Ch.* 174, and 7 *An. de Ch. et Phys.* 307.

which are two holes. Through one of these, the thermometer stem must be passed (the bulb being within the vessel,) so that the part, at which the boiling point is expected, may be just in sight. The other hole may be left open; and the cover being fixed in its place, the vessel, containing a few inches of water at the bottom, is to be set on the fire. The thermometer will presently be wholly surrounded by steam; and when the mercury becomes stationary in the stem, its place must be marked. The scale of Fahrenheit is formed by transferring the intermediate space to paper by a pair of compasses, and dividing it into  $180^{\circ}$ , the lowest being called  $32^{\circ}$ , and the highest  $212^{\circ}$ . The scale of other countries, however, differs considerably; but these variations do not prevent the comparison of observations with different instruments, when the freezing and boiling points of water are agreed upon as fixed data. In the appendix, rules will be given for converting the degrees of other scales to that of Fahrenheit.

III. *The dilatations and contractions of the fluid in the mercurial thermometer, are nearly proportional to the quantities of caloric, which are communicated to the same homogeneous bodies, or separated from them, so long as they retain the same form.*

Thus a quantity of caloric, required to raise a body  $20^{\circ}$  in temperature, by the mercurial thermometer, is nearly double that which is required to raise it  $10^{\circ}$ . Hence there appears to be a pretty accurate proportion between the increments or decrements of heat, and the increments or decrements of expansion in the mercury of a thermometer. On this principle, if equal quantities of hot and cold water be mixed together, and a thermometer be immersed in the hot water, and also in the cold, previously to the mixture, the instrument should point, after the mixture, to the arithmetical mean, or to half the difference of the separate heats, added to the less or subtracted from the greater. This will be proved to be actually the fact, by the following experiment. Mix a pound of water at  $172^{\circ}$  with a pound at  $32^{\circ}$ . Half the excess of the caloric of the hot water will pass to the colder portion; that is, the hot water will be cooled  $70^{\circ}$ , and the cold will receive  $70^{\circ}$  of temperature; therefore  $172 - 70$ , or  $32 + 70 = 102$ ,



will give the heat of the mixture. To attain the arithmetical mean exactly, several precautions must be observed.\*

The experiments of De Luc, however, have shown, that the ratio of expansion does not, *strictly*, keep pace with the actual increments of temperature; and that the amount of the expansion increases with the temperature. Thus if a given quantity of mercury, in being heated from 32 to 122°, the first half of the scale, be expanded 14 parts, in being raised from 122 to 212°, the higher half, it will be expanded 15 parts.

From the inquiries of Mr. Dalton, it appears to follow, that the irregularity of the expansion of mercury is even considerably greater than has been stated by De Luc. By the common mercurial thermometer, we cannot ascertain the true rate of expansion in quicksilver; for it must be obvious that the enlarged capacity of the glass ball, in which it is contained, must considerably affect the result. If the capacity of the ball remained unaltered, we should then be able to determine the actual rate of expansion; but by an increase of temperature its capacity is enlarged, and space is thus found, within the ball, for the expansion of that mercury, which would otherwise be driven into the tube. By knowing the rate of expansion in glass itself, we can correct this error: but a small mistake in this datum will lead us considerably wrong as to the true expansion of quicksilver. The *real* expansion of mercury in glass is *greater* than the *apparent*, by the expansion of the glass itself.

Making due correction for this circumstance, Mr. Dalton has been led to conclude from his experiments, that notwithstanding the apparent diversities of expansion in different fluids, they all actually expand according to the same law; *viz. that the quantity of expansion is as the square of the temperature from their respective freezing points, or from their points of greatest density.* If then a thermometer be constructed, with degrees corresponding to this law, they will be found to differ very considerably from those of the common mercurial thermometer, in which the space between freezing

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\* See Crawford on Animal Heat, p. 95, &c.

and boiling is divided into 180 equal parts. In the Appendix will be found a table showing the correspondence between the old scale and the new one constructed on Mr. Dalton's principle.

The view which has been taken by Mr. Dalton of the thermometer, has drawn the attention of Dr. Ure,\* and of M. M. Petit and Dulong,† to the same subject. The former concludes from his experiments, that taking three thermometric intervals from 32° Fahr. upwards, each of 180°, mercury has actually an increasing rate of expansion, and that 60 parts at 572° are expanded as much by the same power of caloric, as 61 parts at 592°, and 62 parts at 212°. But this small difference, he observes, is compensated by the lessening quantity of quicksilver in the bulb of a thermometer at high temperatures, in consequence of which the mercurial thermometer becomes a true measurer of sensible heat. Petit and Dulong, also, satisfied themselves that the expansibility of mercury slowly increases as the temperature augments. From 32° to 212°, it is scarcely appreciable, and corresponds with the expansion of air, which they take for granted to be perfectly equable. The following Table exhibits the dilatation of mercury for a degree centigrade at the various temperatures (all centigrade‡) indicated in the first column of the table, and measured by an air thermometer.

Temperature.	Expansion of Mercury.	Temp. indicated by the dilatations of the mercury supposed uniform.
0° .....	0 .....	0.00
100 .....	$\frac{1}{5550}$ .....	100.00
200 .....	$\frac{1}{5455}$ .....	204.61
300 .....	$\frac{1}{5366}$ .....	314.15

Comparing the numbers in the first and last columns, it

\* Phil. Trans. 1818.

† Annals of Philos. vol. xiii.

‡ To convert centigrade degrees into those of Fahr. double them, then deduct one tenth, and add the constant number 32. Thus 18° centigrade  $\times 2 = 36$ , from which  $\frac{1}{10}$  subtracted leaves 32.4, and to this adding 32, we have 64.4, Fahr.

appears that up to  $100^{\circ}$ , the mercurial and air thermometers give the same indications; in the second interval, the excess of the former over the latter is  $4.61^{\circ}$ , and in the last interval it increases to  $14.15^{\circ}$ .

The boiling point of mercury, according to these philosophers, is  $680^{\circ}$  Fahr, or, making the due correction for the expansion of glass,  $662^{\circ}$  of Fahr. scale. The experimental result of Mr. Crighton of Glasgow, was  $656^{\circ}$ .

IV. *Uncombined caloric has a tendency to an equilibrium.*—Any number of different bodies at various temperatures, if placed under similar circumstances of exposure, all acquire a common temperature. Thus, if in an atmosphere at  $60^{\circ}$ , we place iron filings heated to redness, boiling water, water at  $32^{\circ}$ , and various other bodies of different temperatures, they will soon affect the thermometer in the same degree. The same equalization of temperature is attained, though less quickly, when a heated body is placed in the vacuum of an air-pump. The rate of cooling in air is to that *in vacuo*, the temperatures being equal, nearly as five to two.

II. *Motion of Free Caloric.*—1. *Its Radiation.*—2. *Its Passage through Solids and Fluids.*

*Caloric escapes from bodies in two different modes.*—Part of it finds its way through space, independently of other matter, and with immeasurable velocity. In this state it has been called radiant heat, or radiant caloric.

RADIANT CALORIC exhibits several interesting properties.

1. *Its reflection.* (a) Those surfaces, that reflect light most perfectly, are not equally adapted to the reflection of caloric. Thus, a glass mirror, which reflects light with great effect when held before a blazing fire, scarcely returns any heat, and the mirror itself becomes warm. On the contrary, a polished plate of tin, or a silver spoon, when similarly placed, reflects, to the hand, a very sensible degree of warmth; and the metal itself remains cool. Metals, therefore, are much better reflectors of caloric than glass; and they possess this property, exactly according to their degree of polish.

(b) Caloric is reflected according to the same law that regulates the reflection of light. This is proved by an interest-

ing experiment of M. Pictet; the means of repeating which may be attained at a moderate expense. Provide two reflectors of planished tin (*a* and *b*, fig. 45), which may be 12 inches diameter, and segments of a sphere of nine inches radius. Parabolic mirrors are still better adapted to the purpose; but their construction is less easy. Each of these must be furnished, on its convex side, with the means of supporting it in a perpendicular position on a proper stand. Place the mirrors opposite to each other on a table, at the distance of from six to 12 feet. Or they may be placed in a horizontal position, as represented in the wood cut given at page 83, an arrangement in some respects more convenient. In the focus of one, let the ball of an air thermometer, *c*, or (which is still better) one of the balls of a differential thermometer, be situated; and in that of the other, suspend a ball of iron, about four ounces in weight, and heated below ignition, or a small matrass of hot water, *d*; having previously interposed a screen before the thermometer. Immediately on withdrawing the screen, the depression of the column of liquid, in the air thermometer, evinces an increase of temperature in the instrument. In this experiment, the caloric flows first from the heated ball to the nearest reflector; from this it is transmitted, in parallel rays, to the surface of the second reflector, by which it is collected into a focus on the instrument. This is precisely the course that is followed by radiant light; for if the flame of a taper be substituted for the iron ball, the image of the candle will appear precisely on that spot (a sheet of paper being presented for its reception) where the rays of caloric were before concentrated.

(*c*) When a glass vessel, filled with ice or snow, is substituted for the heated ball, the course of the coloured liquid in the thermometer will be precisely in the opposite direction; for its ascent will show, that the air in the ball is cooled by this arrangement. This experiment, which appears, at first view, to indicate the reflection of cold, presents, in fact, only the reflection of heat in an opposite direction; the ball of the thermometer being, in this instance, the hotter body. "And since heat emanates from bodies in quantities greater as their temperature is higher, the introduction of a cold body into

the focus of one mirror, necessarily diminishes the temperature of a thermometer in the focus of the other, in the same manner as a black body placed in the focus of the one would diminish the quantity of light in the focus of the other."\*

(d) In Mr. Leslie's "Enquiry into the Nature, &c. of Heat," a variety of important experiments are detailed, which show the influence of covering the reflectors with various substances, or of mechanically changing the nature of their surfaces, on their power of returning caloric.

2. Caloric is *refracted*, also, according to the same law that regulates the refraction of light. This interesting discovery we owe to Dr. Herschell, whose experiments and apparatus, however, cannot be understood without the assistance of a plate. For this reason, I refer to his paper in the 90th vol. of the Philosophical Transactions, or in the 7th vol. of the Philosophical Magazine.

3. The nature of the *surface* of bodies has an important influence over their power of *radiating* caloric.

To exhibit this influence experimentally, let a canister of planished block tin, forming a cube of six or eight inches, be provided, having an orifice at the middle of its upper side, from half an inch to an inch diameter, and the same in height. This orifice is intended to receive a cap having a small hole, through which a thermometer is inserted, so that its bulb may reach the centre of the canister. Let one side of the canister be covered with black paint; destroy the polish of another side, by scratching it with sand-paper; tarnish a third with quicksilver; and leave the fourth bright. Then fill the vessel with boiling water. The radiation of caloric from the blackened side is so much more abundant than from the others, as to be even sensible to the hand. Place it before a reflector (fig. 45), in lieu of the heated iron ball already described. The thermometer, in the focus of the second reflector, will indicate the highest temperature, or most copious radiation of caloric, when the blackened side is presented to the reflector; less when the tarnished or scratched side is turned towards it; and least of all from the polished side.

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\* Davy's Chem. Philos. p. 206.

These varieties in the radiating power of different surfaces, are attended, as might be expected, with corresponding variations in the *rate of cooling*. If water in a tin vessel, all of whose sides are polished, cools through a given number of degrees in eighty-one minutes, it will descend through the same number in seventy-two minutes, if the surface be tarnished with quicksilver. Water, also, enclosed in a clean and polished tin ball, cools about twice more slowly than water in the same ball covered with oiled paper. Blackening the surface with paint, or even a thin coat of varnish, on the same principle, accelerates greatly the rate of cooling. These facts teach us, that vessels, in which fluids are to be long kept hot should have their surfaces brightly polished; and they explain among other things, the superiority of metallic tea-pots over those of earthen ware.

5. Radiant caloric is *absorbed* with different facility by different surfaces. This is only stating, in other terms, that surfaces are endowed with various powers of reflecting caloric; since the power of absorbing caloric is precisely opposite to that of reflecting it. Hence the best reflectors of heat will absorb the least. It may be proper, however, to offer some illustrations of the principle under this form.

(a) Expose the bulb of a sensible thermometer to the direct rays of the sun. On a hot summer's day it will probably rise, in this climate, to  $108^{\circ}$ .\* Cover it with Indian ink, and again expose it in a similar manner. During the evaporation of the moisture it will fall; but as soon as the coating becomes dry, it will ascend to  $118^{\circ}$ , or upwards, of Fahrenheit, or  $10^{\circ}$  higher than when uncovered with the pigment. This cannot be explained, by supposing that the black coating is gifted with the power of retaining caloric, and preventing its escape; because from experiments already related, it appears, that a similar coating accelerates the cooling of a body to which it is applied.

(b) Colour has considerable influence over the absorption of caloric. This is shown by the following very simple experiment of Dr. Franklin.

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\* Watson's Essays. v. 193.

On a winter's day when the ground is covered with snow, take four pieces of woollen cloth, of equal dimensions but of different colours, *viz.* black, blue, brown, and white, and lay them on the surface of the snow, in the immediate neighbourhood of each other. In a few hours, the black cloth will have sunk considerably below the surface; the blue almost as much; the brown evidently less; and the white will remain precisely in its former situation. Thus it appears, that the sun's rays are absorbed by the dark coloured cloth, and excite such a durable heat, as to melt the snow underneath; but they have not the power of penetrating the white. Hence the preference, generally given to dark coloured cloths during the winter season, and to light coloured ones in summer, appears to be founded on reason.

(c) This experiment has been varied by Sir H. Davy, in a manner which may be repeated at any season of the year. Take six similar pieces of sheet copper, each about an inch square, and colour the one white, another yellow, a third red, the fourth green, the fifth blue, and the sixth black. On the centre of one side of each piece, put a small portion of a mixture of oil and wax, or cerate, which melts at about  $76^{\circ}$ . Then expose their coloured surfaces, under precisely equal circumstances, to the direct rays of the sun. The cerate on the black plate will begin to melt perceptibly before the red; the blue next; then the green and the red; and, lastly, the yellow. The white will scarcely be affected, when the black is in complete fusion.

Caloric passes, also, but much more slowly, through solid and liquid bodies, which are then termed CONDUCTORS of caloric.

1. Solid bodies convey heat in all directions, upwards, downwards, and laterally; as may be shown, by heating the middle of an iron rod, and holding it in different directions.

2. Some bodies conduct caloric much more quickly than others. Coat two rods, of equal length and thickness, the one of glass, the other of iron, with wax, at one end of each only; and then apply heat to the uncoated ends. The wax will be melted vastly sooner from the end of the iron rod, than

from the glass one; which shows, that iron conducts heat more quickly than glass.

Even the different metals possess very different powers of conducting caloric. An approximation to the degree in which they possess this property, may be attained by the following method, originally employed by Dr. Ingenhouz. Procure several solid cylinders, or rods, of the same size and shape, but of different metals. They may be six inches long, and one 4th of an inch in diameter. Coat them, within about an inch of one end, with bees-wax, by dipping them into this substance when melted, and allowing the covering to congeal. Let an iron heater be provided, in which small holes have been drilled, that exactly receive the clean ends of the cylinders. After heating it below ignition, insert the cylinders in their places. The conducting power may be estimated by the length of wax coating melted from each in a given time. According to the experiments of Dr. Ingenhouz, the metals may be arranged in the following order: Silver possesses the highest conducting power; next gold; then copper and tin, which are nearly equal; and, below these platina, iron, steel, and lead, which are greatly inferior to the rest.

It is chiefly owing to the different conducting powers of bodies, that they affect us, when we touch them, with different sensations of cold. Thus, if we apply the hand in succession to a number of bodies (as a piece of wood, another of marble, &c.), they appear cold in very different degrees. And as this sensation is occasioned by the passage of caloric out of the hand into the body which it touches, that body will feel the coldest, which carries away heat the most quickly; or which, in other words, is the best conductor. For the same reason, of two bodies which are heated to the same degree, and both considerably above the hand, the best conductor is the hottest to the touch. Thus the money in our pockets often feels hotter than the clothes which contain it.

3. Liquid and aciform bodies convey heat on a different principle from that observed in solids, *viz.* by an actual change in the situation of their particles. That portion of the fluid, which is nearest to the source of heat, is expanded, and becoming specifically lighter, ascends, and is replaced by a



colder portion from above. This, in its turn, becomes heated and dilated, and gives way to a second colder portion; and thus the process goes on, as long as the fluid is capable of imbibing heat.

(a) Take a glass tube, eight or ten inches long, and about an inch in diameter. Pour into the bottom part, for about the depth of an inch, a little water tinged with litmus, and then fill up the tube with common water, pouring on the latter extremely gently, so as to keep the two strata quite distinct. If the upper part of the tube be first heated, the coloured liquor will remain at the bottom; but if the tube be afterwards heated at the bottom, the infusion will ascend, and will tinge the whole mass of fluid.

(b) Into a cylindrical glass jar, four inches diameter, and 12 or 14 deep, let a circular piece of ice be fitted  $3\frac{1}{2}$  inches thick, and of rather less diameter than the jar. Or water may be poured into the jar to the depth of  $3\frac{1}{2}$  inches, and allowed to congeal by exposure to a freezing atmosphere, or by surrounding it with a mixture of snow and salt. The ice is to be secured in its place by two slips of wood, crossing each other like two diameters of a circle, set at right angles to each other. Pour, over the cake of ice, water of  $32^{\circ}$  temperature, to the depth of two inches; and on its surface let there float a shallow circular wooden box, perforated with holes. From the cock of a tea-urn, filled with boiling water, and raised so that its spout may be above the top of the jar, suspend a number of moistened threads, the lower ends of which must rest on the surface of the box. By this arrangement, when the cock is turned, the hot water will trickle down the threads, and will have its fall considerably broken. It will then spread over the surface of the box, and pass through the perforated holes to the cold water beneath, over which it will float without mixing with it. Let the jar be thus completely filled with hot water. The ice will remain unmelted for several hours at the bottom of the vessel.

(c) Fill a similar jar with hot water; and, having provided a cake of ice, of equal size with the former one, let it be placed on the surface of the water. In about three minutes, the whole will be melted. Both these experiments are more

striking, if the water, used for forming the cakes of ice, be previously coloured with litmus; for, in the latter experiment, the descending currents of cold water are thus made apparent.

(d) These experiments may be varied, by freezing, in the bottom of a tube one inch wide, a portion of water, about two inches in depth. Then fill the tube with water of the common temperature, and hold it inclined over an Argand's lamp, so that the upper portion only of the tube may be heated. When thus disposed, the water may be made to boil violently at the surface, and yet the ice will not be melted. But if the experiment be reversed, and (the ice floating on the surface) heat be applied to the bottom of the tube, the ice will be liquefied in a few seconds.

(e) Substituting water of the temperature of  $41^{\circ}$  for the boiling water used in experiment (c), Count Rumford found, that, in a given time, a much greater quantity of ice was melted by the cooler water. This appears, on first view, rather paradoxical. The fact, however, is explained by a remarkable property of water, *viz.* that when cooled below  $40^{\circ}$  it ceases to contract, and experiences, on the contrary, an enlargement of bulk. Water, therefore, at  $40^{\circ}$  (at the bottom of which is a mass of ice at  $32^{\circ}$ ), is cooled by contact with the ice, and is expanded at the same moment. It therefore ascends, and is replaced by a heavier and warmer portion from above.

It is in consequence of the same property that the surface of a deep lake is sometimes covered with ice, even when the water below is only cooled to  $40^{\circ}$ ; for the superficial water is specifically lighter than the warmer water beneath it, and retains its place, till it is changed into ice. This property of water is one of the most remarkable exceptions to the law, that bodies are expanded by an increase, and contracted by a diminution, of temperature.

From these facts, Count Rumford concluded, that water is a perfect non-conductor of caloric, and that it propagates caloric in one direction only, *viz.* upwards, in consequence of the motions which it occasions among the particles of the fluid. The Count inferred also, that if these motions could be suspended, caloric would cease to pass through water; and, with

the view of deciding this question, he made the following experiments, which admit of being easily repeated. A cylindrical tin vessel must previously be provided, two inches in diameter, and  $2\frac{1}{2}$  inches deep, having a moveable cover, perforated with a small aperture, for transmitting the stem of a thermometer, which is to be inserted so that its bulb may occupy the centre of the vessel.

(*f*) Fill this vessel with water of the temperature of the atmosphere; let the cover be put in its place; and let the whole apparatus, except the scale of the thermometer, be immersed in water, which is to be kept boiling over a lamp. Observe how long a time is required to raise the water from its temperature at the outset to  $180^{\circ}$ , and remove it from its situation. Note, also, how long it takes to return to its former temperature.

(*g*) Repeat the experiment, having previously dissolved in the water 200 grains of common starch. The thermometer will now require about half as long again to arrive at the same temperature. A similar retardation, and to a greater amount, is produced by the mixture of eider-down, cotton-wool, and various other substances, which are not chemically soluble in water, and which can diminish its conducting power in no other way than by obstructing the motion of its particles.

This inference, however, respecting the complete non-conducting power of water, has been set aside by the subsequent inquiries of Dr. Thomson and Dr. Murray, especially by a most decisive experiment of the latter. To establish the conducting power of water, it was justly deemed indispensable, that caloric should be proved to be propagated through that fluid downwards. This, on actual trial, it appeared to be; but it was objected, that the sides of the containing vessel might be the conductor. To obviate this objection, Dr. Murray contrived to congeal water into the form of a jar, capable of holding liquids. This was separately filled with linseed oil and with mercury. At a proper distance below the surface, the bulb of a thermometer was placed; and on the surface of the liquid rested a flat iron vessel, containing boiling water. Under these circumstances, the thermometer invariably rose; and though it ascended only a very few de-

grees, yet it must be recollected, that the cooling power of the sides of the vessel would effectually prevent any considerable elevation of temperature. This experiment, in conjunction with others, decisively proves that water is a conductor, though a slow or imperfect one, of caloric.



### SECTION III.

#### *Caloric the Cause of Liquidity.*

ALMOST every solid is capable of passing to the fluid state on the application of a sufficient degree of heat, which is not the same for all solids, but differs for each. In many solids the transition to the liquid form is sudden, while others pass through various stages of liquidity, before they become completely fluid. The metals are examples of the first, and wax or tallow of the second kind of liquefaction. In the former it is more easy to determine what has been called the *fusing* or *melting point*, which is constant in the same solid. When the natural form of a body is that of a liquid, and it only occasionally assumes the solid form, we call the temperature at which it is solidified the *freezing* or *congealing point*; and this is also constant in the same liquid, but different in various liquids, as will more clearly appear from the following examples.

I. *The temperature of melting snow, or of thawing ice, is uniformly the same at all times, and in all places.*—This may be ascertained by the thermometer, which will always, when immersed in liquefying ice or snow, point to  $32^{\circ}$  of Fahrenheit, whatsoever may be the height of the barometer, or the elevation, above the sea, of the place where the experiment is made.\*

II. *The sensible heat, or temperature of ice, is not changed by liquefaction.*—A thermometer in pounded ice stands at  $32^{\circ}$ , and at the very same point in the water which results from the liquefaction of ice.

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\* Shuckburgh, Philosophical Transactions, lxix.

III. *Yet ice, during liquefaction, must absorb much caloric.*—Expose a pound of water at  $32^{\circ}$ , and a pound of ice at  $32^{\circ}$ , in a room, the temperature of which is several degrees above the freezing point, and uniformly the same during the experiment. The water will arrive at the temperature of the room, several hours before the ice is melted; and the ice, when first melted, will have, as before its liquefaction, the temperature of  $32^{\circ}$ . Yet the ice must, during the whole of this time, have been imbibing caloric, because (according to Experiment IV. § 2.) a colder body can never be in contact with a warmer one, without receiving caloric from it. The caloric, therefore, which has entered the ice, but is not to be found in it by the thermometer, is said to have *become latent*. As it is the cause of the liquefaction of the ice, it is sometimes called *caloric of fluidity*.

IV. *The quantity of caloric that enters into a pound of ice, and becomes latent, during liquefaction, may be learned by experiment.*—To a pound of water, at  $172^{\circ}$ , add a pound of ice at  $32^{\circ}$ . The temperature will not be the arithmetical mean ( $202^{\circ}$ ), but much below it, *viz.*  $32^{\circ}$ . All the excess of caloric in the hot water has therefore disappeared. From  $172^{\circ}$  take  $32^{\circ}$ ; the remainder,  $140^{\circ}$ , shows the quantity of caloric that enters into a pound of ice during liquefaction; that is, as much caloric is absorbed by a pound of ice, during its conversion into water, as would raise a pound of water from  $32^{\circ}$  to  $172^{\circ}$ .

It is from the property of its uniformly absorbing the same quantity of caloric for conversion into water, that ice has been ingeniously applied, by Lavoisier and Laplace, to the admeasurement of the heat, evolved in certain operations. Let us suppose the body (from which the caloric, evolved either by simple cooling or combustion, is to be measured) to be inclosed in a hollow sphere of ice, with an opening at the bottom. When thus placed, the heat which is given out will be all employed in melting the ice; and will produce this effect in direct proportion to its quantity. Hence the quantity of ice, which is converted into water, will be an accurate measure of the caloric, that is separated from the body submitted to experiment. In this way, Lavoisier ascertained that equal

weights of different combustible bodies melt, by burning, very different weights of ice. The apparatus which he employed for this purpose, he has called the *calorimeter*. Its construction can scarcely be understood without the plate, which accompanies the description in his "Elements of Chemistry;" and I consider it unnecessary to copy it into this work, because the instrument is liable to several causes of inaccuracy.

V. *The heat rendered latent by the fusion of various bodies is not a constant quantity, but varies for each individual body.* This is shown by the following results of the experiments of the two Drs. Irvine.

	Caloric of fluidity.	Do. reduced to the sp. heat of water.
Sulphur . . . . .	143.68° Fahr.	27.14
Spermaceti . . . . .	145	
Lead. . . . .	162	5.6
Bees-wax . . . . .	175	
Zinc . . . . .	493	48.3
Tin . . . . .	500	33.
Bismuth . . . . .	550	23.25

VI. *Other examples of the absorption of caloric, during the liquefaction of bodies,* are furnished by the mixture of snow and nitric acid, or of snow and common salt, both of which, in common language, produce intense cold.

1. Dilute a portion of nitric acid with an equal weight of water: and, when the mixture has cooled, add to it a quantity of light fresh-fallen snow. On immersing the thermometer in the mixture, a very considerable reduction of temperature will be observed. This is owing to the absorption, and intimate fixation, of the free caloric of the mixture, by the liquefying snow.

2. Mix quickly together equal weights of fresh-fallen snow at 32°, and of common salt cooled, by exposure to a freezing atmosphere, down to 32°. The two solid bodies, on admixture, will rapidly liquefy; and the thermometer will sink 32°, or to 0; or, according to Sir C. Blagden, to 4° lower.\* To understand this experiment, it must be recollected, that the

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\* Philosophical Transactions, lxxviii. 281.

snow and salt, though at the freezing temperature of water, have each a considerable portion of uncombined caloric. Now salt has a strong affinity for water; but the union cannot take place while the water continues solid. In order, therefore, to act on the salt, the snow absorbs all the free caloric required for its liquefaction; and during this change, the free caloric, both of the snow and of the salt, amounting to  $32^{\circ}$ , becomes latent, and is concealed in the solution. This solution remains in a liquid state at 0, or  $4^{\circ}$  below 0 of Fahrenheit; but if a greater degree of cold be applied to it, the salt separates in a concrete form.

3. Most neutral salts, also, during solution in water absorb much caloric; and the cold, thus generated, is so intense as to freeze water, and even to congeal mercury. The former experiment, however (*viz.* the congelation of water), may easily be repeated on a summer's day. Add to 32 drachms of water, 11 drachms of muriate of ammonia, 10 of nitrate of potash, and 16 of sulphate of soda, all finely powdered. The salts may be dissolved separately, in the order set down. A thermometer, put into the solution, will show, that the cold produced is at or below freezing; and a little water, in a thin glass tube, being immersed in the solution, will be frozen in a few minutes. Various other freezing mixtures are described in Mr. Walker's papers in the Philosophical Transactions for 1787, 88, 89, 95, and 1801. Of these the table, given in the Appendix, for which I am indebted to the obliging communication of the author, contains an arranged abstract.

4. Crystallized muriate of lime, when mixed with snow, produces a most intense degree of cold. This property was discovered some years ago by M. Lovitz, of St. Petersburg, and has been since applied, in this country, to the congelation of mercury on a very extensive scale. The proportions which answer best, are about equal weights of the salt finely powdered, and of fresh-fallen and light snow. On mixing these together, and immersing a thermometer in the mixture, the mercury sinks with great rapidity. For measuring exactly the cold produced, a spirit-thermometer, graduated to  $50^{\circ}$  below 0 of Fahrenheit, or still lower, should be employed.

A few pounds of the salt are sufficient to congeal a large mass of mercury. By means of 13 pounds of the muriate, and an equal weight of snow, Messrs. Pepys and Allen froze 56 pounds of quicksilver into a solid mass. The mixture of the whole quantity of salt and snow, however, was not made at once, but part was expended in cooling the materials themselves.

On a small scale it may be sufficient to employ two or three pounds of the salt. Let a few ounces of mercury, in a very thin glass retort, be immersed, first in a mixture of one pound of each; and, when this has ceased to act, let another similar mixture be prepared. The second will never fail to congeal the quicksilver. The salt thus expended may be again evaporated, and crystallized for future experiments.

In plate iv. fig. 42, a very simple and cheap apparatus is represented, which I have generally employed to freeze mercury. The dimensions will be given in the description of the plates.\*

The reader, who wishes for farther particulars respecting these experiments, is referred to the Philosophical Magazine, iii. 76.

VII. *On the contrary, liquids, in becoming solid, evolve or give out caloric, or, in common language, produce heat.*

1. Water, if kept perfectly free from agitation, may be cooled down several degrees below  $32^{\circ}$ ; but, on shaking it, it immediately congeals, and the temperature rises to  $32^{\circ}$ .

2. Expose to the atmosphere, when at a temperature below freezing (for example, at  $25^{\circ}$  of Fahrenheit), two equal quantities of water, in one only of which about a fourth of its weight of common salt has been dissolved. The saline solution will be gradually cooled, without freezing, to  $4^{\circ}$ . The pure water will progressively descend to  $32^{\circ}$ , and will there remain stationary a considerable time before it congeals. Yet while thus stationary, it cannot be doubted, that the pure water is yielding caloric to the atmosphere, equally with the saline solution; for it is impossible that a warmer body can be surrounded by a cooler one, without imparting caloric to

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\* See Appendix.



the latter. The reason of this equable temperature is well explained by Dr. Crawford. (*On Heat*, p. 80.) Water, he observes, during freezing, is acted upon by two opposite powers: it is deprived of caloric by exposure to a medium, whose temperature is below  $32^{\circ}$ ; and it is supplied with caloric, by the evolution of that principle from itself, viz. of that portion which constituted its fluidity. As these powers are exactly equal, the temperature of the water must remain unchanged, till the caloric of fluidity is all evolved.

3. The evolution of caloric, during the congelation of water, is well illustrated by the following experiment of Dr. Crawford:—Into a round tin vessel put a pound of powdered ice; surround this by a mixture of snow and salt in a larger vessel; and stir the ice in the inner one, till its temperature is reduced to  $+ 4^{\circ}$  of Fahrenheit. To the ice thus cooled, add a pound of water at  $32^{\circ}$ . One 5th of this will be frozen; and the temperature of the ice will rise from  $4^{\circ}$  to  $32^{\circ}$ . In this instance, the caloric, evolved by the congelation of one 5th of a pound of water, raises the temperature of a pound of ice  $28^{\circ}$ .

4. If we dissolve sulphate of soda in water, in the proportion of one part to five, and surround the solution by a freezing mixture, it cools gradually down to  $31^{\circ}$ . The salt, at this point, begins to be deposited, and stops the cooling entirely. This evolution of caloric, during the separation of a salt, is exactly the reverse of what happens during its solution.\*

5. To a saturated solution of sulphate of potash in water, or of any salt that is insoluble in alcohol, add an equal measure of alcohol. The alcohol, attracting the water more strongly than the salt retains it, precipitates the salt, and considerable heat is produced.

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\* Blagden, *Philosophical Transactions*, lxxviii. 290.

## SECTION IV.

*Caloric the Cause of Vapour.*

I. *Every liquid, when of the same degree of chemical purity, and under equal circumstances of atmospheric pressure, has one peculiar point of temperature, at which it invariably boils.*— Thus, pure water always boils at  $212^{\circ}$ , alcohol of sp. gr. 0.813 at  $173^{\circ}$ , and ether at  $96^{\circ}$ , Fabr.; and, when once brought to the boiling point, no liquid can be made hotter, however long the application of heat be continued. The boiling point of water may be readily ascertained, by immersing a thermometer in water boiling, in a metallic vessel, over the fire. As there is some danger in applying heat directly to a vessel containing either ether or alcohol, the ebullition of these fluids may best be shown, by immersing the vessel containing them in water, the temperature of which may be gradually raised. The appearance of boiling is owing to the formation of vapour at the bottom of the vessel, and its escape through the heated fluid above it. That the steam, which escapes, is actually formed at the bottom, and not at the top of the water, may be seen by boiling some water in a Florence flask, or other transparent vessel, over an Argand's lamp. The bubbles of vapour will all ascend from the bottom of the vessel. A few exceptions to the fixity of the boiling point of liquids, arising chiefly from the material of which the containing vessel is made, have been stated by Gay Lussac.\*

II. *Steam has exactly the same temperature as boiling water.*—Let a tin vessel be provided, having two holes in its cover, one of which is just large enough to admit the stem of a thermometer. Fill it partly with water, and let the bulb of the thermometer be an inch or two above the surface of the water, leaving the other aperture open for the escape of vapour. When the water boils, the thermometer, surrounded by steam, will rise to  $212^{\circ}$ , which is precisely the temperature

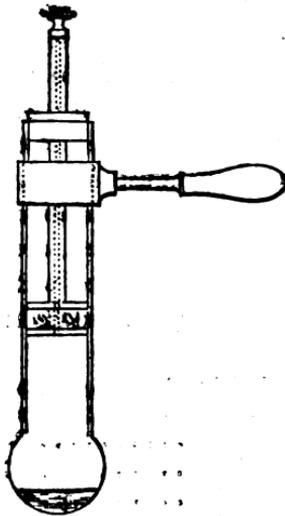
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\* Ann. de Chim. et Phys. vii. 307, or Journ. of Science, v. 361.

of the water beneath; yet water, placed on a fire, continues to receive heat, very abundantly, even when boiling hot; and as this heat is not appreciable by the thermometer, it must exist in the steam, in a latent state.

III. *Perfectly formed steam is completely invisible.*—We may satisfy ourselves of this by boiling strongly a small quantity of water in a flask; for perfect transparency will exist in the upper part of the vessel. It is only when it begins to be condensed, that steam becomes visible. We have a proof also of the same fact in the thick fogs which are produced by a sudden transition from warm to cold weather; the vapour, which was imperceptible at the higher temperature, being condensed and rendered visible by the lower.

The perfect transparency of steam, and also two other important properties on which depends its use as a moving power, viz. its elasticity and its condensibility by a reduced temperature, are beautifully shown by a little apparatus contrived by Dr. Wollaston, of which a sketch is annexed. It consists of a glass tube about 6 inches long and  $\frac{3}{4}$  inch bore, as cylindrical as possible, and blown out a little at the lower end. It has a wooden handle, to which is attached a brass clip embracing the tube; and within is a piston, which, as well as its rod, is perforated, as shown by the dotted lines.



This canal may be occasionally opened or closed by a screw at the top; and the piston rod is kept in the axis of the cylinder by being passed through a piece of cork fixed at the top of the tube. When the instrument is used, a little water is put into the bottom; the piston is then introduced with its aperture left open; and the water is heated over a spirit lamp. The common air is thus expelled from the tube, and when this may be supposed to be effected, the aperture in the rod is closed by the screw. On ap-

plying heat, steam is produced, which drives the piston upwards. On immersing the bulb in water, or allowing it to cool spontaneously, a vacuum is produced in the tube, and the piston is forced downwards by the weight of the atmosphere. These appearances may be alternately produced by repeatedly heating and cooling the water in the ball of the instrument. In the original steam engine, the vapour was condensed in the cylinder, as it is in the glass tube; but in the engine as improved by Mr. Watt, the steam is pumped into a separate vessel, and there condensed; by which the loss of heat, occasioned by cooling the cylinder every time, is avoided.

IV. *The boiling point of the same fluid varies, under different degrees of atmospheric pressure.*—Thus water, which has been removed from the fire, and has ceased to boil, has its ebullition renewed when it is placed under a receiver, the air of which is quickly exhausted by an air pump. Alcohol and ether, confined under an exhausted receiver, boil violently at the temperature of the atmosphere. In general, liquids boil *in vacuo*, with about  $124^{\circ}$  less of heat, than are required under a mean pressure of the atmosphere;\* water, therefore, in a vacuum must boil at  $88^{\circ}$ , and alcohol at  $49^{\circ}$  Fahr. Even the ordinary variations in the weight of the air, as measured by the barometer, are sufficient to make a difference in the boiling point of water of several degrees between the two extremes,† as shown in the following table.

Height of Barometer.	Boiling point of water.	Height of Barometer.	Boiling point of water.
26 .....	204.91 <sup>o</sup>	29 .....	210.19 <sup>o</sup>
26.5 .....	205.79	29.5 .....	211.07
27 .....	206.67	30 .....	212
27.5 .....	207.55	30.5 .....	212.88
28 .....	208.43	31 .....	213.76
28.5 .....	209.31		

On ascending considerable heights, as to the tops of moun-

\* Black's Lectures, i. 151.

† Sir G. Shuckburgh, in Philosophical Transactions, lxxix. 375, and Gen. Roy in ditto, lxvii. 687.

tains, the boiling point of water gradually falls on the scale of the thermometer. Thus on the summit of Mont Blanc, water was found by Saussure to boil at  $187^{\circ}$  Fahrenheit. On this fact is founded the use of the thermometer in the measurement of heights, which though originally suggested by Fahrenheit, has only lately been made conveniently practicable, in consequence of the invention of a thermometer, adapted to the purpose, by the Rev. Mr. Wollaston.\* Without entering into minute details, it would not be possible to give a clear idea of the instrument. It may be sufficient to state that each degree about the boiling point is made to occupy a space, that admits of being distinctly divided into 1000 parts. And as each degree of Fahrenheit is equivalent to 0.589 of an inch of the barometer, which indicates an elevation of 530 feet, it follows that one thousandth part of a degree will be equivalent to a difference in height of about six inches. In fact, the height of a common table produces a manifest difference in the boiling point of water, as ascertained by this sensible instrument.

The influence of a diminished pressure in facilitating ebullition may, also, be illustrated by the following very simple experiment:—Place, over a lamp, a Florence flask, about three fourths filled with water; let it boil briskly during a few minutes; and, immediately on removing it from the lamp, cork it tightly, and suddenly invert it. The water will now cease to boil; but, on cooling the convex part of the flask by a stream of cold water, the boiling will be renewed. Applying boiling water from the spout of a tea-kettle to the same part of the flask, the water will again cease to boil. This renewal of the ebullition, by the application of cold (an apparent paradox), is owing to the formation of an imperfect vacuum over the hot water, by the condensation of steam; and the suspension of boiling, on re-applying the heat, to the renewed pressure on the surface of the hot water, occasioned by the formation of fresh steam.

From these facts, it may be inferred, that the particles of

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\* Phil. Trans. 1817, p. 184.

caloric are mutually repulsive, and that they communicate this repulsive tendency to other bodies in which caloric is contained. This repulsive power tends to change solids into fluids, and liquids into æriform bodies, and is chiefly counteracted by the pressure of the atmosphere.

Were this counteracting cause removed, many bodies, which at present have a liquid form, would cease to be such, and would be changed into a gaseous state. Precisely the same effect, therefore, results from the prevalence of either of these forces. Add to certain liquids a quantity of caloric, in other words, place them in a high temperature, and they immediately assume an æriform state: or, their temperature remaining the same, diminish the weight of the atmosphere; and the caloric, which they naturally contain, exerts its repulsive tendency with equal effect, and they are in like manner converted into gases. These facts are best shown by the following experiments on ether:

1. Ether, at the temperature of  $96^{\circ}$ , exists in the state of a gas. This may be shown by filling a jar with water a few degrees above this temperature, and inverting it in a vessel of the same. Then introduce a little ether, by means of a small glass tube closed at one end. The ether will rise to the top of the jar, and, in its ascent, will be changed into gas, filling the whole jar with a transparent, invisible, elastic fluid. On permitting the water to cool, the ethereal gas is condensed, and the inverted jar again becomes filled with water.

2. Ether is changed into gas by diminishing the weight of the atmosphere. Into a glass tube, about six inches long, and half an inch in diameter, put a tea-spoonful of ether, and fill up the tube with water; then, pressing the thumb on the open end of the tube, place it, inverted, in a jar of water. Let the whole be set under the receiver of an air pump, and the air exhausted. The ether will be changed into gas, which will expel the water entirely from the tube. On re-admitting the air into the receiver, the gas is again condensed into a liquid form.

It is evidently unnecessary that a liquid should boil *in vacuo*, in order to be converted into vapour; for all liquids have in

fact, at every temperature, a tendency to assume the state of gas, and several, which exhibit, at the common temperature of the atmosphere, no appearance of ebullition, are nevertheless convertible into vapour, at that temperature, under an exhausted receiver. The quantity of vapour produced *in vacuo*, varies with the space, the temperature, and the nature of the liquid. 1st, It is proportional to the space, for a double space gives occasion to the formation of a double quantity of vapour; and if a given volume of vapour be mechanically compressed into half its bulk, one half will be re-converted into water. 2dly, It increases with the temperature, but in a greater proportion. 3dly, It is different for different liquids; and it may be observed that liquids, which enter most easily into ebullition, are generally, though with some exceptions, those which at a given temperature afford the densest vapour. Thus the vapour of ether is more dense than that of water. The caloric required to produce this sort of evaporation, which may be called *spontaneous*, in order to distinguish it from that produced by obvious sources of heat, is supplied in the first instance by the liquid itself, the temperature of which is observed to fall, and is regained by contact with surrounding bodies.

Spontaneous evaporation goes on, also, from the surface of liquids exposed to the atmosphere, and a quantity of vapour is produced which, from the same liquid, is determined by the pressure and the temperature. If to a given volume of dry atmospheric air confined over mercury, we admit a small quantity of water, the volume of the air is increased by the admixture of aqueous vapour. Substituting at the same temperature and pressure, any other gas for atmospheric air, an expansion is produced to precisely the same amount; and it is remarkable that the quantity and force of vapour, in a given volume of air or of gas of extreme moisture, is precisely the same as in Toricellian vacuum of like volume.\* These facts show, as will afterwards more fully appear, that spontaneous evaporation is entirely independent of any affinity of air for water, and is to be explained by the general laws regulating the production and force of vapour.

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\* Dalton's New System, p. 183.

V. *On the contrary, by considerably increasing the pressure, water may be heated to above 400° Fahrenheit, without being changed into vapour.*—This experiment requires, for its performance, a strong iron vessel, called a Papin's digester, a plate of which may be seen in Gren's Chemistry. That the boiling point of water, and the temperature of steam, are raised by an increased pressure, may be equally well shown, however, by means of the small boiler, represented plate v. fig. 46, which will be found extremely useful in experiments on this subject. Its precise size, and directions for its construction, will be given in the Description of the Plates.

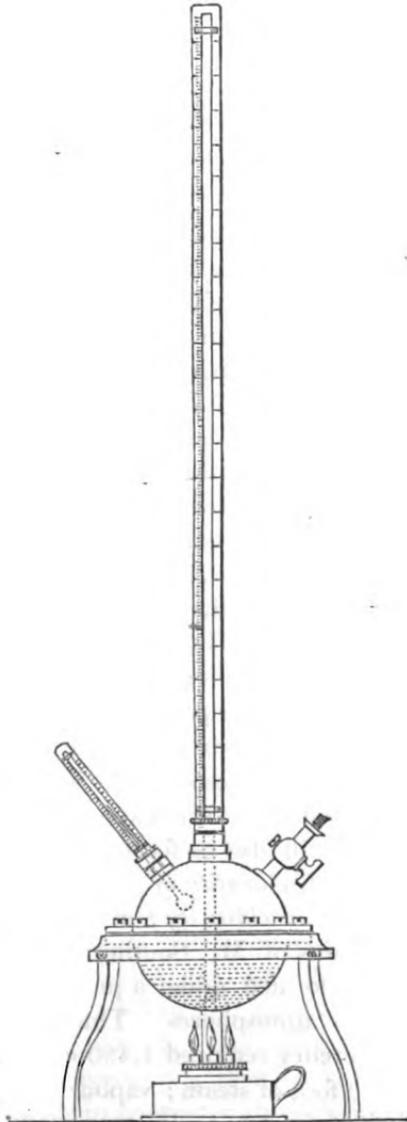
On the cock *c* may be screwed, occasionally, a valve, loaded in the proportion of 14 pounds to the square inch; or a guage adapted to show the density of the steam, by the diminution of bulk in a confined portion of air, which will occupy a bulk inversely proportionate to the compressing force (fig. 46, *f*.) The boiler being rather more than half filled with water, and the perforated cap *d* being screwed into its place, the ball of the thermometer will be an inch or more above the surface of the water, and will indicate its temperature, as well as that of the steam, both being, necessarily, in all cases, precisely the same. Allowing the steam to escape through the cock *c*, before affixing the valve, the temperature of the steam, under a mean atmospheric pressure, will be 212°. When an additional atmosphere is added by the weighted valve, it will rise to 250°; by a valve twice as heavy as the first, or loaded in the proportion of 42 pounds to the square inch (= three atmospheres), the temperature of the steam will be raised to more than 270°. This is as far as it is safe to carry the experiment.

An apparatus adapted to the same purposes, has been contrived, also, by Dr. Marcet, and may be procured from the makers of philosophical instruments in London. It consists of two hemispheres (see the figure), generally of brass, which are fixed together by flanches and screws. At the upper part are three openings, into one of which a cock may be screwed; into the other a thermometer graduated to 250°, or upwards; and into the central one is fixed a long glass tube open at both ends, and reaching to within about one-eighth of an inch of the bottom of the



boiler. When the apparatus is used, mercury sufficient to fill the tube is first put into the vessel, and over this a quantity of water sufficient to occupy about half its capacity is poured, and the cock being shut, the heat of a spirit lamp with three or four wicks is applied. With this boiler precisely the same experiments may be made as with that which I have already described, the only difference being in its form, and in the gauge for measuring the force of the steam which is generated; for this, by its pressure, drives the mercury up the tube, and by the height of the column exhibits, in a more striking manner, the correspondence between the elasticity of the steam and its temperature.

The elasticity of the vapour of water from 32° to 212° Fahr. had been experimentally determined by Mr. Dalton, who, from his results, had calculated its force at temperatures above the ordinary boiling point. It was still, however, desirable to ascertain, by actual experiment, the elastic force



of vapour above 212°, and this has been attempted by Professor Robison, Mr. Southern, and Dr. Ure. Mr. Southern's experiments were made many years ago, but were not published till very lately, in Dr. Brewster's edition of Prof. Robison's Works. The following table expresses the elasticity o

aqueous vapour according to his experiments, under one, two, four, and eight atmospheres.

Atmospheres.	Pressure in Inches of Mercury.	Temperature Fahr.
1 .....	29.8 .....	212°
2 .....	59.6 .....	250.3
4 .....	119.2 .....	293.4
8 .....	238.4 .....	343.6

Dr. Ure's experiments were published in the Philosophical Transactions for 1818, and their general results are contained in a table, which will be found in the Appendix. Between 32° and 212°, an almost exact coincidence may be observed between the experiments of Dalton and of Ure; but this ceases above the boiling point of water; for there Mr. Dalton's numbers were calculated on the presumption that the same law of progression obtains in the higher as in the lower ranges, which does not appear to be correctly the fact.

Dr. Ure has examined, also, the elastic forces of the vapours of alcohol, ether, oil of turpentine, and naphtha, and has exhibited the results in the form of a table. To the experiments on ether it has however been objected by Mr. Dalton, that they were made on that fluid in an impure state, as is evident from its boiling point, which Dr. Ure states at 104° or 105°; whereas the point, at which pure ether boils under the pressure of the atmosphere, is 96° Fahr. Mr. Dalton has, therefore, from his own experiments, constructed a fresh table, which will also be found in the Appendix.

VI. *The density of steam is nearly if not accurately proportional to its elasticity; at least this may be affirmed of it within the limits of Mr. Southern's experiments, which extended to steam formed under a pressure of 120 inches of mercury, or of four atmospheres. Thus steam of elasticity = 40 inches of mercury required 1.430 cubic inches of water to form each cubic foot of steam; vapour of 80 inches required 2.940 cubic inches of water; and vapour = 120 inches force required for each cubic foot 4.279 cubic inches of water. The elasticities, therefore, and the quantities of water, in these experiments, have the same common multiple; in other words, steam of double, triple, &c. elastic force contains, in an equal volume, twice, thrice, &c. the weight of water.*

VII. *The latent heat of the vapours of fluids, though constant for vapour of the same kind, and of a given elasticity, differs in different vapours.*

The latent heat of the vapours of different liquids has been investigated, so far as I know, only by Dr. Ure. His method was to distil off a known quantity of each liquid, and to observe the temperature gained by the water employed to condense its vapour. From the results, he has constructed the following Table. (Phil. Trans. 1818.)

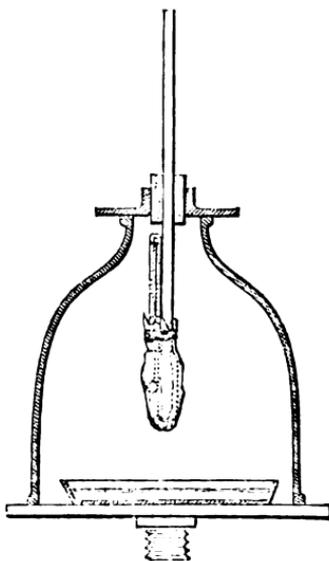
*General Table of latent Heat of Vapours.*

Vapour of water at its boiling point .....	967°
alcohol (sp. gr. 0.825).....	442
sulph. ether (boiling point 104°)....	302.379
petroleum .....	177.87
oil of turpentine (do. about 310°) ...	177.87
nitric acid (sp. gr. 1.494, boiled at 165°)	591.99
liquid ammonia (sp. gr. 0.978).....	837.28
vinegar (sp. gr. 1.007) .....	875.00

VIII. *The absorption of caloric, during evaporation, shown by experiment.*—Moisten a thermometer with alcohol, or with ether, and expose it to the air, repeating these operations alternately. The mercury of the thermometer will sink at each exposure, because the volatile liquor, during the evaporation, robs it of its heat. In this way (especially with the aid of an apparatus described by Mr. Cavallo, in the Philosophical Transactions, 1781, p. 509), water may be frozen in a thin and small glass ball, by means of ether. The same effect may be obtained, also, by immersing a tube, containing water at the bottom, in a glass of ether, which is to be placed under the receiver of an air pump; or the ether may be allowed to float on the surface of the water. During the exhaustion of the vessel, the ether will evaporate rapidly; and, robbing the water of heat, will completely freeze it; thus exhibiting the singular spectacle of two fluids in contact with each other, one of which is in the act of boiling, and the other of freezing, at the same moment.

By a little modification of the experiment, mercury itself, which requires for congelation a temperature of almost 40° below 0 of Fahrenheit, may be frozen, as was first shown by

Dr. Marcet.\* A conical receiver, open at the top, is placed on the plate of an air pump, and a small tube, with a cylindrical bulb at its lower end, is suspended within the receiver, through the aperture, by means of a brass plate, perforated in its centre, and fitting the receiver air tight, when laid upon its open neck. The tube passes through this plate, to which it is fitted by a leather adjustment, or simply by a cork secured with sealing wax. The bulb is then wrapped up in a little cotton wool, or, what is better, in a small bag of fine fleecy hosiery; in which a small spirit thermometer, graduated below  $40^{\circ}$  Fahr., may also be included; and, after being dipped into sulphuret of carbon or ether,† the apparatus is quickly placed under the receiver, which is



exhausted as rapidly as possible. In two or three minutes the temperature sinks to about  $45^{\circ}$  below 0, at which moment the quicksilver in the stem suddenly descends with great rapidity. If it be desired to exhibit the mercury in a solid state, common tubes may be used, which have originally been about an inch diameter, but have been flattened by pressure, when softened by the blow-pipe. The experiment succeeds, when the temperature of the room is as high as  $+40^{\circ}$  Fahrenheit.

IX. *The fixation of caloric in water, by its conversion into steam, may be shown by the following experiments:—*1. Let a pound of water at  $212^{\circ}$ , and eight pounds of iron filings at  $300^{\circ}$ , be suddenly mixed together. A large quantity of vapour will be instantly generated; and the temperature of the mixture will be only  $212^{\circ}$ ; but that of the vapour produced is also not more than  $212^{\circ}$ ; and the steam must therefore contain, in a latent or combined form, all the caloric which raised

\* 34 Nich. Journal, 119.

† In exhausting a vessel containing either of these fluids, the valves of the air pump must be metallic.

the temperature of eight pounds of iron filings from  $212^{\circ}$  to  $300^{\circ}$ .

2. When a quantity of water is heated several degrees above the boiling point in a close vessel, and a cock is then suddenly opened, the steam rushes out with prodigious noise and violence, and the heat of the water is reduced in three or four seconds to the boiling temperature. The water, however, constituting the steam which has escaped, amounts to only a very trifling quantity, and yet it has been sufficient to carry off the whole excess of heat from the water in the digester.

3. The quantity of caloric, which becomes latent during the formation of steam, may be approximated, by repeating the following experiment of Dr. Black: He placed two cylindrical flat-bottomed vessels of tin, five inches in diameter, and containing a small quantity of water at  $50^{\circ}$ , on a red hot iron plate, of the kind used in kitchens. In four minutes the water began to boil, and in twenty minutes the whole was boiled away. In four minutes, therefore, the water received  $162^{\circ}$  of temperature, or  $40\frac{1}{4}^{\circ}$  in each minute. If we suppose, therefore, that the heat continues to enter the water at the same rate, during the whole ebullition, we must conclude that  $40\frac{1}{4}^{\circ} \times 20 = 810^{\circ}$  have entered the water, and are contained in the vapour.

It has been found by experiment that 75 pounds of Newcastle coal, or 100 pounds of coal of medium quality, applied in the best manner, are required for the vaporization of 12 cubic feet, or about  $89\frac{3}{4}$  wine gallons, of water. A pound of coal, on the average, may be considered as equivalent to convert a gallon of water into vapour. Wood charcoal, by combustion, is capable of melting 94 times its weight of ice, and of evaporating 13 times its weight of water, previously at  $32^{\circ}$  Fahrenheit. Peat of the best quality, when properly applied, evaporates 10 times its weight of water, but, as commonly used, only 4 or 5 times. Even with the assistance of heated air, only six times its weight can be evaporated, though Curaudau pretends to have evaporated 25 times its weight.\* From evidence given before the House of Commons on the Gas Light Bill,  $17\frac{7}{8}$  pounds of good London coke appear to

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\* 79 An. Ch. 86.

be capable of raising from 66 to 70 pounds of water into vapour, or about 4 times their weight.\*

X. *Water, by conversion into steam, has its bulk prodigiously enlarged, viz. according to Mr. Watt's experiments, about 1800 times, or, according to Gay Lussac, only 1698 times.*—A cubic inch of water (or 252 grains) occupies, therefore, when converted into steam, of temperature  $212^{\circ}$ , and force equal to 30 inches of mercury, the space of nearly a cubic foot. The specific gravity of aqueous vapour under the ordinary pressure of the air, is to that of perfectly dry air, taking Gay Lussac's data, as 10 to 16, or 0.62349 to 1. The specific gravity which it ought to have from theory is 0.620, for this should result from condensing into one volume two volumes of hydrogen gas, sp. gr. 0.0688, and one volume of oxygen gas, sp. gr. 0.1025. The experimental result of Gay Lussac was obtained by comparing air and steam at the common temperature of  $212^{\circ}$  Fahr.† But as all gases and vapours are expanded or contracted to the same amount by equal variations of temperature, it must be obvious that the same relation will continue between air and aqueous vapour at all other degrees of heat, provided both are subjected to a common temperature and pressure.

XI. *On the contrary, vapours, during their conversion into a liquid form, evolve, or give out, much caloric.*—The heat given out, by the condensation of steam, is rendered apparent by the following experiment. Mix 100 gallons of water at  $50^{\circ}$  with 1 gallon of water at  $212^{\circ}$ ; the temperature of the water will be raised about  $1\frac{1}{2}^{\circ}$ . Condense by a common still-tub, 1 gallon of water, from the state of steam, by 100 gallons of water, at the temperature of  $50^{\circ}$ . The water will be raised  $11^{\circ}$ . Hence, 1 gallon of water, condensed from steam, raises the temperature of 100 gallons of cold water  $9\frac{1}{2}^{\circ}$  more than 1 gallon of boiling water; and, by an easy calculation, it appears that the caloric imparted to the 100 gallons of cold water by 8 pounds of steam, if it could be condensed in 1 gallon of water, would raise it to  $950^{\circ}$ .‡ The quantity of ice, which is melted by steam of ordinary density, is invariably  $7\frac{1}{2}$  times the weight of the steam.

\* See also Count Rumford's Researches on the Heat developed in Combustion. Phil. Mag. xli. xlii. and xliii.

† Ann. de Chim. et de Phys. ii. 135.

‡ Black's Lectures, i. 169.

For exhibiting the latent heat of steam, by means of a small apparatus, which may be placed on a table, and with the assistance only of a lamp, the boiler already described (fig. 46) will be found extremely well adapted. The right angled pipe *e* must be screwed, however, into its place, and must be made to terminate at the bottom of a jar, containing a known quantity of water of a given temperature. This conducting pipe and the jar should be wrapped round with a few folds of flannel. The apparatus being thus disposed, let the water in the boiler be heated by an Argand's lamp, with double concentric wicks, till steam issues in considerable quantity through the cock *c*, which is then to be closed. The steam will now pass through the right angled pipe into the water contained in the jar, which will condense the steam, and will have its temperature very considerably raised. Ascertain the augmentation of temperature and weight; and the result will show, how much a given weight of water has had its temperature raised by a certain weight of condensed steam. To another quantity of water, equal in weight and temperature to that contained in the jar at the outset of the experiment, add a quantity of water at  $212^{\circ}$ , equal in weight to the condensed steam; it will be found, on comparison of the two resulting temperatures, that a given weight of steam has produced, by its condensation, a much greater elevation of temperature, than the same quantity of boiling water. This will be better understood by the following example, taken from actual experiment:

Into eight ounces of water, at  $50^{\circ}$  Fahrenheit, contained in the glass jar, *f*, fig. 46, steam was passed from the boiler, till the temperature of the water in the jar rose to  $173^{\circ}$ . On weighing the water, it was found to have gained  $8\frac{1}{2}$  drachms; that is, precisely  $8\frac{1}{4}$  drachms of steam had been condensed, and had imparted its heat to the water.—To facilitate the explanation of this experiment, it is necessary to premise the following remarks.

To measure the whole quantities of caloric contained in different bodies, is a problem in chemistry which has not yet been solved. But the quantities of caloric, added to, or subtracted from, different bodies (setting out from a given tem-

perature) may, in many cases, be measured and compared with considerable accuracy. Thus, if, as has been already stated, two pounds of water at  $120^{\circ}$  be mixed with two pounds at  $60^{\circ}$ , half the excess of caloric in the hot water will pass to the colder portion; that is, the hot water will be cooled  $30^{\circ}$ , and the cold will receive  $30^{\circ}$  of temperature; and if the experiment be conducted with proper precautions,  $90^{\circ}$ , the arithmetical mean of the temperature of the separate parts, will be the temperature of the mixture. If three pounds of water at  $100^{\circ}$  be mixed with one pound at  $60^{\circ}$ , we shall have the same quantity of heat as before, *viz.* four pounds at  $90^{\circ}$ . Hence if the quantity of water be multiplied by the temperature, the product will be a comparative measure of the quantity of caloric which the water contains, exceeding the zero of the thermometer employed.

Thus in the last example,

$$\begin{aligned} 3 \times 100 &= 300 = \text{the caloric above zero in the first portion.} \\ 1 \times 60 &= 60 = \text{the caloric above zero in the second do.} \end{aligned}$$

The sum,  $360 =$  the caloric above zero in the mixture. Dividing  $360$  by  $4$ , the whole quantity of water, we obtain  $90^{\circ}$ , the temperature of the mixture.

This method of computation may be conveniently applied to a variety of cases. Thus, in the foregoing experiment,  $8\frac{1}{2}$  drachms of steam at  $212^{\circ}$ , added to  $64$  drachms of water at  $50^{\circ}$ , produced  $72\frac{1}{2}$  drachms of water at  $173^{\circ}$ . Now,

$$\begin{aligned} 72\frac{1}{2} \times 173 &= 12542\frac{1}{2} = \text{whole heat of the mixture.} \\ 64 \times 50 &= 3200 = \left\{ \begin{array}{l} \text{heat of } 64 \text{ drachms, one of the} \\ \text{component parts.} \end{array} \right. \\ \hline 9342\frac{1}{2} &= \left\{ \begin{array}{l} \text{heat of } 8\frac{1}{2} \text{ drachms, the other} \\ \text{component part.} \end{array} \right. \end{aligned}$$

Therefore  $9342\frac{1}{2}$  divided by  $8\frac{1}{2} = 1099$ , should have been the temperature of the latter portion (*viz.*  $8\frac{1}{2}$  drachms,) had none of its heat been latent: and  $1099 - 212 = 887$  gives the latent heat of the steam. This result does not differ more than might be expected, owing to the unavoidable inaccuracies of the experiment, from Mr. Watt's determination, which



states the latent heat of steam at  $900^{\circ}$ , or from that to  $950^{\circ}$ .\* Lavoisier, with the aid of the calorimeter, makes it  $1000^{\circ}$ , or a little more;† Mr. Southern,  $945$ ; and Dr. Ure,  $967$ .

XII. *The same weight of steam contains, whatever may be its density, the same quantity of caloric; its latent heat being increased, in proportion as its sensible heat is diminished; and the reverse.*—This principle, though scarcely admitting of illustration by any easy experiment, is one of considerable importance; and an ignorance of it has been the occasion of many fruitless attempts to improve the economy of fuel in the steam engine. The fact, so far as respects steam of lower density than that of 30 inches of mercury, was long ago determined experimentally by Mr. Watt.‡ As the boiling point of liquids is known to be considerably reduced by a diminished pressure, it seemed reasonable to suppose that, under these circumstances, steam might be obtained from them with a less expenditure of fuel. Water, Mr. Watt found, might easily be distilled in vacuo when at the temperature of only  $70^{\circ}$  Fahrenheit. But, by condensing steam formed at this temperature, and observing the quantity of heat which it communicated to a given weight of water, he determined that its latent heat, instead of being only  $955^{\circ}$ , was between  $1200^{\circ}$  and  $1300^{\circ}$ .

The same principle may be explained also by the following illustration, which was suggested to me by Mr. Ewart. Let us suppose that in a cylinder, furnished with a piston, we have a certain quantity of steam, and that it is suddenly compressed, by a stroke of the piston, into half its bulk. None of the steam will in this case be condensed; but it will acquire double elasticity, and its temperature will be considerably increased. Now if we either suppose the cylinder incapable of transmitting heat, or take the moment instantly following the compression before any heat has had time to escape, it must be evident that the sensible and latent heat of the steam, taken together before compression, are precisely equal to the sensible and latent heat taken together of the denser steam. But in the dense steam, the sensible heat is increased, and the latent heat proportionally diminished. The explanation of

\* Black's Lectures, i. 174.

† Ibid. i. 175.

‡ Ibid. i. 190.

this fact will be furnished by a principle to be hereafter explained, viz. that the capacities of elastic fluids for caloric are uniformly diminished by increasing their density.

Direct experiments to ascertain the latent heat of steam, formed under higher pressures than that of the atmosphere, have been made by Mr. Southern, of Soho, and by Mr. Sharpe, of Manchester.\* Those of the latter were first published; but were subsequent in point of time to the experiments of Mr. Southern, which, though only lately made public,† were instituted many years ago. They consisted in ascertaining the augmentation of weight and increase of temperature, gained by a given quantity of water, from the condensation of known volumes of aqueous vapour of different densities. The results presented slight differences in the latent heat of steam of different densities, but of so small an amount as to arise probably from unavoidable sources of error. The following table exhibits the principal results obtained by Mr. Southern.

Temperature of Steams.	Elasticity of ditto in inches of Mercury.	Latent Heat.
229 .....	40 .....	942°
270 .....	80 .....	942°
295 .....	120 .....	950°

The experiments of Mr. Sharpe, and also a recent series by Clement and Desormes, (of which an abstract is given in the Appendix to Thenard's *Traité de Chimie*, vol. iv. p. 262, 3me. edition,) establish the same general law. This law is of great importance in practice, since it shows that no essential saving of fuel can be reasonably expected from using, as a moving power, steam formed under high pressures. On the contrary, it seems probable that the higher the temperature of the water in the boiler, the greater will be the loss of heat by the escape of hot air through the chimney. Nevertheless, there are certain cases in which high pressure steam may be advantageously applied to various manufacturing processes, as a means of communicating heat, when the temperature is required to exceed 212° Fahrenheit.

A remarkable fact has been observed respecting steam of

\* Manchester Society's Memoirs. Vol. 2. New Series.

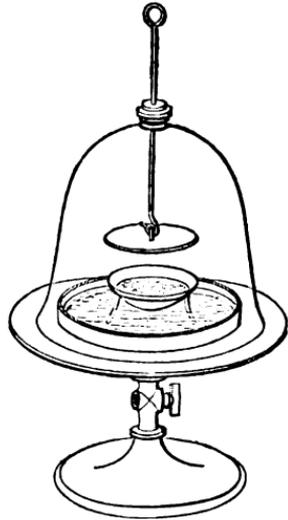
† Brewster's Edition of Prof. Robison's Works.

great elasticity; viz. that when allowed to escape suddenly from a cock or small aperture in the boiler, the hand may be held close to the place at which it issues, without being scalded by it; and even the water of the boiler itself does not scald under these circumstances. Both the issuing steam and water must, necessarily, therefore, be considerably under the temperature of  $212^{\circ}$ , and are, in fact, found to be so by the thermometer. This is probably owing to the sudden rarefaction of the issuing steam in the first case, or sudden production of steam of great rarity in the second; for this rarefaction, or sudden production of steam, instantly renders latent a large quantity of heat, and prevents it from producing those effects, which are due only to caloric of temperature. There is still, however, some difficulty, in conceiving, why highly compressed steam, on being allowed to escape from an orifice, should fall *below*  $212^{\circ}$ , since that is the temperature which is due to it under the mean pressure of the atmosphere.

XIII. *The evaporation of water is carried on much more rapidly under a diminished pressure, especially if the vapour, which is formed, be condensed as soon as it is produced, so as to maintain the vacuum.*

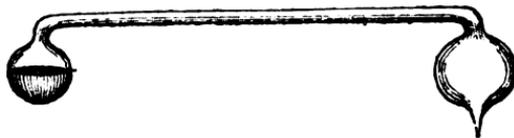
On this principle depends Mr. Leslie's new and ingenious mode of freezing water, in an atmosphere of any common temperature, by producing a rapid evaporation from the surface of the water itself. The water to be congealed is contained in a shallow vessel, which is supported above another vessel, containing strong sulphuric acid, or dry muriate of lime; or even dried garden mould or parched oatmeal. Any substance, indeed, that powerfully attracts moisture, may be applied to this purpose. The whole is covered by the receiver of an air pump, which is rapidly exhausted; and as soon as this is effected, crystals of ice begin to shoot in the water, and a considerable quantity of air makes its escape, after which the whole of the water becomes solid. The rarefaction required is to about 100 times; but to support congelation, after it has taken place, 20 or even 10 times are sufficient. The sulphuric acid becomes very warm; and it is remarkable, that if the vacuum be kept up, the ice itself evaporates. In five or six days, ice of an inch in thickness will entirely disappear. The acid continues to act, till it has absorbed an equal volume of water.

An elegant manner of making the experiment is to cover the vessel of water with a plate of metal or glass fixed to the end of a sliding wire, which must pass through the neck of the receiver, and be, at the same time, air tight, and capable of being drawn upwards. (See the annexed figure.) When the receiver is exhausted, the water will continue fluid, till the cover is removed, when, in less than five minutes, needle shaped crystals of ice will shoot through it, and the whole will soon become frozen.



In this interesting process, if it were not for the sulphuric acid, an atmosphere of aqueous vapour would fill the receiver; and, pressing on the surface of the water, would prevent the further production of vapour. But the steam which rises, being condensed the moment it is formed, the evaporation goes on very rapidly, and has no limits but the quantity of the water, and the diminished concentration of the acid.\*

It is on the same principle, that the instrument invented by Dr. Wollaston, and termed by him the *Cryophorus* or *Frost-bearer*, is founded. It may be formed by taking a glass tube, having an internal diameter of about  $\frac{1}{4}$ th of an inch, the tube being bent to a right angle at the distance of half an inch from each ball, thus:



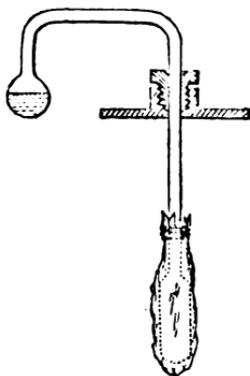
One of these balls should be about half filled with water, and the other should be as perfect a vacuum as can readily be obtained, the mode of effecting which is well known to those accustomed to blow glass. One of the balls is made to ter-

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\* The most complete account of this new mode of freezing is to be found in the Supplement, now publishing, to the Encycl. Brit. Art. COLD

minate in a capillary tube; and when the water in the other ball has been boiled over a lamp a considerable time, till all the air is expelled, the capillary extremity, through which the steam is still issuing with violence, is held in the flame of the lamp, till the force of the vapour is so far reduced, that the heat of the flame has power to seal it hermetically.

When an instrument of this kind is well prepared, if the empty ball be immersed in a mixture of snow and salt, the water in the other ball, though at the distance of two or three feet, will be frozen solid in the course of a very few minutes. The experiment may be rendered even more striking, if performed according to Dr. Marcet's modification of it: the empty ball, covered with a little moist flannel, is to be suspended, in the manner shown by the annexed sketch, within a receiver, over a shallow vessel of strong sulphuric acid, and the receiver is then to be exhausted. In both cases, the vapour present in the empty ball is condensed by the common operation of cold; and the vacuum, produced by this condensation, gives opportunity for a fresh quantity to arise from the opposite ball, with a proportional reduction of the temperature of its contents.



The large quantity of caloric, latent in steam, renders its application extremely useful for practical purposes. Thus, water may be heated, at a considerable distance from the source of heat, by lengthening the conducting pipe *e*, fig. 46. This furnishes us with a commodious method of warming the water of baths, which, in certain cases of disease, it is of importance to have near the patient's bed-room; for the boiler, in which the water is heated, may thus be placed on the ground-floor, or in the cellar of a house; and the steam conveyed by pipes into an upper apartment. Steam may also be applied to the purpose of heating or evaporating water, by a modification of the apparatus. Fig. 46, *g*. represents the apparatus for boiling water by the condensation of steam, without adding to its quantity; a circumstance occasionally of considerable importance. The steam is received between the

vessel, which contains the water to be heated, and an exterior case; it imparts its caloric to the water, through the substance of the vessel; is thus condensed, and returns to the boiler by the perpendicular pipe. An alteration of the form of the vessel adapts it to evaporation (fig. 46, *h*). This method of evaporation is admirably suited to the concentration of liquids, that are decomposed, or injured, by a higher temperature than that of boiling water, such as medicinal extracts; to the drying of precipitates, &c. In the employment of either of these vessels, it is expedient to surround it with some slow conductor of heat. On a small scale, a few folds of woollen cloth are sufficient; and, when the vessel is constructed of a large size for practical use, this purpose is served by the brick-work in which it is placed.

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#### SECTION V.

##### *Caloric the Cause of permanently elastic Fluidity.—General Properties of Gases.*

From the facts which have been detailed in the last section, it appears that in vapours, strictly so called, such as the steam of water, caloric is retained with but little force; for it quits the water when the vapour is merely exposed to a lower temperature. But, in permanently elastic fluids, caloric is held very forcibly, and no diminution of temperature, that has ever yet been effected, can separate it from some of them. Thus the air of our atmosphere, in the most intense artificial or natural cold, still continues in the æriform state. Hence is derived one character of gases, *viz.* that they remain æriform under almost all variations of pressure and temperature, and in this class are also included those aerial bodies, which, being immediately condensed by contact with water, require confinement over mercury. The following experiment will show, that the caloric contained in gases, is chemically combined; or at least that it is inappreciable by the thermometer.

Into a small retort (plate ii. fig. 26, *b*) put an ounce or two of well dried common salt, and about half its weight of sulphuric acid. By this process, a great quantity of gas is produced, which might be received and collected over mercury. But,

to serve the purpose of this experiment, let it pass through a glass balloon, *c*, having three openings, into one of which the neck of the retort passes, while, from the other, a tube *e* proceeds, which ends in a vessel of water, *f*, of the temperature of the atmosphere. Before closing the apparatus, let a thermometer, *d*, be included in the balloon, to show the temperature of the gas. It will be found that the mercury, in this thermometer, will rise only a few degrees, whereas the water, in the vessel which receives the bent tube, will soon become boiling hot. In this instance, caloric flows from the lamp to the muriatic acid, and converts it into gas; but the heat, thus expended, is not indicated by the thermometer. The caloric, however, is again evolved, when the gas is condensed by water. In this experiment, we trace caloric into a latent state, and again into the state of free or uncombined caloric.

A considerable part of the caloric, which exists in gases in a latent state, may be rendered sensible by rapid mechanical compression. Thus if air be suddenly compressed in the ball of an air-gun, the quantity of caloric liberated by the first stroke of the piston, is sufficient to set fire to a piece of the tinder called *amadou*.\* A flash of light is said, also, to be perceptible at the moment of condensation. This fact has been applied to the construction of a portable instrument for lighting a candle. It consists of a common syringe, concealed in a walking stick. At the lower extremity, the syringe is furnished with a cap, which receives the substance intended to be fired, and which is attached to the instrument by a male and female screw. The rapid depression of the piston condenses the air, and evolves sufficient heat to set the tinder on fire.† When, on the contrary, air is suddenly rarefied to many times its volume, its temperature falls sufficiently to sink a very sensible thermometer  $50^{\circ}$  of Fahr., its sensible heat passing in this case instantly into a latent form. (See Gay Lussac, *Ann. de Chim. et de Phys.* ix. 305.)

For demonstrating the influence of variations of atmospheric pressure on the formation of gases, better experiments

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\* *Philosophical Magazine*, xiv. 363, and xl. 424.

† *Ibid*, xxxi. 130.

cannot be devised than those of Lavoisier.\* But as some students, who have the use of an air-pump, may not possess the apparatus described by Lavoisier (the glass bell and sliding wire), it may be proper to point out an easier mode of showing the same fact. This proof is furnished by the experiment already described, in which sulphuric ether is made to assume alternately an aëriform and liquid state, by removing and restoring the pressure of the atmosphere.

Gases, when once formed, undergo a considerable change of bulk by variations of external pressure. The general law, which has been established on this subject is, that the *volume of gases is inversely as the compressing force*. If, for example, we have a quantity of gas occupying 60 cubic inches, under the common pressure of the atmosphere, it will fill the space of only 30 cubic inches, or one half, under a double pressure; of 20 inches, or one 3d, under a triple pressure; of 15 inches, or one 4th, under four times the pressure; and so on. When the pressure is sudden, heat is evolved from all gases, and it appears, from Gay Lussac's experiments, that different gases, when equally compressed, give out different quantities of heat, bearing probably a proportion to their specific heats.

The law of the dilatibility of gases by heat has already been stated to be an enlargement of about  $\frac{1}{273}$ th part of their bulk for each degree of Fahrenheit's scale, between the freezing and boiling points of water. At a temperature capable of rendering glass luminous (probably about 1035° Fahr.), 1 volume becomes about 2.5.†

When a body heated to a certain point is placed in different gases, under circumstances otherwise similar, it is found to cool with very different velocities; in other words, the *power of elastic fluids to conduct heat differs for different gases*. Mr. Dalton has given a series of experiments on this subject, and Sir H. Davy, having raised the same thermometer to the same temperature, 160° Fahr., exposed it to equal volumes (21 cubic inches) of the following gases at 52° Fahr.

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\* See his Elements, chap. 1.

† Davy, Phil. Trans. 1817. p. 54.



The times for cooling down to  $106^{\circ}$  were for

	Min.	Sec.
Atmospheric air . . . . .	2	0
Hydrogen. . . . .	0	45
Olefiant gas . . . . .	1	15
Coal gas . . . . .	0	55
Azote . . . . .	1	30
Oxygen . . . . .	1	47
Nitrous Oxide . . . . .	2	30
Carbonic Acid . . . . .	2	45
Chlorine . . . . .	3	6

It appears from this Table, that the powers of elastic fluids to abstract or conduct away heat from solid surfaces, is in some inverse ratio to their density. The nature of the surface of the hot body, it has been shown by Dulong and Petit, does not affect the conducting power of gaseous bodies; but the state of the gases themselves, as to moisture or dryness, has a considerable influence; for moist gases, as is shown by Count Rumford's experiments, conduct heat much more rapidly than dry ones.

Before dismissing the consideration of the gases in general, there are a few properties, which it may be proper to notice, with the view of comparing the degree in which they belong to different individuals of the class.

I. The exact *specific gravity* of the different gases is a most important element, in calculating the proportion of the ingredients of compounds, into which they enter. Nothing, indeed, can show the importance of this object more strikingly, than the fact, that on the precise specific gravities of hydrogen and oxygen gases, depend the whole series of numbers, which are used to express the weights of the atoms of bodies on the Daltonian theory. The following Table exhibits the specific gravities of the most important of this class of bodies.

TABLE OF THE SPECIFIC GRAVITY OF GASES.\*

Barometer 30. Thermometer 60°.

NAMES OF GASES.	Specific gravity.	Wt. of 100 cub. inches.		Authorities.
		Grains.		
Atmospheric air .....	1.0000	30.50		Shuckburgh.
Ditto .....	1.0000	30.199		Brande.
<b>SIMPLE GASES.</b>				
Oxygen .....	1.1088	33.82		Allen and Pepys.
Ditto .....	1.1111	33.888		Thomson.
Ditto .....	1.1026	33.629		Berzelius and Dulong.
Chlorine .....	2.5082	76.500		Davy.
Ditto .....	2.5000	76.250		Thomson.
Iodine (vapour) .....	8.678	244.679		Gay Lussac.
Hydrogen .....	0.0694	2.116		Thomson.
Ditto .....	0.0688	2.098		Berzelius and Dulong.
Nitrogen .....	0.9722	29.652		Thomson.
Ditto .....	0.9760	29.768		Berzelius and Dulong.
Carbon (vapour) .....	0.482	12.870		Gay Lussac.
Sulphur (ditto) .....	1.1111	33.888		Thomson.
Phosphorus (ditto) .....	0.8333	25.416		Ditto.
<b>COMPOUND COMBUSTIBLE.</b>				
Ammonia .....	0.5960	18.18		Allen and Pepys.
Ditto .....	0.5931	18.08		Thomson.
Ditto .....	0.5912	18.03		Berzelius and Dulong.
Carbureted hydrogen .....	0.5555	16.944		Thomson.
Ditto .....	0.5590	17.049		Berzelius and Dulong.
Bi-carbureted ditto (olefiant) .....	0.9722	29.652		Thomson.
Ditto .....	0.9804	29.90		Berzelius and Dulong.
Phosphureted hydrogen .....	0.9722	29.652		Thomson.
Biphosphureted ditto (hydro-phos) .....	0.9653	29.441		Ditto.
Sulphureted hydrogen .....	1.1805	36.007		Ditto.
Sulphuret of carbon .....	2.6447	80.663		Ditto.
Arsenureted hydrogen .....	0.5290	16.130		Tromsdorff.
Cyanogen .....	1.8055	55.069		Gay Lussac.
Ditto .....	1.8188	55.473		Berzelius and Dulong.
Ether sulphuric (vapour) .....	2.5808	78.714		Berzelius and Dulong.
— muriatic (ditto) .....	2.2190	67.679		Thomson.
— hydriodic (ditto) .....	5.4750	166.987		Ditto.
— chloric (ditto) .....	3.4750	105.257		Ditto.
Alcohol (ditto) .....	1.6004	48.812		Berzelius and Dulong.
Turpentine, oil of (ditto) .....	5.0130	152.896		Thomson.
<b>OXIDES.</b>				
Aqueous vapour .....	0.6235	19.016		Gay Lussac.
Nitrous oxide .....	1.5277	46.597		Thomson.
Ditto .....	1.5273	46.582		Berzelius and Dulong.

\* Gay Lussac's Table, which is more copious, but in which the numbers are not reduced to a mean of the barometer and thermometer, is copied into Thomson's Annals, ix. 16.; a Table by Professor Meinecke of Halle is inserted in the Journal of Science, &c. iii. 415. Dr. Thomson's elaborate paper on this subject is printed in the 16th volume of Annals of Philosophy; and Berzelius and Dulong's in the 15th volume of Annales de Chim. et de Physique.

Table of Gases continued.

NAMES OF GASES.	Specific gravity.	Wt. of 100 cub. inches.	Authorities.
<i>Oxides continued.</i>			
Nitric oxide.....	1.0416	Grains, 31.770	Thomson.
Ditto .....	1.0010	30.530	Berzelius and Dulong.
Carbonic oxide .....	0.9722	29.652	Thomson.
Ditto .....	0.9727	29.667	Berzelius and Dulong.
<b>ACIDS.</b>			
Carbonic .....	1.5277	46.597	Thomson.
Ditto .....	1.5240	46.481	Berzelius and Dulong.
Chlorocarbonic (Phosgene).....	3.4722	105.902	Thomson.
Chlorocyanic (vapour).....	2.1520	65.636	Ditto.
Fluoboric.....	2.3709	72.312	Ditto.
Fluo-silicic.....	3.5735	108.002	Ditto.
Hydriodic.....	4.3750	133.434	Ditto.
Hydro-cyanic (vapour).....	0.9368	28.572	Ditto.
Muriatic.....	1.2847	39.183	Ditto.
Nitric.....	2.4250	73.96	Sir H. Davy.
Sulphurous .....	2.2222	67.777	Thomson.
Sulphuric (vapour).....	2.7777	84.699	Ditto.

II. *All solid bodies, that possess a certain degree of porosity, are capable of absorbing gases.* This was first observed in charcoal, the power of which to condense different gases will be fully described in the section on that substance. It has been found, also, by Saussure, jun. to belong to a stone called meerscham, to adhesive slate, asbestos, rock cork, and other minerals; and to raw silk and wool. The following general principles are deducible from the experiments of Saussure.\*

1. It is necessary to deprive the solid of the air which it naturally contains. When of a nature not to be injured by heat, this is most effectually done by igniting the solid, and quenching it under mercury, where it is to be kept, till admitted to a given volume of the gas to be absorbed. Solids that are decomposable by heat may be deprived, though less effectually, of air, by placing them under a receiver, which must then be exhausted by the air-pump.

2. The same solid absorbs different quantities of different gases. Charcoal for instance condenses 90 times its bulk of ammoniacal gas, and not quite twice its bulk of hydrogen.

3. Solids, chemically the same, absorb different quantities of the same gas, according to their state of mechanical aggre-

\* Thomson's Annals, vi. 241.

gation. Thus the dense charcoal of box-wood absorbed  $7\frac{1}{2}$  volumes of air, while a light charcoal, prepared from cork, did not absorb a sensible quantity.

4. Different solids absorb different quantities of the same gas; the quantity of carbonic acid absorbed by charcoal being about seven times greater than that absorbed by meerschaum.

5. When the solid exerts no chemical action on the gas, the absorption is terminated in 24 or 36 hours.

6. The effect of moistening the solid is to retard the absorption and to diminish its amount: and when a gas has actually been absorbed, it is again driven out unchanged, partly by water of the ordinary temperature, and entirely by exposure to a boiling heat.

7. During the absorption of a gas by a solid, the temperature of the latter rises several degrees, and bears a proportion to the absorbability of the gas, and the rapidity with which it is condensed.

8. Solids condense a greater number of volumes of the more absorbable gases, under a rare than under a dense atmosphere; but if the absorption be reckoned by weight, it is most considerable under the latter state.

9. When a solid saturated with any one gas is introduced into an atmosphere of any other gas, a portion of the first is expelled, and a part of the second takes its place.

III. *Gases are absorbed by liquids.* On this subject the following general principles may be laid down.

1. The same liquid absorbs different quantities of different gases. Thus water takes up its own bulk of carbonic acid, and not one fiftieth of its bulk of hydrogen gas.

2. Different liquids absorb different quantities of the same gas. Alcohol, for instance, absorbs almost twice as much carbonic acid, as is taken up by an equal volume of water.

3. The absorption is promoted by first freeing the liquid from air, either by long continued boiling in a vessel with a narrow neck, or by the air-pump. It requires, also, brisk and long continued agitation, especially with the less absorbable gases.

4. It does not appear that the gases are absorbed by all liquids in the same order. For example, of four gases, naphtha absorbs most olefiant gas; oil of lavender most nitrous oxide:

olive oil most carbonic acid; and solution of muriate of potash most carbonic oxide.

5. The viscosity of liquids, though it does not much influence the amount absorbed, occasions a longer time to be spent in effecting the absorption. On the other hand, the amount of any gas which is absorbed by water, is diminished by first dissolving in the water any saline substance.

6. In general the lightest liquids possess the greatest power of absorbing gases; whereas, when there is no evident chemical action, the heaviest gases are absorbed most copiously and rapidly by the same liquid.

7. The temperature of a liquid is raised by the absorption of a gas, in proportion to the amount and the rapidity of the absorption.

8. In all liquids the quantities of gases absorbed are directly as the pressure. For example, a liquid, which absorbs its own bulk of gas under the pressure of the atmosphere, will still absorb its own bulk of the same gas under double, triple, &c. pressure; but its own bulk of gas, twice compressed, is equal to double its bulk of gas ordinarily compressed, and so on. The proofs of this law, I have given at length in the Philosophical Transactions for 1803.

9. When water, or probably any other liquid, is agitated with a limited quantity of any mixture of two gases, it does not absorb one gas to the exclusion of the other, but absorbs a portion of both. In this case, the density of each gas in the water or liquid has a constant relation to that without, *for the same gas*. Thus in carbonic acid gas, the density is the same within and without the water; in olefiant gas and phosphureted hydrogen, the density within is 1-8th of that without; in oxygen and carbureted hydrogen, &c. the density within is 1-27th of that without; in azote and hydrogen, it is about 1-50th, according to Dalton, though he originally stated it to be 1-64th, under the impression that the distances of the particles within were always some multiple of those without. This concise enunciation of the general law, deduced by Mr. Dalton from his experimental enquiries, will be better understood by the illustrations contained in a paper published in the Annals of Philosophy, vii. 216, where the reader will find a formula for ascertaining the quantities of mixed gases absorbed by water.

The principle, on which gases are absorbed and retained by liquids, is still a subject of controversy. By Berthollet, Thomson, Saussure, and the generality of chemists, it is ascribed, in all cases, to the exertion of a chemical affinity between the gas and the liquid; but it is contended by Mr. Dalton and myself that the effect in most cases is chiefly, if not wholly, mechanical. The discussion would lead me into details of too great a length: and I refer, therefore, for a statement of the argument, to two papers which I have published in the 8th and 9th volumes of Nicholson's Journal; to Mr. Dalton's *New System of Chemical Philosophy*; and to his essay, in the 7th volume of Dr. Thomson's *Annals*, which contains a reply to the objections, advanced against the mechanical theory by Saussure, in the 6th volume of the same work.

IV. The velocities, with which different gases, when condensed artificially by the same degree of pressure, escape through a capillary tube, has been shown by Mr. Faraday to vary very considerably.\* The following table exhibits the comparative times required by some of the gases to escape from a vessel in which they were all equally compressed at the outset, till their density arrived at an atmosphere and a quarter.

Carbonic acid required . . . . .	156.5 minutes.
Olefiant gas . . . . .	135.5
Common air . . . . .	128
Coal gas . . . . .	100
Hydrogen . . . . .	57

These differences cease to exist at low pressures; for equal volumes of hydrogen and olefiant gases passed through the same tube, at equal low pressures, in almost the same time. Through small needle holes, hydrogen gas, pressed by a small column of mercury, escaped about three times more quickly than olefiant gas. Increasing the pressure, the same proportions were observed; and also, though not to the same degree, when the gases were expelled through slits cut by a penknife. Both glass and metal tubes produced the effect, and it was heightened as the gas was made to pass more slowly

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\* *Journal of Science, &c.* iii. 354. vii. 106.

through the tube, and this whether the increased time were caused by diminished pressure, increased length of tube, or diminished diameter. The specific gravity of the gases seems to have no influence, for carbonic acid, olefiant, and oxygen gases, under the same pressure and other equal circumstances, required respectively 4' 6'', 3' 3'', and 5' 45'', for the escape of the same quantity of gas, numbers, as will be seen from the foregoing Table of Specific Gravity of Gases, bearing no proportion to their relative weights. What is singular in these results is, that the ratio for the same gas varies with the pressure, and that this variation differs in different gases. Thus the one which passes with the greatest facility at low pressures, passes with the least at high pressures.

This investigation has been pursued and extended by M. Girard. (*An. de Chim. et de Phys.* xvi. 129.) He was permitted to use for his experiments the gazometer and pipes belonging to one of the gas lighting establishments at Paris. The gases operated upon were common air, and carbureted hydrogen, which, when allowed to escape at different distances from the gazometer, through equal apertures in a three inch pipe, and under the same pressure, gave the following results:

The distances being . . . . .	1288,	3758,	6228
The quantities of carb. hyd. were	1281,	710,	541
Ditto of common air . . . . .	902,	541,	394

The escape of carbureted hydrogen, therefore, considerably exceeded that of common air, but not in proportion to its inferior specific gravity, which is not much more than half that of the atmosphere, while the excess in the escape of the lighter gas is far from being double that of the heavier. Similar results were obtained when the gases were expelled through tubes of 7 lines in diameter, or through an aperture in the side of the gazometer, the lighter gas being discharged in both cases the most abundantly. In the latter case, each gas escaped 11 times faster, than when it had to traverse a tube of the same diameter as the hole, and 127 metres in length. In all cases, equal quantities of gas, in any one experiment, escaped in equal times.

These phenomena of the movement of gases through pipes,

M. Girard shows, are exactly the same as those of the linear movement of incompressible fluids; and he draws several conclusions, which are important to those practically engaged in operations that require the transmission of gases through long tubes; for which, however, I must refer the reader to the memoir itself.

V. The colour of the electric spark, when transmitted through different gases, has been observed by De Grotthus\* to be as follows :

In atmospheric air of double density, the spark was more brilliant, but not coloured.

In hydrogen gas . . . . .	purple.
— phosphureted hydrogen . . . . .	red.
— ammonia . . . . .	red.
— dry carbonic acid gas . . . . .	violet.
— oxygen gas . . . . .	ditto.
— aqueous vapour . . . . .	orange.
— vapour of ether } . . . . .	celadon green.
— ditto of alcohol }	

The general inference from his experiments is, that the intensity of electric light is always in a direct proportion to the density of the gas, and in the inverse proportion to the conducting power of the gas for electricity.

VI. The comparative soniferous properties of the gases have been determined by Messrs. Kerby and Merrick; but as these belong rather to mechanical than to chemical science, I shall content myself with referring to the account of them in the 27th and 33d volumes of Nicholson's Journal, and in the 45th volume of the Philosophical Magazine.

## SECTION VI.

### *Specific Caloric.*

**EQUAL weights of the same body, at the same temperature, contain the same quantities of caloric. But equal weights of**

\* 82 An. de Chim. 34.



*different* bodies, at the same temperature, contain unequal quantities of caloric. The quantity of caloric, which one body contains, compared with that contained in another, is called its *specific caloric*; and the power or property, which enables bodies to retain different quantities of caloric, has been called *capacity for caloric*. The term *specific heat* has been employed also to denote the quantity of caloric which a body requires, in order to be heated a single degree, or through a certain number of degrees, relatively to that required by any other body to produce the same change. The method of determining the specific caloric of different bodies, is as follows:

It has already been observed, that equal weights of the *same* body, at different temperatures, give, on admixture, the arithmetical mean. Thus, the temperature of a pint of hot water and a pint of cold, is, after mixture, very nearly half way between that of the two extremes. But this is not the case, when equal quantities of *different* bodies, at different temperatures, are employed.

(a) If a pint of quicksilver at  $100^{\circ}$  Fahrenheit, be mixed with a pint of water at  $40^{\circ}$ , the resulting temperature will not be  $70^{\circ}$  (the arithmetical mean), but only  $60^{\circ}$ . Here the quicksilver loses  $40^{\circ}$  of heat, which nevertheless raise the temperature of the water only  $20^{\circ}$ : in other words, a larger quantity of caloric is required to raise the temperature of a pint of water, than that of a pint of mercury, through the same number of degrees. Hence it is inferred, that water has a greater capacity for caloric than is inherent in quicksilver.

(b) The experiment may be reversed, by heating the water to a greater degree than the quicksilver. If the water be at  $100^{\circ}$ , and the mercury at  $40^{\circ}$ , the resulting temperature will be nearly  $80^{\circ}$ ; because the pint of hot water contains more caloric, than is necessary to raise the quicksilver to the arithmetical mean.

(c) Lastly, if we take two measures of quicksilver to one of water, it is of no consequence which is the hotter; for the resulting temperature is always the mean between the two extremes; for example,  $70^{\circ}$ , if the extremes be  $100^{\circ}$  and  $40^{\circ}$ . Here, it is manifest, that the same quantity of caloric, which makes one measure of water warmer by  $30^{\circ}$ , is sufficient for

making two measures of quicksilver warmer by the same number. Quicksilver has, therefore, a less capacity than water for caloric, in the proportion, when equal measures are taken, of one to two.

If, instead of equal *bulks* of quicksilver and water, we had taken equal *weights*, the disparity between the specific caloric of the mercury and water would have been still greater. Thus a pound of water at  $100^{\circ}$ , mixed with a pound of mercury at  $40^{\circ}$ , gives a temperature of  $97\frac{1}{2}^{\circ}$ , or  $27\frac{1}{2}^{\circ}$  above the arithmetical mean. In this experiment, the water, being cooled from  $100^{\circ}$  to  $97\frac{1}{2}^{\circ}$ , has lost a quantity of caloric reducing its temperature only  $2\frac{1}{2}^{\circ}$ ; but this caloric, communicated to the pound of mercury, has occasioned, in its temperature, a rise of no less than  $57\frac{1}{2}^{\circ}$ . Therefore, a quantity of caloric, necessary to raise the temperature of a pound of water  $2\frac{1}{2}^{\circ}$ , is sufficient to raise that of a pound of mercury  $57\frac{1}{2}^{\circ}$ ; or, by the rule of proportion, the caloric, which raises the temperature of a pound of water  $1^{\circ}$ , will raise that of a pound of quicksilver about  $23^{\circ}$ . Hence it is inferred, that the quantity of caloric contained in water, is to that contained in the same *weight* of quicksilver as  $23^{\circ}$  to  $1^{\circ}$ . Or, stating the caloric of water at  $1^{\circ}$ , that of quicksilver will be  $\frac{1}{23}$  part of  $1^{\circ}$ , or  $0.0435$ .\*

In a similar manner may the specific heats of other bodies be ascertained. If a pound of water at  $100^{\circ}$ , and the same weight of oil at  $50^{\circ}$ , be mixed, the resulting temperature is not  $75^{\circ}$ , (the mean) but  $83\frac{1}{3}^{\circ}$ ; the water, therefore, has lost only  $16\frac{2}{3}^{\circ}$ , while the oil has gained  $33\frac{1}{3}^{\circ}$ . Or if equal weights of water at  $50^{\circ}$ , and oil at  $100^{\circ}$ , be mixed, the resulting temperature is  $66\frac{2}{3}^{\circ}$ , so that the oil has given out  $33\frac{1}{3}^{\circ}$ , and the water has increased only  $16\frac{2}{3}^{\circ}$ . (Dr. Thomson's Chemistry, vol. i.) Hence the heat, which raises a given weight of water  $1^{\circ}$ , will raise the same weight of oil  $2^{\circ}$ ; and as the specific heats are inversely as the changes of temperature, the specific heat of water may be called 1, and that of oil 0.5.

In some instances, it is not possible intimately to mix together the bodies under examination. When the specific heat

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\* The above numbers, which differ from those commonly stated, are given on the authority of Mr. Dalton.

of a solid mass of metal is to be ascertained, it may be heated throughout to a certain degree, and then surrounded by water of  $32^{\circ}$ , observing the increase of temperature which is gained by the water, and calculating the specific heat in the same manner as before. This was the method of Wilcke; but Lavoisier and Laplace substituted ice for water, placing, by means of an apparatus called the *Calorimeter*, the heated body in the centre of a quantity of ice, and determining the caloric evolved, by the quantity of ice melted in each instance.

When this comparison is extended to a great variety of bodies, they will be found to differ very considerably in their capacities for caloric. The results of numerous experiments of this kind are comprised in a table of specific caloric.\*

The capacities of bodies for caloric influence, considerably, the rate at which they are heated and cooled. In general, those bodies are most slowly heated, and cool most slowly, which have the greatest capacities for heat.† Thus, if water and quicksilver be set, in similar quantities, and at equal distances before the fire, the quicksilver will be much more rapidly heated than the water; and, on removal from the fire, it will cool with proportionally greater quickness than the water. By ascertaining then the comparative rates of cooling, we may determine, with tolerable exactness, the specific caloric of bodies.

It has been doubted whether the specific heats of bodies are permanent so long as they retain their form; in other words, whether a quantity of heat, which raises a body through a certain number of degrees at any one temperature, will raise it through an equal number of degrees at other temperatures. This subject, to which Mr. Dalton had formerly turned his attention,‡ has been lately investigated more completely by Petit and Dulong.§ They heated the body to be tried to the required temperatures, and ascertained what number of degrees of heat it communicated to a certain quantity of water. Repeating these trials at various points of the thermometric scale, they found that the specific heats of bodies

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\* See the Appendix.  
New System, vol. i. p. 53.

† See Martine, on Heat, page 74.  
§ Annals of Philosophy, xiii.

are greater at high than at low temperatures. Thus the specific heat of iron was found to be as follows :

Centigrade.	Specific heat.
From 0 to 100° .....	0.1098
..... 0 to 200° .....	0.1150
..... 0 to 300° .....	0.1218
..... 0 to 350° .....	0.1255

The same law was found to extend to various other bodies, as is shown by the following Table :

	Sp. heats between 0° and 100° cent.	Sp. heats between 0° and 300° cent.
Mercury .....	0.0330	0.0350
Zinc .....	0.0927	0.1015
Antimony .....	0.0507	0.0549
Silver .....	0.0557	0.0611
Copper .....	0.0949	0.1013
Platinum .....	0.0355	0.0355
Glass .....	0.1770	0.1900

Another important law, deduced by Petit and Dulong, from their researches on heat is, that *the atoms of all simple bodies have precisely the same specific heat*. This will appear from the following Table, the third column of which expresses differences so small, that they may reasonably be imputed to unavoidable inaccuracies in the method of determining the true weights of the atoms.

	Sp. heats, that of water being 1.	Wght. of the atoms, that of oxyg. being 1.	Product of the weight of the atom by the Sp. heat.
Bismuth .....	0.0288	13.300	0.3830
Lead .....	0.0293	12.950	0.3794
Gold .....	0.0298	12.430	0.3704
Platinum .....	0.0314	11.160	0.3740
Tin .....	0.0514	7.350	0.3779
Silver .....	0.0557	6.750	0.3759
Zinc .....	0.0927	4.030	0.3736
Tellurium .....	0.0912	4.030	0.3675
Copper .....	0.0949	3.957	0.3755
Nickel .....	0.1035	3.690	0.3819
Iron .....	0.1100	3.392	0.3731
Cobalt .....	0.1498	2.460	0.3685
Sulphur .....	0.1188	2.011	0.3780

The determination of the *specific heat* of gases is a difficult and important problem, which has successively employed the labour and ingenuity of Crawford, Lavoisier and De la Place, Leslie, Gay Lussac, Dalton, Delaroche and Berard, and Clement and Desormes. The details of the experiments of Delaroche and Berard are given in the 85th volume of the *Annales de Chimie*, preceded by an historical review of the labours of their predecessors. The following Table contains the general results :

TABLE OF THE SPECIFIC HEATS OF SOME GASES:

NA <sup>M</sup> ES OF GASES.	Under equal volumes.	Under equal weights.	Specific gravities.
Atmospheric air .....	1.0000	1.0000	1.0000
Hydrogen gas .....	0.9033	12.340	0.0732
Oxygen gas .....	0.9765	0.8848	1.1036
Nitrogen gas .....	1.0000	1.0318	0.9691
Nitrous oxide .....	1.3503	0.8878	1.5209
Olefiant gas .....	1.5530	1.5763	0.9885
Carbonic oxide .....	1.0340	1.0805	0.9569
Carbonic acid .....	1.2583	0.8280	1.5196

Taking water as unity, the specific heats of the gases are as follow :

*Table of the Specific Heats of the Gases, water being taken as unity.*

Water .....	1.0000
Atmospheric air .....	0.2669
Hydrogen gas .....	3.2936
Carbonic acid .....	0.2210
Oxygen .....	0.2361
Azote .....	0.2754
Protoxide of azote .....	0.2369
Olefiant gas. ....	0.4207
Oxide of carbon .....	0.2884
Steam of water .....	0.8470

After having thus determined the specific heats of the gases, MM. de la Roche and Berard ascertained that the specific heat of any one gas, considered with respect to its volume,

augments with its density, but in a proportion less than the increase of density. On this subject, M. M. Clement and Desormes have given the following results :

	Under the pressure of in. of mer.	Sp. heat.
Atmospheric air . . . . .	39.6 . . . . .	1.215
Ditto . . . . .	29.84 . . . . .	1.000
Ditto . . . . .	14.92 . . . . .	0.693
Ditto . . . . .	7.44 . . . . .	0.540
Ditto . . . . .	3.74 . . . . .	0.368
Azotic gas . . . . .	29.84 . . . . .	1.000
Oxygen . . . . .	29.84 . . . . .	1.000
Hydrogen . . . . .	29.84 . . . . .	0.664

## CHAPTER IV.

## OF LIGHT.

THE laws of light, so far as they relate to the phenomena of its movement, and to the sense of vision, constitute the science of OPTICS; and are the objects, therefore, not of Chemistry, but of Natural Philosophy. It may be proper, however, by a brief statement of its physical properties, to recal them to the memory of the reader.

1. The light of the sun moves with the velocity of 200,000 miles in a second of time, in consequence of which it passes through the whole distance between the sun and the earth in about eight minutes.

2dly. While it continues to move through a transparent medium of uniform density, its motion is in perfectly straight lines, but in passing obliquely out of one medium into another, it undergoes a change of direction. If the new medium be denser than the old, the ray of light is bent or *refracted* nearer to the perpendicular; but in passing out of a denser into a rarer medium it is *refracted* from the perpendicular; and there is a constant proportion between the sine of the angle of incidence and that of refraction. Transparent media, also, not only cause a change of the direction of a ray, but decompose it into its constituent parts, an effect which has been called *dispersion*.

3. In general the amount of refraction is proportional to the density of a body, but inflammable substances cause a greater refraction than might have been inferred from their densities, and the refractive power of the same inflammable substance bears a proportion to its perfection, insomuch that this property may be used as a test of its purity. Thus Dr. Wollaston found that genuine oil of cloves has a refractive power of 1.535, while that of an inferior quality did not ex-

ceed 1.498. The powers of the gases to refract light are exhibited in the following table by MM. Biot and Arago, from which it appears that the combustible gases surpass the others in this property, and that hydrogen gas exceeds them all.

*Table of the Refracting Powers of different Gases. (Therm. 32° Fahr. Bar. 30 in.)*

Atmospheric air .....	1.00000
Carbonic acid .....	1.00476
Azotic gas .....	1.03408
Muriatic acid gas .....	1.19625
Oxygen gas .....	1.86161
Carbureted hydrogen .....	2.09270
Ammonia .....	2.16851
Hydrogen gas .....	6.61436

4. When a ray of light arrives at the common surface of two media, and, instead of passing from the one into the other, is turned back into the first, this turning back is called *reflection*. The angles of incidence and reflection are, in this case, always equal, whatever may be the obliquity of the incident ray.

5. All objects seen by reflection or refraction appear in that place or direction from whence the rays were last reflected or refracted to the eye.

6. There are certain bodies (Iceland spar for example) which exhibit a double image of any object that is viewed through them, or are said to *refract doubly*. In this case, one portion of the light is refracted according to the common law, the other undergoes an extraordinary refraction, in a plane parallel to the diagonal which joins the two obtuse angles of the crystal. If the ray, which has thus suffered double refraction, be made to fall on another crystal placed parallel to the first, no new division of the rays will happen; but if the second crystal be placed in a transverse direction, that part of the ray, which before suffered ordinary refraction, will now undergo extraordinary refraction; and that which un-



derwent extraordinary refraction will now suffer ordinary refraction.

7. A ray of light, falling upon a polished surface of glass at an angle of  $35^{\circ} 25'$ , is reflected in a straight line at the same angle. . But if a second plate of glass be so placed that the reflected ray will fall upon it likewise at an angle of  $35^{\circ} 25'$ , and if the second plate be slowly turned round its axis, without varying the angle which it makes with the ray that falls upon it, a curious phenomena is observed. If the planes of reflection be parallel to each other, the ray of light is reflected from the second glass in the same manner as from the first. But if the second glass be turned round a quadrant of a circle, so as to make the planes of reflection perpendicular to each other, the whole of the ray will pass through the second glass, and none of it will be reflected. When the second glass is turned round another quadrant of a circle, so as to make the reflecting planes again parallel, the ray will be reflected by the second glass as at first; but when turned round three quadrants, the whole light will be again transmitted, and none of it reflected. Under certain circumstances, therefore, light can penetrate through glass when in one position, but not in another. In the latter case, it has been termed by Malus *polarised light*, on the supposition that the light has been bent into another position, as the needle is by a magnet.\* For a popular statement of the discoveries of Malus, the reader is referred to the 33d vol. of Nicholson's Journal, p. 344; for those of Dr. Brewster to the Phil. Trans. for 1813 and following years; and for the experiments of Biot and Arago to the 94th vol. of Annales de Chimie, or to the *Traité de Physique* of the former philosopher.

Light is capable of producing also important chemical effects, and of entering into various chemical combinations. Its action is, for the most part, exerted in de-oxidizing bodies; and facts of this kind cannot be perfectly understood, until two important classes of bodies have been described, *viz.* those o oxides and of acids. In this place, therefore, I shall state only

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\* Thomson's Chemistry, i. 16.

a few of its least complicated effects; and shall trace its agency on individual bodies, as they become the objects of experiment in the sequel.

I. Light, in the state in which it reaches the organ of vision, it is well known, is not a simple body, but is capable of being divided, by the prism, into seven primary rays or colours, viz. red, orange, yellow, green, blue, indigo, and violet. These are refrangible in the above order, the red being least refrangible, and the violet most so. The image formed by the different rays, thus separated, constitutes the SOLAR SPECTRUM. If it be divided into 300 parts, the red will occupy 45 of these parts, the orange 27, the yellow 48, the green 60, the indigo 40, and the violet 80. Dr. Wollaston found, however, that when a beam of light only  $\frac{1}{10}$ th of an inch broad is received by the eye, at the distance of ten feet, through a clear prism of flint glass, only four colours are seen, viz. red, yellowish green, blue, and violet. The different coloured rays, being collected by a lens into a focus, again produce uncoloured light.

II. Heat and light are not present, in corresponding degrees, in different parts of the solar spectrum. With respect to the *illuminating* power of each colour, Dr. Herschell found that the red rays are far from having it in an eminent degree. The orange possess more of it than the red; and the yellow rays illuminate objects still more perfectly. The maximum of illumination lies in the brightest yellow or palest green. The green itself is nearly equally bright with the yellow; but from the full deep green the illuminating power decreases very sensibly. That of the blue is nearly on a par with that of the red; the indigo has much less than the blue, and the violet is very deficient.\*

III. The *heating* power of the rays follow a different order. —If the bulb of a very sensible air thermometer be moved in succession, through the differently coloured rays, it will be found to indicate the greatest heat in the red rays; next in the green; and so on, in a diminishing progression, to the

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\* Philosophical Transactions, 1800, page 267.

violet. The precise effects of the different rays, determined by Dr. Herschell's experiments, are as follows :

The thermometer rose	
In the blue,	in 3 minutes from 55° to 56°
— green,	in 3 ——— 54 to 58
— yellow,	in 3 ——— 56 to 62
— full red,	in 2½ ——— 56 to 72
— confines of red,	in 2½ ——— 58 to 73½

IV. When the thermometer is removed entirely out of the confines of the red rays, but with its ball still in the line of the spectrum, it rises even higher than in the red rays; and continues to rise, till removed half an inch beyond the extremity of the red rays. In this situation, quite out of the visible light, the thermometer rose in 2½ minutes from 61 to 79. The ball of the thermometer, employed for this purpose, should be extremely small,\* and should be blackened with Indian ink. An air thermometer is better adapted than a mercurial one, to exhibit the minute change of temperature that ensues. These INVISIBLE HEAT-MAKING RAYS may be reflected by the mirror, and refracted by the lens, exactly in the same manner as the rays of light.

A fact has been ascertained by Dr. Delaroché, which seems to point out a close connection between heat and light, and a gradual passage of the one into the other. The rays of invisible heat pass through glass with difficulty, at a temperature below that of boiling water, but they traverse it with a facility always increasing with the temperature, as it approaches the point when bodies become luminous. From these experiments it would appear that the modification, whatever it be, which must be impressed on the invisible rays, to render them capable of penetrating through glass, makes them approach more and more to the state in which they must be, when they enter the eye, and occasion the sensation of vision.

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\* Excellent thermometers for this purpose, and others requiring great sensibility, are made by Mr. Crichton, of Glasgow, and Mr. Cary, of London.

The experiments of Dr. Herschell, already confirmed by Sir H. Englefield and other philosophers, were found correct in the main, when repeated by Mr. Berard,\* who observed the same progressive heating power in the rays from the violet to the red. But he found the greatest heating power in the red extremity of the spectrum, and not beyond it. He fixed it at the point, where the bulb of the thermometer was still entirely covered by the red ray; and the thermometer sunk progressively, in proportion as the distance of its bulb from the red ray increased. Entirely out of the visible spectrum, where Herschell fixed the maximum of heat, its elevation above the ambient air was only one-fifth of what it had been in the red ray itself. The reflection of invisible radiant heat, Mr. Berard found, follows precisely the same law as that of light, and that the rays of heat are capable of polarization equally with those of light.

V. Beyond the confines of the spectrum on the other side, *viz.* a little beyond the violet ray, the thermometer is not affected; but in this place it is remarkable, that there are also invisible rays of a different kind, which exert all the chemical effects of the rays of light, and with even greater energy. One of the chemical properties of light, it will hereafter be stated, is, that it speedily changes, from white to black, the fresh-precipitated muriate of silver.† This effect is produced most rapidly by the direct light of the sun; and the rays, as separated by the prism, have this property in various degrees. The blue rays, for example, effect a change of the muriate of silver in 15 seconds, which the red require 20 minutes to accomplish; and, generally speaking, the power diminishes as we recede from the violet extremity. But entirely out of the spectrum, and beyond the violet rays, the effect is still produced. Hence it appears, that the solar beams consist of three distinct kinds of rays; of those that excite heat, and promote oxidation; of illuminating rays; and of DE-OXIDIZING OR HYDROGENATING RAYS. It has lately, also, been asserted by Morrichini, that the violet rays have a magnetising power, and are capable of reversing the poles of a needle al-

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\* Thomson's Annals, ii. 163.

† See chap. ix. sect. 35.

ready magnetic.\* A striking illustration of the different power of the various kinds of rays is furnished, by their effect on phosphorus. In the rays beyond the red extremity, phosphorus is heated, smokes, and emits white fumes; but these are presently suppressed, on exposing it to the de-oxidizing rays, which lie beyond the violet extremity.

“I found,” says Sir H. Davy,† “that a mixture of chlorine and hydrogen acted more rapidly upon each other, combining without explosion, when exposed to the red rays, than when placed in the violet rays; but that solution of chlorine in water became solution of muriatic acid most rapidly, when placed in the most refrangible rays of the spectrum. Puce-coloured oxide of lead, when moistened, gradually gained a tint of red in the least refrangible rays, and at last became black, but was not affected in the most refrangible rays; and the same change was produced by exposing it to a current of hydrogen gas. The oxide of mercury, procured by a solution of potash and calomel, exposed to the spectrum, was not changed in the most refrangible rays, but became red in the least refrangible ones, which must have depended on its absorbing oxygen. The violet rays produced, upon moistened red oxide of mercury, the same effects as hydrogen gas.”

The experiments of Berard‡ confirm those of Ritter and Wollaston. To show the disproportion between the energies of the different rays, he concentrated, by means of a lens, all that part of the spectrum, which extends from the green to the extreme violet; and, by another lens, all that portion, which extends from the green to the extremity of the red. In the focus of this last half, though intensely bright to the eyes, muriate of silver remained above two hours unaltered; but in that of the former half, though much less bright, it was blackened in less than six minutes.

VI. There is an exception, however, as stated by Dr. Wof-

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\* *Ann. de Chim. et Phys.* iii. 323; *Jour. of Science*, v. 138; and *Thomson's Annals*, xii. 1.

† *El. of Chem. Phil.* p. 211.

‡ *Thomson's Annals*, ii. 165, and xvi. 6; also *Brewster's Ed. Journal*, i. 239; and *Silliman's American Journal*, i. 89.

laston, to the de-oxidizing power of the rays above-mentioned. The substance, termed gum-guaiacum, has the property, when exposed to the light, of being changed from a yellowish colour to green; and this effect he has ascertained to be connected with the absorption of oxygen. Now in the most refrangible rays, which would fall beyond the violet extremity, he found that this substance became green, and was again changed to yellow by the least refrangible. This is precisely the reverse of what happens to muriate of silver, which is blackened, or de-oxidized, by the most refrangible; and has its colour restored, or is again oxygenized, in the least refrangible rays.

VII. Certain bodies have the property of absorbing the rays of light in their totality; of retaining them for some time; and of again evolving them unchanged, and unaccompanied by sensible heat. Thus, in an experiment of Du Fay, a diamond exposed to the sun, and immediately covered with black wax, shone in the dark, on removing the wax, at the expiration of several months. Bodies, gifted with this property, are called SOLAR PHOSPHORI. Such are Canton's, Baldwin's, Homberg's, and the Bolognian phosphori, which will be described hereafter. To the same class belong several natural bodies, which retain light, and give it out unchanged. Thus snow is a natural solar phosphorus. So also is, occasionally, the sea when agitated; putrid fish have a similar property; and the glow-worm belongs to the same class. These phenomena are independent of every thing like combustion; for artificial phosphori, after exposure to the sun's rays, shine in the dark, or when placed in the vacuum of an air-pump, or under water, &c. where no air is present to effect combustion.

VIII. From solar phosphori, the extrication of light is facilitated by the application of an elevated temperature; and, after having ceased to shine at the ordinary temperature, they again emit light when exposed to an increase of heat. Several bodies, which do not otherwise give out light, evolve it, or become phosphorescent, when heated. Thus, powdered fluuate of lime becomes luminous, when thrown on an iron plate raised to a temperature rather above that of boiling water;

and one of its varieties, known to mineralogists under the name of *chlorophane*, gives out abundantly an emerald green light by the mere heat of the hand; and after being exposed to the sun, or even to a candle, continues to shine in a dark place for some time.\* The yolk of an egg, when dried, becomes luminous, on being heated; and so also does tallow during liquefaction. To exhibit the last mentioned fact, it is merely necessary to place a lump of tallow on a coal, heated below ignition, making the experiment in a dark room.

IX. Attrition, also, evolves light. Thus, two pieces of common bonnet cane, rubbed strongly against each other in the dark, emit a faint light. Two pieces of borax or of quartz have the same property much more remarkably.

X. Light is disengaged in various cases of chemical combination. Whenever combustion is a part of the phenomena, this is well known to happen; but light is evolved, also, in other instances, where nothing like combustion goes forward. Thus, fresh prepared pure magnesia, added suddenly to highly concentrated sulphuric acid, exhibits a red heat.

XI. For measuring the relative intensities of light from various sources, an instrument has been contrived, called the **PHOTOMETER**. That of Count Rumford, described in the 84th volume of the *Philosophical Transactions*, being founded on optical principles, does not fall strictly within the province of this work. It is constructed on the principle, that the power of a burning body, to illuminate any defined space, is directly as the intensity of the light, and inversely as the square of the distance. If two unequal lights shine on the same surface at equal obliquities, and an opaque body be interposed between each of them and the illuminated surface, the two shadows must differ in intensity or blackness; for the shadow formed by intercepting the greater light will be illuminated by the lesser light only; and, reversely, the other shadow will be illuminated by the greater light; that is, the stronger light will be attended with the deeper shadow. But it is easy, by removing the stronger light to a greater distance, to render the shadow, which it produces, not deeper than that

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\* Thomson's *Annals*, ix. 17.

of the smaller, or of precisely the same intensity. This equalization being effected, the quantity of light emitted by each lamp, or candle, will be as the square of the distance of the burning body from the white surface.

The photometer of Mr. Leslie is founded on a different principle, *viz.* that light, in proportion to its absorption, produces heat. The degree of heat produced, and consequently of light absorbed, is measured by the expansion of a confined portion of air. A minute description of the ingenious instrument contrived by Mr. Leslie with this view, may be seen in his work on Heat, or in the 3d vol. of Nicholson's 4to. Journal. In its construction, it bears a considerable resemblance to the differential thermometer, already described, and represented plate i. fig. 7. As both the balls of the latter instrument, however, are transparent, no change ensues in the situation of the coloured liquid when it is exposed to the variations of light. But, in the photometer, one of the balls is rendered opaque, either by tinging the glass, or by covering it with a pigment; and hence this ball, absorbing the incident light which passes freely through the transparent one, the air included in it becomes warmer than that of the other ball, and, by its great elasticity, forces the liquid up the opposite leg of the instrument. A graduated scale measures the amount of the effect; and a glass covering defends the photometer from being influenced by the temperature of the atmosphere.

Mr. Brande has ascertained that by substituting ether, as in Dr. Howard's modification of the differential thermometer, the sensibility of the photometer is greatly increased, and that it becomes most delicately susceptible of the impression of light. An instrument of this sort he found fully adequate to determine the comparative illuminating powers of different gases, which cannot be done when the photometer is filled with air.\*

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\* Journal of Science, viii. 220.



## CHAPTER V.

## ON THE CHEMICAL AGENCIES OF COMMON AND GALVANIC ELECTRICITY.

THAT branch of natural science which comprehends the phenomena of Galvanism, and the general principles under which they are arranged, is only of recent origin. It was not till the year 1791, that Galvani, an Italian philosopher, being engaged in a course of experiments on animal irritability, observed accidentally the contractions, which are excited in the limbs of frogs, by applying a conductor of electricity between a nerve and a muscle. The theory, which he framed to account for this phenomenon, was, that the different parts of an animal are in opposite states of electricity, and that the effect of the metal is merely to restore the equilibrium. The analogy, however, was afterwards shown to be without foundation, by Volta, who excited similar contractions by making a connection between two parts of a nerve, between two muscles, or between two parts of the same muscle; but to produce the effect, two different metals were found to be essential. Hence he was led to infer that, by the contact of different metals, a small quantity of electricity is excited: and to the agency of this electricity, first upon the nerves, and through their mediation on the muscles, he ascribed the phenomena in question.

Several years elapsed, during which the action of galvanic electricity on the animal body, and the discussion of its cause, occupied the attention of philosophers. Early in 1800, the subject took a new turn, in consequence of the discovery by Signor Volta of the Galvanic Pile; \* a discovery which has furnished us with new and important instruments of analysis, capable, if any such there are, of leading to a knowledge of the true elements of bodies. From this period, discoveries have multiplied with a rapidity, and to an extent, which sur-

\* Philosophical Transactions, 1800; or Philosophical Magazine, vii 287.

pass any thing before known in the history of science; and the facts are now become so numerous, that an arrangement and classification of them seem to be preferable to an historical detail in the order of time. The method, which appears to me best calculated to give a distinct view of the subject, is to describe,

I. The construction of galvanic apparatus, and the circumstances essential to the excitement of this modification of electricity :

II. The facts, which establish its identity with the electricity excited by ordinary processes :

III. The agency of the electric or galvanic fluid in producing chemical changes :

IV. The theory, by which these changes, in the present state of our knowledge, are best explained :

V. The hypotheses, which have been framed to account for the origin of the electricity, excited by galvanic arrangements :  
And

VI. I shall offer a very general view of the phenomena of electro-magnetic motion, which, with the principles deducible from them, promise to throw light on some of the most interesting, but obscure operations of nature.

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## SECTION I.

### *Of the construction of Galvanic Arrangements.*

FOR the excitation of ordinary electricity, it is well known that a class of substances are required, called *electrics*, by the friction of which the electric fluid is accumulated, and from which it may be collected by a different class of bodies termed *non-electrics* or *conductors*. When friction, for example, is applied to the glass cylinder or plate of an electrical machine, that part of the glass, which is in contact with the rubber, attracts the electric fluid from it, as well as from all other conducting bodies, with which the rubber is connected. The glass, regaining instantly its natural state, repels the electric

fluid, which is received by the prime conductor, placed for that purpose. All then that is effected, by the action of the machine, is a disturbance of the natural quantity of electricity in bodies, or a transfer of it from some to others, in consequence of which, while the latter acquire a redundance, the former become proportionally deficient in their quantity of electricity.

The conditions necessary to the excitement of galvanic electricity are altogether different; for the class of bodies, termed electrics, have now no longer any share in the phenomena. All that is required is the simple contact of *different* conducting bodies with each other; and it has even been found by Des-saignes that two discs of *the same* metal, heated to different temperatures, give sufficient electricity to excite contractions in the legs of a frog, prepared for the purpose. Conductors of electricity have been divided into *perfect* and *imperfect*, the former comprehending the metals, plumbago and charcoal, the mineral acids, and saline solutions; the latter, or imperfect, including water, alcohol and ether, sulphur, oils, resins, metallic oxides, and compounds of chlorine.

The least complicated galvanic arrangement is termed a SIMPLE GALVANIC CIRCLE. It consists of three conductors, two of which must be of the one class, and one of the other class. In the following Tables, constructed by Sir H. Davy, some different simple circles are arranged in the order of their powers, the most energetic occupying the highest place.

*Table of some Electrical Arrangements, which by combination form Voltaic Batteries, composed of two Conductors and one imperfect Conductor.*

Zinc, Iron, Tin, Lead, Copper, Silver, Gold, Platina, Charcoal.	Each of these is the positive pole to all the metals below it, and negative with respect to the metals above it in the column.	Solutions of nitric acid, of muriatic acid, of sulphuric acid, of sal ammoniac, of nitre, of other neutral salts.
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*Table of some Electrical Arrangements consisting of one perfect Conductor and two imperfect Conductors.*

Solution of sulphur and potash, of potash, of soda.	Copper, Silver, Lead, Tin, Zinc, Other Metals, Charcoal.	Nitric acid, Sulphuric acid, Muriatic acid, Any solutions containing acid.
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In explanation of these Tables, Sir H. Davy observes, that in all cases when the fluid menstrea afford oxygen, those metals, which have the strongest attraction for oxygen, are those which form the positive pole. But when the fluid menstrea afford sulphur to the metals, the metal which, under the existing circumstances, has the strongest attraction for sulphur, determines the positive pole. Thus, in a series of copper and iron plates, introduced into a porcelain trough, the cells of which are filled with water or with acid solutions, the iron is positive and the copper negative; but when the cells are filled with solution of sulphuret of potash, the copper is positive and the iron negative. When one metal only is concerned, the surface opposite the acid is negative, and that in contact with solution of alkali and sulphur, or of alkali, is positive.\*

The powers of simple galvanic circles are but feeble; but they may be made sufficiently apparent by the following experiments.

1. When a piece of zinc is laid upon the tongue, and a piece of silver under it, no sensation is excited, so long as the metals are kept apart; but, on bringing them into contact, a metallic taste is distinctly perceived. In this case we have an example of the arrangement of two perfect conductors (the metals) with one imperfect one (the tongue, or rather the fluids which it contains). The metallic taste arises, in all probability, from the excitement of a small quantity of electricity by the contact of the metals, and its action on the nerves of the tongue.

\* El. of Chem. Phil. p. 148.

2. A piece of zinc, immersed under water which is freely exposed to the atmosphere, oxidizes very slowly; but when placed in the same situation, in contact with a piece of silver, its oxidation is much more rapid. By immersing iron and silver (also in contact with each other) under diluted muriatic acid, the action of the acid upon the iron is considerably increased; and hydrogen gas is evolved from the water, not only where it is in contact with the iron, but where it touches the silver. These facts explain, why, in the sheathing of ships, it is necessary to use bolts of the same metal which forms the plates; for if two different metals be employed, they both oxidate or rust very speedily, in consequence of their forming, with the water of the ocean, a simple galvanic circle.

*Of compound Galvanic Circles or Batteries.*

Galvanic batteries are formed by multiplying those arrangements, which compose simple circles. Thus if plates of zinc and of silver, and pieces of woollen cloth of the same size as the plates and moistened with water, be piled upon each other (fig. 77. pl. ix), in the order of zinc, silver, cloth; zinc, silver, cloth; and so on, for twenty or more repetitions, we obtain a galvanic battery; termed, from its discoverer, the *Pile of Volta*. The power of such a combination is sufficient to give a smart shock, as may be felt by grasping in the hands, which should be previously moistened, two metallic rods, and touching with these the upper and lower extremities of the pile. The shock may be renewed at pleasure; until, after a few hours, the activity of the pile begins to abate, and finally ceases altogether.

The metals, composing a galvanic battery, may be more conveniently arranged in the form of a trough, a happy invention of Mr. Cruikshank. In a long and narrow wooden trough, made of baked wood, grooves are cut, opposite to and at the distance of between  $\frac{1}{4}$  and  $\frac{3}{4}$  of an inch from each other; and into these are let down, and secured by cement, square plates of zinc and copper, previously united together by soldering. (See figs. 37 and 78.) The space, therefore, between each pair of plates, forms a cell for the purpose of

containing the liquid, by which the combination is to be made active. The advantage of this contrivance, over the pile, is partly that it is much more easily put in order; but, besides this, it is a more efficient instrument. When constructed in the way which has been described, it affords an example of a galvanic combination of *the first kind*, formed by two perfect and one imperfect conductor. But it admits of being modified, by cementing, into the grooves, plates of one metal only, and filling the cells, alternately, with two different liquids, as diluted nitric acid and solution of sulphuret of potash. In this case, we have a battery of *the second order*, formed by the repetition of one perfect and two imperfect conductors. For all purposes of experiment, the first kind of arrangement is universally preferred.

Another modification of the apparatus, which may be called the *Chain of Cups*, was proposed by Volta at the same time that he communicated his invention of the Pile; and, from the experiments of Mr. Children,\* it appears to be a very useful and powerful one. It consists of a row of glasses (see fig. 75), such as wine glasses or small tumblers, for the purpose of containing any fluid that may be selected. Into each of these glasses is plunged a plate of zinc and another of copper, each not less than an inch square, which are not to touch each other. The plates of different cups are connected by metallic wires or arcs, in such a manner that the zinc of the first cup communicates with the copper of the second; the zinc of the second with the copper of the third; and so on through the whole row. The shock is felt on dipping the fingers of one hand into the fluid of the first cup, and those of the other hand into the last of the series. The superiority of this arrangement consists in both surfaces of each metallic plate being exposed to the action of the liquid; whereas, by soldering the plates together, one of the surfaces of each is protected from the liquid, and contributes nothing to the effect. The common trough has lately been made to combine this advantage, by dividing it into cells, not by plates of metal, but by partitions of glass. Into each of these cells

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\* Philosophical Transactions, 1809, p. 32.

filled with the proper liquid, a plate of each metal is introduced, but not so as to touch each other. A communication is then made, by a metallic arc, between the zinc plate of each cell and the copper one of the next, precisely as in the chain of cups. More lately the troughs themselves have been made of earthen ware, and the partitions of the same material; the apparatus being completed, in other respects, in the manner already described. The plates, also, are now so suspended that when not in use, they may all be lifted out of the cells at once.\* And it has been recently ascertained that the power of a battery is increased at least one half by placing in each cell one zinc and two copper plates, so that each surface of zinc may be opposed to a surface of copper.†

The size of the plates has been varied from one or two inches to several feet. The large battery, described by Mr. Children in the *Philosophical Transactions* for 1815, consisted of plates each six feet by two feet eight inches, equal to 32 square feet; and the cells were capable of containing about 945 gallons of liquid. For ordinary purposes, plates of two inches square are sufficient; but for the decomposition of several bodies, not less than 100 pairs of plates, each four inches square, are required.‡ The enlargement of the size of the troughs, so as to contain this number, would be extremely inconvenient; and we may therefore combine the power of several troughs, by uniting the zinc end of the one with the copper end of the other, by the intervention of a metallic wire, or by an arc of silver or zinc.

A convenient and powerful galvanic battery has been constructed by Dr. Hare of Philadelphia, of zinc and copper sheets formed into coils. The zinc sheets were about nine inches by six; the copper fourteen by six; more of the latter metal being necessary, as, in every coil, it was made to commence within the zinc, and completely to surround it without.

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\* See Pepys in *Journal of Science*, &c. i. 193.

† *Phil. Trans.* 1815.

‡ Some useful information respecting the number and size of plates, adapted to different purposes, is given by Mr. Singer in *Nicholson's Journal*, xxiv. 174.

The sheets were coiled so as not to leave between them an interstice wider than a quarter of an inch. Each coil was in diameter about two inches and a half; their number amounted to 80; and by means of a lever they were made all to descend together into 80 glass jars, 2 inches and  $\frac{3}{4}$ ths diameter inside, and eight inches high, duly placed to receive them. The effects of this apparatus, in producing ignition, appear to have been very striking, especially at the moment of immersion, when Dr. Hare found the effect to be by much the most powerful.\* An apparatus of 80 coils produced a vivid ignition in charcoal; and when the points of the charcoal were drawn three-fourths of an inch apart from each other, a most brilliant arc of flame extended between them.

It may be sufficient to add, in general terms, that every combination, which is capable of forming a simple galvanic circle, may, by sufficient repetition, be made to compose a battery. The combinations, also, which are most active in simple circles, are observed to be more efficient in compound ones. The foregoing tables of Sir H. Davy express, therefore, the powers of compound as well as of simple arrangements.

To construct a battery of the first order, it is essential that a fluid be employed, which exerts a chemical action upon one of the metals. Pure water, entirely deprived of air, appears to be inefficient. In general, indeed, the galvanic effect is, within certain limits, proportional to the rapidity with which the more oxidable metal is acted upon by the intervening fluid. Spring water was found sufficient, in Mr. Children's immense battery, to produce the ignition of platina wire. The fluid generally used is nitric acid, diluted with 20 or 30 times its weight of water. Mr. Children recommends a mixture of three parts fuming nitrous acid, and one sulphuric, diluted with thirty parts of water. Directions, also, respecting the best kind and density of acids, for producing galvanic electricity, are given by Mr. Singer. From his experiments it appears, that acid of different densities is required for different purposes. The best wire melting charge is formed with ten

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\* Silliman's Journal, *vi.* 105.



gallons of water, five pounds of nitric acid, and half a pound of muriatic acid.

The power of the apparatus has been found to be increased, when insulated by non-conductors; and when surrounded by an atmosphere of oxygen gas; not sufficiently, however, to make it necessary to resort to either of these expedients in ordinary cases. Oxygen gas disappears in this process, when carried on under a receiver; and, after all the oxygen is absorbed, the effect ceases, and is renewed by introducing a fresh portion. A battery, also, which has ceased to be efficient, has its activity renewed by emptying the cells of their liquor, and uncovering the plates. When the cells are filled with diluted nitric acid, the apparatus continues active, even under the exhausted receiver of an air-pump, or in an atmosphere of carbonic acid or nitrogen gases. But if the cells be filled with water only, all action is suspended, by placing it under any of these circumstances. Hence it appears that the oxidation of one or both of the metals, composing the trough, is essential to the excitement of galvanic electricity.

The *electric column* may be classed among galvanic arrangements. It was originally contrived by M. de Luc, who formed it of discs of Dutch gilt paper, alternated with similar discs of laminated zinc. These were piled on each other in a dry state, and the instrument, instead of being soon exhausted, like the pile with humid substances, was found to continue active for some years.\* A similar pile may be formed by laying a mixture of very finely powdered zinc with common glue and a little sugar, by means of a brush, on the back of Dutch gilt paper; and, when dry, cutting it into discs, which are to be piled on each other†. Zamboni of Verona has constructed a pile of slips of silver paper, on the unsilvered side of which is spread a layer of black oxide of manganese and honey. These papers are piled on each other to the number of 2000; then covered externally with a coating of shell lac; and enclosed in a hollow brass cylinder. Two of these piles are placed at the distance of four or five inches from each other; and between them is suspended on a pivot a light me-

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\* Nicholson's Journal, vol. xxvi.

† Phil. Mag. xlviii. 265.

tallic needle, which is attracted alternately to the one pile and the other, so that it moves between them like a pendulum. This instrument has been applied to the measurement of time, by causing it to give motion to the pendulum of a clock.\*



## SECTION II.

### *On the mutual Relation of Electricity and Galvanism.*

Is the influence, it may now be inquired, which is called into action in a way so different from that employed for the excitation of ordinary electricity, identical with it or of a different kind? This question will be decided by examining whether any of those phenomena, which are occasioned by the agency of the electric fluid, are produced also by that of galvanism; and we shall find the following striking resemblances:

1. The sensation, produced by the galvanic shock, is extremely similar to that which is excited by the discharge of a Leyden jar. Both influences, also, are propagated through a number of persons, without any perceptible interval of time.

2. Those bodies, which are conductors of electricity, are also conductors of the galvanic fluid, as the metals, charcoal, and a variety of liquids. Again, it is not transmitted by glass, sulphur, and the whole class of electrics, which do not convey ordinary electricity. Among liquids, those only are conductors of electricity and galvanism, which contain oxygen as one of their elements.†

3. The galvanic fluid passes through air and certain other non-conductors, in the form of sparks; accompanied with a snap or report; and, like the electric fluid, it may be made to inflame gun-powder, phosphorus, and mixtures of hydrogen and oxygen gases. It has been found, also, by Mr. Children, that in the Voltaic apparatus there is, what is called in electricity, a *striking distance*. With a power of 1250 pairs of four inch plates, he found this distance to be one 50th of

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\* Phil. Mag. xlv. 261. and Ann. de Ch. et de Phys. xi. 190.

† Cruickshank, in Nicholson's 4to. Journal, iv. 258.

an inch, the thickness of a plate of air, through which the galvanic discharge is able to pass in the form of a spark. Increasing the number of plates, the striking distance will be greater; and the reverse when it is diminished. It is also increased by rarefying the air, through which the spark is transmitted.

4. The Voltaic apparatus is capable of communicating a charge to a Leyden jar, or even to a battery. If the zinc end of a pile (whether it be uppermost or the contrary) be made to communicate with the inside of a jar, it is charged positively. If circumstances be reversed, and the copper end be similarly connected, the jar is charged negatively.\* The shocks do not differ from those of a jar or battery, charged to the same intensity by a common electrical machine.

5. Galvanism, even when excited by a single galvanic circle only (such as a piece of zinc, a similar one of copper, and a piece of cloth moistened with a solution of muriate of ammonia), distinctly affects the gold leaf of the condensing electrometer. If the zinc end be uppermost, and be connected directly with the instrument, the electricity indicated is positive; if the pin of the electrometer touch the copper, the electricity is negative. A pile consisting of sixty combinations produces the effect still more remarkably.†

6. The chemical changes produced by galvanic and common electricity, so far as they have hitherto been examined, are precisely similar. These will form the subject of the following section.

### SECTION III.

#### *On the Chemical Agencies of Electricity and Galvanism.*

THE effects of the electric or galvanic fluids, in producing chemical decomposition, cannot be described, without intro-

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\* Cuthbertson's *Practical Electricity and Galvanism*, p. 261; Volta, in *Nicholson's Journal*, 8vo. i. 140; Van Marum, in *Philosophical Magazine*, xii. 162; Singer, p. 126.

† *Nicholson*, 8vo. i. 139, and ii. 281; Cuthbertson, p. 264; and Singer p. 317; where the cautions necessary to the success of this delicate experiment are particularly described.

ducing to the reader the names of several substances, with which, in the present state of his knowledge, he may be supposed to be unacquainted. This difficulty is unavoidable; for it is impossible to explain the general laws of electro-chemical action, without a variety of particular instances. In general, however, it will be found that a minute acquaintance with the bodies, which are brought in illustration, is by no means essential; and that it is sufficient to consider them abstractedly as composed of two ingredients, which are in opposite electrical states, and are subject to the laws of electrical attraction and repulsion.

The most simple chemical effect, produced alike by the agency of electricity and galvanism, is the *ignition* and *fusion* of *metals*. When a piece of watch-pendulum wire is placed in the circuit of a common electrical battery, containing not less than three or four square feet of coating, at the moment of the discharge the wire becomes red-hot; but continues so only for a few seconds; no longer, indeed, than if it had been ignited in any other way.\* The same effect may be produced by making a piece of wire the medium of communication between the opposite extremities of a galvanic trough; but, in this case, the heat continues sensibly longer, than when it is excited by an electrical explosion. Indeed a platina wire may be kept ignited *in vacuo*, for an unlimited time, by Voltaic electricity. Water, surrounding a wire so placed, may be made to boil briskly.

By means of his large battery, Mr. Children not only ignited wire of considerable thickness; but a bar of platina,  $\frac{1}{8}$ th of an inch square and  $2\frac{1}{4}$  inches long, was ignited, and even fused at one end. The facility of being ignited in the different metals appeared to be inversely proportional to their power of conducting heat. Thus platina, which has the lowest conducting power, was most easily ignited; and silver, which conducts heat better than any other metal, was ignited with greater difficulty than any of the rest.

It does not appear, however, that a very powerful combination is required to produce ignition, if the wire be made of

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\* On the quantity of coated surface required for igniting different lengths of wire, the reader may consult Mr. Cuthbertson's book, p. 161, &c.

proportionately small diameter. Dr. Wollaston has ascertained that a wire  $\frac{1}{3000}$  of an inch in diameter may be ignited by a single zinc plate only one inch square, provided each of its surfaces be opposed to a surface of copper or some other metal. The liquor which he employed was a mixture of one measure of sulphuric acid with 50 measures of water. Any farther diminution in the diameter of the wire he found to be unfavourable to the effect, in consequence of the increase of the cooling power of the atmosphere.\*

When the power of an electrical battery is increased, metallic wires, by transmitting the discharge through them, may be melted and dispersed in the form of smoke, or of an impalpable powder lighter than air. The galvanic discharge, also, is capable of fusing metallic wires; but being less violent, it does not scatter their particles to a distance. Even wire formed of the most infusible of the metals, platina, acquires a white heat, and melts into globules.

With a still more powerful electrical battery (one for example containing about 18 square feet) metallic wires are not only melted, but undergo absolute *combustion*. Lead and tin wire emit a yellow light, and copper and silver a green one. If the experiment be made on wire confined in a glass receiver, which contains a measured quantity of air, the bulk of the air, and its proportion of oxygen, are both found to be diminished.† The metals are converted into oxides of different colours; lead, tin, and zinc, into white oxides; platina, gold, silver, and copper, into oxides of a dark colour. The experiment may be pleasingly varied by passing the discharge through wires, stretched over panes of glass or sheets of paper, at a small distance from their surface. The metallic oxide which is produced is forcibly driven into the glass or paper; and produces beautiful figures, varying in colour with the metal employed.‡ It appears, also, from Mr. Singer's experiments, that the oxides of some of the compound metals,

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\* Thomson's Annals, vi. 209.

† Cuthbertson, p. 199.

‡ Cuthbertson, p. 226; and Wilkinson's Elements of Galvanism, in the 9th plate of which these appearances are represented.

when thus treated, (brass wire for instance) are exhibited in a completely separate state.

The combustion of metals may be effected, also, by galvanic electricity; but for this purpose the form of very thin leaves is preferable to that of wire. The plates, composing the galvanic trough, should, for this purpose, be not less than four inches square, the larger, indeed, the better; and several troughs should be joined together, so as to form an aggregate of not less than 100 or 150 pairs of plates. The galvanic influence is to be conveyed by wires brought from each extremity of the arrangement, and placed in contact with the opposite surfaces of the leaf. For the protection of the fingers, the wires should be inclosed in glass tubes. When thus exposed, the metals burn, or rather deflagrate, with great brilliancy.

Gold emits a very vivid white light, inclining a little to blue, and leaves an oxide, whose colour verges towards that of mahogany. Copper presents similar phenomena.

The flame of silver is a vivid green, somewhat like that of a pale emerald, and the light is more intense than that of gold. Lead gives a vivid light of a dilute bluish purple. Tin a light similar to that of gold; and zinc a bluish white flame fringed with red.\* In all these cases, provided the power be sufficiently strong, the deflagration is kept up, for some time, without intermission.

But a much more remarkable action is exerted by the electric and galvanic fluids, in disuniting the elements of several combinations. One of the first discoveries of the chemical agency of the pile was its power of decomposing water. Two pieces of any metallic wire are thrust through separate corks, which are fitted into the open ends of a glass tube in such a way, that the extremities of the wires, when the corks are in their places, may not be in contact, but may be at the distance from each other of about a quarter of an inch (see fig. 77, *a*). If the parts of the wire, which project from without the tube, be made to communicate, the one with the zinc or positive

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\* Philosophical Magazine, xi. 284, and xv. 96.

end, and the other with the copper or negative end, of a galvanic battery, a remarkable appearance takes place. The wire, connected with the zinc or positive end of the pile or trough, where it is in contact with the water, if of an oxidable metal, is rapidly oxidized; while from the negative wire a stream of small bubbles of gas arises. But if the wires employed be of a metal which is not susceptible of oxidation, such as gold or platina, gas is then extricated from both wires, and, by a simple contrivance, may be separately collected. The apparatus for this purpose is shown by fig. 76, where the wires *p* and *n*, instead of being introduced into a straight tube, are inclosed in a syphon, and terminate before they reach the end, in which a small hole is to be ground. When a stream of galvanic electricity is made to act upon water thus confined, oxygen gas is found, at the close of the experiment, in the leg connected with the positive end of the battery, and hydrogen gas in that connected with the negative end; and in the proportions which, by their union, compose water. At an early period of the inquiry, it was found, however, by Mr. Cruickshank, that the water surrounding the positive wire became impregnated with a little acid; and that around the negative wire with a little alkali. If instead of water we employ a metallic solution, the metal is revived round the negative wire *n*, and no hydrogen gas is liberated.

The gases constituting water, it was afterwards discovered by Sir H. Davy, may be separately produced from two quantities of water, not immediately in contact with each other. The fact is of peculiar importance, from its resemblance to other more recent ones, which have led that distinguished philosopher to the discovery of the general laws of electrochemical action. Two glass tubes (*p* and *n*, pl. ix. fig. 79), about one third of an inch diameter and four inches long, having each a piece of gold wire sealed hermetically into one end and the other end open, were filled with distilled water, and placed inverted in separate glasses filled, also, with that fluid. The two glasses, *a* and *b*, were made to communicate, either by dipping the fingers of the right hand into one glass, and those of the left into the other, or by interposing fresh animal muscle, or a living vegetable, or even moistened thread,

as shown at *c*. The gold wires, projecting from the sealed ends of these tubes, were then connected, the one with the positive, the other with the negative end of the trough. Gas was immediately evolved from both wires. At the close of the experiment, in the tube *p* oxygen gas was found; in the negative tube *n* hydrogen. The proportions by measure were, as nearly as possible, those which result from the decomposition of water, *viz.* two of hydrogen to one of oxygen gas.\* Now if these gases arose, as they necessarily must, from the decomposition of the same portion of water, that portion of water must have been contained either in the tube *p* or in the tube *n*. In the former case, the hydrogen gas, found after the process in *n*, must have passed invisibly from *p* to *n*; through the intermediate substance *c*. Or, if the water was decomposed in *n*, then the reverse process must have happened with respect to the oxygen; and it must have been transmitted, in a like imperceptible manner, from *n* to *p*. Facts of this kind, evincing the transference of the elements of a combination, to a considerable distance, through intervening substances, and in a form that escapes the cognizance of our senses, however astonishing, it will appear from the sequel, are sufficiently numerous and well established. It appears, also, from the experiments of Mr. Porrett, that water may be forced, contrary to its gravity, through the compact substance of a bladder, from the positive to the negative wire of a galvanic battery, composed of plates only  $1\frac{1}{4}$  inch square.†

Different chemical compounds require, for the disunion of their elements, galvanic arrangements of various powers and intensities. The decomposition of water is easily effected by a series of fifty pairs of plates, each one or two inches square. But for those which remain to be described, instruments of much greater power are necessary.

The apparatus, employed in the masterly experiments of Sir H. Davy, which have laid the groundwork of this new science, was extremely simple. In cases, where liquid substances were operated upon, he employed occasionally the agate cups *p* and *n*, fig. 80, each of which was capable of

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\* N'cholson's Journal, 4to. iv. 276.

† Thomson's Annals, viii. 74



holding about sixty grains of water. They were connected together, as shown in the figure at *a*, by the fibres of a peculiar flexible mineral called amianthus; and into each was inserted a platina wire, the bent extremity of which is seen, in each figure, projecting above the cup. When the vessels were in actual use, the wire of *p* was connected with the zinc or positive end of a powerful galvanic series; and that of *n*, with the copper or negative extremity. For the agate cups two hollow gold cones were occasionally substituted (*p* and *n*, fig. 81,) the wire projecting from *p* being connected with the positive, and that from *n* with the negative end of a trough or series of troughs. Solid bodies were submitted to the galvanic influence, either by immersing small pieces of them in the gold cones; or, at other times, by making the cups themselves of the substance intended to be decomposed. Or if it was desirable to preserve them from contact with water, they were laid on a small insulated dish of platina, with the inferior surface of which, immediately under the substance used, a wire from one end of the battery was connected, while the substance itself was made to communicate by another wire, with the opposite extremity of the apparatus.

When the gold cones were both filled with a solution of sulphate of potash (a salt composed of potash and sulphuric acid,) after exposure, during a sufficient time, to a powerful galvanic arrangement, pure potash was found in the negative cone *n*, and sulphuric acid in the positive cone *p*. The decomposition was quite complete; for the liquid in *n* contained no acid, and that in *p* no alkali.

The experiment was repeated with several other neutral salts;\* and with the invariable result, that the acid collected in the positive cone, and the alkali in the negative one. Strong solutions, or those in which the salt bore a considerable proportion to the water, were more rapidly acted upon than weak ones. Metallic salts were, also, decomposed. The acid appeared, as before, in the positive cone, and the metal

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\* Minute directions for exhibiting the transfer of acid and alkali, by means of a power not exceeding thirty pairs of two inch plates, are given by Mr. Singer. (Nicholson's Journal, xxiv. 178.)

was deposited, sometimes with a little oxide, in the negative one.

Salts, which are either insoluble, or very sparingly soluble, in water, had their elements disunited in the following manner. Cups were constructed of them, precisely resembling the gold cones, which, as the salts were hard and compact in their texture, was easily effected. These, after being filled with water, were connected, by platina wires, with the opposite ends of a galvanic battery, the vessels themselves communicating, as before, by means of moistened amianthus. At the conclusion of the experiment, sulphuric acid (when the cups were made of sulphate of lime) was found in the positive cup, and lime water in the negative one. Sulphate of strontites, fluoate of lime, and sulphate of barytes, were decomposed, though less easily, by the same expedient. In all these cases the acid element was found at the positive side, and the earthy one at the negative side, of the arrangement.

These facts evidently point out a transference of the elements of combinations from one electrified vessel or surface to another differently electrified. But the principle is made much more apparent by a little variation of the experiment. Thus, if solution of sulphate of potash be electrified in the positive cone  $p$ , water alone being contained in  $n$ , after a sufficient continuance of the electrical action  $p$  will be found to contain diluted sulphuric acid; and the potash will be discovered in the water of  $n$ . The alkali must necessarily, therefore, have passed, in an imperceptible form, along the connecting amianthus from the vessel  $p$  to the vessel  $n$ . Reversing the experiment, and filling  $n$  with solution of sulphate of potash, the alkali remains in this cone, and the acid is transferred to the opposite side  $p$ . In one experiment, in which nitrate of silver was placed in the positive cup, and pure water in the negative one, the whole of the connecting amianthus was covered with revived silver.

In the farther prosecution of the inquiry, Sir H. Davy succeeded in discovering a still more extraordinary series of facts. When an intermediate vessel ( $i$ , fig. 82) was placed between the positive and negative cups  $p$  and  $n$ , and was connected with both of them by moistened amianthus, it was

found that acids may actually be made to pass from *n* to *p*, through the intermediate solution in *i*, without combining with it. Thus, solution of sulphate of potash being put into the negative cup *n*, solution of pure ammonia into *i*, and pure water into *p*, in half an hour sulphuric acid was found in the water of the positive cup, though to have reached this it must have been transferred from *n* through the intermediate solution of ammonia. Muriatic acid, also, from muriate of soda, and nitric acid from nitrate of potash, were transferred from the negative to the positive side through an interposed solution of alkali. And contrariwise, alkalies and metallic oxides were transmitted from the positive to the negative side, through intervening solutions of acids.

It is necessary, however, that the solution, contained in the intermediate vessel *i*, should not be capable of forming an insoluble compound with the substance intended to be transmitted through it. Thus sulphuric acid, in its passage from sulphate of potash in the negative cup through the vessel *i* containing a solution of pure barytes, is detained by the barytes, and falls down in the state of an insoluble compound with that earth.

Bodies, the composition of which is considerably more complicated, are, also, decomposed by galvanic electricity. Thus from certain minerals, containing acid and alkaline matter in only very minute proportion, these ingredients are separately developed. Basalt, for example (a kind of stone which, in 100 grains, contains only  $3\frac{1}{4}$  grains of soda and half a grain of muriatic acid), gave, at the end of ten hours, evident traces of alkali round the negative, and of acid round the positive wire. A slip of glass, also, negatively electrified in one of the gold cones, had soda detached from it, and sustained a loss of weight.

It may now be understood, why, by the agency of galvanism on water, alkali appears at the negative and acid at the positive wire. The fact was, for some time, not a little perplexing to Sir H. Davy; till, at length, he ascertained that all water, however carefully distilled, contains neutral salts in a state of solution. From these impurities, the alkaline and acid elements are separated, agreeably to a law, which has

already been explained. In the same way, also, the muriatic acid and alkali are accounted for, which some chemists have obtained by galvanizing what was before considered as pure water; a fact which has been urged in proof of the synthetical production of both those bodies. Absolutely pure water, it has been demonstrated by Sir H. Davy, yields nothing but hydrogen and oxygen gases.

All the effects of galvanic arrangements, in producing chemical decompositions, it has been found, may be obtained by ordinary electricity. Its adaptation to this purpose was first successfully attempted by Dr. Wollaston.\* The apparatus, which he employed, was similar to that already represented (fig. 77, *a*), excepting that the wires, instead of being exposed to the fluid contained in the tube, throughout their whole length, were covered with wax, and the points only were laid bare. Or (which was found to answer still better) the wires were inclosed in capillary glass tubes, which were sealed at their extremities, and then ground away, till the points alone were exposed. The conducting wires, thus arranged, were then introduced into a tube, or other vessel containing the liquid to be operated on, and were connected, the one with the positive, the other with the negative, conductor of an electrical machine, disposed for positive and negative electricity.† When solution of sulphate of copper was thus electrized, the metal was revived round the negative pole. On reversing the apparatus, the copper was re-dissolved, and appeared again at the other wire, now rendered negative.

When gold wires, from  $\frac{1}{100}$  to  $\frac{1}{1300}$  of an inch in diameter, thus inclosed, were made to transmit electricity, a succession of sparks afforded a current of gas from water. When a solution of gold in nitro-muriatic acid was passed through a capillary tube; the tube then heated to drive off the acid; and afterwards melted and drawn out, it was found that the mere current of electricity, without sparks, evolved gas from water.

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\* Philosophical Transactions, 1801.

† See Cuthbertson's Practical Electricity.

Sir H. Davy has since proved that by a similar apparatus, solution of sulphate of potash is decomposed, potash appearing at the negative, and sulphuric acid at the positive pole.\*

  
SECTION IV.*Theory of the Changes produced by Galvanic Electricity.*

A FACT of considerable importance, in explaining the phenomena that form the subject of the last section, was discovered several years ago by Mr. Bennett, and has since been confirmed by the experiments of Volta and Davy. Different bodies, it is found, acquire, when brought into contact either by their whole surfaces or by a single point, different states with respect to their quantities of electricity. The best method of performing the experiment is to take two discs or plates, the one of copper, the other of zinc, each about four inches diameter, and furnished with an insulating glass handle; to apply them for an instant to each other by their flat faces; and afterwards, to bring them separately into contact with the insulated plate of the condensing electrometer. The instrument indicates, by the divergence of its gold leaves, the kind of electricity acquired by each of the plates, which in the zinc plate is shown to be positive, and in the copper plate negative.†

It had been established, also, by Sir H. Davy, in 1801, that when a galvanic arrangement of *the second kind* is constructed, by alternating metallic plates with strata of different fluids, alkaline solutions always receive electricity *from* the metal, and acids on the contrary transmit it *to* the metal. When an arrangement, for example, is made of water, tin, and solution of potash, the current of electricity is from the tin to the alkali. But, in an arrangement of nitric acid, tin, and water, the circulation of electricity is from the acid to

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\* Philosophical Transactions, 1806.

† Volta, in Nicholson's Journal, 8vo. i. 136. Wilkinson, ii. 40, 50, 131. Cuthbertson, 267.

the tin, If then the alkali, after having acquired electricity from the metal, could be suddenly separated from the combination, there can be no doubt that it would be found in a positive state. For the contrary reason, the acid, having given electricity to the metal, must, if it could be detached, be found negative.

Still more satisfactory evidence has been since obtained of the electrical state of the acids and alkalies, by examining what kind of electricity they impart to an insulated metallic plate. Various dry acids, being touched on an extensive surface by a plate of copper insulated by a glass handle, the copper was found after contact to have become positively electrified, and the acid negatively. On the contrary, making the experiments with dry earths in a similar manner, the metal became negative. The alkalies gave less distinct results, owing to their attraction for moisture. Bodies, moreover, possessing opposite electrical energies towards one and the same body, are found to possess them with regard to each other. Thus when lime and oxalic acid were brought into contact, the earth was found to be positive, and the acid negative. Sulphur appears to be in the positive state. Oxygen, judging from those compounds in which it is loosely combined, is negative; and hydrogen, by the same test, positive.

Now, if the common laws of electrical attraction and repulsion operate, as there is every reason to believe they must, among bodies so constituted, it will follow that hydrogen, the alkalies, metals, and oxides, being positively electrified, will be repelled by surfaces which are in the same state of electricity as themselves, and will be attracted by surfaces that are negatively electrified. And, contrariwise, oxygen, and the acids (in consequence of the oxygen they contain), being in a negative state, will be attracted by positive surfaces and repelled by negative ones.

To apply this theory to the simplest possible case, the decomposition of water, the hydrogen of this compound, being itself positively electrified, is repelled by the positive wire and attracted by the negative one; while, on the contrary, oxygen, being negative, is repelled by the negative wire, and attracted by the positive one. The flame of a candle, which

consists chiefly of ignited charcoal, when placed between a positive and negative surface, bends towards the latter; but the flame of phosphorus, consisting chiefly of acid matter, when similarly placed, takes a direction towards the positive surface. In the case of neutral salts, the negative acid is attracted by the positive wire; and the positively electrified alkali by the negative wire.

Thus then a power has been discovered, superior in its energy to chemical affinity, and capable either of counteracting it, or of modifying it according to circumstances. The chemical attraction between two bodies may be destroyed, by giving one of them an electrical state opposite to its natural one; or the tendency to union may be increased, by exalting the natural electrical energies.

All bodies, indeed, that combine chemically, so far as they have hitherto been examined, have been found to possess opposite states of electricity. Thus copper and zinc are in opposite states to each other; so are gold and mercury; sulphur and metals, acids and alkalies. By bringing two bodies into the same electrical state, which were before capable of union, we destroy their tendency to combination. Thus zinc or iron, when negatively electrified, will not unite with oxygen. Even after combination, it is thought by Sir H. Davy not improbable, that bodies may still retain their peculiar states of electricity. If oxygen prevail, in any compound, over the combustible or positive base, the compound is negative, as in certain metallic oxides. But the combustible ingredient may be in such proportion, as to predominate, and to give to the compound a positive energy. When precise neutralization is attained, bodies that had before exhibited electrical effects are deprived of this property.

It is an interesting question, but one which can scarcely be determined in the present state of the science, whether the power of electrical attraction and repulsion be identical, as Sir H. Davy has suggested, with chemical affinity; or whether it may not rather be considered, like caloric, as a distinct force, which only modifies that of chemical attraction. On the former hypothesis, two bodies, which are naturally in opposite electrical states, may have these states sufficiently exalted, to

give them an attractive force superior to the cohesive affinity opposed to their union; and a combination will take place, which will be more or less energetic, as the opposed forces are more or less equally balanced. Again, when two bodies, repellent of each other, act upon a third with different degrees of the same electrical energy, the combination will be determined by the degree. Or, if bodies, having different degrees of the same electrical energy with respect to a third, have likewise different energies with respect to each other, there may be such a balance of attracting and repelling forces as to produce a triple compound.

This hypothesis, it is remarked by Sir H. Davy, agrees extremely well with the influence of *mass*, which has been so well illustrated by Berthollet; for many particles, acting feebly, may be equal in effect to fewer acting more powerfully. Nor is it at all contradictory to the observed influence of caloric over chemical union; for an increase of temperature, while it gives greater freedom of motion to the particles of bodies, exalts all their electrical energies. This Sir H. Davy ascertained with respect to an insulated plate of copper and another of sulphur, when heated below  $212^{\circ}$  Fahr.; and at a still higher temperature these bodies, as is well known, combine with the extrication of heat and light, the usual accompaniments of intense chemical action.

On the supposition that electricity is a force, which only modifies the action of chemical affinity, we may regard it, when it promotes combination, as producing this effect by counteracting cohesive attraction. When it impedes combinations, or destroys those which are already formed, it probably acts as a force co-operating with elasticity.



## SECTION V.

### *Theory of the Action of the Galvanic Pile.*

Two theories have been framed to account for the phenomena of the Galvanic Pile, and of all similar arrangements.



The first, originating with Volta, was suggested by the fact which may be considered, indeed, as fundamental to it—that electricity is excited by the mere contact of different metals. When a plate of copper and another of zinc are made to touch by their flat surfaces, as was stated in the last section, the zinc, after separation, exhibits positive electricity, and the copper negative. It is natural, therefore, to conclude that a certain quantity of electricity has moved from the copper to the zinc. On trying other metals, Volta found that similar phenomena take place; and by a series of experiments he was led to arrange their powers in the following order, it being understood that the first gives up its electricity to the second; the second to the third; the third to the fourth, and so on.

Silver.

Copper.

Iron.

Tin.

Lead.

Zinc.

The metals, then, have been denominated by Volta, from this property, *motors* of electricity; and the process, which takes place, *electro-motion*, a term since sanctioned by the adoption of it by Sir H. Davy.

It is on this transference of electricity from one body to another by simple contact, that Volta explains the action of the instrument discovered by himself, and of all similar arrangements. The interposed fluids, on his hypothesis, have no effect as chemical agents in producing the phenomena, and act entirely as conductors of electricity. Without disputing, however, the accuracy or value of the facts which suggested his theory, it is sufficient for its refutation that it is irreconcilable with other phenomena; and especially with the observation, that the chemical agency of the liquids, on the more oxidizable metal of galvanic arrangements, is essential to their sustained activity. It has been proved, indeed, that the phenomena begin and terminate with the oxidation; and that the energy of the pile bears a pretty accurate proportion to the

rapidity of the process. Hence it seems, on first view, an obvious inference, that the oxidation of the metal is the primary cause of the evolution of electricity in galvanic arrangements. It has been proved, however, that it is not necessary to the excitement of electricity, that the amalgam should be oxidated; for the machine continues to act, when inclosed in hydrogen gas or carbonic acid; and the electric column of M. de Luc is composed of dry substances. Even in this instrument, the oxidation of the metals appears to be essential to its activity, for when the column is hermetically confined in a given portion of air, the phenomena cease in time, in consequence of the loss of its oxygen.

But though the chemical agency of the fluids which are employed is now admitted, on all hands, to be essential to the excitement of this kind of electricity, yet it is by no means universally agreed that we are to consider it as the first in the order of phenomena. It has been suggested by Sir H. Davy, as a correction of the theory of Volta, that the electro-motion, occasioned by the contact of metals, is the primary cause of the chemical changes; and that these changes are in no other way efficient, than as they restore the electric equilibrium. To explain this, let us suppose that in any three pairs of plates of a galvanic trough the zinc plates  $z$  1,  $z$  2,  $z$  3 (fig. 78), are in the state of positive, and the copper plates  $c$  1,  $c$  2,  $c$  3, in that of negative electricity. The liquid, in any cell after the first, will be in contact, on the one side, with positively electrified zinc, and on the other with negatively electrified copper. And if the elements composing the fluid be themselves in different states of electricity, the negatively electrified element will be attracted by the zinc, and the positively electrified element by the copper. Thus when solution of muriate of soda in water is the fluid, the oxygen and the acid will pass to the zinc or positive plate, and the alkali to the copper one; while the hydrogen, having no affinity for copper, escapes. The electric equilibrium will be restored, but only for a moment; for, as the interposed fluid is but a very imperfect conductor of electricity, the zinc and copper plates will, by their electromotive power, again assume their states of opposite electricity; and these changes will go on, as long as

any muriate of soda remains undecomposed. In a Voltaic arrangement, therefore, the electrical energies of the metals with respect to each other, or to the substances dissolved in water, are the causes disturbing the equilibrium; and the chemical changes are the causes that restore it.

No theory of the galvanic pile, however, can be considered as complete, that does not account for the accumulation of electricity at the zinc end of the apparatus. On the theory that the oxidation of the zinc is the source of the evolved electricity, the fact has been ingeniously explained by Dr. Bostock. He takes it for granted that the electric fluid has an affinity for hydrogen; and supposes that the electricity, evolved at the surface of the first zinc plate, is carried, united to hydrogen, through the fluid of the cell to the opposite copper plate. Here the hydrogen and electricity separate; the former flies off in the state of gas, and the latter passes onwards to the next zinc plate. Being in some degree accumulated in this plate, it is disengaged by the action of the fluid in a more concentrated state than before. And in the same manner, by multiplying the number of pairs, it may be made to exist, in the zinc end of the pile, in any assignable degree of intensity.

On this theory, the electricity evolved is actually *generated* by the chemical action of the interposed fluids on every zinc plate of the series; and its accumulation is the aggregate of what is thus evolved. The concentration, which takes place at the zinc end of the arrangement, admits, however, of being explained by the hypothesis of Volta, especially as modified by Sir H. Davy. Taking the first cell as an example, the fluid interposed between the positive zinc plate  $\alpha$  1, fig. 78, and negative copper plate  $c$  2, being itself a conductor of electricity, must in time produce an equilibrium between these two plates; but this can only be done by the passage of a certain quantity of electricity across the fluid. The absolute quantity of electricity will, therefore, be diminished in the first pair, and increased in the second. In like manner, the second zinc plate will give up part of its electricity to the third copper plate, and the second pair of plates will be de-

prived of part of its electricity. The electricity, thus lost by the second pair, it will regain from the first pair of plates. By multiplying, in this way, the number of plates, every successive pair, as we advance in the series, has a tendency to diminish the quantity of electricity in the first, and to have its own state of electricity proportionally exalted.

When a communication is made between two extremities of a series, for example between  $z^3$  or its contiguous cell, and  $c^1$ , the opposite electricities tend to an equilibrium. The third pair gives up a share of its electricity to the first; and the intermediate pair, being placed between equal forces, remains in equilibrio. Hence, in every galvanic arrangement, there is a pair of plates at the centre, which is in its natural state of electricity. The effect of such a communication must necessarily be to reduce the pile to a state of inactivity, if there did not still exist some cause sufficient to destroy the equilibrium. On the hypothesis of Volta, this can be nothing else than the property of electro-motion in the metals, which originally produced its disturbance.

Such are the hypotheses that have been framed to explain the phenomena of the Voltaic pile. In the present state of the science, neither of them is entitled to be received as altogether satisfactory; and I have stated them rather with the view of exciting them of satisfying inquiry.\* On the theory of galvanic electricity, it only remains to point out its difference from the electricity developed by ordinary processes; and to explain the different effects, which are produced by varying the size of the plates in galvanic arrangements.

Though the identity of common and galvanic electricity appears to be sufficiently established, yet in some of their phenomena, which have already been described, there is a con-

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\* The reader, who wishes to pursue the subject, may consult an essay by the author, in Nicholson's Journal, xxxv. 259; M. De Luc's papers, xxxii. 271, and xxxvi. 97; Mr. Singer on the Electrical Column, xxxvi. 378, and his work on Galvanic Electricity; Dr. Bostock's Essay in Thomson's Annals, iii. 32; Sir H. Davy's chapter on Electrical Attraction and Repulsion, in his Elements of Chem. Philos. p. 125; and the 1st. vol. of Gay Lussac and Thenard's Recherches.

siderable difference. To explain these, it was long ago suggested by Mr. Nicholson,\* that the electricity, excited by the common machine, is developed in much smaller quantity, but in a higher state of concentration or intensity than the electricity of galvanism. Hence, its velocity is much more rapid; and hence it readily passes through plates of air and other non-conductors, that are scarcely permeable by galvanic electricity. By virtue of the same property it disperses the metals in the form of smoke; while the utmost effect of a Voltaic arrangement is to melt them into globules. By doubling the quantity of galvanic electricity, also, we ignite only a double length of metallic wire, and the ignition is more permanent; but the intensity of common electricity is such, that by doubling its quantity we ignite four times the length of wire, and the effect is little more than momentary.†

The comparative quantities of electricity evolved by the common machine and by a Voltaic apparatus, have been made a subject of calculation by Mr. Nicholson. A pile consisting of 100 half crowns, with the same number of pieces of zinc, produced, he found, 200 times more electricity than could be obtained, in an equal time, from a 24 inch plate machine in constant action. Van Marum has, also, observed that a single contact of a Leyden jar or battery with a Voltaic pile charges it to the same degree, as six contacts with the prime conductor of a powerful machine.

It might naturally be expected that a proportion would be observed between the quantity of surface composing galvanic arrangements, and their power of action; and such, with some limitation, is the fact. With plates of the same size, the effect, generally speaking, is proportional to the number. But by enlarging the size, without increasing the number, neither the shock nor the power of decomposing water and other imperfect conductors, is proportionally increased. A remarkable proof of this is, that Mr. Children's great battery of 20 double plates, 4 feet by 2, had no more effect on the human body, or in decomposing water, than a battery con-

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\* See his Journal, 4to. iv. 244.

† Cuthbertson, p. 278.

taining the same number of small plates. On the contrary, to obtain a great increase of effect in the combustion of metals, it is necessary to enlarge considerably the size of the plates. Thus 100 plates of four inches square produce, in this way, an incomparably greater effect, than the same surface divided into four times the number.

The effect of multiplying the number of plates, it has already been observed, is, that we obtain electricity of a higher intensity, and it was supposed by Volta\* that the proportion is, as nearly as can be judged, an arithmetical one. If, for example, we have a certain intensity with 20 pairs, it should be doubled by 40, trebled by 60, and so on. It has been shown, however, by Sir H. Davy,† that by increasing the number of plates, the quantities of gas, evolved from water, were nearly as the squares of the numbers. By a sufficient increase, the most astonishing effects may be produced. Thus the combination belonging to the Royal Institution, which contains 2000 double plates, each having a surface of 32 square inches, when in action, melts platinum, as easily as wax is melted by a candle, and fuses quartz, the sapphire, lime, and magnesia. By enlarging the size, without increasing the number, it has also been shown that we gain, not in intensity, which remains exactly the same, but in quantity. Now, for the combustion of metals, what we principally want is a large quantity of electricity; for as they are perfect conductors, it finds a ready passage through them even when of low intensity. On the contrary, to find its way through fluids and other imperfect conductors, it must be evolved in a high state of concentration. The facts, therefore, accord sufficiently well with the explanation, to entitle it to be received as a probable hypothesis.

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\* Nicholson's Journal, 8vo. i. 139.

† Elements of Chem. Philos. p. 155.

## SECTION VI.

*Of Electro-Magnetic Phenomena.*

ALL the effects of galvanic arrangements, that have hitherto been described, are produced in bodies when interposed between the extremities of conductors proceeding from the positive and negative poles; in other words, so placed that the galvanic current is *imperfectly* continued through the body intended to be acted upon. It was not known that the electric current, passing *uninterruptedly* through a wire connecting the two ends of a galvanic battery, is capable of being manifested by any effect, till Professor Oersted, of Copenhagen, in the winter of 1819, discovered an unequivocal test of its passage in its effect on the magnetic needle. The opposite poles of a battery of sufficient magnitude, in full action, were joined by a metallic wire, which, for shortness, he calls the *uniting conductor*, or *uniting wire*. This wire was either placed horizontally, (see pl. iv. fig. 37.) or bent in any other direction required by the nature of the experiment. When the wire was placed horizontally *over*, and parallel to a magnetic needle properly suspended, and at a distance not exceeding three quarters of an inch, the needle was moved, and the end of it next to the negative pole of the battery turned westwards. The circumstances of the experiment remaining in every respect the same, except that the uniting wire was placed *under* the needle instead of over it, the declination of the needle was in an opposite direction; for the pole next the negative end of the battery now turned eastwards. Again, when the connecting wire and needle were situated in the same horizontal plane, no declination took place, either to the east or west, but an *inclination*, or vertical dip of the needle was observed. When the uniting wire was west of the needle, the pole next to the negative end of the battery was depressed; when the wire was to the east, the same pole was elevated.

When the uniting wire was situated perpendicularly to the plane of the magnetic meridian, the needle, whether above

or below the wire, remained at rest, unless the pole were very near the wire. In that case, the pole was *elevated*, if the negative electricity entered from the west side; and *depressed*, if from the east. M. Von Buch has since, however, shown that this state of rest does not continue in two of the four positions of the wire, provided a sufficient galvanic power be employed in the experiment. (Ann. of Phil. N.S. ii. 285.)

When the uniting wire was perpendicularly opposite to the north pole of the suspended needle, and the upper extremity of the wire connected with the *negative* end of the battery, the pole, when brought near the wire, moved towards the east. But when the wire was opposite to a point between the pole and the middle of the needle, the pole moved westwards. When the upper end of the wire was made to receive *positive* electricity, the phenomena were reversed.

The amount of these effects diminished with the decreasing power of the battery, and with the distance of the needle from the uniting wire. This wire, it was found, may consist of almost any metal; nor does it lose its effect though interrupted by a column of water, provided the column does not extend to several inches in length. It is remarkable, also, contrary to what is observed in any other effect of electricity or galvanism, that the influence of the uniting wire passes to the needle through plates of glass, metal, or wood, the disc of an electrophorus, or a stone-ware vessel of water; nor does the sudden interposition of any of these bodies destroy or sensibly diminish the effect. On needles of brass, glass, or gum lac, no effect whatever is produced.

The common electrometer indicates the tension or intensity of electricity; but, till the discovery of M. Oersted, we had no instrument to show the direction of its current. The effect on the needle depends, indeed, entirely on the current. So long as this current is interrupted, no effect is produced on the needle; but the moment it is restored, the north pole of the needle is turned to the left of the observer, supposing him to have his face directed towards that pole. This may be more briefly expressed by saying, that the north pole is carried to the left of the current which acts upon the needle. We



thus acquire a *galvanometer*, capable of pointing out the direction of the electric current under all circumstances.

By an instrument nicely constructed on this principle, M. Ampère ascertained that the current in the voltaic battery itself, from the negative to the positive extremity, has the same influence on the needle, as that current, which, in the uniting wire, goes on the contrary from the positive to the negative pole. This is best shown by two needles, the one placed upon the pile, the other above or under the conductor. In each, the north pole of the needle will be seen turned to the left of the current near which it is placed: the two needles are both carried to the same side, and are nearly parallel, when one is above the pile, and the other beneath the conductor.

When two rectilinear portions of two conducting wires, joining the extremities of two voltaic piles, are so disposed that the one is fixed and the other suspended so as to be moveable, the latter will approach the former if the currents be in the same sense, and will be repelled when the currents are in opposite directions. In common electrical attractions and repulsions, electricities of the same name are mutually repulsive, and opposite electricities attract each other. But in the attractions and repulsions of electric currents, it is precisely the reverse, the repulsion taking place only when the wires are so situated that the currents are in opposite directions. The attractions and repulsions of these currents, unlike the mutual action of bodies electrized in the common way, takes place equally *in vacuo* as in air.

The discovery of M. Oersted was limited to the action of the electric current on needles previously magnetized. But it was afterwards, and about the same time, ascertained both by Sir H. Davy and M. Arago, that magnetism may be developed, in steel not previously possessing it, by being placed in the electric current, and may even be excited in the uniting wire itself. Both philosophers ascertained, independently of each other, that the uniting wire, becoming a magnet, attracts iron filings, and collects sufficient to acquire the diameter of a common quill. The moment the connexion is broken, all the filings drop off;\* and the attraction diminishes also

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\* M. Arago afterwards determined that the wire retains its magnetism for a few instants after the connexion is broken, but that it soon ceases.

with the decaying energy of the pile. Filings of brass or copper, or wood shavings, are not attracted at all.

The communication of magnetic properties to a steel needle was effected, by Sir H. Davy and M. Arago, in different ways. The former observed that steel needles, placed upon the connecting wire, became magnetic; those parallel to the wire acted like the wire itself; those placed across it each acquired two poles. Such as were placed *under* the wire, the positive end of the battery being east, had north poles on the south of the wire, and south poles to the north. The needles *above* were in the opposite direction, and this was constantly the case, whatever might be the inclination of the needle to the wire. On breaking the connexion, the steel needles, placed *across* the uniting wire, retained their magnetism, while those placed *parallel* to it lost it at the moment of disunion. Contact with the uniting wire was not found necessary, for the effect was produced though thick glass intervened. Increasing the size of the plates of the battery increased the magnetic effect of the connecting wires; thus the wire uniting the poles of a battery of 60 pairs of plates did not take up half so much filings, as when the battery was arranged so as to form 30 pairs of twice the size.

Similar effects were produced in Sir H. Davy's experiments by the electricity excited by a common machine. A battery of 17 square feet, discharged through a silver wire 1-20th of an inch diameter, rendered bars of steel, two inches long and from 1-10th to 1-20th thick, so magnetic as to lift up pieces of steel wire and needles; and the effect was communicated to needles at the distance of five inches from the wire, even with the intervention of water or of thick plates of glass or metal. Various other important facts respecting the communication of magnetism are described in the paper of the same author, published in the Philosophical Transactions for 1821, all tending to establish the conclusion that magnetism is produced whenever concentrated electricity is passed through space.

On the suggestion of M. Ampère, M. Arago communicated magnetism to the needle in a different manner. A copper wire, by being rolled round a solid rod, was twisted into a spiral so as to form a *helix*. It was easy, by passing the wire

round the rod, in one direction or the other, to form a *dextrorsal* helix, proceeding from the right hand towards the left, as in the tendrils of many plants; or a *sinistrorsal*, or left helix, proceeding downwards from the left hand to the right above the axis. Into the cavity of a spiral thus formed, connecting the two poles of a battery, a steel needle wrapped in paper was introduced; and in order to exclude all influence of the magnetism of the earth, the conchoidal part of the wire was kept constantly perpendicular to the magnetic meridian. In a few minutes the needle had acquired a sufficiently strong dose of magnetism; and the position of the north and south poles exactly agreed with Mr. Ampère's notion, that the electric current traverses the connecting wire in a direction from the zinc extremity of the pile to the copper extremity.

In another experiment, using one copper wire, two symmetrical spirals were formed, each nearly two inches long, and separated by a rectilinear piece of the same metal, the spirals of the two being turned in contrary senses. Within each of these spirals a needle, properly guarded, was included, and the connexion made between the two ends of a galvanic battery. The result was that both the needles were magnetized, but in exactly opposite senses. When a right helix had been used, that end of the needle, which had been placed towards the negative pole of the battery, pointed to the north, and the other end to the south; but with a left helix, that end of the needle which had been nearest the positive pole of the battery pointed north, and the other end south. In one case, when the connecting wire had been twisted into three consecutive helices, the middle one being different from the other two, a single piece of steel wire, sufficiently long to pass through all three, being inclosed in a glass tube, was placed within them. On being removed, it was found to have acquired six poles: first a north pole, a little further on a south pole, then another south pole, a north pole, another north pole, and at the further end a south pole.

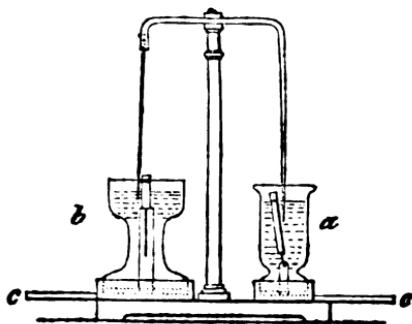
The electricity of a common machine, it was afterwards ascertained by the Chev. Yelin, when passed along a helix,

either in simple electrical sparks, or discharges from a battery, has the effect of rendering an included needle magnetic. In varying these experiments, M. Bockman ascertained that no modification of the effect was produced by altering the diameter of the helix from half an inch to 13 inches. With a helix of 34 inches diameter, and a coated surface of 300 square inches, much less magnetism was, however, imparted; and with one of 84 inches it was scarcely perceptible. It was found that a needle outside of the helix was magnetized as much as one within; that after being once fully magnetised, a continuation of the discharges diminished its power; and that five jars, each of 300 square inches, did not produce, by repeated discharges, much more effect than one of them.

Any wire, through which a current of electricity is passing, has a tendency to revolve round a magnetic pole, in a plane perpendicular to the current; and that without any reference to the axis of the magnet, the pole of which is used. Also a magnetic pole has a tendency to revolve round such a wire.

Suppose the wire perpendicular, its upper end positive, or attached to the positive pole of a voltaic battery, and its lower end negative; and let the centre of a watch dial represent the magnetic pole: if it be a north pole, the wire will rotate round it in the direction that the watch hands move; if it be a south pole, the motion will be in the opposite direction. From these two, the motions which would take place if the wire were inverted, or the pole changed or made to move, may be readily ascertained, since the relation now pointed out remains constant.

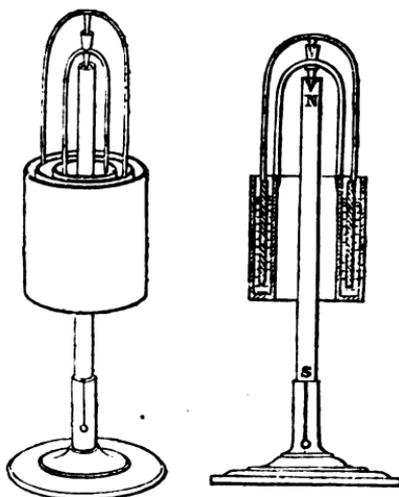
The apparatus in the sketch is the ingenious invention of Mr. Faraday, and is intended to illustrate these motions. The central pillar supports a piece of thick copper wire, which, on the one side, dips into the mercury contained in a small



glass cup, *a*. To a pin at the bottom of this cup a small cylindrical magnet is attached by a piece of thread, so that one pole shall rise a little above the surface of the mercury, and be at liberty to move round the wire. The bottom of the cup is perforated, and has a copper pin passing through it, which, touching the mercury in the inside, is also in contact with the wire that proceeds outwards on that side the instrument. On the other side of the instrument, *b*, the thick copper wire, soon after turning down, terminates, but a thinner piece of wire forms a communication between it and the mercury in the cup beneath. As freedom of motion is required in this wire, it is made to communicate with the former by a ball and socket joint, the ball being held in the socket by a piece of thread; or else the ends are bent into hooks, and the one then hooked on to the other. As good metallic contact is required, the parts should be amalgamated, and a small drop of mercury placed between them, and the lower ends of the wire should also be amalgamated. Beneath the hanging wire a small circular magnet is fixed in the socket of the cup, *b*, so that one of its poles is a little above the mercury. As in the former cup, a metallic connexion is made through the bottom from the mercury to the external wire.

If now the poles of a battery be connected with the horizontal external wires *cc*, the current of electricity will be through the mercury and the horizontal wire on the pillar which connects them, and it will now be found that the moveable part of the wire will rotate round the magnetic pole in the one cup, *b*, and the magnetic pole round the fixed wire in the other cup, *a*, in the direction before mentioned.

By using a delicate apparatus, the magnetic pole of the earth may be made to put the wire in motion. The rotation then takes place round a line parallel to the dipping needle: hence the rotating wire must always be inclined, so that the solid it describes in revolving, if a cone, and not a mere circle, should include a line parallel to the dip which passes through its apex.

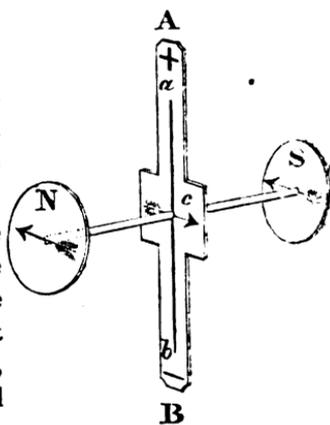


Another ingenious contrivance for illustrating the rotatory motion of the wire round the pole of a magnet, has been invented by M. Ampère, and has the advantage of comprising within itself the voltaic combination which is employed. It consists of a cylinder of copper about 2 inches high, and  $1\frac{1}{4}$  inch internal diameter, within which is a smaller cylinder about 1 inch diameter. (See the wood cut.) The two cylinders are fixed together by a bottom, having a hole in its centre the size of the smaller cylinder, leaving a circular cell which may be filled with acid. A piece of strong copper wire is fastened across the top of the inner cylinder, and from the middle of it rises at a right angle a piece of copper wire, supporting a very small metal cup containing a few globules of mercury. A cylinder of zinc, open at each end, and about  $1\frac{1}{4}$  inch diameter, completes the voltaic combination. To the latter cylinder a wire, bent like an inverted U, is soldered at opposite sides; and in the bend of this wire a metallic point is fixed, which, when fixed in the little cup of mercury, suspends the zinc cylinder in the cell, and allows it a free circular motion. On the suggestion of Mr. Barlow, Mr. Newman has lately fixed an additional point directed downwards from the central part of the stronger wire, which point is adapted

to a small hole at the top of a bar magnet. When the apparatus with one point only is charged with diluted acid, and set on the end of a magnet placed vertically, the zinc cylinder revolves in a direction determined by the magnetic pole which is uppermost. With two points, the copper revolves in one direction, and the zinc in a contrary one. The magnet employed should be a powerful one.

As it is not easy always to bear in mind the direction in which the different poles of a magnet tend to revolve round the galvanised wire, or in which the wire tends to revolve round each respective magnetic pole, the following contrivance, invented by Dr. Roget, which he has been so good as to communicate to me, will be found very useful in aiding our conceptions, while studying the circumstances of an experiment, or anticipating the result of any new combination.

AB. (see the wood cut) is a slip of card, on each side of which a line  $ab$  is drawn along the middle of its length, the end  $a$  being marked  $+$ , the end  $b$   $-$ , and the centre  $c$  being crossed by an arrow at right angles to it, directed as in the figure. Through the centre and at right angles to the plane of the slip of card, there is made to pass a slender stem of wood, at the two ends of which are fixed, in planes parallel to the slip of card AB, the circular discs of card,



marked respectively with the letters N and S, and with arrows parallel to, but pointing in a contrary direction to the one at  $c$ . The same marks must be put on the reverse of each of the three pieces of card, so that when held in different situations they may be seen without turning the instrument.

If the line  $ab$  be supposed to represent the galvanic wire, (the direction of the current of electricity being denoted by the signs  $+$  and  $-$ , at the ends of the line,) the arrow at the centre will point out the direction in which it tends to move, when under the influence of the north pole of a magnet situ-

ated at N; or of a south pole situated on the other side at S: and, *vice versa*, the arrows at N and S will indicate the directions in which the north and south pole, respectively, tends to revolve round the galvanised wire in its vicinity, with relation to the direction of the current of electricity that is passing through it.

It must be observed that the poles N and S are here not considered as in connexion with each other, or as forming parts of one magnet: their operations are exhibited singly, and quite independently of each other. The advantage of this little instrument consists in its being capable of being held in any situation, and thus easily adapted to the circumstances of any fact or experiment, of which we may wish to examine the theory.

The above is but a very imperfect outline of the important facts already known respecting electro-magnetism; but it would lead me into details too extensive for this work to go farther into the subject. I refer, therefore, to the original memoirs of Oersted,\* Arago,† Ampère,‡ Sir H. Davy,§ Faraday,|| and others; and those, who wish only for a general view of the subject, will find it in an "Historical Sketch of Electro-magnetism," published in the 2d and 3rd volumes, N.S. of the *Annals of Philosophy*. It is necessary, however, before dismissing the subject, to offer a brief view of the explanation which has been given of the leading phenomena.

The theory of Oersted, which, though it appears to have led him to his principal discoveries, is not stated in a very intelligible manner, rests on the assumption of two different and opposite electricities, positive and negative, the former of which is developed by the more oxidizable, the latter by the less oxidizable metal of galvanic arrangements. Each of these forces has a repulsive activity for itself, and an attractive activity for the opposite force. In the wire connecting the two opposite poles of a galvanic battery, and in the space around it, there are, he supposes, two currents, the one of

\* *Ann. of Phil.* xiii. and N.S. ii.

† *Ann. de Chim. et Phys.* xv. 93.

‡ *Ann. de Chim. et Phys.* xv. 59.

§ *Phil. Trans.* 1821.

¶ *Quar. Journ.* xii. 47. 416.



positive, the other of negative electricity, moving in spiral and opposite directions; and an effect is supposed to take place in the wire and around it, dependent on the union of these electricities, to which he gives the name of the *electric conflict*. By this conflict, all non-magnetic bodies appear to be penetrable, while magnetic bodies, or rather their magnetic particles, resist its passage, and are, therefore, moved by the impetus of the contending powers. All the effects on the north pole of the needle may be understood by supposing that negative electricity moves in a spiral line bent to the right, propelling the north pole, but not acting on the south pole. To positive electricity a contrary motion is ascribed, and a power of acting on the south pole, but not on the north. This theory requires, therefore, that there be two electric fluids: but in the opinion of Dr. Wollaston, which on every obscure topic of science is entitled to the greatest deference, the phenomena may be equally well explained by a single electro-magnetic current, passing round the axis of the wire, in a direction determined by the position of the voltaic poles. The assumption of such a current is, it must be confessed, altogether gratuitous; but, without such a supposition, it is not easy to conceive any adequate cause for the motions that are observed in the magnetic needle, when brought within the influence of the uniting wire. Further researches will probably unfold the causes of these interesting phenomena, and class them under general laws, founded on a more extensive induction of facts than we now possess, notwithstanding the zeal and genius that have already been devoted to the enquiry.

## CHAPTER VI.

## OF ELECTRO-NEGATIVE BODIES.

IN conformity with the principle of arrangement which has been explained in the Introduction, I shall commence with that class of bodies, the individuals of which are chiefly distinguished by the property of being attracted by positively electrified surfaces, and repelled by negative ones, and the natural state of which may, therefore, from the common laws of electrical attraction and repulsion, be inferred to be negative. They may be termed, for the sake of brevity, *electro-negative bodies*. Though highly important from their extensive influence as chemical agents, yet their number is but small; for they consist only of OXYGEN, CHLORINE, IODINE, and a fourth body, which is only very imperfectly known to us, FLUORINE. These bodies have been classed together from another circumstance of resemblance, that of being what has been termed *supporters of combustion*. But to the latter principle of arrangement may be objected the more extensive use, which is now made in chemistry, of the term *combustion*, to express all chemical combinations, which are accompanied with the extrication of heat and light. Now these appearances constantly attend the union of some of the simple combustible bodies with each other, (sulphur and copper for instance); and we must seek, therefore, for similitudes of a more comprehensive kind, on which to found the classification of chemical substances. In the present state of our knowledge, none appears to me preferable to that which distributes them into two great classes; the ELECTRO-NEGATIVE, or bodies that are attracted by the positive pole of a galvanic or electrical arrangement, which are the four already mentioned; and the ELECTRO-POSITIVE, or those that are attracted by the negative pole. The latter class, it will afterwards appear, contains a much greater number of individuals, and may itself, with great advantage to perspicuity and order, be divided into several subordinate genera.

## SECTION I.

*Of Oxygen.*

WE have no knowledge of the properties of oxygen in a state of complete separation. In the most simple form, under which we can procure it, it is combined with caloric, and probably with light and electricity, constituting oxygen gas.

This gas was discovered by Dr. Priestley in August 1774. He first obtained it from that oxide of mercury, which is procured by the long exposure of quicksilver to a boiling heat, and which had then the name of *mercurius calcinatus per se*. After investigating its properties with considerable skill, he gave it the name of *dephlogisticated air*. In the following year, Scheele discovered it without any knowledge of the previous experiments of Priestley, and called it *empyreal air*. It has been termed, also, *vital air*; but all these have given place to the name proposed by Lavoisier, which it now bears, and which though objectionable on some accounts, it is scarcely desirable to change.

I. *Oxygen gas may be procured from various substances.*

1. From the black oxide of manganese, heated to redness in a gun-barrel, or in an iron or earthen retort; or, from the same oxide, heated by a lamp in a retort or gas-bottle, with half its weight of strong sulphuric acid. One pound of manganese is capable of furnishing from 40 to 50 wine pints of gas. But as manganese is often contaminated with a small proportion of carbonate of lime, it is advisable, before using it, to wash it with muriatic or nitric acid diluted with 15 or 20 parts of water; then with distilled water; and afterwards to dry it at a moderate heat.

2. From the red oxide of lead (the common red lead used by painters), heated either with or without half its weight of concentrated sulphuric acid.

3. From various other oxides, as will be hereafter mentioned.

4. From nitrate of potash (common saltpetre) made red-hot in a gun-barrel, or in an earthen retort.

5. From chlorate of potash, heated in a small coated glass retort, over an Argand's lamp. The oxygen gas thus produced, is much purer than that obtained in any other mode, especially the last portions, which should be kept separate. It will be found, also, to be much less contaminated with common air, if heated in a small matrass, which is best when of green glass. The chlorate of potash may be introduced while the tube is straight, which allows us to use one of very small diameter. After this, it may be bent by a spirit lamp, as represented in the annexed cut.



All these substances, after having yielded oxygen gas, are found considerably diminished in weight; and calculating each cubic inch of gas to be equal to one third of a grain, the loss of weight by the oxides will be found equivalent to that of the gas generated.

II. This gas has the following properties :

1. *It is not absorbed by water ;\** or, at least, is so sparingly absorbed, that, when agitated in contact with water, no perceptible diminution takes place.

2. *It is rather heavier than common air.* Messrs. Allen and Pepys determined 100 cubic inches to weigh 33.82 grains, the barometer being 30, and thermometer 60°; from whence its specific gravity may be deduced to be 1.1088. By Biot and Arago its specific gravity is stated to be 1.10359; by Thénard 1.1025; by Berzelius and Dulong 1.1026; and by Dr. Thomson 1.1117. Reckoning 100 cubic inches of atmospheric air to weigh 30.5 grains, 100 cubic inches of oxygen should weigh, according to Berzelius, 33.629 grains, or according to Dr. Thomson 33.906 grains.

3. *It refracts the rays of light less than any other gas.*

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\* In this as in several other instances, where a gas is said not to be absorbed by water, the assertion is not to be taken strictly, but merely as implying that only a minute and difficultly appreciable portion is absorbed. The precise proportion of each gas absorbed by water is stated in chap. viii. sec. i. art. 1. in the form of a table.

4. When suddenly and strongly compressed, not only heat is evolved, but the gas becomes luminous, a property belonging to no other simple gas except chlorine.

5. *All combustible bodies burn in oxygen gas with greatly increased splendour.*

(a) A lighted wax taper, fixed to an iron wire, and plunged into a vessel of this gas, burns with great brilliancy, pl. iv. fig. 38. If the taper be blown out, and let down into a vessel of the gas while the snuff remains red-hot, it instantly rekindles, with a slight explosion.

(b) A red-hot bit of charcoal, fastened to a copper wire, and immersed in the gas, burns vividly and throws out beautiful sparks.

(c) The light of phosphorus, burnt in this gas, is the brightest that can be in any mode produced; if we except, perhaps, the ignition of charcoal by voltaic electricity. Let the phosphorus be placed in a small hemispherical tin cup, which may be raised by means of the wire stand, pl. ii. fig. 25, two or three inches above the surface of water contained in a broad shallow dish. Fill a bell-shaped receiver, having an open neck at the top, to which a stopper is ground, with oxygen gas; and, as it stands inverted in water, press a circular piece of pasteboard, rather exceeding the jar in diameter, over its mouth. Cover the phosphorus instantly with the jar of oxygen gas, retaining the pasteboard in its place, till the jar is immediately over the cup. When this has been skilfully managed, a very small portion only of the oxygen gas will escape. The stopper may now be removed, when the water will rise to the same level within as without the jar, and the phosphorus may be kindled by a heated copper wire. Its combustion will be extremely brilliant.

(d) Substitute, for the phosphorus in experiment c, a small ball formed of turnings of zinc, in which about a grain of phosphorus is to be inclosed; and set fire to the phosphorus as before. The zinc will be inflamed, and will burn with a beautiful white light. A similar experiment may be made with metallic arsenic, which may be moistened with spirit of turpentine. The filings of various metals may also be inflamed, by placing them in a small cavity, formed in a piece of

charcoal, igniting the charcoal, and blowing, on the part containing the metal, a stream of oxygen gas from a bladder.

(e) Procure some thin harpsichord wire, and twist it round a slender rod of iron or glass, so as to coil it up in a spiral form. Then withdraw the rod, and tie a little thread or flax round one end of the wire, for about one 20th of an inch; which end is to be dipped into melted sulphur. The other end of the wire is to be fixed into a cork; so that the spiral may hang vertically (fig. 39). Fill, also, with oxygen gas, a bottle capable of holding about a quart, and set it with its mouth upwards. Then light the sulphur, and introduce the wire into the bottle of gas, suspending it by the cork. The iron will burn with a most brilliant light, throwing out a number of sparks, which fall to the bottom of the bottle, and generally break it. This accident, however, may frequently be prevented by pouring sand into the bottle, so as to lie about half an inch deep on the bottom (see pl. iv. fig. 39). According to Mr. Accum,\* a thick piece of iron or steel, such as a file, if made sharp pointed, may be burnt in oxygen gas. A small bit of wood is to be stuck upon its extremity, and set on fire, previously to immersion in the gas.

(f) A little of Homberg's pyrophorus, a substance to be hereafter described, when poured into a bottle full of this gas, immediately flashes like inflamed gunpowder.

From this detail of its properties, it appears, therefore, that oxygen gas is eminently a *supporter of combustion*. It was long, indeed, supposed to be the only supporter, and the presence of oxygen was imagined to be essential to combustion. It will appear, however, in the sequel, that other simple bodies, capable of existing in an aërial form, are equally entitled to rank as supporters of combustion. Among these are chlorine, iodine, and possibly fluorine. But they do not all support the combustion of the same substances; charcoal, for example, does not burn in chlorine, and potassium is the only body that is known to burn in the vapour of iodine.

III. *During every combustion in oxygen gas, the gas suffers a considerable diminution.*—To exhibit this, experimentally, in

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\* Nicholson's Journal, 8vo. i. 320.

a manner perfectly free from all sources of error, would require such an apparatus, as few beside adepts in chemistry are likely to possess. The apparatus adapted to this purpose is described in the 6th chapter of Lavoisier's Elements. The fact may, however, be shown, less accurately, by the combustion of phosphorus, in the manner which has been already described. The first effect of the combustion will be a depression of the water within the jar; but when the combustion has closed, and the vessel has cooled, a considerable absorption will be found to have ensued.

Those persons, who are possessed of a mercurial apparatus, may repeat this experiment in a less exceptionable manner. On the surface of the quicksilver let a small hemispherical cup float, made of untinned sheet-iron; and, in order to keep it from the sides of the jar, it may rest on a wire-stand, shaped like the figure 43, plate iv. Let a jar, the height and diameter of which must be regulated by the size of the mercurial trough, be filled with oxygen gas over water, and be removed, by means of a piece of pasteboard, as before described, to the mercurial bath, inverting it dexterously over the tin cup. If the phosphorus had been previously set on fire, a large quantity of the gas, expanded by the heat, would have escaped, and would have prevented the accurate measurement of the absorption. After drying the surface of the mercury within the jar by blotting paper, a portion of the included gas must, therefore, be removed. This is done by an inverted syphon, one leg of which is to be introduced (in the same manner as is shown at fig. 41, *g*) within the jar, before placing it over the mercury; and the gas will be forced through the open extremity of the other, when the jar is pressed down into the quicksilver. When the proper quantity has been expelled, remove the syphon. The cup, containing the phosphorus, will thus rest on the surface of the quicksilver within the jar, and above the level of the mercury without. The phosphorus is to be inflamed by passing a crooked iron wire, made red hot, through the quicksilver. On the first impression of the heat arising from its combustion, the included gas will be considerably expanded; but when the phosphorus has ceased to burn, a considerable absorption

will be found to have taken place, the amount of which may be measured by ascertaining the height of the quicksilver within the jar, before and after the experiment. The quantity of phosphorus employed should be very small, and should not bear a greater proportion than that of 10 grains to each pint of gas; otherwise the combustion will go on so far, as to endanger the breaking of the jar, by the approach of the inflamed phosphorus.

In this process, a dense white vapour is produced, which concretes on the inner surface of the jar in solid flakes. This substance has strongly acid properties; and, being formed by the union of oxygen with phosphorus, is termed the phosphoric acid.

The diminution of the volume of oxygen gas, by the combustion of other bodies, may be ascertained in a similar manner. When the substance employed is not easily set on fire, it is proper to enclose, along, and in contact with it, a small bit of phosphorus, the combustion of which excites sufficient heat to inflame iron-turnings, charcoal, &c. In the instance of charcoal, however, though that substance undergoes combustion, no absorption ensues; because, as will appear in the sequel, the product is a gas, occupying exactly the same bulk as the oxygen gas submitted to experiment.

IV. *During the combustion of bodies in oxygen gas, a large quantity of caloric is liberated.*—Lavoisier has endeavoured to prove (Elements of Chemistry, chap. ix.) that a given weight of oxygen abandons very different quantities of heat, when combined with different inflammable bodies. For example, the caloric disengaged from 1 pound of oxygen, during the combustion of its equivalent of phosphorus, he estimates to be sufficient to melt between 66 and 67 pounds of ice; of charcoal, between 37 and 38 pounds; and of hydrogen, 52 pounds of ice. There can be little doubt that the heat, evolved in these combustions, as well as the light, has its origin partly from the oxygen gas, and partly from the combustible body; but the precise quantity due to each can scarcely be considered as yet determined. Nor must it be understood, that the transition of oxygen from the gaseous to a more dense state is essential to the phenomena of combustion; for besides that



we have several examples of true combustion where oxygen is not at all concerned, as in those effected by chlorine, the principle must now be still more limited by a variety of cases, to be afterwards mentioned, which show that active and vivid combustion is sometimes attended, not with a condensation of the bodies that combine, but on the contrary with a great enlargement of volume; and, what is still more remarkable, that in some instances the new compounds, formed by combustion, have as great a capacity for heat as their constituent principles. (See Petit and Dulong's Memoir. Ann. de Ch. et Phys. x. 395.)

V. *All bodies, by combustion in oxygen gas, acquire an addition to their weight; and the increase is in proportion to the quantity of gas absorbed, viz. about one third of a grain for every cubic inch of gas.*—To prove this by experiment, requires also a complicated apparatus. But sufficient evidence of the general fact of an increase of weight may be obtained by the following very simple experiment. Fill the bowl of a tobacco pipe with iron wire coiled spirally, and of known weight: let the end of the pipe be slipped into a brass tube, which is screwed to a bladder filled with oxygen gas: heat the bowl of the pipe, and its contents, to redness in the fire, and then force through it a stream of oxygen gas from the bladder. The iron wire will burn; will be rapidly oxydized; and will be found, when weighed, to be considerably heavier than before. When completely oxydized in this mode, 100 parts of iron wire gain an addition of about 30.

VI. The substances, capable of uniting with oxygen, afford one or other of the following products; 1st, *an acid*; 2dly, *an alkali or earth*; or 3dly, *an oxide*. It is not easy to give precise definitions of these three classes of compounds. Of the acids, for instance, there are some which, though entitled to that epithet by their general qualities of chemical combination, are not sour to the taste; and others which do not redden vegetable blue colours. Nor is oxygen an element essential to the acidity of a compound, for some bodies are rendered acid by union with chlorine, and others by combination with hydrogen. The theory of Lavoisier, therefore, which considered oxygen as the essential principle of acidity,

and in conformity to which its present name was assigned to it,\* can no longer be received as correct. The name, however, may be retained, to avoid the inconvenience of changing one so long and generally received.

Alkalis and earths are chiefly distinguished by acting as bases, with which the acids combine, with the loss generally of the separate characters of each. The alkalis are soluble in water, and change some vegetable blues to green; and the earths are either not soluble at all or sparingly soluble in that fluid; but in the quality of insolubility they agree with many of the third class of compounds, *viz.* oxides, especially with those derived from the metals, which also serve as bases to the acids.

In many instances, a combustible body, which affords an acid when united with a certain quantity of oxygen, gives an *oxide* when combined with a less quantity; and the acid may be brought back to the state of an oxide by separating part of its oxygen. We have examples, also, furnished chiefly by a few of the metals, in which the same body, combined with a small proportion of oxygen, gives an oxide that is capable of uniting with acids, and of composing salts, and again, united with more oxygen, yields an acid which is susceptible, with alkalis and earths, of forming saline compounds.

VII. *Oxygen gas supports, eminently, animal life.*—It will be found that a mouse, a bird, or other small animal, will live four or five times longer in a vessel of oxygen gas, than another animal of the same kind and size will live in a jar of atmospherical air of the same dimensions.

VIII. *This effect seems connected with the absorption of oxygen by the blood.*—Pass up a little dark-coloured blood into a jar partly filled with oxygen gas, and standing over mercury. The gas will be in part absorbed, and the colour of the blood will be changed to a bright and florid red. This change to red may be shown, by putting a little blood into a common vial filled with oxygen gas, and shaking it in contact with the gas.

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\* From *ὄξος*, acid, and *γενωμαί*, to generate.

## SECTION II.

*Of Chlorine.*

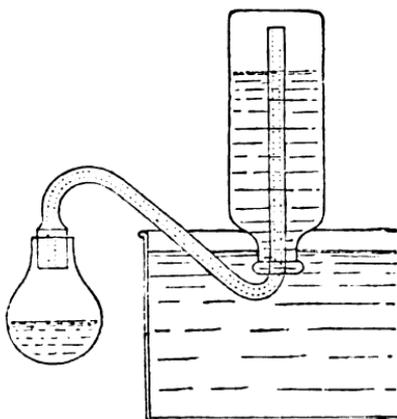
Chlorine was discovered by Scheele in the year 1774, and first described by him in an Essay on Manganese, under the name of *dephlogisticated marine acid*. It was afterwards termed in the French nomenclature *oxygenated muriatic acid*, and by Dr. Pearson *oxymuriatic acid*, a name generally received in this country, till superseded by that which it now almost universally bears. The simplest state, in which we are able to examine its properties, is that of a gas.

I. This gas may be formed by either of the following processes :

Process 1. Into a stoppered retort introduce eight ounces of liquid muriatic acid, sp. gr. 1.160, and four ounces of finely powdered manganese, and apply the heat of a lamp. A gas will be produced, which may be received, in the usual manner, over water of the temperature of 80° or 90° Fahrenheit. From the foregoing materials about 160 cubical inches may be obtained.

Process 2. Grind together in a mortar eight ounces of muriate of soda (common salt) with three ounces of powdered manganese; put them into a stoppered retort, and pour on them four ounces of sulphuric acid, which have been diluted previously with four ounces of water, and suffered to cool after dilution. Or the proportions recommended by Thenard may be employed, *viz.* 4 parts of muriate of soda, 1 part of oxide of manganese, water and sulphuric acid each 2 parts. On applying a gentle heat, gas will be produced, as in Process 1. But as the gas is absorbed by contact with cold water, though not rapidly, it should be received, when it is intended to be kept, in bottles filled with, and inverted in, water of the temperature of 80° or 90° Fahr. and provided with accurately ground stoppers. It will be found also much to diminish the loss of gas by absorption, if it be made to issue from a gas bottle, the

tube of which is sufficiently long to reach nearly to the bottom of the inverted receiving bottle; for the gas is thus prevented from passing in bubbles through a long column of water. (See the annexed cut). The stopper must be introduced under water, while the receiving bottle remains quite full of the gas, so that no water may be left in the bottle, along with the gas.



II. Chlorine gas has the following properties :

(a) It has a yellowish green colour; and this property has suggested the name *chlorine*.\*

(b) It has a pungent and suffocating smell. In experiments on this gas, great care should be taken that it does not escape, in any considerable quantity, into the apartment; for its action on the lungs is extremely painful and injurious.

(c) It is heavier than common air (taking the statement of Gay Lussac) in the proportion of 2.470 to 1.000 by experiment, or 2.4216 by calculation; and 100 cubic inches should, therefore, weigh 75.33 grains. Sir H. Davy found them to weigh between 76 and 77 grains, at a mean temperature and pressure, the latter of which numbers would make its specific gravity 2.5082. Dr. Thomson fixes its sp. gr. at 2.500, which, taking his statement of the sp. gr. of hydrogen to be correct, viz. 0.0694, would make it 36 times the weight of hydrogen. From other data, it had been calculated to be only  $33\frac{1}{2}$  times heavier than hydrogen gas.

(d) By a temperature of  $+ 40^{\circ}$  Fahr. it is reduced into a liquid form, and is condensed on the sides of the vessel. But if the gas be previously dried by exposure to muriate of

\* From  $\chi\lambda\omega\rho\varsigma$ , green.

lime, it bears the most intense artificial cold without condensation.\*

When a receiver, filled with this gas, not artificially dried, is surrounded by snow, or pounded ice, the gas forms on its inner surface a solid concretion, of a yellowish colour, resembling, in its ramifications, the ice which is deposited on the surface of windows during a frosty night. By a moderate increase of heat, such as to  $50^{\circ}$  Fahrenheit, this crust melts into a yellowish oily liquid, which, on a farther elevation of temperature, passes to the state of a gas.

(e) When suddenly and considerably condensed by mechanical pressure, not only heat is evolved, as from all other gases, but light also; a property peculiar to this gas and oxygen among the simple gases.

(f) It is not changed by being transmitted through ignited porcelain tubes, nor by a succession of electrical discharges through it.

(g) When a burning taper is introduced into a vessel of chlorine gas, the flame becomes red, a dense smoke arises, and the taper is soon extinguished. Phosphorus, however, takes fire the moment it is introduced, and burns vehemently; and many of the metals, when brought in a finely divided state into contact with the gas, exhibit a brilliant combustion.

(h) It is not at all acted upon by oxygen gas, but with hydrogen gas a remarkable series of phenomena take place which will presently be described.

(i) Chlorine gas, in its ordinary state, destroys all vegetable colours. This may be shown by passing, into the gas confined by water, a piece of paper stained with litmus, the colour of which will immediately disappear. Hence the application of this gas to the purpose of bleaching, its power of effecting which may be shown by confining, in the gas, a pattern of unbleached calico, which has been previously boiled in a weak solution of caustic potash, and then washed in water, but not dried. Chlorine gas, however, which has been carefully dried by solid chloride of calcium, and into which

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\* Sir H. Davy, Phil. Trans. 1811, p. 30.

perfectly dry litmus paper is introduced, produces no change of colour in the litmus, a sufficient proof that its bleaching power depends on the presence and decomposition of water.

(k) This gas is absorbed by water; slowly, if allowed to stand over it quiescent, but rapidly when agitated.

1. The best method of effecting the impregnation of water with this gas, is by means of a Woulfe's apparatus, the bottles of which should be surrounded by ice-cold water. The quantity of the gas, which water is capable of absorbing, appears, from the concurrent testimony of Davy and Dalton, to be twice its bulk. The former has remarked that water, apparently saturated with chlorine by agitation with it in a narrow vessel, takes up a further portion of the gas when exposed with a broad surface.

2. The watery solution, if perfectly free from common muriatic acid, has not the taste of an acid, but an astringent one. Its purity from muriatic acid may be ascertained by a solution of nitrate of mercury, which is not precipitated by pure chlorine.

3. The watery solution has the colour and peculiar smell of the gas, and has a similar property of discharging vegetable colours. Hence it may be employed in bleaching.

4. When the watery solution of chlorine is exposed to a temperature only a little above that of freezing water, the gas, which is combined with it, separates in the form of a liquid, heavier than water.

5. Chlorine is not altered by the temperature of boiling water; for its solution may be raised in distillation, and again condensed without change.

6. When the solution of chlorine in water is exposed to the direct rays of the sun, oxygen gas is obtained, and the acid passes to the state of muriatic acid. Placed in the current of the electric fluid, the chlorine, and the oxygen of the water, arrange themselves at the positive, and the hydrogen at the negative pole.

Chlorine is susceptible of combination with various other bodies, and the compounds possess, in many instances, remarkable properties. At present we shall describe those only which result from the union of chlorine with oxygen.

ART. 1.—*Protoxide of Chlorine or Euchlorine.*

When chlorate or hyper-oxy muriate of potash (a salt which will be afterwards described) is distilled, at a gentle heat, with weak muriatic acid, a gas may be collected over mercury, which is found to differ essentially from chlorine. Its colour has a dense tint of brilliant yellow green; and its smell resembles that of burnt sugar, mixed with the peculiar smell of chlorine. Water takes up eight or ten times its volume, and acquires an orange tint. It has been called by its discoverer, Sir H. Davy, *Euchloric gas*, or simply *Euchlorine*. Gay Lussac has proposed for it the name of oxide of chlorine; but it may, with more propriety, be called *Protoxide of Chlorine*.

Euchlorine explodes by a gentle heat, applied to the vessel which contains it, and five parts in volume become six, consisting of a mixture of oxygen and chlorine gases, in such proportions that euchlorine must be composed of two in volume of chlorine and one of oxygen, the latter being condensed into half its bulk, or by weight of

Chlorine.....	81.44	.....	100.
Oxygen .....	18.56	.....	22.79.

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100.

These proportions indicate that euchlorine is constituted of one atom of chlorine = 36, + one atom of oxygen = 8, and hence its atom must weigh 44.

When detonated with twice its volume of hydrogen gas, there is a condensation of more than two thirds of the mixture, and liquid muriatic acid is formed.

Mercury has no action on euchlorine at common temperatures. Antimony and copper burn in it, if introduced previously heated. Sulphur and phosphorus decompose it; and charcoal already ignited burns in it with a dull red light. Nitrous gas condenses it with red fumes.

Euchlorine destroys vegetable colours; but it first gives the blue a tint of red.

In almost all cases of vivid combustion, there is a condensation of the bodies which unite; but in the decomposition of

euchlorine by heat, we have the remarkable phenomenon of an explosion, accompanied with heat and light, and yet with an expansion of the elements, which are separated from each other.

ART. 2.—*Deutoxide or Peroxide of Chlorine.*

Another compound of chlorine and oxygen, containing a larger proportion than euchlorine, of the latter element, was discovered by Sir H. Davy,\* and has since been made the subject of a series of experiments by Count Stadion of Vienna.† As it exhibits no acid properties, it may be called *peroxide of chlorine*, a name, it appears to me, preferable to that of *deutoxide*, which has also been applied to it, because intermediate compounds will probably be discovered between this oxide and the protoxide already described.

To procure it, 50 or 60 grains of the powdered chlorate of potash are to be mixed with a small quantity of concentrated sulphuric acid. When thoroughly incorporated, a solid mass will result, of a bright orange colour. This is to be introduced into a small retort of glass, which is to be exposed to the heat of water gradually warmed, but prevented from attaining the boiling point by an admixture of spirit of wine. Count Stadion obtained it by fusing a small quantity of chlorate (hyper-oxy muriate) of potash, in a retort. Over this, when cool, he poured concentrated sulphuric acid, and exposed the retort to water for three hours, gradually raising its temperature to  $212^{\circ}$ . The gas may be received over mercury, on which it has no action at common temperatures.

It has a lively yellow colour, much more brilliant than that of euchlorine; is much more rapidly absorbed by water; and has a peculiar aromatic smell, not mixed with any smell of chlorine. According to Davy, it destroys vegetable blue colours, without first reddening them; but Count Stadion asserts that it does not change blue paper. When heated to about the temperature of  $212^{\circ}$  Fahr. or, according to Count Stadion, to between  $112^{\circ}$  and  $114^{\circ}$ , it explodes with more violence, and a greater expansion of volume, than euchlorine,

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\* Phil. Trans. 1815, Part II.

† Thomson's Annals, ix. 22.



producing much light. After explosion over mercury, from 2.7 to 2.9 volumes appear, for every two of gas decomposed; and, of these two, as Count Stadion also admits, are oxygen and the rest chlorine. A little chlorine is absorbed, however, by the mercury, and it is reasonable, Sir H. Davy thinks, to conclude that the deep yellow gas is, in reality, composed of two in volume of oxygen, and one of chlorine, condensed into two volumes. If this be correct, the gas must consist, by weight, of one atom of chlorine 36, and four atoms of oxygen 32, and its atom will weigh 68. But if, as Stadion asserts, it gives two volumes of chlorine and three of oxygen, it should consist of one atom of chlorine and only three of oxygen.

It is not decomposed, at common temperatures, by any combustible body, except phosphorus, which occasions an explosion when introduced into it, and burns, in the liberated gases, with great brilliancy.

Its saturated solution in water, which contains seven volumes of gas, is of a deep yellow colour. It does not taste sour, but extremely astringent and corroding; and it leaves on the tongue a disagreeable and lasting impression. The solution may be kept in the dark unchanged, but when exposed to the sun's rays it is decomposed, and chlorine and chloric acid are obtained.

### ART. 3.—*Chloric Acid.*

A third compound of chlorine and oxygen was pointed out by Mr. Chevenix, some time before it was obtained in a separate form, as existing in the class of salts called by him hyper-oxy muriates. For the method of exhibiting it in a distinct state, we are indebted to Vauquelin\* and Gay Lussac.† The following is the process: To a solution of pure chlorate of barytes (the mode of preparing which will be described chap. ix, sect. 5.) add by degrees dilute sulphuric acid, as long as it occasions any precipitation. This separates the barytes, and leaves the chloric acid combined with water only. It is important to add no more sulphuric acid than is barely suffi-

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\* Ann. de Chim. xcv. 102.

† Ibid. xci. 111.

cient; for the slightest excess renders the chloric acid impure. If the right quantity has been used, the liquid obtained should remain perfectly transparent, when, taking two separate portions of it, we add to the one dilute sulphuric acid, and to the other chlorate of barytes. If either of these agents occasions a precipitate, we must add it by degrees till the effect ceases. The clear liquid is then to be decanted by a syphon, and reserved for use. It is a solution of chloric acid in water; and has the following properties.

1. It is free from colour; its taste is acid and astringent; and its smell, when concentrated and a little heated, is moderately pungent.

2. It reddens the infusion of litmus. Paper stained with litmus, though it does not immediately lose its colour, yet is deprived of it in a day or two if left in the liquid; or more rapidly if taken out of the liquid and exposed to the air, in consequence of the solution becoming more concentrated.

3. It does not precipitate either silver, mercury, or lead, from nitric acid.

4. It is volatilized by heat, but not without a partial decomposition into chlorine and oxygen. Hence it afterwards precipitates the nitrate of silver.

5. Muriatic acid decomposes it, and both acids, if mixed in just proportion, are changed entirely into chlorine.

6. Chloric acid is decomposed, also, by sulphureted hydrogen and by sulphurous acid. In the first case, chlorine and sulphur are separated, and water is formed. In the second, sulphuric acid is formed, and chlorine set at liberty. None of the acids, which are saturated with oxygen, have any action on chloric acid.

7. All the metals that are capable of decomposing water, decompose also the chloric acid, and afford compounds of chlorine with a metallic oxide.

According to the experiments of Vauquelin, chloric acid is composed of

Chlorine . . . . .	35	. . . . .	100	. . . . .	54
Oxygen . . . . .	65	. . . . .	185	. . . . .	100

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100

This determination differs materially from that of Gay Lussac, according to whom 32.304 oxygen convert 28.924 chlorine into chloric acid, and hence it should be composed of

Chlorine . . . . .	47.3	. . . . .	100	. . . . .	90
Oxygen . . . . .	52.7	. . . . .	110	. . . . .	100
100.					

The result of Gay Lussac is by much the more probable of the two, and would make the chloric acid consist of one atom of chlorine + 5 atoms of oxygen (together = 76) while Vauquelin's numbers would indicate no less than 8 atoms of oxygen. Mr. Chenevix formerly stated the composition of the hyper-oxy muriatic or chloric acid to be 65 oxygen + 35 muriatic acid. To accommodate this view to the new theory, 10.4 taken from the oxygen and added to the muriatic acid will give 45.4 and 54.6, numbers not very different from those of Gay Lussac.

It is proper, however, to add that the existence of a simple combination of chlorine and oxygen has been disputed by Sir H. Davy, who considers the liquid, obtained by Gay Lussac, as constituted of two proportions (atoms) of hydrogen, one of chlorine, and six of oxygen. To this the latter has replied, that the hydrogen is not an element of the acid itself, but of water with which the acid is united, as is the case with liquid sulphuric and nitric acids. The reader who takes an interest in this controversy, may find it in the first volume of *Annales de Chimie et de Physique*, and of the *Journal of Science and the Arts*; and the argument for the existence of hydrogen in certain acids as an essential and acidifying principle, and not as a constituent of water, has, also, been ably supported by Dr. Murray, in a late volume of the *Edinburgh Transactions*.

#### ART. 4.—*Perchloric Acid.*

In obtaining peroxide of chlorine by Sir H. Davy's or by Count Stadion's process, a peculiar salt is formed, which was first noticed by the latter philosopher. It is mixed with bisulphate of potash, which may be separated by a second crys-

tallization, and the peculiar salt then appears in octohedral crystals. It requires 55 times its weight of water at 60° for solution, but dissolves freely in boiling water. In alcohol it is quite insoluble. When distilled with an equal weight of sulphuric acid, at a temperature of 280° Fahr. it is decomposed: and an acid (of whose properties, however, we have not a distinct account) may be distilled over. When the salt is distilled alone at 412°, it is converted into chloride of potassium (dry muriate of potash) and oxygen gas, in the following proportions. One hundred parts by weight afford

Chloride of potassium . . . . .	54.08	containing	{	28.49	potassium
			}	25.59	chlorine
Oxygen . . . . .	45.92				
		<hr style="width: 50%; margin: 0 auto;"/>			
		100.			

Hence it appears that 25.59 chlorine are united with 45.92 oxygen, which is nearly in the proportion of 36 chlorine to 64 oxygen. Per-chloric acid will therefore consist of one atom of chlorine = 36, united with eight atoms of oxygen = 64; and the weight of its atom will be 100.

### SECTION III.

#### *Of Iodine, and its Compounds with Oxygen and Chlorine.*

IODINE was discovered accidentally, about the beginning of the year 1812, by M. Courtois, a manufacturer of saltpetre at Paris. In the processes for procuring soda from the ashes of sea weeds, he found his metallic vessels much corroded; and in searching for the cause, he made this discovery. Specimens of the new substance were given to MM. Desormes and Clement, who read a short memoir upon it, at a meeting of the Institute of France, in November 1813. Its properties and combinations have since been ably investigated by Vauquelin; \* by Gay Lussac; † by Sir H. Davy; ‡ and by Gaultier de Claubry and Colin. §

\* 90 Ann de Chim. 206.

† 91 Ann. de Chim.

‡ Phil. Trans. 1814.

§ 90, 91, & 93 Ann. de Chim.

When all the soda has been separated by crystallization from a solution of kelp or barilla, or from the ley of ashes of marine plants, that afford the mineral alkali, in order to procure iodine from the residuary liquor, concentrated sulphuric acid is to be poured upon it, in a retort furnished with a receiver. The iodine passes into the receiver, under the form of beautiful violet vapours, which are condensed in crystalline plates, having the aspect of plumbago. To purify it from the redundant acid, that comes over with it, the iodine may be redistilled from water, containing a very small quantity of potash, and afterwards dried by pressing it between folds of blotting paper.\*

*General Properties.*—Iodine is a solid, at the ordinary temperature of the atmosphere. It is often in scales, resembling those of micaceous iron ore; sometimes in large and brilliant rhomboidal plates; and occasionally in elongated octohedrons.† Its colour is bluish black; its lustre metallic, it is soft and friable, and may easily be rubbed to a fine powder. Its taste is very acrid, though it is sparingly soluble in water, which does not take up above one 7000th part of its weight, and it is poisonous if taken in a large dose. Its specific gravity, at 60° Fahrenheit, is 4.946. It is a non-conductor of electricity; and possesses, in a high degree, the electrical properties of oxygen and chlorine, being determined to the positive pole of a galvanic arrangement. When applied to the skin, it produces a yellow stain, but this disappears as the iodine evaporates.

Iodine is fusible at 225° Fahrenheit, and, under the ordinary pressure of the atmosphere, is volatilized at a temperature somewhere near 350°, forming a gas 125 times denser than hydrogen, which last number represents the weight of its atom. According to Gay Lussac, the specific gravity of its vapour, compared with air, is 8.678. Hence 100 cubic inches should weigh 269 grains. The volatilization of iodine at the heat of boiling water, which happens when it is distilled with that

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\* More minute directions for its preparation are given in the *Phil. Mag.* xl. 57, 141, and 209.

† Dr. Wollaston has described the form of its crystal in *Thomson's Annals*, v. 237. See also *Journ. of Science*, &c. v. 364.

fluid, depends on its affinity for aqueous vapour. The colour of its vapour is a beautiful violet, and hence its name (from *ἰώδης*, violaceus).

### ART. 1.—Iodine and Oxygen.

*Action of Oxygen.*—Iodine undergoes no change by being heated in contact with oxygen gas, or with chlorate of potash. By the intervention of protoxide of chlorine, however, it admits of being combined with oxygen, and it then furnishes a peculiar acid with that body.

*Action of Protoxide of Chlorine.*—When iodine is exposed to euchlorine, Sir H. Davy has discovered,\* that there is an immediate action; its colour changes to bright orange; and a liquid is formed. By the application of a gentle heat, the orange compound of chlorine and iodine is expelled, and a compound of oxygen and iodine remains. This substance is a white semi-transparent solid; it has no smell, but a strong astringent sour taste. Its specific gravity is such that it sinks in sulphuric acid.

When decomposed by heat in a pneumatic apparatus, it is resolved into oxygen gas and pure iodine; and it is, therefore, termed by Sir H. Davy, *oxyiodine*; by Gay Lussac *acide iodique anhydre*.† Thirteen grains afforded 9.25 cubical inches of oxygen gas, = 3.14 grains. Hence it is composed of

Iodine . . . .	75.85 . . . .	100. . . .	314.8
Oxygen . . . .	24.15 . . . .	31.84 . . . .	100.
	100.	131.84	414.8

Iodic acid, therefore, is constituted of

5 atoms of oxygen = . . . . .	40
1 atom of iodine = . . . . .	125
	165

And the weight of its atom is . . . . . 165

It presents, then, in its composition, a striking analogy with

\* Phil. Trans. 1815, part 2.

† The term *anhydrous*, which will be often used, is derived from a Greek word signifying *without water*.

chloric acid, which is composed of 5 atoms of oxygen and 1 atom of chlorine.

Anhydrous iodic acid is very soluble in water, and is slightly deliquescent. Its solution, called by Gay Lussac *acide iodique*, first reddens, and then destroys, vegetable blues, and reduces other vegetable colours to a dull yellow. When evaporated sufficiently, it becomes a thick pasty substance, and at length, by a cautiously regulated heat, yields the anhydrous acid unaltered.

When heated in contact with inflammable bodies, or with the more combustible metals, detonations are produced. Its solution in water rapidly corrodes all the metals, and even acts on gold and platinum, but especially on the first.

When its solution is poured into solutions of alkalis, or alkaline earths, or when made to act on their carbonates, triple compounds are formed of oxygen, iodine, and the metallic bases, called by Sir H. Davy, *oxyiodes*; and by Gay Lussac, perhaps more properly, *iodates*. With solution of ammonia, it composes iodate of ammonia; and from the soluble salts of barytes and strontites, it precipitates their respective iodates. Forty-eight grains of iodate of potassium, when decomposed by heat, afforded Sir H. Davy 31 cubic inches = 10.5 grains of oxygen gas.

Iodic acid enters into combination with all those fluid or solid acids, which it does not decompose. Sulphuric acid, dropped into a saturated solution of it in hot water, precipitates a solid, which, on cooling, forms rhomboidal crystals of a pale yellow colour. This compound is fusible; and, with a heat properly regulated, may be sublimed unaltered. Hydronic and hydrophosphoric acids afford analogous compounds. Oxalic and liquid muriatic acids decompose it. All its acid combinations redden vegetable blues; dissolve gold and platinum; and when added to alkalis or earths, afford common neutral salts, and their respective iodates. In their crystalline state, the compounds of iodic and other acids are most probably hydrates; the acids carrying with them, into combination with iodic acid, their definite proportion of water.

ART. 2.—*Iodine and Chlorine.*

Iodine absorbs less than one-third its weight of chlorine, and forms a peculiar acid which may be called *chloriode*, or the *chloriodic acid*, and its compounds *chloriodates*. According to Gay Lussac, indeed, two compounds result, the one of a fine orange-yellow colour, containing the largest proportion of chlorine, the other orange-red. Both are solid and crystalline; deliquesce when exposed to the air; are fusible into an orange liquid; and give an orange coloured gas. The watery solution takes more iodine, and acquires a deeper colour; but if agitated with chlorine, it is deprived of colour, and when poured in that state, into solution of potash, the deflagrating salt is precipitated. From liquid ammonia, the colourless liquid precipitates a white detonating compound; but the coloured solution throws down the darker compound, which detonates on the slightest touch, and is, indeed, identical with that procured by the direct action of iodine on ammonia.

Chloriodic acid (or *chlorure of iodine*, as it is called by Gay Lussac) precipitates the salts of iron, lead, tin, and copper; probably in the state of iodates.

It has been observed by Gay Lussac, that, in order to convert the whole of a quantity of alkali into the deflagrating salt, without any of the hydriodate, (which otherwise is produced in greater proportion than the iodate) it is necessary, first, to combine the iodine with chlorine; and, after dissolving the compound in water, to saturate it with alkali.

*Nature of Iodine.*—Iodine, from all that we yet know respecting it, is to be considered as a simple or elementary body, having a very striking analogy with chlorine, which it resembles, 1stly, in forming one acid by uniting with hydrogen, and a different acid with oxygen; 2dly, in its effects on vegetable colours; 3dly, in its affording, with the fixed alkalies, salts which nearly approach in characters to chlorates; and 4thly, in its electrical habitudes. Its discovery, indeed, lends strong support to that theory, which considers chlorine as a simple body, and muriatic acid as a compound of chlorine and hydrogen. In the property of forming an acid, whether it



be united with hydrogen or with oxygen, iodine bears, also, an analogy to sulphur; and it is remarked by Gay Lussac of the combinations of chlorine, iodine, and sulphur, with the elements of water, that while the acids, which they respectively form with oxygen, have their elements strongly condensed, those formed with hydrogen have their elements very feebly united. Sulphur has the strongest affinity for oxygen, then iodine, and lastly chlorine. But for hydrogen, chlorine has a stronger attraction than iodine, and iodine than sulphur; whence it appears that the affinity of each of those bodies for oxygen is inversely proportionate to its affinity for hydrogen.

*The source of iodine in nature* has been investigated by M. Gaultier de Claubry.\* His first experiments were directed to the analysis of the several varieties of *Fucus*, the combustion of which furnishes the soda of sea-weeds. Before these vegetables are destroyed by combustion, he ascertained that iodine exists in them in the state of *hydriodate of potash*; and that calcination only destroys the vegetable matters, with which it is combined. As the hydriodate of potash is a deliquescent salt, it remains in the mother liquor, after separating the carbonate of soda, and most of the other salts, by crystallization. In the course of these experiments, M. de Claubry found that starch is one of the most delicate tests of the presence of iodine, and if added to any liquid containing it, with a few drops of sulphuric acid, iodine is indicated by a blue colour, of greater or less intensity. In this way, he detected iodine in the decoction of several varieties of *Fucus*; but he was unable to discover the slightest trace of it in sea-water. The *Fucus Saccharinus* yielded it most abundantly; and in order to obtain it by the cheapest and easiest process, he recommends that we should submit this *fucus*, dried and reduced to powder, to distillation with sulphuric acid.

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\* Ann. de Chim. xciii. 75, 118.

## SECTION IV.

*Of Fluorine.*

THE experiments of Sir H. Davy led him, in 1808, to conclude, chiefly from the action of potassium on silicated fluoric gas, that the fluoric acid is a compound of oxygen with a combustible basis. But as all acids, so constituted, are decomposed by galvanic electricity, their base being determined to the negative, and their oxygen to the positive pole, he has since \* submitted liquid fluoric acid to this test, after having ascertained, by the result of its combination with ammoniacal gas, that in its strongest form, it contains no water. Considerable difficulty was experienced in making the necessary exposure of the liquid to electricity, (partly in consequence of the dangerous fumes which it emitted,) and also in collecting the products. At the negative pole, a gas was evolved, which, from its inflammability, appeared to be hydrogen. The platina wire at the positive pole was rapidly corroded, and covered with a chocolate powder, the properties of which seem not to have been examined.

When fluat of ammonia was treated with potassium, no evidence was obtained of its containing oxygen. Charcoal, also, intensely ignited in fluoric acid gas, gave no carbonic acid. The most simple way of explaining the phenomena appears, therefore, to Sir H. Davy, to be by the supposition, that the fluoric acid, like the muriatic, is composed of hydrogen, and a peculiar base, possessing, like oxygen and chlorine, a negative electrical energy, and hence determined to the positive surface. For this base, which, like chlorine, he believes to combine at once with metals, the name of *fluorine* has been proposed. This substance, from its strong affinities and decomposing agencies, has not yet been exhibited in a separate state; nor have any of the attempts to detach it from its combinations by chlorine or oxygen, (on the presumption that the attraction of one of those bodies for the metals might be superior to that of fluorine,) been hitherto successful.

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\* Phil. Trans. 1813, part 2; and 1814, part 1.

The number representing the atom of *fluorine*, as deduced from the composition of fluor spar, is 17.1; and fluor spar must be composed of 20 calcium and 17.1 fluorine. On the whole, Sir H. Davy is disposed to estimate the weight of the atom of fluorine at less than half that of chlorine, and to fix it at 33, which is equivalent, on Mr. Dalton's scale, to 16.5.

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### ELECTRO-POSITIVE BODIES.

The bodies which are determined to the negative pole of a galvanic arrangement, and whose inherent electrical state may, therefore, be presumed to be positive, have been sometimes termed *simple combustible bodies*. To this title, however, the same objections exist, which have been before urged against that of *supporters of combustion* as applied to electro-negative substances; and it may be added that one body at least (azote) may with propriety be included among electro-positive bodies, which cannot be considered as combustible, and to which it would otherwise be difficult to assign a place. The electro-positive class comprehends, as we have already observed, all the objects of chemical science, with the exception of the four that have been already described; and from their great number it becomes desirable to distribute them into subordinate and less comprehensive divisions. They may be considered, then, either as elementary or compound. The elementary, or those which have not been as yet resolved into a more simple state, may be divided into,

I. Those, which, by combination with oxygen or hydrogen, are capable of being converted into acids, but which have no metallic properties.

II. Those which either decidedly rank as metals, or are so nearly allied to metals in their general habitudes, as to render it improper to assign to them any other place in a chemical arrangement. In the class of metals will be found a few bodies which yield acids when united with oxygen, and one or two which are even acidified by combination with hydrogen.

## CHAPTER VII.

OF SIMPLE ACIDIFIABLE BODIES (NOT METALLIC), AND THEIR COMBINATIONS WITH OXYGEN, CHLORINE, IODINE, AND FLUORINE.

THIS subdivision comprehends hydrogen, nitrogen, charcoal, boron, phosphorus, sulphur, and selenium, bodies extremely different from each other in their external appearance and physical characters, but still agreeing in the property of being convertible into acids. Of these, hydrogen is acidifiable only by chlorine; nitrogen, charcoal, and boron by oxygen only; while sulphur and selenium are acidifiable both by hydrogen and oxygen. In selecting the order in which they should be described, I have been governed chiefly by the importance of their compounds, and by the extent of their influence over chemical phenomena. For this reason, I begin with hydrogen, because there are few chemical changes in which water is not concerned, either by acting as a solvent, or by furnishing oxygen or hydrogen to the bodies with which it is brought into contact.

## SECTION I.

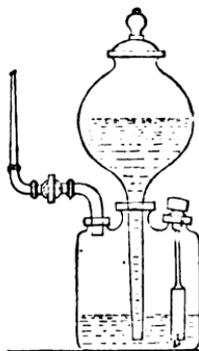
*Of Hydrogen.*

THE most simple form, in which HYDROGEN has hitherto been obtained, is in that of a gas, that is, in a state of union with caloric, and perhaps with electricity and light. From this combination we are not able to separate it, except by availing ourselves of the affinity of some other substance, in which case the hydrogen separates from the caloric, and forms, with the body which has been added, a new combination. Of its nature we know but little; but as it has not yet been resolved into any more simple form, it is still arranged among

elementary bodies. The date of the discovery of hydrogen gas does not appear to be clearly ascertained; but it seems to have been first attentively examined by Mr. Cavendish. It has been termed *inflammable*, or *light inflammable* air, and received its present appellation for a reason which will be stated in the sequel.

I. *To procure hydrogen gas*, let sulphuric acid, previously diluted with five or six times its weight of water, be poured on iron filings or turnings, or on small iron nails; or (which is still better) pour sulphuric acid, diluted with eight parts by weight of water, on zinc,\* granulated by pouring it melted into cold water, and contained in a gas bottle or small retort. An effervescence will ensue, and the escaping gas may be collected in the usual manner. According to Mr. Cavendish, one ounce of zinc gives 356 oz. measures = about 676 cubic inches, and 1 oz. of iron filings, 412 oz. m. = 782 cubic inches, of hydrogen gas. An ingenious apparatus for obtaining it instantaneously in a laboratory is described by Gay Lussac, in the 5th vol. of *Ann. de Chim. et Phys.* p. 300; and the annexed cut shows its construction.

It consists of a three necked glass bottle, one of whose openings has a stopper from which is suspended a small cylinder of zinc. To the opposite aperture is fixed a bent brass tube furnished with a stop cock, on which may be screwed either a small jet for burning the gas, or a tube to conduct it wherever it may be required. The upper vessel is of glass, and ground to fit the middle neck, its pipe reaching within a small distance of the bottom of the bottle. To use the apparatus, the lower vessel is filled with sulphuric acid properly diluted, and the zinc cylinder is then introduced, the stopper being closed to which it is affixed, and the cover of the upper vessel removed. The gas, which is generated, drives the diluted acid into the upper vessel, and the further production



\* Zinc may be purchased at the brass-founders or copper-smiths, under the name of speltre.

of it ceases, when the zinc is completely uncovered. We have then the bottle filled with gas; and can at any time expel it by opening the cock, and allowing the atmosphere to press on the surface of the liquid in the globular vessel.

Hydrogen gas, thus obtained, is not to be considered as absolutely pure. An observation of Mr. Cuthbertson long ago rendered it probable that, when disengaged by zinc, it contains a portion of that metal; and, when generated by means of iron, it is apt to contain a little carbureted hydrogen. Mr. Donovan has also shown,\* that, when procured from zinc and dilute sulphuric acid, it is contaminated with sulphureted hydrogen and carbonic acid; and he recommends that to obtain pure hydrogen, we should first agitate common hydrogen with lime-water during a few minutes, next with a little nitrous acid, afterwards with solution of green sulphate of iron, and finally with water. It appears to me, however, that as the only impurities, discovered by Mr. Donovan in hydrogen gas, were carbonic acid and sulphureted hydrogen, they may be equally well removed by the simple process of washing the crude gas either with lime-water or with a solution of caustic potash; and Berzelius and Dulong, indeed, in their recent experiments, seem to have trusted entirely to the latter agent.

II. This gas has the following properties :

1. *It remains permanent over water, or is not absorbed in a proportion exceeding  $\frac{1}{30}$ th the bulk of the water.*

2. *It is not altered either by intense heat or by electric discharges. It refracts light more powerfully than any other gas.*

3. *As commonly procured, it has a disagreeable smell; but pure hydrogen gas was found by Mr. Donovan to be free from all odour.*

4. *It is inflammable.* This may be shown by the following experiments :

(a) Fill a small jar with the gas, and, holding it with the mouth downwards, bring the gas into contact with the flame of a candle. The air will take fire, and will burn silently with a lambent flame.

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\* Phil. Mag. xlviii. 138.

(b) Fill with this gas a bladder which is furnished with a stop-cock, and with a small pipe, of diameter less than that of a common tobacco pipe. Press the air out through the pipe, and, on presenting a lighted candle, the stream will take fire, and continue to burn with a pale and feeble flame, not well adapted to the purpose of artificial light.

Persons, who are provided with the jars represented pl. ii. fig. 22, *a*, may screw to the cock a brass pipe with a small aperture. On pressing the jar, filled with hydrogen gas, into the water, and opening the cock, the gas will be forced out in a stream, which may be set on fire. On this principle are founded the artificial fireworks without smell or smoke. They consist of pipes, having variously sized apertures, some of which have a rotatory motion; and to give greater brilliancy or variety of colour to the flame, the hydrogen gas is impregnated either with sulphuric ether, or some other substance that admits of being readily diffused through it.

(c) In a strong bottle, capable of holding about four ounces of water, mix two parts of common air and one of hydrogen gas. On applying a lighted candle, or a red hot wire, the mixture will burn, not silently, as in experiment (*a*), but with a sudden and loud explosion. If a larger bottle be used, it should be wrapped round with a handkerchief, to prevent the glass from doing any injury, in case the bottle should be burst.\*

Mr. Cavendish made a number of experiments on the effects of firing different proportions of hydrogen gas and common air. (Phil. Trans. vol. lvi.) Nine parts of air with one of hydrogen did not fire easily, and gave a feeble sound; and four parts of hydrogen with one of air caught fire without noise, and continued to burn only in the neck of the bottle. Four parts of hydrogen and six of air gave the loudest sound. He found indeed that it was necessary that the mixture should contain more air than inflammable gas; otherwise the whole of the latter is not consumed. From theory, five volumes of common air should be sufficient for two of hydrogen, for these are ade-

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\* These experiments may also be made advantageously by means of an apparatus sold under the name of the inflammable air-pistol.

quate to saturate one volume of oxygen which is contained in 5 of atmospheric air; but it is probable that a small excess of common air will render the combustion more perfect.

(*d*) The same experiment may be repeated with oxygen gas, instead of atmospherical air; changing the proportions, and mixing only one part of oxygen gas with two of hydrogen. The report will be considerably louder. The bottle should be a very strong one, and should be wrapped round with several folds of cloth to prevent an accident.

In this case also the combustion is imperfect, if much more or much less oxygen be employed, than is required to saturate the hydrogen. When the oxygen is  $9\frac{1}{2}$  times the volume of the hydrogen, or when, on the other hand, it is reduced to one-tenth of the bulk of the latter gas, the combustion in both cases is incomplete, and a portion of the hydrogen remains uncombusted. Sir H. Davy found that one measure of hydrogen and oxygen gases, mixed in due proportion for perfect combustion, was rendered unflammable by eight additional measures of hydrogen, or nine of oxygen.

(*e*) The combustion of these two gases may be made over water, by means of the electric spark. Procure a strong tube, about three quarters of an inch diameter, and 12 inches long, closed at one end (plate ii. fig. 29, *b*.) About a quarter or half an inch from the sealed end, let two small holes be drilled, opposite to each other, and into each of these let a brass conductor be cemented, so that the two points may be distant from each other within the tube, about one 8th of an inch. An apparatus, serving the same purpose, and much more easily constructed, may be formed by hermetically sealing a piece of brass wire, or, still better, platina wire, into the end of a glass tube (fig. 29, *a*). With this conductor, an interrupted circuit may be formed, by introducing into the tube a longer wire, one end of which terminates one 10th of an inch from the upper one, while the other extends beyond the aperture of the tube. (See fig. 84.) Into this tube, standing over water, pass about half a cubic inch of a mixture of hydrogen and oxygen gases, in the proportion of two measures of the former to one of the latter. Hold the tube firmly, and pass an electric spark through the mixed gases. For relieving the



shock which is sometimes considerable on firing, an ingenious contrivance of Sir H. Davy, described in the *Philosophical Magazine*, xxxi. 3, may be employed; or the one proposed by Dr. Ure, in the 12th vol. of *Annals of Philosophy*, p. 381. The first effect of the combustion is a sudden and considerable enlargement of volume, which, from some experiments of Sir H. Davy (on *Flame*, p. 90) probably amounts to 15 times the original bulk of the mixture. After this the gases, if pure, and in the proper proportion, will be found to have disappeared entirely.

It has been asserted by Grotthus, that a mixture of two measures of hydrogen gas with one of oxygen, cannot be inflamed by the electric spark, when expanded to 16 times its volume by diminished pressure; nor, when dilated by heat to only six times its volume. In the latter case, even a lighted taper, he asserts, does not kindle the mixture; but water is formed silently by a continued succession of electric sparks.\*

Oxygen and hydrogen gases, in the proportions to form water, it is admitted by Sir H. Davy, will not explode by the electric spark when mechanically rarefied 18 times; but when the tube containing the expanded gases was artificially heated so as nearly to soften, and the electric spark then passed, a feeble flash of light was visible, which is not consistent with the last mentioned experiments of Grotthus. Sir H. Davy found, also, that dilatation by heat, instead of diminishing the explosiveness of a mixture of hydrogen and oxygen gases in the proportions that saturate each other, on the contrary enabled them to explode at lower temperatures. Thus a mixture of two volumes of hydrogen and one of oxygen, being expanded by a spirit lamp to  $2\frac{1}{2}$  volumes, instantly exploded when the upper part of the tube containing it was made red hot by another spirit lamp. He even found that a heat much below redness (somewhere between the boiling point of mercury, and the greatest heat that can be given short of rendering glass luminous in the dark) occasions a mixture of hydrogen and oxygen gases to unite without violence or evolution of light; but that if, to a mixture so circumstanced, a red heat be suddenly applied, an explosion always takes place. (*On Flame*, p. 68.)

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\* 82 Ann. de Chimie, 37.

A glowing coal, if red in day light, and free from ashes, uniformly explodes a mixture of hydrogen and oxygen gases; but if its redness is barely visible in the shade, it will not explode them, but will cause their slow combination. This is not owing to rarefaction; for if an iron wire heated to whiteness be placed upon the coal within the vessel, the mixture instantly detonates.

It is rarely that oxygen and hydrogen gases can be used in such a state of purity as to leave absolutely no residuum. To determine, indeed, the purity either of the oxygen or hydrogen gas employed, it is sometimes necessary so to adjust their proportions, that the whole mixture may not be condensed by firing. If, for example, we wish to know the purity of a quantity of oxygen gas, we are to use about three times its bulk of hydrogen. Let us suppose that 100 measures of oxygen are detonated with 300 of hydrogen gas, and that the total 400 is reduced by firing to 130; the diminution of volume will be 270. This number, divided by three, gives 90 for the quantity of oxygen; that is, the oxygen gas employed must have contained 10 *per cent.* of nitrogen, or of some foreign gas not condensable by hydrogen.

If atmospherical air be employed, a diminution, though not equal in amount, will be produced by the union of the hydrogen with the oxygen gas contained in the air; and if a sufficient quantity of hydrogen gas be employed, the whole of the atmospherical oxygen will thus be removed. On this principle is founded the EUDIOMETER OF VOLTA, which may be constructed by graduating either of the tubes already described into equal parts.\* If, in one of these tubes, we mix 300 parts of common air, and 200 of pure hydrogen gas, there will remain, after the explosion excited by passing an electric spark between the two wires, about 305 measures. There will, therefore, have been a diminution of 195 measures, of which pretty exactly one 3d may be estimated to be pure oxygen. In this instance, therefore, 65 of oxygen have been lost by 300 of air, or 21 and a fraction *per cent.*

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\* A Volta's Eudiometer, invented by Gay Lussac, is described in *An. de Chim. et Phys.* iv. 188. See also Dr. Hare, in *Silliman's American Journal*, ii. 312.

The general rule for ascertaining the purity of atmospheric air by hydrogen gas, may be stated as follows: Add to three measures of the air under examination, two measures of pure hydrogen gas; inflame the mixture by electricity; observe the diminution when the vessel has cooled; and, dividing its amount by three, we obtain pretty nearly the quantity of oxygen gas which has been condensed.

In the reverse process, *i. e.* in determining the purity of hydrogen gas, we mix it with more oxygen gas than is required for saturation. Suppose that to 100 of hydrogen gas we add 100 of oxygen, and that 80 measures remain after detonation. The diminution will have been 120 measures; and of these, two thirds or 80 measures are hydrogen. Hence the inflammable gas under examination, must contain 20 *per cent.* of some other gas, which is most probably nitrogen. In this way we determine the proportions of hydrogen and nitrogen in any mixture composed of those two gases only.

(*f*) The diminution of hydrogen and oxygen gases, by the union of their bases, may be shown also by their slow combustion. Fill a tall jar with oxygen gas, and fill also, with hydrogen gas, a bladder furnished with a stop-cock, and with a long brass pipe bent like the letter S, and drawn out to a fine point (plate iv. fig. 41.) On pressing the bladder, a stream of gas will issue from the pipe, which may be set on fire, and brought cautiously under the tall inverted jar of oxygen gas. By this contrivance, the stream of hydrogen gas will be burnt in a confined portion of oxygen gas; and, on continuing the combustion a sufficient length of time, the water will be seen to rise gradually within the jar. On the first impression of the heat, indeed, a quantity of gas will escape from the jar, which will render it difficult to ascertain what degree of absorption has actually taken place. But this loss may be prevented, by using a jar with a neck at the top, to which a compressed bladder is firmly tied. The expanded air, instead of escaping through the water, will now fill the bladder at the top; and, when the experiment has closed, and the vessels have cooled, it may be ascertained, by pressing out the gas from the bladder, what quantity of oxygen gas has been consumed.

The same experiment may be more accurately and ele-

gantly made with the assistance of an apparatus which I have described in the Philosophical Transactions for 1808. The description cannot be understood without the plate, which is there given, and which has been copied into the Philosophical Magazine, xxxii. and Nicholson's Journal, xxi. The fact may, also, be shown by substituting, for the bladder (*e*, fig. 41), a small gazometer, containing a measured quantity of hydrogen gas. Let the bent pipe be screwed on the cock of the gazometer; and over its open end, placed perpendicularly, invert a jar of oxygen gas. This jar must be provided at the top with a metallic conductor, screwed into a brass cap, as represented in fig. 41; which shows also the level of the water within the jar, attained by means of a siphon. After noting the height of the water within, let a rapid succession of electric sparks be passed between the two conductors; and, on opening the cock at this instant, the stream of oxygen gas will be inflamed. The end of the pipe must then be so far depressed, that the cement of the brass cap may not be melted by the flame; and the outer surface of the top of the vessel should be kept cool. When the gas is first lighted, the oxygen gas will be suddenly expanded; but, presently a rapid diminution will go on, till the water rises above the end of the pipe, and extinguishes the flame. If pure oxygen gas be employed, it will be found, after the experiment, uninjured in its quality, and will support the combustion of burning bodies as well as before.

When the above experiment is made with the substitution of common air for oxygen gas, a diminution takes place, but much less considerable, *viz.* not amounting to one 6th of the original bulk of the gas.

(*g*) When a stream of hydrogen gas is burned under a tube 18 or 24 inches long, a musical sound is produced. The experiment may be made in the following manner:

Into a glass bottle are put iron filings and sulphuric acid, diluted with five or six parts of water; and a cork is fitted into the neck, through which a glass tube is passed, having its upper extremity drawn out to a capillary bore. By setting fire to the hydrogen gas,\* which escapes from this extremity,

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\* The gas must not be inflamed till it has been produced for some time,

a continued current or jet of flame is produced, which is allowed to pass into a tube either of glass, earthen ware, or metal. If the tube be not too large, the flame becomes smaller as it is depressed; and when the tube covers the flame to a considerable depth, very clear sounds are produced. But, on the contrary, if the tube be too narrow, the flame will be extinguished; and, in proportion as the tube is enlarged, the sound diminishes: so that there is a certain limit at which it totally ceases. The same happens when the tube is too long. The sounds may be raised at pleasure, by either using tubes of various figures or dimensions, or made of different substances.\*

(h) It has been discovered by M. Biot that a mixture of hydrogen and oxygen gases may be made to explode by mechanical compression. A mixture of these two gases was introduced into a strong metallic syringe, furnished with a glass bottom, and a sudden stroke given to the piston. An extremely brilliant light appeared, accompanied with a loud detonation; and the glass bottom was forcibly driven out. The repetition of this experiment, it is obvious, must be attended with some difficulty and danger.† The heat given out by the sudden compression of the gases is probably the cause of the combustion which is excited.

The combustion of hydrogen and oxygen gases was many years ago successfully applied by Dr. Hare of Philadelphia to the purpose of exciting an intense heat by the blow-pipe. The peculiar construction of the apparatus cannot be understood without a plate, which may be seen in the *Annales de Chimie*, tom. xlv. or in the 14th volume of the *Philosophical Magazine*. It may be sufficient here to state, that the gases are contained each in a separate gasholder; that they are expelled by the pressure of a column of water obtained by lengthening the pipe *b*, fig. 36; and that their mixture does not take place till they nearly reach the aperture of the pipe, at the extremity of which they are inflamed. This last pre-

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and has expelled all the common air of the bottle; otherwise an explosion will happen, and the bottle will be burst, with some danger to the operator.

\* See Nicholson's Journal, 8vo. i. 129, and iv. 23.

† See Nicholson's Journal, xii. 212.

caution is of considerable importance, because a violent and dangerous explosion would otherwise happen. To guard the more effectually against this accident, it is advisable to affix a valve, opening outwards, in the pipe proceeding from each gasholder, just before the junction of the two.

The power of hydrogen and oxygen gases to produce an intense degree of heat, has been much increased, in consequence of a suggestion of Mr. Newman to Professor Clarke of Cambridge, that the gases should be previously mixed, then condensed into a metallic reservoir, and made to pass through a capillary tube before being set on fire.\* (See plate x, fig. 4, 5, 6, and the Description of the Plates at the end of vol. ii.) The temperature thus produced was found adequate to the instantaneous fusion of the most refractory substances. Platinum, for instance, was not only immediately melted, but set on fire and consumed like iron wire in oxygen gas, with vivid scintillation. Considerable danger, however, arises to the operator, from the liability of the condensed gases to explode and burst the apparatus. Several expedients have been tried for the purpose of obviating this risk, the most effectual of which, suggested by Professor Cumming, consists in interposing, between the flame and the main reservoir of gases, a cylinder containing a little water or oil, through which, by means of a valve at the bottom, the gas is allowed to pass.† All, therefore, that can happen is the explosion of the mixed gases between the inflamed jet and the surface of the oil or water, where the quantity is not sufficient to occasion any serious mischief. The more effectually to guard against danger, Dr. Clarke has since, on the suggestion of Dr. Wollaston, interposed a fagot of capillary tubes of the smallest possible diameter, between the stop-cock and the orifice of the pipe at which the gases are inflamed.‡ Addi-

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\* Journal of Science, &c. ii. 104.

† Journal of Science, &c. ii. 379, where a plate of the improved apparatus is given.

‡ Thomson's Annals, ix. 327. Other improvements are suggested in the Journ. of Science, iii. 376; Edin. Journal, ii. 187; and Ann. of Philos. N. S. i. 428. The fullest information respecting the construction and use of this instrument may be found in Dr. Clarke's book on the Gas Blow-pipe, 8vo. London, 1819.

tional safety may, also, be given to the apparatus by interposing, between the operator and the reservoir, a strong screen, through which the piston rod of the syringe may be worked horizontally, and the flame may thus be kept up for a length of time proportionate to the size of the reservoir, from which the mixed gases are drawn.\* This modification of the instrument renders it applicable to some of the arts, in which not only an intense but a long continued heat is required.

4. *Hydrogen gas, though inflammable itself, extinguishes burning bodies.*—Bring an inverted jar, filled with this gas, over the flame of a candle; and suddenly depress the jar, so that the lighted wick may be wholly surrounded by the gas. The candle will be immediately extinguished.

5. *It is fatal to animals.*—This may be shown by confining, in the gas, a mouse or other small animal. It may, indeed, be breathed for some time, without inconvenience, when the lungs at the outset are filled with common air; but if a forcible expiration be made, before drawing in the hydrogen gas, only two or three inspirations of the latter can be made, and even these produce great feebleness and oppression about the chest. It has been found, also, to change the tone of the voice. This effect is observed, on the person speaking immediately after ceasing to breathe it; but it soon goes off. (Journ. of Science, ix. 182.)

6. *It is considerably lighter than atmospherical air, and indeed is the lightest of all elastic fluids.*—The earlier attempts to ascertain its specific gravity appear to have given too large numbers, probably on account of the impurity of the gas submitted to experiment. Kirwan made 100 cubic inches (thermometer 60°, barometer 30) to weigh 2.613 grains; Lavoisier 2.372; and Fourcroy, Vauquelin, and Seguin, 2.75. Even MM. Biot and Arago found the same quantity to weigh 2.23, which would make the specific gravity of the gas 0.07321. Dr. Thomson, by recent experiments (Ann. Phil. xvi. 168), reduces it to 0.06940, which is precisely the number deduced by Dr. Prout from the composition and specific gravity of am-

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\* Thomson's Annals, x. 373. Other improvements of the apparatus are described in the same work, x. 366.

monia. It does not appear, however, that Dr. Thomson operated on the gas artificially dried, and the aqueous vapour diffused through his gas would a little increase its specific gravity. Berzelius and Dulong, having taken the precaution to dry their hydrogen gas, found its specific gravity to be only 0.0688, from whence, taking 100 cubic inches of atmospheric air at 31 grains, we find 100 cubic inches of dry hydrogen gas, at a mean of the barometer and thermometer, to weigh 2.13 grains. (Ann. de Chim. et Phys. xv. 393.)

(a) Let a jar filled with this gas stand, for a few seconds, with its open mouth upwards. On letting down a candle, the gas will be found to have escaped.

(b) Place another jar of the gas inverted, or with its mouth downwards. The gas will now be found to remain a short time in the jar, being prevented from escaping upwards by the bottom and sides of the vessel.

(c) Fill, with hydrogen gas, a bladder furnished with a stop-cock; and adapt to this a common tobacco pipe. Dip the bowl of the pipe into a lather of soap, and, turning the cock, blow up the lather into bubbles. These bubbles, instead of falling to the ground, like those commonly blown by children, will rise rapidly into the air. On this property of hydrogen gas, is founded its application to the raising of balloons.

(d) The experiment may be varied by filling the bladder with a mixture of two parts of hydrogen gas, and one of oxygen gas. Bubbles, blown with this mixture, take fire on the approach of a lighted candle, and detonate with a loud report. It is proper, however, not to set them on fire, till they are completely detached from the bowl of the pipe; otherwise the contents of the bladder will be exploded, with considerable danger to the operator.

In this place a property of hydrogen gas may be described, which it possesses in common with all other æriform bodies, viz. a tendency to diffusion through any other elastic fluid, with which it may be brought into contact. Common or inelastic fluids are capable of remaining in contact with each other for a long time without admixture. Thus if we half fill



a wine glass with spirit of wine tinged with any colouring ingredient, and then, by means of the dropping tube, fig. 15, introduce under it a quantity of water, the spirit floats on the water, and the two surfaces remain perfectly distinct, provided we carefully avoid agitation or unequal changes of temperature. But this is not the case with elastic fluids or gases, which, it has been discovered by Mr. Dalton,\* penetrate each other, and become thoroughly mixed under all circumstances. The fact, with respect to hydrogen and oxygen gases, may be proved by a very simple apparatus.

Provide two glass vials, each of the capacity of about an ounce measure, and also a tube open at both ends, 10 inches long and one 20th inch bore. At each end, the tube is to be passed through a perforated cork, adapted to the necks of the vials. Fill one of the bottles with hydrogen gas, and the other with oxygen gas; place the latter on a table with its mouth upwards, and into this insert the tube secured by its cork. Then, holding the hydrogen bottle with its mouth downwards, fit it upon the cork at the top of the tube. The two bottles, thus connected, are to be suffered to remain in this perpendicular position. After standing two or three hours, separate the vials, and apply a lighted taper to their mouths, when it will almost certainly occasion an explosion in both. The hydrogen gas, though sixteen times lighter than the oxygen, must, therefore, have descended through the tube from the upper into the lower vial; and the oxygen gas, contrary to what might have been expected from its greater weight, must have ascended through the tube, and displaced the lighter hydrogen.

Experiments of this kind, it has been shown by Mr. Dalton, may be extended to all the other gases; but to prove the effect, tests of a different kind are necessary, which require a previous knowledge of the properties of these gases. They establish the conclusion, *that elastic fluids, which have a sufficiently free communication with each other, tend to mutual diffusion, and that this tendency is even sufficient to overcome the obstacle of specific gravity, the heavier rising into the*

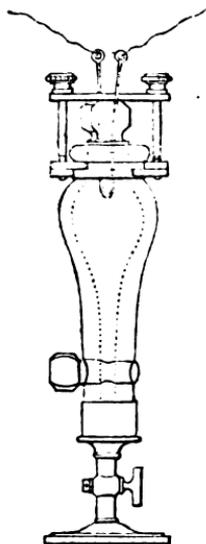
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\* Manchester Memoirs, vol. i. new series.

lighter, and the reverse. It is obvious, therefore, that different elastic fluids, when once thoroughly mixed, cannot separate, and arrange themselves according to their respective specific gravities.

ART. 1.—*Hydrogen with Oxygen.—Synthesis, or Composition, of Water.*

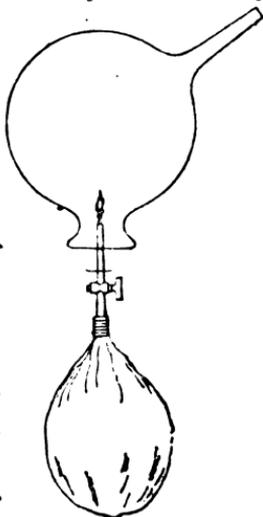
It has already been stated, that oxygen and hydrogen gases, when fired over water in the proper proportions, wholly disappear. To ascertain the nature of the product thus formed, the experiment must be repeated over mercury in a similar manner, by means of the detonating tube (pl. ii. fig. 28.,) or (which is still better) in a very strong glass vessel, (see the annexed figure) capable of holding about half a pint, and furnished, (besides the proper contrivance at the top, for taking an electric spark in it,) with a brass cap and cock, by means of which it can be screwed to the transfer plate of an air pump. When exhausted, it may be filled with a mixture of oxygen and hydrogen gases, in the proportion of one measure of the former to two of the latter, and an electric spark may be passed through the mixture. After the explosion, when time has been given to the vessel to cool, a sensible quantity of moisture will have condensed on the inner surface of the vessel, and by repeating the operation frequently, a sufficient quantity of fluid may be collected to show that water is the only product. The water, produced in this mode, is not, however, to be considered as a compound of the two gases, but only of their bases; for the light and caloric, which constituted the gases, escape, in considerable part, during the combustion. Every gas, it must be remembered, has at least two ingredients; the one, gravitating matter, which, if separate, would probably exist in a solid or liquid form; the other, an extremely subtile fluid, termed caloric. In the example before us, caloric (and perhaps elec-



tricity and light) is a common ingredient both of hydrogen and oxygen gases; but the two gases differ in having different bases. The basis of the one is called hydrogen, of the other oxygen; and water may, therefore, be affirmed to be a compound, not of hydrogen and oxygen gases, but of hydrogen and oxygen. Its composition may be proved in two modes; by synthesis, *i. e.* by joining together its two elementary ingredients; and by analysis, in other words, by separating its constituent parts, and again exhibiting them in a distinct form.

I. Fill, with hydrogen gas, a bladder, furnished with a stop-cock and bent pipe (fig. 41, *e*). Then pour into a shallow earthen dish as much quicksilver as will about half fill it, and invert over this a glass bell, full of common air and perfectly dry. Expel the hydrogen gas through the pipe; light the stream, and bring it under the glass bell, by raising this, and depressing it into the mercury, as soon as the inflamed gas is introduced. A portion of air will escape, at first, in consequence of the rarefaction. As the combustion continues, water will form, and will condense on the sides of the glass. This water is produced by the union of hydrogen with the oxygen contained in atmospheric air.

II. Those persons who are not possessed of a sufficient quantity of quicksilver to make the above experiment, may substitute the following: procure a large glass globe, capable of holding three or four quarts, and having two openings, one of which may resemble the pipe of a quilled receiver. In order to increase the condensing surface, the latter may be covered by a cylinder of thin glass closed at one end. In flame a stream of hydrogen gas, proceeding from a bladder (see the figure) and introduce it into the cavity of the globe. The rarefied and vitiated air will ascend through the aperture of the globe, and a constant supply of fresh air will be furnished from beneath. By this combustion, a quan-



tity of water will be generated, which will be condensed on the inner surface of the vessel.

III. A simple and ingenious apparatus, less costly than any other adapted to the purpose of exhibiting the composition of water, was invented by the late Mr. Cuthbertson. It is described and figured in Nicholson's Journal, 4to. ii. 235; or in the Philosophical Magazine, ii. 317; \* and also in plate iv. of this work, figs. 33 and 34.

In using this apparatus, however, instead of two glass receivers for the oxygen and hydrogen gases, standing inverted in a trough of water, I employ a couple of gazometers; and with this alteration, the experiment is more easily managed, as well as more striking. The apparatus, thus modified, consists of a large glass receiver or bottle *a* (pl. iv. fig. 34), with an opening at the bottom, into which is cemented a piece of brass, perforated with two holes. This brass piece is represented of a larger size in fig. 33; the aperture *a* conveying the oxygen gas, and *b* the hydrogen. Before commencing the experiment, the cock *e*, fig. 34, is screwed, by means of a collar-joint,† to the cock *b* of the gazometer, fig. 35, containing oxygen gas; and to the cock *d*, by the same means, is affixed another gazometer, filled with hydrogen gas.

When it is intended to ascertain, accurately, the proportions of gases consumed and of water generated, the receiver *a*, previously weighed, is first exhausted by an air-pump, with which it may be connected by the female screw at *c*. The quantity of common air left in the receiver may be determined, by enclosing a guage within it: or after exhausting the receiver, oxygen gas may be admitted; its contents pumped out a second time; and again renewed by fresh oxygen from the gazometer, the quantity of which may be measured by the graduated scale. The receiver being thus filled with

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\* In the same volume of the Philosophical Magazine, an interesting account may be consulted of the principal experiments on the composition of water, accompanied by neat and perspicuous engravings of the apparatus employed in them.

† See pl. v. fig. 47; and the corresponding description of the structure of this joint, in the explanation of the plates at the end of the work.

oxygen gas, and accurately closed by a cock at *c*, a succession of sparks is to be passed, from the prime conductor of an electrical machine, between the platina knob of the bent wire within the receiver, and the point of the brass cone. While the sparks are transmitted, the cock *d* is to be opened. A stream of hydrogen gas will immediately issue from the aperture at the point of the cone, and will be inflamed by the electric spark, as represented fig. 33. The cock *e* is now to be opened, and the size of the flame of hydrogen gas regulated by partly shutting the cock *d*. As the volume of hydrogen gas consumed is double that of the oxygen; and the pipe, which transmits it, is of less diameter than that conveying the latter, about twice the pressure is required to expel the hydrogen. This is given, by lessening, in that proportion, the weight of the counterpoises (*ee*, fig. 35) of the gazometer containing hydrogen.

During the combustion, the moveable vessel *c*, fig. 35, of each gazometer descends; and, by observing the graduated scales, it will be seen that the hydrogen vessel falls twice as much as that which holds the oxygen gas. It is necessary to keep the receiver *a* cool by means of wet cloths; and, when this is done, the water, which is produced, will condense into drops on the inside of the receiver, and collect at the bottom. At the conclusion of the experiment, the receiver is to be again weighed, and the increase noted. The quantity of gases consumed is to be observed, and their actual weight computed, by means of the table given in the Appendix. It will be found, that the weight of water produced is very nearly equal to that of the two gases expended: that is to say, for every hundred grains of water generated in the receiver, 88.3 grains of oxygen gas, and 11.7 grains of hydrogen gas (equal by measure to about 250 cubic inches of the former, and 500 of the latter), will have disappeared from the gazometers.

#### *Of the Proportion of the Elements of Water.*

The precise determination of the proportions of oxygen and hydrogen in water, is a problem of great importance, not only on account of the fact itself, but of its influence on the general

theory of chemistry. The results of almost all the earliest experiments tended to prove, that water is a compound of 85 parts by weight of oxygen, and 15 of hydrogen. These numbers were afterwards corrected by Fourcroy and his associates to 85.7 of oxygen, and 14.3 of hydrogen; and in 1805 it was shown by Humboldt and Gay Lussac, that the quantity of aqueous vapour, which gases always contain, being subtracted, it is a nearer approximation to truth to state the proportions at 87.4 and 12.6. It is admitted, on all hands, that water is formed by the union of two volumes of hydrogen gas, and one volume of oxygen gas. The greatest deviation from those numbers that has ever been contended for, is that 100 measures of oxygen gas combine with 197 measures of hydrogen. A difference, however, so difficult to ascertain, on account of its minuteness, may be neglected; and it may be safely assumed, that the general statement of one volume of oxygen to two of hydrogen is correct.

In determining the proportion of the elements of water, every thing will depend, therefore, on the precision with which the specific gravities of oxygen and hydrogen gases are ascertained. Taking the results of Biot and Arago (viz. 1.10359 for oxygen gas, and 0.07321 for hydrogen gas), the proportion of the elements of water should be as 1.10359 to 0.14642; and 100 grains should be composed of

Oxygen .....	88.286
Hydrogen .....	11.714
	—————
	100.

These proportions scarcely differ from those formerly determined by Berzelius (81 An. Ch. 25), viz.

Oxygen . . .	88.246 . . .	750.77 . . .	100
Hydrogen ..	11.754 . . .	100. . . .	13.33
	—————	—————	—————
	100.	850.77	113.33

The most recent experiments, however, on the specific gravities of oxygen and hydrogen gases, lead to an alteration in the statement of the composition of water, as determined by its synthesis. According to the results of Dr. Thomson,

oxygen gas is precisely 16 times heavier than hydrogen gas, and according to Berzelius and Dulong a little more than 16 times; but if we take 16 to 1 as the nearest approximation, it will follow, since water consists of two volumes of hydrogen and one of oxygen, that eight parts by weight of oxygen and one of hydrogen constitute water, or, according to the last mentioned chemists it consists of

Oxygen .....	88.9
Hydrogen .....	11.1

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100.

And if water be constituted of one atom of oxygen united with one atom of hydrogen, the atom of oxygen will be represented by 8, and that of hydrogen by 1; or, representing oxygen by 10, hydrogen will be denoted by 1.250. It must be allowed, however, to be possible, though it is a much less probable view of the subject, that water may be a compound of two atoms of hydrogen with one of oxygen, which would double the weight of the atom of oxygen, and make it 16. But it admits of being proved to be consistent with mechanical principles, that the most energetic combination of any two elements is that in which they are united particle to particle. Until, therefore, the contrary can be established, we may assume, with Mr. Dalton, that water is a binary compound of 1 atom of oxygen, and 1 atom of hydrogen: and, adding the weights of these atoms together ( $8 + 1$ ), an atom of water will weigh 9. The same proportions, expressed by different numbers, as proposed by Dr. Wollaston, will make the relative weight of an atom of water  $10 + 1.250 = 11.250$ ; the only difference in this way of stating the fact, being, that oxygen, instead of hydrogen, is made the decimal unit.

By the combustion of hydrogen gas, either in oxygen gas or in atmospheric air, a large quantity of heat is evolved, the source of which, as well as of the light which is also extricated, is probably to be traced both to the oxygen gas and to the combustible body. Several attempts have been made to measure the caloric thus set at liberty. Lavoisier, with the aid of his calorimeter, obtained results which led him to assign  $295\frac{1}{4}$  lbs. of ice as the quantity melted by the combustion of a pound of

hydrogen gas. Dr. Crawford, by a different process, made it 480 lbs.; and Mr. Dalton, from experiments on the rise of temperature produced in a known quantity of water by burning a given volume of hydrogen, calculates the ice melted by the combustion of a pound of hydrogen to be 320 lbs. The wide difference between these several numbers shows the necessity of fresh experiments on the subject.

*Analysis, or Decomposition, of Water.*

The analytic experiments on water are of two kinds: 1st, Such as present us with one of its ingredients only, in a separate and distinct form: 2dly, Such as present us with its two component principles, hydrogen and oxygen, mixed together in the state of gas.

I. Of the first kind are the following:

1. Procure a gun-barrel, the breech of which has been removed, so as to form a tube open at each end. Fill this with iron wire, coiled up in a spiral form. To one end of the barrel adapt a small glass retort, partly filled with water, and to the other a bent glass tube, the open end of which terminates under the shelf of the pneumatic cistern. Let the barrel be placed horizontally (or rather with that end, to which the retort is fixed, a little elevated) in a furnace, which has two openings in its body opposite to each other. (Pl. iv. fig. 40.) Light a fire in the furnace; and, when the gun-barrel has become red-hot, apply a lamp under the retort. The steam of the water will pass over the red-hot iron, and will be decomposed. Its oxygen will unite with the iron; and its hydrogen will be obtained in the form of a gas. This is the readiest and cheapest mode of procuring hydrogen gas, when wanted in considerable quantity.

2. The same experiment may be repeated; substituting an earthen tube for a gun-barrel, and weighing the iron wire accurately, both before and after the experiment. The iron will have gained weight very considerably; and, if attention be paid to the weight of the water that escapes decomposition, by an addition to the apparatus (fig. 40, *e*), and to the weight of the hydrogen gas obtained, it will be found, that the weight gained by the iron, added to that of the hydrogen



gas, will make up exactly the weight of the water that has disappeared.

3. Water may be decomposed, in a similar apparatus, over charcoal instead of iron. The products, however, are different in this case, as will appear from a subsequent section.

4. Another mode of effecting the decomposition of water yet remains to be mentioned, in which not the hydrogen, but the oxygen, is obtained in a gaseous state. This is by the action of living vegetables, either entire, or by means of their leaves only. Fill a clear glass globe with water, and put into it a number of green leaves, from almost any tree or plant. A sprig or two of mint will answer the purpose perfectly well. Invert the glass, or place it, with its mouth downwards, in a vessel of water. Expose the whole apparatus to the direct light of the sun, which will then fall on the leaves surrounded by water. Bubbles of air will soon begin to form on the leaves, and will increase in size, till at last they rise to the top of the vessel. This process may be carried on as long as the vegetable continues healthy; and the gas, when examined, will prove to be oxygen gas, nearly pure. In this experiment, the hydrogen combines with the plant, to the nourishment and support of which it contributes, while the oxygen is set at liberty.

II. The processes, by which the elementary parts of water are separated from each other, and are both obtained in an æriform state, as a mixture of hydrogen and oxygen gases, are dependent on the agency of electricity.

1. The first of these experiments requires for its performance the aid of a powerful electrical machine. This fact was the discovery of a society of Dutch chemists; and the principal circumstance, in the experiment, is the transmission of electrical shocks, through a confined portion of water. The apparatus employed, in the experiment of Messrs. Dieman and Van Troostwyk, is a glass tube, about one 8th of an inch diameter, and 12 inches long, one of the ends of which is sealed hermetically, a gold wire being inserted at this end, and projecting about an inch and a half within the tube. About the distance of five 8ths of an inch from the extremity of this, another wire is to be fixed, which may extend to the

open end of the tube. The tube is next to be filled with distilled water, and to be placed inverted in a vessel of the same. When thus disposed, electrical shocks are to be passed between the two ends of the wire, through the water; and, if these shocks be sufficiently strong, bubbles of air will be formed at each explosion, and will ascend till the upper part of the wire is uncovered by the water. As soon as this is effected, the next shock that is passed will set fire to the mixed gases, and the water will rise again in the tube, a very small quantity of gas remaining. Now, as hydrogen and oxygen gases, in a state of admixture, are the only ones that are capable of being inflamed by the electric spark; and as there is nothing in the tube, beside water, that can afford them in this experiment, we may safely infer, that the evolved hydrogen and oxygen gases arise from decomposed water.

2. An improved apparatus, exhibiting the same experiment, with less trouble to the operator, has been invented by Mr. Cuthbertson, and is described and figured in Dr. Pearson's paper in the Philosophical Transactions for 1797, or in Nicholson's Journal, vols. i. and ii. 4to.

3. The decomposition of water by galvanic electricity is a process singularly adapted to demonstrate the fact in a simple and elegant manner. The manner of conducting it, as well as the results, have been fully explained, in treating of the general principles of electro-chemical science.

#### *Properties of Water.\**

I. *Water contains air.*—This may be shown by placing a glass vessel of water under the receiver of an air-pump. During the exhaustion of the receiver, bubbles of air will be seen to ascend very plentifully. Much air escapes also from water, during boiling, and may be collected by a proper apparatus. The same fact may also be exhibited, by filling a barometer tube, about 32 inches long, sealed at one end, with quicksilver, except about four inches, and the remainder with water. On inverting the open end of the tube in quick-

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\* Whenever in the course of this work water is mentioned as an agent in any chemical operation, pure distilled water is to be understood.

silver, bubbles of air will, in a short time, rise from the water.

The kind of gas, extricated from the water of a spring at a considerable distance from the surface, I have made the subject of experiment.\* From 100 cubic inches of the water, or about  $3\frac{1}{2}$  wine pints, 4.76 cubic inches of gas were separated, of which 3.38 were carbonic acid gas, and 1.38 air of the same standard as that of the atmosphere. It is probable, however, that the proportion of gaseous contents differs in the water of different springs, for Mr. Dalton states the average of his experiments to be about 2 inches from 100 of water, and that the air expelled, after losing 5 or 10 per cent. of carbonic acid by the action of lime-water, consisted of 38 per cent. oxygen and 62 nitrogen.†

Every gas is absorbed by water, which has been deprived of all or the greatest part of its air by long boiling. The quantity, however, which water is capable of absorbing, varies considerably with respect to the different gases. Those gases, of which only a small proportion is absorbed, require violent and long continued agitation in contact with water. The following table has been drawn up by Mr. Dalton from the combined results of his own experiments and mine.

Water absorbs, at the mean pressure and temperature of the atmosphere,

Of carbonic acid gas . . . . .	its own bulk.
sulphureted hydrogen . . . . .	do.
nitrous oxide . . . . .	do.
olefiant gas. . . . .	$\frac{1}{8}$ .
oxygen gas. . . . .	$\frac{1}{7}$ .
nitrous gas. . . . .	do.
carbureted hydrogen. . . . .	do.
carbonic oxide. . . . .	$\frac{1}{8}$ .
azotic gas . . . . .	do.
hydrogen gas . . . . .	do.

The accuracy of these results has been called in question by Saussure,‡ who, from a series of experiments of his own, has

\* Philosophical Transactions, 1803.

† New System, p. 271.

‡ Thomson's Annals, vi. 340.

deduced the numbers expressed in the second column of the following Table.

Gases.	100 volumes of water absorb (Dalton and Henry)	100 volumes of water absorb (Saussure)
Sulphureted hydrogen . . . . .	100	253
Carbonic acid . . . . .	100	106
Nitrous oxide. . . . .	100	76
Olefiant gas. . . . .	12.5	15.3
Oxygen. . . . .	3.7	6.5
Carbonic oxide . . . . .	1.56	6.2
Azotic. . . . .	1.56	4.1
Hydrogen . . . . .	1.56	4.6

Absolutely pure water (not merely freed from air by boiling) according to recent experiments of Mr. Dalton, takes up  $2\frac{1}{2}$  per cent. of its bulk of azotic gas, and two per cent. of hydrogen. In the other gases, with the exception of carbonic oxide, which he had already in his System, p. 375, corrected to 1-27th the bulk of the water, he is disposed to abide by his original numbers, and to consider those of Saussure as much greater than the truth.\*

II. *Water is contained in the air of the atmosphere, even during the driest weather.*—Expose to the air, in a shallow vessel, a little sub-carbonate of potash or common salt of tartar. In a few days it will have become moist, or *deliquiated*. On the same principle, water exposed to the air, in a shallow vessel, disappears, being dissolved by the atmosphere. Saussure states the quantity of water in a cubic foot of air, charged with moisture at 65° of Fahrenheit, to be 11 grains. The quantity of water, that may be extracted from 100 cubical inches of air, at 57° Fahrenheit, is 0.35 of a grain; but, according to Clement and Desormes, at 54° Fahrenheit, only 0.236 of a grain can be detached by exposure to muriate of lime. The experiments, both of these chemists and of Mr. Dalton, concur in proving that at the same temperature, equal bulks of all the different gases give up the same quantity of water to deliquescent salts. The portion of humidity, which they thus

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\* Thomson's Annals, vii. 215.

abandon, has been called *hygrometric water*. Whether they contain a still farther quantity in a state of more intimate union, and not separable by deliquescent substances, is still undetermined.

III. Several bodies absorb water from the atmosphere, which can scarcely be supposed to have an affinity for it, and again give it up, on the application of a gentle heat. Such are almost all substances in the state of powder; porous paper; soils which have been artificially dried; parched oat-meal; and even the filings of metals. Some powders retain the moisture they have absorbed, till a considerable heat is applied.\* The nature of this combination is not exactly understood.

There are two different theories of the state, in which water exists in the atmosphere and in other gases. By most writers, it has been considered as united to air by chemical affinity; and, when abstracted by other bodies, (as sulphuric acid, lime, and the whole class of deliquescent salts) the effect has been ascribed to the superior affinity of those bodies for water. Mr. Dalton first took a different view of the subject, *viz.* that the vapour of water, mixed with air and other gases, differs in no respect from pure steam, and is subject to the same laws. It constitutes, indeed, in his opinion, a distinct and independent atmosphere, the elastic force of which forms, at different temperatures, different proportions of the elastic force of the whole; for example, at the temperature of 65° Fahrenheit, it gives to air  $\frac{1}{30}$  of its elasticity. According to this view, a volume of air or gas at any temperature, saturated with moisture, contains as much steam as could exist at that temperature in a vacuum of equal capacity. This theory appears to have much more probability, than that which explains the phenomena by chemical affinity; and it is supported, especially, by the absorption of caloric having been ascertained to be of the same amount in spontaneous as in forced evaporation. It steers clear, also, of the inconsistency attending the supposition, that the vapour, contained in the atmosphere at ordinary temperatures, is in a different state from that existing in a

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\* Berzelius, 79 An. Chim. 118.

Toricellian vacuum; and again, that water below  $212^{\circ}$  Fahr. is chemically combined with the atmosphere, and above  $212^{\circ}$  assumes a new form, and becomes a distinct elastic fluid called *steam*. It is certainly much more reasonable to suppose that water, whenever it exists as an elastic fluid, whether distinct from or mixed with others, is maintained as such, by one and the same cause, *viz.* the caloric which enters into it; and not by chemical solution in any gas or mixture of gases.

It may be asked, indeed, why the diffusion of vapour in the atmosphere is not instantaneous as it is *in vacuo*? This appears to be owing to the *vis inertiae* of the particles of air, and the resistance is probably similar to that which a stream of water meets in descending through a bed of pebbles. The evaporation of water, we find, is accelerated either by raising its temperature; by increasing its surface; or by causing a current of air to pass over it. In the first case, the force of the vapour, or its power of overcoming obstacles, is increased; and the quantity of water evaporated in a given time bears, as Mr. Dalton found, a proportion to the force of vapour of the same temperature: Thus the forces of vapour at  $212^{\circ}$ ,  $180^{\circ}$ ,  $164^{\circ}$ ,  $152^{\circ}$ ,  $144^{\circ}$ , and  $138^{\circ}$  are equal to 30, 15, 10,  $7\frac{1}{3}$ , 6, and 5 inches of mercury respectively, and the grains of water evaporated *per minute* in those temperatures were 30, 15, 10, 7, 6, and 5 also, or numbers proportional to these. The evaporation from a vessel containing water at  $212^{\circ}$  in a still atmosphere, Mr. Dalton found, was increased one half by a current, and a still stronger current, he thinks it probable, would have doubled it. In this case, the removal of a mechanical obstacle conspires with the force of the vapour; and as steam rises only from the surface of water, it is obvious that increase of surface must quicken evaporation by augmenting the quantity of vapour of a given force. Another circumstance, influencing the rate of evaporation, is the force of the vapour actually existing in the atmosphere at the time, for the less this force, or in other words the less the quantity of vapour in the air, the more rapid is the evaporation from a given surface of water of a given temperature. Hence an increase of temperature in the air quickens evaporation by enabling the atmosphere to hold steam of greater force; and

by a current of heated air, we apply two causes conjointly both of which tend to quicken evaporation.

The method of finding the force of vapour in the atmosphere, employed by Mr. Dalton, is extremely simple and elegant. A glass jar, or a common tumbler (the thinner the glass the better) may be filled with cold spring water fresh from the well. If dew be immediately formed on the outside, the water is poured out and allowed to stand awhile to increase in heat; the glass is then well dried with a linen cloth, and the water poured in again. This operation is continued till dew ceases to be formed, and then the temperature of the water is to be observed, and opposite to it in the Table (see the Appendix) will be found the force of vapour in the atmosphere. This must be done either in the air or at an open window; because the air within is generally more humid than that without. Spring water in this country is commonly about 50° Fahr., and will mostly answer the purpose during the three hottest months of the year: in other seasons, artificial cold, produced by dissolving a little of any fit neutral salt in the water, is required.

In the torrid zone, the aqueous atmosphere is equal to a pressure of six tenths of an inch of mercury, and increases even to one inch. In this climate, Mr. Dalton has observed it above half an inch in summer; but in winter it is sometimes so low as one tenth, or even half a tenth; and at the same place, and during the same season, it is constantly varying with the temperature of the air. It is easy then to see, at any time, what proportion it constitutes of the whole weight of the atmosphere by taking the *dew point*; observing the barometer at the time when the experiment is made; and referring to Mr. Dalton's Table of the Force of Vapour.

Besides this method of determining the degree of moisture of the air by ascertaining the *dew point*, a variety of instruments have been also contrived for the same purpose. They are called *Hygrometers*, and consist, for the most part, of some substance, such as a human hair or a fine slip of whalebone, which is elongated by a moist atmosphere, and shortened by a dry one. The extreme points are attained by placing it, first in air artificially dried, and then in air ren-

dered as humid as possible. The degree of expansion or contraction is rendered more sensible by connecting it with an axis, which moves a circular index, like the finger of a clock. Mr. Leslie, by a slight modification of his differential thermometer, makes it serve the purpose of an hygrometer; for if one of the balls be covered with silk, and then moistened with water, the rate of evaporation will be shown by the degree of cold produced, as indicated by the descent of the liquid in the opposite leg of the instrument. The drier the air, the quicker will be the evaporation, and the greater the effect in moving the liquid within the instrument.

IV. *Water enters into combination with various solid bodies, and entirely loses its fluid form.* In many instances, it unites in a definite proportion; and it is retained by so powerful an affinity, as not to be separated by a very high temperature. Such compounds are termed *hydrates*, or, as Gay Lussac has proposed, *hydroxures*.\* The pure alkalies, potash, and soda, retain, for example, even after fusion, about  $\frac{1}{3}$  their weight of water, which can only be separated by some body having a stronger affinity for the alkali. In all hydrates, at least one atom of water must be present, or it must be contained in them in such quantity, as to bear the proportion of 9 at least to the weight of the atom or atoms with which it is united. If, for example, the weight of the atom of potash be 48, we cannot have a true binary compound of water and potash, in which the former bears to the latter a less proportion than that of 9 to 48. And if, in any instance, water is obtained from a compound in a proportion less than that of the weight of the atom of water, to the weight of the atom or atoms of the body with which it is associated, we may take for granted that it is held mechanically and accidentally, and not as a true chemical constituent. Such appears to be the nature of the union of water with certain neutral salts (common salt and sulphate of potash for example) which contain only 1 or 2 per cent of their weight of water.

V. *Water dissolves a great variety of solid bodies.*—The substances, on which it exerts this effect, are said to be soluble in

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\* Ann. de Chim. et Phys. i. 170.



water ; and there are various degrees of solubility. See chap. i. and the table in the Appendix.

VI. *During the solution of bodies in water, a change of temperature ensues.*—In most instances, an absorption of caloric (in other words, a production of cold) is attendant on solution, as in the examples given in the chapter on caloric. But, in other cases, caloric is evolved, or heat is produced. Thus, common salt of tartar, during solution in water, raises the temperature of its solvent ; and caustic potash, in a state of dryness, does the same still more remarkably. But carbonated and pure potash, when crystallized, observe the usual law, and absorb caloric during solution. Now as their difference, in the crystallized and uncrystallized state, depends chiefly on their containing in the former, but not in the latter, water chemically combined, we may infer, that the cold, produced during the solution of salts, is occasioned by the conversion of the water, which exists in these bodies, from a solid to a liquid form. Some doubt, it must be acknowledged, is thrown on this conclusion by the observation of Gay Lussac, that a saturated solution of nitrate of ammonia, when mixed with water of the same temperature, is cooled 8 or 9 degrees.\*

VII. *During the solution of salts in water, a quantity of air is disengaged.*—This air was partly contained mechanically in the salt, and partly in the water. That it does not arise entirely from the former source, is proved by varying the experiment in the following manner. Let an ounce or two of sulphate of soda be put into a vial, and on this let as much water be poured as will completely fill the bottle. The air contained in the pores of the salt will be thus disengaged ; but only a small portion of the salt will be dissolved. Let the vial be shaken, and the whole of the salt will disappear ; a fresh portion of air being liberated during its solution.

VIII. *During the solution of bodies, the bulk of water changes.*—Take a glass globe, furnished with a long narrow neck (commonly termed a matrass, see fig. 4), and put into it an ounce or two of sulphate of soda. Then, add as much water

as will fill the globe, and about three 4ths of the neck. This should be done with as little agitation as possible, in order that the salt may not dissolve, till required. Mark, by tying a little thread, or by a scratch with a file, the line where the water stands; and then agitate the matrass. The salt will dissolve; air will be set at liberty; and, during the solution, the water will sink considerably below its level. The contraction of bulk is owing to the diminution of temperature; and, when the water has regained its former temperature, it will be found that its bulk is increased by the addition of the salt. The late Bishop Watson observed, that water exhibits a manifest augmentation of bulk, by dissolving only the two thousandth part of its weight of salt; a fact sufficiently decisive against that theory, which supposes pores in water capable of receiving saline bodies without an augmentation of volume.

IX. *Water appears to have its solvent power increased, by diminishing the pressure of the atmosphere.*—Into a Florence flask, put half a pound of sulphate of soda; pour on it barely a pint of water, and apply heat so as to boil the water. The whole of the salt will be dissolved. Boil the solution for several minutes pretty strongly, so as to drive out the air; and cork the bottle tightly, immediately on its removal from the fire. To prevent more completely the admission of air, tie the cork over with bladder. As the vessel cools, an imperfect vacuum will be formed over the solution; for the steam, which arises during the ebullition, expels the air, and takes its place. The steam is condensed again, when the vessel cools. The solution, when perfectly cold, may be shaken without any effect ensuing, so long as the vessel is kept closely stopped; but, on removing the cork and shaking the vessel, the solution will immediately congeal, and heat will be produced. This experiment, besides the principle which it is peculiarly intended to illustrate, exemplifies also the general rule already laid down, that caloric is always evolved, during the transition of bodies from a fluid to a solid state; and it furnishes a fact exactly the reverse of that in which cold is produced, or caloric absorbed, during the solution of salts. It is proper, however, to remark that the observa-

tions of Dr. Coxe, of Philadelphia,\* have thrown some doubt over the cause of these phenomena, which appears to require farther investigation. From his experiments, the exclusion of air does not seem to be absolutely necessary; for saline solutions continued fluid, if perfectly at rest, though freely exposed to the atmosphere, but immediately became solid when shaken.\* The efficacy of mechanical disturbance in promoting saline crystallization, under circumstances where it has been ascribed to the renewed contact of air with the surface of the solution, is illustrated also by some experiments of Dr. Ure.†

X. It is unnecessary to add any thing to what has been already said in a former section, respecting the combination of caloric with water constituting steam; or to the history of the phenomena attending its conversion into ice; except that, during the latter change, its bulk is enlarged in the proportion of nine to eight, and that, in consequence of this expansion, water, during congelation, is capable of bursting the strongest iron vessels, and becomes specifically lighter. Hence, ice swims always on the surface of the water.

It is remarkable, that this enlargement of the bulk of water begins, long before its temperature has descended to the freezing point, *viz.* at about 40° Fahrenheit. Let a thermometer bulb, and part of its tube, having a wide bore, be filled with water tinged with a little litmus, which may be introduced by the same means as those already directed for filling with quicksilver. Immerse the bulb in water of the temperature of 40°; and, when the included water may be supposed to have attained the same degree of heat, remove the instrument successively into water of the temperature of 36° and 32°. At each immersion, the water will rise in the tube. Bring its temperature again to 40°, and it will descend to the same point as before. Place it in water of 50°, and it will again be expanded. Precisely similar effects, therefore, appear to result, in these experiments, from two opposite causes; for the bulk of water is alike increased by reducing or raising its temperature. The point, at which water is of the greatest density,

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\* Thomson's Annals, vi. 101.

† Journal of Science, &c. v. 106.

was fixed by De Luc at  $41^{\circ}$  Fahr.; by Sir C. Blagden and Mr. Gilpin at  $39^{\circ}$ ; and by Dr. Hope and Count Rumford, somewhere between  $39^{\circ}$  and  $40^{\circ}$ . It is contended, however, by Mr. Dalton, that, in the apparent expansion by a lower temperature, there is a deception, arising from the contraction of the glass, which must lessen the capacity of the bulb, and force the water up the stem. He apprehends, therefore, that the point of greatest density has been fixed too high by Count Rumford, Dr. Hope, and other philosophers, and that it is in reality  $36^{\circ}$  of Fahrenheit, or  $4^{\circ}$  above the freezing point. M. Biot infers also that the true maximum of density is at  $38.16$  of Fahr.\*

#### *Deutoxide or Peroxide of Hydrogen.*

Only one compound of hydrogen and oxygen, namely water, was known until, in July 1818, M. Thenard discovered, that by a process somewhat difficult and complicated, an additional dose of oxygen may be communicated to that fluid; and a compound obtained, which is possessed of a new and very remarkable train of properties.

To obtain this product, it is necessary to employ a substance, the nature and preparation of which will be described in the section on *barium*, viz. the *peroxide* of that metal. This compound, when acted upon by liquid hydro-chloric (muriatic) acid, abandons part of its oxygen, and is reduced to the state of protoxide (baryta), which unites with the muriatic acid, while the oxygen unites with the water. Sulphuric acid, added to the compound fluid, carries down the barytes, and sets muriatic acid at liberty, which is ready to act upon a fresh quantity of the peroxide of barium. This operation may be several times repeated, and at each repetition the water becomes charged with an additional quantity of oxygen. When the process has been carried far enough, sulphate of silver is added, to precipitate the free muriatic acid, which it replaces by a quantity of free sulphuric acid; but the latter is easily separated by adding a due proportion of barytes. This is a general outline of the process, to insure the perfect success of which seems to require many precautions, and especially the greatest attention

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\* Thomson's Annals, ix. 434.

to the purity of the peroxide of barium. Very minute instructions for the preparation of this oxygenated water are given by its discoverer, M. Thenard; but they would occupy too much room here, and I refer therefore for a detail of them to his Memoir on the subject.\*

The peroxide of hydrogen is liquid and colourless like water. It has scarcely any smell, but when applied to the tongue whitens it, thickens the saliva, and produces a taste like that of some strong metallic solutions. It attacks the skin with great rapidity, bleaches it, and occasions a smarting, the duration of which differs in different persons, and in the same person according to the quantity applied. Its specific gravity is 1.452, and when poured into water it descends through it like syrup, though easily dissolved by agitation. Its tendency to the vaporous form is much less than that of water, and hence, when very dilute, it may be concentrated by exposing it under the receiver of an air-pump, along with any strongly deliquescent substance. If continued long in this situation, however, it at length disappears. In its most concentrated form, it has not been congealed by any degree of artificial cold yet applied to it.

When once prepared, it is necessary to keep it surrounded by ice, for a temperature of 58° Fahr. is sufficient to decompose it, and to liberate oxygen gas in great abundance. The action of heat varies with its degree of concentration. Seven or eight grains of the sp. gr. 1.452 are sufficient to occasion a violent explosion; and therefore to obtain safely the whole of its excess of oxygen above that constituting water, it is necessary, before applying heat, to dilute it with about 20 parts by weight of water. By experiments of this kind, carefully made, M. Thenard ascertained that, admitting water to be composed of 11.71 hydrogen and 88.29 oxygen, this new compound contains exactly double that quantity of oxygen, or 11.71 hydrogen, and 176.58 oxygen, or

Hydrogen .....	1
Oxygen .....	16

If water then be a compound of one atom of hydrogen and

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\* Ann. de Chim. et Phys. viii, ix.; Ann. of Philos. xiii, xiv, xv; and Quarterly Journ. vi. 150, 379. viii. 114, 154.

one of oxygen, the peroxide must consist of one atom of hydrogen and two of oxygen, and its representative number (hydrogen being unity) will be 17, or oxygen being 10 it will be 21.250.

Light does not exert any speedy operation on the peroxide of hydrogen. Of the metals, tin, iron, antimony, and tellurium, bring it back rapidly to the state of water. Some metals, as silver, platina, gold, &c., when finely divided and added to it, liberate its oxygen without themselves undergoing any change, in a way which is not easily explained. Others (arsenic, molybdena, tungsten, potassium, sodium, &c.) liberate one part of the oxygen and absorb the rest. Acids render it a more stable compound. For example, when to diluted peroxide of hydrogen, effervescing from the application of an increased temperature, we add phosphoric, sulphuric, muriatic, arsenic, acetic, tartaric, citric, or oxalic acid, the discharge of gas is suspended. Carbonic and boracic acids do not produce this effect, on account probably of their feeble powers as acids. Sulphurous and hydriodic acids, and sulphureted hydrogen, decompose the peroxide, and possess themselves of its oxygen.

The following substances, when added to the concentrated peroxide, occasion explosions of greater or less violence; oxide of silver, peroxide of lead, peroxide of manganese artificially prepared, osmium, silver, and platina, the two last in the finest state of division in which they can be obtained by chemical precipitation.

**ART. 2.—Hydrogen with Chlorine.—Hydro-Chloric or Muriatic Acid.**

Chlorine and hydrogen gases act with considerable energy upon each other, and with different phenomena accordingly as the experiment is conducted.

1. If a phial be entirely filled with a mixture of hydrogen and chlorine gases in equal proportions, and a well ground stopper be introduced; no action takes place, provided light is carefully and completely excluded, even by standing some time; but on applying a lighted taper, the gases immediately explode.

2. Let a jar, fig. 22. *a*, guarded from the light, be half filled with chlorine gas and half with hydrogen, and a stout vessel capable of holding 4 or 6 cubical inches, and provided with a fit contrivance for passing an electric spark through it, (see page 244) be first exhausted by the air-pump, and then screwed upon *a*, and filled with the mixed gases. An electric spark may now be passed through the mixture, when a detonation will ensue, to avoid any injury from which the vessel should be wrapped in several folds of cloth. If the cock, attached to the vessel, be opened under mercury in about a quarter of an hour, none of that fluid will enter, proving that the volume of gas after the experiment is not diminished; but if it be removed to a vessel of water, and left there for a few minutes, the water will be found to have ascended and entirely filled the vessel. Hence a gas must have been generated by the combustion, which, though not absorbable by mercury, is condensable by water.

3. Let a stout and well stoppered vial, capable of holding three or four ounce measures, be filled over water with equal volumes of chlorine and hydrogen gases, and a ground stopper introduced. Expose it to the ordinary day-light, guarding it from the direct rays of the sun, and in 12 or 14 hours the colour of the chlorine will have disappeared; and on withdrawing the stopper under water, the vial will be immediately filled with that fluid.

4. If the experiment be repeated, with this difference that the phial is exposed to the direct rays of the sun, the combination will take place rapidly, and a detonation will ensue, which will probably drive out the stopper. But if this should not happen, the stopper may be removed under water, which will ascend and completely fill the bottle as in experiment 3.

This effect of solar light, in promoting the action of chlorine and hydrogen gases on each other, was discovered by Gay Lussac, and, without any knowledge of his experiments, about the same period by Mr. Dalton. The agency of light may be beautifully shewn by filling a tube about half an inch diameter, and 12 inches long, with the mixed gases, and alternately shading it with an opaque cover, and exposing it to the sun's rays.

The moment the tube is exposed even to the diffused light of day, a cloudiness will appear within it, and the water will ascend more or less rapidly according to the intensity of the light. The effect even of a passing cloud is distinctly seen in retarding the rapidity of the combination, which is very striking in the full solar light. Blue light, it has been observed by Seebeck,\* is more effectual than red; but neither occasions the rapid union which is excited by the direct rays of the sun. It is probable that in this case, the combination is favoured by increase of temperature, for it has been observed by Sir H. Davy that a mixture of chlorine and hydrogen inflames at a much lower temperature than one of oxygen and hydrogen gases, and produces a more considerable degree of heat in combustion. He ascertained, also, that the former mixture will bear a much greater rarefaction than the latter, without losing its explosive property. Oxygen and hydrogen gases ceased to explode when rarified 18 times, but chlorine and hydrogen were still combustible, when mechanically expanded to 24 times their volume.

5. It had been supposed that the direct beams of the sun were necessary to explode a mixture of chlorine and hydrogen gases; but Professor Silliman, in the *American Journal of Science* (iii. 342) has related the accidental explosion of a mixture of the gases, in the quantity that filled a Florence oil flask, not only when no direct solar light fell upon it, but when the diffuse light of day was rendered more feeble than common by a thick snow storm. This fact is important, as furnishing a caution against mixing the two gases in considerable quantities.

6. Mr. Brande found (*Phil. Trans.* 1820) that the intense light, issuing from charcoal points connected with a powerful galvanic battery, was as effectual as solar light in acting on hydrogen and chlorine gases, and causing them to detonate; but he could not produce an analogous effect by any other terrestrial light. The moon's rays, also, he found to be quite inefficient on a mixture of these two gases.

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\* 34 *Nicholson's Jour.* p. 220.



*Muriatic or Hydrochloric Acid Gas.*

When one volume of hydrogen gas has been made to combine, either silently or explosively, with one volume of chlorine, the product is two volumes of a new gas, differing essentially from either of its components, and especially in being instantly absorbed by water. To preserve it, therefore, in a gaseous state, it is necessary to confine it by quicksilver.

As the elements of the new gas unite without condensation, its specific gravity will necessarily be the mean between those of its components, which, taking hydrogen at 0.0688, and chlorine at 2.500, is 1.2844, a number almost exactly agreeing with the experimental result of Dr. Thomson, but exceeding that of Biot and Arago. On this occasion, as on others, there is perhaps reason to believe that we are not in possession of the true relative weights of the gases. But admitting the relative weights of hydrogen and chlorine under equal volumes to be as 1 to 36, and that hydrochloric acid gas is constituted of an atom of each, the compound atom will be equivalent to 37.

To obtain hydrochloric acid gas in sufficient quantity for the exhibition of its properties, the direct combination of chlorine and hydrogen gases is not an eligible process. It may be procured much more conveniently in the following manner. Let the tubulated gas bottle (plate ii. fig. 17) be about one-fourth, or one-third, filled with well dried muriate of soda (common salt) in lumps, not in powder. To this adapt the acid-holder, filled with concentrated sulphuric acid; and let the aperture of the bent pipe terminate under a jar filled with, and inverted in, quicksilver. Open the communication between the acid and the salt, by turning the cock; and immediately on the contact of these two bodies, an immense quantity of muriatic acid gas will be disengaged. A common or tubulated gas bottle, or tubulated retort, will answer sufficiently well for procuring the gas. The first portions, that come over, may be allowed to escape under a chimney; because they are contaminated by the admixture of common air present in the bottle. The subsequent portions may be preserved for use; and the pure gas will exhibit the following qualities:

(a) It has a very pungent smell; and is sufficiently caustic to blister the skin, when applied to it for some time.

(b) When brought into contact with common air, it occasions a white cloud. This is owing to its union with aqueous vapour, which is always present in the atmosphere.

(c) It extinguishes a lighted candle. Before the flame goes out, the upper part of it assumes a greenish hue, the cause of which has not yet been explained. A white vapour also surrounds the extinguished wick, owing to the combination of water, produced by the combustion of the candle, with the muriatic acid gas.

(d) It is heavier than common air. Gay Lussac states its specific gravity at 1.278, and hence 100 cubic inches weigh, as nearly as possible, 39 grains; according to Sir H. Davy between 39 and 40, or to Mr. Brande 38.8. Biot and Arago make its specific gravity, by experiment, 1.2474, or, by calculation 1.2505. Dr. Thomson finds it, by experiment, 1.28436; by calculation, 1.28472.

(e) When a succession of electrical discharges is passed through muriatic acid gas in contact only with glass, by means of an apparatus which I have described in the Phil. Trans. for 1812, the gas is partly resolved into its elements, and after taking out the undecomposed muriatic acid gas by a few drops of water, we find a residuum of chlorine and hydrogen gases, in quantity never exceeding  $\frac{1}{3}$  the bulk of the original gas. When the disengaged gases rise above this proportion, they re-combine and form muriatic acid again. If the experiment be made over mercury, the presence of chlorine is rendered evident by its effect on the surface of that fluid.

(f) When a mixture of oxygen and muriatic acid gases is either electrified, or transmitted through a red hot porcelain tube, the oxygen unites with the hydrogen of the acid, and the chlorine of the latter is set at liberty.

(g) Muriatic acid gas effects the liquefaction of a piece of ice, almost as rapidly as it would be melted by a red-hot iron.

(h) It is very rapidly absorbed by water. A drop or two of water, admitted to a large jar full of this gas, causes the whole of it instantly to disappear. According to Mr. Kirwan, an ounce-measure troy of water absorbs 800 cubical

inches (*i. e.* 421 times its bulk) of muriatic acid gas; and the water, by this absorption, is increased about one-third its original volume. Sir H. Davy (*Elements*, p. 252) found that at 40° Fahr. water absorbs about 480 times its bulk of muriatic acid gas, and forms a solution of specific gravity 1.2109. One hundred grains of this acid, decomposed by nitrate of silver, indicated 40.8 of acid gas to have been condensed in it. Berthollet has shown that 100 grains of water absorb 12.467 grains (= about 32 cubic inches) of muriatic acid gas, deprived of all redundant water by passing it through a tube surrounded by a freezing mixture. By this absorption, he obtained an acid of the specific gravity 1061.4; and hence it follows that acid of this density contains, in 100 grains, only 8.55 of real acid.

It is in this state of watery combination that muriatic acid is kept for chemical purposes, and all the processes for preparing the liquid acid have for their object the disengagement of muriatic acid gas, and its absorption by water. This may be effected in the following manner.

*Process for preparing Liquid Hydrochloric or Muriatic Acid.*

Into a tubulated retort, placed in a sand-bath, put eight parts of dried chloride of sodium (common salt); and, to the tubulure, lute the bent tube (fig. 26, *a*,) with fat lute. To the neck of the retort, affix a tubulated receiver (fig. 30, *b*) by means of the same lute; and to the aperture of this adapt a tube, twice bent at right angles, and furnished with Welter's contrivance for preventing absorption (fig. 31, *b*), the longer leg of which terminates beneath the surface of water contained in a two-necked bottle. From the other neck, let a second right-angled pipe proceed; and this may terminate in a similar manner, in a second bottle containing water; the total quantity of which, in all the bottles, may be about five parts. Let the junctures be all carefully luted; and, when they are sufficiently hardened, pour very gradually, through the bent tube, five and a half parts by weight of strong sulphuric acid, making the additions at several distant intervals. On each affusion of the acid, a large quantity of muriatic acid gas will be liberated, and

will be absorbed by the water of the first bottle, till this has become saturated. It will then pass on to the second bottle, and be there condensed. The water employed may amount to half the weight of the salt, and may be equally distributed between the two bottles. These it is better to surround with cold water, or, still preferably, with ice or snow; because the condensation of the gas evolves considerable heat, which prevents the water from attaining its full impregnation. When the whole of the sulphuric acid has been added, and the gas no longer issues, let a fire be lighted in the furnace, beneath the sand-bath, removing the bent tube *a*, and substituting a well-ground glass stopper. This will renew the production of gas; and the temperature must be preserved, as long as gas continues to be evolved. At this period it is necessary to keep the luting, which connects the retort and receiver, perfectly cool; otherwise it will be apt to melt. To this juncture, indeed, I prefer the application of the clay and sand lute; but to apply this properly requires a little practice. Towards the close of the process, a dark-coloured liquid is condensed in the first receiver, consisting of a mixture of sulphuric and muriatic acids. When nothing more comes over, the operation may be suspended, and the liquid in the two receivers must be preserved in bottles with ground stoppers. It consists of liquid muriatic or hydro-chloric acid.

The liquid muriatic acid may also be obtained by diluting the sulphuric acid with the water necessary for the condensation of the gas, and adding the dilute acid, when cold, to the salt in the retort. To the retort, an adopter may be united with the clay and sand lute; and this may terminate in a large tubulated receiver, from the aperture of which a right-angled Welter's tube is conveyed beneath a few ounces of water, contained in a two-necked bottle. A fire must then be lighted under the sand-bath, and continued as long as any liquid comes over. The adopter and receiver must be kept cool, by the constant application of moistened cloths.

The proportions, directed by the London College of Physicians, in their Pharmacopœia of 1809, are those recommended by Vauquelin, *viz.* four parts of dried salt, three of sulphuric acid, and three of water, of which last one-third is

to be employed in diluting the acid, and two-thirds to be put into the receiver. Mr. R. Phillips had stated, that the water and acid are in unnecessary excess; and that the most economical proportions are 32 parts of salt, and 21.9 (say 22) of sulphuric acid of density 1.850, which may be diluted with one-third its weight of water, the remaining two-thirds being placed, as before, in the receiver.\* He has since, however, found reason to acquiesce in the greater economy of the proportions of the Edinburgh Pharmacopœia, which directs equal weights of common salt and sulphuric acid; for when no more sulphuric acid is used than the scale of equivalents requires, about one-sixth of the common salt escapes decomposition.

If the muriatic acid, thus obtained, should contain sulphuric acid, which may be discovered by muriate of barytes occasioning a white precipitate, the acid is to be re-distilled from a fresh portion of common salt. When prepared by Woulfe's apparatus, the product in the second bottle is always perfectly pure.

The acid, formed by the process of the College, has the specific gravity only of about 1.142; that of commerce is generally about 1.156; but by Woulfe's apparatus, and especially when the bottles are surrounded by ice or snow, it approaches 1.500. A fluid ounce of the specific gravity 1.142 dissolves 204 grains of marble; and the same quantity of sp. gr. 1.174 decomposes 240 grains. The intermediate degree of specific gravity, however, which has been mentioned (*viz.* 1.156 or thereabouts), is best adapted for keeping; for the denser acid emits a large quantity of fumes, which are extremely inconvenient, besides being injurious to all metallic instruments.

The *caput mortuum* consists of sulphate of soda with some undecomposed muriate of soda. The former may be obtained, in a crystallized form, by first driving off, by a strong heat, the excess of sulphuric acid that adheres to it; and then dissolving it in hot water. The product of sulphate of soda exceeds that of the muriate employed, in the proportion of about eight to five.

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\* On the London Pharmacop. p. 10.

Liquid muriatic acid has the following properties :

1. It emits white suffocating fumes. These consist of muriatic acid gas, which becomes visible by contact with the moisture of the air.

2. When heated in a retort, or gas bottle, muriatic acid gas is disengaged, and may be collected over mercury.

3. Liquid muriatic acid is not decomposed by the contact of charcoal, essential oils, or other combustible bodies.

4. When diluted with water, an elevation of temperature is produced, much less remarkable, however, than that occasioned by diluting sulphuric acid; and when the mixture has cooled to its former temperature, a diminution of volume is found to have ensued. The capacity of the diluted acid for heat, Dr. Ure has found to be less than the mean capacity of the strong acid and of water, which sufficiently accounts for the increased temperature.\*

5. In a perfectly pure state liquid muriatic acid is quite colourless; but it has frequently a yellowish hue. This may proceed, either from a portion of chlorine, or of muriate of iron, but most commonly of the latter. This colour is instantly destroyed by a few drops of muriate of tin; but this addition, instead of diminishing, obviously increases the impurity of the acid.

6. Muriatic acid combines readily with alkalies, and with most of the earths, both in their pure and carbonated states.

7. Liquid muriatic acid is specifically heavier than water. The correspondence between its specific gravity, and the quantity of real acid, which it contains, is shown by the following Table, given by Sir H. Davy in his *Elements of Chemical Philosophy*. It is constructed from experiments made with great care by Mr. E. Davy in the Laboratory of the Royal Institution.

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\* Thomson's Annals, x. 273.

*Table showing the Quantity of real Acid in Liquid Muriatic Acid of different Specific Gravities. (Temp. 45° Fahr. Barom. 30.)*

Specific Gravity.	100 Grains contain of Muriatic Acid Gas.	Specific Gravity.	100 Grains contain of Muriatic Acid Gas.
1.21	42.43	1.10	20.20
1.20	40.80	1.09	18.18
1.19	38.38	1.08	16.16
1.18	36.36	1.07	14.14
1.17	34.34	1.06	12.12
1.16	32.32	1.05	10.10
1.15	30.30	1.04	8.08
1.14	28.28	1.03	6.06
1.13	26.26	1.02	4.04
1.12	24.24	1.01	2.02
1.11	22.3		

The proportion of dry or real muriatic acid, in liquid acid of different densities, has also been investigated by Dr. Ure, who has ascertained that acid of density 1.192 contains in 100 parts by weight 28.3 of real muriatic acid; and has given some general formulæ for deducing the proportion of real acid, in liquid acid of various specific gravities.\* Of these, the most useful is the following rule for finding the quantity of real acid in liquid acid of any given density. Multiply the decimal part of the number denoting the specific gravity by 147, the product will be very nearly the per centage of dry acid, or by 197 when we want to know the per centage of the acid gas.

Examples. 1. The specific gravity being 1.141; required the proportion of dry acid in 100 parts.

$0.141 \times 147 = 20.72$ . By the Table it is 20.66.

2. The specific gravity being 1.960, required the quantity of acid gas.

$0.960 \times 197 = 18.9$ . By the Table it is 18.8.

The first rule shows directly the increase of weight, which any alkaline or earthy base will acquire by combining with the liquid acid. Thus if we unite 100 grs. of liquid acid of sp.

\* Thomson's Annals, x. 369.

gr. 1.134 with lime, the base will on evaporation to dryness be found to have gained 16.7 grains.

The Table, deduced from Dr. Ure's experiments, may be found in the Appendix at the end of vol. ii. As it does not include acid of greater specific gravity than 1.1920, if we wish to find the real acid in a liquid of greater density, it may be diluted with a known quantity of water, till brought within the range of the table.

8. When liquid muriatic acid is brought into contact with any substance containing oxygen in a state of loose combination, the hydrogen of the acid unites with the oxygen and forms water, while the chlorine is liberated in a gaseous state. It is in this way that chlorine is procured for the purposes of chemistry and the arts; but instead of liquid muriatic acid it is usual to substitute materials capable of furnishing the acid gas (*viz.* common salt, sulphuric acid, and oxide of manganese) as already described in the chapter on chlorine.

*On the Theories which have prevailed respecting Chlorine and Muriatic Acid.*

There are few subjects, respecting which the opinions of chemists have undergone such frequent changes, as concerning the nature of chlorine and of muriatic acid. The view originally taken by Scheele, the illustrious discoverer of the former substance, was, that the muriatic acid is compounded of a certain base and an imaginary principle called *phlogiston*; and that by the action of certain bodies, it becomes *dephlogisticated*, or deprived of that supposed principle of inflammability.\* It was afterwards found, however, that all bodies, which are capable of producing this change in muriatic acid, contain oxygen, and that their proportion of oxygen is diminished by the process. It appeared, therefore, to be an obvious conclusion, that what takes place in the action of metallic oxides on muriatic acid is simply the transference of oxygen from the oxide to the muriatic acid; and conformably with this theory, the resulting gas received the name of *oxygenated muriatic*, or *oxymuriatic acid*. Sir H. Davy was led, by his earlier experiments, to modify, in some degree,

\* On Manganese, § xxiii. xxiv.



this view of the theory of the process; and to consider the muriatic acid as a compound of a certain basis with water, and the oxymuriatic as a compound of the same basis with oxygen. This modification was rendered necessary by the fact, that when a metallic oxide is heated in muriatic acid gas, oxymuriatic acid is obtained, and water appears in a separate state. It was evident, therefore, that muriatic acid gas must either contain water ready formed; or the elements of water; or hydrogen, capable of composing water with the oxygen of the oxide. But, at a subsequent period, that distinguished philosopher was induced, by the experiments of Gay Lussac and Thenard, as well as by his own researches, to form a different theory on the subject. Oxymuriatic acid he now considers as a simple or undecomposed substance; and muriatic acid as a compound of that simple substance with hydrogen. To convert the muriatic acid into chlorine, we have only, according to this view, to abstract hydrogen from the muriatic acid; and this, it is believed, is all that is effected by the action of those oxides, which are adapted to the purpose. Again, to convert chlorine into muriatic acid, we have only to supply it with hydrogen; and accordingly the simple mixture of one measure of each of those gases, when exposed for a short time to the sun's rays, or exploded by an electric spark, affords two measures of muriatic acid gas.

The oxymuriatic acid or *chlorine* (as Sir H. Davy proposes to call it, in order to avoid all connection of its name with hypothetical views) is supposed, also, to unite at once with the metals, without requiring, like the sulphuric, nitric, and other acids, that the metals should first be in the state of oxides. In proof of this theory, it appears to be sufficiently established, that no oxygen can be obtained either alone, or in combination with combustible bodies added for the purpose, from the compounds of chlorine and metals. The analyses, however, of the metallic muriates, as they were formerly considered, remain unimpeached by this change of theory. All that is necessary, to transmute in idea a muriate into a compound of chlorine, is to deduct the oxygen from the metallic oxide; and, adding it to the muriatic acid, to consider the sum as chlorine. For example, muriate of soda, deprived of all water, consists,

On the old theory, of muriatic acid . . . . .	46
Soda composed of . . . . .	$\left\{ \begin{array}{l} \text{Oxygen} \dots 13.5 \\ \text{Sodium} \dots 40.5 \end{array} \right\}$
	100.

On the new theory, chloride of sodium consists of	
Sodium . . . . .	40.5
Chlorine, $46 + 13.5 =$ . . . . .	59.5
	100.

On the discarded theory of oxymuriatic acid, that supposed compound was stated to be constituted of

Oxygen . . . . .	22.65	. . . . .	100	. . . . .	29.28
Muriatic acid ..	77.35	. . . . .	341.5	. . . . .	100.
	100.		441.5		129.28

According to this view, the atom of muriatic acid, hydrogen being unity, and oxygen 8, would be nearly 28; and this + 8, (1 atom of oxygen) would give 36 for the atom of oxymuriatic acid. The latter number, indeed, still represents the atom of chlorine, as deduced from the fact that it unites with an equal volume of hydrogen gas, and is 36 times specifically heavier than that inflammable gas.

It is remarkable that there is hardly any fact, connected with the chemical history of chlorine and muriatic acid, that does not admit of being equally well explained upon the hypothesis that chlorine is a compound, as upon that of its being a simple substance. On the whole, however, the weight of evidence certainly appears to be very much in favour of the new, or rather the revived opinion of its elementary nature, especially since the discovery of iodine; and I have little scruple, therefore, in adopting it, as affording the most simple and satisfactory explanation of phenomena, as well as the best groundwork for a perspicuous arrangement of the objects of chemistry. Still, however, it must be allowed, that there are objections against its implicit acceptance, which this is not the proper place for stating at length.\* I shall only observe,

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\* The reader who wishes to examine fully the evidence for both opinions, is referred to the controversy between Drs. Murray and J. Davy in the 34th volume of Nicholson's Journal; to Sir H. Davy's paper in the

that not the least important of these objections is, the instantaneous conversion, which the theory of chlorine supposes, of the metallic combinations of that body, called *chlorides*, into muriates, when the former are dissolved in water, the oxygen of which is imagined to pass, in a moment, to the metal, while the hydrogen is attracted by the chlorine. In the present state of the inquiry, indeed, we stand in need of some fact, which will admit of explanation only on one of the opposed theories; and which shall serve the purpose of an *experimentum crucis*.

ART. 3.—*Hydrogen with Iodine.*

The affinity of iodine for hydrogen is very strong, and it absorbs that basis from hydrogen gas, and detaches it from several of its combinations, affording, as the result, a distinct and well characterized acid.

If iodine be heated in dry hydrogen gas, an expansion of volume takes place; an acid gas is formed, which is very absorbable by water, and acts so much on mercury that it cannot be preserved long over that metal. A similar gaseous compound is formed, by exposing iodine to sulphureted hydrogen gas. But the acid gas is best prepared, in quantity, by the action of moistened iodine and phosphorus on each other, the phosphorus being in excess, and the mixture distilled in a retort. The gas may be received into a vessel filled with common air, which it expels by its superior gravity. Gay Lussac recommends, instead of a retort, a small bent tube, which, after putting the iodine into it, is to be inverted over mercury; the air, which it contains, is to be expelled by a glass rod, that almost fills its capacity; and the phosphorus is to be brought into contact with the iodine, by introducing it through the mercury. As soon as the contact takes place, the acid gas is disengaged, and may be collected by putting the open end of the tube under a glass jar standing inverted in mercury.

No sooner does the gas come into contact with mercury, than it begins to be decomposed; and if the contact be pro-

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Phil. Trans. for 1818, p. 169; to the 8th volume of Trans. of the Royal Society of Edinburgh; the Annals of Philosophy, xii. 379, and xiii. 26, 285; and to a paper by Mr. R. Phillips, in the new series of that work, vol. i. p. 27, on the action of chlorides on water.

longed a sufficient time, or agitation be used, the decomposition is complete. The iodine unites with the mercury; and there remains hydrogen gas, in volume exactly one half that of the acid gas. It is decomposed, in a similar manner, by all metals, except gold and platinum.

The acid gas is colourless, its taste is very sour, and its smell resembles that of muriatic acid gas. Its specific gravity was found by experiment to be 4.449; by calculation it should have been 4.428. Compared with hydrogen its specific gravity is 62.5 to 1. 100 cubic inches weigh 133.6 grains.

The acid gas is rapidly decomposed by being heated in contact with oxygen gas, which detaches the hydrogen. Chlorine also instantly deprives it of hydrogen, and produces muriatic acid gas; and the iodine re-appears in the form of a beautiful violet vapour. When mixed with proto-phosphureted hydrogen, both gases are condensed into white cubical crystals, which are volatilized at a moderate heat without fusion or decomposition.\* It is composed, by weight, according to Gay Lussac, of 100 iodine and 0.849 hydrogen; but, correcting the specific gravity of hydrogen gas to 0.0694, its true composition will be, by weight,

Hydrogen.....	1
Iodine.....	125

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Weight of its atom ..... 126

For this compound Sir H. Davy proposed the name of *hydro-ionic acid*, and Gay Lussac that of *hydriodic acid*. I prefer the latter, because it is easier, by varying its termination, to express its combinations with alkaline and other bases.

*Hydriodic Acid Gas* is plentifully absorbed by water; the solution is fuming, and has the density of 1.7. To prepare this liquid in quantity, Gay Lussac recommends to put powdered iodine into water, and to pass sulphureted hydrogen gas through the mixture. The hydrogen unites with the iodine, and the sulphur is precipitated. The liquid may be concentrated by evaporation. Till it attains the temperature of 257°, water only distils; above this point, the acid itself is

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\* 6 Ann. de Chim. et Phys. 305.

volatilized, and remains stationary at  $262\frac{1}{4}^{\circ}$ , its density being then 1.7.

The liquid acid is slowly decomposed by contact with air, its hydrogen being attracted by the oxygen of the atmosphere, and a portion of iodine liberated, which gives the liquor a colour, of intensity proportionate to the quantity of free iodine. Concentrated sulphuric acid, nitric acid, and chlorine, decompose it, and separate iodine. With solutions of lead, it gives a fine orange precipitate; with solution of peroxide of mercury, a red one; and with silver, a white precipitate, insoluble in ammonia.

When submitted to Galvanic electricity, the liquid hydriodic acid is rapidly decomposed; iodine appears at the positive, and hydrogen at the negative pole. It dissolves zinc and iron, with a disengagement of hydrogen gas, which proceeds from the water. It has no action on mercury, though the gas so powerfully affects that metal. It is decomposed by those oxides, which hold their oxygen loosely, and combines with the rest, forming a genus of neutral salts, called *hydriodates*.

In general, the hydriodates are readily soluble in water. Those of potash and barytes are not decomposed by heat, except oxygen is in contact with them; the salt with base of lime is wholly, and that with base of magnesia partially, decomposed at high temperatures.

ART. 4.—*Hydrogen with Fluorine.—Of Hydro-fluoric acid.*

Though it has not yet been demonstrated that hydrogen is the acidifying principle of this acid, yet there appears every reason to believe that in the same manner as hydro-chloric acid is constituted of chlorine united with hydrogen, this acid also consists of a peculiar base belonging, like chlorine, to the electro-negative class of bodies, and rendered acid by combination with hydrogen. To this basis, though not yet exhibited in a separate state, the name of *fluorine* has been given, and the acid has been termed *hydro-fluoric*.

Hydro-fluoric acid may be obtained in a liquid state by distilling powdered fluor spar, (a mineral found abundantly in Derbyshire,) with twice its weight of strong sulphuric acid. A leaden retort and receiver must be used; to the first a moderate heat must be applied, and the receiver must be sur-

rounded by pounded ice or snow. An ingenious apparatus for this purpose is described and represented by Mr. Knight, in the 17th vol. of the Philosophical Magazine.

When the liquid acid is obtained, it must be preserved in leaden or silver bottles with air-tight stoppers of the same material. Its volatility, however, is such that it is difficult to confine it. Its specific gravity was found by Sir H. Davy to be 1.0609, but it is increased by the gradual additions of water to 1.25, a property observed in no other liquid. When suddenly mixed with water, it becomes very hot and enters into ebullition. It emits very penetrating and noxious vapours, and acts strongly on glass, destroying the polish of its surface, and corroding it deeply. Hence it has been used for etching on glass. When applied to the skin it raises painful pustules, or if in sufficient quantity occasions deep and dangerous ulcers.

When brought into contact with potassium, a violent detonation ensues, and hydrogen gas is disengaged, a solid white substance being at the same time formed. This substance is probably a compound of potassium and fluorine, or a *fluoride of potassium*. Common fluor spar is believed to be a *fluoride of calcium*, and the number deduced from the composition of that substance, as representing the atom of fluorine, is 16, to which adding an atom of hydrogen, we obtain 17 for the atom of hydro-fluoric acid.

By combination with silica, and also with boracic acid, hydro-fluoric acid becomes capable of forming a permanent gas, which property does not belong to it in a pure state. These compounds will be described under the respective heads of silica and of boracic acid.

*Charcoal* does not combine with iodine.

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## SECTION II.

### *Of Nitrogen or Azote.*

AFTER separating, from any quantity of atmospherical air, all the oxygen which it contains, there remains a gas which was called by Lavoisier *azotic gas*, a name applied to it in con-

sequence of its unfitness for supporting animal life: and derived from the Greek privative  $\alpha$  and  $\zeta\omega\acute{\nu}$  *vita*. This, however, as being merely a negative property, has since been deemed an improper foundation for its nomenclature: and the term NITROGEN gas has been substituted; because one of the most important properties of its base is, that by union with oxygen it composes nitric acid. By this appellation, therefore, I shall hereafter distinguish it.

I. Nitrogen gas may be procured, though not absolutely pure, yet sufficiently so for the purpose of exhibiting its general properties, in any of the following manners: 1. Mix equal weights of iron filings and sulphur into a paste with water, and place the mixture, in a proper vessel, over water, supported on a stand: then invert over it a jar full of common air, and allow this to stand exposed to the mixture for a day or two. The air contained in the jar will gradually diminish, as will appear from the ascent of the water within the jar, till at last only about four 5ths of its original bulk will remain. The vessel containing the iron and sulphur must next be removed, by withdrawing it through the water; and the remaining air may be made the subject of experiment.

2. A quicker process, for procuring nitrogen gas, consists in filling a bottle, about one 4th, with the solution of nitrous gas in liquid sulphate of iron, or with liquid sulphuret of lime, and agitating it with the air which fills the rest of the bottle. During the agitation the thumb must be firmly placed over the mouth of the bottle; and, when removed, the mouth of the bottle must be immersed in a cup full of the same solution, which will supply the place of the absorbed air. The agitation, and admission of fluid, must be renewed, alternately, as long as any absorption takes place.

3. Atmospheric air, also, in which phosphorus has burned out, affords, when time has been allowed for the condensation of the phosphoric acid, tolerably pure nitrogen gas.

4. Azotic gas may be procured from the lean part of flesh meat (beef for example), which may be put into a gas bottle, along with very dilute nitric acid. By a heat of about  $100^{\circ}$ , the gas is disengaged, and may be collected over water. Its source has been satisfactorily traced to the animal substance, no part of it proceeding from the nitric acid.

5. It may be obtained by the action of chlorine on ammonia, in a manner which will be afterwards described in speaking of that alkali.

II. Nitrogen gas has the following properties:

1. It is not absorbed by water.

2. *It is a little lighter than atmospheric air*, 100 cubic inches being found by Sir H. Davy to weigh 90.04 grains under a pressure of 30 inches, and at the temperature of 55° Fahrenheit. At 60° Fahrenheit 100 inches weigh, therefore, 29.73 grains. According to Biot and Arago, its specific gravity is 0.96913. Dr. Thomson makes it 0.9722; and Berzelius and Dulong 0.9760.

3. It immediately extinguishes a lighted candle, and all other burning substances. Even phosphorus, in a state of active inflammation, is instantly extinguished when immersed in nitrogen gas. This is best shown by placing the burning phosphorus in a tin cup, raised by a stand over the surface of the water, and quickly inverting over it a jar filled with nitrogen gas.

4. It is fatal to animals that are confined in it.

5. When mixed with pure oxygen gas, in the proportion of four parts to one of the latter, it composes a mixture resembling atmospheric air in all its properties. Of this any one may be satisfied, by mixing four parts of azotic gas with one of oxygen gas, and immersing, in the mixture, a lighted taper. The taper will burn as in atmospherical air.

#### *Composition of Nitrogen.*

That nitrogen is not an element, but itself a compound, has been long suspected, and various attempts have been made to discover its ingredients. Berzelius, from the combination of experiment with much theoretical reasoning, has deduced, that nitrogen is compounded of oxygen and an unknown base, in the following proportions:\*

Base . . . . .	44.32 . . . . .	79.64 . . . . .	100.00
Oxygen . . . . .	55.68 . . . . .	100 . . . . .	125.51
	100	179.64	225.51

\* 2 Thomson's Annals, 284.



This base, it must be observed, however, is purely hypothetical; and, as it has never yet been exhibited in a separate state, we cannot at present know any thing of its properties. Berzelius has proposed for it the name of *nitricum*.

The experiments of Sir H. Davy,\* directed to the decomposition of nitrogen, on the presumption of its being an oxide, have not been attended with any better success. Potassium was ignited, by intense Voltaic electricity, in nitrogen gas; and the result was, that hydrogen appeared, and some nitrogen was found deficient. This, on first view, would lead to the suspicion that nitrogen was decomposed. But, in subsequent experiments, in proportion as the potassium was more free from a coating of potash, which would introduce water, so, in proportion, was less hydrogen evolved, and less nitrogen found deficient. The general tenor of these inquiries, therefore, lends no strength to the opinion that nitrogen is a compound body.

#### ART. 1.—*Nitrogen with Oxygen.—Atmospheric Air.*

THE atmosphere is a collection of elastic fluids, retained on the surface of the earth by their gravitation. Its weight was first ascertained by Galileo, and applied by Toricelli to explain the rise of water in pumps, and of mercury in barometrical tubes; and by Paschal to the mensuration of the height of mountains. At the level of the ocean it is adequate to sustain a column of water having the altitude of 35 feet, or one of mercury of the height of 30 inches, and it presses with the weight of about 15 pounds on every square inch of surface. As we ascend, the atmosphere decreases in density in a geometrical proportion to equal ascents. Thus at three miles in height, the density of the atmosphere is one half what it is at the earth's surface, or equal to a column of 15 inches of mercury; at six miles, the barometer would stand at  $\frac{1}{4}$  the usual height, or at  $7\frac{1}{2}$  inches; at nine miles of elevation, at  $3\frac{1}{2}$  inches; and at 15 miles nearly at 1 inch. Hence the greatest part of the atmosphere is always within 15 or 20 miles of the earth's surface; though, from the refraction of the sun's light,

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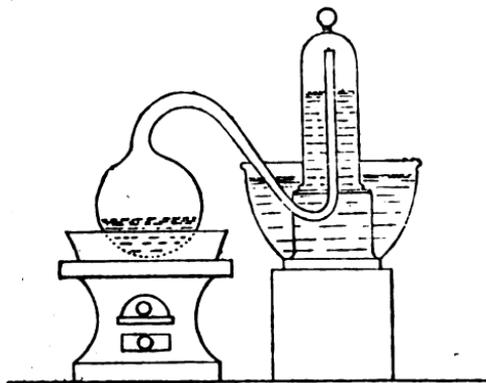
\* Phil. Trans. 1810.

it may be inferred to extend from 40 to 45 miles in height. Beyond the former limit it appears highly probable, indeed, from the recent observations of Dr. Wollaston, (Phil. Trans. 1822) that our atmosphere does not reach at all; the force of gravity downwards, upon a single particle, being there equal to the resistance arising from the repulsive force of the medium. We have no evidence, then, of the existence of similar matter round any other planet; and, on the contrary, it has been ascertained, by the observations of Captain Kater, that no retardation of the motion of Venus can be perceived in her progress towards the sun, as would happen if the latter were encompassed by a refracting atmosphere. The approach, also, of Jupiter's satellites to the body of that planet is uniformly regular, till they appear in actual contact, showing that there is not that extent of atmosphere, which Jupiter should attract to himself from an infinitely divisible medium filling all space. These observations are favourable, as Dr. Wollaston remarks, to the existence of particles of matter no longer divisible, for if an elastic fluid like our atmosphere consist of such particles, we can scarcely doubt that all other bodies are similarly constituted; and may without hesitation conclude that those equivalent quantities, which we have learned to appreciate by proportionate numbers, do really express the relative weights of elementary atoms, the ultimate objects of chemical research.

The great body of air, constituting our atmosphere, is in a state of constant motion, not only from its accompanying the earth in its rotation round its axis, but it flows also from the equator towards the poles, and contrariwise. Over the torrid zones, the air is expanded by heat, and acquires a tendency to ascend, while the air from the temperate and frigid zones presses forward to supply the vacancy. In the torrid zones, the upper regions of the atmosphere meet with less lateral pressure than is necessary to support them, and the air, therefore, overflows in both directions, so that currents northward and southward are established in the higher regions of the atmosphere. Thus a constant circulation is maintained, and a cause established for supporting a temperature on the earth's surface, approaching much more nearly to uniformity, than it could have been without such a provision of nature.

It has already been stated that the air of our atmosphere, besides small proportions of aqueous vapour and carbonic acid, is principally constituted of two different gases, viz. oxygen gas, and azotic or nitrogen gas, the former of which seems to be the only ingredient on which the effects of the air, as a chemical agent, depend. Hence combustible bodies burn in atmospheric air, only in consequence of the oxygen gas which it contains; and, when this is exhausted, air is no longer capable of supporting combustion.\* Its analysis is most satisfactorily demonstrated by the action of heated mercury, as was first effected by Lavoisier in the following manner.

Into a small matrass, capable of holding from 45 to 50 cubical inches, pour about 1500 grains of mercury, and let its neck be so bent that its extremity may open into a known quantity of atmospheric air confined in a glass receiver over mercury. (See the annexed cut.) The receiver should not be more than one



third full of air, in order to allow space for its expansion by heat; and the body of the matrass must be surrounded by dry sand, contained in the sand pot of a distilling furnace. The vessels being thus disposed, a fire is to be lighted in the furnace, and kept up for several days, so as to maintain the quicksilver

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\* Certain combustible bodies even cease to burn in atmospheric air, long before its oxygenous portion is consumed, for reasons that will hereafter be given.

nearly at the boiling point, which is thus freely exposed to the air in the bell as well as to that in the matrass. At first, the air is rarefied by heat; but when the fire has been supported for two or three days, its volume begins to diminish, and at the end of the fifth day, when the vessels have cooled, it is found that about one sixth the bulk of the original air has disappeared. What remains is completely altered in its properties. It immediately extinguishes flame, and is fatal to any small animal that may be inclosed in it. The mercury, also, may be observed to have undergone a change; and scaly particles of a flea colour may be seen floating on its surface.

When these particles are collected, and subjected to a heat approaching to redness, in a coated glass tube, a quantity of gas may be collected by a proper apparatus, the volume of which will be found equivalent to that which has disappeared. Its properties, when examined, answer to those of oxygen gas, which is thus decisively proved to be a constituent part of the air of our atmosphere, the other ingredient of which is shown to be an elastic fluid incapable either of supporting combustion or animal life. The analysis, however, effected in this way, is not adequate to disclose the true proportion of the gases constituting the atmosphere, for mercury has not a sufficiently strong attraction for oxygen to separate the whole of that existing in the air, which amounts to about one fifth of the whole volume. This separation may be completely effected by other methods to be presently described, proving that atmospheric air is composed of one volume of oxygen gas, and four of nitrogen, besides small proportions of carbonic acid and aqueous vapour, the latter varying with the temperature.

This process is extremely tedious; but evidence of the nature of atmospheric air may be obtained much more expeditiously by the following experiments.

I. Burn phosphorus, in the manner described, substituting, for oxygen gas, common atmospherical air. The combustion will, in this instance, be less vivid; will cease sooner; and the absorption, when the vessels have cooled, will be much less considerable than in the former case.

The phosphorus, however, will have absorbed the whole

of the oxygen gas contained in the air submitted to experiment; and hence it may be employed for measuring the quantity of oxygen gas in a given bulk of atmospherical air. This may be accomplished either by its slow or rapid combustion. Berthollet proposes\* to expose a cylinder of phosphorus, fastened to a glass rod, in a narrow glass vessel, graduated into equal parts, and standing full of air over water. (See fig. 24.) The phosphorus immediately begins to act, without visible combustion, on the included air; and in six or eight hours its effect is completed. The residuary azotic gas has its bulk enlarged about one 40th, by absorbing a little phosphorus; and for this allowance must be made in measuring the diminution.

In the eudiometer of Seguin, the rapid combustion of phosphorus is employed with the same view. A glass tube, open at one end only, about an inch in diameter, and eight or ten high, is filled with, and inverted in, mercury. A small bit of phosphorus, dried with blotting paper, is then introduced, and, by its inferior specific gravity, rises to the top of the tube where it is melted, by bringing a red-hot poker near to the outer surface of the glass. When the phosphorus is liquefied, a measured portion of the air to be examined is admitted, by a little at once, into the tube. The phosphorus inflames at each addition, and the mercury rises. When all the air under examination has been added, the red-hot poker is again applied to ensure the completion of the process, and the residuary gas is transferred into a graduated measure, where its bulk is carefully ascertained. In this instance, about one 40th the volume of the residuary gas is to be deducted from the apparent quantity of azotic gas, because, in this case also, a small portion of phosphorus is dissolved by the latter, and occasions a trifling expansion. With this deduction, atmospheric air loses pretty accurately 21 parts out of every 100; and contains, therefore, 21 *per cent.* of oxygen, and 79 of azote by measure.† And it is remarkable,

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\* Annales de Chimie, xxiv. 78.

† Various other methods of analyzing atmospherical air will be described in the course of the work, references to which may be found in the Index, article Eudiometer. One of the quickest and most satisfactory is described in the section on Hydrogen Gas.

that no appreciable difference exists between the proportions of oxygen and azote in the atmospheres of distant places; from which it appears, that the purity and salubrity of air depend on some other circumstances than the proportion of these its chief elements.

II. The inferior fitness of atmospherical air to that of oxygen gas, for supporting combustion, may be shown, also, by a comparative experiment with two candles. Provide a circular piece of lead, three inches diameter, and half an inch thick, from the centre of which proceeds a perpendicular iron wire, six or eight inches high; to the end of this wire fasten a piece of wax taper. Set the candle, supported by its stand, on the shelf of a pneumatic cistern; and place, also, the conducting pipe from the bladder (*e*, fig. 41), in the position shown by the figure; the cock *d*, however, being shut. Then, having the syphon *g* in the inverted position shown in the plate, sink the whole apparatus into the water. Part of the air in the jar *a* will escape through the syphon, and will be replaced by water. When we have left, in the jar, the proper quantity of air, the syphon must be removed, and the jar returned to its place. The level of the water will now be considerably higher within than without the receiver; and its height must be noted. On passing a succession of electrical sparks from the conducting wire to the bent pipe, and opening the cock *d* from the bladder filled with hydrogen gas, we shall have a small flame, which is to be extinguished as soon as, by its means, we have lighted the candle. The candle may be suffered to burn till it is extinguished; and the duration of its burning, and the diminution it occasions in the air, are to be noted. When the combustion is repeated in the same manner, but with the substitution of oxygen gas, it will be found to last considerably longer, and the diminution of volume in the gas will be much greater; or the experiment will be still more striking, if made at the same time with two receivers, the one containing common air, the other oxygen gas.

Of the fifty-one simple or elementary bodies, nine only are incapable of being acted upon at any temperature by the oxygen present in atmospheric air. These are chlorine, iodine, azote, silver, gold, platina, rhodium, palladium, and iridium. All the rest absorb oxygen from the atmosphere, either at the

ordinary temperature, or at a more elevated one which differs for different individuals.

III. Take two tubes, each a few inches long, closed at one end, and divided into 100 aliquot parts. Fill the one with atmospherical air, the other with oxygen gas, and invert them in two separate cups filled with a solution of sulphuret of potash. The sulphuret will ascend gradually within the tube of common air, till, after a few days, about four fifths of its original volume will remain; but, in that containing oxygen, it will ascend much higher, and if the gas be pure, will even absorb the whole.

The explanation of this fact is, that liquid sulphuret of potash has the property of absorbing oxygen, but not nitrogen. It therefore acts on atmospherical air, only as long as any oxygen gas remains, and may be employed as a means of ascertaining the quantity of this gas in the atmosphere at different times, and in distant places. An improved instrument,\* thus graduated, has been employed by Guyton as an *Eudiometer*.† But an apparatus, of much greater simplicity, and facility of application, is that of Professor Hope of Edinburgh, announced in Nicholson's Journal, 8vo. iv. 210. It consists of a small bottle, of the capacity of 20 or 24 drachms (fig. 20, pl. ii), destined to contain the eudiometric liquid, and having a small stopper at *b*. Into the neck of the bottle a tube is accurately fitted by grinding, which holds precisely a cubic inch, and is divided into 100 equal parts. To use the apparatus, the bottle is first filled with the liquid employed, which is best prepared by boiling a mixture of quicklime and sulphur with water, filtering the solution, and agitating it for some time in a bottle half filled with common air. The tube, filled with the gas under examination (or with atmospherical air, when the quality of this compound is to be ascertained), is next to be put into its place; and, on inverting the instrument, the gas ascends into the bottle, where it is to be brought extensively into contact with the liquid by brisk agitation.

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\* See Nicholson's Philosophical Journal, 4to. i. 268; or Tilloch's Philosophical Magazine, iii. 171.

† Other eudiometers will be described hereafter.

An absorption ensues; and, to supply its place, the stopper *b* is opened under water, a quantity of which rushes into the bottle. The stopper is replaced under water; the agitation renewed; and these operations are performed alternately, till no farther diminution takes place. The tube *a* is then withdrawn, the neck of the bottle being under water, and is held inverted in water for a few minutes; at the close of which the diminution will be apparent. Its amount may be measured by the graduated scale engraved on the tube.

To the eudiometer of Dr. Hope there are, however, a few objections. If the tube *a* and the stopper *b* are not both very accurately ground, air is apt to make its way into the instrument to supply the partial vacuum, occasioned by the absorption of oxygen gas. This absorption causes a diminished pressure within the bottle; and, consequently, towards the close of each agitation, the absorption goes on very slowly. Besides, the eudiometric liquid is constantly becoming more dilute, by the admission of water through *b*. To obviate all these difficulties, I have substituted for the glass bottle, one of elastic gum, as shown by fig. 21, *b*. The tube *a* is accurately ground into a short piece of very strong tube of wider bore, as shown at *c*, the outer surface of which is made rough by grinding, and shaped as represented, that it may more effectually retain the neck of the elastic bottle when fixed by a string. This instrument is used, in every respect, in the same way as Dr. Hope's. The only difficulty is, in returning the whole of the residuary gas into the tube; but the art of doing this will be readily acquired by practice.

An ingenious modification of the eudiometer, which enables us to measure an absorption of only  $\frac{1}{1000}$ th part of the gas employed, is described by Mr. Pepys in the Philosophical Transactions for 1807, or Philosophical Magazine, xxix.

V. *Atmospherical air, when very considerably rarefied, is rendered unfit for supporting combustion.* The general fact that flame ceases in air highly rarefied by the air pump, was well known to the earlier experimenters upon the Boylean vacuum; but the degree of rarefaction, necessary to this effect, has been differently stated. Sir H. Davy (on Flame, p. 57,) found that a jet of inflamed hydrogen from what has been



called the philosophical candle, of about one-sixth of an inch in height, when introduced under a receiver, containing from 200 to 300 cubic inches of air, enlarged as the receiver was exhausted by an air-pump. When the gage indicated a pressure between 4 and 5 times less than that of the atmosphere, the flame was at its maximum size; it then gradually diminished below, but burned above, till the pressure was between 7 and 8 times less. Using a larger jet with the same apparatus, it burned till the pressure was reduced to one-tenth that of the atmosphere; and when a coil of platinum wire was kept in the flame in a state of ignition, the combustion did not cease till the pressure was reduced 13 times. The combustibility of hydrogen in atmospheric air does not, therefore, appear to be increased or diminished by mere rarefaction from the removal of pressure, but to cease in rarefied atmospheres, only when the heat produced is insufficient to keep up the combustion, or at that point when it is incapable of communicating visible ignition to metal.

It is not, however, by the same degree of rarefaction of air, that the combustion of all bodies is suspended; for, as might naturally be expected, those which require least heat for their combustion, burn in more rarefied air than those that require a higher temperature; and again, those that produce much heat in their combustion, burn in more rarefied air than those which evolve little heat. The following table, collected from Sir. H. Davy's experiments, shows the degrees of rarefaction of common air, at which the combustion of some inflammable bodies ceases, both with and without the appendage of a coil of platinum wire.

	Without Platinum.	With Platinum.
Olefiant gas ceases to burn in air } rarefied .....	.....	11 to 12 times.
Carbureted hydrogen .....		4 .....
Carbonic oxide .....		6 .....
Alcohol ..... } Wax taper .....	5 to 6	7 to 8 ....
Sulphureted hydrogen .....	7	.....
Sulphur .....	15 to 20	.....
Phosphorus .....	60 ....	.....

By preserving heat in rarefied air, Sir H. Davy found that the inflammation of bodies may be continued, when, under other circumstances, it would have been extinguished. Thus, when camphor was burned in a glass tube, so as to make the upper part of the tube red hot, the inflammation continued when the rarefaction was 9 times; whereas it would only continue in air rarefied 6 times, when the camphor was burned in a thick metallic tube, which could not be considerably heated by it. By other experiments he has shown, also, that expansion by heat, instead of diminishing the combustibility of gases, enables them, on the contrary, to explode at a lower temperature.

VI. *The power of atmospheric air to support combustion is diminished also by mixing it with some other gases.* Thus, Sir H. Davy found that a candle is instantly extinguished in air mixed with one tenth of silicated fluoric acid gas, or with one sixth of muriatic acid gas. But air, thus rendered inadequate to support the combustion of one sort of inflammable substance, is capable of maintaining that of others, as is proved in an elegant manner by the following experiment of the same philosopher. Into a long bottle with a narrow neck introduce a lighted taper, and let it burn till it is extinguished. Carefully stop the bottle, and introduce another lighted taper; it will be extinguished before it reaches the bottom of the neck; then introduce a small tube containing zinc and diluted sulphuric acid, at the mouth of which the hydrogen is inflamed; the hydrogen will be found to burn, in whatever part of the vessel it is placed. After the hydrogen is extinguished, introduce lighted sulphur; this will burn for some time; and, after its extinction, phosphorus will be as luminous as in the open air, and, if heated in the bottle, will produce a pale yellow flame of considerable density. (Davy on Flame, p. 82.)

VII. *The mechanical condensation of air does not adapt it for supporting a more vivid combustion.* Sir H. Davy's experiments are the only ones we possess on this subject. He condensed air nearly five times, and then ignited iron wire to whiteness in it, by the Voltaic apparatus, but the combustion took place with very little more brightness than in the common atmosphere, and would not continue as in oxygen; nor did

charcoal burn much more brightly in this compressed air than in common air.

VIII. *Atmospheric air supports animal life, only in consequence of the oxygen gas which it contains.*—Air, after having been received into the lungs, and again expired, is found to have lost a considerable part of its oxygen, *viz.* from 10 to 12 *per cent.* It proves fatal to animals, however, long before this ingredient is wholly exhausted; and hence it appears, that a considerable proportion of oxygen gas is necessary to fit the air for supporting respiration. As the analysis of expired air requires an acquaintance with another gas, not hitherto described, *viz.* carbonic acid, its examination will be postponed to a future occasion.

IX. *Atmospheric air is diminished in volume by animal respiration.*—This may be shown by repeating a very simple experiment, originally contrived by Mayow. He confined a mouse in a small glass jar, and tied the jar over, quickly and firmly, with moistened bladder. The heat of the animal first expanded the air, and rendered the bladder convex outwards; but when the animal after death had become cold, the bladder exhibited a hollow surface, proving that the air within the jar was diminished in its bulk.

The exact amount of the diminution may be shown, by confining a mouse, over water, in a graduated jar, furnished with a stop-cock, and containing common air. As the heat of the animal, however, would occasion the expulsion of part of the air, it is expedient, on first depressing the jar into water, to open the cock, through which a part of the air will escape: the cock is then to be shut, and the height of the water within to be accurately noted. At first, the level will be depressed, in consequence of the expansion of the air by the warmth of the animal; but, after its death, a considerable diminution will be observed.

X. The weight of 100 cubic inches of atmospheric air, at 60° Fahrenheit and 30 inches barometer, is said by Mr. Kirwan to be 30.92 grains. Sir H. Davy states it, when under the same pressure, but at 55° Fahrenheit, to be 31.10 grains, from which it may be deduced that, with the temperature and pressure assumed by Mr. Kirwan, 100 inches would weigh

30.78 grains. Under the same circumstances, Sir George Shuckburgh's experiments fix its weight at 30.5 grains, a number confirmed by the subsequent investigations of Mr. Rice. (Ann. of Phil. vol. xiii.) Mr. Brande, however, (Manual, i. 379,) deduces, from twelve experiments made at the Royal Institution, with great care and an excellent balance, that 100 cubic inches of air, at a mean of the barometer and thermometer, weigh only 30.199 grains. On the whole, perhaps, 30.5 grains may be considered as a near approximation.

All eudiometrical processes, when skilfully performed, concur to prove that, apart from the carbonic acid and aqueous vapour which are present in atmospheric air, 100 volumes consist of 79 oxygen, and 21 nitrogen; or, including the two former ingredients, that it is constituted, at a mean temperature and pressure, of

Nitrogen gas . . . . .	77.5	by measure . . . . .	75.55	by weight.
Oxygen gas . . . . .	21.	.....	23.32	
Aqueous vapour ..	1.42	.....	1.03	
Carbonic acid ....	0.08	.....	0.10	
	<hr/>		<hr/>	
	100.00		100.00	

It is remarkable, also, that with the exception of the aqueous vapour, the quantity of which varies with the temperature, as will presently appear, the other ingredients of the atmosphere bear at all times, in all quarters of the globe, and at all accessible heights above its surface, the same relative proportion to each other. Thus air from the Alps analyzed by Saussure Jun., from Spain by De Marti, from France and Egypt by Berthollet, from England and the coast of Guinea by Davy, from the Peak of Teneriffe and from near the summit of the Andes by Humboldt, and from the height of nearly 22,000 feet by Gay Lussac and Thenard, all gave results approaching as nearly as possible to each other. The unknown ingredients which are occasionally mingled with the atmosphere, and which impart to it deleterious properties, are either of too subtile a nature, or present in too

small a proportion, to be discoverable by our imperfect instruments.

Two views have been taken of the nature of the union, which exists among the several elastic fluids constituting the atmosphere. By the greater part of chemists, it has been considered as a chemical compound, chiefly from the uniformity of its composition, and from the fact that its several ingredients do not separate and arrange themselves according to their respective specific gravities. Mr. Dalton was the first who presented, under a distinct view, the theory, that of the various elastic fluids constituting the atmosphere, the particles of one have neither attractive nor repulsive power towards those of another; but that the weight or pressure, upon any one particle of any fluid mixture of this sort, arises solely from the particles of its own kind.\* According to this hypothesis, oxygen, azotic, and carbonic acid gases (or indeed any number), may exist together under any pressure, and at any temperature, while each of them, however paradoxical it may appear, occupies the whole space allotted for all. Each ingredient of the atmosphere, on this view, exerts its own separate pressure in supporting the mercury of the barometer, and performs the part assigned to it in the following table.

	Inch. of Mercury.
The nitrogen gas exerts a pressure .....	= 23.36
Oxygen gas .....	= 6.18
Aqueous vapour .....	= 0.44
Carbonic acid gas .....	= 0.02
	30.00

To enter fully into the arguments for and against this doctrine, would lead into discussions of too great length for an elementary work; and I shall only, therefore, express my opinion, that on the whole it is more probable, and encumbered with fewer difficulties, than the theory that the constituents of the atmosphere are held united by chemical affinity. It must be

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\* Manchester Memoirs, v. 538.

acknowledged, as has been done by Mr. Dalton,\* that taking the azotic part of the atmosphere as a standard, the oxygen and carbonic acid must observe a decreasing ratio to it in ascending, and the aqueous vapour an increasing one. But on the summit of Mont Blanc (nearly three English miles in perpendicular height) the ratio of the oxygen to the nitrogen would still be very nearly as 20 to 80, and at all ordinary heights, the difference of proportions must be scarcely appreciable.

*General View of the Compounds of Nitrogen and Oxygen.*

When nitrogen and oxygen gases are mingled together, in whatsoever proportions they are employed, no combination ensues. The result is a simple mixture of the two gases, which do not, like inelastic fluids, separate on standing, but remain diffused through each other for an indefinite length of time. When, however, either one or both of these elements is in a condensed state, or deprived of part of that caloric which keeps the gravitating particles of all gases at a distance from each other, they unite and form compounds, distinguished by very striking properties. According to the proportions in which the oxygen and nitrogen exist in these compounds, their qualities undergo a remarkable variation, so that from two elementary bodies, variously united, we have several compounds, totally unlike each other in external qualities, as well as in their chemical relations.

Before describing the compounds of oxygen and nitrogen individually, it will contribute to perspicuity to take a general survey of the whole. Some of them exist essentially in an aëriform state, and are capable of uniting with water and other liquids in small proportion only. Others, again, combine with water to such an extent, that the liquid form is the only one under which they occur to our observation. When entirely deprived of water, they are all essentially gaseous bodies.

In a series of the compounds of nitrogen, founded on their proportion of oxygen, they occupy (excluding atmospherical

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\* Manchester Memoirs, 2d ser. i. 257.

air from the number) the following order, the last containing the largest proportion of oxygen—nitrous oxide—nitric oxide or nitrous gas—hypo-nitrous acid—nitrous acid or nitrous vapour—and nitric acid. The two first are sparingly soluble in water; but the three last unite with it largely, and form liquid compounds of decidedly acid taste and quality.

The following table exhibits the composition of three of these bodies, the calculation being founded on the experiments of Sir H. Davy, published in the year 1800 in his "Researches." Oxygen gas is assumed to weigh 33.8 grains, and nitrogen, 29.5 for 100 cubical inches.

	Proportion of Elements by Weight.		Proportion by Measure.	
	Nitrogen.	Oxygen.	Nitr. gas.	Ox. gas.
Nitrous oxide .....	63.30	36.70	100.	50.63
— gas .....	44.05	55.95	100.	110.
Nitrous acid* .....	29.50	70.50	100.	208.60

From a comparison of the third and fourth columns of the foregoing Table, it is obvious, that in nitrous oxide, the nitrogen is, in volume, very nearly double the oxygen; that in nitrous gas, the two elements exist in almost equal volumes; and that in nitrous acid, the oxygen is a little more than twice the volume of the nitrogen. These coincidences, and others of the same kind, are the foundation of the theory advanced by Gay Lussac; viz. *that compounds, whose elements are gaseous, are constituted either of equal volumes of those elements; or, that if one of the elements exceeds the other, the excess is by some simple multiple of its volume.* That the proportions of nitrogen and oxygen by measure do not, in the foregoing instances, rigorously conform to this law, is ascribed by Gay Lussac to unavoidable inaccuracies, attendant on all delicate processes for determining the constitution of gaseous bodies. In one instance, the coincidence was proved experimentally; for M. Berard, by the combustion of potassium in 100 measures of nitrous gas, obtained exactly 50 measures of nitrogen. Hence the table, corrected to accord with the views of

\* These were at first stated to be the proportions of the elements of *nitric acid*; but they apply more correctly to *nitrous acid*.

Gay Lussac, and enlarged so as to comprehend all the known compounds of nitrogen, will stand as follows :

	Measures of		100 grains contain	
	Nitrogen.	Oxygen.	Nitrogen.	Oxygen.
Nitrous oxide consists of ..	100	50	63.58	36.42
—— gas .....	100	100	46.60	53.40
Hypo-nitrous acid .....	100	150	36.8	63.2
Nitrous acid .....	100	200	30.40	69.60
Nitric acid .....	100	250	25.97	74.03

Supposing the foregoing proportions by volume to be correct, the proportions by weight will be as follows :

	In weight of	
	Nitrogen.	Oxygen.
Nitrous oxide consists of .....	100	+ 57
—— gas .....	100	+ 114
Hypo-nitrous acid .....	100	+ 171
Nitrous acid .....	100	+ 228
Nitric acid .....	100	+ 285

In all these compounds the elements are in a state of condensation, except in nitrous gas, in which the nitrogen and oxygen, according to Gay Lussac, are precisely in the same state of density, as in nitrogen and oxygen gases. In the other compounds, the contraction, he apprehends, is exactly equivalent to the bulk of the oxygen gas. For example, in 100 measures of nitrous oxide, consisting of 100 measures of nitrogen gas and 50 measures of oxygen gas, the condensation is 50 measures. On the same principle 100 measures of nitrogen gas, and 200 of oxygen gas constitute 100 of nitrous acid gas; and 100 measures of nitrogen and 250 of oxygen compose 100 of gaseous nitric acid.

Mr. Dalton, in his "New System of Chemical Philosophy," has given a Table of the Compounds of nitrogen and oxygen, which differs essentially from that of Gay Lussac. This table, however, it is unnecessary to copy, because it has been since materially altered by the author, who has presented it under the following corrected form.\*

\* Thomson's Annals, ix. 193.



	Volumes of		Atoms of		Symbol.*
	Nitrogen.	Oxygen.	Nitrogen.	Oxygen.	
Nitrous oxide . . . .	100	+ 62	2	+ 1	
— gas . . . . .	100	+ 124	1	+ 1	
Hypo-nitrous acid	100	+ 186	2	+ 3	
Nitrous acid . . . .	100	+ 248	1	+ 2	
Nitric acid . . . . .	100	+ 310	2	+ 5	

It will be obvious, from a comparison of this table with the foregoing one, that it assigns to all the compounds of nitrogen, 24 per cent. or very nearly one fourth, more oxygen, than is stated by Gay Lussac to enter into their composition. It is admitted, on all hands, that setting out from nitrous oxide, the other compounds of nitrogen contain proportions of oxygen, which are simple multiples, both in weight and in volume, of that existing in nitrous oxide. The question, which is still disputed by the opponents of the theory of volumes, is whether it be true that one volume of nitrogen unites with either exactly half a volume of oxygen, or with exactly an equal volume, or a double volume, and so on. Analogy is certainly in favour of this opinion; for the instances are numerous, in which gaseous bodies observe the law respecting volumes, deduced by Gay Lussac; and we have not, at present, any well ascertained exception to it. The argument, which, perhaps, weighs most in its favour, when applied to the combinations of nitrogen and oxygen, is that, assuming nitrous oxide to consist of one volume of nitrogen and half a volume of oxygen, and multiplying the oxygen of nitrous oxide by 5, we are led to proportions constituting nitric acid, which almost exactly agree with those deduced by Dr. Wollaston from the experiments of Richter and Phillips.

If it should, hereafter, be unquestionably established that the elements of the compounds of nitrogen and oxygen are truly expressed by the table of Gay Lussac, it will then follow that the number representing the atom of nitrogen (oxy-

\* O representing oxygen, and N nitrogen.

gen being taken at 8) must be 14, or (oxygen being 10) 17.5. In this determination, it is taken for granted that the two elements exist atom to atom in nitrous oxide, and that this, and not nitrous gas, is the true binary compound. But if, with Mr. Dalton, we suppose nitrous oxide to be constituted of two atoms of nitrogen to one of oxygen, we must then express the weight of the atom of nitrogen, either by  $14 \div 2 = 7$ , or, taking oxygen at 10, by  $17.5 \div 2 = 8.75$ . It appears to me, however, most probable, that the former view is the correct one, and that

Nitrous oxide consists of 1 atom of nitrogen + 1 of oxygen.

Nitrous gas . . . . . 1 . . . . . + 2 . . . . .

Hypo-nitrous acid . . . . . 1 . . . . . + 3 . . . . .

Nitrous acid . . . . . 1 . . . . . + 4 . . . . .

Nitric acid . . . . . 1 . . . . . + 5 . . . . .

It is obvious that as the five compounds of nitrogen and oxygen, which have been already described, contain the same elements, and differ only in their proportion, they may be converted into each other, by adding or subtracting a due proportion of oxygen. Thus nitric acid, by contact with some of the oxidizable metals, is converted into nitrous gas; and nitrous gas, by abstracting a farther quantity of oxygen, is changed into nitrous oxide. Again, by adding oxygen to nitrous gas, it may be reconverted into hypo-nitrous, nitrous, or nitric acid, according to the proportion of oxygen which is added, and the circumstances under which the combination is effected.

*Protoxide of Nitrogen.—Nitrous Oxide of Davy.*

1. This compound of oxygen and nitrogen may be obtained by several processes:

(a) By exposing common nitrous gas for a few days to iron filings, or to various other bodies strongly attracting oxygen, the former gas is changed into nitrous oxide.

Some nicety and experience are required to suspend the decomposition before it has gone too far; in which case nitrogen gas is obtained along with nitrous oxide. The sulphite of potash, being incapable of decomposing nitrous oxide, is bet-

ter adapted to the conversion of nitrous gas into that elastic fluid. The process, in all cases, may be suspended, when about two thirds the original bulk of the gas are left.

(b) By dissolving zinc, or tin, in nitric acid, diluted with five or six times its weight of water. Zinc, during this solution, disengages nitrous oxide till the acid begins to exhibit a brownish colour, when the process must be suspended, as nitrous gas is then formed. But by neither of these processes is the gas obtained sufficiently pure for exhibiting its qualities. To procure it in a state of purity, the following process is the best adapted.

(c) To nitric acid, diluted with five or six parts of water, add carbonate of ammonia, till the acid is saturated. Then evaporate the solution by a gentle heat, until a glass rod when dipped into it, and rapidly cooled, is found to have acquired a solid coating; and, to supply the waste of alkali, add, occasionally, a little more of the carbonate. The salt obtained, after the solution has cooled, is next to be put into a glass retort, and distilled with a sand-heat, not exceeding 440° Fahr.\* The heat of an Argand's lamp is more than sufficient, and requires cautious regulation. The salt will presently liquefy, and must be kept gently simmering, avoiding violent ebullition. The gas may be collected over water, and allowed to stand a few hours before it is used, during which time it will deposit a white substance, and will become perfectly transparent.

A gazometer, however, is best adapted for its reception, because all danger is then avoided of the water of the trough being forced into the retort; and because the gas is brought into contact with a much smaller surface of water, which has the property of absorbing a considerable proportion of the gas. On this account, water, which has been once used to confine the gas, may be kept for the same purpose.

The changes that take place, during the conversion of ni-

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\* From the observations of Mr. Sadler (Nicholson's Journal, xv. 286), it appears that the purity of the nitrate of ammonia is of considerable importance; and that its adulteration with muriate diminishes the quantity, and impairs the quality of the gas.

trate of ammonia into nitrous oxide, are the following; Nitric acid is composed of oxygen and nitrous gas; ammonia, of hydrogen and nitrogen. In a high temperature, the nitrous gas combines with an additional dose of nitrogen, and forms nitrous oxide; while the oxygen of the decomposed nitric acid unites with the hydrogen of the ammonia, and forms water. Water and nitrous oxide are, therefore, the only results of the careful decomposition of nitrate of ammonia by heat.

The gas, thus obtained, was termed, by its discoverer Dr. Priestley, *dephlogisticated nitrous air*; by the associated Dutch chemists, *gaseous oxide of azote*. Its most appropriate title is *protoxide of nitrogen*; but, for the sake of brevity, I shall occasionally use, with Sir H. Davy, the name of nitrous oxide.\*

In order to ascertain whether nitrous oxide be adulterated with either common air or oxygen gas, we may mix equal measures of the gas under examination, and of nitrous gas. If any diminution ensue, the presence of one of these may be suspected; and the amount of the diminution will show which of them is contained in it. Nitrous gas, however, is a much more common contamination; for it is generated, along with nitrous oxide, whenever the temperature of the salt is raised too high. Its presence may be detected, either by red fumes and a diminution on the admixture of oxygen gas; or by an absorption being effected, on agitating the gas with a solution of green sulphate of iron, which has no action on pure nitrous oxide.

II. Nitrous oxide gas has the following properties:

(a) It is considerably heavier than common air. At about 55° Fahr. and 30 inches pressure, 100 cubic inches weigh 50.20 grains, or under the same pressure, and at 60° Fahr. 49.68. (Davy.) More recently Sir H. Davy has stated 100 cubic inches to weigh between 48 and 49 grains, and hence its specific gravity should be very nearly 1.6. Colin makes it only 1.5204, or, corrected by calculation, 1.5209: Dr. Thomson 1.5269: and Berzelius and Dulong 1.5273. On the

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\* For a full account of this gas, consult Sir H. Davy's *Researches, Chemical and Philosophical*. London. Johnson, 1809.

theory that it is constituted of one volume of nitrogen, and half a volume of oxygen, 100 cubic inches should weigh  $46\frac{1}{2}$  grains.\*

(b) Sir H. Davy, by passing electric sparks for some time through seven measures of nitrous oxide over mercury, found it reduced to  $6\frac{1}{2}$  measures. The residue was a gas analogous in properties to atmospheric air; and some nitrous acid was also produced. (Researches, p. 282.)

(c) When passed through a porcelain tube, well glazed both inside and outside, and strongly ignited in a furnace, a gas came over which was rendered opaque by dense red vapour, but which, after the spontaneous condensation of this, exhibited very nearly the same properties as atmospheric air. Neither this mode of decomposition, however, nor the last, furnishes results sufficiently exact to give any insight into the proportion of the components of nitrous oxide.

(d) A candle burns in nitrous oxide with a brilliant flame and crackling noise. Before its extinction, the white inner flame becomes surrounded with an exterior blue one.

(e) Phosphorus, introduced into it in a state of inflammation, burns with increased splendour. Phosphorus, however, may be melted and sublimed in this gas, without alteration. It may even be touched with red-hot iron wire, without being inflamed; but when wire intensely heated, or made white-hot, is applied, the phosphorus burns, or rather detonates, with prodigious violence.

(f) Sulphur, introduced into nitrous oxide when burning with a feeble blue flame, is instantly extinguished; but when in a state of an active inflammation, it burns with a vivid and beautiful rose-coloured flame.

(g) Red-hot charcoal burns in nitrous oxide more brilliantly than in the atmosphere. When the experiment is made in a proper apparatus, the results of its combustion are found to be one measure of nitrogen gas and half a measure of carbonic acid (equivalent to half a measure of oxygen) from each measure of nitrous oxide. It must, therefore, consist of

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\* Dalton, Thomson's Annals, ix. 190.

59 parts by weight of nitrogen and 33.8 oxygen,\* or it must contain by weight

Oxygen .....	36.43	.....100	..... 57.
Nitrogen .....	63.57	.....174	.....100.
	100.	274	157.

On the supposition that nitrous oxide is constituted of one atom of nitrogen and one of oxygen, this would make the weight of the atom of nitrogen = 14; for as 57 is to 100 so is 8 to 14.

(h) A mixture of this gas with hydrogen gas detonates loudly, on applying a lighted taper, or passing an electric spark.

When the proportion of hydrogen is nearly equal to that of nitrous oxide, or as 39 to 40, nitrogen gas only remains after the explosion; but when the proportion of hydrogen is smaller, nitric acid is also generated. In general terms, it may be stated that two volumes of nitrous oxide require for decomposition two volumes of hydrogen gas, and leave after combustion two volumes of nitrogen. Now we know that two volumes of hydrogen are equivalent to the saturation of one volume of oxygen, which, with the two remaining volumes of nitrogen, must make up the composition of two volumes of nitrous oxide. In other words, one volume of nitrous oxide consists of one volume of nitrogen + half a volume of oxygen condensed into the space of one volume. By an easy calculation, founded on the specific gravity of its elements, these proportions will be found to answer to 1 atom of nitrogen weighing 14, and 1 atom of oxygen = 8; its representative number will therefore be 22.

Nitrous oxide forms, also (as I have shown, Philosophical Transactions, 1809, page 444), a combustible mixture with ammoniacal gas, 100 measures of the latter requiring for saturation 130 measures of nitrous oxide.

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\* Two hundred cubic inches of nitrogen gas weigh 59 grains, and 100 of oxygen weigh 33.8.

(i) Iron wire burns in this gas with much the same appearance as in oxygen gas, but for a shorter period.

(k) Nitrous oxide is rapidly absorbed by water that has been previously boiled, about one thirtieth the original bulk of the gas remaining uncondensed. A quantity of gas, equal to considerably more than nine-tenths the bulk of the water, may be thus made to disappear. This property furnishes a good test of the purity of nitrous oxide; for the pure gas is almost entirely absorbed by boiled water, which has cooled without the access of air. The gas employed should exceed the water three or four times in bulk, in order to obtain a saturated solution.

Water, that has been saturated with this gas, gives it out again, unchanged, when heated. The impregnated water does not change blue vegetable colours. It has a distinctly sweet taste, and a faint, but agreeable, odour.

(l) Nitrous oxide is not diminished by admixture with either oxygen or nitrous gas, nor is it altered by contact either with chlorine or iodine.

(m) Nitrous oxide is not absorbed by alkalis; but if it be brought into contact with them, when in a nascent state, or before it has assumed the form of a gas, it then enters into combination with alkaline bases. Thus, when a mixture of sulphite of potash and pure potash is exposed to nitrous gas, the gas is de-oxidized by the sulphite, and changed into nitrous oxide, which unites with the alkali. We obtain, therefore, a mixture of sulphate of potash with a compound of nitrous oxide and alkali, the former of which may be separated by priority of crystallization. The latter is composed of about three parts of alkali, and one of nitrous oxide. It is soluble in water; has a caustic taste, of peculiar pungency; and converts vegetable blues to green. Powdered charcoal, mingled with it, and inflamed, burns with bright scintillations. The nitrous oxide is expelled from fixed alkalis by all acids, even by the carbonic.

(n) Animals, when wholly confined in this gas, die speedily.

(o) One of the most extraordinary properties of this gas is exhibited by its action on the human body, when received into

the lungs. When thus employed, it does not prove fatal, because, when admitted into the lungs, it is mixed and diluted with the atmospherical air present in that organ. To administer the gas, it may be introduced into an oiled silk bag or clean bladder, furnished with a stop-cock, and may be breathed repeatedly from the bag and back again, as long as it will last. The sensations that are produced vary greatly in persons of different constitutions; but, in general, they are highly pleasurable, and resemble those attendant on the early period of intoxication. Great exhilaration, an irresistible propensity to laughter, a rapid flow of vivid ideas, and an unusual fitness for muscular exertion, are the ordinary feelings it produces. These pleasant sensations, it must be added, are not succeeded, like those accompanying the grosser elevation from fermented liquors, by any subsequent depression of nervous energy.

*Deutoxide of Nitrogen.—Nitrous Gas, or Nitric Oxide.*

This gas, through discovered by Dr. Hales, was first distinctly examined by Dr. Priestley, and called by him *nitrous air*, a term afterwards changed to *nitrous gas*, then to *nitric oxide*, and more lately to *deutoxide of azote*, or *deutoxide of nitrogen*, which last appears to be its most appropriate title. It is so generally known, however, under the name of nitrous gas, that I shall sometimes, for the sake of brevity, continue so to call it.

Nitrous gas may be easily obtained by pouring, upon filings or turnings of copper contained in a gas bottle, nitric acid of density 1.2 or 1.3, without applying any other heat than that occasioned by the action of the acid and metal on each other. Quicksilver may be substituted for copper, and with either metal a more dilute acid may be employed, but in the latter case it will be found necessary to apply heat to the materials. During this process part of the nitric acid gives oxygen to the copper, and passes to the state of nitrous gas; and the remaining acid unites with the deutoxide of copper, and composes the deuto-nitrate of that metal.

The properties of nitrous gas are the following:—

(a) It is permanent over water; but it is absorbed in the



proportion of about 1 volume to 18 or 20, when agitated with water which has been recently boiled, and has become cold. This solution, according to La Grange, is converted, by long keeping, into nitrate of ammonia, in consequence of the decomposition of the water.

Nitrous gas is rather heavier than common air. One hundred cubic inches at  $55^{\circ}$ , barometer  $30^{\circ}$ , were stated by Sir H. Davy in 1800, to weigh 34.26, or at  $60^{\circ}$  Fahr. 33.80 grains. He has since, however, given the weight of 100 cubic inches at 32 grains, and hence its specific gravity at 1.050. Berard's determination is considerably lower; *viz.* 1.0388 by experiment, or 1.0364 corrected by calculation; Dr. Thomson's 1.0409; and Berzelius and Dulong's does not exceed 1.001.\*

(b) When well washed with water, it is not acid. It will be found not to redden the colour of litmus. This may be shown by introducing a piece of paper, tinged with that substance, into a jar of nitrous gas, standing inverted over water. To accomplish this, the paper should be fastened to the end of a glass rod or a piece of stick. The colour will remain unchanged.

(c) It extinguishes flame, and is fatal to animals. Homberg's pyrophorus, however, is inflamed by it; and charcoal and phosphorus, introduced into it when in a state of actual combustion, continue to burn vehemently.

(d) Mingled with hydrogen gas, it imparts a green colour to its flame. It does not, however, explode with hydrogen in any proportion, nor with any of the varieties of carbureted hydrogen. But, when mixed with ammonia, an electric spark produces a detonation, as I have shown in the Philosophical Transactions for 1809. The proportions, required for mutual saturation, are about 120 measures of nitrous gas to 100 of ammonia.

(e) When mixed with oxygen gas, red fumes arise; heat is evolved; a diminution takes place; and if the two gases be in proper proportion, and perfectly pure, they disappear entirely. Ten measures of oxygen, Mr. Dalton asserts, may be made to condense any quantity of nitrous gas, between 13 and 36

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\* Annales de Chim. et de Phys. tom. xv.

measures, accordingly as the mixture is conducted; and Gay Lussac finds that 100 measures of oxygen gas condense over water from 134 to 365 of nitrous, but in a dry glass vessel only 204, which, allowing for inaccuracies, may be stated at 200. In the latter case the total, 300 measures, become 200 of nitrous acid vapour.

(f) The same appearances ensue, less remarkably, with atmospheric air: and the diminution is proportionate to the quantity of oxygen gas which it contains. On this property of its condensing oxygen, but no other gas, is founded the application of nitrous gas to the purpose of *eudiometry*, or of ascertaining the purity of air. The sources of error, in its employment in this mode, have hitherto been considered such, as to forbid our relying implicitly on the results which it may afford. Learning, however, from Mr. Dalton, that he constantly employs nitrous gas in determining the purity of air, and with perfect satisfaction as to the accuracy of his results, I have obtained from him the following communication. It may be necessary to premise, that for applying nitrous gas to this purpose, two tubes will be found convenient, shaped like fig. 24; each from three to four tenths of an inch in diameter; eight or nine inches long, exclusive of the funnel-shaped part; and accurately graduated into minute aliquot parts. What these parts are, is of no consequence. Hundredth parts of a cubical inch give rather too large divisions of the scale; but if each of these be divided into two, the scale will be sufficiently small. If the tube employed be not long enough to comprise 100 of these parts, the experiment may be made on 50 parts only of atmospherical air; and the results, multiplied by 2, will give the proportion in 100 parts.

“ To use nitrous gas accurately in eudiometry, it is only  
“ requisite to take both gases in a dilute state, namely, con-  
“ taining four or five times their bulk of azotic gas (which  
“ atmospheric air naturally does), or of any other gas not  
“ acted upon by nitrous or oxygen gases. In this case, if an  
“ excess of one gas be used, the other is, in a few minutes, en-  
“ tirely taken up, and in a constant proportion; whatsoever  
“ may be the form of the vessel, or the manner of mixing the  
“ gases. The proportion is 1 of oxygen to 1.7 of nitrous, so

“ that 10-27ths of the diminution over water are oxygen, and  
“ 17-27ths nitrous gas. It is proper, as soon as the greater  
“ part of the diminution has ensued, to transfer the mixture  
“ through water into a graduated vessel, without using any  
“ agitation.

“ If pure nitrous gas be admitted to pure oxygen gas in a  
“ narrow eudiometer tube, so that the oxygen gas is upper-  
“ most, the two unite very nearly in the same uniform pro-  
“ portion as above. If, on the other hand, the nitrous be  
“ the upper gas, a much less quantity of it disappears, *viz.*  
“ 1.24 nitrous to one oxygen. If undiluted nitrous gas be  
“ admitted to pure oxygen gas, in a wide vessel over water,  
“ the whole effect takes place immediately; and one measure  
“ of oxygen will condense 3.4 nitrous gas.

“ To render this rule more intelligible, an example may  
“ be necessary. Let 100 measures of common air be admitted  
“ to 100 measures of a mixture of nitrous gas, with an equal  
“ volume of azotic or hydrogen gas. After standing a few  
“ minutes in the eudiometer, there will be found 144 measures.  
“ The loss 56 being divided by the common divisor, 2.7, gives  
“ 21 nearly for the oxygen gas present in 100 measures of  
“ common air.”

To these directions I may add, that when atmospherical air is the subject of experiment, it is scarcely necessary to dilute the nitrous gas, with any other gas, previously to its use. If a number of experiments be made, it will be proper, in all cases, to let the gases remain together the same definite time (say 10 minutes) before noting the diminution; and it is needless to transfer them into another vessel. If the mixed gas, under examination, contain much more oxygen than is present in atmospherical air, then it is proper to dilute the nitrous gas with an equal bulk of nitrogen or hydrogen gas; and, in this case, the narrower the tube in which the experiment is made, the more accurate will be the result.

Subsequent experience has convinced me that the method, proposed by Mr. Dalton, though sufficiently correct when applied to a mixture of the same, or nearly the same, standard as the atmosphere, cannot be relied on, when the proportion of oxygen is either considerably greater or less. In the

former case, the process gives too great a diminution, sometimes indeed to such an extent as to indicate more oxygen gas, than the whole amount of what was submitted to experiment. When the air, on which we are operating, is of an inferior standard to the atmosphere, we do not learn its full proportion of oxygen. Notwithstanding these objections, however, the method has considerable value, since it may be applied to determine the proportion of oxygen in some mixed gases, to which other eudiometrical tests are not applicable; for example, to mixtures of hydro-carburet and oxygen gases.

The application of nitrous gas to eudiometrical purposes, it has been observed by Gay Lussac, is susceptible of perfect accuracy, provided certain precautions be observed which he has pointed out, and which were suggested by his theoretical views of the constitution of these gases. A narrow tube he finds to be unfit for an eudiometer, his object being to form nitrous acid gas, which is but slowly absorbed by water. Instead therefore of a narrow tube, we must take a wide vessel, such as a small tumbler glass; and to 100 parts of atmospheric air, previously measured, we must add at once 100 measures of nitrous gas. A red fume will appear, which will soon be absorbed without agitation, and in half a minute, or a minute at most, the absorption will be complete. Pass the residuum into a graduated tube, and it will be found, almost invariably, that 84 measures have disappeared. Dividing this number by 4, we have 21 for the quantity of oxygen condensed.

By a series of experiments on mixtures of oxygen and nitrogen gases in various proportions, Gay Lussac found that this eudiometrical process may be depended upon, whether the oxygen exceed or fall short considerably of the proportion contained in atmospheric air.

(g) The generation of an acid, by the admixture of nitrous gas with common air or oxygen gas, may be shown by the following experiment. Paste a slip of litmus-paper within a glass jar, near the bottom; and into the jar, filled with and inverted in water, admit as much nitrous gas, previously well washed, as will displace the water below the level of the

paper. The colour of the litmus will remain unchanged; but, on adding atmospheric air or oxygen gas, it will be immediately reddened.

(h) The acid, thus produced, is either nitrous or hypo-nitrous, according to the circumstances of the experiment, the presence of water favouring the production of the latter, and its absence promoting that of nitrous acid.\* The nature of the product may be shown, in a general way, as follows: Into a jar, filled with and inverted in mercury, pass a small quantity of a solution of pure potash; and, afterward, measures of oxygen and nitrous gases, separately, and in proper proportion. On removing the solution from the jar, exposing it for some time to the atmosphere, and afterward evaporating it, crystals of nitrate of potash will be formed, a salt which is ascertained to be formed of potash and nitric acid.

(i) Nitrous gas is decomposed by exposure to almost all bodies that attract oxygen. Thus, iron filings decompose it, and become oxydized, affording a proof of the presence of oxygen in this gas. During this process, water, ammonia, and nitrous oxide, in the proportion of one volume from two of nitrous gas, are generated. Sulphuret of potash, &c., have a similar effect. Sulphuret of barytes gives one half its volume of nitrogen. Mixed with sulphurous acid, nitrous gas is decomposed, and this acid is changed into the sulphuric, but not unless water is present.† Nitrous gas does not, with hydrogen gas, afford a mixture that can be exploded by the electric spark; but with ammoniacal gas it may be fired in a Volta's eudiometer over mercury. The oxygen of the nitrous gas unites with the hydrogen of the ammonia, and the nitrogen of both gases is set at liberty.

Bodies, that have a still more powerful affinity for oxygen, decompose nitrous gas into its *ultimate* elements. Charcoal ignited in 100 measures, gives 50 measures of nitrogen gas, and 50 of carbonic acid. Arsenic, zinc, or potassium, when heated in it, evolve half its volume of nitrogen. Nitrous gas should consist, therefore, of 1 volume of oxygen + 1 volume

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\* Dalton, in Thomson's Annals, x. 39.

† Nicholson's Journal, xvii. 43.

of nitrogen, neither of which elements is in a state of condensation. We may therefore consider nitrous gas as constituted of one atom of nitrogen = 14, and two atoms of oxygen = 16, and its representative number will be 30. Its composition then is

	Vols.		By weight.	
Nitrogen....	1	.....	46.60	..... 100
Oxygen.....	1	.....	53.40	..... 114
	<u>2</u>		<u>100.</u>	<u>214</u>

No distinct information is obtained respecting the constitution of nitrous gas by the long continued action of electricity. One half the azote, according to Mr. Dalton, is liberated, and the remainder unites with the evolved oxygen and composes nitrous acid (System, p. 334.)

(k) Nitrous gas and chlorine, when both perfectly dry, have no action whatsoever on each other; but, if water be present, there is an immediate decomposition, its hydrogen combining with the chlorine to form muriatic acid, and its oxygen with the nitrous gas to form nitrous acid.

(l) Nitrous gas is absorbed by the green sulphate and muriate of iron,\* which do not absorb nitrogen gas. To ascertain, therefore, how much nitrogen gas a given quantity of nitrous gas contains, let it be agitated in a graduated tube with one of these solutions. This analysis is necessary, previously to deducing, from its effects on atmospheric air, the proportion of oxygen gas; for we must subtract from the residuum the quantity of nitrogen introduced by the nitrous gas.

From the important use which is now made in eudiometry of this solution of nitrous gas in sulphate of iron, it may be proper to describe the mode of its preparation.

Dissolve as much of the green sulphate of iron in water as the water will take up, or dissolve iron filings in sulphuric acid, diluted with five or six parts of water, leaving an excess of the iron, in order to ensure the perfect saturation of the acid. Fill a wide-mouthed bottle with this solution, invert it

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\* For an account of these salts, see chap. ix. sect. 16.

in a cupful of the same, and into the inverted bottle receive the nitrous gas, as it is generated by the proper materials, shaking the inverted bottle frequently. The colour of this solution will be changed to black, and the production of gas and the agitation are to be continued, till the absorption can be carried no farther. The impregnated solution should be preserved in a number of small bottles, not holding more than an ounce or two each. The most commodious method of applying this solution, is by means of Dr. Hope's eudiometer, already described.

### *Of Hypo-nitrous Acid.*

When 400 measures of nitrous gas and 100 measures of oxygen (in which, taken together, the nitrogen and oxygen are to each other by measure as 100 to 150) are mixed together over a solution of potash confined by mercury, we obtain 100 measures of a compound, called by Gay Lussac *per-nitrous acid*.\* Mr. Dalton, who obtained it several years ago, and then considered it as nitrous acid, proposed to call it *sub-nitrous acid*;† but the name hypo-nitrous seems to me more conformable to the analogy of similar acids having sulphur and phosphorus for their basis. This new compound is so far hypothetical, that it has never yet been exhibited in a separate form; for when a stronger acid is added, to expel it from the potash, it is resolved into nitrous gas and nitrous acid.

Hypo-nitrous acid is, also, frequently generated, when nitrous and oxygen gases, or nitrous gas and common air, are mingled together in eudiometrical processes. At the same time nitrous and nitric acids are produced, in proportions to the hypo-nitrous and to each other, which are modified by the circumstances of the experiment.‡

Calculating from the proportions of its elements and their state of condensation, 100 cubic inches of hypo-nitrous acid

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\* Ann. de Chim. et Phys. i. 400.

† Thomson's Annals, vol. ix.

‡ Dalton, Thomson's Annals, x. 83.

gas must weigh 80.2 grains; and it must consist in 100 grains of

	Vols.	Atoms.	By weight.	
Nitrogen.....	1	.... 1	.... 36.8	.... 100
Oxygen .....	1.5	.... 3	.... 63.2	.... 171.74
	2.5		100.	

Hypo-nitrous acid unites with sulphuric acid, either concentrated or a little diluted, and, at a moderate temperature, the compound forming elongated four-sided prisms. These crystals, and even the liquid in which they shoot, give nitrous gas when brought into contact with water. A similar solid is obtained by passing nitrous acid vapour into sulphuric acid; and it appears, also, to be identical with the crystalline solid formed, by Clément and Desormes, by the mixture of oxygen gas, sulphurous acid, nitrous gas, and the vapour of water. The last-mentioned compound had been supposed to consist of nitrous gas and sulphuric acid; but sufficient reasons have been given by Gay Lussac for the new view of it, which has just been stated.

#### *Nitrous Acid.*

It has been a subject of controversy whether an acid, entitled to this denomination, and holding the same relation to the nitric, which the sulphurous bears to the sulphuric, has really existence; but it is now generally admitted, that the nitrous acid is as much a distinct and peculiar compound as any other of the compounds of nitrogen.

The proportions of its elements have been investigated by Sir H. Davy,\* who finds that two measures of nitrous gas and one of oxygen (= 1 volume of nitrogen and 2 of oxygen), both freed from moisture, and mixed together in a vessel previously exhausted of air, are condensed into half their volume,† and form a deep orange-coloured elastic fluid,

\* Elements of Chem. Philosophy.

† Gay Lussac states the condensation at two thirds of the volume of the mixture. Ann. de Chim. et Phys. i. 403.



which may be called *nitrous acid gas*. It has the following properties :

A taper burns in it with considerable brilliancy. Sulphur when inflamed does not continue to burn in it ; but phosphorus burns vividly. Charcoal continues to burn in it with a dull red light. Water absorbs it, and gains a tint of green. It reddens litmus paper, has a sour taste, a strong smell, and turns animal substances yellow. One hundred cubic inches, calculating from the condensation of its elements assumed by Davy, must weigh 65.3 grains, at mean temperature and pressure, and it must contain in 100 grains,

Nitrogen . . . .	30.32	.....	100	.....	40.4
Oxygen . . . . .	69.68	.....	230	.....	100.
		—————			
			100.		

Its atomic constitution is 1 atom of nitrogen = 14, + 4 atoms of oxygen = 32, and its representative number is 46 ; or in volumes it consists of one of nitrogen and two of oxygen condensed into the space of one volume.

To form liquid nitrous acid, nothing more is necessary than to saturate water with this vapour. The water becomes first green, then blue, and finally an orange colour more or less deep. The latter may be brought to the state of green or blue by adding more or less water. Hence the colour depends merely on the circumstance of density.

The properties of liquid nitrous acid, Berzelius remarks,\* differ from those of nitric acid ; for while the latter boils at 236°, nitrous acid of the same density boils at 160°. The purely acid part he infers to be composed of 36.9 nitrogen + 63.1 oxygen. With bases, it forms a class of salts, which, he asserts, differ entirely from those containing nitric acid. On the other hand, we have the testimony of Gay Lussac, that the nitrous acid is decomposed with so much facility by contact with alkaline solutions, as to be incapable of forming a distinct class of salts. With solution of potash, for example, he found that it affords pernitrite and nitrate, but nothing that can properly be called a nitrite of potash.†

\* 13 Ann. de Chim. 10.

† Ann. de Chim. et Phys. i. 409.

*Nitric Acid.*

I. The direct combination of nitrogen and oxygen, affording a decisive synthetic proof of the nature of this acid, may be effected by passing electric sparks through a mixture of nitrogen and oxygen gases. The experiment is an extremely laborious one, and requires, for its performance, a powerful electrical machine; but those who are disposed to repeat it, may proceed as follows:

Let the tube, fig. 84, *c*, be filled with, and inverted in, mercury. Pass into it a portion of atmospherical air, or an artificial mixture of nitrogen and oxygen gases, in the proportion of one of the former to two of the latter.—Let an iron wire, lengthened out with one of platinum, be introduced within the tube, so that the latter metal only may be in contact with the mixed gases; and let the end of this wire be distant about one fourth of an inch from the extremity of the upper conducting one. When the apparatus is thus disposed, pass a series of electric sparks or shocks through the gases for several hours. The mixture will be diminished in bulk; will redden litmus-paper when enclosed in it; and will exhibit distinctly the smell of nitrous acid. If the experiment be repeated, with the addition of a few drops of solution of potash, in contact with the gases, we shall obtain a combination of nitric acid with potash.

This interesting experiment on the generation of nitric acid we owe to Mr. Cavendish, who discovered the fact in the year 1785.\* The proportions, which he found to be necessary for mutual saturation, were five parts of oxygen gas and three of common air, or seven parts of oxygen gas to three of nitrogen gas. The acid, thus obtained, being constituted of 100 measures of nitrogen + 233 oxygen, appears therefore to have been intermediate between nitrous and nitric acid, or more probably consisted of both those acids in a state of mixture. No evolution either of light or heat attends this combination, which is very slowly and gradually effected.

Pure nitric acid then is to be considered as a gaseous body,

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\* Philosophical Transactions, lxxv.

having the specific gravity, compared with that of common air, of 2.440. One hundred cubic inches, according to Sir H. Davy, weigh 76 grains at  $55^{\circ}$  Fahr. and under 30 inches pressure, or, corrected to the temperature of  $60^{\circ}$  Fahr., 75.21 grains. According to the experiments of Sir H. Davy, published in 1800, it is composed, in 100 grains, of  $29\frac{1}{4}$  azote, and  $70\frac{1}{4}$  oxygen. This approximation differs but little from the proportions deducible from the synthetic experiments of Cavendish, *viz.* 27.8 nitrogen to 72.2 oxygen. The later results of Sir H. Davy have led him, however, to believe, that 4 in volume of nitrous gas and 2 of oxygen gas, when condensed in water, absorb 1 in volume of oxygen to become nitric acid. We have then 2 volumes of oxygen (contained in 4 of nitrous gas) + 2 + 1 = 5 volumes of oxygen, to 2 of nitrogen, or  $2\frac{1}{2}$  volumes of oxygen to one of nitrogen, for the constituents of nitric acid in a gaseous state; and estimating the oxygen gas, existing in nitrous gas, at one half its volume, and taking the specific gravities of oxygen and nitrogen gases at the numbers already given, 100 parts by weight of nitric acid will consist of

Oxygen .....	74.13	.....	286
Nitrogen.....	25.87	.....	100
	100.		386

In investigating what number should be used as the equivalent of nitric acid, Dr. Wollaston was led to inquire into the composition of that acid; and, from his own experiments, and those of Richter and Phillips, he infers the oxygen, which nitric acid contains, to be by weight to the nitrogen, as 50 to 17.54. Hence nitric acid, as it exists in nitre, will be composed, by weight, of

Oxygen .....	74.03	.....	100	.....	285
Nitrogen .....	25.97'	.....	35	.....	100
	100.		135		385

By an easy calculation, it will be found that the nitrogen, in 100 grains of nitric acid thus constituted, is equal in volume to 88 cubic inches, and the oxygen to 219. But as 88 to 219, so is 100 to 249; and on this view of the nitric acid, it is

composed of 1 volume of nitrogen and  $2\frac{1}{2}$  volumes of oxygen, which agrees with the result of Sir H. Davy, and with the latest determination of Gay Lussac.\* Nitric acid, then, will consist of 5 atoms of oxygen = 40, and 1 atom of nitrogen = 14; and its atom will weigh 54.

The formation of liquid nitric acid, by the direct union of oxygen and nitrogen gases, or even by condensing oxygen and nitrous gases into water, is a process too tedious to be practicable on the large scale. The following is the method commonly employed for obtaining liquid nitric acid.

*Process for preparing Liquid Nitric Acid.*

Into a glass retort, which may be either tubulated or not, put four parts by weight of nitrate of potash, reduced to a coarse powder, and pour upon it three parts of concentrated sulphuric acid. Apply a tubulated receiver, of large capacity, between which, and the retort, an adopter may be interposed; these junctures being luted with a mixture of pipe-clay, sifted sand, and cut tow or flax.—To the tubulure of the receiver, a glass tube may be fixed by means of the fat lute, and may terminate in another large receiver, containing a small quantity of water.

If the operator wishes to collect the gaseous products also, this second receiver should be provided with a tubulure, to which a bent pipe may be luted, terminating under one of the inverted funnels in the shelf of the pneumatic trough. Apply heat to the retort, through the intervention of a sand-bath. The first product, that passes into the receiver, is generally of a red colour, and of a smoking quality. These appearances gradually diminish; and if the materials used were clean, the acid will come over pale, and even colourless. Afterwards it gradually re-assumes a red colour, and smoking property. These appearances go on increasing till the end of the operation; and the whole product, mingled together, has either a yellow or an orange colour, according to the temperature employed.

The proportions, recommended in the new London Phar-

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\* Ann. de Chim. et Phys. i. 404.

macopœia for the preparation of nitric acid, are two pounds of nitrate of potash, deprived by heat of its water of crystallization, and two pounds of sulphuric acid. These are directed to be mixed in a glass retort, and distilled in a sand-bath, until a red vapour arises. The acid in the receiver is to be mixed with an ounce of nitrate of potash, and again distilled in a similar manner. After the second distillation, its specific gravity is 1.500; and one fluid-ounce, Mr. Phillips finds, decomposes 476 grains of marble. But he objects to the proportion of sulphuric acid, in the process of the College, as unnecessarily large. If, however, it be required to decompose the whole of any portion of nitre, it is necessary to use as much sulphuric acid, as will form, with the alkali of the nitre, *bi-sulphate* of potash, *viz.* 97 parts of acid, of density 1.85, to 100 parts of nitre.

The nitric acid, which first passes over, has the greatest specific gravity. In an experiment of Dr. Perceval of Dublin, the product was taken in three portions; the first of which had the specific gravity of 1.494, the second of 1.485, and the third of 1.442.\* Gay Lussac, by two successive distillations of nitric acid of specific gravity 1.3 from four times its weight of sulphuric acid, brought it to the density of 1.510. In this state, he found it to be decomposed by heat or light with extraordinary facility.†

In the large way, and for purposes of the arts, it is usual to substitute earthen or cast-iron retorts, made extremely thick, for those of glass. An earthen head is adapted, and this is connected with a range of proper condensers. The strength of the acid is varied also, by putting more or less water into the receiver. What is called double aqua fortis varies in its specific gravity from 1.3 to 1.4.

Nitric acid, obtained by this process, is never perfectly pure. It contains, generally, both sulphuric and muriatic acids; the former of which is indicated by a white precipitate, on adding a solution of nitrate of barytes to a little of the acid diluted with 8 or 10 parts of water; and the latter, by a milkiness produced by nitrate or sulphate of silver. The sulphuric acid may be separated, either by a second distillation from a por-

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\* Transactions of the Irish Academy, iv. 37.

† Ann. de Chim. et Phys. vol. i.

tion of very pure nitre, equal in weight to one eighth of that originally employed, or by adding nitrate of barytes; allowing the precipitate to settle; decanting the clear liquid, and distilling it. Muriatic acid is separated by the addition of nitrate of silver. An immediate milkiness ensues, and fresh additions must be made of nitrate of silver, as long as it occasions this appearance. Then allow the precipitate to subside; decant the clear liquid, and re-distil it; leaving one eighth or one tenth in the retort. The product will be pure nitric acid. Nitrate of lead may be substituted for nitrate of silver.\* The nitric acid may also be obtained free from muriatic acid, if a perfectly pure nitrate of potash be employed for distillation. This purification is effected by repeated solutions of the nitre in boiling distilled water, and re-crystallizations.

Nitric acid, obtained in this manner, is defective also in another respect; for it is not perfectly oxygenated, but holds in solution a considerable quantity of nitrous gas or nitrous acid. To expel the latter, put the acid into a retort, to which a receiver is applied, the two vessels not being luted, but joined merely by paper. Apply a very gentle heat for several hours to the retort, changing the receiver as soon as it becomes filled with red vapours. The nitrous gas will thus be expelled, and the nitric acid will remain in the retort in a state of purity, and as limpid and colourless as water. It must be kept in a bottle secluded from the light.

One hundred parts of nitrate of potash, according to La Grange, yield by this process 43 of acid, or, according to my experience, above 50; but if the process of the College be followed, 100 of fused nitre afford about  $66\frac{1}{2}$  of acid. Even this, however, is not the whole of what was contained in the salt; for a part is decomposed by the temperature necessary to the operation. Accordingly, a large quantity of oxygen gas is disengaged during the distillation, and may be collected by an obvious addition to the apparatus.

In the retort, there remains a compound of potash with more sulphuric acid than is essential to its saturation, or a bi-sulphate of potash. On submitting this to a pretty strong heat, the excess of sulphuric acid is expelled; and the residue,

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\* See Nicholson's Journal, xi. 134.

dissolved and evaporated, affords crystallized sulphate of potash.

*Properties of Liquid Nitric Acid.*

The liquid nitric acid has the following properties:

(a) It is heavier than water, in the proportion of 1.5 or upwards to 1. Proust obtained it as high as 1.62; and the specific gravity of real nitric acid, which cannot, however, be obtained separately, may be calculated at 1.75. In its heaviest form, it still contains a portion of water, which is essential to its existence in a liquid state, and without which its elements would separate from each other. In acid of the sp. gr. 1.50, the water amounts, calculating from the data furnished by Dr. Wollaston, to 25.11 grains in 100 grains of acid; or, according to Mr. R. Phillips, to 25.09. According to Sir H. Davy, the strongest acid (sp. gr. 1.55) contains 14.4 parts of water in 100; and acid of sp. gr. 1.42 contains 25.2 of water in 100.\* We have not, however, at present, documents sufficient for the construction of an accurate Table of the quantities of *real nitric acid* in acids of different densities. The Table published by Mr. Dalton,† that philosopher has since found reason to believe to be inaccurate; and one which he communicated to me for the last edition of this work, does not appear to be entitled to greater reliance. Dr. Ure has constructed two Tables (for which see the Appendix), the first from experiments on the mixture of nitric acid of specific gravity 1.500 with water in the proportions of 95 + 5, 90 + 10, 80 + 20, &c.; and the second from the calculation of the intermediate terms by a law of progression, which may be thus stated: The specific gravity of dilute acid, containing 10 parts in the hundred of acid of density 1.500, is by experiment 1.054. Taking this number as the root, its successive powers will give us the successive densities, at the terms of 20, 30, 40 per cent, &c. Thus  $1054^2 = 1.111$  is the specific gravity corresponding to 20 strong acid + 80 water;  $1054^3 = 1.234$  the density of 30 strong acid + 70 water; and hence any one term being given the whole series may be found. In the construction of this table, however, there appears to have been an error in assuming that nitric acid of sp.

\* Elements, p. 265.

† New System, p. 355.

gr. 1.500 contains in 100 parts 79.7 of real acid; for this considerably exceeds the proportion deduced by any of the philosophers whose results have been quoted.

(*b*) Hydro-nitric acid is perfectly limpid and colourless, and emits white fumes when exposed to the air.

(*c*) It gives a yellow stain to the skin.

(*d*) It boils at 248° Fahrenheit, and may be distilled over, without any essential change. This, however, is true only of acid of the specific gravity 1.42; for an acid, weaker than this, is strengthened by being boiled; while an acid, stronger than 1.42, becomes weaker by boiling. All the varieties of nitric acid, therefore, are brought, by sufficient boiling, to the specific gravity 1.42.

(*e*) Hydro-nitric acid may be frozen by the application of a sufficiently low temperature. Like sulphuric acid, there is a certain point of density at which it most readily congeals. Mr. Cavendish has described this, not by its specific gravity, but by the quantity of marble which it is capable of dissolving. When it takes up  $\frac{4.16}{1000}$ ths of its weight, in which case its specific gravity is 1.3, the acid freezes at 2° below 0 Fahrenheit. When considerably stronger and capable of dissolving  $\frac{3.61}{1000}$ ths, it required cooling to — 41.6; and when so much diluted as to take up only  $\frac{3.76}{1000}$ ths, it did not congeal till cooled to — 40.3.\*

(*f*) Strong hydro-nitric acid absorbs moisture from the atmosphere; in consequence of which it increases in weight, and diminishes in specific gravity.

(*g*) When two parts of the acid are suddenly diluted with one of water, an elevation of temperature is produced to about 112° Fahrenheit; and the admixture of 58 parts by weight of acid of specific gravity 1.50 with 42 parts of water, both at 60° Fahrenheit, gives a temperature of 140°.† When more water is added to this diluted acid, its temperature is reduced. Snow or ice, added to the cold dilute acid, is instantly liquefied, and an intense degree of cold is produced.

(*h*) It becomes coloured by exposure to the sun's light, passing first to a straw colour, and then to a deep orange. This effect is produced by the union of the light of the sun with

\* Phil. Trans. 1788.

† Dr. Ure, Journ. of Science, iv. 298.



oxygen, in consequence of which the proportion of the acidifying principle to the nitrogen is diminished.

By exposing it to the sun's rays in a gas bottle, the bent tube of which terminates under water, oxygen gas may be procured.

(i) This acid retains its oxygen with but little force.—Hence it is decomposed by all combustible bodies, which are oxygenized by it, with more or less rapidity in proportion to their affinity for oxygen.

1. When brought into contact with hydrogen gas at a high temperature, by transmitting them together through an ignited porcelain tube, a violent detonation ensues. This experiment, therefore, requires great caution. 2. Poured on perfectly dry and powdered charcoal, it excites the combustion of the charcoal, which becomes red-hot, and emits an immense quantity of fumes. 3. It also inflames essential oils (as those of turpentine and cloves,) when suddenly poured on them. In these experiments, the acid should be poured out of a bottle, tied to the end of a long stick; otherwise the operator's face and eyes may be severely injured. 4. Nitric acid is decomposed, by boiling it in contact with sulphur, which attracts the oxygen, and forms sulphuric acid.

(k) The hydro-nitric acid is also decomposed by metals; as iron, tin, zinc, copper, &c. and with different phenomena, according to the affinity of each metal for oxygen. This may be seen, by pouring some strong nitric acid on iron filings, or powdered tin. The acid must be of greater density than 1.48, otherwise it will not produce the effect. Violent heat, attended with red fumes, will be produced, and the metals will be oxidized.

(l) Liquid nitric acid absorbs nitrous gas, and undergoes a considerable change of colour and properties. The gas may be transmitted, as it issues from the materials that afford it, through a quantity of colourless nitric acid, which first passes to straw yellow, and becomes gradually deeper in its colour, till at length it assumes a deep orange, and emits red coloured fumes. According to Dr. Priestley (on Air, 2d edit. i. 383), 100 parts of nitric acid of specific gravity 1.4 absorb in two days 90 parts by weight of nitrous gas.\* Seven parts of gas, he states, are sufficient to give the acid an orange hue; when 18

\* There appears to be some error in this statement, for according to Sir

have been absorbed it becomes green ; and when it has taken up all that it is capable of condensing, it emits an immense quantity of red fumes. The gas thus absorbed may be expelled again by a gentle heat, or by diluting the acid with water.

Sir H. Davy, in the year 1800, gave the following table, showing the proportion of nitrous gas in nitrous acid of different colours.

	Sp. Gr.	100 parts by weight contain		
		Real Acid.	Nit. Gas.	Water.
Pale yellow . . . . .	1.502	90.5	1.2	8.3
Bright ditto . . . . .	1.50	88.94	2.96	8.1
Dark orange . . . . .	1.480	86.84	5.56	7.6
Light olive . . . . .	1.479	86.	6.45	7.55
Dark olive . . . . .	1.478	85.4	7.1	7.50
Bright green . . . . .	1.476	84.8	7.76	7.44
Blue green . . . . .	1.475	84.6	8.	7.40

Mere dilution with water is sufficient to vary these colours. Thus the dark orange-coloured acid, by dilution, passes through the shades of blue, olive, and bright green. Nitric acid, also, by absorbing nitrous gas, has its specific gravity diminished. Colourless acid, for example, when rendered of pale yellow, becomes lighter in the proportion of 1.51 to 1.502.

#### *Nitro-Muriatic Acid.*

This acid may be formed most commodiously by mixing two parts by weight of colourless nitric acid with one of liquid muriatic acid. Proust employs only one of nitric to four of muriatic acid. Though the acids are both perfectly pale, yet the mixture becomes of a deep red colour, a brisk effervescence takes place, and pungent vapours of chlorine are evolved.

Considerable light has been thrown on the nature of this acid by the experiments of Sir H. Davy,\* who has rendered it probable that its peculiar properties are owing to a mutual

II. Davy 100 parts of nitric acid, when saturated with nitrous gas, hold only 9 or 10 of the latter; and into acid of sp. gr. 1.3, Mr. Dalton could not condense above 20 times its bulk, or a little more than 2 per cent. by weight.

\* Journal of Science, &c. i. 67.

decomposition of the nitric and muriatic acids, the oxygen of the former uniting with the hydrogen of the latter, in consequence of which water, chlorine, and nitrous acid, are the results. For every 101 parts in weight of real nitric acid (equivalent to 118 of hydro-nitric acid) which are decomposed, 67 parts of chlorine, he calculates, are produced. According to this view, it is not correct to say that *aqua regia* oxidates gold or platinum, since it merely causes their combination with chlorine. By long continued and gentle heat, nitro-muriatic acid may be entirely deprived of chlorine, and it then loses its power of acting on gold and platinum.

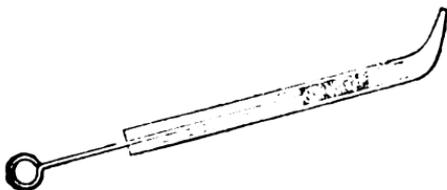
The nitro-muriatic acid does not form, with alkaline or other bases, a distinct genus of salts, entitled to the name of nitro-muriates; for, when combined with an alkali, or an earth, the solution yields, on evaporation, a mixture of a muriate and a nitrate; and metallic bodies dissolved in it yield muriates only. The most remarkable property of nitro-muriatic acid (that of dissolving gold, from whence it has been called *aqua regia*) will be described in the chapter on that metal.

#### *Combination of Nitrogen with Chlorine.*

Chlorine has no action whatsoever on nitrogen gas, nor on nitrous gas or nitrous oxide, when both gases are perfectly dry; but a compound of chlorine and nitrogen may be formed, by passing chlorine gas through a solution of nitrate of ammonia, or of almost any ammoniacal salt, of the temperature of 80° to 90° Fahrenheit. The chlorine gas is rapidly absorbed, and a film appears on the surface, which soon collects into yellowish drops, that sink to the bottom of the liquor.

Mr. Brande recommends, as the simplest method of forming it, to fill a perfectly clean glass basin with a solution of about one part of sal ammoniac in twelve of water, and to invert into it a tall jar of chlorine gas. The saline solution gradually rises into the glass, a film forms upon its surface, and it acquires a deep yellow colour. At length small globules, resembling yellow oil, collect upon its surface, and successively fall into the basin beneath, from whence they are most conveniently removed by drawing them into a small and perfectly clean glass syringe, made of a glass tube drawn to a

pointed orifice, and having a copper wire, with a little tow wrapped round it for a piston. In this way a globule may be drawn into the tube, and transferred to any other vessel.



This yellowish and oily fluid is the most powerfully detonating compound with which we are acquainted. When gently warmed, it explodes with so much violence, that it is not safe to employ a quantity larger than a grain of mustard seed. Its discoverer, M. Dulong,\* was severely wounded in his first experiments on this substance; and Sir H. Davy had a serious injury done to his eyes in repeating them. It is expedient, therefore, to proceed with great caution.

When a globule of this fluid is thrown into olive oil, turpentine or naphtha, it explodes even without heat, and so violently, as to shatter any glass vessel. The same effect ensues when it touches phosphorus, or phosphorized alcohol or ether; but pure alcohol seems to deprive it of its explosive property, and renders it a white oily matter.

The specific gravity of the fluid, Sir H. Davy has determined to be 1.653, water being 1.† It is not congealed, by exposure to the cold produced by snow and muriate of lime.

Messrs. Porrett, Wilson, and Kirk, have published an elaborate memoir on this compound in Nicholson's Journal, xxxiv. 180, and have described at great length the appearances attending its formation, and the results of acting upon it with a great variety of substances. These experiments tend to show that it will not explode at any temperature much under 212° Fahr. nor without the contact of a combustible body; that it may be distilled at or below 160°, and does not become solid at - 16°. Though the class of bodies termed combustible act upon it most remarkably, yet there are some bodies of that description, camphor for instance, with which it seemed to unite without

\* See Ann. de Chim. vol. 85.

† Phil. Trans. 1813.

decomposition; nor did the metals, resins, or sugar, cause it to explode. It detonated with the following only, out of 125 substances that were tried.

Supersulphureted hydrogen.	Oil of tar.
Phosphorus.	Oil of amber.
Phosphuret of lime.	Oil of petroleum.
Caoutchouc.	Oil of orange peel.
Myrrh.	Naphtha.
Palm oil.	Metallic soaps.
Ambergris.	Fused potash.
Whale oil.	Solution of ammonia.
Linseed oil.	Phosphureted hydrogen gas.
Olive oil.	Nitrous gas.
Ditto camphoreted.	Phosphureted camphor.
Ditto sulphureted.	Oil of turpentine.

The products of its detonation are chlorine and nitrogen gases, but it is impossible to determine the bulk of those elements which are afforded by a given weight. The best method of analyzing it, is by its action on mercury, which unites with the chlorine, and sets the nitrogen free. From various experiments of this kind, Sir H. Davy concludes that it is composed of four in volume of chlorine to one in volume of nitrogen, or of

Chlorine . . . . .	91.2
Nitrogen . . . . .	8.8
	100.

These proportions correspond best with the opinion, that it is constituted of one atom of nitrogen to four atoms of chlorine; it will be represented therefore by  $14 + (36 \times 4 =)$  144, making together 158; but its analysis is not sufficiently correct to render these numbers worthy of implicit reliance.

#### *Of the Compound of Nitrogen with Iodine.*

Iodine cannot be brought to act directly upon nitrogen, but when iodine is kept in a solution of ammonia in water, it is gradually converted into a brownish black substance which is an *iodide of nitrogen*. This may be collected, and dried at a very gentle heat on bibulous paper.

This compound evaporates spontaneously in the open air. It explodes with great violence when touched or when heated, and is converted into nitrogen gas and iodine, but all attempts to collect the products have failed, and we are ignorant therefore of the proportion of its components.

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### SECTION III.

#### *Of Carbon, and its compounds with Oxygen, Chlorine, and Iodine.*

CHARCOAL, in the form under which it ordinarily occurs, contains several ingredients that are not essential to it; and it is to the pure carbonaceous principle, divested of these impurities, that the term Carbon is alone properly applied. The diamond, which Sir I. Newton had sagaciously inferred to be a combustible body, from its powers of refracting light, was first shown by Guyton to contain carbon,\* and his experiments led him to conclude that the diamond is the only form of pure carbon; and that charcoal is a compound of carbon and oxygen, or an oxide of carbon. The experiments of Messrs. Allen and Pepys have, however, gone far towards proving that the diamond and charcoal, though so widely remote from each other in external characters, are, as to their chemical nature, identically the same; and that the difference between them, in all probability, results merely from the respective states of aggregation of their particles.

Some doubts, it must be confessed, were thrown on this conclusion by an experiment of Sir H. Davy, in which an inflammable gas was obtained, by igniting charcoal in a Toricellian vacuum, by a powerful Voltaic battery. But the hydrogen, thus evolved, may reasonably be ascribed to water, from which it is extremely difficult, if not impossible, to free charcoal. The absence of oxygen from charcoal was proved, by heating it with potassium, for no potash was produced; but when potassium was heated with diamond, there was an indistinct appearance of the production of that alkali. The subsequent experiments of the same philosopher† tend to es-

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\* *Annales de Chimie*, xxxi.

† *Phil. Trans.* 1814, p. 557.

tablish, that charcoal invariably contains either hydrogen or water; for when it is burned in pure and dry oxygen gas, some moisture is always deposited. The quantity, however, is so small, that hydrogen cannot exist in charcoal as an essential ingredient, or in any definite proportion. The diamond appears to be absolutely free both from water and hydrogen; and it is in this respect only, and in the mechanical arrangement of its particles, that we have any evidence of its differing from charcoal. If proof were wanted of the identity of the two substances, it is furnished by the fact that the diamond converts iron into steel, under circumstances quite free from all sources of fallacy.\*

To obtain charcoal free from contamination, pieces of oak, willow, hazle, or other woods, deprived of the bark, may be buried in sand in a crucible, which is to be exposed, covered, to the strongest heat of a wind-furnace. For purposes of accuracy, charcoal must be used when recently prepared, and before it has had time to become cold; or if it cannot be had fresh made, it must be heated again to redness under sand in a crucible. A remarkably pure charcoal may be obtained by passing the vapour of oil of turpentine, or of spirit of wine, through a red hot tube. It then appears in the form of a black impalpable powder. In the experiments of Sir H. Davy, this sort of charcoal, by combustion in oxygen gas, gave a much smaller product of moisture than any other.

From 100 parts of each of the following woods Messrs. Allen and Pepys obtained the annexed quantities of charcoal; *viz.* from fir, 18.17; *lignum vitæ*, 17.25; box, 20.25; beech, 15; oak, 17.40; mahogany, 15.75.

In the large way, charcoal is now most commonly prepared in this country by the distillation of wood in cast iron cylinders. The loppings of young trees, commonly called crop wood, are generally employed; and, besides the charcoal, liquid products of value are collected, especially an impure vinegar called *pyroligneous acid*. The process is described at length by Mr. Parkes in the 2d volume of his "Chemical Essays," p. 271.

The charcoal of wood, besides its use as a fuel, is necessary to the preparation of that kind of iron which is used for wire;

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\* Phil. Trans. 1815, p. 371.

to the cementation of steel; and to the preparation of gunpowder. The charcoal prepared from coal, called *coke*, is less pure, and, beside other substances, generally contains sulphur; but it has the advantage of being heavier and more compact, in consequence of which it is better adapted for burning in furnaces in which there is a powerful blast of air.

Lamp black, a necessary ingredient of printing ink, is the condensed soot collected from the refuse resin of turpentine makers.

Charcoal has the following properties:

1. In its aggregated state it is black, perfectly insipid, and free from smell; insoluble in water, brittle, and easily pulverized. In close vessels, and entirely secured from contact with air, it is unchanged by any degree of heat. A gas, however, may be collected from it by distillation, which consists of hydrogen and carbon, and perhaps a little oxygen. Berthollet has found, also, in the æriform products of its distillation, a considerable proportion of nitrogen.\*

In the section on carbonic acid, it will be explained what is meant by the *vapour* of *charcoal*, and it may be sufficient at present to observe that this term is not applicable to charcoal in any state in which it can be experimentally exhibited, but to that state in which it exists in gaseous combination with other bodies.

2. Charcoal has the singular property of absorbing gases without alteration. Fill a jar with common air, or any other gas, and place it over dry mercury: take a piece of charcoal, red-hot from the fire, and plunge it in the mercury of the bath: when cold, let it be passed into the vessel of gas, without bringing it into contact with the atmosphere. A considerable diminution of the gas will be effected; and in 24 or 36 hours its absorption will be completed.

Count Morozzo has given the following table of the quantities of different gases, absorbed in the foregoing manner by charcoal. In each experiment, he employed a piece of that substance 1 inch long and  $\frac{3}{4}$  of an inch diameter. The receiver containing gas was 12 inches long and 1 inch diameter.

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\* Mémoires d'Arcueil, ii. 484.



Gas absorbed.	Inches.	Gas absorbed.	Inches.
Atmospheric air .....	3½	Nitrous .....	6⅝
Carbonic acid .....	11	Hydrogen .....	2⅞
Ammonia .....	11	Oxygen .....	2⅞
Muriatic acid .....	11	Sulphurous acid .....	5½
Sulphureted hydrogen ..	11		

This property of charcoal has been made the subject of a valuable set of experiments by Saussure.\* Charcoal of box-wood he found to absorb, in less than 24 hours, of

	Volumes.
Aminoniacal gas .....	90
Muriatic acid .....	85
Sulphurous acid .....	65
Sulphureted hydrogen .....	55
Nitrous oxide .....	40
Carbonic acid .....	35
Olefiant gas .....	35
Carbonic oxide .....	9.42
Oxygen .....	9.25
Azote .....	7.5
Hydrogen .....	1.75

Most of the phenomena attending this absorption have already been described, in speaking of the absorption of gases by solids. It appears to be entirely a mechanical effect; for even those gases that have an affinity for charcoal (hydrogen and oxygen for instance), are given out unchanged at the heat of boiling water. The densest and heaviest kinds of charcoal are most remarkable for this property, which is much diminished by pulverizing them; and it does not exist at all in plumbago or in stone coal.

3. From the experiment of Rouppe,† it appears, that if charcoal, which has imbibed oxygen gas, be brought into contact with hydrogen gas, water is generated; but Saussure, by a careful repetition of it, could not obtain the same result.

4. Charcoal, by long exposure to the atmosphere, absorbs one twentieth of its weight, three fourths of which are water.‡

The charcoal of different woods, Messrs. Allen and Pepys found to increase very differently in weight; that from fir

\* Thomson's Annals, vi. 241.

† Ann. de Chim. xxxii, 1.

‡ Clement and Desormes.

gained, by a week's exposure, 13 per cent. ; that from *lignum vitæ*, in the same time, 9.6 ; from box, 14 ; beech, 16.3 ; oak, 16.5 ; mahogany, 18. The absorption goes on most rapidly during the first 24 hours ; and by much the largest part of what is absorbed consists of water merely.

5. Charcoal resists the putrefaction of animal substances. A piece of flesh-meat, which has begun to be tainted, may have its sweetness restored by rubbing it daily with powdered charcoal ; and may be preserved sweet for some time by burying it in powdered charcoal, which is to be renewed daily. Putrid water is also restored by the application of the same substance ; and water may be kept unchanged at sea, by perfectly charring the inner surface of the casks which are used to contain it.\* It produces, also, a remarkable effect in destroying the taste, odour, and colour of many vegetable and animal substances. Common vinegar, by being boiled on it, is rendered perfectly limpid. Rum and other varieties of ardent spirit, which are distinguished by peculiar colours and flavours, lose both by maceration with powdered charcoal. The colour of litmus, indigo, and other pigments, dissolved or suspended in water, is destroyed. Putrid animal fluids, and air contaminated with offensive fumes, are, also, completely deprived of their odour. These effects are most certainly produced by animal charcoal;† which is best adapted for this purpose when obtained by calcining bones in close vessels.

6. Charcoal is a very slow conductor of caloric. The experiments of Guyton have determined, that caloric is conveyed through charcoal more slowly than through sand, in the proportion of three to two. Hence powdered charcoal may be advantageously employed to surround substances which are to be kept cool in a warm atmosphere ; and also to confine the caloric of heated bodies. It affords, however, an easy transmission to the electric fluid.

7. The weight of the atom of charcoal is inferred by Mr. Dalton to be 5.4, that of oxygen being 7. But if the weight of the atom of oxygen be corrected to 8, the atom of charcoal will then weigh 6. The evidence in favour of this conclusion will be stated in the following section. The specific gravity,

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\* Lovitz, *Ann. de Chim.* tom. xiv.

† 79 *Ann. de Chim.* 80 ; *Journ. of Science, &c.* iv. 367.

which it would have, if reducible into a vaporous form, is calculated by Gay Lussac to be 0.416.

*Combustion of Carbon.*

If a small piece of charcoal be exposed red-hot to atmospheric air, it exhibits scarcely any signs of combustion, and soon becomes cold; but Sir H. Davy has observed that dry charcoal converts oxygen gas pretty rapidly, though imperceptibly, into carbonic acid, at a temperature a little above the boiling point of quicksilver,\* and, according to Saussure, the oxygen gas, which is absorbed by charcoal, becomes converted in time into carbonic acid, at the common temperature of the atmosphere. If a piece of charcoal, heated to about 800° or 1000° Fahrenheit, or nearly to redness, be introduced into a receiver filled with oxygen gas, it continues to burn with greatly increased splendour, and with bright scintillations; and if the charcoal be pure, and its proportion rightly adjusted, it is entirely consumed. When the quantity burnt is considerable, a manifest production of water takes place, and the inner surface of the glass vessel becomes covered with moisture, which disappears, however, on standing. This portion of water owes its origin to the union of oxygen with the hydrogen, which, it appears from Sir H. Davy's experiments and from the results of its distillation, all charcoal contains.

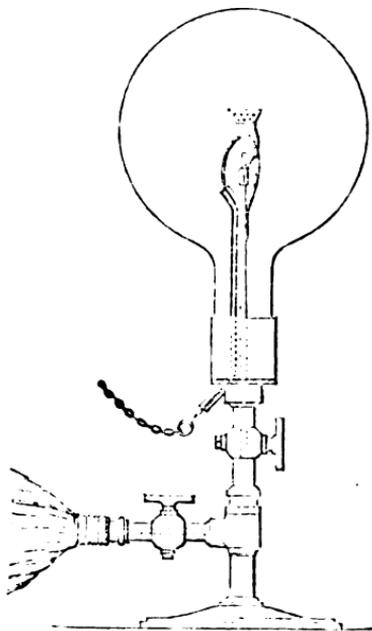
The diamond, also, which was formerly considered as an incombustible substance, may be consumed by a sufficiently intense heat, even in atmospherical air. The Florentine academicians, in the year 1694, appear first to have ascertained this fact, by exposing diamonds to the focus of a powerful burning lens. Their experiment has been repeated by subsequent chemists, with various modifications. It has been found by Sir George Mackenzie that diamonds burn in atmospheric air, when exposed on a muffle, to the temperature of about 1½° Wedgwood. In oxygen gas the diamond takes fire, when the focus of a powerful lens is thrown upon it; and continues to burn, though removed out of the focus, with a steady brilliant light, visible in the strongest sunshine.† The portion of diamond, which remains unconsumed, is not ren-

\* Phil. Trans. 1817, p. 16.

† Davy, in Phil. Trans. 1814.

dered black, as has been asserted, but is found to have lost its lustre, like glass acted on by fluoric acid. When the vessel has become cold, no production whatsoever of moisture is visible. By effecting its combustion in this way, Guyton thought he had determined that the diamond, in an equal weight, contains more real carbon than exists in common charcoal. His experiments, however, have not been confirmed by those of other chemists. One fact, however, has been contributed on this subject by Guyton, which is of considerable value. The diamond, he first ascertained, is destroyed when thrown into red-hot and melted nitre; and this property, it will afterwards appear, has been successfully applied by Mr. Tennant to the determination of the nature of the diamond, and of the proportion of ingredients in carbonic acid.

At the Royal Institution, an apparatus is employed for the combustion of the diamond, from which, with Mr. Brande's permission, the annexed sketch has been taken. It consists of a glass globe, capable of holding about 140 cubical inches, which, when used, is first exhausted, and then filled with oxygen gas. In the centre of this globe is supported a small hemispherical cup of platinum, pierced with small holes. This is destined for containing the diamonds; and beneath it, at the distance of about  $\frac{3}{4}$  of



an inch, is the orifice of a small pipe, from which a jet of hydrogen gas may be forced, by opening the cock and pressing the bladder. This stream of hydrogen being lighted by electric sparks, taken by means of a contrivance usually employed for such purposes, ignites the diamonds, and, when they are white-hot, the gas is extinguished by shutting the cock. The diamonds continue to burn till they are so much reduced in

size that the cooling power of the platinum, with which they are in contact, prevents their farther combustion. After the apparatus has cooled, the gas within the globe will be found, when examined by rules which will presently be given, to have undergone an essential change, and to be partly converted into carbonic acid.

To collect the entire products of the combustion of carbon, in either of its forms, requires rather a complicated apparatus. Lavoisier burnt charcoal in a known quantity of oxygen gas, which was confined by mercury, the charcoal being set on fire by a bent iron wire heated to redness,\* and introduced through the quicksilver. Messrs. Allen and Pepys collected the products of the combustion of charcoal and of the diamond, by burning them separately in a platinum tube, set horizontally in a charcoal furnace, and connected at each extremity with a mercurial gazometer. A correct idea of this arrangement will easily be obtained by imagining that to each end of the tube *c*, fig. 40, the pipe *b* of a gazometer, like that shown fig. 35, is connected. At the outset of the experiment, one of the gazometers was filled with a known quantity of the purest oxygen gas, and the other was empty. The tube was then made red-hot; and the gas, being forced alternately from one gazometer to the other, was repeatedly brought into contact with the red-hot charcoal or diamond. The volume of the gas was found to be entirely unaltered; but it had received an addition to its weight precisely equal to what the charcoal or diamond, on weighing, was ascertained to have lost; and it was partly converted into a gas, totally different in its properties from oxygen gas, and called carbonic acid. It appears, therefore, that oxygen gas, by conversion into carbonic acid, undergoes neither expansion nor condensation. This conclusion is farther established by the recent experiments of Sir H. Davy, on the combustion of the diamond in oxygen gas.

#### *Carbonic Acid.*

From the quantity of charcoal or diamond consumed in the experiments of Allen and Pepys, and the quantity of oxygen converted into carbonic acid, it is easy to infer the proportion

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\* Elements of Chemistry, pl. iv. fig. 3.

of carbon and oxygen in the new compound. Reducing these to centesimal proportion, for every 28 or 29 grains of the combustible base which disappeared, 100 grains of carbonic acid (= about 201 cubic inches) were generated; and it is remarkable that these proportions agree exactly with those originally stated by Lavoisier. The same quantity of carbonic acid resulted, also, from the combustion of between 28 and 29 grains of diamond. Hence it may be inferred, that the actual quantity of carbon in equal weights of diamond and charcoal is very nearly the same; and that charcoal is not, as has hitherto been supposed, an oxide of carbon; their only difference consisting in the presence of hydrogen in charcoal, in so small a proportion as not materially to diminish the quantity of carbonic acid produced by its combustion. If this inference required confirmation, it is furnished by its agreement with Mr. Tennant's experiments on the combustion of the diamond, published in 1797. Two grains and a half of diamond (that philosopher found), when consumed in a tube of gold by means of nitre, gave nine grains of carbonic acid, which, in 100 parts, should contain, therefore, as nearly as possible, 28 parts of diamond or carbon. The mean of a number of Messrs. Pepys and Allen's experiments give the following statement of the composition of carbonic acid :

Carbon .....	28.60	.....	100
Oxygen .....	71.40	.....	250
	<hr style="width: 50%; margin: 0 auto;"/>		
	100.		

It is remarkable, also, that these numbers are precisely those which result from the experiments of Clement and Desormes.\* They differ, however, a little, from those of Saussure, jun., who states the carbon in 100 grains of carbonic acid at between 27.04 and 27.38 grains. The results of Gay Lussac, which are conformable with the views of Berzelius, and, as nearly as possible with those of Dr. Wollaston, are,

Carbon .....	27.376	.....	100.	.....	37.55
Oxygen .....	72.624	.....	265.12	.....	100.
	<hr style="width: 50%; margin: 0 auto;"/>			<hr style="width: 50%; margin: 0 auto;"/>	
	100.		365.12		137.55

\* Ann. de Chim, xxxix. 42.

Mr. Dalton assumes the composition of carbonic acid to be, in round numbers, 28 of charcoal and 72 of oxygen; from whence he deduces the weight of the atom of charcoal to be 5.4. But if the atom of oxygen weigh 8, and if the proportions just assigned be correct, the atom of charcoal will weigh 6, and that of carbonic acid (considering it as a ternary compound of two atoms of oxygen and one of charcoal) will be  $16 + 6 = 22$ . On the theory of volumes, its constitution has been stated by Gay Lussac to be 1 volume of gaseous carbon + 1 volume of oxygen, condensed into the space of 1 volume, and the density of the vapour of charcoal has been estimated to be equal to the density of carbonic acid, less that of oxygen gas, or to  $1.5245 - 1.1025 = 0.422$ . When two volumes of carbonic oxide are converted into carbonic acid, we add a volume of oxygen equal to that already existing in two measures of the former gas, *viz.* one volume, and obtain two volumes of carbonic acid, which gas may therefore be considered, under this aspect, as constituted of one volume of oxygen + half a vol. of carbonic oxide condensed into one volume. This view of the constitution of carbonic acid and carbonic oxide rests, however, it is evident, upon the presumption, that the general law, deduced by the last mentioned philosopher from a variety of other cases, applies in this instance; *viz.* that *gaseous compounds either contain equal volumes of their elements, or that if either exceed, the excess is by some simple multiple of the smaller volume.*

In addition to the proofs of the constitution of carbonic acid, derived from its synthesis, we have also the evidence of its analysis, which may be effected by several processes.

1. By passing a succession of electrical discharges through a quantity of carbonic acid gas confined over mercury, I have found that the gas is separated into oxygen, and a gas called carbonic oxide, which consists of oxygen united with a larger proportion of carbon than exists in carbonic acid. When the carbonic acid, which escapes decomposition, has been washed out by solution of potash, an electric spark inflames the residuary mixture; the oxygen and carbonic oxide again uniting, and re-composing carbonic acid.\*

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\* Phil. Trans. 1809, p. 448.

2. When a mixture of carbonic acid and hydrogen gases is electrified, the hydrogen combines with part of the oxygen of the acid, and reduces it to the state of carbonic oxide. The same products are obtained, by transmitting a mixture of two parts of hydrogen gas and one of carbonic acid through a glazed porcelain tube strongly ignited. The hydrogen, uniting with a part of the oxygen of the carbonic acid, brings the latter to the state of carbonic oxide, at the same time that water is formed.

3. When potassium is heated in carbonic acid gas, Sir H. Davy has found that the metal inflames; part of it is oxidated at the expense of the acid; and part of it unites with the charcoal, which is precipitated.

4. By simply heating phosphorus in carbonic acid gas, no step is made towards the decomposition of the latter. But by applying phosphorus to some of the combinations of carbonic acid, the phosphorus is oxygenated, and carbon appears in a separate form. The original discovery of this fact is due to Mr. Tennant,\* and the details of the experiment have been ably followed up by Dr. Pearson.†

To exhibit this fact, provide a tube of very thin glass, about one-third of an inch wide, and 18 or 20 inches long, sealed at one end. Coat it, within about an inch of the sealed extremity, with a lute of sand and clay; and when this is dry, put into it as much purified phosphorus, in small pieces, as will fill the uncoated part. Then cover the phosphorus with carbonate of lime, or carbonate of soda which has been deprived of its water of crystallization. Let the part of the tube, which contains the carbonate, be made red-hot by means of a portable furnace; and, at this moment, apply heat to the part containing the phosphorus, sufficient to melt and raise it into vapour. The vapour of the phosphorus, coming into contact with the red-hot carbonate, will decompose the carbonic acid; and charcoal will be found in the residue of the process, in the form of a very light and black powder.

To procure carbonic acid, sufficiently pure for the exhibition of its properties, the combustion of charcoal is far from

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\* Phil. Trans. 1791, p. 182.

† Ibid, 1792, p. 289.



being the best process. The student may, therefore, have recourse to another, the rationale of which he will not, at present, understand; but which will be explained afterwards. Into a common gas bottle, put a little powdered marble or chalk; and pour on this sulphuric acid, diluted with five or six times its weight of water: or upon small fragments of marble about the size of horse beans, contained in a gas bottle, pour muriatic acid diluted with 8 or 10 times its weight of water, which disengages the gas more slowly and conveniently. This gas may be received over mercury; but a mercurial apparatus is not absolutely essential, since the gas may be collected over water, if used immediately when procured. Carbonic acid may, also, be separated by heat alone, from carbonate of lime. For this purpose, coarsely powdered chalk or marble may be put into the iron vessel *a*, fig. 85, which may be connected, by means of the conducting pipe *b*, with a gazometer. The receiving cylinder of the latter, after a sufficiently long continuance of heat to the bottle *a*, will be filled with carbonic acid gas, contaminated, however, by a small proportion of carbonic oxide, and sometimes a little hydrogen.

#### *Properties of Carbonic Acid.*

(*a*) *It extinguishes flame.*—Set a vessel, filled with the gas, with its mouth upwards, and let down a lighted candle. The candle will instantly be extinguished.

A person, says Dr. Priestley, who is quite a stranger to the properties of this kind of gas, will be agreeably amused with extinguishing lighted candles, or blazing chips of wood, on its surface. For the smoke readily unites with this kind of air; so that little or none of it escapes into the atmosphere. It is remarkable, that the upper surface of this smoke, floating in the fixed air, is smooth and well defined; whereas the lower surface is exceedingly ragged, several parts hanging down to a considerable distance within the body of the carbonic acid, and sometimes in the form of balls, connected to the upper stratum by slender threads, as if they were suspended. The smoke is also apt to form itself into broad flakes, exactly like clouds. Making an agitation in this air,

the surface of it (which still continues exactly defined) is thrown into the form of waves ; and if, by this agitation, any of the carbonic acid be thrown over the sides of the vessel, the smoke, which is mixed with it, will fall to the ground, as if it were so much water.

(*b*) *It is fatal to animals.*—Put a mouse, or other small animal, into a vessel of the gas, and cover the vessel, to prevent the contact of common air. The animal will die in the course of a minute or two.

By means of this gas, butterflies, and other insects, the colours of which it is desirable to preserve, for the purpose of cabinet specimens, may be suffocated better than by the common mode of killing them with the fumes of sulphur.

(*c*) *This gas is heavier than common air.*—According to Sir H. Davy, 100 cubic inches, at 55° Fahrenheit, and 30 inches of the barometer, weigh 47.5 grains; and at 60°, with the same pressure, would weigh 47.11. Messrs. Allen and Pepys determined that 100 cubic inches, at 60° Fahrenheit, and 30 inches barometer, weigh 47.26 grains. Its specific gravity, according to Biot and Arago, is 1.5196; and hence, if 100 cubic inches of atmospheric air weigh 30.5 grains, the same bulk of carbonic acid gas should weigh 46.34 grains. Dr. Ure finds it to weigh 46.4. Dr. Thomson states its specific gravity to be 1.5266, and Berzelius and Dulong 1.5240. It will be a sufficiently near approximation to take the weight of 100 cubical inches at 46.5 grains, at a mean of the barometer and thermometer.

To show the superior specific gravity of this gas in a general way, the following experiment will be sufficient. Let a long glass tube, proceeding from a gas bottle, containing powdered marble and dilute sulphuric acid, be twice bent at right angles; let the open end of the longer leg reach the bottom of a glass jar, perfectly dry within, and standing with its mouth uppermost. The carbonic acid will expel the common air from the jar, because it is heavier.—This superior gravity may be farther shown as follows: When the jar is perfectly filled with the gas (which may be known by a lighted candle being instantly extinguished when let down into it), take another jar, of rather smaller size, and place at the bottom

of it a lighted taper, supported by a stand: then pour the contents of the first-mentioned jar into the second, as if you were pouring water. The candle will be instantly extinguished, as effectually as if it had been immersed in water.

It is owing to its superior gravity, that carbonic acid gas is often found at the bottom of grottoes, of deep wells, and of mines, the upper part of which is entirely free from it. Hence the precaution, used by the sinkers of wells, of letting down a candle before they venture to descend in person.

(d) *Carbonic acid gas is absorbed by water.*—Fill partly a jar with this glass, and let it stand inverted a few hours over water. An absorption will gradually go on, till at last none will remain. This absorption is infinitely quicker when agitation is used. Repeat the above experiment, with this difference, that the jar must be shaken strongly. A very rapid diminution will now take place. In this manner water may be charged with rather more than its own bulk of carbonic acid gas; and it acquires, when thus saturated, a very brisk and pleasant taste. This impregnation is most commodiously effected by an apparatus, sold in the glass shops, under the name of Nouth's machine.

The influence of pressure, in occasioning water to absorb a large quantity of carbonic acid, may be illustrated by an apparatus, which I have described in the Philosophical Transactions for 1803, but which cannot be understood without the engraving that accompanies it. From an extensive series of experiments with this apparatus, I have deduced, as a general law, that water takes up the same volume of compressed carbonic acid gas, as of gas under ordinary pressure. And since the space occupied by any gas is inversely as the compressing force, it follows that the quantity of gas, forced into water, is directly as the pressure. Thus, if water under common circumstances takes up an equal bulk of carbonic acid, under the pressure of two atmospheres it will absorb twice its bulk; under three atmospheres three times its bulk, and so on.

(e) *From water, thus impregnated, carbonic acid is again set at liberty, on boiling the water, or by exposing it under the receiver of an air-pump.*—During exhaustion, the gas will escape so rapidly, as to present the appearance of ebullition; and

will be much more remarkable than the discharge of air from a jar full of common spring water, confined at the same time, under the receiver, as a standard of comparison.

(f) *Carbonic acid is expelled from water by freezing.*—If the impregnated water be rapidly congealed, by surrounding it with a mixture of snow and salt, the frozen water has more the appearance of snow than of ice, its bulk being prodigiously increased by the immense number of air bubbles. When water, thus congealed, is liquefied again, it is found, by its taste, and other properties, to have lost nearly the whole of its carbonic acid.

(g) *Carbonic acid gas, when combined with water, reddens vegetable blue colours.*—This may be shown by dipping into water, thus impregnated, a bit of litmus paper, or by mixing, with a portion of it, about an equal bulk of the infusion of litmus. This fact establishes the title of the gas to be ranked among acids. When an infusion of litmus, which has been thus reddened, is either heated, or exposed to the air, its blue colour is restored, in consequence of the escape of the carbonic acid. This is a marked ground of distinction from most other acids, the effect of which is permanent, even after boiling.

(h) *Carbonic acid gas precipitates lime water.*—This character of the gas is necessary to be known, because it affords a ready test of the presence of carbonic acid whenever it is suspected. Pass the gas, as it proceeds from the materials, through a portion of lime water. This, though perfectly transparent before, will instantly grow milky: Or, mix equal measures of water saturated with carbonic acid and lime water. The same precipitation will ensue. By means of lime water, the whole of any quantity of carbonic acid, existing in a mixture of gases, cannot, however, be removed, as Saussure, jun. has shown; but recourse must be had, in order to effect its entire absorption, to a solution of caustic potash or soda.

(i) *By the application of the test (h) it will be found, that carbonic acid is generated in several cases of combustion.*—1. Let the chimney of a small portable furnace, in which charcoal is burning, terminate, at a distance sufficiently remote to allow of its being kept cool, in the bottom of a barrel provided

with a moveable top, or of a large glass vessel having two openings. A small jar of lime water being let down into the tub or vessel, and agitated, the lime water will immediately become milky. The gas will also extinguish burning bodies, and prove fatal to animals that are confined in it. Hence the danger of exposure to the fumes of charcoal, which, in several instances, have been known to be fatal. These fumes consist of a mixture of carbonic acid and nitrogen gases, with a very small proportion of oxygen gas. 2. Fill the pneumatoc-chemical trough with lime water, and burn a candle, in a jar filled with atmospheric air, over the lime water till the flame is extinguished. On agitating the jar, the lime water will become milky. The same appearances will take place, more speedily and remarkably, if oxygen gas be substituted for common air. The carbonic acid, thus formed during combustion, by its admixture with the residuary air, renders it more unfit for supporting flame, than it otherwise would be from the mere loss of oxygen. Hence, if a candle be burnt in oxygen gas, it is extinguished long before the oxygen is totally absorbed, because the admixture of carbonic acid with oxygen gas, in considerable proportion, unfits it for supporting combustion. Whenever any substance, by combustion in oxygen gas or common air over lime water, gives a precipitate, soluble with effervescence in muriatic acid, we may confidently infer that it contains carbon.

(k) *The respiration of animals is another source of carbonic acid.*—On confining an animal in a given portion of atmospheric air, over lime water, this production of carbonic acid is evinced by a precipitation. The same effect is also produced more remarkably in oxygen gas. The production of carbonic acid, by respiration, may be proved, also, by blowing the air from the lungs, with the aid of a quill, through lime water, which will immediately grow milky. The carbonic acid, thus added to the air, unfits it for supporting life, not merely by diminishing the proportion of oxygen gas, but apparently by exerting a positively noxious effect. Hence a given quantity of air will support an animal much longer, when the carbonic acid is removed as fast as it is formed, than when suffered to remain in a state of mixture. It has been

found, that an atmosphere, consisting of oxygen gas and carbonic acid, is fatal to animals, though it should contain a larger proportion of oxygen than the air we commonly breathe.

(l) *Carbonic acid is at all times present in the air of the atmosphere.*—This might naturally be expected, from the immense quantity which is constantly produced by respiration and combustion. Its presence is demonstrated by leaving a shallow vessel of lime water exposed to the atmosphere; for its surface is soon covered with a solid pellicle, which, when removed, is succeeded by another, and so on, till the water is deprived of almost all the lime which it held in solution. From the precipitate, thus formed, carbonic acid is disengaged by dilute acids. It has been discovered not only in air at ordinary heights, but was ascertained by Saussure to exist in the atmosphere on the summit of Mont Blanc, nearly 16,000 feet above the level of the sea, and was found by Humboldt in air brought down by Garnerin from the height of several thousand feet, to which he had ascended in an air balloon. (*Jour. de Phys.* xlvii. 202.)

The proportion of carbonic acid in atmospheric air, is estimated by Mr. Dalton not to exceed one thousandth or  $\frac{1}{1000}$ th of its bulk. Saussure, jun. examined its proportion in the air of an open field, a few miles from Geneva.\* In January, the mean of three experiments showed 4.79 parts in 10,000; in July and August, 7.18 parts in the same volume, which is considerably short of the proportion determined by Mr. Dalton. The difference between the quantities discovered in summer and winter, though on first view very small, viz.  $2\frac{3}{10}$  volumes in ten thousand, would constitute so large a quantity, when the whole atmosphere is taken into the account, that the fact can scarcely be considered as determined without repeated and careful experiments. The uniformity of its proportion is surprising, when we consider the enormous volumes that are constantly generated by respiration and combustion, which scarcely seem to affect its relative quantity even in the atmospheres of large manufacturing towns.

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\* *Ann. de Chim. et Phys.* ii. 199; and iii. 170.

(m) *Carbonic acid retards the putrefaction of animal substances.*—This may be proved, by suspending two equal pieces of flesh meat, the one in common air, the other in carbonic acid gas, or in a small vessel through which a stream of carbonic acid is constantly passing. The latter will be preserved untainted some time after the other has begun to putrefy.

(n) *Carbonic acid gas exerts powerful effects on living vegetables.*—These effects, however, vary according to the mode of its application.

Water, saturated with this gas, proves highly nutritious to plants, when applied to their roots. The carbonic acid is decomposed, its carbon forming a component part of the vegetable, and its oxygen being liberated in a gaseous form.

On the contrary, carbonic acid, when a living vegetable is confined in the undiluted gas over water, is injurious to the health of the plant, especially in the shade. The late Mr. Henry, however, long ago found that a certain quantity of fixed air, applied as an atmosphere, is favourable to vegetation; and M. Saussure, of Geneva, has determined more recently, that the mixture of more than  $\frac{1}{4}$  of carbonic acid with common air is always injurious; but that in this proportion it promotes the growth of plants, and is manifestly decomposed. It is this process of nature that appears to be the principal means of preventing an excess of carbonic acid in the general mass of the atmosphere, which, without some provision of this kind, must gradually, in the course of ages, be rendered less and less fit for respiration.

#### *Gaseous Oxide of Carbon, or Carbonic Oxide.*

This gas appears to have been first obtained by Dr. Priestley, by the distillation of charcoal with oxide of zinc; but he was not aware of its composition, which was first pointed out by the late Mr. Cruickshank, of Woolwich,\* and afterwards more particularly by Clement and Desormes.† The Dutch Society of Chemists objected to its being regarded as a dis-

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\* Nicholson's Journal, 4to. vol. v.

† Ann. de Ch. xxxix. 26.

tinct species, and considered it only as a variety of carbureted hydrogen;\* but these objections were not entitled to any weight, and have been completely set aside by farther investigations.

It may be procured by any of the following processes :

1. By the distillation of the white oxide of zinc with one eighth of its weight of charcoal, in an earthen or glass retort; from the scales which fly from iron in forging, mixed with a similar proportion of charcoal; from the oxides of lead, manganese, or, indeed, of almost every imperfect metal, when heated in contact with powdered charcoal. It may also be obtained from the substance which remains after preparing acetic acid from acetate of copper.

2. From well dried carbonate of barytes or of lime (common chalk), distilled with about one fifth of charcoal, or with rather a larger proportion of dry iron or zinc filings, which afford it quite free from hydrogen.

8. By transmitting carbonic acid gas over charcoal ignited in a porcelain tube, the acid gas combines with an additional dose of charcoal; loses its acid properties; and is converted into carbonic oxide. An ingenious apparatus, contrived by M. Baruel, and extremely useful for this and similar purposes, is described and represented by a plate, in the 11th volume of Nicholson's Journal.

The last product of the distillation is the purest, but still contains carbonic acid, which must be separated by washing the gas with lime liquor or solution of potassa.

Its properties are as follow :

(a) It has an offensive smell.

(b) It is lighter than common air, in the proportion of 0.9694 according to Thomson, or 0.9727 according to Berzelius and Dulong. One hundred cubical inches weigh 30 grains, the temperature being 55° Fahrenheit, and pressure 29.5 (Cruickshank); or at temperature 60°, and barometer 30, 100 cubic inches weigh 30.19 grains. Its specific gravity, from calculation, according to Gay Lussac, should be .96782.

(c) It is inflammable, and, when set fire to, as it issues from

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\* Ann. de Ch. xliii.



the orifice of a small pipe, burns with a blue flame. The temperature of an iron wire heated to dull redness was found by Sir H. Davy sufficient to kindle it. When mixed with common air, it does not explode like other inflammable gases, unless in very few proportions,\* but burns silently with a lambent blue flame. A mixture of two measures with one measure of common air may, however, be exploded by a lighted taper, or even by red-hot iron or charcoal.

(d) When a stream of this gas is burnt, in the manner described in speaking of hydrogen gas, no water is condensed on the inner surface of the glass globe, a proof that the gaseous oxide contains no hydrogen.

(e) It is sparingly soluble in water; is not absorbed by liquid caustic alkalies; nor does it precipitate lime water.

(f) It is extremely noxious to animals; and fatal to them if confined in it. When respired for a few minutes, it produces giddiness and fainting.†

(g) When 100 measures of carbonic oxide are fired over mercury in a detonating tube, with 45 of oxygen gas, the total 145 are diminished to 90, which, if the gases employed be pure, consist entirely of carbonic acid. Proportions, differing a little from these, have been stated by Berthollet, viz. that 100 measures of carbonic oxide are saturated by 50 measures of oxygen, and give 100 of carbonic acid; and these last proportions are coincident, also, both with the theory and experience of Gay Lussac.

(h) It is not expanded by electric shocks, nor does it appear to undergo any change by electrization.

(i) When carbonic oxide, mingled with an equal bulk of hydrogen gas, is passed through an ignited tube, the tube becomes lined with charcoal. In this temperature, the hydrogen attracts oxygen more strongly than it is retained by the charcoal, and water is formed. It was found, also, by Gay Lussac, to be decomposed by the action of potassium, which combines with the oxygen and precipitates charcoal.

According to Mr. Cruickshank, it contains per cent. about 70 oxygen, and 30 carbon by weight; or the former is to the latter as 21 to 8.6, or as 21 to 9. Gay Lussac, however,

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\* Dalton's System, p. 373.

† See Phil. Mag. xliii. 367.

makes it to consist of 43 charcoal and 57 oxygen; Berzelius of 44.28 charcoal and 55.72 oxygen, proportions which agree, within a small fraction, with those of Clement and Desormes. It contains, therefore, just half the oxygen that exists in carbonic acid; and it is constituted of one atom of charcoal and one atom of oxygen, and weighs, according to Mr. Dalton,  $7 + 5.4 = 12.4$ , or, by the corrected numbers,  $8 + 6 = 14$ .

On the theory of volumes it consists of 1 volume of oxygen + 1 vol. of gaseous carbon, the oxygen being in such a state of expansion as to occupy the space of two volumes. Thus we have  $1.1025$  (the specific gravity of oxygen)  $+ 2 = .551 + .422$  (the specific gravity of gaseous carbon)  $= .973$ , the specific gravity of carbonic oxide, as determined by Gay Lussac.

#### ART. 2.—*Carbon with Chlorine.*

Several attempts had been made to effect the combination of chlorine with carbon, by igniting charcoal in chlorine gas; but, though unsuccessful, there appeared to be no reason for inferring a want of affinity between those two elements, which, from other phenomena, it seemed reasonable to conclude might be rendered efficient, by bringing the two bodies into contact in a state favourable to their union. The most probable method seemed to be to employ some compound, in which carbon exists in a minute state of division, and yet not of such intimate combination, as to preclude its union with chlorine. Mr. Faraday, therefore, to whom we are indebted for a masterly set of experiments on this subject, which ended in his effecting the object in view, employed a compound of charcoal and hydrogen, to be hereafter described under the name of olefiant gas, as best adapted to the purpose. At present it is only necessary to observe, that olefiant gas is a compound of 1 atom of carbon with 1 atom of hydrogen; that when mixed with an equal volume of chlorine, the three elements all unite and form a ternary liquid compound of chlorine, carbon, and hydrogen; and that, by subjecting this triple compound to the repeated action of fresh quantities of chlorine, the hydrogen may be entirely abstracted, and a binary compound of chlorine and carbon produced.

To prepare this substance, a retort or other glass vessel of

the capacity of about 200 cubic inches, provided with a brass cap and stop-cock, is first to be exhausted by the air pump, and then made to communicate with a jar filled with chlorine. It is next to be screwed on a vessel full of olefiant gas, and as much as can find admission having entered, the cock is to be shut, and the whole left for a short time. When the fluid, composed of chlorine and olefiant gases, has formed and condensed on the sides of the vessel, the vessel is again to be placed over olefiant gas, and a further portion admitted. This process is to be repeated, till all the chlorine has united to form the fluid, and the vessel remains full of olefiant gas. Chlorine is then to be admitted by repeated portions, in consequence of which more of the fluid is formed, and ultimately a large portion is obtained, with an atmosphere of chlorine above it. The vessel is now to be exposed to the sun's rays, which cause the immediate formation of muriatic acid gas. This may be absorbed by admitting a small portion of water; and then another atmosphere of chlorine is to be introduced. Again exposed to the light, this will partly combine with the carbon, and partly form muriatic acid gas, which, being, as before, absorbed by water, leaves space for more chlorine. Repeating this action, the fluid gradually becomes thick and opaque, from the formation of crystals in it, which at last adhere to the sides of the vessel as it is turned round: and ultimately the vessel contains only chlorine, with the accumulated impurities of the gases; a strong solution of muriatic acid coloured blue by its action on the brass; and the solid substance in question.

In order to cleanse the substance, the remaining gases are first to be blown out of the vessel by a pair of bellows, and the vessel is then to be filled with water to wash away the muriatic acid and other soluble matters. The new substance is then to be detached from the inside of the vessel, and poured with the water into a jar. A little alcohol will remove the last portions which adhere to the glass, and, when poured into the water, will precipitate the new compound, which must be collected on a filtre, and dried as much as possible by pressure between folds of bibulous paper. It must next be introduced into a glass tube, and sublimed by a spirit lamp. A part will

be decomposed, but the sublimed portion is to be dissolved in alcohol, and poured into a weak solution of potash, by which the new substance is thrown down, and the muriatic acid neutralized and separated. Then wash away the potash and muriate by repeated affusions of water, until the substance remains pure; collect it on a filter, and dry it, first by pressure between folds of paper, and afterwards by sulphuric acid under the exhausted receiver of an air pump. It will now appear as a white pulverulent substance; and, if perfectly pure, will not, when a little is sublimed in a tube, leave the slightest trace of carbon, or afford any muriatic acid. A small portion, dissolved in ether, should give no precipitate with nitrate of silver. If not quite pure, it must be re-sublimed, washed, and dried, as often as is necessary.

To this compound Mr. Faraday has given the name of *per-chloride of carbon*. When pure, it is, immediately after fusion, a transparent colourless substance, having scarcely any taste. Its odour is aromatic, and approaches that of camphor. Its specific gravity is as nearly as possible 2. Its refractive power is high, being above that of flint glass (1.5767.) It is very friable, easily breaking down on pressure, and when scratched, has much of the feel and appearance of white sugar. It does not conduct electricity. It is crystallizable, and the varieties of its form, which are very numerous and interesting, result from a primitive octohedron.

It volatilizes slowly at common temperatures, and, like camphor, passes towards the light. At 320° Fahr. it fuses, and boils at 360°. When condensed from these rapid sublimations, it is in so transparent and colourless a state, that it is difficult to perceive where it is lodged.

It is not readily combustible. When held in the flame of a spirit lamp, it burns with a red flame, emitting much smoke and acid fumes; but when removed from the lamp, combustion ceases. In an atmosphere of pure oxygen, it burns with a brilliant light.

It is very sparingly soluble in water, either hot or cold, but dissolves readily in alcohol, especially if heated. The solution is decomposed when poured into water, and gives regular crystals on cooling or evaporation, but does not, with ni-

trate of silver, form the chloride of that metal. Ether, particularly when heated, dissolves it, even more readily than alcohol. It is soluble also in volatile oils, and in fixed oils, but the latter solutions assume a charred appearance when heated.

It is not changed by solutions of pure alkalis, even when applied boiling hot; nor is it attacked by concentrated and heated muriatic, nitric, or sulphuric acids.

When transmitted in vapour mixed with oxygen gas through a red hot tube, there is a decomposition, and mixtures of chlorine, carbonic acid, carbonic oxide, and chloro-carbonic acid, are evolved. It is decomposed also by per-oxide of mercury with the aid of heat.

Chlorine has no action on it. Iodine either unites with it, or at high temperatures takes away a portion of chlorine. Hydrogen gas, when transmitted along with it through red-hot tubes, decomposes it, and muriatic acid and charcoal are produced.

Sulphur, at moderate temperatures, unites with it; at higher ones, removes one portion of chlorine. The same effect is produced by phosphorus. Charcoal is quite inefficient on it. Most of the metals decompose it with the aid of heat, forming chlorides, and charcoal being liberated. Per-oxides produce with it, at a high temperature, chlorides and carbonic acid; protoxides afford chlorides and carbonic oxide.

In forming this substance, Mr. Faraday believes that five volumes of chlorine gas saturate one of olefiant, and produce four volumes of muriatic acid gas; that three volumes of the chlorine combine with the two volumes of charcoal existing in the olefiant gas to form the crystalline solid; and that when chlorine acts on the fluid compound of chlorine and olefiant gas, for every volume of chlorine that combines, an equal volume of hydrogen is separated. The results of its decomposition by per-oxide of copper, confirm these views, and tend to establish that the composition of per-chloride is

3 atoms of chlorine .....	=	108
ditto of carbon .....	=	12

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Weight of its atom .... 120

*Proto-chloride of Carbon.*

By passing the vapour of per-chloride of carbon over fragments of rock crystal ignited in a glass tube, the upper part of which is bent up and down two or three times, so that the angles may form receivers for the new compound, a partial decomposition is effected; one portion of chlorine is separated and escapes; and the remainder, continuing united to the carbon, forms a fluid substance, which may be collected and purified by repeated distillations. This is the *proto-chloride of carbon*.

It is a highly limpid and perfectly colourless fluid; its specific gravity is 1.5526; it is a non-conductor of electricity; its refractive power is 1.4875, being very nearly that of camphor. It is not combustible, except when held in the flame of a spirit lamp, and then it burns with a bright yellow light, much smoke, and fumes of muriatic acid.

It does not become solid at 0° Fahr. When its temperature is raised under the surface of water to between 160° and 170°, it is converted into vapour, and remains in that state till the temperature is lowered. When its vapour is passed over ignited fragments of rock crystal, it undergoes a partial decomposition.

It is not miscible with water, but is soluble in alcohol, ether, and fixed and volatile oils. Neither alkaline solutions nor strong acids produce any effect upon it. It is not decomposed by solutions of silver. Oxygen gas, at high temperatures, forms with it carbonic oxide, and chlorine is liberated. Hydrogen, under the same circumstances, forms muriatic acid with its chlorine, and charcoal appears. The metals, at high degrees of heat, absorb the chlorine, and liberate charcoal; oxides, according to their proportion of oxygen, form with it either carbonic acid or carbonic oxide.

By analysis, effected by per-oxide of copper, it is shown to be constituted of

1 atom of chlorine .....	36
1 ditto of carbon .....	6

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Weight of its atom ..... 42

*Sub-chloride of Carbon.*

A third compound of chlorine and carbon was brought over from Sweden by M. Julin, of Abo, where it had been accidentally formed during the distillation of nitric acid from crude nitre and sulphate of iron. The quantity produced at each process did not exceed a few grains, which condensed in fine white feathery crystals in a glass tube connecting the first and second receiver. Its properties are described by M. Julin as follows: (Ann. of Phil. N. S. i. 216.)

It is white; consists of small soft adhesive fibres; sinks slowly in water; is insoluble in it whether hot or cold; is tasteless; has a peculiar smell, somewhat resembling spermaceti; is not acted upon by concentrated and boiling acids or alkalies, except that some of them dissolve a small portion of sulphur; dissolves in hot oil of turpentine and in alcohol, but most of it crystallizes in needles on cooling; burns in the flame of a lamp with a greenish blue flame, and a slight smell of chlorine; when heated melts, boils, and sublimes between  $350^{\circ}$  and  $450^{\circ}$  Fahr., or sublimes slowly at a heat of  $250^{\circ}$ , forming long needles. Potassium burns with a vivid flame in its vapour, and charcoal is deposited; and a solution of the residuum in nitric acid gives a copious precipitate with nitrate of silver.

A small quantity of this substance, having been put into the hands of Messrs. R. Phillips and Faraday, has been made by them the subject of analysis. They found that it might readily be purified from sulphur by boiling in liquid potash, washing in water, drying, and subliming, when it formed beautiful acicular crystals, in the form of four-sided prisms.

It was decomposed into chlorine and charcoal by being passed over red hot fragments of rock crystal. Its vapour, being detonated over mercury with excess of oxygen, gave carbonic acid gas and chloride of mercury. When heated with phosphorus, iron, or tin, chlorides of those substances were formed, and charcoal deposited. Its analysis was effected in two ways; by being transmitted over ignited per-

oxide of copper, and over dry quick-lime. Both processes gave results which conspire to show that it is constituted of

1 atom of chlorine .....	36
2 atoms of carbon .....	12

—————  
Weight of its atom .... 48

Messrs. Phillips and Faraday have not given any name to this compound. It may be called, provisionally, the sub-chloride of carbon.

Thus we have three distinct compounds of chlorine and carbon, viz.

	At. of Chlor.	At. of Carb.
The per-chloride .....	3	+ 2
The proto-chloride .....	1	+ 1
The sub-chloride .....	1	+ 2

It is probable that another chloride of carbon will hereafter be found, consisting of two atoms of chlorine and one of carbon.

#### SECTION IV.

##### *Boron.*

BORON was first obtained by Sir H. Davy in 1808 by the action of Voltaic electricity on boracic acid. When that acid, slightly moistened with water, was exposed between two surfaces of platina to a battery of 500 pairs of plates, an olive brown matter began immediately to appear on the negative surface, and gradually increased in quantity. This substance was found not to be acted on by water, but to dissolve with effervescence in warm nitric acid. When heated to redness on platina, it burned slowly, and boracic acid was regenerated. Hence the name of *boron* has been applied to it.

The same substance was afterwards obtained more abundantly by Gay Lussac and Thenard, by the action of potassium. Equal parts of potassium and very pure and vitreous boracic acid were put into a copper tube, which was gradually heated to



redness. At the temperature of  $302^{\circ}$  Fahr. the mixture became suddenly red, and the metal disappeared by acting on the boracic acid. By washing the residuum with warm water, a greenish brown or olive substance was obtained, which is the base or radical of boracic acid.

This substance is insoluble in water, it is destitute of taste, and does not affect vegetable blue colours. Mixed with chlorate or nitrate of potash, and projected into a red hot crucible, it burns vividly, and boracic acid is reproduced. In close vessels it may be exposed to a strong heat, without undergoing any change except an increase of density, for it now sinks in sulphuric acid of sp. gr. 1.844. It is a non-conductor of electricity.

When heated to  $600^{\circ}$  Fahr. in the open air, it burns vividly, absorbs oxygen, and affords boracic acid; but the coating, which it acquires of that acid, soon stops the combustion. The quantity of oxygen absorbed by a given weight has been investigated by Gay Lussac and Thenard, and by Sir H. Davy. According to the latter, 100 parts of boron absorb 174 of oxygen. Berzelius investigated the same problem indirectly, and was led to conclude that 100 of boron unite with 300 of oxygen to form boracic acid. Dr. Thomson,\* after pursuing the same enquiry by different means, infers that 100 grains of boron condense 266.6 grains of oxygen, which are in the proportions of 6 to 16, indicating that the composition of boracic acid agrees exactly with that of the carbonic, as to the relative proportions of base and oxygen. According to this view, the atom of boron weighs 6; and each atom, to form boracic acid, combines with two atoms of oxygen, ( $8 \times 2 = 16$ ) and the atom of acid weighs 22. These results, however, are still liable to considerable uncertainty.

*Boron with Oxygen.—Boracic acid.*

I. This acid is very rarely to be found native; having been discovered hitherto only in the Lipari islands, and in the hot springs of Sasso in the Florentine territory. For pur-

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\* Ann. of Phil. N.S. ii. 131.

poses of experiment, it is obtained from the purified borax of commerce, by one of the following processes :

1. To a solution of borax, in boiling water, add half its weight of sulphuric acid, previously diluted with an equal quantity of water. Evaporate the solution a little; and, on cooling, shining scaly crystals will appear, which consist of boracic acid. Let them be well washed with distilled water, and dried on filtering paper.

2. Let any quantity of borax be put into a retort, with half its weight of sulphuric acid, and half its weight of water. Boracic acid may be obtained by distillation, and may be purified, by washing in water, &c., as before. By neither of these processes, however, is it obtained perfectly pure; for electrical analysis discovers in it a minute portion both of alkali and of sulphuric acid. (Davy.)

II. Boracic acid has the following qualities :

1. It has the form of thin white scales, is destitute of smell; and nearly so of taste. Its specific gravity is 1.479.

2. It fuses, when heated, and loses its water of crystallization, which, according to Dr. Thomson, amounts to 44.5 from 100 of the crystals. If the heat be increased suddenly, before it has lost its water of crystallization, it sublimes; but, otherwise, it melts into a glass, which is permanent in the strongest fire, and has the specific gravity 1.803.

3. It is generally described as soluble in twelve parts of cold water, and in three or four of boiling water; but, according to Sir H. Davy, even boiling water does not take up above  $\frac{1}{50}$  of its weight.

4. This solution reddens vegetable blue colours, and effervesces with alkaline carbonates. It is remarkable, however, that it reddens turmeric in the same manner as alkalis. (Faraday.)

5. It is soluble in alcohol, and the solution burns with a beautiful green flame.

*Boron with chlorine.*—Boron burns with considerable splendor in chlorine gas, but the compound which it forms has not been investigated. The same may be said of its combination with iodine.

*Fluoboric Acid.*

With the view of obtaining fluoric acid gas perfectly free from water, Sir H. Davy and Gay Lussac appear to have had recourse to the same expedient, *viz.* that of distilling perfectly dry boracic acid with fluate of lime. When these substances were exposed to a strong heat in an iron tube, in the proportion of one part of the former to two of powdered fluor spar, a gas was collected in great quantity, which exhibited singular properties, and to which Messrs. Gay Lussac and Thenard have given the name of *gas fluoborique* or fluoboric acid gas. It may, also, be obtained by distilling in a retort one part of vitreous boracic acid with two of fluor spar and 12 of sulphuric acid. One hundred cubic inches weigh 73.5 grains.

This gas, according to the latter chemists, appears to contain no water, and to have so strong an affinity for it, as to take it from other gases which hold water in combination. Hence, when mixed with most of those gases, on which it does not exert a chemical action, such as atmospheric air, it loses its transparency and becomes cloudy.

With ammoniacal gas it unites in two proportions. If the alkaline gas be put first into the tube, equal measures combine together, and the compound is neutral. But if we admit fluoboric gas by bubbles to the alkaline gas, we obtain a compound, with an excess of base, consisting of one measure of fluoboric gas to two of ammonia.

Fluoboric gas is absorbed copiously by water, which takes up 700 times its bulk, and acquires the specific gravity 1.77. The saturated solution has the causticity and aspect of strong sulphuric acid; requires for ebullition a temperature considerably exceeding 212° Fahrenheit; and is condensed again in stræ which contain much gas. From analogy, Gay Lussac supposes that nitric and even sulphuric acids would, if they could be obtained free from water, be equally elastic with this acid.

When potassium or sodium was heated in fluoboric gas, Gay Lussac and Thenard obtained fluate of potash or soda, and the base of the boracic acid was separated.

The liquid acid acts almost as intensely as sulphuric acid on vegetable substances. It blackens paper, and affords a true ether with alcohol. It has no effect in corroding glass.

From analysis, Gay Lussac and Thenard, as well as Sir H. Davy, have determined it to be a compound of boracic and fluoric acids, in proportions not yet ascertained.



## SECTION V.

### *Phosphorus.*

PHOSPHORUS was discovered about the year 1669 by Brandt, an alchemist of Hamburgh, while employed in the research after the art of converting the baser metals into gold and silver; and afterwards by Kunckel, a German chemist. But the method of preparing it was not publicly divulged by either of those persons; and it was not till 1737, that a commission, appointed by the French Academy of Sciences, was instructed by a stranger in the process. It consisted in evaporating putrid urine to dryness, and distilling the residuum at an intense heat in a stoneware retort. Margraff improved the process by adding a salt of lead to the urine; and in 1769 Gahn, of Sweden, having discovered the phosphoric acid in bones, invented the method of preparing phosphorus which is now generally followed.

I. Phosphorus is an inflammable substance, and is distinguished by the following external characters.

(a) It has generally a flesh-red colour, but, when carefully purified, may be obtained colourless, and perfectly transparent. Its specific gravity is 1.77. It is necessary to preserve it under water in well-closed bottles.

(b) It is so soft that it readily yields to the knife.

(c) It melts at about  $109^{\circ}$  or  $110^{\circ}$  Fahrenheit, and boils at  $550^{\circ}$ . When melted, it must be covered with water, in order to prevent it from inflaming. Exposed to a heat of between  $140^{\circ}$  and  $160^{\circ}$  Fahrenheit, and suddenly cooled, it becomes black; but, if slowly congealed, it remains transparent and colourless: when cooled at a moderate rate, it assumes the

semi-transparency of horn. According to Thenard, however, it is not all phosphorus that exhibits these properties, but only that which has undergone repeated distillations.

(d) In the atmosphere it emits a white smoke, and a peculiar smell; and a faint and beautiful light arises from it; but these appearances do not take place in air which has been artificially dried.

If a cylinder of phosphorus be introduced into a vessel of oxygen gas over mercury, at a temperature not exceeding  $80^{\circ}$  Fahrenheit, no perceptible absorption will happen in 24 hours; but if, the temperature remaining the same, the pressure be diminished to  $\frac{1}{8}$ th or  $\frac{1}{10}$ th that of the atmosphere, the phosphorus will be surrounded by white vapours, will become luminous in the dark, and will absorb oxygen. Under ordinary pressures, a higher temperature is required to produce this effect; but it is remarkable, that if the density of the oxygen be reduced in the above proportion, by mixing it with azote, hydrogen, or carbonic acid, the phosphorus becomes luminous. Hence phosphorus absorbs oxygen from atmospheric air with an extrication of light.

II. Phosphorus is inflamed by the application of a very gentle heat. According to Dr. Higgins, a temperature of  $60^{\circ}$  is sufficient to set it on fire, when perfectly dry. It burns when heated to about  $148^{\circ}$ , with a very brilliant light, a white smoke, and a suffocating smell, and may even be inflamed in an atmosphere rarefied sixty times. (Van Marum.)

1. It may be set on fire by friction. Rub a very small bit between two pieces of brown paper; the phosphorus will inflame, and will set the paper on fire also.

2. In oxygen gas it burns with a very beautiful light; and also in nitrous oxide, and chlorine gases. The product of the rapid combustion of phosphorus in oxygen gas is exclusively phosphoric acid.

III. Phosphorus is volatile at  $550^{\circ}$ . Hence it may be raised by distillation; but, to prevent its taking fire on the application of heat, the retort should previously be filled with azotic or hydrogen gas, and the mouth of the retort be immersed in water.

To accomplish this, the quantity of phosphorus, which it is

intended to rectify, should first be put into the retort, with a sufficient portion of water to cover it. The water must then be made hot enough to melt the phosphorus, which, on cooling, forms a compact mass, of the shape of the bottom of the retort. When cold, fill the retort, and its neck also, with water, and invert it in water. Displace the water by hydrogen gas, forced from a bladder through a bent pipe; keep the finger on the open end of the retort neck; place it in a sand bath; and immerse the mouth of it in water. Then apply heat very cautiously. A bladder should also be provided, furnished with a stop-cock and brass pipe, and filled with hydrogen gas. During the distillation, the gas, in the retort, is absorbed, and it is necessary to add more from the bladder, otherwise the water will rush into the retort, and occasion an explosion. By distillation, in this mode, phosphorus is rendered much purer. In the neck of the retort a substance is condensed of a beautiful red or carmine colour, which is a combination of carbon and phosphorus, or a *phosphuret of carbon*. Thenard observes that phosphorus, however frequently distilled, cannot be freed entirely from charcoal, a minute quantity of which does not impair its whiteness or transparency.

The only information, which we possess, respecting the nature of phosphorus, is derived from the electro-chemical researches of Sir H. Davy. When acted upon by a battery of 500 pairs of plates in the same manner as sulphur, gas was produced in considerable quantities, and the phosphorus became of a deep red-brown colour. The gas proved to be phosphureted hydrogen, and was equal in bulk to about four times the phosphorus employed. Hence hydrogen may possibly be one of its components; but no confirmation of the truth of this view is derived from the recent experiments of the same philosopher, which, indeed, are rather contradictory to it.

#### ART. 1.—*Phosphorus and Oxygen.*

Phosphorus may be oxygenized in various modes.\*

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\* On the oxides of phosphorus, see Nicholson's Journal, vi. 134.

(a) By exposure to atmospheric air. Let a stick of phosphorus be placed in a funnel, the pipe of which terminates in an empty bottle. The phosphorus will be slowly oxygenized, and, after some time, will be changed into an acid, which will fall into the bottle in a liquid state.

A large quantity of acid may be obtained, if a number of sticks be thus exposed: and as they would be in danger of taking fire, if heaped together, each stick should be enclosed in a glass tube, of rather larger diameter than itself. These tubes must be disposed round a funnel, the pipe of which terminates in a bottle. The whole should be covered by a bell-shaped receiver, the air of which is to be frequently changed. The acid thus obtained is a mixture of *phosphorous* and *phosphoric* acids, &c. Dulong, indeed, believes it to be a distinct compound, for which he has proposed the name of *phosphatic acid*.\* But this view of its composition is not supported by the recent investigations of Sir H. Davy, who still considers it as a mixture of the two well-known acids of phosphorus.

Phosphorus, kept under water in a bottle partly filled with that fluid, and into which fresh air is occasionally admitted, becomes slowly oxygenized, partly into a soluble compound which the water takes up, and partly into a white substance that invests the sticks of phosphorus with an insoluble crust. This appears to be an oxide of phosphorus.

When phosphorus is burned in a quantity of atmospheric air much short of that which is required to consume it, the unburned portion consists of a red oxide, mixed with unconsumed phosphorus and phosphoric acid. The red substance is an oxide of phosphorus, but neither the precise composition of this nor of the white oxide has been yet ascertained. It has been conjectured, indeed, that the white compound is a *hydrate*, composed of water united with the red oxide.

When phosphorus is burnt in highly rarified air, three products are formed—a red solid comparatively fixed, and requiring a heat above  $212^{\circ}$  for its fusion—a white and easily volatile substance, which is combustible, soluble in water, and has acid properties—and a substance, which is strongly acid and not

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\* Phil. Mag. xlviii. 273.

volatile, even at a white heat. The first appears to be a mixture of unburned phosphorus and phosphorous acid; the second to be phosphorous acid; and the third to be phosphoric acid.

(b) Phosphorus inflames vividly in oxygen gas. When burnt in this manner, every hundred parts of phosphorus, according to Lavoisier, gain an addition of 154. From this result, a subsequent one of Sir H. Davy scarcely differs, viz. that 100 grains of phosphorus condense 450 cubic inches, or 153 grains, of oxygen gas; but having examined the subject anew, with every attention to the accuracy of his results, and with the advantage of improved methods of operating, he found that, taking an average of three experiments, 100 grains of phosphorus condense only 135 grains of oxygen. In this estimate, 100 cubic inches of oxygen gas are assumed to weigh 33.9 grains, the barometer being at 28.8 inches, and Fahrenheit's thermometer at from 46° to 49°.

(c) By the nitric acid. If phosphorus be cautiously added, by small fragments at once, to nitric acid, heated in a retort, the nitric acid is decomposed, and its oxygen, uniting with the phosphorus, constitutes phosphoric acid. A tubulated retort must be used for this purpose; and its neck may terminate in the apparatus already described for procuring nitric acid. By this contrivance a considerable quantity of nitric acid will be saved. The liquid, remaining in the retort, may be heated in an open capsule to a thick consistence, in order to expel the redundant nitric acid, and also to drive off a portion of ammonia, which Mr. R. Phillips has observed to be formed during the action of the nitric acid, the nitrogen of which unites with hydrogen liberated at the same moment by the decomposition of water.

#### *Phosphorous Acid.*

Phosphorous acid cannot, according to Sir H. Davy, be obtained pure by exposing cylinders of phosphorus to atmospheric air; for, when thus prepared, it always contains phosphoric acid. It can only be procured in a state of purity, first, by subliming phosphorus through corrosive sublimate;



then mixing the product with water and heating it, till it becomes of the consistence of syrup. The liquid obtained is a compound of pure phosphorous acid and water, which becomes solid and crystalline on cooling. It is acid to the taste, reddens vegetable blues, and unites with alkalis.

The theory of this process is, that when the compound of phosphorus and chlorine, formed in the first operation, is brought into contact with water, the water is decomposed; its hydrogen uniting with chlorine composes muriatic acid; and its oxygen combining with phosphorus forms phosphorous acid. From this mixture of acids, heat expels the muriatic.

The phosphorous acid exhales a disagreeable foetid odour; and yields, when strongly heated, penetrating white vapours. When heated in a glass ball, blown at the end of a small tube, a gas issues from the orifice of the tube, which inflames on coming into contact with the atmosphere. Hence it appears to contain an excess of phosphorus. The residuum in the ball is phosphoric acid. From the experiments of Rose on the phosphoric acid, Gay Lussac infers that phosphorous acid must consist of

Phosphorus...	56.81	....	100	....	132
Oxygen .....	43.19	....	76	....	100
			100.		

These proportions do not differ materially from those stated by Dulong, who makes phosphorous acid to consist of 100 phosphorus + 74.88 oxygen.\* They agree, also, still more nearly, with the following statement of Berzelius, according to whom this acid consists of

Phosphorus .....	56.524	.....	100.
Oxygen .....	43.476	.....	76.92
			100.†

Sir H. Davy, however, after a careful investigation of the constitution of phosphorous acid, has more lately been led to

\* Phil. Mag. *xlvi*. 273.

† Ann. de Chim. et Phys. *ii*. 227.

conclude that the oxygen, which it contains, is just one half of that existing in phosphoric acid; or that, in the former, 100 grains of phosphorus are united with only 67.5 of oxygen. Hence 100 grains of phosphorous acid must consist of

Phosphorus .....	59.7
Oxygen.....	40.3
	100.

And phosphorous acid, being probably constituted of 1 atom of oxygen, + 1 atom of phosphorus, the weight of the latter atom may be inferred to be 11.62, or in round numbers 12. Phosphorous acid, then, will be represented by  $12 + 8 = 20$ .

*Hypo-phosphorous or Per-phosphorous Acid.*

When phosphuret of barytes, carefully prepared, is made to act on water, two distinct compounds are generated, *viz.* phosphate of barytes, which, being insoluble, is readily separated by filtration; and a soluble salt of barytes, which passes through the filter. To the latter compound, sulphuric acid is to be added, in quantity just sufficient to separate the barytes. The acid solution which remains, when concentrated by evaporation, yields a viscous fluid, strongly acid and uncrystallizable. By a still stronger heat, this substance is decomposed; phosphureted hydrogen is developed; a little phosphorus is sublimed; and phosphoric acid remains in the retort.\*

The compounds of this new acid, with alkaline and earthy bases, are remarkable for their extreme solubility. Those of barytes and strontites crystallize with great difficulty. The *hypo-phosphites* of potash, soda, and ammonia, are soluble, in all proportions, in highly rectified alcohol. That of potash is even more deliquescent than muriate of lime. They absorb oxygen slowly from the air, and when heated in a retort give the same products as the acid itself.

In order to ascertain the proportions of the elements of this

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\* Dulong, 48 Phil. Mag. 271.

acid, Dulong, its discoverer, converted a known quantity of it into phosphoric acid by means of chlorine, whence he infers it to consist of

Phosphorus . . . . .	72.75 . . . . .	100
Oxygen . . . . .	27.25 . . . . .	37.44
	<hr style="width: 10%; margin: 0 auto;"/>	
	100.	

These results are calculated on the supposition that hypo-phosphorous or per-phosphorous acid is a binary compound of oxygen and phosphorus; but it is doubtful whether it may not be a triple compound of oxygen, phosphorus, and hydrogen, or a *hydracid*; in which case its proper appellation would be *hydro-phosphorous acid*.

In his able investigation of the compounds of phosphorus, Sir H. Davy admits the existence of the new acid of Dulong, but deduces different proportions of its elements. The oxygen of this acid he infers to be precisely half of that which exists in phosphorous acid; or that 100 of phosphorus are united with 33.750 oxygen. But it has been already shown to be probable that phosphorous acid is composed of an atom of each of its elements; and it may, therefore, be inferred that hypo-phosphorous acid is constituted of one atom of oxygen weighing 8, and two atoms of phosphorus weighing  $12 \times 2 = 24$ , and the weight of the compound atom may be represented by 32.

#### *Phosphoric Acid.*

I. To prepare this acid, the combustion of phosphorus may be employed; but the following is the most economical method.

On 20 pounds of bone, calcined to whiteness and finely powdered, pour 20 quarts of boiling water, and add  $16\frac{1}{2}$  pounds\* of sulphuric acid, diluted with an equal weight of water. Let these materials be well stirred together, and be kept in mixture about 24 hours. Let the whole mass be next put into a conical bag of sufficiently porous and strong linen in order to separate the clear liquor, and let it be washed wi

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\* These are the proportions recommended by Pelletier and Dalton. A much less quantity of sulphuric acid is generally prescribed.

water, till the water ceases to have much acidity to the taste. Evaporate the strained liquor in earthen vessels, placed in a sand-heat, and, when reduced to about half its bulk, let it cool. A white sediment will form in considerable quantity, which must be allowed to subside; the clear solution must be decanted, and boiled to dryness in a glass vessel. A white mass will remain, which is the dry phosphoric acid. This may be fused in a crucible, and poured out on a clean copper dish. A transparent glass is obtained, which is the phosphoric acid in a glacial state; not, however, perfectly pure, but containing sulphate and phosphate of lime.—According to Fourcroy and Vauquelin, it is, in fact, a super-phosphate of lime, containing, in 100 parts, only 30 of uncombined phosphoric acid, and 70 of neutral phosphate of lime; but when prepared with the full proportion of sulphuric acid, Mr. Dalton finds only from 8 to 12 per cent of the calcareous phosphate. To separate the latter, Dr. Higgins neutralized the acid liquor, obtained by the action of sulphuric acid on bones, with carbonate of ammonia; the neutral liquor was decanted and evaporated till a portion of it taken out deposited crystals on cooling; and was then poured while hot into a thin glass balloon, which was placed on the sand bed of a reverberatory furnace. The mouth of the balloon being covered with an inverted crucible, the fire was gradually raised till the sand pot was obscurely red. In this way, the sulphate of ammonia, and ammonia that neutralized the phosphoric acid, were both expelled; and the phosphoric acid remained in the form of a transparent colourless glass, still retaining a minute quantity of ammonia.\* The glacial acid may also be prepared from perfectly pure phosphoric acid, which has been made by acting on phosphorus with nitric acid. It is remarkable that, according to the experiments of Berthier, it contains at least one fourth its weight of water, a proportion which could scarcely have been expected in so hard a substance.

To procure the phosphoric acid in quantity, and at the same time perfectly pure, the oxygenation of phosphorus by

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\* Minutes of a Society, p. 254.

nitric acid is the most effectual though an expensive process (c, of the preceding article). The acid may be evaporated to dryness in a glass capsule; and the dry mass, when fused, affords *glacial phosphoric acid*.

II. The phosphoric acid has the following properties :

(a) When pure it dissolves readily in water. That obtained immediately from bones is rendered insoluble by the admixture of earthy salts. But the glacial acid prepared with nitric acid is readily soluble.

(b) It is not volatile, nor capable of being decomposed by heat only, nor does it emit any smell when heated.

(c) It is composed, according to the experiments of Rose on the combustion of phosphorus in oxygen gas, (the correctness of which is admitted by Dr. Wollaston, in his table of equivalents,) of

Phosphorus.....	46.72	.....	100.
Oxygen .....	63.28	.....	114.6
	<hr style="width: 50%; margin: 0 auto;"/>		
	100.		

Dulong investigated the composition of phosphoric acid, by finding how much chlorine is absorbed by phosphorus previously combined with a base. He then deduced the oxygen, from the quantity known to be the equivalent of the chlorine, which had disappeared. In this way, he estimates the composition of phosphoric acid to be

Phosphorus.....	44.48	.....	100.
Oxygen .....	55.52	.....	124.8
	<hr style="width: 50%; margin: 0 auto;"/>		
	100.		

Berzelius, by a still more complicated process, obtained results, the average of which gives 100 phosphorus to 127.5 oxygen.\*

But if 235 parts of phosphoric acid, as appears from the recent experiments of Sir H. Davy, with which those of Dr.

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\* Ann. de Chim. et Phys. ii. 222.

Thomson agree, consist of 100 phosphorus, and 135 oxygen, 100 grains must contain

Phosphorus .....	42.55
Oxygen .....	57.45
	100.

This would very nearly accord with the notion, that phosphoric acid is constituted of one atom of phosphorus, weighing 12 and two atoms of oxygen = 16, and the weight of the atom of phosphoric acid will, therefore, be 28. It appears, then, that we have three acids with base of phosphorus, which are constituted as follows :

	Atoms of Phosph.	+ Atoms of Oxyg.	Weight of Atom.
Hypo-phosphorous acid.....	2	+ 1	.... 32
Phosphorous acid.....	1	+ 1	.... 20
Phosphoric acid.....	1	+ 2	.... 28

(d) When distilled in an earthen retort with half its weight of powdered charcoal, glacial phosphoric acid is decomposed; its oxygen, uniting with the carbon, forms carbonic acid, and phosphorus, in quantity equal to about  $\frac{1}{4}$  of the acid, rises in a separate state. This is the usual and best mode of obtaining phosphorus.

The phosphoric acid of bones may either be employed for this purpose in the state of glass, finely powdered; or to the evaporated acid, when acquiring a thick consistence, powdered charcoal may be added, in sufficient quantity to give it solidity. In the latter mode, however, unless the heat is very cautiously raised, the materials are apt to swell, and to boil over. The mixture of acid and charcoal is to be put into a stone-ware retort, coated with Willis's lute, the neck of which is lengthened out by a tin pipe. The open end of the pipe is to be immersed in a vessel of water. The heat is to be slowly raised, and at length made very intense. An enormous quantity of gas escapes, which takes fire on coming into contact with the atmosphere; and the phosphorus distils over in drops, which congeal in the water. As it is apt also to condense in, and to stop up, the neck of the retort and tin-

pipe, it must be occasionally melted out of these, by a shovel full of hot cinders, held under them. The process is rather a troublesome one; and though it is proper that the student should perform it, in order to complete a course of experiments, it will be found more economical to purchase the phosphorus which may be required for use.

Phosphorus may also be procured, by adding to urine a solution of lead in nitric acid, which precipitates a phosphate of lead. This, when well washed, dried, and distilled in a stone-ware retort, yields phosphorus.\* Or a solution of phosphate of soda (which may be bought at the druggists), mixed with one of acetite of lead, in the proportion of one part of the former salt to  $1\frac{1}{4}$  of the latter, yields a precipitate of phosphate of lead, from which phosphorus may be procured by distillation with charcoal, but at considerably more expence.

#### ART. 2.—*Combinations of Phosphorus with Chlorine.*

There are two compounds of chlorine and phosphorus.

1. *Bi-chloride or Per-chloride.* When phosphorus is introduced into chlorine gas, it takes fire spontaneously, and burns with a pale flame; and a white solid condenses on the sides of the vessel. In an experiment of Sir H. Davy, conducted with great care, 4 grains of phosphorus condensed 31.9 cubic inches (barometer 30.1, thermometer  $46^{\circ}$ ) of chlorine gas, equivalent to very nearly  $24\frac{1}{4}$  grains, or six times its weight. Therefore 100 grains of phosphorus, to form this compound, condense 600 grains of chlorine; and as 36 of chlorine appear, from a variety of facts, to be equivalent to 8 of oxygen, the above 600 grains are, by the rule of proportion, the equivalent of 135 of oxygen; and thus is derived a collateral proof that phosphoric acid is constituted of 100 phosphorus + 135 oxygen by weight.

The solid compound of phosphorus and chlorine is volatile at a temperature below  $212^{\circ}$  Fahrenheit. It acts violently on water, the hydrogen of which forms; with the chlorine, muriatic acid; while the oxygen forms, with the phosphorus, phosphoric acid. When transmitted with oxygen gas through

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\* See Crell's Journal, Translation, iii. 36.

a red hot porcelain tube, chlorine is evolved, and phosphoric acid is formed, showing that, at high temperatures, the affinity of oxygen for phosphorus is stronger than that of chlorine.

2. *Chloride or Proto-chloride.* Though this compound may be obtained by heating the per-chloride with a due proportion of phosphorus, yet a better method of preparing it is (as Sir H. Davy recommends) to pass the vapour of phosphorus over corrosive sublimate, heated in a glass tube. By this process, proto-chloride of mercury (calomel) is formed, and the remaining atom of chlorine unites with the phosphorus. The result is a liquid of the specific gravity 1.45, which does not itself redden litmus paper, though its fumes produce this effect, in consequence of being rendered acid by contact with the moisture of the air. The acid, which results from its action on water, is the phosphorous, which is best procured by the intervention of this chloride. At the same time muriatic acid is formed, by the union of chlorine with the hydrogen of the water.

In this chloride, the chlorine exists in half the quantity which constitutes the perchloride, that is, 100 grains of phosphorus are united with 300 of chlorine. But in phosphorous acid, 100 grains of phosphorus are combined with 67.5 of oxygen, which last number is, therefore, the equivalent of 300 chlorine. Now as 67.5 to 300, so is 8 to 36; indicating that in the *chloride* of phosphorus, its elements are united atom to atom; while in the *per-chloride*, two atoms of chlorine are combined with one of phosphorus.

	Atoms of Phosph.	Atoms of Chlor.	Weight of Atom
Chloride of phosphorus	1	+ 1	.. 48
Perchloride	. . . . . 1	+ 2	.. 84

### ART. 3.—*Phosphorus with Iodine.*

*Phosphorus and Iodine* combine at the temperature of the atmosphere, according to Sir H. Davy, evolving much heat, but no light; but, according to Thenard, with a disengagement both of light and heat. The result is an *iodide of phosphorus*, of a reddish brown colour, the solidity, fusibility, and volatility of which vary with the proportions of its ingredients.



If both the phosphorus and iodine are dry, no gas is given out during their combination; but, when slightly moistened, hydriodic acid is formed, by the union of iodine with the hydrogen of the water; a little subphosphureted hydrogen is produced; and phosphorous acid remains in solution. The hydriodic acid gas is also formed, when the phosphuret of iodine, produced from dry materials, is added to water.

SECTION VI.

*Sulphur.*

I. THE sulphur, which occurs as an article of commerce, is a mineral production, and is brought to this country chiefly from Sicily. That which is procured in our own island, is generally of very inferior quality, and contains a portion of the metal, from combination with which it has been separated. It is met with under two different forms; of a compact solid, which has generally the shape of long rolls or sticks; and of a light powder called *flowers of sulphur*. In general, the latter may be considered as most pure; but the two varieties, it will presently appear, are readily convertible into each other by the modified application of heat. Its specific gravity is 1.98 or 1.99. When rubbed it emits a peculiar smell, and becomes negatively electric.

II. Sulphur is readily fused and volatilized. When heated to 170° of Fahrenheit, it begins to evaporate, and to produce a very disagreeable smell; at 185° or 190° it begins to melt; and at 220° is completely fluid. If the heat be rapidly increased, it loses at 350° its fluidity, and becomes firm, and of a deeper colour. It regains its fluidity, if we reduce the temperature; and this may be repeated at pleasure, in close glass vessels, if the changes of heat be not slow; otherwise it is volatilized. It sublimes at 600°; and, according to the greater or less quickness of the process, and the size of the condensing chamber, may be collected either in a solid form or in that of flowers. (Thenard, i. 197.)

III. If, after being melted, it be suffered to cool, it congeals

in a crystalline form, but so confusedly, that we cannot define the shape of the crystals, farther than that they are slender interlaced fibres. If a large mass be kept fluid below, while it congeals at the surface, the crystallization there is much more distinct. When sulphur in complete fusion, *viz.* at  $300^{\circ}$ , is poured into water, it becomes tenacious like wax, and may be applied (as is done by Mr. Tassie) to take impressions from engraved stones, &c. These impressions are quite hard, when the sulphur has become cold. It is then of a red colour, and of the specific gravity 2.325.

IV. At the temperature of about  $290^{\circ}$  Fahrenheit, sulphur is converted into vapour; and if this operation be conducted in close vessels, the volatilized sulphur is again collected in a solid form. What remains has been called *sulphur vivum*. This affords an example of the process of *sublimation*, which differs from distillation, in affording a solid product, while the latter yields a condensed liquid. In this mode, sulphur may, in part, be purified; and its purification is completed, by boiling it repeatedly in distilled water; then in twice or thrice its weight of nitro-muriatic acid, diluted with one part of distilled water; and, finally, by washing it with distilled water, till this comes off tasteless, and incapable of changing the blue colours of vegetables.

V. When flowers of sulphur are digested in alcohol, no union takes place; but if the two bodies be brought into contact, when both are in a state of vapour, they enter into chemical union. This may be shown by an ingenious experiment of La Grange, the apparatus for performing which is represented in the first plate of his "Manual." Into a glass alembic (see the plates to this work, fig. 2) put a little sulphur; over this suspend a small bottle filled with alcohol; and apply a receiver to the pipe of the alembic, the head being put into its place. Lute the junctures, and apply a gentle heat to the alembic. The sulphur will now be raised in vapour; and the vapour surrounding the bottle of alcohol, the latter will be volatilized, and will meet in this state the fumes of sulphur. A combination will take place between the two bodies, and sulphurized alcohol will pass into the receiver. On pouring this preparation into water, the sulphur will be precipitated.

Sulphur is perfectly soluble in boiling oil of turpentine, which may be employed as a means of determining its purity.

VI. Though it had already been suspected (chiefly from the experiments of M. Berthollet, jun.) that sulphur contains hydrogen, yet the first unequivocal evidence of the fact was furnished by Sir H. Davy. A bent glass tube, having a platinum wire hermetically sealed into its upper extremity, was filled with sulphur. The sulphur was melted by heat; and a proper connection being made with the Voltaic apparatus of 500 double plates, each six inches square and highly charged, a most intense action took place. A very brilliant light was emitted; the sulphur soon entered into ebullition; elastic matter was evolved in great quantities; and the sulphur, from being of a pure yellow, became of a dark reddish brown tint. The gas was found to be sulphureted hydrogen, or hydrogen gas holding sulphur in solution; and its quantity, in about two hours, was more than five times the volume of the sulphur employed.

Another proof of the presence of hydrogen in sulphur is derived from the action of potassium; for these two bodies combine with great energy, and evolve sulphureted hydrogen, with intense heat and light.

Lastly, when dry sulphur is burned in dry oxygen gas, Sir H. Davy is of opinion that, besides sulphuric acid, a portion of water is also formed; but he is still doubtful whether the hydrogen in sulphur can be considered as any thing more than an accidental ingredient. This view of the subject is embraced, also, by Berzelius,\* who found, by heating sulphur with oxide of lead, that the quantity of water produced is much too minute to indicate any definite proportion of hydrogen in sulphur.

Another ingredient of sulphur, it appeared probable from the experiments of Sir H. Davy, is oxygen. For potassium, after being made to act on sulphureted hydrogen gas, evolved less hydrogen from water, than it ought to have done. It has since, however, been proved by Gay Lussac,† that when all sources of fallacy are avoided, a given weight of potassium,

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\* 79 Ann. de Chim. 119.

† Ann. de Chim. vol. lxxiii.

which has been exposed to sulphureted hydrogen, separates exactly the same volume of hydrogen gas from water, as an equal weight of recent metal. Potassium, therefore, acquires no oxygen, from the sulphur which is contained in sulphureted hydrogen.

#### ART. 1.—*Sulphur with Oxygen.*

Sulphur is inflammable, and appears susceptible of two distinct combustions, which take place at different temperatures.\* At 140° or 150° Fahrenheit, it begins sensibly to attract oxygen; and if the temperature be raised to 180° or 190°, the combination becomes pretty rapid, accompanied by a faint blue light. But the heat evolved is scarcely sensible; at least it is so weak, that the sulphur may thus be burned out of gunpowder, and the powder be rendered useless without inflaming it. At a temperature of 300°, its combustion, though still feeble compared with that of some other bodies, is much more active, and accompanied with a redder light. When set on fire in oxygen gas, it burns with a very beautiful and brilliant light; but of a given quantity of oxygen gas, it is not possible to condense the whole by this combustion, for reasons which hereafter will be stated. The product of these combustions, when examined, will be found to be sulphurous and sulphuric acid, but chiefly the former, and if water be carefully excluded, sulphurous acid only is formed. It is necessary, therefore, in order to produce sulphuric acid, to make the experiment over water.

#### *Sulphuric Acid.*

Sulphuric acid has been known ever since the time of Basil Valentine, who appears to have discovered it about the close of the 15th century. It was first extracted from sulphate of iron by distillation, and afterwards formed by the combustion of a mixture of about 1 part of nitre, and 6 or 8 of sulphur in large glass vessels over water. For glass vessels, in process of time, large leaden chambers, having a stratum of water floating on the bottom, came to be substituted. The history of the

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\* For an account of the oxides of sulphur, see Dr. Thomson's paper in Nicholson's Journal, vi. 101.

successive improvements of its manufacture in this country has been given at length by Mr. Parkes, in the second volume of his *Chemical Essays*.

The properties of this acid may be exhibited by a portion of that usually found in the shops. They are as follows:

(a) Sulphuric acid has a thick and oily consistence; as may be seen by pouring it from one vessel into another.

(b) In a pure state, it is perfectly limpid and colourless.

(c) When mixed suddenly with water, considerable heat is produced. Four parts, by weight, of concentrated sulphuric acid, and one of water, when mixed together, each at the temperature of  $50^{\circ}$  Fahrenheit, have their temperature raised to  $300^{\circ}$ . When an ounce of water has been suddenly mixed with three of sulphuric acid, and the mixture been suffered to cool to the temperature of the atmosphere, an additional half oz. of water raises it to  $86^{\circ}$ , a second to  $96^{\circ}$ , and a third to  $104^{\circ}$ .\* The greatest elevation of temperature, Dr. Ure finds to be occasioned by the sudden mixture of 73 parts by weight of strong sulphuric acid with 27 of water. This rise of temperature takes place, because the affinity or capacity of the compound of sulphuric acid and water for caloric, is less than that of the acid and water separately. A diminution of bulk also ensues; that is, one measure of acid and one of water do not occupy the space of two measures, but about  $\frac{1}{3}$ th less; and the greatest condensation results, when those proportions are used, which give the greatest increase of temperature. Owing to the heat produced by its admixture with water, the dilution, for ordinary purposes, should be conducted very gradually; and the acid should be added to the water by small portions at once, agitating the mixture after each addition, and allowing each portion to cool before a fresh addition is made. On the principle of its attraction for water is to be explained, also, the rapid increase of weight which the sulphuric acid acquires when exposed to air. In one day, three parts of concentrated sulphuric acid, exposed to the atmosphere, are increased in weight one part; and one ounce, by twelve months' exposure, has been found to gain an addition of  $6\frac{1}{2}$ .

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\* Philips on the London Pharmac. p. 34.

(d) Perfectly pure sulphuric acid remains quite limpid during dilution. The sulphuric acid, however, commonly found in the shops, under the name of oil of vitriol, on admixture with water, deposits a white powder, in considerable quantity, consisting of various impurities, but chiefly of sulphate of lead. Berzelius has found, also, a minute quantity of titanium in sulphuric acid of English manufacture, and tellurium in acid prepared at Stockholm.\* By evaporating 100 parts of sulphuric acid of commerce in a platinum dish, Dr. Ure has obtained from one half to three quarters of a grain of solid matter, consisting of about two parts of sulphate of potash and one of sulphate of lead.†

(e) Sulphuric acid is nearly twice as heavy as water. The specific gravity of the strongest pure acid that can be obtained, is 1.850; but even this contains 19 (according to Dr. Wollaston, 18.44) per cent. of water, which appears essential to its constitution, and can only be separated by combining the acid with a base. Dr. Ure states that genuine commercial acid should not exceed 1.8485. When denser, its purity may be suspected. It has been ascertained, by Mr. Dalton, that acid, of nearly the maximum strength, has its specific gravity very little altered, by adding or subtracting small portions of water. Thus acids, containing 81 and 80 per cent. of acid, do not differ more than 1 in the third place of decimals; nor is the specific gravity proportionally changed by dilution till it falls as low as 1.78. The strength of the more concentrated acid may be better ascertained, by observing how much water is required, to bring it down to the specific gravity 1.78. The boiling point, also, Mr. Dalton has discovered, is a much better test of its strength; and he has constructed the following useful Table, in which account is taken of all these circumstances.

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\* Thomson's Annals, x. 464.

† Journ. of Science, iv. 115.

*Mr. Dalton's Table of the Quantity of real Acid in 100 Parts of Liquid Sulphuric Acid, at the Temperature 60° Fahrenheit.*

Atoms Acid Water.	Real Acid per cent. by Weight.	Real Acid per cent. by Measure.	Specific Gravity.	Boiling Point.
1 + 0	100	unknown.	unknown.	unknown.
1 + 0	81	150	1.850	620°
	80	148	1.849	605°
	79	146	1.848	590°
	78	144	1.847	575°
	77	142	1.845	560°
	76	140	1.842	545°
	75	138	1.838	530°
	74	135	1.833	515°
	73	133	1.827	501°
	72	131	1.819	487°
	71	129	1.810	473°
	70	126	1.801	460°
	69	124	1.791	447°
1 + 2	68	121	1.780	435°
	67	118	1.769	422°
	66	116	1.757	410°
	65	113	1.744	400°
	64	111	1.730	391°
	63	108	1.715	382°
	62	105	1.699	374°
	61	103	1.684	367°
	60	100	1.970	360°
1 + 3	58.6	97	1.650	350°
	50	76	1.520	290°
	40	56	1.408	260°
1 + 10	30	39	1.30 +	240°
1 + 17	20	24	1.200	224°
1 + 38	10	11	1.10—	218°

It has been ascertained by Dr. Ure that by adding about  $2\frac{1}{4}$  per cent. of its weight of sulphate of potash to concentrated oil of vitriol, its specific gravity may be increased to 1.860. The only mode, therefore, of ascertaining exactly the strength of oil of vitriol is by saturating a known quantity with an alkali; and it may be assumed as sufficiently correct, that

100 grains of dry sub-carbonate of soda neutralize 92 grains of pure liquid sulphuric acid ; or that 100 grains of the acid require 108, or 108.5, of the sub-carbonate for saturation.

It is sometimes of importance to the chemical artist to know the proportion, not of *real acid*, but of *acid of commerce*, in diluted sulphuric acid of different specific gravities. An approximation to the true proportion may be obtained, by increasing the numbers, indicating the real acid, one fourth. For example, acid of the specific gravity 1.200, contains, according to the above table, 20 per cent. of real acid ; which, increased one fourth, gives 25 per cent. of acid of sp. gr. 1.849. A very copious Table of the quantities of sulphuric acid of commerce in acid of different densities, constructed by Mr. Parkes from actual experiment, is given in the 40th volume of the *Philosophical Magazine*, and in vol. ii. of his *Chemical Essays*, p. 144. Its length only prevents me from inserting it here. The shorter Table of Vauquelin, in the 30th volume of *Nicholson's Journal*, is rendered less fit for the English chemist, because the acid, employed in the experiments on which it is founded, is inferior in density to the average acid sold in this country. In taking the specific gravity of sulphuric acid, it is of importance to attend to its temperature,\* which must be examined by a thermometer, having its bulb perfectly dry. According to Dr. Ure, 10° Fahrenheit make a difference in the density of oil of vitriol of 0.005. With due attention to this, and other necessary precautions, Dr. Ure has constructed a Table, which, as it is of moderate length, and exhibits at one view the proportion not only of real or dry acid, but of liquid acid, in sulphuric acid of different specific gravities, I shall insert in the Appendix. In the memoir of which the Table forms a part, Dr. Ure has endeavoured to establish some general formulæ for calculating the proportion of oil of vitriol in dilute acid of any specific gravity, and also for finding the specific gravity corresponding to a given proportion of acid.†

(f) Sulphuric acid, by a sufficient reduction of its temperature, may be frozen ; and under favourable circumstances,

\* See Parkes's *Essays*, ii. 461.

† *Journ. of Science*, iv. 127.



it assumes a regular crystalline form, a considerable degree of solidity or hardness, and a density exceeding that which it possessed in a fluid state. From the experiments of Mr. Keir\* it follows that there is a certain point of specific gravity (*viz.* 1.780), at which the sulphuric acid most readily congeals; and when of this degree of strength it requires even a less degree of cold than is sufficient to freeze water, its congealation taking place at  $+45^{\circ}$  Fahrenheit. From the specific gravity of 1.786, on the one hand, to 1.775, on the other, it freezes at  $32^{\circ}$  Fahrenheit. It is singular that it remains congealed, at a temperature higher than that originally required for freezing it. Acid, for example, which did not become solid till its temperature was reduced to  $32^{\circ}$ , remained frozen at  $45^{\circ}$ . When of the specific gravity of 1.843, or as nearly as possible of that of commerce, it was found by Mr. Macnab † to freeze at  $-15^{\circ}$  Fahrenheit: but this acid, mixed with rather more than half its weight of water, required for congealation the temperature of  $-36^{\circ}$  Fahrenheit.

(g) To purify sulphuric acid, it must be distilled in a glass retort, placed in the sand-bed of a reverberatory furnace. This process requires considerable care. But to those who have sufficient experience in chemical operations, the following instructions may be useful; especially as it is indispensable, in all experiments of research, to employ an acid purified by distillation.

The furnace, in which this process is conducted, should have a contrivance for supporting a sand-bath within it at a proper height; and an opening in the side, for transmitting the neck of the retort. (Pl. vii. fig. 62, 63.) The retort must be coated with clay and sand over its whole body, and also over that part of the neck which is exposed to the fire. It is then to be placed, the coating being previously dry, in the sand-bath, about one half filled with sulphuric acid; and a receiver must be applied, but not luted on. The fire must now be lighted, and raised with extreme caution. The first portion that comes over, amounting to about one sixth, consists chiefly of water, and may be rejected. This is followed

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\* Philosophical Transactions, lxxvii. 267.

† Ibid. lxxvi. 241.

by the concentrated acid; and, at this period, there is great risk that the neck of the retort will be broken, by the contact of the condensed acid, which has a very high temperature, and which frequently cracks the glass, as effectually as the application of a red-hot iron. The fire must be regulated by the register door of the ash-pit, so that several seconds may elapse between the fall of the drops into the receiver. The process may be continued as long as any acid is condensed. The retorts, employed for this purpose, should be most attentively annealed.

The difficulty of rectifying sulphuric acid is much diminished, by using a retort of the capacity of from two to four quarts, when a pint of the acid is employed, and by connecting its neck with the receiver by means of an adapter three or four feet long. The retort may be set over a charcoal fire, and the flame made to play gently on its bottom. No luting is to be employed, and the receiver is to be surrounded with cold water. With this arrangement, and a cautious regulation of the heat, Dr. Ure finds that sulphuric acid may be distilled without much risk, in a continuous gentle stream.\* The sudden explosions, that occasionally happen during the process, may be prevented either by putting into the retort a few sharp pointed pieces of glass, or some slips of platinum as recommended by Mr. Brande.

Sulphuric acid may be less perfectly purified by diluting it with an equal weight of water, allowing the impurities to settle, decanting the clear liquor, and evaporating it to the proper degree in a glass retort.

(h) The proportion of the elements of sulphuric acid has been investigated by several chemists. Berthollet oxygenated 17.846 parts of sulphur by nitric acid, and obtained a quantity of sulphuric acid, which gave 127.515 parts of sulphate of barytes. Hence 100 parts of sulphur would have formed 230.79 parts of real sulphuric acid (= about 292 of density 1.85); but this product falls short of what ought to have resulted. Klaproth, Richter, and Bucholz, obtained results nearly agreeing with each other. Berzelius, to avoid all fal-

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\* Journal of Science, iv. 116.

lacy from the hydrogen contained in sulphur, combined it, in the first place, with lead, which, like other metals, always evolves much hydrogen, and then oxygenated the sulphuret. If two volumes of sulphurous acid gas, and one of oxygen, constitute sulphuric acid, it follows that the oxygen in the latter is a multiple of that in the former by  $1\frac{1}{2}$ ; and sulphurous acid being constituted of 100 sulphur + 99.44 oxygen, sulphuric acid will consist of 100 sulphur + 149.16 oxygen; or it will contain as nearly as possible 40 sulphur and 60 oxygen in 100 real acid. The following Table exhibits the proportions, deduced from different experiments, in 100 parts of real acid :

	Sulphur.	Oxygen.
From the experiments of Berthollet ..	43.28	.. 56.72
————— Klaproth ...	42.20	.. 57.80
————— Bucholz ....	42.50	.. 57.50
————— Berzelius ..	39.92	.. 60.08
Proportions admitted by Dr. Wollaston ..	40.0	.. 60.0

If the proportions be taken at 40 sulphur and 60 oxygen, and if the acid consists, as Mr. Dalton supposes, of 1 atom of sulphur and 3 atoms of oxygen, the atom of sulphur will weigh 16; for as  $(60 \div 3 = )$  20 is to 40 so is 8 to 16; the weight of an atom of real sulphuric acid will be 40; and the liquid acid, containing an atom of water, = 9, will be represented by the number 49. Mr. Dalton's numbers are 13 for the atom of sulphur, 34 for that of sulphuric acid, and 42 for the liquid acid, the difference being occasioned by his taking oxygen at 7, instead of 8.

A coincidence has been pointed out by Berzelius, which is very remarkable, and is deemed by him sufficiently general, to be admitted as a law; *viz.* that in any combination of two oxygenated bodies with each other, the oxygen of the one is either a multiple or divisor of that of the other, by some simple number. Sulphuric acid, of 1.850 density, affords an illustration of this principle; for it consists of 81 real acid and 19 water; and it will be found that the oxygen in the acid is, as nearly as possible, 48; and the oxygen in the water 16, so that in this case the multiple is 3, for  $16 \times 3 = 48$ . Various

other examples of the same general principle will be given, in treating of metallic oxides. In all neutral compounds of sulphuric acid with alkaline, earthy or metallic bases, the acid contains a quantity of oxygen, which exceeds that in the base by the same multiple 3.

(i) Sulphuric acid is decomposed, at the temperature of the atmosphere, by inflammable substances, and acquires a dark colour. The addition of a little brown sugar, or a drop of olive oil, to a portion of the acid, imparts to it a brownish hue, which in time changes to black. Hence this acid should always be kept in bottles with glass stoppers; for a small bit of straw or cork, if dropped into a considerable quantity of sulphuric acid, changes it in the manner that has been pointed out.

(k) In high temperatures, sulphuric acid is still farther decomposed by combustible bodies.

1. Hydrogen gas, brought into contact with sulphuric acid, in a state approaching ignition, decomposes it, and water and sulphurous acid are formed. This, however, is a dangerous and difficult process, which it is not advisable to repeat.

2. According to Gay Lussac, sulphuric acid is decomposed by heat alone; and is resolved into two volumes of sulphurous acid gas, and one of oxygen gas. This experiment is best performed by passing the acid through a red-hot tube of glass or porcelain, which should not exceed two tenths of an inch in diameter. The acid is also decomposed by platina wires, communicating with the extremities of a galvanic pile. At the end of the negative wire, flocculi of sulphur appear, and at the positive end oxygen gas is evolved; and a brownish tint is produced by the formation, doubtless, of sulphate of platinum.

3. Sulphur, by being boiled in sulphuric acid, partly deoxygenates it, and converts a portion of it into sulphurous acid, which comes over in a gaseous state.

4. Into a glass retort, put such a quantity of sulphuric acid as will fill about one fourth part of it, and add a small portion of powdered charcoal. On applying the heat of a lamp, gas will be produced very abundantly. Let this gas be conveyed

by a tube fixed to the mouth of a retort, and bent in the proper manner, into an inverted jar of water; or, if it can be had, into an inverted jar of quicksilver in a mercurial apparatus. During this operation, the carbon attracts part of the oxygen of the sulphuric acid, and forms carbonic acid gas. But the sulphur is not entirely disoxygenated; and a compound is therefore formed of sulphur and oxygen, containing less oxygen than the sulphuric acid. This compound exists in the state of a gas, and its properties may next be examined. To avoid, however, the complication which the admixture of carbonic acid with this new product introduces into the experiment, it may be proper to prepare it in a mode less objectionable, but the *rationale* of which cannot at present be explained. This consists in dissolving two parts, by weight, of quicksilver in one of sulphuric acid, and boiling the mass to dryness, in a glass capsule, or in the bottom of a broken Florence flask. The dried mass is next to be distilled in a strong sand-heat; a glass globe being interposed between the retort and the receiving mercurial trough, to condense any sulphuric acid that may escape decomposition. (See pl. iii. fig. 31.) The gas thus obtained is termed, conformably to the principles of the new nomenclature, *sulphurous acid*.

#### *Sulphurous Acid Gas.*

Sulphurous acid may be formed, 1st, by burning sulphur at a low temperature in common air, under a glass bell; and if slips of linen cloth, dipped in a solution of potash, be exposed to the vapour, the alkali forms a combination with the sulphurous acid, which may afterwards be washed off and evaporated. The dry salt, distilled with liquid tartaric acid, gives sulphurous acid gas.

2dly. It is formed, exclusively, when sulphur is burned in dry oxygen gas. The gas, when restored to its original temperature, is found to be contracted  $\frac{1}{7}$ th or  $\frac{1}{5}$ th of its bulk; but this is probably owing to the hydrogen contained in sulphur, for there is every reason to believe that oxygen gas, by becoming sulphurous acid, is not at all changed in volume.

3dly. By heating red oxide of mercury with one fourth of

its weight of sulphur, sulphurous acid is produced in the proportion of about a cubic inch for every five grains of the oxide.

4thly. By boiling 1 part by weight of mercury with six or seven of sulphuric acid to dryness in a glass retort, and then raising the heat, sulphurous acid gas is formed, and may be collected and preserved over quicksilver. Half an ounce of mercury is sufficient for the production of several pints of the gas.

Its properties are the following :

(a) It has a pungent and suffocating smell, exactly resembling that which arises from burning sulphur.

(b) It is more than twice as heavy as atmospherical air. One hundred cubic inches are stated by Mr. Kirwan to weigh 70.215 grains, which would make its specific gravity 2.265. By Sir H. Davy, the same volume is said to weigh 68 grains : this would give the specific gravity of 2.23, which agrees almost exactly with the statement of Thenard (i. 685.) According to a calculation of Gay Lussac, founded on the proportion of its elements, its specific gravity should be 2.30314. Berzelius finds it by experiment to be 2.247.\*

(c) Monge and Clouet assert, that if the gas be exposed, at the same time, to a temperature of 31° Fahrenheit, and to great pressure, it assumes a fluid state.

(d) It extinguishes burning bodies ; and kills animals, when respired.

(e) It has the property of whitening or bleaching silk, and of giving it lustre, and removes fruit stains from woollen cloth.

(f) Of sulphurous acid, water absorbs 33 times its bulk, or one eleventh of its weight, caloric is evolved, and the solution at 68° has the specific gravity 1.0513. Mr. Dalton states the quantity absorbed to be only 22 times the bulk of the water. From the solution, when recently prepared, the gas may be separated by heat, but not by congelation.

(g) The watery solution does not redden infusion of litmus, as acids in general do, but totally destroys its colour. Hence its use in bleaching several vegetable and animal products.

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\* Ann. de Chim. et Phys. v. 178.

It restores the colour of syrup of violets, which has been reddened by other acids.\*

(h) Sulphuric acid, saturated with this gas, which may be effected by passing the gas through the acid, acquires a strong smell, a yellowish brown colour, smokes when exposed to the air, and has the property of assuming a solid form, by a moderate reduction of its temperature. When distilled, the first product, which is a compound of the two acids, assumes a solid form. It has been called *glacial sulphuric acid*. It has, however, been asserted by Vogel,† that the presence of sulphurous acid is not the cause of the glacial quality of oil of vitriol; and that, when converted to this state, by boiling in contact with sulphur, it contains no sulphurous acid. The nature of the change he has not yet fully explained.

(i) Sulphurous acid is absorbed by crystallized borax, and, by means of this property, Cluzel observes, may be separated from carbonic acid, and some other gases.‡

Sulphurous acid is again converted to the state of sulphuric by restoring oxygen to it.

1. A mixture of oxygen and sulphurous acid gases, both perfectly dry, and standing over mercury, is not diminished by remaining in contact with each other during some months; but if a small quantity of water be added, the mixture begins to diminish, and sulphuric acid is formed. Or if water impregnated with sulphurous acid be exposed to oxygen gas in a tube, the oxygen in 10 or 14 days is imbibed, and sulphuric acid formed. The same gases in a state of mixture, by the action of electricity, or by being driven through a red-hot porcelain tube, afford sulphuric acid. The proportions required for mutual saturation are two measures of sulphurous acid and one of oxygen gas.

2. To a portion of water saturated with sulphurous acid gas add a little oxide of manganese, a substance that contains much oxygen, loosely combined. The pungent smell of the water, and the other characteristics of sulphurous acid, will soon disappear.

3. Sulphurous acid gas is condensed into sulphuric acid by

\* Nicholson's Journal, xvii. 306.

† 84 Ann. de Chim. 283.

‡ 83 Ann. de Chim. 259.

admixture with chlorine gas; but not unless the gases are in contact with water. In the latter case, the hydrogen of the water unites with the chlorine, and the oxygen with the sulphurous acid.

Dry nitrous acid gas is also inefficient on dry sulphurous acid; but when placed in contact with a small quantity of water, all these bodies act mutually and rapidly on each other; the nitrous acid gas yields a portion of its oxygen to the sulphurous acid, from whence result nitrous gas and sulphuric acid, which, both combining with water, form white flakes upon the inside of the balloon. These flakes are made up of congeries of small crystalline needles. Water, brought into contact with these crystals, dissolves the sulphuric acid, and the nitrous gas is liberated with effervescence. By means therefore of a small quantity of nitrous gas, we may transform a large quantity of sulphurous acid into sulphuric acid, provided the acid gas be mingled with half its volume of oxygen, or with an equivalent quantity of atmospheric air. The phenomena are beautifully exhibited by admitting, into an exhausted and dry glass balloon, first 30 measures of sulphurous acid, next 15 of oxygen, and then 5 of nitrous gas. No perceptible change takes place, till a little water is introduced, sufficient to moisten the inside of the vessel, when the small quantity of red nitrous acid, formed on adding the nitrous gas, disappears, and composes the crystalline substance already described. When these crystals have been deposited on the inside of the balloon, and a small quantity more of water is admitted, there is an immediate effervescence from the escape of nitrous gas, which, meeting with oxygen gas, again becomes nitrous acid, and this, acting upon the sulphurous acid, the same combinations ensue as before, and may be repeated as long as sufficient sulphurous acid and oxygen remain.

It is by a series of operations of this kind, that the formation of sulphuric acid is effected in the ordinary process for preparing it. The nitric acid, present in the saltpetre, abandons part of its oxygen to one portion of the sulphur, which, becoming sulphuric acid, unites with the potash of the nitre. At the same moment nitrous gas is set at liberty, which, with



the oxygen present in the air of the chamber, composes nitrous acid gas. Another portion of sulphur is converted into sulphurous acid, which becomes sulphuric acid by depriving the nitrous acid of oxygen, the latter acid being brought back to the state of nitrous gas. This gas, absorbing the atmospheric oxygen, again becomes nitrous acid, which changes a fresh portion of sulphurous into sulphuric acid. This theory was first suggested by MM. Clément and Desormes. It has been since modified by Gay Lussac, who supposes that nitrous acid, and not nitrous gas, is disengaged from nitrate of potash. But even if this be admitted, the subsequent steps of the process are still explicable on the original theory, which satisfactorily explains why so small a proportion of nitre as one eighth is adequate to the conversion of sulphur into sulphuric acid, though capable of supplying only a very small share of the oxygen essential to this change.

(k) When the temperature of sulphurous acid gas is greatly reduced, by surrounding it with a mixture of snow and muriate of lime, it is changed into a liquid.

(l) If sulphurous acid gas and fresh muriate of tin are brought into contact over mercury, the volume of the gas is speedily diminished, sulphur is deposited, and the proto-muriate becomes a per-muriate of tin. (Accum.)

(m) It is decomposed, when submitted to the heat of ignition, in contact with certain combustible bodies. Thus, when a mixture of sulphurous acid and hydrogen gases are driven through a red-hot porcelain tube, the oxygen of the acid combines with the hydrogen, and forms water, and sulphur is obtained in a separate form. The sulphurous acid is decomposed, also, when transmitted over red-hot charcoal; and, as appears from Gay Lussac's experiment, by potassium.

From the testimony of the same chemist we learn that 100 parts of sulphur, to become sulphurous acid, unite with 95 oxygen. The following Table shows the numbers derived from different authorities. Sulphurous acid contains per cent.

	Sulphur.	Oxygen.
According to Gay Lussac . . . .	51.30 . . . . .	48.70
———— Berzelius . . . . .	50.03 . . . . .	49.97
———— Thomson . . . . .	53.0 . . . . .	47.0

The determination of Berzelius, of 100 sulphur to 99.44 oxygen, agrees best with the specific gravity of the gas; for if 100 cubic inches weigh 68, and 100 cubic inches of oxygen 34, the remaining 34 must consist of sulphur. Its atomic constitution, according to Mr. Dalton, is 1 atom of sulphur + 2 atoms of oxygen; and the weight of its atom will, therefore, be  $16 + 16 = 32$ .

The combinations of sulphurous acid with alkaline and earthy bases, called *sulphites*, will be described individually in their proper places.

#### *Of Hypo-sulphurous Acid.*

This acid, like the hypo-nitrous, exists only in combination with salifiable bases, forming compounds which were first examined in 1813 by Gay Lussac, and were called by him *sulphureted sulphites*. Beside other methods of preparing these salts, he found that they might be obtained by digesting the solution of a sulphite with sulphur, an additional quantity of which might thus be made to combine with the sulphurous acid. It had also been long ago observed by Mr. Higgins of Dublin, that liquid sulphurous acid dissolves iron without effervescence; and Berthollet afterwards showed that in this case the iron is oxidized at the expence of the sulphurous acid, and that sulphur is disengaged, which immediately unites with the sulphite of iron, forming a sulphureted sulphite. Dr. Thomson appears to have been the first\* who took a just view of these phenomena. The new compound he found to be a neutral salt, containing a peculiar acid of sulphur, to which he gave the name of *hypo-sulphurous acid*, and to its compounds that of *hypo-sulphites*. These compounds have been since examined with great ability by Mr. Herschell,† who has not, however, succeeded completely in his attempt to exhibit the acid in a separate state; nor indeed does it appear capable of existing permanently when uncombined with a base. From the experiments of Dr. Thomson and Mr. Herschell, it may be inferred to be a compound of 1

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\* System of Chemistry, 5th edition.

† Edinburgh Philosophical Journal, i. 8, and 36.

atom of sulphur + 1 atom of oxygen, and its representative number will be  $16 + 8 = 24$ . Its properties will again come under review in speaking of the several hypo-sulphites.

*Hypo-sulphuric Acid.*

This acid was discovered by Welter and Gay Lussac.\* Their process for forming it consists in passing a current of sulphurous acid through water, in which finely powdered peroxide of manganese is kept mechanically suspended. There is immediately produced a perfectly neutral solution, consisting of hypo-sulphate and common sulphate of manganese. When the solution is sufficiently concentrated, pure barytes is added to the previously heated liquor, and agitated along with it, taking care to employ an excess of the earth. All the oxide of manganese is thus separated; and, sulphate of barytes being insoluble, the filtered liquor contains only the hypo-sulphate of barytes, and also the redundant portion of that earth. The latter is to be separated by a stream of carbonic acid, and subsequent ebullition to expel any excess of carbonic acid. The hypo-sulphate is then to be crystallized, dissolved in water, and decomposed by just the quantity of sulphuric acid, which is required to precipitate the barytes. The filtered liquor is to be concentrated, by exposing it under the exhausted receiver of an air-pump, along with a vessel of sulphuric acid, till it has attained the density of 1.347. If continued to be exposed, it is resolved into sulphurous acid which exhales, and sulphuric acid which remains liquid.

Oxygen gas, atmospheric air, chlorine, concentrated nitric acid, and red sulphate of manganese, are all inert on it at common temperatures. Zinc is dissolved by it, and hydrogen gas is disengaged by the decomposition of water, and there remains in solution hypo-sulphuric acid combined with oxide of zinc. It completely saturates salifiable bases, and affords neutral and soluble compounds with barytes, strontites, lime, and protoxide of lead; whereas sulphuric acid yields insoluble compounds with all those bases. At common temperatures these salts are permanent, but, when heated, sulphurous acid

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\* Ann. de Chim. et de Phys. x. 312.

escapes, and they pass to the state of sulphates, which are still neutral.

Hypo-sulphuric acid has been inferred to be composed of 100 parts of sulphur + 125 oxygen, setting apart that which is in the water essential to its existence; or we may consider it as a compound of 100 parts of sulphurous acid + 125 of sulphuric. Hence we have the four following acids with base of sulphur:

	Sulphur.	Oxygen.	Sulphur.	Oxygen.
1. Hypo-sulphurous acid.	100	+ 50	or 1 atom	+ 1 atom.
2. Sulphurous acid . . . . .	100	+ 100	or 1 atom	+ 2 atoms.
3. Sulphuric acid. . . . .	100	+ 150	or 1 atom	+ 3 atoms.
4. Hypo-sulphuric. . . . .	100	+ 125	or 2 atoms	+ 5 atoms.

#### ART. 2.—*Sulphur with Chlorine.*

Sulphur, when heated in contact with chlorine gas, or even when exposed to it at common temperatures, absorbs it, and forms a singular compound first described by Dr. Thomson,\* and afterwards investigated by Berthollet, jun.† Ten grains absorb nearly 30 cubic inches of gas, which is nearly in the proportion of 16 (the weight of an atom of sulphur) to 36 (the weight of an atom of chlorine). It appears, indeed, to be a true chloride of sulphur.

This fluid is volatile below 200° Fahrenheit. Its colour is red by reflected light, but yellowish green by transmitted light. It emits fumes, which are peculiarly acrid, and which excite a copious flow of tears. Its specific gravity is 1.6. When agitated with about an equal volume of water, an active ebullition and great disengagement of heat take place; sulphur is deposited; and the residuary liquid contains muriatic and sulphurous, and a small quantity of sulphuric, acids. Hence the water is decomposed, and while its hydrogen unites with the chlorine, its oxygen combines with the greater part of the sulphur. Alcohol and ether are decomposed with appearances of still more intense action, and it disunites also the elements of ammonia.

\* Nicholson's Journal, 8vo. vol. vi.

† Mem. d'Arcueil, tom. i.

Mercury acts strongly upon this liquid; its surface is first tarnished, great heat is evolved, and a grey powder is formed, which is a mixture of sulphur and chloride of mercury.

It reddens vegetable blue colours; but not till, by its action on water or on hydrogen, muriatic acid has been produced. Some chemists have considered it as an acid, and have proposed to call it the *chloro-sulphuric acid*; but besides being deficient in the other qualities of acids, it does not, like them, unite with salifiable bases.

#### *Sulphur with Iodine.*

Sulphur and iodine unite at a gentle heat, and a black radiated compound is formed, resembling sulphuret of antimony. It is easily decomposed at a degree of heat a little above that at which it was produced, and iodine is detached from it in vapour. Its precise composition is unknown.

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## SECTION VII.

### *Of Selenium.*

IN the chambers for manufacturing sulphuric acid, from the sulphur which is procured at Fahlun in Sweden, a reddish mass is deposited, which is principally sulphur. This substance, in burning, gave out an odour, which induced Berzelius to suspect that it contained tellurium, but on a minute examination he discovered, instead of that metal, a body with entirely new properties, to which he has given the name of *selenium*. The process, by which it was extracted, is described in the 13th vol. of *Annals of Philosophy*, p. 403; but as the source of it is extremely rare, it will be sufficient to refer to Berzelius's description. For the same reason, I shall give only a short account of this substance, confining myself to such of its properties, as are important from their influence on the general doctrines of chemistry.

The colour of selenium varies a good deal. When rapidly

cooled, its surface has a dark brown hue, and its fracture the colour of lead. Its powder has a deep red colour, but it sticks together when pounded, and then assumes a grey colour and a smooth surface. It softens at  $212^{\circ}$  Fahr., and completely fuses at a few degrees higher. While cooling, it has a considerable degree of ductility, and may be kneaded between the fingers, and drawn out into fine threads, which have a strong metallic lustre, an imperfect degree of transparency; and are red by transmitted, but grey by reflected light. When slowly cooled, it assumes a granulated fracture, and is extremely like a piece of cobalt. At a temperature nearly equal to that of boiling mercury, selenium enters into ebullition; and condenses, either into opaque metallic drops, or, when a retort with a large neck is used, into flowers of a fine cinnabar colour. Its vapour has a deep yellow colour, more intense than that of chlorine, but not so deep as that of sulphur.

When heated before the blow-pipe, it tinges the flame of a fine azure blue, and exhales so strong a smell of horse-radish, that a fragment, not exceeding  $\frac{1}{50}$  of a grain, is sufficient to fill the air of a large apartment.

*Selenium and Oxygen.*—Oxide of selenium is formed by heating selenium in a close phial with common air, which acquires a very strong smell of horse-radish. Water agitated with this air imbibes the odour of the gas, and reddens litmus feebly, but this appears to be owing to the production of a small quantity of selenic acid. Selenic oxide gas is very sparingly soluble in water, and does not impart any taste to it. It does not combine with liquid alkalis. Its precise composition is unknown; but it appears to belong to the same class of oxides as carbonic oxide.

*Selenic Acid.*—Selenium dissolves in nitric and nitro-muriatic acids, and when the solution is evaporated in a retort, so as to expel the excess of those acids, there remains a white saline mass, which sublimes on raising the temperature, and forms a vapour, the colour of which closely resembles that of chlorine. In the cold part of the apparatus, selenic acid condenses in very long four-sided needles. These crystals, when first taken out of the retort, have a dry aspect and a

peculiar lustre. Exposed to the air, they adhere to each other, and the lustre becomes dull, but they do not liquefy.

Selenic acid has a sour taste, and leaves a slightly burning sensation on the tongue. It is very soluble in cold water, and dissolves in almost every proportion in boiling water. A saturated solution crystallizes, when rapidly cooled, in small grains, and when slowly cooled in striated prisms. The crystals dissolve in great abundance in alcohol, and the solution, when distilled, yields a fluid having an ethereal smell.

Selenic acid unites with different bases, and forms a class of salts called *Selenates* or *Seleniates*, which will be described with their respective bases.

Selenic acid is easily reduced both in the moist and the dry way. When a plate of zinc or polished iron is introduced into a solution of selenic acid mixed with muriatic acid, selenium is precipitated in the form of red, or brown, or blackish flakes. It is revived, also, by sulphureted hydrogen and sulphurous acid gases.

From his investigation of selenic acid, Berzelius has inferred it to consist of

Selenium .....	71.261	.....	100.00
Oxygen .....	28.739	.....	40.33
	—————		
	100.		

On the supposition that it is constituted of an atom of base + 2 atoms of oxygen, the equivalent number for selenium will be 41, and for selenic acid 57.

*Selenium and Chlorine.*—Selenium absorbs chlorine gas, and becomes hot and forms a brown liquid, which, by an additional quantity of chlorine, is converted into a white solid mass. This is stated by Berzelius to be a compound of muriatic and selenic acids, but it is probably composed of chloride of selenium and the latter acid. It has not yet been accurately separated into its component parts, for when heat is applied, both substances are sublimed.

The remaining compounds of selenium will be described hereafter in their proper places. At present, it is only necessary to observe farther, that while this body possesses some

of the characters of metals, (the metallic lustre for example,) it is destitute of others that are essential to its arrangement in that class. It has more transparency than any metal, and is distinguished, also, from the metals, by the want of power to conduct electricity or heat. In some respects it resembles tellurium; but, on the whole, its properties are most analogous to those of sulphur; and it may be regarded as forming the connecting link between metals and non-metallic combustibles.



## CHAPTER VIII.

### OF THE COMBINATION OF SIMPLE ACIDIFIABLE BODIES, (NOT METALLIC), WITH EACH OTHER.

#### SECTION I.

##### *Hydrogen with Nitrogen.—Ammonia.*

##### ART. 1.—*Preparation and Qualities of Ammonia.*

I. AMMONIA, in a liquid form, had been long known to chemists, both Basil Valentine, and Raymond Lully having described the methods of procuring it; but Dr. Black was the first who distinguished between its pure or caustic, and its mild or carbonated state, and Dr. Priestley first exhibited it in a gaseous form, to which he gave the name of *alkaline air*. To procure it in this state, one of the following processes may be employed.

(a) Mix together equal parts of muriate of ammonia and dry quicklime, each separately powdered; and introduce them into a small gas bottle or retort. Apply the heat of a lamp, and receive the gas, that is liberated, over mercury.

(b) To a saturated solution of ammonia in water or the pure liquid ammonia, in a gas bottle, apply the heat of a lamp; and collect the gas, as in *a*.

II. This gas has the following properties:

(a) It has a strong and very pungent smell.

(b) It immediately extinguishes flame; and is fatal to animals. Before, however, a candle is extinguished, by immersion in this gas, the flame is enlarged, by the addition of another, of a pale yellow colour, which descends from the mouth to the bottom of the jar. If the flame of the candle be only in part surrounded with the gas, this yellowish flame rises a few lines above the other.

(c) It is lighter than atmospheric air. Hence a jar filled with this gas, and placed with its mouth upwards, is soon

found to exchange its contents for common air, which, being heavier, descends, and displaces the ammoniacal gas. By the experiments of Messrs. Allen and Pepys,\* undertaken at the desire of Sir. H. Davy, 100 cubic inches of ammonia were found to weigh 18.18 grains, barometer 30, thermometer 60°. According to Gay Lussac, its specific gravity is to that of common air as 0.5967 to 10; and hence, (taking 100 cubic inches of air at 30.5 grains) 100 cubic inches of ammonia weigh 18.17 grains. Mr. Dalton assumes, that at a mean temperature and pressure, 100 cubic inches weigh 18.6 grains; and hence that its specific gravity is 6, air being 10. It does not appear that in any of these trials, the gas was artificially dried. To effect its desiccation, potash or quicklime are best adapted; for dry muriate or chloride of lime, as well as several other chlorides, absorb it rapidly.†

(d) Ammoniacal gas is not sufficiently inflammable to burn when in contact with common air. But, when expelled from the extremity of a pipe, having a small aperture surrounded by oxygen gas, I have found that it may be kindled, and it then burns with a pale yellow flame, the products of its combustion being water and nitrogen gas.

(e) Ammoniacal gas may be decomposed by transmitting it through a red-hot porcelain tube, which should be either well glazed internally, or covered externally with a lute. It has been ascertained by Thenard,‡ that when any of the five following metals are enclosed in the tube, they promote the decomposition of ammonia in the order set down, viz. iron, copper, silver, gold and platinum; iron being most effectual, and platinum least. Iron, after the process, is found to be rendered brittle, and copper still more so. The gas obtained always consists of 3 parts hydrogen by measure, and 1 nitrogen. None of the metals is either increased or diminished in weight; and they can only, therefore, act as conductors of heat. Yet it is singular that iron decomposes a much larger quantity than platinum, and at a lower temperature.

(f) It has been asserted by Guyton, that ammoniacal gas is reduced to a liquid state at 70° below 0 of Fahrenheit; but

\* Philosophical Transactions, 1808, page 39.

† Journal of Science, v. 74.

‡ 85 Ann. de Chim. 61.

it may be questioned whether the drops of liquid, which he observed, were any thing more than the watery vapour, which the gas always contains, condensed by the cold, and saturated with ammonia. (Ann. de Chim. xxix. 290.)

(g) Ammonia is rapidly absorbed by water. A drop or two of water being admitted to a jar of this gas, confined over mercury, the gas will be immediately absorbed, and the mercury will rise, so as to fill the whole of the jar, provided the gas be sufficiently pure. Ice produces the same effect, in a still more remarkable manner. From Sir H. Davy's early experiments, it appeared that 100 grains of water absorb 34 grains of ammoniacal gas, or 190 cubic inches. Therefore a cubic inch of water takes up 475 cubic inches of the gas. More recently he has stated that at 50° Fahrenheit, water absorbs 670 times its bulk, and acquires the specific gravity .875.\*

Alcohol, also, absorbs several times its bulk, and affords a solution of ammonia, which possesses the strong smell, and other properties, of the gas.

(h) Water, by saturation with this gas, acquires its peculiar smell; and constitutes what has been called liquid ammonia; or, more properly, solution of pure ammonia in water. The method of effecting this impregnation is as follows:

*Process for obtaining Solution of Ammonia in Water.*

The following process is given by Mr. R. Phillips, as preferable to that of the London Pharmacopœia.†

On 9 oz. of well-burnt lime, pour half a pint of water, and when it has remained in a well closed vessel for nearly an hour, add 12 ounces of muriate of ammonia, and about 3½ pints of boiling water. When the mixture has cooled, filter the solution; and, having put it into a retort, distil off 20 fluid ounces. The solution will have the specific gravity 0.954, which is quite as strong as it can be conveniently kept. If the solution be required to be more strongly impregnated, this will be best effected by passing ammoniacal gas through

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\* Elements of Chem. Phil. p. 263.

† Remarks on the London Pharm. p. 34.

it, from a mixture of equal parts of powdered lime and muriate of ammonia, by means of an apparatus similar to that described for the preparation of muriatic acid.

The strength of a solution of ammonia is influenced by two circumstances, the temperature of the liquid, and the pressure on its surface, for ammonia is not retained in water without external force. The intervals of temperature, required to double the force of ammoniacal vapour, were ascertained by Mr. Dalton to increase in ascending. When mixed with common air, its elasticity is not altered; thus when ammoniacal gas of 15 inches force is mixed with a given volume of dry air, the air it doubled in bulk.

Solutions of ammonia, when mixed with water, were found by Sir H. Davy, not to be sensibly condensed; and, therefore, if the quantity of ammonia in a solution of given specific gravity be determined, it is easy to calculate the quantity in solutions of other densities. The two following Tables, it may be observed, do not exactly agree in their results, the quantity of ammonia, in solutions of the same density, being from 15 to 20 per cent. less in Mr. Dalton's Table than in Sir H. Davy's. The numbers in the latter, marked with an asterisk, were found by experiment, and from these the others were deduced.

*Sir H. Davy's Table of the Quantities of Ammoniacal Gas in Solutions of different Densities (Temp. 50° Fahrenheit, Barometer, 29.8.)*

100 parts of Specific Gravity.		Of Ammonia.	100 parts of Specific Gravity.		Of Ammonia.
.8750*	contain	32.5	.9435	contain	14.53
.8875		29.25	.9476		13.46
.9000		26.	.9513		12.40
.9054*		25.37	.9545		11.56
.9166		22.07	.9573		10.82
.9255		19.54	.9597		10.17
.9326		17.52	.9619		9.60
.9385		15.88	.9692*		9.50

*Mr. Dalton's Table of the Quantities of Ammonia in Solutions of different Specific Gravities.*

Specific Gravity.	Grains of Ammonia in 100 water-grain measures of liquid.	Grains of Ammonia in 100 grains of liquid.	Boiling point of the liquid in degrees of Fahrenheit.	Volumes of gas condensed in a given volume of liquid.
850	30	35.3	26°	494
860	28	32.6	38°	456
870	26	29.9	50°	419
880	24	27.3	62°	382
890	22	24.7	74°	346
900	20	22.2	86°	311
910	18	19.8	98°	277
920	16	17.4	110°	244
930	14	15.1	122°	211
940	12	12.8	134°	180
950	10	10.5	146°	147
960	8	8.3	158°	116
970	6	6.2	173°	87
980	4	4.1	187°	57
990	2	2.	196°	28

ART. 2.—*Analysis of Ammonia.*

(1) Ammoniacal gas is decomposed by electricity; and its bulk, as Dr. Priestley first observed, is thus gradually enlarged. Into a glass tube, having a conductor sealed hermetically into one end (fig. 29), and standing inverted over mercury, pass about one tenth of a cubic inch of ammoniacal gas; and transmit through it a succession of electrical discharges from a Leyden jar. The arrangement of the apparatus, for this purpose is shown in fig. 84, pl. ix. When two or three hundred discharges have been passed, the gas will be found to have increased to almost twice its original bulk, and to have lost its property of being absorbed by water. Mix it with a quantity of oxygen gas, equal to between one third and one half of its bulk, and pass an electric spark through the mixture. An explosion will immediately happen; and the quantity of gas will be considerably diminished. Note the amount

of the diminution by firing; divide it by 3; and multiply the product by 2. The result shows the quantity of hydrogen gas in the mixed gases which have been generated by electricity; for two measures of hydrogen are saturated by one of oxygen gas.

Suppose, for example, that we expand 10 measures of ammonia to 18; and that, after adding 8 measures of oxygen gas, we find the whole (= 26 measures) reduced by firing to 6 measures; the diminution will be 20. Dividing 20 by 3 we have 6.66, which multiplied by 2 gives 13.32 measures of hydrogen gas from 10 of ammonia. Deducting 13.32 from 18, we have 4.68 for the nitrogen gas contained in the product of electrization. Therefore 10 measures of ammonia have been destroyed, and expanded into

13.32 measures of hydrogen gas,  
4.68 ————— nitrogen gas.

According to the above proportions, 100 cubic inches of ammonia, which weigh about 18 grains, if they could be decomposed by electricity, would give about 133 cubic inches of hydrogen weighing 3.5 grains, and 46 of nitrogen weighing 14.4 grains, in all 17.9 grains, or one tenth of a grain less than the ammonia decomposed. Mr. Dalton obtained 185 measures of gas by decomposing 100 measures of ammonia; and, by comparing the products with the original gas, he finds that the weight of the former rather exceeds that of the latter; thus,

	Grains
100 measures of ammonia × sp. gr.	.6 = 60
produce {	51.8 nitrogen, which × sp. gr. .967 = 50.09
	133.2 hydrogen, which × sp. gr. .08 = 10.65
	60.74

The excess of 3-4ths of a grain in 60 he considers as too small to affect the conclusion, and as arising from unavoidable inaccuracies in some of the data.

It is contended by Gay Lussac and Thenard, and the pro-

bable accuracy of their result is admitted by Sir. H. Davy\* and by Dr. Wollaston, that 200 measures of ammonia are resolvable, by complete decomposition, into 300 of hydrogen and 100 of nitrogen. This proportion is consistent with the theory of combination in definite volumes. There is, however, considerable difficulty in ascertaining the precise amount of the gases evolved from ammonia; for if either the gas itself, or the mercury which confines it, contain any moisture, the product of gas, resulting from its decomposition, will exceed what it ought to be. The problem is one of great importance to the atomic theory, because from the proportion of the elements of ammonia, is deduced the weight of the atom of nitrogen. This will differ considerably, according to the statement, which we may adopt, of the amount of gases obtained by decomposing ammonia; their proportion to each other; and the exact specific gravities of hydrogen and nitrogen gases. From the data supplied by Mr. Dalton, the weight of nitrogen in ammonia should be to that of hydrogen nearly as 5 to 1, and, if ammonia be a binary compound, the atom of nitrogen will, therefore, be represented by 5, and that of ammonia by  $5 + 1 = 6$ . On the scale of Dr. Wollaston, nitrogen is represented by 17.54; which, with 3 atoms or proportions of hydrogen ( $1.32 \times 3 = 3.96$ ), gives 21.5 for the equivalent of ammonia, oxygen being considered as 10. But if hydrogen be made the decimal unit, and it be admitted that the three volumes of hydrogen in ammonia represent 3 atoms, and the 1 vol. of nitrogen one atom, then the weights of the atoms of hydrogen and nitrogen will be as their specific gravities, viz. as .0694 to .970, or as 1 to 14. Ammonia, according to this view, will be constituted of three atoms of hydrogen =  $3 + 1$  atom of nitrogen = 14, and its representative number will be 17.

(2) In the Philosophical Transactions for 1809, I have described a property of ammonia, which forms the basis of a very easy and quick mode of analyzing that alkali. When mingled with oxygen gas it may be inflamed by the electric spark, precisely like a mixture of hydrogen and oxygen gases.

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\* Elements of Chem. Phil. p. 269.

To obtain accurate results, however, it is necessary to use less oxygen at first, than is sufficient to saturate the whole hydrogen of the alkali. This is easily calculated. If, for example, we take 10 measures of ammonia, we must use less oxygen than will saturate 13 or 14 measures of hydrogen gas, the quantity which exists in 10 of ammonia; and which require about 7 of oxygen gas. It will be advisable, therefore, not to add above 4 or 5 of oxygen. The whole (suppose 15) will probably, after firing, be reduced to about 9. To the remaining gas admit 4 or 5 measures more of oxygen; and on passing the electric spark again, a second explosion will happen, with a diminution of about 6 measures. But, in the first explosion, the whole of the oxygen disappears, and it must therefore have saturated a quantity of hydrogen equal to 10 measures; besides which, two thirds of the second diminution ( $6 \div 3 \times 2$ ) = 4 measures are owing to the condensation of hydrogen. Hence the whole hydrogen is  $10 + 4 = 14$ . The nitrogen, the whole of which exists in the product of the first detonation, is ascertained by deducting from it (viz. from 9 in the present instance) the second quantity of hydrogen (4) which gives 5 for the nitrogen. These numbers may not, perhaps, be exactly obtained by experiment; and they are given merely as a general illustration of the process.

By experiments of this kind I have determined that 100 measures of ammonia require, for saturating the hydrogen which they contain, between 67 and 68 of pure oxygen gas, and afford

Of hydrogen gas about 136 measures,	
nitrogen gas . . . . .	47 measures.
	<hr style="width: 10%; margin: 0 auto;"/>
	183

(3) *Chlorine and Ammonia*.—Scheele first observed that when liquid solutions of chlorine and ammonia are mixed, or when aëriiform chlorine is passed through liquid ammonia, nitrogen gas is disengaged, and muriatic acid formed. In this case the hydrogen of the ammonia unites with the chlorine, and the nitrogen is liberated. The latter process furnishes a good method of obtaining nitrogen gas.



If into a bottle containing two or three pints of chlorine gas, about a drachm of strong solution of ammonia be poured, the two gases, when diffused through each other, act with sufficient energy to cause a detonation. The impossibility of confining chlorine gas, either by water or mercury, renders its decomposing action on ammonia of little use as a means of analyzing that compound.

The results of the analysis of ammonia furnish a good example of the condensation of the elements of gases, which takes place on chemical union; and if we could, by any means, permanently condense a mixture of 136 measures of hydrogen with 47 of nitrogen into 100 measures, or three volumes of hydrogen and one of nitrogen into one volume, the new gas would constitute ammonia. Simple admixture of these gases, however, even in the same proportions which are obtained by analyzing ammonia, is not sufficient to generate this alkali. The caloric, with which the hydrogen and nitrogen are respectively combined, opposes, by its elasticity, an obstacle to their union, and places them beyond the sphere of their mutual attractions. If these elements are presented to each other when one or both are deprived of part of their caloric, combination then takes place; and the composition of the volatile alkali is proved synthetically, as in the following experiments.

1. When iron filings, moistened with water, are exposed to nitrogen gas confined over mercury, the gas, after some time has elapsed, acquires the smell of volatile alkali. In this case, the iron decomposes the water and seizes its oxygen; while the hydrogen, at the moment of its liberation, unites with nitrogen, and composes ammonia. This state of condensation, or absence of the quantity of caloric necessary to bring it into a gaseous form, has been called the nascent state of hydrogen gas; and the same term has been applied to the bases of other gases when in a similar state.

(2) Another fact, showing the mutual relation of ammonia and of the compounds of nitrogen, was discovered some years ago, by Mr. Higgins of Dublin.\* Moistened some powdered

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\* See his Comparative View of the Phlogistic and Antiphlogistic Theories, 2d edition, p. 300, note.

tin (which is sold under that name by the druggists) with strong nitric acid; and, when the red fumes have ceased to arise, add some quick-lime or solution of pure potash. A strong smell of ammonia will be immediately produced. In this experiment, the tin attracts, at the same instant, the oxygen both of the nitric acid and of the water. Hydrogen and nitrogen are consequently set at liberty; and, before they have assumed the gaseous state, these two bases combine, and constitute ammonia. The ammonia thus generated unites with a portion of undecomposed nitric acid; and is disengaged from this combination by potash or lime, which render it evident to the smell.

3. A similar production of ammonia has been shown by Mr. R. Phillips to take place, when nitric acid is acted upon by phosphorus, which, simultaneously decomposing both water and nitric acid, enables the hydrogen of the former, and the oxygen of the latter, to unite while in a nascent form.

#### ART. 2.—*Salts with base of Ammonia.*

*Chlorine and Ammonia.*—No compound of chlorine and ammonia can exist, for as soon as ammonia is brought into contact with chlorine, it is decomposed in the manner which has been already described.

*Chlorate of Ammonia* may be formed either by saturating carbonate of ammonia with chloric acid, or by precipitating the solution of any earthy chlorate by that carbonate. Chlorate of ammonia forms fine needle shaped crystals, which are extremely soluble in water and in alcohol. It is volatile, and, when thrown upon a red-hot coal, detonates with a red flame. The proportion of its components is not known. (See Vauquelin, Ann. de Chim. xcv. 97.)

*Iodine and Ammonia.*—Dry ammoniacal gas is absorbed by iodine without decomposition. The product is at first very viscid, and has a metallic aspect; but by an excess of ammonia it loses these properties, and becomes of a very deep brownish red. When iodine is added to liquid ammonia, one part of it unites with the hydrogen of the alkali, and forms hydriodic acid, while another portion of the iodine combines

with the azote, and falls down in the form of a black powder. This compound of iodine and azote detonates with a very gentle heat, and even with the slightest touch.

*Iodate of Ammonia.*—This salt is best formed by saturating iodic acid with ammonia. It is deposited in small crystalline grains of an indeterminate form. When these are thrown on a red-hot coal, they detonate with a feeble violet flame and an escape of iodine. When heated in close tubes, the tubes are frequently burst; but Gay Lussac succeeded in collecting the products, which were equal volumes of oxygen and azotic gases. He states its composition at 100 acid + 10.94 ammonia, or 2 vols. of gaseous ammonia, 1 volume of iodine in vapour, and  $2\frac{1}{2}$  volumes of oxygen.

*Hydriodate of Ammonia* is constituted of equal volumes of hydriodic acid gas and ammoniacal gas. It may be formed by mixing the watery solutions of the acid and base. It crystallizes in cubes which are more soluble than sal ammoniac, and nearly as volatile, subliming in close vessels without decomposition.

*Hydro-chlorate of Ammonia, Muriate of Ammonia,  
or Sal-ammoniac.*

Muriate of ammonia may be formed by mixing over mercury equal measures of ammoniacal gas and muriatic acid gas, which are entirely condensed into a white solid. For purposes of experiment, the common sal ammoniac of the shops is sufficient, which is prepared by a circuitous process from an impure carbonate of ammonia, obtained by the distillation of bones, and other animal matters. This carbonate of ammonia, by being kept in contact with sulphate of lime and water, is converted into sulphate of ammonia. This again is decomposed by muriate of soda, which affords muriate of ammonia and sulphate of soda. The latter salt is separated by priority of crystallization, and the muriate of ammonia is then purified by being once or twice sublimed.

It has lately been ascertained by Dr. Marcet, that muriate of ammonia exists in sea water, and may be separated by sublimation from the uncrystallizable part called *bittern*.\*

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\* Phil. Trans. 1822, p. 454.

It is easy to calculate the composition of this salt, for since 100 cubic inches of muriatic acid gas weigh 39 grains, and the same volume of ammonia weighs 18.18 grains, muriate of ammonia must consist of

		Atom.		
Muriatic acid . . . .	68.205	. . . . 1	. . . .	37
Ammonia . . . . .	31.745	. . . . 1	. . . .	17
	100.			54

But in its ordinary state, the salt contains water, the proportion of which, according to Berzelius, is as follows:

		Atom.		
Muriatic acid . . . .	49.55	. . . . 1	. . . .	37
Ammonia . . . . .	31.95	. . . . 1	. . . .	17
Water . . . . .	18.50	. . . . 1	. . . .	9
	100.			63

Muriate of ammonia exhibits the following properties:

(a) It is volatilized, without being liquefied or decomposed, or in other words may be *sublimed*. Sir H. Davy finds that it may even be passed, without alteration, through glass or porcelain tubes heated to redness. When, however, it is transmitted over ignited metals, it is decomposed into its gaseous elements.

(b) It is readily soluble in water, three parts and a half of which, at 60°, take up one of the salt. During its solution much caloric is absorbed. In boiling water, it is still more soluble; and the solution, on cooling, shoots into regular crystals.

(c) It slightly attracts moisture from the air.

(d) On the addition of a solution of pure potash, or pure soda, the alkali is disengaged, as is evinced by the pungent smell that arises on the mixture of these two bodies, though perfectly inodorous when separate.

(e) Though generally considered as a neutral salt, yet, if placed on litmus paper and moistened, Berzelius observes, that the paper is reddened after some moments, as it would be by an acid.

(f) It is decomposed by baryta, strontia, lime, and magnesia.

*Nitrate of Ammonia.*

The most simple mode of preparing this salt is by adding carbonate of ammonia to dilute nitric acid, till saturation has taken place. If the liquor be evaporated, by a heat between  $70^{\circ}$  and  $100^{\circ}$ , to a certain extent, it shoots, on cooling, into crystals, having the shape of six-sided prisms, terminated by long six-sided pyramids. Evaporated at the temperature of  $212^{\circ}$ , it yields, on cooling, thin fibrous crystals; and, when the evaporation is carried so far that the salt immediately concretes on a glass rod by cooling, it then forms a compact and shapeless mass.

The solubility of this salt varies, according to the temperature in which it has been formed. When in crystals, it requires twice its weight of water for solution, or half its weight of boiling water. It deliquesces, in all its forms, when exposed to the atmosphere.

The most important property of this salt is the one which has been already described, *viz.* of yielding, when decomposed by heat, the nitrous oxide. One pound of the compact kind gives, by careful decomposition, nearly five cubic feet of gas, or rather more than 34 doses; so that the expense, estimating the salt at 5s. 10d. the pound, is about 2d. for each dose.

In a temperature of  $600^{\circ}$  this salt explodes, and is entirely decomposed. Hence it was formerly called *nitrum flammans*.

Its composition varies according to the mode of its preparation, and is stated by Sir H. Davy as follows:

Prismatic.	Fibrous.	Compact.
69.5 .....	72.5 .....	74.5 acid
18.4 .....	19.3 .....	19.8 ammonia
12.1 .....	8.2 .....	5.7 water
<hr/>	<hr/>	<hr/>
100.	100.	100.

The prismatic variety is stated by Berzelius,\* who inves-

\* 80 Ann. de Chim. 182.

tigated very carefully the results of its decomposition, to consist of

		Atom.		
Acid . . . . .	67.625	. . . . . 1	. . . . .	54
Base . . . . .	21.143	. . . . . 1	. . . . .	17
Water . . . . .	11.232	. . . . . 1	. . . . .	9
	100.			80

The dry salt, therefore, is constituted of 1 atom of acid + 1 atom of base, and its equivalent is  $54 + 17 = 71$ .

#### *Carbonates of Ammonia.*

*Carbonate of ammonia* consists of one volume of carbonic acid and two volumes of ammonia, which, when mingled over mercury in that proportion, undergo complete condensation. As 100 cubic inches of carbonic acid weigh 46.56 grains, and 200 of ammonia 36.36 grains, in all 82.92 grains, carbonate of ammonia must consist of

		Atom.		
Carbonic acid . . . . .	56.20	. . . . . 1	. . . . .	22
Ammonia . . . . .	43.80	. . . . . 1	. . . . .	17
	100.			39

These proportions differ very little from the experimental results of Gay Lussac (56.02 acid + 43.98 base).

*Bi-carbonate of ammonia* was formed by Berthollet, by impregnating a solution of the common carbonate with carbonic acid gas. It crystallizes, when evaporated by a very gentle heat, in small six-sided prisms, has no smell, and but little taste. It consists, according to Berthollet, exclusive of water, of

		Atoms.		
Carbonic acid . . . . .	71.81	. . . . . 2	. . . . .	44
Ammonia . . . . .	28.19	. . . . . 1	. . . . .	17
	100.			61

*Sesqui-carbonate of Ammonia.*—Besides these two compounds of ammonia and carbonic acid, there is another which is generally met with in the shops under the name of *sub-carbonate of ammonia*. It is produced by exposing to heat, in a proper subliming apparatus, a mixture of muriate of ammonia and carbonate of lime, and if no loss occurred during the opera-

tion, it ought to consist of 1 atom of carbonic acid, 1 of ammonia, and 1 of water. But the heat, which is necessary to the decomposition, expels both ammonia and carbonic acid, and the resulting salt has the following proportions :

	Acid.	Base.	Water.
According to Dr. Ure * . . . . .	54.5	30.5	15.
Mr. Phillips † . . . . .	54.2	29.3	16.5
Mr. Dalton ‡ . . . . .	59.	24.5	16.5

The atomic constitution, nearest to the above proportions, and that which probably belongs to the salt in its perfect state, is as follows :

Acid . . . . .	55.72	3 atoms	66
Base . . . . .	29.	2 atoms	34
Water . . . . .	15.28	2 atoms	18
	100.		118

Viewing it as a compound of  $1\frac{1}{2}$  portions of carbonic acid, 1 ammonia, and 1 of water, it has been called by Mr. Phillips a *sesqui-carbonate*, and if this view be unconnected with the notion of its containing the fraction of an atom, there can be no objection to the name. It is preferable, indeed, to that of sub-carbonate, which should be reserved for the compound, hitherto unknown, of 1 atom of acid and 2 of base.

When the sesqui-carbonate is fresh prepared, it has a crystalline appearance and some transparency, and is hard and compact. It has a pungent smell, and a sharp penetrating taste, and affects vegetable blues as uncombined alkalis do. It dissolves in twice its weight of cold, or an equal weight of boiling water. When exposed to the atmosphere, it loses weight very fast, ceases to be transparent, loses its odour, and becomes brittle and easily reducible to powder. When its chemical composition is now examined, it is found to be identical with the bi-carbonate, or to consist of

Two atoms of acid . . . . .	44
One atom of base . . . . .	17
Two atoms of water . . . . .	18
	79

\* Ann. of Phil. x. 206.

† Quarterly Journ. vii. 294.

‡ Manch. Mem. iii. 32.

It has therefore lost, by exposure, 1 atom of acid and 1 atom of base.

By varying the proportions of the ingredients, and the regulation of the heat, it is possible to obtain a bi-carbonate at once by sublimation. (Annals of Philos. N. S. iii. 110.)

*Borate of Ammonia*, formed by saturating boracic acid with ammonia, crystallizes somewhat like borax. When heated, part of the base is expelled. It consists, according to Berzelius, of

Acid . . . . .	37.95	. . . . .	100.
Ammonia . . . . .	30.32	. . . . .	79.895
Water . . . . .	31.73		
	—————		
	100.		

*Phosphite of Ammonia* is a very soluble salt, and is with difficulty brought to crystallize.

*Hypophosphite of ammonia* is very soluble both in water and alcohol. Its composition has not been ascertained.

*Phosphate of ammonia* may be formed by saturating the superphosphate of lime, resulting from the action of sulphuric acid on bones, with carbonate of ammonia. The liquid, when evaporated spontaneously, crystallizes in low four-sided pyramids with square bases. It is soluble in twice its weight of water at 55° Fahr. When heated, it fuses, swells, and, if the heat be strongly urged, loses its alkaline base, the phosphoric acid being left in a glacial form.

*Sulphite of Ammonia* crystallizes in six-sided prisms terminated by six-sided pyramids. It is soluble in an equal weight of cold, or in less than an equal weight of boiling water. It attracts moisture from the air, and rapidly passes to the state of a sulphate. It is constituted of 100 acid + 53.2 base, or of an atom of each of its elements; and the crystals consist of two atoms of salt and one atom of water.

*Hyposulphite of ammonia*.—According to Mr. Herschell, this is strictly a bi-salt, consisting of 2 atoms of acid and 1 of base. It does not readily crystallize. Its taste is pungent and excessively bitter. When heated, it burns with a feeble flame, and evaporates.

*Sulphate of ammonia* may be formed by uniting 100 parts of



the compact sesqui-carbonate with 88 of sulphuric acid, previously diluted with water. The salt crystallizes in long flattened prisms with six sides, terminated by six-sided pyramids. These crystals have a cool, bitter taste; they slightly attract moisture from the air; are soluble in two parts of water at 60°, or in an equal weight of boiling water. During solution they produce cold. When heated, they sublime; but the constitution of the salt undergoes some change.

It is composed, according to Berzelius, of

Sulphuric acid . . . . .	53.1	. . . .	1 atom	. . . .	40
Ammonia . . . . .	22.6	. . . .	1 do.	. . . .	17
Water . . . . .	24.3	. . . .	2 do.	. . . .	18
	100.				75

When dried as much as possible without decomposing it, Dr. Ure found that it lost an atom of water, or that it consisted of 61 acid + 25.96 ammonia, + 13.04 water.

*Seleniates of ammonia.*—Selenic acid unites with ammonia in three different proportions, forming seleniate, biseleniate, and quadriseleniate. These salts, which are not important, are described by Berzelius. (Ann. de Chim. et Phys. ix. 260.)

## SECTION II.

### *Combinations of Hydrogen with Carbon.*

ONLY two distinct and well-characterized compounds of hydrogen and carbon are at present known; for though it has been contended, by some chemical writers, that these two elements are capable of uniting in almost all proportions, yet there seems no reason for believing that, in this instance, there is any departure from the general law, that bodies combine in proportions which are few in number, and which are either equal, or are simple multiples or divisors of each other.

The union of hydrogen with carbon cannot be effected by heating charcoal in hydrogen gas, for the cohesive attrac-

tion of the particles of charcoal prevents the combination. It may be effected, however, by exposing to a high temperature some of the solid and liquid compounds of hydrogen and charcoal, and it is produced also by several natural operations, especially by animal and vegetable putrefaction. The gas which has a minimum of carbon may be called, simply, carbureted hydrogen gas.

ART. 1.—*Carbureted Hydrogen Gas.*

It has been distinguished also by the name of *heavy inflammable air, gas of marshes, hydro-carburet, proto-carburet of hydrogen*, and has been termed by Dr. Thomson, *bi-hydroguret of carbon*.

This gas may be obtained, mixed, however, with about  $\frac{1}{30}$  of carbonic acid, and  $\frac{1}{15}$  or  $\frac{1}{20}$  of nitrogen gas, by stirring the bottom of almost any stagnant pool of water, especially if formed of clay. When this is done by an assistant, the gas is copiously disengaged in bubbles, which may be collected either in an inverted glass jar, or in an inverted bottle filled with water, into the mouth of which a funnel is fixed. It should be washed, when collected, with lime water or liquid potash.

It may, also, be procured by the purification of gas from coal, by means of chlorine and solution of potash, applied in succession, in a manner which will afterwards be described in speaking of coal gas.

Carbureted hydrogen, thus obtained, is permanent over water, which, after being well purged of air by boiling, is capable of taking up about  $\frac{1}{4}$ th of its bulk. It has very little odour, the strong and disagreeable smell of coal gas being dependent on foreign admixtures. Its specific gravity, from Dr. Thomson's experiments and my own, is 0.555; and hence 100 cubic inches, at a mean of the barometer and thermometer, weigh 16.95 grains.

When set on fire as it issues from a small orifice, it burns with a yellow flame, giving out vastly more light than hydrogen gas. When mixed with atmospheric air, it may be kindled by a lighted taper, and it explodes with violence, provided it forms not less than  $\frac{1}{2}$ th of the mixture, and does not

exceed  $\frac{1}{8}$ th. With oxygen gas, the detonation is louder and more violent; but it is necessary that the oxygen should rather exceed the inflammable gas in volume, and yet should not be more than  $2\frac{1}{4}$  times its bulk. Under a pressure diminished below one-fourth that of the atmosphere, the mixture ceases to be combustible; and its inflammability is also much lessened, by mingling it with carbonic acid and some other gases. To burn it completely, it is necessary to use more than twice its volume of oxygen gas, of which exactly two volumes are consumed, and carbonic acid is produced, equivalent in volume to the inflammable gas. Now we know that in carbonic acid gas there exists exactly its volume of oxygen; and hence one volume of the oxygen spent is found in that compound, and the other volume has formed water with the hydrogen, which last element must have existed in quantity equivalent to twice the bulk of the inflammable gas. The water produced may be collected by the slow combustion of the gas, but this is not necessary for calculating the proportion of its elements, which may be correctly estimated as follows. Since 100 cubic inches (= 16.95 grains) afford by combustion 100 cubic inches of carbonic acid, weighing 46.5 grains, and containing 12.69 grains of carbon, then  $16.95 - 12.69 = 4.26$  is the hydrogen in 100 cubic inches of carbureted hydrogen, which is, therefore, constituted of

	Grains.		Grains.		Grains.
Charcoal . . . .	12.69	. . . .	74.87	. . . .	100.
Hydrogen . . .	4.26	. . . .	25.13	. . . .	33.41
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	16.95		100.		133.41

Or carbureted hydrogen gas may be stated to be composed of 2 volumes of hydrogen and 1 volume of gaseous carbon condensed into 1 volume. But 2 volumes of hydrogen requiring 1 volume of oxygen to form the binary compound, water, which we have already considered to be constituted of an atom of each element, the atomic constitution of carbureted hydrogen will be 1 atom of charcoal (= 6) + 2 atoms of hydrogen (= 2) and the compound atom will weigh 8. From this view of its constitution, the name proposed by Dr. Thomson (bi-hydroguret of carbon) is certainly most appropriate,

and it is only to avoid the inconvenience of laying aside one which is sanctioned by long usage, that I employ that of carbureted hydrogen.

When carbureted hydrogen and chlorine gases are mixed together, no change happens either immediately or on standing, provided light be carefully excluded; but if exposed to the ordinary light of day, and still more rapidly in sunshine, a mutual action ensues. If 4 volumes of chlorine, and 1 of carbureted hydrogen, be thus kept, during a few hours, in a bottle filled entirely with the mixture, and furnished with a well-ground stopper, on removing this under water, a sudden absorption of muriatic acid gas takes place, and 1 volume of carbonic acid remains. Three volumes of chlorine and one of carbureted hydrogen afford a residue of carbonic oxide. In both cases, water is decomposed (for the gases do not act on each other if perfectly dry), the oxygen of the water uniting with the carbon, and its hydrogen with the chlorine. If the quantities be sufficiently large, and the sun's rays fall on the mixture, a detonation ensues, which may also be produced either by an electric spark, or by a lighted taper.

#### ART. 2.—*Bi-carbureted Hydrogen, or Olefiant Gas.*

This gas was discovered by the associated Dutch chemists, and was termed by them *olefiant gas*, from a property which will presently be described. It has since been called *bi-carbureted* or *per-carbureted hydrogen*, and by Dr. Thomson, *hydrouret of carbon*. It may readily be obtained by distilling, in a glass retort, with a gentle heat, three measures of concentrated sulphuric acid, and one measure of alcohol. The mixture soon assumes a black colour and thick consistence, and a gas is disengaged which may be collected over water, and freed from carbonic acid by washing it with liquid potash. If left to stand long over water, it sustains a diminution, that fluid being capable of taking up  $\frac{1}{3}$ th of its volume of the gas.

Bi-carbureted hydrogen, when pure, has very little odour, except when mingled with a little sulphuric ether, which is formed along with it. Its specific gravity is stated by the

Dutch chemists at .909; by my experiments, made several years ago, it is .967; by those of Saussure, jun. .9852; and by Dr. Thomson's latest trials 0.970. According to the last mentioned result, 100 cubic inches, at a mean of the barometer and thermometer, weigh 29.64 grains.

This gas, when set on fire as it issues from the orifice of a small pipe, burns with a remarkably dense and bright flame, very superior to that of simple carbureted hydrogen. When mingled with oxygen gas, it detonates very loudly and forcibly, and if fired by electricity in a Volta's eudiometer, is apt, unless very small quantities be employed, to burst the instrument. One volume requires for saturation three volumes of pure oxygen gas, and affords two volumes of carbonic acid gas. But in order to insure the perfect combustion of the inflammable gas, it should be mixed with 5 times its bulk of oxygen, of at least 90 per cent purity. If too little oxygen be used, charcoal is apt to be precipitated unburned; and the excess of oxygen does no harm, but remains in the mixture. When fired with less than its own bulk of oxygen, the separation of charcoal is very evident, and the bulk of the residue is greater than that of the original gases.

Calculating the constitution of this gas, from the oxygen spent in its combustion and the carbonic acid formed, precisely as was done with respect to carbureted hydrogen, we have the following results, the first column including the composition of 100 cubical inches.

	Grains.	Grains.	Grains.
Charcoal . . . .	25.38 . . . . .	85.63 . . . . .	100.
Hydrogen . . . .	4.26 . . . . .	14.37 . . . . .	16.71
	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
	29.64	100.	116.71

In this gas, therefore, 100 grains of charcoal are united with 16.71 hydrogen, and in the last with 33.41; or, as nearly as possible, olefiant gas contains only one half the hydrogen. Its constitution may hence be stated as follows:

	Vols. of Carb.	Vols. of Hydr.	At. of Carb.	At. of Hydr.
In each volume . . . .	2	+	2	=
	1	+	1	1

The compound atom, therefore, will weigh  $6 + 1 = 7$ . Its greater combustibility evidently depends on its containing, in a given volume, twice the quantity of carbonaceous matter that is present in simple carbureted hydrogen.

When olefiant and chlorine gases are mixed together in equal quantities, an immediate diminution ensues; and this effect takes place, even when the vessel is shaded from the light by an opaque cover. It is therefore wholly independent of the agency of light, and may be made the basis of a method of analyzing a mixture of olefiant and carbureted hydrogen gases. For of the diminution thus produced, one half is due to the olefiant, and one half to the chlorine gas, those gases having been ascertained to saturate each other in equal volumes. Into a graduated tube standing over water, admit 30 or 40 measures of chlorine gas, and note its bulk when actually in the tube, which must be shaded by an opaque cover. Then add a known quantity (suppose 50 measures) of the gas under examination; and, after ten minutes, cautiously lift the outer cover, till the surface of the water appears. If the volume of the two gases has suffered no diminution, we may infer the absence of olefiant gas; but if the united bulk of the two gases be less than the sum of their separate volumes, divide the diminution by 2, and the quotient will show how much olefiant gas has been condensed. In this way I have found that olefiant and carbureted hydrogen gases may be accurately separated from each other; but it is necessary to use a slight excess of chlorine, which may afterwards be removed by washing the residue with liquid potash, and the carbureted hydrogen will then be obtained pure.

By the action of chlorine gas on bi-carbureted hydrogen, a liquid substance is formed, in appearance very much resembling oil, and which, being at first mistaken for oil, occasioned this gas to be called *olefiant*. It possesses, however, very different properties from those of oil, and more nearly approaches in character to ether. It may be collected in quantity, by mixing large volumes of chlorine and bi-carbureted hydrogen, taking care to have an excess of the latter gas; and it may be purified by washing it with water, and then distilling it from dry chloride of calcium. It has an agreeable ethereal smell, and

a not unpleasant taste. Its specific gravity at 45° F. is 1.2201 ; it boils at 152° ; at 49° its vapour is capable of supporting a column of mercury 24.66 inches in length, and the specific gravity of its vapour is to that of air as 3.4434 to 1. It consists of 1 vol. of chlorine + 1 vol. of olefiant gas condensed into 1 vol. ; or by weight of

Chlorine .....	72.5	.....	100
Olefiant gas .....	27.5	.....	38.88
	100.		

Or it is constituted of two atoms of bi-carbureted hydrogen + 1 atom of chlorine gas. It has been called by Dr. Thomson, *chloric ether* ; but a more appropriate name would be *hydro-chloride of carbon*.

When olefiant gas is mixed with eight or nine times its bulk of chlorine, and exposed to the sun's rays, at first the fluid hydro-chloride of carbon is formed, and this, by continuing the exposure, is changed into the crystalline compound of carbon and chlorine, discovered by Mr. Faraday, and already described as the *perchloride of carbon*.

When iodine and olefiant gas are exposed in a similar manner to the sun's rays, the two substances unite, and form colourless crystals. When the redundant iodine has been washed away by liquid potash, and the residue collected and dried, it is a solid white crystalline body, heavier than sulphuric acid ; having a sweet taste and an aromatic smell ; friable, and a nonconductor of electricity ; fusible, and capable of being sublimed at a moderate heat without change ; but decomposed by a strong heat. It is not readily combustible, but, when held in the flame of a spirit lamp, burns, diminishing the flame, and giving off abundance of iodine and some fumes of hydriodic acid. It is insoluble in water, and in acid and alkaline solutions ; but dissolves in alcohol and in ether. It may be termed *hydriodide of carbon*, or *hydro-carburet of iodine*. (Faraday, Phil. Trans. 1821.) From a recent analysis by Mr. Faraday, it appears to consist of 1 atom of iodine + 2 atoms of olefiant gas. (Quarterly Journal, xiii. 429.)

**ART. 3.**—*On the Mixed Combustible Gases from Moist Charcoal, Alcohol, Ether, Coal, Oil, Tallow and Wax.*

The two gases, which have been just described under the names of carbureted and bi-carbureted hydrogen, appear to me to be the only compounds of those elements, that have as yet been proved to be distinct and well-characterized species; though it is extremely probable, as I have shown in the *Phil. Trans.* for 1820, that another gas exists, which was first observed by Mr. Dalton; is heavier and more combustible than olefiant gas; and contains a larger proportion of carbon. It is of mixtures of two or more of those three gases, with occasionally a proportion of carbonic oxide, that the almost infinite variety of aëriform products are constituted, which are obtainable by the exposure of moistened charcoal, of alcohol or ether, of oil, tallow, wax, or coal, to a heat a little above ignition. This view of the subject, at least, appears to me much more probable, than that they are so many distinct compounds of carbon and hydrogen, which, on this theory, would be capable of uniting in all possible proportions with each other.

Of these aëriform compounds, the gases from coal and from oil are of most importance, from their widely extended use in artificial illumination.

*Coal Gas.*—By submitting coal to distillation in an iron retort, besides a portion of tar and solution of carbonate of ammonia, which condense in a liquid form, a large quantity of permanent gas is evolved. This gas I have shown (*Phil. Trans.* 1808 and 1820) is extremely variable in composition and properties, not only when prepared from different coals, but from the same kind of coal under different circumstances. Within certain limits, the more quickly the heat is applied, the greater is the quantity, and the better the quality, of the gas obtained from coal; for too slow a heat expels the inflammable matter in the form of tar. The early products of gas are, also, the heaviest and most combustible, and there is a gradual decline in quality towards the close of the distillation, insomuch that the last products are inferior, by more than one half, to the first. The ge-



neral name of *coal gas* is, therefore, quite indefinite. It is, in fact, a mixture of the two varieties of carbureted hydrogen, with a third which remains to be more fully investigated, as well as with hydrogen gas, carbonic oxide, carbonic acid, nitrogen, and sulphureted hydrogen gases, in ever-varying proportions. To describe the methods of separating these gases from each other, would lead into minute details not suited to an elementary work, and I refer therefore to the papers which I have published in the *Phil. Trans.* for 1808 and 1820, and in the 3d. vol. 2d. Series, of the *Manchester Society's Memoirs, or Annals of Philosophy*, vol. xv.

Coal gas, as generally procured, has a very disagreeable odour, arising from sulphureted hydrogen, and, perhaps, a little sulphuret of carbon; but both these may be washed out of it by cream of lime, with (as I have shown) very little loss of illuminating power, and with an entire removal of all unpleasant smell either before or during burning. The best gas has the specific gravity .650 or upwards; and each volume consumes about  $2\frac{1}{4}$  volumes of oxygen and gives  $1\frac{1}{4}$  volume of carbonic acid; the last portions have a specific gravity as low as .340, and each volume consumes about 8-10ths of a volume of oxygen, and gives about 3-10ths of a volume of carbonic acid. In the best gas, chlorine, applied as directed page 416, detects from 13 to 20 per cent. of olefiant gas, and the remainder is almost pure carbureted hydrogen: but the last products contain little or no olefiant gas, much less carbureted hydrogen, and instead of these, a large proportion of hydrogen and carbonic oxide, both of which afford very little light by their combustion.

It is scarcely possible to assign the quantity of gas, which ought to be obtained from a given weight of coal, but it may be considered as an approach to a general average to state that 112lbs. of good coal are capable of giving from 450 to 500 cubic feet of gas of such quality, that half a cubic foot per hour is equivalent to a mould candle of six to the pound, burning during the same space of time.

*Oil Gas.*—In Nicholson's *Journal* for 1805, I have given an account of some experiments on the gas obtained by the destructive distillation of spermaceti oil, which showed that

of all the artificial gases, this, next to olefiant gas, consumes most oxygen, and is the best adapted to afford light. Since that time, an apparatus has been invented by Messrs. Taylor, of London, which has greatly facilitated the preparation of oil gas on a large scale, and this gas is now much used as a source of artificial light. The process consists in letting whale oil (the purity of which is not essential, since very inferior oil answers the purpose) fall by drops into an iron cylinder placed horizontally in a furnace, and ignited to a cherry redness. From each wine gallon of oil, about 100 cubic feet of gas may with care be obtained, of the specific gravity of more than .900, containing upwards of 40 per cent. of gas condensable by chlorine, and of which 100 volumes consume 260 volumes of oxygen, and yield 158 of carbonic acid. But of gas from Wigan cannel, when the whole product is mingled together, 100 measures do not saturate more than 155 of oxygen, and give 88 measures of carbonic acid. Oil gas, therefore, from this document, may be inferred to contain, in a given volume, twice the quantity of combustible matter that is present in the average of gas from cannel coal; and its illuminating power will be as 2 to 1. The experiments of Mr. Brande led him to conclude, that to produce the light of ten wax candles for one hour, there will be required

2600	cubical inches of olefiant gas
4875	..... oil gas.
13120	..... coal gas.

But it seems probable that the coal gas, employed in these experiments, was below the general standard, and that it is a fair average to consider 1 volume of oil gas as equivalent to 2 or at most 2½ volumes of gas from coal of good quality. This estimate agrees with the experience of the late Mr. Creighton, of Glasgow, author of the excellent article 'Gas Lights,' in the Supplement now publishing to the Encyclop. Britan. Oil gas he considers as superior, in an equal volume, to good average coal gas, in the proportion of only 2 to 1; and he has given the following Table of the comparative expence of lighting with these two gases, and with oil and tallow.

	<i>s.</i>	<i>d</i>
Valuing the quantity of light which 1 lb. of tallow gives in candles at .....	1	0
An equal quantity of light from sperm. oil consumed in an Argand's lamp, will cost .....	0	6½
Do. from whale oil gas .....	0	4½
Do. from coal gas .....	0	2¾

Twenty cubic feet of coal gas, or ten of oil gas, he considers as equivalent to a pound of tallow, and 5000 grains of good sperm. oil to 7000 of tallow, or 1lb. avoirdupois.

The advantages of oil gas over gas from coal are, that smaller distilling vessels are required; that gazometers and conduit pipes of half the capacity are sufficient; that no washing apparatus is necessary; that the trouble and expence of removing waste materials is avoided; and that the gas affords a much brighter light, and with a smaller production of heat, and also of water. When only a moderate quantity of light is required; when it is an object to save room or labour; and in countries where coal is dear, oil gas is entitled to a decided preference; but it cannot be brought into competition with coal gas, where coal is cheap, or where the establishments to be lighted are of very considerable magnitude, and of such a nature as to allow of their being freely ventilated.

Of the comparative value of different compounds of hydrogen and charcoal for the purpose of illumination, it still appears to me that the only accurate test is the one which I proposed in Nicholson's Journal for 1805, viz. the quantities of oxygen gas required to saturate equal volumes. If 100 measures, for instance, of one gas, require for perfect combustion 100 measures of oxygen, and 100 measures of another gas take 200 of oxygen, the value of the second will be double that of the first. Specific gravity, though a guide to a certain extent, is not a sufficient one, for the weight of a gas may be owing to a large proportion of carbonic oxide, which is capable of giving out only a very small quantity of light. Photometrical experiments, also, appear to me to require greater perfection in the instruments that have been invented for that purpose, before we can implicitly trust to results obtained by their means; but there can be no fallacy in the combustion of these gases by oxygen, if conducted with ordinary care,

and especially if, in each instance, an average be taken of two or three trials, which need not occupy more than a few minutes. Nor can it admit of a doubt that, other circumstances being equal, the brilliancy of light, evolved by the combustion of gases which are constituted of purely inflammable matter, will bear a proportion to their densities, perhaps even a greater proportion than one strictly arithmetical; because, while by the combustion of denser gases a higher temperature is produced, the cooling agencies remain the same. It is probable, therefore, that of two gases, composed of the same ingredients, that which has a double density will afford somewhat more than a double quantity of light.

ART. 4.—*On the Fire Damp of Coal Mines, and the Construction and Principle of the Safety-Lamp of Sir H. Davy.*

The fire-damp of coal mines, by an analysis of it which I published in 1806, was shown to be identical in composition with light carbureted hydrogen.\* This conclusion coincides with the subsequent results of Sir H. Davy, who has enlarged our knowledge of the chemical history of the fire-damp, by several important facts,† and has been led, by an ingenious and happy chain of reasoning, to a discovery most important to the interests of humanity. The most readily explosive mixture of fire-damp with common air he found to be one measure of the inflammable gas to seven or eight of air. The mixture was not capable of being set on fire by charcoal in a state of active combustion, nor by iron ignited to a red or even to a white heat, except when in a state of brilliant combustion; in which respects, the fire-damp differs from other combustibile gases.

It was in attempting to measure the expansion, occasioned by the combustion of a mixture of fire-damp and air, that Sir H. Davy discovered a fact, which afterwards led him to the most novel and important results. An explosive mixture could not, he ascertained, be kindled in a glass tube so narrow as  $\frac{1}{4}$  of an inch diameter; and when two separate reservoirs of an explosive mixture were connected by a metallic tube,  $\frac{1}{4}$  of an inch diameter and  $1\frac{1}{2}$  inch in length, and one of the

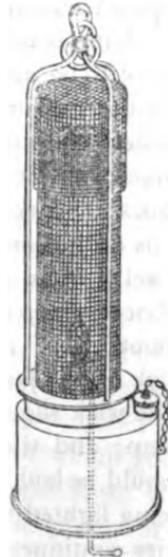
\* Nicholson's Journal, xix. 149.

† Phil. Trans. 1816.

portions of gas was set on fire, the explosion did not extend to the other. Fine wire sieves or wire gauze, interposed between two separate quantities of an explosive mixture, were also found to prevent the combustion of one portions from spreading to the other. A mixture of fire-damp and air, in explosive proportions, was deprived of its power of exploding, by the addition of about  $\frac{1}{4}$  its bulk of carbonic acid or nitrogen gas.

Reflection on these facts suggested to Sir H. Davy the possibility of constructing a lamp,\* in which the flame, by being supplied with only a limited quantity of air, might produce carbonic acid and nitrogen, in such proportion as to destroy the combustibility of explosive mixtures; and which might, also, by the nature of its apertures for giving admittance and exit to the air, be rendered incapable of spreading combustion to the surrounding atmosphere, supposing this to be an inflammable one.

This most desirable object was accomplished by the use of air-tight lanterns, supplied with air through tubes or canals of small diameter, or through apertures covered with wire gauze below the flame, and having a chimney at the upper part on a similar system, for carrying off the foul air. The apparatus was afterwards simplified by covering or surrounding the flame of a lamp or candle with a cylindrical wire sieve, having at least 625 apertures in a square inch. (See the sketch.) Within this cylinder, when the fire damp encompassing it is to the air as 1 to 12, the flame of the wick is seen surrounded by the feeble blue flame of the gas. When the proportion is as 1 to 5, 6, or 7, the cylinder is filled with the flame of the fire-damp; but though the wire gauze becomes red-hot, the exterior air, even when explosive, is not kindled. The lamp is therefore *safe* in the most dangerous atmospheres, and



\* A full history of the Safety Lamp, and of the chemical researches connected with it, has been published by Sir H. Davy, 8vo. printed for R. Hunter, 1818. In the Phil. Mag. l. 387, a document, also, may be found which fully establishes his claim to the priority of the invention.

has been used most extensively in the mines of Whitehaven, Newcastle, and other places, without the occurrence of a single failure or accident.

The effect of the safety-lamp depends on the cooling agency of the wire gauze, exerted on the portion of gas burning within the cylinder. Hence a lamp may be secure, where there is no current of an explosive mixture to occasion its being strongly heated; and yet not safe, when the current passes through it with great rapidity. But any atmosphere, however explosive, may be rendered harmless, by increasing the cooling surface; which may be done, either by diminishing the size of the apertures, or by increasing their depth, both of which are perfectly within the power of the manufacturer of the wire gauze.

When a small coil of platinum wire is hung above the wick of the lamp within the wire gauze cylinder, the metal continues to glow, long after the lamp is extinguished, and affords light enough to guide the miner in what would otherwise be impenetrable darkness. In this case, the combustion of the fire damp is continued so slowly, and at so low a temperature, as not to be adequate to that ignition of gaseous matter which constitutes flame, though it excites a temperature sufficient to render platinum wire luminous. A similar ignition of platinum wire, it has been found, may be supported for many hours, by surrounding the flame of a spirit lamp with small coils of that metal, not exceeding  $\frac{1}{100}$  of an inch in diameter. Twelve coils of this wire, twisted spirally round the tube of a tobacco-pipe, or round any thing that will render the coils about  $\frac{3}{8}$  of an inch in diameter, are to surround, six the wick of the lamp, and six to remain elevated above the wick. The wick should be small, and quite loose in the burner of the lamp; and the fibres of the cotton, surrounded by the coil, should be laid as straight as possible. When the lamp, after being lighted for a few moments, is blown out, the platinum wire continues to glow for several hours, as long as there is a supply of spirit of wine, and to give light enough to read by; and sometimes the heat produced is sufficient to re-kindle the lamp spontaneously.\*

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\* Thomson's Annals, vol. xi.

## SECTION III.

*Hydrogen with Phosphorus.—Phosphureted Hydrogen Gas.*

By heating solid phosphorous acid out of the contact of air, a large quantity of elastic fluid is generated, which may be collected by a proper apparatus, and has characteristic properties. According to Dr. Thomson, the same gas may also be formed by exposing bi-phosphureted hydrogen to the direct rays of the sun, which occasions the precipitation of part of the phosphorus.

It has a disagreeable smell, but is not so offensive as bi-phosphureted hydrogen. It does not burn spontaneously, when brought into contact with air, but detonates violently when heated with oxygen to about  $300^{\circ}$  Fahrenheit; or when a mixture of the two gases is rarefied by diminished pressure.\* It explodes in chlorine with a white flame. Water absorbs about  $\frac{1}{4}$  its volume. Its specific gravity was found by Sir H. Davy to be to that of hydrogen as 12 to 1, or to air as 0.87 to 1. He gave it the name of *hydro-phosphoric gas*, but he has since adopted that of phosphureted hydrogen. Dr. Thomson ascertained its specific gravity, air being 1, to be 0.9653, and he has proposed for it the name of *bi-hydroguret of phosphorus*. By a calculation founded on the proportion of its elements, its true specific gravity should be 0.9722.

Potassium doubles its volume, and the residue is pure hydrogen. Sulphur occasions the formation of sulphureted hydrogen, equal in volume to twice the original gas. Three parts of it in volume condense more than five of oxygen; or, according to Dr. Thomson, 1 volume requires 2 volumes of oxygen for complete combustion, one volume of which goes to the saturation of the hydrogen, and the remaining volume unites with the phosphorus. In this case phosphoric acid is formed. If only  $1\frac{1}{2}$  vol. of oxygen be used, phosphorous acid is produced. One in volume absorbs four of chlorine. It appears to be constituted of two atoms of hy-

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\* 6 Ann. de Chim. et Phys. 304.

drogen and one of phosphorus; and the hydrogen in it is condensed into half its bulk. In that case the weight of its atom will be  $2 + 12 = 14$ .

Its formation appears to be owing to the decomposition of water, the oxygen of which, with part of the phosphorous acid, forms phosphoric acid, while the hydrogen, dissolving the excess of phosphorus existing in another portion of phosphorous acid, composes the peculiar gas.

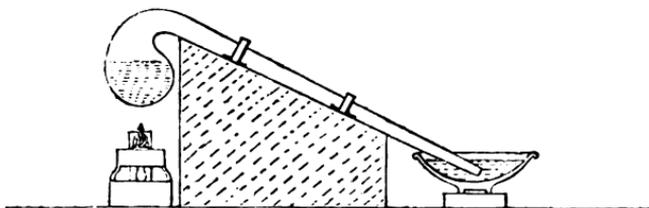
### *Bi-phosphureted Hydrogen Gas.*

I. This gas may be procured, by boiling, in a retort, a little phosphorus with a solution of pure potash, or by throwing into water, acidulated with muriatic acid, and contained in a retort or gas bottle, a few lumps of phosphuret of lime (see chap. ix. § 4); or, indeed, simply by the action of the latter compound upon water. The water is decomposed; its oxygen, uniting with the phosphorus, forms phosphoric acid, which combines with the alkali, while the hydrogen dissolves another portion of phosphorus, constituting bi-phosphureted hydrogen gas, or, as Dr. Thomson terms it, *hydroguret of phosphorus*. This gas may also be obtained, by putting into five parts of water half a part of phosphorus, cut into very small pieces, with one of finely granulated zinc, and adding three parts of strong sulphuric acid. This affords an amusing experiment. The gas is disengaged in small bubbles, which cover the whole surface of the fluid, and take fire on reaching the air; these are succeeded by others, and a well of fire is produced. (Davy.)

In preparing this gas from phosphorus and solution of potash, for exhibiting its spontaneous accension, both the body and neck of the retort should be entirely filled with the solution, which Dr. Coxe, of Philadelphia, recommends to be almost boiling hot. He employs a retort holding from half a pint to a pint; and after introducing both the phosphorus and the solution, fixes its neck on an inclined plane formed of a block of wood, the upper extremity of which is overhung by the body of the retort, while its mouth projects over the lower



end, and is dipped into a small bowl filled with a hot solution of potash, as represented in the figure. The gas, extricated



by the flame of a lamp, accumulates; and, forcing the alkaline solution down the neck, at length escapes, through the hot solution in the bowl, into the air, where it inflames. Should the heat slacken, and an absorption ensue, nothing passes into the retort but the hot solution of alkali from the bowl; and this, as the retort is secured from being displaced, does no harm. In this way, a torrent of gas may be kept up, as long as there remains sufficient of the solution in the retort; and all danger of breaking the retort is avoided.

II. The properties of this gas are the following:

(a) It takes fire immediately on coming into contact with the atmosphere. This may be shown by letting it escape into the air, as it issues from the retort, when a very beautiful appearance will ensue. A circular dense white smoke rises in the form of a horizontal ring, which enlarges its diameter as it ascends, and forms a kind of corona. The gas produces also a flash of light, when admitted into the best vacuum that can be made by an air pump.

(b) When mixed suddenly with oxygen gas, it detonates. One measure requires  $1\frac{1}{2}$  of oxygen for complete saturation; and the product is phosphoric acid. It may also be combined with an equal volume of oxygen, and the product is then phosphorous acid. This experiment should be made cautiously, and in small quantity. But in a tube only three-tenths of an inch in diameter, the mixture does not detonate.

(c) The same phenomenon ensues on mixing it with chlorine gas, or with nitrous oxide. Three volumes of chlorine are condensed by one of bi-phosphureted hydrogen; and the products are muriatic acid and per-chloride of phosphorus.

When 1 vol. of bi-phosphureted hydrogen is mixed with 3 of nitrous oxide, and an electric spark passed through the mixture, there remain after detonation 3 vols. of nitrogen. Hence the phosphureted hydrogen has in this case combined with  $1\frac{1}{2}$  volume of oxygen.

When fired with a similar proportion of nitrous gas, there remains only  $1\frac{1}{2}$  volume of nitrogen; and as nitrous gas contains half its bulk of oxygen, the bi-phosphureted hydrogen must have combined with  $1\frac{1}{2}$  volume of oxygen as before.

When mingled with any of these gases, it should be passed up by not more than a bubble or two at once.

(d) Sulphurous acid and bi-phosphureted hydrogen gases, when mingled together, mutually decompose each other.

(e) It deposits phosphorus, by standing, on the inner surface of the receiver, and loses its property of spontaneous accension, its volume remaining the same. It is, also, decomposed by electricity, without any change of volume.

(f) Its specific gravity is very variable. Sir H. Davy has obtained it, from phosphorus and alkaline lixivium, of all specific gravities from .400 to .700; Mr. Dalton states it at .850, air being 1.000, and Dr. Thomson at .902.2. The quantity absorbed by water is fixed by the former at  $\frac{1}{40}$  its bulk, and by the latter at  $\frac{1}{37}$ . Dr. Thomson makes it  $\frac{1}{30}$ .

(g) Two measures of the gas heated with potassium become three, and phosphuret of potassium is formed.

(h) When iodine is heated in bi-phosphureted hydrogen, iodide of phosphorus, and probably hydriodic acid, are formed.

From all that is known respecting this variety of phosphureted hydrogen, it may be inferred to consist of 1 atom of hydrogen + 1 atom of phosphorus; and the weight of its atom will be represented by 13.

We have, therefore, two compounds of phosphorus and hydrogen, viz.

Phosphureted hydr., or } = { 2 vols. of hydr. } condensed  
Bi-hydroguret of phosp. } = { 1 vol. of phosp. } into 1 vol.

Bi-phosphureted hydr., or } = { 1 vol. of hydr. } condensed  
Hydroguret of phosp. } = { 1 vol. of phosp. } into 1 vol.

And if the specific gravity of the vapour of phosphorus be

correctly assumed at 0.8328, and that of hydrogen at 0.0690, it is easy to estimate what should be the specific gravity of both those gases in a pure state. As the first gas consists of 1 atom of phosphorus + 2 of hydrogen; and the second of 1 of phosphorus + 1 of hydrogen, it must be admitted that the names bi-hydroguret, proposed by Dr. Thomson for the first, and hydroguret for the second, are more appropriate than those which have hitherto been in use.

The existence of different varieties of phosphureted hydrogen has, however, been denied by Mr. Dalton, whose experiments have led him to the conclusion, that the apparent diversities of composition are occasioned by the admixture of various proportions of free hydrogen and phosphureted hydrogen. These two gases admit, he finds, of separation by liquid chloride of lime, which absorbs the phosphureted hydrogen, and not simple hydrogen.

One volume of phosphureted hydrogen, in a pure state, requires, according to Dalton, two volumes of oxygen for saturation. When electrified *per se*, it is expanded one-third of its volume. It is absorbed by eight times its bulk of water. When two parts are mixed with five of nitrous gas, and an electric spark is passed through the mixture, a brilliant explosion takes place; and the results are phosphoric acid and water, and nitrogen gas, less in bulk by 2 or 3 per cent. than half the volume of the nitrous gas.\*



#### SECTION IV.

##### *Hydrogen with Sulphur.*

##### *Sulphureted Hydrogen Gas.*

SULPHURETED hydrogen gas, though known to Rouelle, was first investigated by Scheele in 1777; and afterwards by Bergman, Kirwan, Berthollet, Chaussier, Davy, and Gay Lussac and Thenard. It may be formed by repeatedly subliming sulphur in hydrogen gas; but this process is of little

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\* Thomson's Annals, xi. 7.

use, except to prove its nature by direct synthesis, for it is impossible thus to convert nearly the whole of any quantity of hydrogen into the compound gas. For the purposes of experiment, it may be procured by any one of the following methods; but the fifth is, perhaps, on the whole, the best.

1. By the action of diluted sulphuric acid on sulphuret of iron, prepared in the following manner. A bar of iron is to be heated to a white or welding heat in a smith's forge, and, in this state, is to be rubbed with a roll of sulphur. The metal and sulphur unite, and form a liquid compound, which falls down in drops. These soon congeal; and the compound must be preserved in a well-closed phial.

The sulphuret, prepared by melting iron filings with sulphur in a crucible, does not answer the purpose equally well, because the gas, which it affords, is mixed with a good deal of hydrogen gas.

2. Gay Lussac prepares sulphuret of iron, by introducing into a matrass two parts by weight of iron filings and one of flowers of sulphur. To these, water is added in sufficient quantity to give a thickish consistence; and the matrass is heated a little, to favour the combination, which is indicated by a copious disengagement of heat, and by the whole mass assuming a black colour. From this compound, sulphuric acid, diluted with four times its volume of water, separates sulphureted hydrogen in great abundance. It is better to prepare the compound when wanted, than to keep it ready made, because, unless very carefully preserved from contact with the air, it becomes less fit for the purpose of affording gas.\*

4. The sulphuret of potash, if prepared by boiling flowers of sulphur with liquid potash quite free from carbonic acid, gives pure sulphureted hydrogen, when acted upon by diluted sulphuric or muriatic acid.

5. To a mixture of powdered sulphuret of antimony (crude antimony of the shops) with 5 or 6 times its weight of muriatic acid (sp. gr. 1.160 or thereabouts) contained in a retort or gas bottle, apply the heat of a lamp. Sulphureted hydrogen will be disengaged in great abundance.

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\* Ann. de Chim. et Phys. vii. 314.

Whichever of these processes be followed, it is advisable, as the gas is absorbed quickly by standing over water, to receive it into bottles provided with glass stoppers, and after filling them entirely with the gas, to introduce the stopper.

II. Its properties are the following:

(a) Its smell is extremely offensive, resembling that of putrefying eggs, or of the washings of a gun barrel, to which indeed it imparts their offensive odour.

(b) It appears to be one of the most unrespirable of all the gases, for a small bird died immediately in air containing only  $\frac{1}{1300}$  of its volume of sulphureted hydrogen; a dog perished in air mingled with  $\frac{1}{800}$ ; and a horse in air containing  $\frac{1}{450}$ . (Thenard, i. 723.)

(c) It is inflammable, and burns either silently or with an explosion, according as it is previously mixed, or not, with oxygen gas or atmospheric air. During this combustion, water results from the union of the hydrogen with the oxygen, and sulphurous acid, with a little sulphuric acid, from that of the oxygen and sulphur. Two measures require three of oxygen gas, one measure of which saturates the hydrogen, and two the sulphur.

(d) It tarnishes silver, mercury, and other polished metals, and instantly blackens white paint and solution of acetate of lead. By direct experiments, I have found that one measure of this gas, mixed with 20,000 measures of hydrogen, or of carburated hydrogen, or common air, produces a sensible discoloration of white lead, or of oxide of bismuth, mixed with water and spread upon a piece of card. In this way we may ascertain the presence in coal gas of extremely small quantities of sulphureted hydrogen; and may even form a tolerable estimate of its proportion, when too minute to be otherwise measured, by comparing the shade of colour, with a series that has been prepared for the purpose, by exposing slips of card covered with white lead and water to mixtures of sulphureted hydrogen and common air in known proportions.

(e) Sulphureted hydrogen is absorbed by water, which takes up its own bulk, or according to Saussure twice and a half, or to Gay Lussac, three times, its bulk of the gas; but in order to obtain so considerable an absorption, the gas, submitted

to experiment, should be perfectly free from common hydrogen. Water thus saturated acquires the peculiar smell of the gas. It is this gas which gives to the Harrogate, and some other natural waters, their disagreeable odour. Liquid muriatic acid absorbs at least three times its volume of the gas; and sulphuric acid, diluted with an equal weight of water, once and a half its volume.

(f) Water, saturated with this gas, reddens the infusion of violets, in this respect producing the effect of an acid. From this and other properties, some of the German chemists have proposed for it the name of *hydrothionic acid*; and Gay Lussac has given it the very objectionable name of *hydro-sulphuric acid*, a term which would be much more properly applied to liquid sulphuric acid.

(g) Water impregnated with sulphureted hydrogen, when exposed to the atmosphere, becomes covered with a pellicle of sulphur. Sulphur is even deposited when the water is kept in well-closed bottles.

(h) On the addition of a few drops of nitric or nitrous acid to the watery solution, sulphur is instantly precipitated. In this case the oxygen of the acid combines with the hydrogen of the gas, and the sulphur is separated. The gas itself, also, is decomposed when transmitted through sulphuric, nitric, or arsenic acids.\*

(i) Sulphureted hydrogen is decomposed by mixture with chlorine, which seizes the hydrogen, and sulphur is precipitated. Vogel obtained, also, a liquid, analogous to the chloride of sulphur of Dr. Thomson. **Iodine** decomposes it, and hydriodic acid is formed.

(k) It is decomposed, also, when long kept in a state of mixture with atmospheric air, the oxygen of which combines with the hydrogen, and forms water, while the sulphur is precipitated.

(l) A succession of electric explosions throws down sulphur from it, and the volume of the gas remains unaltered. A similar effect is produced by passing it through an ignited porcelain tube, but it cannot in this way be entirely decomposed. Its

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\* Journ. of Science, &c. ii. 152.

elements are also disunited by exciting vivid ignition, by voltaic electricity, in platina wires surrounded by it; sulphur is deposited, and an equal volume of hydrogen remains.

(*m*) It is decomposed when passed over ignited charcoal, and is converted into carbureted hydrogen gas.

(*n*) Sulphureted hydrogen, both in the state of a gas and of watery impregnation, precipitates all metallic solutions, excepting those of iron, nickel, cobalt, manganese, titanium, and molybdenum.

(*o*) It is copiously absorbed by alkalies, and by all the earths, excepting alumina and zirconia. This property affords a ready method of ascertaining its purity, for if it be agitated with a solution of potash by means of the apparatus represented fig. 20 or 21, the unabsorbed residue will show the amount of the impurity, which is commonly hydrogen gas. Its alkaline and earthy combinations are termed hydro-sulphurets. It unites with an equal volume of ammoniacal gas, or, if transmitted through the watery solution of that gas, it is rapidly absorbed, and the compound, which is very useful as a chemical test, has a yellow colour and a strong smell of sulphureted hydrogen.

(*p*) When three volumes of sulphureted hydrogen gas, and two volumes of sulphurous acid gas, both dry, are mixed together over mercury, they are entirely condensed into a solid body, which adheres firmly to the inside of the vessel. This substance is of an orange yellow colour. Its taste is acid and hot, and it leaves a permanent impression on the mouth. When perfectly dry it does not change litmus paper; but reddens it immediately when moistened. Water, alcohol, nitric acid, and sulphuric acid, decompose it, and disengage sulphur. It does not precipitate the watery solution of barytes. It is decomposed at a moderate heat, and pure sulphur remains. Dr. Thomson, who discovered this compound, considers it as an acid, and terms it *hydro-sulphurous acid*. He states it to be constituted of 5 atoms of sulphur + 4 atoms of oxygen + 3 atoms of hydrogen. (Ann. of Phil. xii. 441.)

(*q*) When potassium or sodium is made to act on sulphureted hydrogen gas, a brilliant combustion takes place; a quantity of hydrogen gas is evolved, precisely equivalent to that which the same weight of metal would have separated

from water; the metal loses its lustre, and becomes greyish, or amber coloured, or reddish; and by the action of diluted muriatic acid, the whole of the sulphureted hydrogen is recovered. This experiment proves, that sulphureted hydrogen, and consequently sulphur, contain no oxygen; for, in that case, the potassium, having had its affinity for oxygen partly satisfied, would not, after being acted on by the gas, evolve the original quantity of sulphureted hydrogen from water. All that appears to take place, during the combustion, is the combination of the metal with sulphur, the liberation of hydrogen, and the formation of a sulphuret of potassium or sodium, which disengages from water exactly as much hydrogen, as would have been evolved by the metal in its separate state, and this hydrogen, while in a nascent state, re-dissolves the sulphur. The results of Sir H. Davy, which are somewhat different from these, are satisfactorily explained by Gay Lussac and Thenard.\*

(r) The specific gravity of sulphureted hydrogen gas has been variously stated. Mr. Kirwan found 100 cubic inches, at 60° Fahrenheit, and 30 inches barometer, to weigh 34.286 grains, which makes its specific gravity 1.124. Sir H. Davy states the weight of the same quantity at 36.5 grains, and its specific gravity, therefore, at 1.196. Gay Lussac and Thenard determined its specific gravity to be 1.1912 by experiment, or 1.1768 by calculation; and 100 cubic inches, according to the first of those two numbers, should weigh 36.33 grains.

The latest attempt to ascertain its specific gravity, is that of Dr. Thomson, the result of which was 1.1788, or, more correctly, he conceives, 1.180. Hence, 100 cubic inches (bar. 30, therm. 60°) would weigh 35.89 grains. To determine its composition, therefore, we have only to subtract the specific gravity of hydrogen from that of the compound gas, and the remainder will show the weight of the sulphur. Thus

Sp. grav. of sulphureted hydrogen gas.....	1.180
————— of hydrogen gas .....	0.069

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1.111

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\* Recherches, i. 202.

† 81 Ann. de Chim. 26.



It is constituted, therefore, of 1 volume of the vapour of sulphur = 1 atom (1.111) + 1 vol. of hydrogen gas = 1 atom (0.069.) But the numbers 0.069 and 1.111 are in the proportion very nearly of 1 to 16, which gives exactly the same relative weight for the ultimate particle of sulphur, as that deduced from the composition of sulphuric acid.

*Bi-sulphureted Hydrogen.*

This compound was discovered by Scheele, and afterwards examined by Berthollet (Ann. de Chim. tom. xxv.) It is obtained when hydro-sulphuret of potash (formed by boiling flowers of sulphur with liquid potash) is poured, by little and little, into muriatic acid. A very small portion only of gas escapes; and while the greater part of the sulphur separates, one portion of it combines with the sulphureted hydrogen; assumes the appearance of an oil; and is deposited at the bottom of the vessel. Or, dissolve sulphur in a boiling solution of pure potash; and into a phial, containing about  $\frac{1}{3}$  its capacity of muriatic acid, of the specific gravity 1.07, pour about an equal bulk of the liquid compound. Cork the phial, and shake it; the hydrogureted sulphur gradually settles to the bottom in the form of a brown, viscid, semifluid mass. Its properties are the following:

1. Its taste and smell resemble those of putrid eggs, but are less offensive. Its precise specific gravity is unknown, but it is heavier than water, and descends through it. It is inflammable, and burns in the air with a smell of sulphurous acid.

2. If gently heated, sulphureted hydrogen gas exhales from it; the bi-sulphuret loses its fluidity; and a residue is left, consisting merely of sulphur.

3. It combines with alkalies and earths; and forms with them a class of substances called hydrogureted sulphurets.

4. It is constituted, according to Mr. Dalton, of two atoms of sulphur = 32, with one atom of hydrogen, and is represented by the number 33. It consists per cent. of

Sulphur . . . . .	96.75
Hydrogen . . . . .	3.25

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100.

There are, therefore, three distinct combinations of sulphur and its compounds with alkalies and earths. The first consist, simply, of sulphur, united with an alkaline or earthy base, and are properly called *sulphurets*. The second are composed of sulphureted hydrogen, united with a base, and are called *hydro-sulphurets*. The third contain bi-sulphureted hydrogen, attached to a base, and constitute *hydrogureted sulphurets*.

The pure sulphurets can exist, as such, only in a dry state; for the moment they begin to dissolve in water, a decomposition of that fluid commences; sulphureted hydrogen is formed; and of this a part is disengaged, while another part, uniting with an additional proportion of sulphur, composes bi-sulphureted hydrogen. This last, uniting with the base, forms an hydrogureted sulphuret. At the same time, it has been stated by Berthollet,\* sulphuric acid is composed, by the action of the sulphur on the oxygen of the water. This, however, Gay Lussac has shown, takes place only when the sulphuret has been formed at an unnecessary degree of heat, and that when carefully prepared, at a heat below redness, the solution of an alkaline sulphuret in water contains sulphurous and hypo-sulphurous acids, but no sulphuric acid.† The sulphurets, also, being partly changed, by solution, into hydrogureted sulphurets, the affusion of an acid throws down a quantity of sulphur. A distinguishing character, also, of solutions of this kind, is, that sulphur is precipitated by passing through them sulphureted hydrogen gas.

According to Proust, if red oxide of mercury be added to solutions of the kind which have just been described, the sulphureted hydrogen is removed, and what remains is a pure liquid sulphuret, from which acids precipitate sulphur only, without any effervescence.

II. The hydrogureted sulphurets are also formed by boiling, along with a sufficient quantity of water, the alkaline, or earthy base, with flowers of sulphur. Thus a solution of pure potash, pure soda, or of baryta or strontia, may be

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\* Ann. de Chim. xxv. 239, 269.

† 6 Ann. de Chim. et Phys. 322.

changed into an hydrogureted sulphuret. To prepare the compound with base of lime, the powdered earth, mixed with sulphur, may be boiled with a proper quantity of water, and the solution filtered or cleared by subsidence. One hundred grains of lime, or 134 of hydrate, dissolve about 215 of sulphur, and afford a liquid of 1.146 specific gravity.

Another method of forming, by a very simple process, the hydrogureted sulphurets, consists in digesting, in a gentle heat, a hydro-sulphuret with powdered sulphur, an additional portion of which is thus dissolved, while part of the sulphureted hydrogen escapes.

Hydrogureted sulphurets have the following properties :

1. They have a deep greenish yellow colour ; an acrid and intensely bitter taste ; and an excessively offensive smell.

2. They deposit sulphur when kept in close vessels ; become much more transparent and lighter coloured ; and less offensive to the smell.

3. They rapidly absorb oxygen from the atmosphere, and from oxygen gas. Hence their employment in eudiometry.\*

4. On the addition of dilute sulphuric, or muriatic, or of certain other acids, they are decomposed. Sulphureted hydrogen gas is evolved, and sulphur is precipitated.

5. When boiled in contact with filings of silver or of copper, and of those metals only, Vauquelin found that they lose their excess of sulphur, and become simple hydro-sulphurets.



## SECTION V.

### *Hydrogen with Selenium.—Selenureted Hydrogen Gas.*

**BERZELIUS**, by fusing together potassium and selenium, and adding water to the fused mass, obtained a hydro-selenuret of potash of a deep ale colour. By pouring diluted muriatic

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\* See page 289.

acid on the concentrated solution of this compound, a gas is disengaged, which has the following properties.\*

It has a smell resembling that of sulphureted hydrogen. It is absorbed to a considerable amount by water, which acquires no colour, but after some minutes becomes slightly opalescent, and deposits a little selenium. The solution has an hepatic taste, reddens litmus paper, and gives a permanent brown stain to the skin. Exposed to the air, it is gradually but completely decomposed. It precipitates all metallic solutions when neutral, even those of zinc and iron, generally of a brown or black colour.

This gas produces violent effects on the organs of respiration, and a sharp and painful sensation in the nose, which is followed by the loss, for a time, of the sense of smelling. A small bubble not larger than a pea, when let up into the nostrils, beside the immediate effects which have been described, produced a mucous discharge which continued 15 days.

To determine its composition, it was transmitted through a solution of acetate of silver, when a selenuret of silver was formed, from the known composition of which Berzelius deduces the composition of this gas to be

Selenium.....	97.4	....	1 atom	....	41
Hydrogen .....	2.6	....	1 do.	....	1
					42
	100.				

This determination of the equivalent of selenium does not essentially differ from that deducible from the composition of selenic acid.

Selenium agrees then with sulphur and with tellurium, in affording a weak acid when united with hydrogen; an acid which, in all three cases, forms salts with those oxides only whose radicals have a stronger affinity for oxygen than hydrogen has; while it reduces all other oxides, and forms compounds of their respective metals with selenium.

† Ann. of Phil. xiv. 100.

## SECTION VI.

*Nitrogen with Carbon.*ART. 1.—*Carburet of Nitrogen, or Cyanogen.*

CYANOGEN was discovered by Gay Lussac in 1815, in the course of his researches into the properties of the compound, then called *prussiate of mercury*. Its properties have since also been investigated by Vauquelin.

To obtain cyanogen, it is necessary first to boil fine powdered red oxide of mercury with twice its weight of prussian blue and a sufficient quantity of water. The compound is perfectly neutral, and crystallizes in long four-sided prisms truncated obliquely. It still, however, contains a little iron, which may be separated by digesting the liquor, before evaporation, with a little more of the oxide of mercury, and saturating the excess of this oxide with a little prussic acid, or even with a little diluted muriatic acid. The prussiate of mercury, thus obtained neutral and crystallized, must be carefully and completely dried at a temperature below that of boiling water, and then exposed to heat in a small glass retort, or in a tube closed at one extremity. It first blackens, then liquefies, and the cyanogen comes over in the form of a gas, which may be collected over mercury. In the retort there remains a charry matter of the colour of soot, and as light as lamp black.\*

1. Cyanogen is a true gas, or permanently elastic fluid. Its smell is strong, penetrating, and disagreeable. It burns with a bluish flame mixed with purple. Its specific gravity is to that of common air as 1.8064 to 1. Hence 100 cubic inches at 60° Fahr. weigh 55 grains.

2. Water at the temperature of 60° Fahr. absorbs almost  $4\frac{1}{2}$  times its volume, and pure alcohol 23 times its volume. The watery solution reddens litmus; this, however, is scarcely to be considered as an effect of cyanogen, but of the products

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\* Gay Lussac, *Ann. de Chim.* vol. xcvi. ; or Thomson's *Annals*, viii. 37.

to which it gives rise by the decomposition of water. (Vanquelin in Ann. of Phil. xiii. 490.)

3. When 100 measures of cyanogen are detonated, in a Volta's eudiometer, with 250 measures of oxygen gas, 200 measures of carbonic acid result, and 100 measures of nitrogen. There remain, also, 50 measures of oxygen gas undensified. From these data, it is calculated by Gay Lussac, that cyanogen is composed of two volumes of the vapour of charcoal and one volume of nitrogen, condensed into a single volume. Its density ought, therefore, to be  $0.9722 + 0.832 = 1.8042$ , a number not very remote from that obtained by experiment.

4. Analysis by more complicated methods affords the same result, coinciding with that in which cyanogen yields, by a decomposition effected by means of oxygen, twice its volume of carbonic acid and an equal volume of nitrogen. No water whatsoever is formed during its combustion, if the gas be perfectly free from prussic acid vapour, a sufficient proof of the absence of hydrogen from the composition of cyanogen.

5. Phosphorus, sulphur, and iodine, may be sublimed in it without producing any change; but when heated in contact with cyanide of mercury, compounds of those bodies with cyanogen are formed. (Davy, Journ. of Science, vol. i.)

6. The solutions of pure alkalies and alkaline earths absorb cyanogen; and the liquid obtained, when poured into a solution of black oxide of iron, affords prussian blue, but not without the addition of an acid. At the same time, carbonic acid gas escapes, in volume equivalent to the cyanogen absorbed, and there is a perceptible smell of prussic acid. These changes will be more evident from the following recapitulation:

$$1 \text{ vol. of } \left\{ \begin{array}{l} = 2 \text{ vol. char-} \\ \text{cyanogen} \left\{ \begin{array}{l} \text{coal and 1 vol.} \\ \text{nitrogen.} \end{array} \right. \end{array} \right\} \text{ decomposes } \left\{ \begin{array}{l} = 1 \text{ vol. oxygen} \\ \text{and 2 vol. hy-} \\ \text{drogen.} \end{array} \right. \left. \begin{array}{l} 1 \text{ atom of} \\ \text{water.} \end{array} \right.$$

One volume of charcoal, uniting with one volume of oxygen, forms one volume of carbonic acid; the remaining volume of charcoal, uniting with half a volume of nitrogen and half a volume of hydrogen, composes prussic acid; and the residuary

half volume of nitrogen and  $1\frac{1}{4}$  volume of hydrogen compose together one volume of ammonia.

7. It will afterwards be shown, that when to two volumes of charcoal and one volume of nitrogen, together constituting cyanogen, one volume of hydrogen is joined, and the whole four volumes are condensed into two, we obtain *prussic* or *hydro-cyanic acid*. Cyanogen agrees then with chlorine and iodine, in being acidifiable by union with hydrogen. Hence its compounds with metallic bases have been called by Gay Lussac *cyanures*, as those of chlorine are called *chlorures*; but having elsewhere expressed a preference for the name of *chlorides*, I shall, from analogy, give to the compounds of cyanogen the name of *cyanides*.

ART. 2.—*Hydro-cyanic or Prussic Acid.*

From the *prussiate*, or more correctly *cyanide of mercury*, which has been already described, hydro-cyanic acid may be obtained by distillation with muriatic acid, taking care to employ a proportion of the latter which is not sufficient to saturate the metallic base of the salt. The neck of the retort must be prolonged, for about two feet, by a glass tube of at least half an inch bore placed horizontally, and containing in the  $\frac{1}{4}$ d next the retort, small pieces of white marble, in the other  $\frac{3}{4}$ ds fused chloride of calcium. To the end of this tube a small receiver must be luted, and be kept cool by a freezing mixture. Hydro-cyanic acid, along with muriatic acid and watery vapour, will be disengaged on gently heating the retort, the two last of which will be condensed by the materials in the tube, while the first, by successively heating the different parts of the tube, may be driven onwards to the receiver.

On repeating this process, Vauquelin found the product of hydro-cyanic acid so extremely small, that he was induced to seek for a better method of obtaining it. He succeeded by passing a current of sulphureted hydrogen gas, disengaged from sulphuret of iron and sulphuric acid, very slowly, through a glass tube slightly heated and filled with cyanide of mercury, its extremity ending in a receiver which was kept cool by a mixture of snow and salt. The process was

carried on till the smell of sulphureted hydrogen, which for a long time could not be perceived, was discovered in the receiver. The hydro-cyanic acid amounted in weight to  $\frac{1}{3}$ th the cyanide of mercury. To avoid any inconvenience from the process being carried too far, some carbonate of lead was placed at the end of the tube next the receiver, in order to absorb the sulphureted hydrogen that might pass undecomposed.

The hydro-cyanic acid is subject to spontaneous decomposition, and the more so the greater its state of concentration. For medical use, into which it has been of late years introduced, it may be obtained by dissolving 60 grains of cyanide of mercury in each ounce of water, and passing a current of sulphureted hydrogen gas through the solution, till the liquid contains a slight excess of it, which may be separated by a little carbonate of lead; after which the fluid may be filtered.

The process adopted at Apothecaries' Hall, London, is the following. One pound of cyanide of mercury is put into a tubulated retort with six pints of water and one pound of muriatic acid, sp. gr. 1.15; a capacious receiver is luted to the retort; and six pints are distilled over. The specific gravity of the product is 0.995; it must be preserved in bottles excluded from the light, and being subject to decomposition should not be long kept. (Brande's Manual, i. 140.) The specific gravity of the acid is considered by Dr. Ure as an inadequate test of its strength; and he recommends the following as a more simple method of analysis. "To 100 grains, or any other convenient quantity, of the acid, contained in a small vial, add, in succession, small quantities of the peroxide of mercury in fine powder, till it ceases to be dissolved on agitation. The weight of the oxide taken up, being divided by four, gives a quotient representing the quantity of real prussic acid present. By weighing out beforehand on a watch glass 40 or 50 grains of the peroxide, the residual weight of it shows at once the quantity expended." (Quarterly Journal, xiii. 312.)

Concentrated hydro-cyanic acid, prepared by the process of Gay Lussac or Vauquelin, is a limpid and colourless fluid.



It acts as a quick and virulent poison. It has a great tendency to decompose by keeping. Its taste is at first cool, but soon becomes hot and acrid. Though rectified from chalk, it still reddens litmus paper slightly. Its specific gravity at  $45^{\circ}$  Fahr. is .7058. It is highly volatile, and boils at  $79^{\circ}$  Fahr.; at  $68^{\circ}$  it supports a column of mercury of very nearly 15 inches; and it increases, five fold, the bulk of any gas with which it is mixed. It congeals at the temperature produced by snow and salt, and liquefies at  $5^{\circ}$  Fahr. A drop of it placed on paper becomes solid instantly, because the cold, produced by the evaporation of one portion, reduces the temperature of the remainder below its freezing point. Liquid hydro-cyanic acid forms prussian blue directly, both with iron and its oxide, and without the presence of either acid or alkali. The explanation of this fact will be given hereafter. It does not prove, as Vauquelin supposes, that prussian blue is a hydro-cyanate of iron.

Hydro-cyanic acid may also be collected in a gaseous form over mercury, by heating in a retort the crystallized ferrocyanate of potash with dilute sulphuric acid. This gas is absorbable by water and alcohol. It is speedily fatal when received into the lungs of small animals. At a temperature between  $86^{\circ}$  and  $95^{\circ}$  Fahr., the acid gas forms with oxygen gas a mixture which detonates on passing an electric spark. A quantity equal to 100 measures condense 125 measures of oxygen, and there result 100 measures of carbonic acid and 50 measures of nitrogen. But as the carbonic acid contains only its own volume of oxygen, there remain 25 measures of the latter gas which must have been converted into water by 50 measures of hydrogen existing in the prussic acid vapour. From these and other facts, Gay Lussac infers that it is composed of one volume of the vapour of charcoal, half a volume of hydrogen, and half a volume of nitrogen, condensed into one volume.

When potassium is heated in hydro-cyanic vapour, it evolves hydrogen gas equal to half the volume of the vapour. The other elements of the gas unite with the potassium. Thus the hydro-cyanic acid is resolved into hydrogen and cyanogen, which last, uniting with the potassium, forms a cyanide of that metal. As hydro-cyanic acid is constituted of equal volumes of those two gases, united without condensation, the

specific gravity of the acid gas ought to be the mean of those of its component, viz. 0.9560 very nearly. This differs very little from the result of experiments, viz. 0.9476. Its constituents, therefore, are by weight,

Cyanogen .....	100
Hydrogen .....	3.846

or two atoms of charcoal = 12, + 1 of nitrogen = 14, + 1 of hydrogen; and its equivalent number is 27.

The salts formed by the union of this acid with salifiable bases are called *hydro-cyanates*, but they are not permanent, and have no useful properties. They are decomposed by the weakest acids, such as the carbonic.

*Hydro-cyanate of ammonia* crystallizes in cubes or in very small prisms. Its volatility is such that at a temperature of 72° Fahr. its vapour supports a column of upwards of 15 inches of mercury; and at 97° Fahr. it is equal to the pressure of the atmosphere. Dr. Thomson finds that when prussian blue is exposed to a red heat in a copper tube, and the products received over mercury, the glass receiver is coated with transparent crystals of this salt. The solution of this salt precipitates several metallic solutions not affected by hydro-cyanic acid, which, according to Scheele, acts only on nitrates of silver and mercury, and on carbonate of iron. (Ann. of Phil. xv. 394.)

#### ART. 3.—*Chloro-cyanic Acid.*

Chloro-cyanic acid was discovered by Berthollet, who found that hydro-cyanic acid, by absorbing chlorine, acquires new properties, and no longer forms a blue precipitate with the solutions of iron. Supposing it to result from the union of oxygen with the prussic acid, he gave to the new compound the name of *oxy-prussic acid*. The nature of this combination has since been investigated by Gay Lussac. To prepare it, a current of chlorine gas may be passed through a solution of hydro-cyanic acid in water, till the liquid discolours the solution of indigo in sulphuric acid. By agitating this liquid with mercury, and by distilling at a gentle heat, an elastic fluid is formed. This, however, is not pure chloro-cyanic acid, for at temperatures from 60° to 70° Fahr., and

under common pressures, that acid can only exist as a liquid. It is a mixture of carbonic acid and chloro-cyanic acids, in proportions not yet determined.

The mixture of carbonic and chloro-cyanic acids is colourless; it has a very penetrating smell, and excites a flow of tears; its density, determined by calculation, is 2.123, air being 1. It reddens litmus, is not inflammable, and does not detonate by passing an electric spark through a mixture of the gas, with twice its volume of hydrogen or of oxygen; but with a mixture of the two, it burns vividly, with the production of a blueish white flame and of an extremely dense white vapour, which has the smell of nitrous gas and the taste of a mercurial salt.

When potassium is heated in the mixed gases, the chloro-cyanic acid is entirely decomposed; the chlorine and cyanogen are absorbed; and the carbonic acid mingled with it undergoes a decomposition more or less complete.

The watery solution of the mixed acids does not precipitate either barytic water or nitrate of silver; but from the latter it produces, after being mixed with potash and then with nitric acid, a precipitate of chloride of silver.

Alcaline solutions absorb it rapidly, but do not destroy its odour, except when they are in excess. These compounds, on the addition of acids, are decomposed; a brisk effervescence arises in consequence of the escape of carbonic acid, water and chloro-cyanic acids are reciprocally decomposed, and muriatic acid and ammonia are generated.

A characteristic property of this acid is, that with the intervention of potash, it forms green precipitates from solutions in which the iron is oxidized to a minimum. The experiment only succeeds when we first add the chloro-cyanic acid to the metallic solution, then a little alkali, and finally a small portion of acid.

According to the analysis of Gay Lussac, this acid is constituted of

1 vol. of gaseous carbon	}	condensed into 1 volumc.
$\frac{1}{2}$ a volume of nitrogen . .		
$\frac{1}{4}$ ————— chlorine . .		

In other words 1 vol. of chlorine and 1 vol. of cyanogen produce by combining 2 vols. of chloro-cyanic acid. Hence its density should be the mean of those of its components.

ART. 4.—*Of Sulpho-cyanic Acid.*

This acid was discovered by Mr. Porrett, to whom we are indebted for a number of curious and interesting experiments on all the acids having cyanogen for their base. He gave it the name of *sulphureted chyazic acid*, the term chyazic being compounded of the first letter of carbon, the first syllables of hydrogen and azote, with the usual termination signifying an acid. He considered it as a compound of sulphur with hydrocyanic acid, but since the researches of Gay Lussac, it may rather be regarded as a compound of sulphur with cyanogen.

The original process of Mr. Porrett is somewhat complicated and tedious. The following method was contrived by Grotthus, and improved by Vogel. Mix equal weights of pulverised ferro-cyanate (commonly called prussiate) of potash and flowers of sulphur, and expose the mixture in a flask to a heat sufficient to melt the sulphur, keeping it melted for several hours. When cold, reduce the mass to powder, and digest it in water enough to take up every thing soluble. Filter the liquor, and drop into it a sufficient quantity of potash to precipitate any iron that may be held in solution. The liquid, thus prepared, is a solution of sulpho-cyanate of potash in water, and the acid ingredient may be obtained, mixed with water, by distilling it with sulphuric acid.

Sulpho-cyanic acid, thus obtained, is a transparent liquid, colourless, or with a slight pinkish hue, with an odour as strong as, and somewhat resembling, that of acetic acid. The strongest obtained by Mr. Porrett had the specific gravity 1.022. It dissolves a little more sulphur at a boiling temperature; but most of this is separated again on cooling. In this state it throws down oxide of silver from the nitrate of a dark colour; but otherwise the precipitate is white.

Sulpho-cyanic acid boils at  $216\frac{1}{2}^{\circ}$ ; and at  $54\frac{1}{2}^{\circ}$  crystallizes in six-sided prisms. When thrown into a red hot platinum crucible, sulphur is disengaged, and a blue flame is produced.

It is partially decomposed by being transmitted through a red-hot porcelain tube; and if brought into contact with ignited iron turnings, sulphuret of iron is formed, and hydro-cyanic acid and sulphureted hydrogen disengaged.

By a sufficient quantity of chlorine, the whole of the sulphur is converted into sulphuric acid, and hydro-cyanic acid is disengaged. Iodine produces a similar effect.

With protoxide of copper, it affords a white insoluble sulpho-cyanate. From the analysis of this salt, Mr. Porrett drew his inference respecting the composition of the acid, which he conceived to consist of one third by weight of the elements of hydro-cyanic acid, and two thirds of sulphur. According to Dr. Thomson (System, 6th edit. ii. 306.) it is constituted of

2 atoms of sulphur .....	32
2 atoms of charcoal .....	12
1 atom of nitrogen .....	14
1 atom of hydrogen .....	1
	—

Hence its equivalent number is ..... 57

It is capable of uniting with salifiable bases, and composes a genus of salts called *sulpho-cyanates*. Many of these have been investigated by Mr. Porrett.

#### ART. 5. — *Ferro-cyanic Acid.*

The ferro-cyanic acid may be prepared by the following process: dissolve in cold water any quantity of the salt called triple prussiate (ferro-cyanate) of baryta, and for every ten grains so dissolved add a quantity of sulphuric acid equivalent to 2.53 grains of real acid; stir the mixture; and set it aside for some time. The baryta and sulphuric acid are precipitated in combination; and the ferro-cyanic acid may be decanted for use. Its characters are the following:

It has a pale lemon yellow colour; has no smell; and is not poisonous in small quantities. It is decomposed by a gentle heat, or by exposure to a strong light, in which case hydro-cyanic acid is formed, and also white triple prussiate of

and it is only to avoid the inconvenience of laying aside one which is sanctioned by long usage, that I employ that of carbureted hydrogen.

When carbureted hydrogen and chlorine gases are mixed together, no change happens either immediately or on standing, provided light be carefully excluded; but if exposed to the ordinary light of day, and still more rapidly in sunshine, a mutual action ensues. If 4 volumes of chlorine, and 1 of carbureted hydrogen, be thus kept, during a few hours, in a bottle filled entirely with the mixture, and furnished with a well-ground stopper, on removing this under water, a sudden absorption of muriatic acid gas takes place, and 1 volume of carbonic acid remains. Three volumes of chlorine and one of carbureted hydrogen afford a residue of carbonic oxide. In both cases, water is decomposed (for the gases do not act on each other if perfectly dry), the oxygen of the water uniting with the carbon, and its hydrogen with the chlorine. If the quantities be sufficiently large, and the sun's rays fall on the mixture, a detonation ensues, which may also be produced either by an electric spark, or by a lighted taper.

#### ART. 2.—*Bi-carbureted Hydrogen, or Olefiant Gas.*

This gas was discovered by the associated Dutch chemists, and was termed by them *olefiant gas*, from a property which will presently be described. It has since been called *bi-carbureted* or *per-carbureted hydrogen*, and by Dr. Thomson, *hydroguret of carbon*. It may readily be obtained by distilling, in a glass retort, with a gentle heat, three measures of concentrated sulphuric acid, and one measure of alcohol. The mixture soon assumes a black colour and thick consistence, and a gas is disengaged which may be collected over water, and freed from carbonic acid by washing it with liquid potash. If left to stand long over water, it sustains a diminution, that fluid being capable of taking up  $\frac{1}{3}$ th of its volume of the gas.

Bi-carbureted hydrogen, when pure, has very little odour, except when mingled with a little sulphuric ether, which is formed along with it. Its specific gravity is stated by the

Dutch chemists at .909; by my experiments, made several years ago, it is .967; by those of Saussure, jun. .9852; and by Dr. Thomson's latest trials 0.970. According to the last mentioned result, 100 cubic inches, at a mean of the barometer and thermometer, weigh 29.64 grains.

This gas, when set on fire as it issues from the orifice of a small pipe, burns with a remarkably dense and bright flame, very superior to that of simple carbureted hydrogen. When mingled with oxygen gas, it detonates very loudly and forcibly, and if fired by electricity in a Volta's eudiometer, is apt, unless very small quantities be employed, to burst the instrument. One volume requires for saturation three volumes of pure oxygen gas, and affords two volumes of carbonic acid gas. But in order to insure the perfect combustion of the inflammable gas, it should be mixed with 5 times its bulk of oxygen, of at least 90 per cent purity. If too little oxygen be used, charcoal is apt to be precipitated unburned; and the excess of oxygen does no harm, but remains in the mixture. When fired with less than its own bulk of oxygen, the separation of charcoal is very evident, and the bulk of the residue is greater than that of the original gases.

Calculating the constitution of this gas, from the oxygen spent in its combustion and the carbonic acid formed, precisely as was done with respect to carbureted hydrogen, we have the following results, the first column including the composition of 100 cubical inches.

	Grains.	Grains.	Grains.
Charcoal . . . .	25.38 . . . . .	85.63 . . . . .	100.
Hydrogen . . .	4.26 . . . . .	14.37 . . . . .	16.71
	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
	29.64	100.	116.71

In this gas, therefore, 100 grains of charcoal are united with 16.71 hydrogen, and in the last with 33.41; or, as nearly as possible, olefiant gas contains only one half the hydrogen. Its constitution may hence be stated as follows:

	Vols. of Carb.	Vols. of Hydr.	At. of Carb.	At. of Hydr.
In each volume . . . .	2	+	2	=
			1	+
				1

other examples of the same general principle will be given, in treating of metallic oxides. In all neutral compounds of sulphuric acid with alkaline, earthy or metallic bases, the acid contains a quantity of oxygen, which exceeds that in the base by the same multiple 3.

(i) Sulphuric acid is decomposed, at the temperature of the atmosphere, by inflammable substances, and acquires a dark colour. The addition of a little brown sugar, or a drop of olive oil, to a portion of the acid, imparts to it a brownish hue, which in time changes to black. Hence this acid should always be kept in bottles with glass stoppers; for a small bit of straw or cork, if dropped into a considerable quantity of sulphuric acid, changes it in the manner that has been pointed out.

(k) In high temperatures, sulphuric acid is still farther decomposed by combustible bodies.

1. Hydrogen gas, brought into contact with sulphuric acid, in a state approaching ignition, decomposes it, and water and sulphurous acid are formed. This, however, is a dangerous and difficult process, which it is not advisable to repeat.

2. According to Gay Lussac, sulphuric acid is decomposed by heat alone; and is resolved into two volumes of sulphurous acid gas, and one of oxygen gas. This experiment is best performed by passing the acid through a red-hot tube of glass or porcelain, which should not exceed two tenths of an inch in diameter. The acid is also decomposed by platina wires, communicating with the extremities of a galvanic pile. At the end of the negative wire, flocculi of sulphur appear, and at the positive end oxygen gas is evolved; and a brownish tint is produced by the formation, doubtless, of sulphate of platinum.

3. Sulphur, by being boiled in sulphuric acid, partly de-oxygenates it, and converts a portion of it into sulphurous acid, which comes over in a gaseous state.

4. Into a glass retort, put such a quantity of sulphuric acid as will fill about one fourth part of it, and add a small portion of powdered charcoal. On applying the heat of a lamp, gas will be produced very abundantly. Let this gas be conveyed



by a tube fixed to the mouth of a retort, and bent in the proper manner, into an inverted jar of water; or, if it can be had, into an inverted jar of quicksilver in a mercurial apparatus. During this operation, the carbon attracts part of the oxygen of the sulphuric acid, and forms carbonic acid gas. But the sulphur is not entirely disoxygenated; and a compound is therefore formed of sulphur and oxygen, containing less oxygen than the sulphuric acid. This compound exists in the state of a gas, and its properties may next be examined. To avoid, however, the complication which the admixture of carbonic acid with this new product introduces into the experiment, it may be proper to prepare it in a mode less objectionable, but the *rationale* of which cannot at present be explained. This consists in dissolving two parts, by weight, of quicksilver in one of sulphuric acid, and boiling the mass to dryness, in a glass capsule, or in the bottom of a broken Florence flask. The dried mass is next to be distilled in a strong sand-heat; a glass globe being interposed between the retort and the receiving mercurial trough, to condense any sulphuric acid that may escape decomposition. (See pl. iii. fig. 31.) The gas thus obtained is termed, conformably to the principles of the new nomenclature, *sulphurous acid*.

#### *Sulphurous Acid Gas.*

Sulphurous acid may be formed, 1st, by burning sulphur at a low temperature in common air, under a glass bell; and if slips of linen cloth, dipped in a solution of potash, be exposed to the vapour, the alkali forms a combination with the sulphurous acid, which may afterwards be washed off and evaporated. The dry salt, distilled with liquid tartaric acid, gives sulphurous acid gas.

2dly. It is formed, exclusively, when sulphur is burned in dry oxygen gas. The gas, when restored to its original temperature, is found to be contracted  $\frac{1}{3}$ th or  $\frac{1}{5}$ th of its bulk; but this is probably owing to the hydrogen contained in sulphur, for there is every reason to believe that oxygen gas, by becoming sulphurous acid, is not at all changed in volume.

3dly. By heating red oxide of mercury with one fourth of

which has been exposed to sulphureted hydrogen, separates exactly the same volume of hydrogen gas from water, as an equal weight of recent metal. Potassium, therefore, acquires no oxygen, from the sulphur which is contained in sulphureted hydrogen.

#### ART. 1.—*Sulphur with Oxygen.*

Sulphur is inflammable, and appears susceptible of two distinct combustions, which take place at different temperatures.\* At 140° or 150° Fahrenheit, it begins sensibly to attract oxygen; and if the temperature be raised to 180° or 190°, the combination becomes pretty rapid, accompanied by a faint blue light. But the heat evolved is scarcely sensible; at least it is so weak, that the sulphur may thus be burned out of gunpowder, and the powder be rendered useless without inflaming it. At a temperature of 300°, its combustion, though still feeble compared with that of some other bodies, is much more active, and accompanied with a redder light. When set on fire in oxygen gas, it burns with a very beautiful and brilliant light; but of a given quantity of oxygen gas, it is not possible to condense the whole by this combustion, for reasons which hereafter will be stated. The product of these combustions, when examined, will be found to be sulphurous and sulphuric acid, but chiefly the former, and if water be carefully excluded, sulphurous acid only is formed. It is necessary, therefore, in order to produce sulphuric acid, to make the experiment over water.

#### *Sulphuric Acid.*

Sulphuric acid has been known ever since the time of Basil Valentine, who appears to have discovered it about the close of the 15th century. It was first extracted from sulphate of iron by distillation, and afterwards formed by the combustion of a mixture of about 1 part of nitre, and 6 or 8 of sulphur in large glass vessels over water. For glass vessels, in process of time, large leaden chambers, having a stratum of water floating on the bottom, came to be substituted. The history of the

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\* For an account of the oxides of sulphur, see Dr. Thomson's paper in Nicholson's Journal, vi. 101.

successive improvements of its manufacture in this country has been given at length by Mr. Parkes, in the second volume of his *Chemical Essays*.

The properties of this acid may be exhibited by a portion of that usually found in the shops. They are as follows:

(a) Sulphuric acid has a thick and oily consistence; as may be seen by pouring it from one vessel into another.

(b) In a pure state, it is perfectly limpid and colourless.

(c) When mixed suddenly with water, considerable heat is produced. Four parts, by weight, of concentrated sulphuric acid, and one of water, when mixed together, each at the temperature of  $50^{\circ}$  Fahrenheit, have their temperature raised to  $300^{\circ}$ . When an ounce of water has been suddenly mixed with three of sulphuric acid, and the mixture been suffered to cool to the temperature of the atmosphere, an additional half oz. of water raises it to  $86^{\circ}$ , a second to  $96^{\circ}$ , and a third to  $104^{\circ}$ .\* The greatest elevation of temperature, Dr. Ure finds to be occasioned by the sudden mixture of 73 parts by weight of strong sulphuric acid with 27 of water. This rise of temperature takes place, because the affinity or capacity of the compound of sulphuric acid and water for caloric, is less than that of the acid and water separately. A diminution of bulk also ensues; that is, one measure of acid and one of water do not occupy the space of two measures, but about  $\frac{1}{3}$ th less; and the greatest condensation results, when those proportions are used, which give the greatest increase of temperature. Owing to the heat produced by its admixture with water, the dilution, for ordinary purposes, should be conducted very gradually; and the acid should be added to the water by small portions at once, agitating the mixture after each addition, and allowing each portion to cool before a fresh addition is made. On the principle of its attraction for water is to be explained, also, the rapid increase of weight which the sulphuric acid acquires when exposed to air. In one day, three parts of concentrated sulphuric acid, exposed to the atmosphere, are increased in weight one part; and one ounce, by twelve months' exposure, has been found to gain an addition of  $6\frac{1}{2}$ .

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\* Philips on the London Pharmac. p. 24.

(d) Perfectly pure sulphuric acid remains quite limpid during dilution. The sulphuric acid, however, commonly found in the shops, under the name of oil of vitriol, on admixture with water, deposits a white powder, in considerable quantity, consisting of various impurities, but chiefly of sulphate of lead. Berzelius has found, also, a minute quantity of titanium in sulphuric acid of English manufacture, and tellurium in acid prepared at Stockholm.\* By evaporating 100 parts of sulphuric acid of commerce in a platinum dish, Dr. Ure has obtained from one half to three quarters of a grain of solid matter, consisting of about two parts of sulphate of potash and one of sulphate of lead.†

(e) Sulphuric acid is nearly twice as heavy as water. The specific gravity of the strongest pure acid that can be obtained, is 1.850; but even this contains 19 (according to Dr. Wollaston, 18.44) per cent. of water, which appears essential to its constitution, and can only be separated by combining the acid with a base. Dr. Ure states that genuine commercial acid should not exceed 1.8485. When denser, its purity may be suspected. It has been ascertained, by Mr. Dalton, that acid, of nearly the maximum strength, has its specific gravity very little altered, by adding or subtracting small portions of water. Thus acids, containing 81 and 80 per cent. of acid, do not differ more than 1 in the third place of decimals; nor is the specific gravity proportionally changed by dilution till it falls as low as 1.78. The strength of the more concentrated acid may be better ascertained, by observing how much water is required, to bring it down to the specific gravity 1.78. The boiling point, also, Mr. Dalton has discovered, is a much better test of its strength; and he has constructed the following useful Table, in which account is taken of all these circumstances.

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\* Thomson's Annals, x. 464.

† Journ. of Science, iv. 115.

*Mr. Dalton's Table of the Quantity of real Acid in 100 Parts of Liquid Sulphuric Acid, at the Temperature 60° Fahrenheit.*

Atoms Acid Water.	Real Acid per cent. by Weight.	Real Acid per cent. by Measure.	Specific Gravity.	Boiling Point.
1 + 0	100	unknown.	unknown.	unknown.
1 + 0	81	150	1.850	620°
	80	148	1.849	605°
	79	146	1.848	590°
	78	144	1.847	575°
	77	142	1.845	560°
	76	140	1.842	545°
	75	138	1.838	530°
	74	135	1.833	515°
	73	133	1.827	501°
	72	131	1.819	487°
	71	129	1.810	473°
	70	126	1.801	460°
	69	124	1.791	447°
1 + 2	68	121	1.780	435°
	67	118	1.769	422°
	66	116	1.757	410°
	65	113	1.744	400°
	64	111	1.730	391°
	63	108	1.715	382°
	62	105	1.699	374°
	61	103	1.684	367°
	60	100	1.970	360°
1 + 3	58.6	97	1.650	350°
	50	76	1.520	290°
	40	56	1.408	260°
1 + 10	30	39	1.30 +	240°
1 + 17	20	24	1.200	224°
1 + 38	10	11	1.10—	218°

It has been ascertained by Dr. Ure that by adding about  $2\frac{1}{2}$  per cent. of its weight of sulphate of potash to concentrated oil of vitriol, its specific gravity may be increased to 1.860. The only mode, therefore, of ascertaining exactly the strength of oil of vitriol is by saturating a known quantity with an alkali; and it may be assumed as sufficiently correct, that

100 grains of dry sub-carbonate of soda neutralize 92 grains of pure liquid sulphuric acid; or that 100 grains of the acid require 108, or 108.5, of the sub-carbonate for saturation.

It is sometimes of importance to the chemical artist to know the proportion, not of *real acid*, but of *acid of commerce*, in diluted sulphuric acid of different specific gravities. An approximation to the true proportion may be obtained, by increasing the numbers, indicating the real acid, one fourth. For example, acid of the specific gravity 1.200, contains, according to the above table, 20 per cent. of real acid; which, increased one fourth, gives 25 per cent. of acid of sp. gr. 1.849. A very copious Table of the quantities of sulphuric acid of commerce in acid of different densities, constructed by Mr. Parkes from actual experiment, is given in the 40th volume of the Philosophical Magazine, and in vol. ii. of his Chemical Essays, p. 144. Its length only prevents me from inserting it here. The shorter Table of Vauquelin, in the 30th volume of Nicholson's Journal, is rendered less fit for the English chemist, because the acid, employed in the experiments on which it is founded, is inferior in density to the average acid sold in this country. In taking the specific gravity of sulphuric acid, it is of importance to attend to its temperature,\* which must be examined by a thermometer, having its bulb perfectly dry. According to Dr. Ure, 10° Fahrenheit make a difference in the density of oil of vitriol of 0.005. With due attention to this, and other necessary precautions, Dr. Ure has constructed a Table, which, as it is of moderate length, and exhibits at one view the proportion not only of real or dry acid, but of liquid acid, in sulphuric acid of different specific gravities, I shall insert in the Appendix. In the memoir of which the Table forms a part, Dr. Ure has endeavoured to establish some general formulæ for calculating the proportion of oil of vitriol in dilute acid of any specific gravity, and also for finding the specific gravity corresponding to a given proportion of acid.†

(f) Sulphuric acid, by a sufficient reduction of its temperature, may be frozen; and under favourable circumstances,

\* See Parkes's Essays, ii. 461.

† Journ. of Science, iv. 127.

it assumes a regular crystalline form, a considerable degree of solidity or hardness, and a density exceeding that which it possessed in a fluid state. From the experiments of Mr. Keir\* it follows that there is a certain point of specific gravity (*viz.* 1.780), at which the sulphuric acid most readily congeals; and when of this degree of strength it requires even a less degree of cold than is sufficient to freeze water, its congelation taking place at  $+45^{\circ}$  Fahrenheit. From the specific gravity of 1.786, on the one hand, to 1.775, on the other, it freezes at  $32^{\circ}$  Fahrenheit. It is singular that it remains congealed, at a temperature higher than that originally required for freezing it. Acid, for example, which did not become solid till its temperature was reduced to  $32^{\circ}$ , remained frozen at  $45^{\circ}$ . When of the specific gravity of 1.843, or as nearly as possible of that of commerce, it was found by Mr. Macnab † to freeze at  $-15^{\circ}$  Fahrenheit: but this acid, mixed with rather more than half its weight of water, required for congelation the temperature of  $-36^{\circ}$  Fahrenheit.

(g) To purify sulphuric acid, it must be distilled in a glass retort, placed in the sand-bed of a reverberatory furnace. This process requires considerable care. But to those who have sufficient experience in chemical operations, the following instructions may be useful; especially as it is indispensable, in all experiments of research, to employ an acid purified by distillation.

The furnace, in which this process is conducted, should have a contrivance for supporting a sand-bath within it at a proper height; and an opening in the side, for transmitting the neck of the retort. (Pl. vii. fig. 62, 63.) The retort must be coated with clay and sand over its whole body, and also over that part of the neck which is exposed to the fire. It is then to be placed, the coating being previously dry, in the sand-bath, about one half filled with sulphuric acid; and a receiver must be applied, but not luted on. The fire must now be lighted, and raised with extreme caution. The first portion that comes over, amounting to about one sixth, consists chiefly of water, and may be rejected. This is followed

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\* Philosophical Transactions, lxxvii. 267.

† Ibid. lxxvi. 241.

by the concentrated acid; and, at this period, there is great risk that the neck of the retort will be broken, by the contact of the condensed acid, which has a very high temperature, and which frequently cracks the glass, as effectually as the application of a red-hot iron. The fire must be regulated by the register door of the ash-pit, so that several seconds may elapse between the fall of the drops into the receiver. The process may be continued as long as any acid is condensed. The retorts, employed for this purpose, should be most attentively annealed.

The difficulty of rectifying sulphuric acid is much diminished, by using a retort of the capacity of from two to four quarts, when a pint of the acid is employed, and by connecting its neck with the receiver by means of an adopter three or four feet long. The retort may be set over a charcoal fire, and the flame made to play gently on its bottom. No luting is to be employed, and the receiver is to be surrounded with cold water. With this arrangement, and a cautious regulation of the heat, Dr. Ure finds that sulphuric acid may be distilled without much risk, in a continuous gentle stream\*. The sudden explosions, that occasionally happen during the process, may be prevented either by putting into the retort a few sharp pointed pieces of glass, or some slips of platinum as recommended by Mr. Brande.

Sulphuric acid may be less perfectly purified by diluting it with an equal weight of water, allowing the impurities to settle, decanting the clear liquor, and evaporating it to the proper degree in a glass retort.

(h) The proportion of the elements of sulphuric acid has been investigated by several chemists. Berthollet oxygenated 17.846 parts of sulphur by nitric acid, and obtained a quantity of sulphuric acid, which gave 127.515 parts of sulphate of barytes. Hence 100 parts of sulphur would have formed 230.79 parts of real sulphuric acid (= about 292 of density 1.85); but this product falls short of what ought to have resulted. Klaproth, Richter, and Bucholz, obtained results nearly agreeing with each other. Berzelius, to avoid all fal-

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\* Journal of Science, iv. 116.



lacy from the hydrogen contained in sulphur, combined it, in the first place, with lead, which, like other metals, always evolves much hydrogen, and then oxygenated the sulphuret. If two volumes of sulphurous acid gas, and one of oxygen, constitute sulphuric acid, it follows that the oxygen in the latter is a multiple of that in the former by  $1\frac{1}{2}$ ; and sulphurous acid being constituted of 100 sulphur + 99.44 oxygen, sulphuric acid will consist of 100 sulphur + 149.16 oxygen; or it will contain as nearly as possible 40 sulphur and 60 oxygen in 100 real acid. The following Table exhibits the proportions, deduced from different experiments, in 100 parts of real acid :

	Sulphur.	Oxygen.
From the experiments of Berthollet ..	43.28	.. 56.72
————— Klaproth ...	42.20	.. 57.80
————— Bucholz ...	42.50	.. 57.50
————— Berzelius ..	39.92	.. 60.08
Proportions admitted by Dr. Wollaston ..	40.0	.. 60.0

If the proportions be taken at 40 sulphur and 60 oxygen, and if the acid consists, as Mr. Dalton supposes, of 1 atom of sulphur and 3 atoms of oxygen, the atom of sulphur will weigh 16; for as  $(60 \div 3 = )$  20 is to 40 so is 8 to 16; the weight of an atom of real sulphuric acid will be 40; and the liquid acid, containing an atom of water, = 9, will be represented by the number 49. Mr. Dalton's numbers are 13 for the atom of sulphur, 34 for that of sulphuric acid, and 42 for the liquid acid, the difference being occasioned by his taking oxygen at 7, instead of 8.

A coincidence has been pointed out by Berzelius, which is very remarkable, and is deemed by him sufficiently general, to be admitted as a law; *viz.* that in any combination of two oxygenated bodies with each other, the oxygen of the one is either a multiple or divisor of that of the other, by some simple number. Sulphuric acid, of 1.850 density, affords an illustration of this principle; for it consists of 81 real acid and 19 water; and it will be found that the oxygen in the acid is, as nearly as possible, 48; and the oxygen in the water 16, so that in this case the multiple is 3, for  $16 \times 3 = 48$ . Various

other examples of the same general principle will be given, in treating of metallic oxides. In all neutral compounds of sulphuric acid with alkaline, earthy or metallic bases, the acid contains a quantity of oxygen, which exceeds that in the base by the same multiple 3.

(i) Sulphuric acid is decomposed, at the temperature of the atmosphere, by inflammable substances, and acquires a dark colour. The addition of a little brown sugar, or a drop of olive oil, to a portion of the acid, imparts to it a brownish hue, which in time changes to black. Hence this acid should always be kept in bottles with glass stoppers; for a small bit of straw or cork, if dropped into a considerable quantity of sulphuric acid, changes it in the manner that has been pointed out.

(k) In high temperatures, sulphuric acid is still farther decomposed by combustible bodies.

1. Hydrogen gas, brought into contact with sulphuric acid, in a state approaching ignition, decomposes it, and water and sulphurous acid are formed. This, however, is a dangerous and difficult process, which it is not advisable to repeat.

2. According to Gay Lussac, sulphuric acid is decomposed by heat alone; and is resolved into two volumes of sulphurous acid gas, and one of oxygen gas. This experiment is best performed by passing the acid through a red-hot tube of glass or porcelain, which should not exceed two tenths of an inch in diameter. The acid is also decomposed by platina wires, communicating with the extremities of a galvanic pile. At the end of the negative wire, flocculi of sulphur appear, and at the positive end oxygen gas is evolved; and a brownish tint is produced by the formation, doubtless, of sulphate of platinum.

3. Sulphur, by being boiled in sulphuric acid, partly deoxygenates it, and converts a portion of it into sulphurous acid, which comes over in a gaseous state.

4. Into a glass retort, put such a quantity of sulphuric acid as will fill about one fourth part of it, and add a small portion of powdered charcoal. On applying the heat of a lamp, gas will be produced very abundantly. Let this gas be conveyed

by a tube fixed to the mouth of a retort, and bent in the proper manner, into an inverted jar of water; or, if it can be had, into an inverted jar of quicksilver in a mercurial apparatus. During this operation, the carbon attracts part of the oxygen of the sulphuric acid, and forms carbonic acid gas. But the sulphur is not entirely disoxygenated; and a compound is therefore formed of sulphur and oxygen, containing less oxygen than the sulphuric acid. This compound exists in the state of a gas, and its properties may next be examined. To avoid, however, the complication which the admixture of carbonic acid with this new product introduces into the experiment, it may be proper to prepare it in a mode less objectionable, but the *rationale* of which cannot at present be explained. This consists in dissolving two parts, by weight, of quicksilver in one of sulphuric acid, and boiling the mass to dryness, in a glass capsule, or in the bottom of a broken Florence flask. The dried mass is next to be distilled in a strong sand-heat; a glass globe being interposed between the retort and the receiving mercurial trough, to condense any sulphuric acid that may escape decomposition. (See pl. iii. fig. 31.) The gas thus obtained is termed, conformably to the principles of the new nomenclature, *sulphurous acid*.

#### *Sulphurous Acid Gas.*

Sulphurous acid may be formed, 1st, by burning sulphur at a low temperature in common air, under a glass bell; and if slips of linen cloth, dipped in a solution of potash, be exposed to the vapour, the alkali forms a combination with the sulphurous acid, which may afterwards be washed off and evaporated. The dry salt, distilled with liquid tartaric acid, gives sulphurous acid gas.

2dly. It is formed, exclusively, when sulphur is burned in dry oxygen gas. The gas, when restored to its original temperature, is found to be contracted  $\frac{1}{3}$ th or  $\frac{1}{5}$ th of its bulk; but this is probably owing to the hydrogen contained in sulphur, for there is every reason to believe that oxygen gas, by becoming sulphurous acid, is not at all changed in volume.

3dly. By heating red oxide of mercury with one fourth of

its weight of sulphur, sulphurous acid is produced in the proportion of about a cubic inch for every five grains of the oxide.

4thly. By boiling 1 part by weight of mercury with six or seven of sulphuric acid to dryness in a glass retort, and then raising the heat, sulphurous acid gas is formed, and may be collected and preserved over quicksilver. Half an ounce of mercury is sufficient for the production of several pints of the gas.

Its properties are the following :

(a) It has a pungent and suffocating smell, exactly resembling that which arises from burning sulphur.

(b) It is more than twice as heavy as atmospherical air. One hundred cubic inches are stated by Mr. Kirwan to weigh 70.215 grains, which would make its specific gravity 2.265. By Sir H. Davy, the same volume is said to weigh 68 grains : this would give the specific gravity of 2.23, which agrees almost exactly with the statement of Thenard (i. 685.) According to a calculation of Gay Lussac, founded on the proportion of its elements, its specific gravity should be 2.30314. Berzelius finds it by experiment to be 2.247.\*

(c) Monge and Clouet assert, that if the gas be exposed, at the same time, to a temperature of 31° Fahrenheit, and to great pressure, it assumes a fluid state.

(d) It extinguishes burning bodies ; and kills animals, when respired.

(e) It has the property of whitening or bleaching silk, and of giving it lustre, and removes fruit stains from woollen cloth.

(f) Of sulphurous acid, water absorbs 33 times its bulk, or one eleventh of its weight, caloric is evolved, and the solution at 68° has the specific gravity 1.0513. Mr. Dalton states the quantity absorbed to be only 22 times the bulk of the water. From the solution, when recently prepared, the gas may be separated by heat, but not by congelation.

(g) The watery solution does not redden infusion of litmus, as acids in general do, but totally destroys its colour. Hence its use in bleaching several vegetable and animal products.

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\* Ann. de Chim. et Phys. v. 178.

It restores the colour of syrup of violets, which has been red-  
dened by other acids.\*

(h) Sulphuric acid, saturated with this gas, which may be effected by passing the gas through the acid, acquires a strong smell, a yellowish brown colour, smokes when exposed to the air, and has the property of assuming a solid form, by a moderate reduction of its temperature. When distilled, the first product, which is a compound of the two acids, assumes a solid form. It has been called *glacial sulphuric acid*. It has, however, been asserted by Vogel,† that the presence of sulphurous acid is not the cause of the glacial quality of oil of vitriol; and that, when converted to this state, by boiling in contact with sulphur, it contains no sulphurous acid. The nature of the change he has not yet fully explained.

(i) Sulphurous acid is absorbed by crystallized borax, and, by means of this property, Cluzel observes, may be separated from carbonic acid, and some other gases.‡

Sulphurous acid is again converted to the state of sulphuric by restoring oxygen to it.

1. A mixture of oxygen and sulphurous acid gases, both perfectly dry, and standing over mercury, is not diminished by remaining in contact with each other during some months; but if a small quantity of water be added, the mixture begins to diminish, and sulphuric acid is formed. Or if water impregnated with sulphurous acid be exposed to oxygen gas in a tube, the oxygen in 10 or 14 days is imbibed, and sulphuric acid formed. The same gases in a state of mixture, by the action of electricity, or by being driven through a red-hot porcelain tube, afford sulphuric acid. The proportions required for mutual saturation are two measures of sulphurous acid and one of oxygen gas.

2. To a portion of water saturated with sulphurous acid gas add a little oxide of manganese, a substance that contains much oxygen, loosely combined. The pungent smell of the water, and the other characteristics of sulphurous acid, will soon disappear.

3. Sulphurous acid gas is condensed into sulphuric acid by

\* Nicholson's Journal, xvii. 306.

† 84 Ann. de Chim. 283.

‡ 83 Ann. de Chim. 259.

admixture with chlorine gas; but not unless the gases are in contact with water. In the latter case, the hydrogen of the water unites with the chlorine, and the oxygen with the sulphurous acid.

Dry nitrous acid gas is also inefficient on dry sulphurous acid; but when placed in contact with a small quantity of water, all these bodies act mutually and rapidly on each other; the nitrous acid gas yields a portion of its oxygen to the sulphurous acid, from whence result nitrous gas and sulphuric acid, which, both combining with water, form white flakes upon the inside of the balloon. These flakes are made up of congeries of small crystalline needles. Water, brought into contact with these crystals, dissolves the sulphuric acid, and the nitrous gas is liberated with effervescence. By means therefore of a small quantity of nitrous gas, we may transform a large quantity of sulphurous acid into sulphuric acid, provided the acid gas be mingled with half its volume of oxygen, or with an equivalent quantity of atmospheric air. The phenomena are beautifully exhibited by admitting, into an exhausted and dry glass balloon, first 30 measures of sulphurous acid, next 15 of oxygen, and then 5 of nitrous gas. No perceptible change takes place, till a little water is introduced, sufficient to moisten the inside of the vessel, when the small quantity of red nitrous acid, formed on adding the nitrous gas, disappears, and composes the crystalline substance already described. When these crystals have been deposited on the inside of the balloon, and a small quantity more of water is admitted, there is an immediate effervescence from the escape of nitrous gas, which, meeting with oxygen gas, again becomes nitrous acid, and this, acting upon the sulphurous acid, the same combinations ensue as before, and may be repeated as long as sufficient sulphurous acid and oxygen remain.

It is by a series of operations of this kind, that the formation of sulphuric acid is effected in the ordinary process for preparing it. The nitric acid, present in the saltpetre, abandons part of its oxygen to one portion of the sulphur, which, becoming sulphuric acid, unites with the potash of the nitre. At the same moment nitrous gas is set at liberty, which, with

the oxygen present in the air of the chamber, composes nitrous acid gas. Another portion of sulphur is converted into sulphurous acid, which becomes sulphuric acid by depriving the nitrous acid of oxygen, the latter acid being brought back to the state of nitrous gas. This gas, absorbing the atmospheric oxygen, again becomes nitrous acid, which changes a fresh portion of sulphurous into sulphuric acid. This theory was first suggested by MM. Clément and Desormes. It has been since modified by Gay Lussac, who supposes that nitrous acid, and not nitrous gas, is disengaged from nitrate of potash. But even if this be admitted, the subsequent steps of the process are still explicable on the original theory, which satisfactorily explains why so small a proportion of nitre as one eighth is adequate to the conversion of sulphur into sulphuric acid, though capable of supplying only a very small share of the oxygen essential to this change.

(k) When the temperature of sulphurous acid gas is greatly reduced, by surrounding it with a mixture of snow and muriate of lime, it is changed into a liquid.

(l) If sulphurous acid gas and fresh muriate of tin are brought into contact over mercury, the volume of the gas is speedily diminished, sulphur is deposited, and the proto-muriate becomes a per-muriate of tin. (Accum.)

(m) It is decomposed, when submitted to the heat of ignition, in contact with certain combustible bodies. Thus, when a mixture of sulphurous acid and hydrogen gases are driven through a red-hot porcelain tube, the oxygen of the acid combines with the hydrogen, and forms water, and sulphur is obtained in a separate form. The sulphurous acid is decomposed, also, when transmitted over red-hot charcoal; and, as appears from Gay Lussac's experiment, by potassium.

From the testimony of the same chemist we learn that 100 parts of sulphur, to become sulphurous acid, unite with 95 oxygen. The following Table shows the numbers derived from different authorities. Sulphurous acid contains per cent.

	Sulphur.	Oxygen.
According to Gay Lussac . . . .	51.30 . . . . .	48.70
———— Berzelius . . . . .	50.03 . . . . .	49.97
———— Thomson . . . . .	53.0 . . . . .	47.0

The determination of Berzelius, of 100 sulphur to 99.44 oxygen, agrees best with the specific gravity of the gas; for if 100 cubic inches weigh 68, and 100 cubic inches of oxygen 34, the remaining 34 must consist of sulphur. Its atomic constitution, according to Mr. Dalton, is 1 atom of sulphur + 2 atoms of oxygen; and the weight of its atom will, therefore, be  $16 + 16 = 32$ .

The combinations of sulphurous acid with alkaline and earthy bases, called *sulphites*, will be described individually in their proper places.

#### *Of Hypo-sulphurous Acid.*

This acid, like the hypo-nitrous, exists only in combination with salifiable bases, forming compounds which were first examined in 1813 by Gay Lussac, and were called by him *sulphureted sulphites*. Beside other methods of preparing these salts, he found that they might be obtained by digesting the solution of a sulphite with sulphur, an additional quantity of which might thus be made to combine with the sulphurous acid. It had also been long ago observed by Mr. Higgins of Dublin, that liquid sulphurous acid dissolves iron without effervescence; and Berthollet afterwards showed that in this case the iron is oxidized at the expence of the sulphurous acid, and that sulphur is disengaged, which immediately unites with the sulphite of iron, forming a sulphureted sulphite. Dr. Thomson appears to have been the first\* who took a just view of these phenomena. The new compound he found to be a neutral salt, containing a peculiar acid of sulphur, to which he gave the name of *hypo-sulphurous acid*, and to its compounds that of *hypo-sulphites*. These compounds have been since examined with great ability by Mr. Herschell,† who has not, however, succeeded completely in his attempt to exhibit the acid in a separate state; nor indeed does it appear capable of existing permanently when uncombined with a base. From the experiments of Dr. Thomson and Mr. Herschell, it may be inferred to be a compound of 1

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\* System of Chemistry, 5th edition.

† Edinburgh Philosophical Journal, i. 8, and 36.



atom of sulphur + 1 atom of oxygen, and its representative number will be  $16 + 8, = 24$ . Its properties will again come under review in speaking of the several hypo-sulphites.

#### *Hypo-sulphuric Acid.*

This acid was discovered by Welter and Gay Lussac.\* Their process for forming it consists in passing a current of sulphurous acid through water, in which finely powdered peroxide of manganese is kept mechanically suspended. There is immediately produced a perfectly neutral solution, consisting of hypo-sulphate and common sulphate of manganese. When the solution is sufficiently concentrated, pure barytes is added to the previously heated liquor, and agitated along with it, taking care to employ an excess of the earth. All the oxide of manganese is thus separated; and, sulphate of barytes being insoluble, the filtered liquor contains only the hypo-sulphate of barytes, and also the redundant portion of that earth. The latter is to be separated by a stream of carbonic acid, and subsequent ebullition to expel any excess of carbonic acid. The hypo-sulphate is then to be crystallized, dissolved in water, and decomposed by just the quantity of sulphuric acid, which is required to precipitate the barytes. The filtered liquor is to be concentrated, by exposing it under the exhausted receiver of an air-pump, along with a vessel of sulphuric acid, till it has attained the density of 1.347. If continued to be exposed, it is resolved into sulphurous acid which exhales, and sulphuric acid which remains liquid.

Oxygen gas, atmospheric air, chlorine, concentrated nitric acid, and red sulphate of manganese, are all inert on it at common temperatures. Zinc is dissolved by it, and hydrogen gas is disengaged by the decomposition of water, and there remains in solution hypo-sulphuric acid combined with oxide of zinc. It completely saturates salifiable bases, and affords neutral and soluble compounds with barytes, strontites, lime, and protoxide of lead; whereas sulphuric acid yields insoluble compounds with all those bases. At common temperatures these salts are permanent, but, when heated, sulphurous acid

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\* Ann. de Chim. et de Phys. x. 312.

escapes, and they pass to the state of sulphates, which are still neutral.

Hypo-sulphuric acid has been inferred to be composed of 100 parts of sulphur + 125 oxygen, setting apart that which is in the water essential to its existence; or we may consider it as a compound of 100 parts of sulphurous acid + 125 of sulphuric. Hence we have the four following acids with base of sulphur :

	Sulphur.	Oxygen.	Sulphur.	Oxygen.
1. Hypo-sulphurous acid.	100	+ 50	or 1 atom	+ 1 atom.
2. Sulphurous acid . . . . .	100	+ 100	or 1 atom	+ 2 atoms.
3. Sulphuric acid. . . . .	100	+ 150	or 1 atom	+ 3 atoms.
4. Hypo-sulphuric. . . . .	100	+ 125	or 2 atoms	+ 5 atoms.

#### ART. 2.—*Sulphur with Chlorine.*

Sulphur, when heated in contact with chlorine gas, or even when exposed to it at common temperatures, absorbs it, and forms a singular compound first described by Dr. Thomson,\* and afterwards investigated by Berthollet, jun.† Ten grains absorb nearly 30 cubic inches of gas, which is nearly in the proportion of 16 (the weight of an atom of sulphur) to 36 (the weight of an atom of chlorine). It appears, indeed, to be a true chloride of sulphur.

This fluid is volatile below 200° Fahrenheit. Its colour is red by reflected light, but yellowish green by transmitted light. It emits fumes, which are peculiarly acrid, and which excite a copious flow of tears. Its specific gravity is 1.6. When agitated with about an equal volume of water, an active ebullition and great disengagement of heat take place; sulphur is deposited; and the residuary liquid contains muriatic and sulphurous, and a small quantity of sulphuric, acids. Hence the water is decomposed, and while its hydrogen unites with the chlorine, its oxygen combines with the greater part of the sulphur. Alcohol and ether are decomposed with appearances of still more intense action, and it disunites also the elements of ammonia.

\* Nicholson's Journal, 8vo. vol. vi.

† *Mem. d'Arcueil*, tom. i.

Mercury acts strongly upon this liquid; its surface is first tarnished, great heat is evolved, and a grey powder is formed, which is a mixture of sulphur and chloride of mercury.

It reddens vegetable blue colours; but not till, by its action on water or on hydrogen, muriatic acid has been produced. Some chemists have considered it as an acid, and have proposed to call it the *chloro-sulphuric acid*; but besides being deficient in the other qualities of acids, it does not, like them, unite with salifiable bases.

#### *Sulphur with Iodine.*

Sulphur and iodine unite at a gentle heat, and a black radiated compound is formed, resembling sulphuret of antimony. It is easily decomposed at a degree of heat a little above that at which it was produced, and iodine is detached from it in vapour. Its precise composition is unknown.



### SECTION VII.

#### *Of Selenium.*

IN the chambers for manufacturing sulphuric acid, from the sulphur which is procured at Fahlun in Sweden, a reddish mass is deposited, which is principally sulphur. This substance, in burning, gave out an odour, which induced Berzelius to suspect that it contained tellurium, but on a minute examination he discovered, instead of that metal, a body with entirely new properties, to which he has given the name of *selenium*. The process, by which it was extracted, is described in the 13th vol. of *Annals of Philosophy*, p. 403; but as the source of it is extremely rare, it will be sufficient to refer to Berzelius's description. For the same reason, I shall give only a short account of this substance, confining myself to such of its properties, as are important from their influence on the general doctrines of chemistry.

The colour of selenium varies a good deal. When rapidly

cooled, its surface has a dark brown hue, and its fracture the colour of lead. Its powder has a deep red colour, but it sticks together when pounded, and then assumes a grey colour and a smooth surface. It softens at  $212^{\circ}$  Fahr., and completely fuses at a few degrees higher. While cooling, it has a considerable degree of ductility, and may be kneaded between the fingers, and drawn out into fine threads, which have a strong metallic lustre, an imperfect degree of transparency; and are red by transmitted, but grey by reflected light. When slowly cooled, it assumes a granulated fracture, and is extremely like a piece of cobalt. At a temperature nearly equal to that of boiling mercury, selenium enters into ebullition; and condenses, either into opaque metallic drops, or, when a retort with a large neck is used, into flowers of a fine cinnabar colour. Its vapour has a deep yellow colour, more intense than that of chlorine, but not so deep as that of sulphur.

When heated before the blow-pipe, it tinges the flame of a fine azure blue, and exhales so strong a smell of horse-radish, that a fragment, not exceeding  $\frac{1}{50}$  of a grain, is sufficient to fill the air of a large apartment.

*Selenium and Oxygen.*—Oxide of selenium is formed by heating selenium in a close phial with common air, which acquires a very strong smell of horse-radish. Water agitated with this air imbibes the odour of the gas, and reddens litmus feebly, but this appears to be owing to the production of a small quantity of selenic acid. Selenic oxide gas is very sparingly soluble in water, and does not impart any taste to it. It does not combine with liquid alkalis. Its precise composition is unknown; but it appears to belong to the same class of oxides as carbonic oxide.

*Selenic Acid.*—Selenium dissolves in nitric and nitro-muriatic acids, and when the solution is evaporated in a retort, so as to expel the excess of those acids, there remains a white saline mass, which sublimes on raising the temperature, and forms a vapour, the colour of which closely resembles that of chlorine. In the cold part of the apparatus, selenic acid condenses in very long four-sided needles. These crystals, when first taken out of the retort, have a dry aspect and a

peculiar lustre. Exposed to the air, they adhere to each other, and the lustre becomes dull, but they do not liquefy.

Selenic acid has a sour taste, and leaves a slightly burning sensation on the tongue. It is very soluble in cold water, and dissolves in almost every proportion in boiling water. A saturated solution crystallizes, when rapidly cooled, in small grains, and when slowly cooled in striated prisms. The crystals dissolve in great abundance in alcohol, and the solution, when distilled, yields a fluid having an ethereal smell.

Selenic acid unites with different bases, and forms a class of salts called *Selenates* or *Seleniates*, which will be described with their respective bases.

Selenic acid is easily reduced both in the moist and the dry way. When a plate of zinc or polished iron is introduced into a solution of selenic acid mixed with muriatic acid, selenium is precipitated in the form of red, or brown, or blackish flakes. It is revived, also, by sulphureted hydrogen and sulphurous acid gases.

From his investigation of selenic acid, Berzelius has inferred it to consist of

Selenium . . . . .	71.261	. . . . .	100.00
Oxygen . . . . .	28.739	. . . . .	40.93
	—————		
	100.		

On the supposition that it is constituted of an atom of base + 2 atoms of oxygen, the equivalent number for selenium will be 41, and for selenic acid 57.

*Selenium and Chlorine.*—Selenium absorbs chlorine gas, and becomes hot and forms a brown liquid, which, by an additional quantity of chlorine, is converted into a white solid mass. This is stated by Berzelius to be a compound of muriatic and selenic acids, but it is probably composed of chloride of selenium and the latter acid. It has not yet been accurately separated into its component parts, for when heat is applied, both substances are sublimed.

The remaining compounds of selenium will be described hereafter in their proper places. At present, it is only necessary to observe farther, that while this body possesses some

of the characters of metals, (the metallic lustre for example,) it is destitute of others that are essential to its arrangement in that class. It has more transparency than any metal, and is distinguished, also, from the metals, by the want of power to conduct electricity or heat. In some respects it resembles tellurium; but, on the whole, its properties are most analogous to those of sulphur; and it may be regarded as forming the connecting link between metals and non-metallic combustibles.

## CHAPTER VIII.

OF THE COMBINATION OF SIMPLE ACIDIFIABLE BODIES,  
(NOT METALLIC), WITH EACH OTHER.

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### SECTION I.

*Hydrogen with Nitrogen.—Ammonia.*

ART. 1.—*Preparation and Qualities of Ammonia.*

I. AMMONIA, in a liquid form, had been long known to chemists, both Basil Valentine, and Raymond Lully having described the methods of procuring it; but Dr. Black was the first who distinguished between its pure or caustic, and its mild or carbonated state, and Dr. Priestley first exhibited it in a gaseous form, to which he gave the name of *alkaline air*. To procure it in this state, one of the following processes may be employed.

(a) Mix together equal parts of muriate of ammonia and dry quicklime, each separately powdered; and introduce them into a small gas bottle or retort. Apply the heat of a lamp, and receive the gas, that is liberated, over mercury.

(b) To a saturated solution of ammonia in water or the pure liquid ammonia, in a gas bottle, apply the heat of a lamp; and collect the gas, as in *a*.

II. This gas has the following properties:

(a) It has a strong and very pungent smell.

(b) It immediately extinguishes flame; and is fatal to animals. Before, however, a candle is extinguished, by immersion in this gas, the flame is enlarged, by the addition of another, of a pale yellow colour, which descends from the mouth to the bottom of the jar. If the flame of the candle be only in part surrounded with the gas, this yellowish flame rises a few lines above the other.

(c) It is lighter than atmospheric air. Hence a jar filled with this gas, and placed with its mouth upwards, is soon

found to exchange its contents for common air, which, being heavier, descends, and displaces the ammoniacal gas. By the experiments of Messrs. Allen and Pepsys,\* undertaken at the desire of Sir. H. Davy, 100 cubic inches of ammonia were found to weigh 18.18 grains, barometer 30, thermometer 60°. According to Gay Lussac, its specific gravity is to that of common air as 0.5967 to 10; and hence, (taking 100 cubic inches of air at 30.5 grains) 100 cubic inches of ammonia weigh 18.17 grains. Mr. Dalton assumes, that at a mean temperature and pressure, 100 cubic inches weigh 18.6 grains; and hence that its specific gravity is 6, air being 10. It does not appear that in any of these trials, the gas was artificially dried. To effect its desiccation, potash or quicklime are best adapted; for dry muriate or chloride of lime, as well as several other chlorides, absorb it rapidly.†

(d) Ammoniacal gas is not sufficiently inflammable to burn when in contact with common air. But, when expelled from the extremity of a pipe, having a small aperture surrounded by oxygen gas, I have found that it may be kindled, and it then burns with a pale yellow flame, the products of its combustion being water and nitrogen gas.

(e) Ammoniacal gas may be decomposed by transmitting it through a red-hot porcelain tube, which should be either well glazed internally, or covered externally with a lute. It has been ascertained by Thenard,‡ that when any of the five following metals are enclosed in the tube, they promote the decomposition of ammonia in the order set down, viz. iron, copper, silver, gold and platinum; iron being most effectual, and platinum least. Iron, after the process, is found to be rendered brittle, and copper still more so. The gas obtained always consists of 3 parts hydrogen by measure, and 1 nitrogen. None of the metals is either increased or diminished in weight; and they can only, therefore, act as conductors of heat. Yet it is singular that iron decomposes a much larger quantity than platinum, and at a lower temperature.

(f) It has been asserted by Guyton, that ammoniacal gas is reduced to a liquid state at 70° below 0 of Fahrenheit; but

\* Philosophical Transactions, 1808, page 39.

† Journal of Science, v. 74.

‡ 85 Ann. de Chim. 61.



it may be questioned whether the drops of liquid, which he observed, were any thing more than the watery vapour, which the gas always contains, condensed by the cold, and saturated with ammonia. (Ann. de Chim. xxix. 290.)

(g) Ammonia is rapidly absorbed by water. A drop or two of water being admitted to a jar of this gas, confined over mercury, the gas will be immediately absorbed, and the mercury will rise, so as to fill the whole of the jar, provided the gas be sufficiently pure. Ice produces the same effect, in a still more remarkable manner. From Sir H. Davy's early experiments, it appeared that 100 grains of water absorb 34 grains of ammoniacal gas, or 190 cubic inches. Therefore a cubic inch of water takes up 475 cubic inches of the gas. More recently he has stated that at 50° Fahrenheit, water absorbs 670 times its bulk, and acquires the specific gravity .875.\*

Alcohol, also, absorbs several times its bulk, and affords a solution of ammonia, which possesses the strong smell, and other properties, of the gas.

(h) Water, by saturation with this gas, acquires its peculiar smell; and constitutes what has been called liquid ammonia; or, more properly, solution of pure ammonia in water. The method of effecting this impregnation is as follows:

*Process for obtaining Solution of Ammonia in Water.*

The following process is given by Mr. R. Phillips, as preferable to that of the London Pharmacopœia.†

On 9 oz. of well-burnt lime, pour half a pint of water, and when it has remained in a well closed vessel for nearly an hour, add 12 ounces of muriate of ammonia, and about 3½ pints of boiling water. When the mixture has cooled, filter the solution; and, having put it into a retort, distil off 20 fluid ounces. The solution will have the specific gravity 0.954, which is quite as strong as it can be conveniently kept. If the solution be required to be more strongly impregnated, this will be best effected by passing ammoniacal gas through

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\* Elements of Chem. Phil. p. 263.

† Remarks on the London Pharm. p. 34.

it, from a mixture of equal parts of powdered lime and muriate of ammonia, by means of an apparatus similar to that described for the preparation of muriatic acid.

The strength of a solution of ammonia is influenced by two circumstances, the temperature of the liquid, and the pressure on its surface, for ammonia is not retained in water without external force. The intervals of temperature, required to double the force of ammoniacal vapour, were ascertained by Mr. Dalton to increase in ascending. When mixed with common air, its elasticity is not altered; thus when ammoniacal gas of 15 inches force is mixed with a given volume of dry air, the air it doubled in bulk.

Solutions of ammonia, when mixed with water, were found by Sir H. Davy, not to be sensibly condensed; and, therefore, if the quantity of ammonia in a solution of given specific gravity be determined, it is easy to calculate the quantity in solutions of other densities. The two following Tables, it may be observed, do not exactly agree in their results, the quantity of ammonia, in solutions of the same density, being from 15 to 20 per cent. less in Mr. Dalton's Table than in Sir H. Davy's. The numbers in the latter, marked with an asterisk, were found by experiment, and from these the others were deduced.

*Sir H. Davy's Table of the Quantities of Ammoniacal Gas in Solutions of different Densities (Temp. 50° Fahrenheit, Barometer, 29.8.)*

100 parts of Specific Gravity.		Of Ammonia.	100 parts of Specific Gravity.		Of Ammonia.
.8750*	contain	32.5	.9435	contain	14.53
.8875		29.25	.9476		13.46
.9000		26.	.9513		12.40
.9054*		25.37	.9545		11.56
.9166		22.07	.9573		10.82
.9255		19.54	.9597		10.17
.9326		17.52	.9619		9.60
.9385		15.88	.9692*		9.50

*Mr. Dalton's Table of the Quantities of Ammonia in Solutions of different Specific Gravities.*

Specific Gravity.	Grains of Ammonia in 100 water-grain measures of liquid.	Grains of Ammonia in 100 grains of liquid.	Boiling point of the liquid in degrees of Fahrenheit.	Volumes of gas condensed in a given volume of liquid.
850	30	35.3	26°	494
860	28	32.6	38°	456
870	26	29.9	50°	419
880	24	27.3	62°	382
890	22	24.7	74°	346
900	20	22.2	86°	311
910	18	19.8	98°	277
920	16	17.4	110°	244
930	14	15.1	122°	211
940	12	12.8	134°	180
950	10	10.5	146°	147
960	8	8.3	158°	116
970	6	6.2	173°	87
980	4	4.1	187°	57
990	2	2.	196°	28

ART. 2.—*Analysis of Ammonia.*

(1) Ammoniacal gas is decomposed by electricity; and its bulk, as Dr. Priestley first observed, is thus gradually enlarged. Into a glass tube, having a conductor sealed hermetically into one end (fig. 29), and standing inverted over mercury, pass about one tenth of a cubic inch of ammoniacal gas; and transmit through it a succession of electrical discharges from a Leyden jar. The arrangement of the apparatus, for this purpose is shown in fig. 84, pl. ix. When two or three hundred discharges have been passed, the gas will be found to have increased to almost twice its original bulk, and to have lost its property of being absorbed by water. Mix it with a quantity of oxygen gas, equal to between one third and one half of its bulk, and pass an electric spark through the mixture. An explosion will immediately happen; and the quantity of gas will be considerably diminished. Note the amount

of the diminution by firing ; divide it by 3 ; and multiply the product by 2. The result shows the quantity of hydrogen gas in the mixed gases which have been generated by electricity ; for two measures of hydrogen are saturated by one of oxygen gas.

Suppose, for example, that we expand 10 measures of ammonia to 18 ; and that, after adding 8 measures of oxygen gas, we find the whole (= 26 measures) reduced by firing to 6 measures ; the diminution will be 20. Dividing 20 by 3 we have 6.66, which multiplied by 2 gives 13.32 measures of hydrogen gas from 10 of ammonia. Deducting 13.32 from 18, we have 4.68 for the nitrogen gas contained in the product of electrization. Therefore 10 measures of ammonia have been destroyed, and expanded into

13.32 measures of hydrogen gas,  
4.68 ————— nitrogen gas.

According to the above proportions, 100 cubic inches of ammonia, which weigh about 18 grains, if they could be decomposed by electricity, would give about 133 cubic inches of hydrogen weighing 3.5 grains, and 46 of nitrogen weighing 14.4 grains, in all 17.9 grains, or one tenth of a grain less than the ammonia decomposed. Mr. Dalton obtained 185 measures of gas by decomposing 100 measures of ammonia ; and, by comparing the products with the original gas, he finds that the weight of the former rather exceeds that of the latter ; thus,

	Grains
100 measures of ammonia × sp. gr.	.6 = 60
produce { 51.8 nitrogen, which × sp. gr. .967	= 50.09
{ 133.2 hydrogen, which × sp. gr. .08	= 10.65
	60.74

The excess of 3-4ths of a grain in 60 he considers as too small to affect the conclusion, and as arising from unavoidable inaccuracies in some of the data.

It is contended by Gay Lussac and Thenard, and the pro-

bable accuracy of their result is admitted by Sir. H. Davy\* and by Dr. Wollaston, that 200 measures of ammonia are resolvable, by complete decomposition, into 300 of hydrogen and 100 of nitrogen. This proportion is consistent with the theory of combination in definite volumes. There is, however, considerable difficulty in ascertaining the precise amount of the gases evolved from ammonia; for if either the gas itself, or the mercury which confines it, contain any moisture, the product of gas, resulting from its decomposition, will exceed what it ought to be. The problem is one of great importance to the atomic theory, because from the proportion of the elements of ammonia, is deduced the weight of the atom of nitrogen. This will differ considerably, according to the statement, which we may adopt, of the amount of gases obtained by decomposing ammonia; their proportion to each other; and the exact specific gravities of hydrogen and nitrogen gases. From the data supplied by Mr. Dalton, the weight of nitrogen in ammonia should be to that of hydrogen nearly as 5 to 1, and, if ammonia be a binary compound, the atom of nitrogen will, therefore, be represented by 5, and that of ammonia by  $5 + 1 = 6$ . On the scale of Dr. Wollaston, nitrogen is represented by 17.54; which, with 3 atoms or proportions of hydrogen ( $1.32 \times 3 = 3.96$ ), gives 21.5 for the equivalent of ammonia, oxygen being considered as 10. But if hydrogen be made the decimal unit, and it be admitted that the three volumes of hydrogen in ammonia represent 3 atoms, and the 1 vol. of nitrogen one atom, then the weights of the atoms of hydrogen and nitrogen will be as their specific gravities, viz. as .0694 to .970, or as 1 to 14. Ammonia, according to this view, will be constituted of three atoms of hydrogen =  $3 + 1$  atom of nitrogen = 14, and its representative number will be 17.

(2) In the Philosophical Transactions for 1809, I have described a property of ammonia, which forms the basis of a very easy and quick mode of analyzing that alkali. When mingled with oxygen gas it may be inflamed by the electric spark, precisely like a mixture of hydrogen and oxygen gases.

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\* Elements of Chem. Phil. p. 269.

To obtain accurate results, however, it is necessary to use less oxygen at first, than is sufficient to saturate the whole hydrogen of the alkali. This is easily calculated. If, for example, we take 10 measures of ammonia, we must use less oxygen than will saturate 13 or 14 measures of hydrogen gas, the quantity which exists in 10 of ammonia; and which require about 7 of oxygen gas. It will be advisable, therefore, not to add above 4 or 5 of oxygen. The whole (suppose 15) will probably, after firing, be reduced to about 9. To the remaining gas admit 4 or 5 measures more of oxygen; and on passing the electric spark again, a second explosion will happen, with a diminution of about 6 measures. But, in the first explosion, the whole of the oxygen disappears, and it must therefore have saturated a quantity of hydrogen equal to 10 measures; besides which, two thirds of the second diminution ( $6 \div 3 \times 2$ ) = 4 measures are owing to the condensation of hydrogen. Hence the whole hydrogen is  $10 + 4 = 14$ . The nitrogen, the whole of which exists in the product of the first detonation, is ascertained by deducting from it (viz. from 9 in the present instance) the second quantity of hydrogen (4) which gives 5 for the nitrogen. These numbers may not, perhaps, be exactly obtained by experiment; and they are given merely as a general illustration of the process.

By experiments of this kind I have determined that 100 measures of ammonia require, for saturating the hydrogen which they contain, between 67 and 68 of pure oxygen gas, and afford

Of hydrogen gas about 136 measures,  
nitrogen gas . . . . . 47 measures.

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183

(3) *Chlorine and Ammonia*.—Scheele first observed that when liquid solutions of chlorine and ammonia are mixed, or when aëriform chlorine is passed through liquid ammonia, nitrogen gas is disengaged, and muriatic acid formed. In this case the hydrogen of the ammonia unites with the chlorine, and the nitrogen is liberated. The latter process furnishes a good method of obtaining nitrogen gas.

If into a bottle containing two or three pints of chlorine gas, about a drachm of strong solution of ammonia be poured, the two gases, when diffused through each other, act with sufficient energy to cause a detonation. The impossibility of confining chlorine gas, either by water or mercury, renders its decomposing action on ammonia of little use as a means of analyzing that compound.

The results of the analysis of ammonia furnish a good example of the condensation of the elements of gases, which takes place on chemical union; and if we could, by any means, permanently condense a mixture of 136 measures of hydrogen with 47 of nitrogen into 100 measures, or three volumes of hydrogen and one of nitrogen into one volume, the new gas would constitute ammonia. Simple admixture of these gases, however, even in the same proportions which are obtained by analyzing ammonia, is not sufficient to generate this alkali. The caloric, with which the hydrogen and nitrogen are respectively combined, opposes, by its elasticity, an obstacle to their union, and places them beyond the sphere of their mutual attractions. If these elements are presented to each other when one or both are deprived of part of their caloric, combination then takes place; and the composition of the volatile alkali is proved synthetically, as in the following experiments.

1. When iron filings, moistened with water, are exposed to nitrogen gas confined over mercury, the gas, after some time has elapsed, acquires the smell of volatile alkali. In this case, the iron decomposes the water and seizes its oxygen; while the hydrogen, at the moment of its liberation, unites with nitrogen, and composes ammonia. This state of condensation, or absence of the quantity of caloric necessary to bring it into a gaseous form, has been called the nascent state of hydrogen gas; and the same term has been applied to the bases of other gases when in a similar state.

(2) Another fact, showing the mutual relation of ammonia and of the compounds of nitrogen, was discovered some years ago, by Mr. Higgins of Dublin.\* Moisten some powdered

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\* See his Comparative View of the Phlogistic and Antiphlogistic Theories, 2d edition, p. 300, note.

tin (which is sold under that name by the druggists) with strong nitric acid; and, when the red fumes have ceased to arise, add some quick-lime or solution of pure potash. A strong smell of ammonia will be immediately produced. In this experiment, the tin attracts, at the same instant, the oxygen both of the nitric acid and of the water. Hydrogen and nitrogen are consequently set at liberty; and, before they have assumed the gaseous state, these two bases combine, and constitute ammonia. The ammonia thus generated unites with a portion of undecomposed nitric acid; and is disengaged from this combination by potash or lime, which render it evident to the smell.

3. A similar production of ammonia has been shown by Mr. R. Phillips to take place, when nitric acid is acted upon by phosphorus, which, simultaneously decomposing both water and nitric acid, enables the hydrogen of the former, and the oxygen of the latter, to unite while in a nascent form.

#### ART. 2.—*Salts with base of Ammonia.*

*Chlorine and Ammonia.*—No compound of chlorine and ammonia can exist, for as soon as ammonia is brought into contact with chlorine, it is decomposed in the manner which has been already described.

*Chlorate of Ammonia* may be formed either by saturating carbonate of ammonia with chloric acid, or by precipitating the solution of any earthy chlorate by that carbonate. Chlorate of ammonia forms fine needle shaped crystals, which are extremely soluble in water and in alcohol. It is volatile, and, when thrown upon a red-hot coal, detonates with a red flame. The proportion of its components is not known. (See Vauquelin, Ann. de Chim. xcv. 97.)

*Iodine and Ammonia.*—Dry ammoniacal gas is absorbed by iodine without decomposition. The product is at first very viscid, and has a metallic aspect; but by an excess of ammonia it loses these properties, and becomes of a very deep brownish red. When iodine is added to liquid ammonia, one part of it unites with the hydrogen of the alkali, and forms hydriodic acid, while another portion of the iodine combines



with the azote, and falls down in the form of a black powder. This compound of iodine and azote detonates with a very gentle heat, and even with the slightest touch.

*Iodate of Ammonia.*—This salt is best formed by saturating iodic acid with ammonia. It is deposited in small crystalline grains of an indeterminate form. When these are thrown on a red-hot coal, they detonate with a feeble violet flame and an escape of iodine. When heated in close tubes, the tubes are frequently burst; but Gay Lussac succeeded in collecting the products, which were equal volumes of oxygen and azotic gases. He states its composition at 100 acid + 10.94 ammonia, or 2 vols. of gaseous ammonia, 1 volume of iodine in vapour, and  $2\frac{1}{2}$  volumes of oxygen.

*Hydriodate of Ammonia* is constituted of equal volumes of hydriodic acid gas and ammoniacal gas. It may be formed by mixing the watery solutions of the acid and base. It crystallizes in cubes which are more soluble than sal ammoniac, and nearly as volatile, subliming in close vessels without decomposition.

*Hydro-chlorate of Ammonia, Muriate of Ammonia,  
or Sal-ammoniac.*

Muriate of ammonia may be formed by mixing over mercury equal measures of ammoniacal gas and muriatic acid gas, which are entirely condensed into a white solid. For purposes of experiment, the common sal ammoniac of the shops is sufficient, which is prepared by a circuitous process from an impure carbonate of ammonia, obtained by the distillation of bones, and other animal matters. This carbonate of ammonia, by being kept in contact with sulphate of lime and water, is converted into sulphate of ammonia. This again is decomposed by muriate of soda, which affords muriate of ammonia and sulphate of soda. The latter salt is separated by priority of crystallization, and the muriate of ammonia is then purified by being once or twice sublimed.

It has lately been ascertained by Dr. Marcet, that muriate of ammonia exists in sea water, and may be separated by sublimation from the uncrystallizable part called *bittern*.\*

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\* Phil. Trans. 1822, p. 454.

It is easy to calculate the composition of this salt, for since 100 cubic inches of muriatic acid gas weigh 39 grains, and the same volume of ammonia weighs 18.18 grains, muriate of ammonia must consist of

		Atom.		
Muriatic acid . . . .	68.205	. . . . 1	. . . .	37
Ammonia . . . . .	31.745	. . . . 1	. . . .	17
	100.			54

But in its ordinary state, the salt contains water, the proportion of which, according to Berzelius, is as follows:

		Atom.		
Muriatic acid . . . .	49.55	. . . . 1	. . . .	37
Ammonia . . . . .	31.95	. . . . 1	. . . .	17
Water . . . . .	18.50	. . . . 1	. . . .	9
	100.			63

Muriate of ammonia exhibits the following properties:

(a) It is volatilized, without being liquefied or decomposed, or in other words may be *sublimed*. Sir H. Davy finds that it may even be passed, without alteration, through glass or porcelain tubes heated to redness. When, however, it is transmitted over ignited metals, it is decomposed into its gaseous elements.

(b) It is readily soluble in water, three parts and a half of which, at 60°, take up one of the salt. During its solution much caloric is absorbed. In boiling water, it is still more soluble; and the solution, on cooling, shoots into regular crystals.

(c) It slightly attracts moisture from the air.

(d) On the addition of a solution of pure potash, or pure soda, the alkali is disengaged, as is evinced by the pungent smell that arises on the mixture of these two bodies, though perfectly inodorous when separate.

(e) Though generally considered as a neutral salt, yet, if placed on litmus paper and moistened, Berzelius observes, that the paper is reddened after some moments, as it would be by an acid.

(f) It is decomposed by baryta, strontia, lime, and magnesia.

*Nitrate of Ammonia.*

The most simple mode of preparing this salt is by adding carbonate of ammonia to dilute nitric acid, till saturation has taken place. If the liquor be evaporated, by a heat between  $70^{\circ}$  and  $100^{\circ}$ , to a certain extent, it shoots, on cooling, into crystals, having the shape of six-sided prisms, terminated by long six-sided pyramids. Evaporated at the temperature of  $212^{\circ}$ , it yields, on cooling, thin fibrous crystals; and, when the evaporation is carried so far that the salt immediately concretes on a glass rod by cooling, it then forms a compact and shapeless mass.

The solubility of this salt varies, according to the temperature in which it has been formed. When in crystals, it requires twice its weight of water for solution, or half its weight of boiling water. It deliquesces, in all its forms, when exposed to the atmosphere.

The most important property of this salt is the one which has been already described, *viz.* of yielding, when decomposed by heat, the nitrous oxide. One pound of the compact kind gives, by careful decomposition, nearly five cubic feet of gas, or rather more than 34 doses; so that the expense, estimating the salt at 5s. 10d. the pound, is about 2d. for each dose.

In a temperature of  $600^{\circ}$  this salt explodes, and is entirely decomposed. Hence it was formerly called *nitrum flammans*.

Its composition varies according to the mode of its preparation, and is stated by Sir H. Davy as follows :

Prismatic.	Fibrous.	Compact.
69.5	72.5	74.5 acid
18.4	19.3	19.8 ammonia
12.1	8.2	5.7 water
<hr/>	<hr/>	<hr/>
100.	100.	100.

The prismatic variety is stated by Berzelius,\* who inves-

\* 80 Ann. de Chim. 182.

tigated very carefully the results of its decomposition, to consist of

		Atom.		
Acid . . . . .	67.625	1	54	
Base . . . . .	21.143	1	17	
Water . . . . .	11.232	1	9	
	100.		80	

The dry salt, therefore, is constituted of 1 atom of acid + 1 atom of base, and its equivalent is  $54 + 17 = 71$ .

#### *Carbonates of Ammonia.*

*Carbonate of ammonia* consists of one volume of carbonic acid and two volumes of ammonia, which, when mingled over mercury in that proportion, undergo complete condensation. As 100 cubic inches of carbonic acid weigh 46.56 grains, and 200 of ammonia 36.36 grains, in all 82.92 grains, carbonate of ammonia must consist of

		Atom.		
Carbonic acid . . . . .	56.20	1	22	
Ammonia . . . . .	43.80	1	17	
	100.		39	

These proportions differ very little from the experimental results of Gay Lussac (56.02 acid + 43.98 base).

*Bi-carbonate of ammonia* was formed by Berthollet, by impregnating a solution of the common carbonate with carbonic acid gas. It crystallizes, when evaporated by a very gentle heat, in small six-sided prisms, has no smell, and but little taste. It consists, according to Berthollet, exclusive of water, of

		Atoms.		
Carbonic acid . . . . .	71.81	2	44	
Ammonia . . . . .	28.19	1	17	
	100.		61	

*Sesqui-carbonate of Ammonia.*—Besides these two compounds of ammonia and carbonic acid, there is another which is generally met with in the shops under the name of *sub-carbonate of ammonia*. It is produced by exposing to heat, in a proper subliming apparatus, a mixture of muriate of ammonia and carbonate of lime, and if no loss occurred during the opera-

tion, it ought to consist of 1 atom of carbonic acid, 1 of ammonia, and 1 of water. But the heat, which is necessary to the decomposition, expels both ammonia and carbonic acid, and the resulting salt has the following proportions :

	Acid.	Base.	Water.
According to Dr. Ure * . . . . .	54.5	30.5	15.
Mr. Phillips † . . . . .	54.2	29.3	16.5
Mr. Dalton ‡ . . . . .	59.	24.5	16.5

The atomic constitution, nearest to the above proportions, and that which probably belongs to the salt in its perfect state, is as follows :

Acid . . . . .	55.72	3 atoms	66
Base . . . . .	29.	2 atoms	34
Water . . . . .	15.28	2 atoms	18
	100.		118

Viewing it as a compound of  $1\frac{1}{2}$  portions of carbonic acid, 1 ammonia, and 1 of water, it has been called by Mr. Phillips a *sesqui-carbonate*, and if this view be unconnected with the notion of its containing the fraction of an atom, there can be no objection to the name. It is preferable, indeed, to that of sub-carbonate, which should be reserved for the compound, hitherto unknown, of 1 atom of acid and 2 of base.

When the sesqui-carbonate is fresh prepared, it has a crystalline appearance and some transparency, and is hard and compact. It has a pungent smell, and a sharp penetrating taste, and affects vegetable blues as uncombined alkalis do. It dissolves in twice its weight of cold, or an equal weight of boiling water. When exposed to the atmosphere, it loses weight very fast, ceases to be transparent, loses its odour, and becomes brittle and easily reducible to powder. When its chemical composition is now examined, it is found to be identical with the bi-carbonate, or to consist of

Two atoms of acid . . . . .	44
One atom of base . . . . .	17
Two atoms of water . . . . .	18
	79

\* Ann. of Phil. x. 206.

† Quarterly Journ. vii. 294.

‡ Manch. Mem. iii. 32.

It has therefore lost, by exposure, 1 atom of acid and 1 atom of base.

By varying the proportions of the ingredients, and the regulation of the heat, it is possible to obtain a bi-carbonate at once by sublimation. (Annals of Philos. N. S. iii. 110.)

*Borate of Ammonia*, formed by saturating boracic acid with ammonia, crystallizes somewhat like borax. When heated, part of the base is expelled. It consists, according to Berzelius, of

Acid . . . . .	37.95	. . . . .	100.
Ammonia . . . . .	30.32	. . . . .	79.895
Water . . . . .	31.73		

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100.

*Phosphite of Ammonia* is a very soluble salt, and is with difficulty brought to crystallize.

*Hypophosphite of ammonia* is very soluble both in water and alcohol. Its composition has not been ascertained.

*Phosphate of ammonia* may be formed by saturating the superphosphate of lime, resulting from the action of sulphuric acid on bones, with carbonate of ammonia. The liquid, when evaporated spontaneously, crystallizes in low four-sided pyramids with square bases. It is soluble in twice its weight of water at 55° Fahr. When heated, it fuses, swells, and, if the heat be strongly urged, loses its alkaline base, the phosphoric acid being left in a glacial form.

*Sulphite of Ammonia* crystallizes in six-sided prisms terminated by six-sided pyramids. It is soluble in an equal weight of cold, or in less than an equal weight of boiling water. It attracts moisture from the air, and rapidly passes to the state of a sulphate. It is constituted of 100 acid + 53.2 base, or of an atom of each of its elements; and the crystals consist of two atoms of salt and one atom of water.

*Hyposulphite of ammonia*.—According to Mr. Herschell, this is strictly a bi-salt, consisting of 2 atoms of acid and 1 of base. It does not readily crystallize. Its taste is pungent and excessively bitter. When heated, it burns with a feeble flame, and evaporates.

*Sulphate of ammonia* may be formed by uniting 100 parts of

the compact sesqui-carbonate with 88 of sulphuric acid, previously diluted with water. The salt crystallizes in long flattened prisms with six sides, terminated by six-sided pyramids. These crystals have a cool, bitter taste; they slightly attract moisture from the air; are soluble in two parts of water at 60°, or in an equal weight of boiling water. During solution they produce cold. When heated, they sublime; but the constitution of the salt undergoes some change.

It is composed, according to Berzelius, of

Sulphuric acid . . . . .	53.1	. . . .	1 atom	. . . .	40
Ammonia . . . . .	22.6	. . . .	1 do.	. . . .	17
Water . . . . .	24.3	. . . .	2 do.	. . . .	18
	100.				75

When dried as much as possible without decomposing it, Dr. Ure found that it lost an atom of water, or that it consisted of 61 acid + 25.96 ammonia, + 13.04 water.

*Seleniates of ammonia.*—Selenic acid unites with ammonia in three different proportions, forming seleniate, biseleniate, and quadriseleniate. These salts, which are not important, are described by Berzelius. (Ann. de Chim. et Phys. ix. 260.)

## SECTION II.

### *Combinations of Hydrogen with Carbon.*

ONLY two distinct and well-characterized compounds of hydrogen and carbon are at present known; for though it has been contended, by some chemical writers, that these two elements are capable of uniting in almost all proportions, yet there seems no reason for believing that, in this instance, there is any departure from the general law, that bodies combine in proportions which are few in number, and which are either equal, or are simple multiples or divisors of each other.

The union of hydrogen with carbon cannot be effected by heating charcoal in hydrogen gas, for the cohesive attrac-

tion of the particles of charcoal prevents the combination. It may be effected, however, by exposing to a high temperature some of the solid and liquid compounds of hydrogen and charcoal, and it is produced also by several natural operations, especially by animal and vegetable putrefaction. The gas which has a minimum of carbon may be called, simply, carbureted hydrogen gas.

ART. 1.—*Carbureted Hydrogen Gas.*

It has been distinguished also by the name of *heavy inflammable air, gas of marshes, hydro-carburet, proto-carburet of hydrogen*, and has been termed by Dr. Thomson, *bi-hydroguret of carbon*.

This gas may be obtained, mixed, however, with about  $\frac{1}{10}$  of carbonic acid, and  $\frac{1}{3}$  or  $\frac{1}{4}$  of nitrogen gas, by stirring the bottom of almost any stagnant pool of water, especially if formed of clay. When this is done by an assistant, the gas is copiously disengaged in bubbles, which may be collected either in an inverted glass jar, or in an inverted bottle filled with water, into the mouth of which a funnel is fixed. It should be washed, when collected, with lime water or liquid potash.

It may, also, be procured by the purification of gas from coal, by means of chlorine and solution of potash, applied in succession, in a manner which will afterwards be described in speaking of coal gas.

Carbureted hydrogen, thus obtained, is permanent over water, which, after being well purged of air by boiling, is capable of taking up about  $\frac{1}{8}$ th of its bulk. It has very little odour, the strong and disagreeable smell of coal gas being dependent on foreign admixtures. Its specific gravity, from Dr. Thomson's experiments and my own, is 0.555; and hence 100 cubic inches, at a mean of the barometer and thermometer, weigh 16.95 grains.

When set on fire as it issues from a small orifice, it burns with a yellow flame, giving out vastly more light than hydrogen gas. When mixed with atmospheric air, it may be kindled by a lighted taper, and it explodes with violence, provided it forms not less than  $\frac{1}{7}$ th of the mixture, and does not



exceed  $\frac{1}{8}$ th. With oxygen gas, the detonation is louder and more violent; but it is necessary that the oxygen should rather exceed the inflammable gas in volume, and yet should not be more than  $2\frac{1}{4}$  times its bulk. Under a pressure diminished below one-fourth that of the atmosphere, the mixture ceases to be combustible; and its inflammability is also much lessened, by mingling it with carbonic acid and some other gases. To burn it completely, it is necessary to use more than twice its volume of oxygen gas, of which exactly two volumes are consumed, and carbonic acid is produced, equivalent in volume to the inflammable gas. Now we know that in carbonic acid gas there exists exactly its volume of oxygen; and hence one volume of the oxygen spent is found in that compound, and the other volume has formed water with the hydrogen, which last element must have existed in quantity equivalent to twice the bulk of the inflammable gas. The water produced may be collected by the slow combustion of the gas, but this is not necessary for calculating the proportion of its elements, which may be correctly estimated as follows. Since 100 cubic inches (= 16.95 grains) afford by combustion 100 cubic inches of carbonic acid, weighing 46.5 grains, and containing 12.69 grains of carbon, then  $16.95 - 12.69 = 4.26$  is the hydrogen in 100 cubic inches of carbureted hydrogen, which is, therefore, constituted of

	Grains.		Grains.		Grains.
Charcoal . . . .	12.69	. . . .	74.87	. . . .	100.
Hydrogen . . . .	4.26	. . . .	25.13	. . . .	33.41
	<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>		<hr style="width: 50%; margin: 0 auto;"/>
	16.95		100.		133.41

Or carbureted hydrogen gas may be stated to be composed of 2 volumes of hydrogen and 1 volume of gaseous carbon condensed into 1 volume. But 2 volumes of hydrogen requiring 1 volume of oxygen to form the binary compound, water, which we have already considered to be constituted of an atom of each element, the atomic constitution of carbureted hydrogen will be 1 atom of charcoal (= 6) + 2 atoms of hydrogen (= 2) and the compound atom will weigh 8. From this view of its constitution, the name proposed by Dr. Thomson (bi-hydroguret of carbon) is certainly most appropriate,

and it is only to avoid the inconvenience of laying aside one which is sanctioned by long usage, that I employ that of carbureted hydrogen.

When carbureted hydrogen and chlorine gases are mixed together, no change happens either immediately or on standing, provided light be carefully excluded; but if exposed to the ordinary light of day, and still more rapidly in sunshine, a mutual action ensues. If 4 volumes of chlorine, and 1 of carbureted hydrogen, be thus kept, during a few hours, in a bottle filled entirely with the mixture, and furnished with a well-ground stopper, on removing this under water, a sudden absorption of muriatic acid gas takes place, and 1 volume of carbonic acid remains. Three volumes of chlorine and one of carbureted hydrogen afford a residue of carbonic oxide. In both cases, water is decomposed (for the gases do not act on each other if perfectly dry), the oxygen of the water uniting with the carbon, and its hydrogen with the chlorine. If the quantities be sufficiently large, and the sun's rays fall on the mixture, a detonation ensues, which may also be produced either by an electric spark, or by a lighted taper.

#### ART. 2.—*Bi-carbureted Hydrogen, or Olefiant Gas.*

This gas was discovered by the associated Dutch chemists, and was termed by them *olefiant gas*, from a property which will presently be described. It has since been called *bi-carbureted* or *per-carbureted hydrogen*, and by Dr. Thomson, *hydroguret of carbon*. It may readily be obtained by distilling, in a glass retort, with a gentle heat, three measures of concentrated sulphuric acid, and one measure of alcohol. The mixture soon assumes a black colour and thick consistence, and a gas is disengaged which may be collected over water, and freed from carbonic acid by washing it with liquid potash. If left to stand long over water, it sustains a diminution, that fluid being capable of taking up  $\frac{1}{4}$ th of its volume of the gas.

Bi-carbureted hydrogen, when pure, has very little odour, except when mingled with a little sulphuric ether, which is formed along with it. Its specific gravity is stated by the

Dutch chemists at .909; by my experiments, made several years ago, it is .967; by those of Saussure, jun. .9852; and by Dr. Thomson's latest trials 0.970. According to the last mentioned result, 100 cubic inches, at a mean of the barometer and thermometer, weigh 29.64 grains.

This gas, when set on fire as it issues from the orifice of a small pipe, burns with a remarkably dense and bright flame, very superior to that of simple carbureted hydrogen. When mingled with oxygen gas, it detonates very loudly and forcibly, and if fired by electricity in a Volta's eudiometer, is apt, unless very small quantities be employed, to burst the instrument. One volume requires for saturation three volumes of pure oxygen gas, and affords two volumes of carbonic acid gas. But in order to insure the perfect combustion of the inflammable gas, it should be mixed with 5 times its bulk of oxygen, of at least 90 per cent purity. If too little oxygen be used, charcoal is apt to be precipitated unburned; and the excess of oxygen does no harm, but remains in the mixture. When fired with less than its own bulk of oxygen, the separation of charcoal is very evident, and the bulk of the residue is greater than that of the original gases.

Calculating the constitution of this gas, from the oxygen spent in its combustion and the carbonic acid formed, precisely as was done with respect to carbureted hydrogen, we have the following results, the first column including the composition of 100 cubical inches.

	Grains.	Grains.	Grains.
Charcoal . . . .	25.38 . . . . .	85.63 . . . . .	100.
Hydrogen . . .	4.26 . . . . .	14.37 . . . . .	16.71
	<hr/>	<hr/>	<hr/>
	29.64	100.	116.71

In this gas, therefore, 100 grains of charcoal are united with 16.71 hydrogen, and in the last with 33.41; or, as nearly as possible, olefiant gas contains only one half the hydrogen. Its constitution may hence be stated as follows:

	Vols. of Carb.	Vols. of Hydr.	At. of Carb.	At. of Hydr.
In each volume . . . .	2	+ 2	= 1	+ 1

The compound atom, therefore, will weigh  $6 + 1 = 7$ . Its greater combustibility evidently depends on its containing, in a given volume, twice the quantity of carbonaceous matter that is present in simple carbureted hydrogen.

When olefiant and chlorine gases are mixed together in equal quantities, an immediate diminution ensues; and this effect takes place, even when the vessel is shaded from the light by an opaque cover. It is therefore wholly independent of the agency of light, and may be made the basis of a method of analyzing a mixture of olefiant and carbureted hydrogen gases. For of the diminution thus produced, one half is due to the olefiant, and one half to the chlorine gas, those gases having been ascertained to saturate each other in equal volumes. Into a graduated tube standing over water, admit 30 or 40 measures of chlorine gas, and note its bulk when actually in the tube, which must be shaded by an opaque cover. Then add a known quantity (suppose 50 measures) of the gas under examination; and, after ten minutes, cautiously lift the outer cover, till the surface of the water appears. If the volume of the two gases has suffered no diminution, we may infer the absence of olefiant gas; but if the united bulk of the two gases be less than the sum of their separate volumes, divide the diminution by 2, and the quotient will show how much olefiant gas has been condensed. In this way I have found that olefiant and carbureted hydrogen gases may be accurately separated from each other; but it is necessary to use a slight excess of chlorine, which may afterwards be removed by washing the residue with liquid potash, and the carbureted hydrogen will then be obtained pure.

By the action of chlorine gas on bi-carbureted hydrogen, a liquid substance is formed, in appearance very much resembling oil, and which, being at first mistaken for oil, occasioned this gas to be called *olefiant*. It possesses, however, very different properties from those of oil, and more nearly approaches in character to ether. It may be collected in quantity, by mixing large volumes of chlorine and bi-carbureted hydrogen, taking care to have an excess of the latter gas; and it may be purified by washing it with water, and then distilling it from dry chloride of calcium. It has an agreeable ethereal smell, and

a not unpleasant taste. Its specific gravity at 45° F. is 1.2201; it boils at 152°; at 49° its vapour is capable of supporting a column of mercury 24.66 inches in length, and the specific gravity of its vapour is to that of air as 3.4434 to 1. It consists of 1 vol. of chlorine + 1 vol. of olefiant gas condensed into 1 vol.; or by weight of

Chlorine .....	72.5	.....	100
Olefiant gas .....	27.5	.....	38.88
	<hr style="width: 10%; margin: 0 auto;"/>		
	100.		

Or it is constituted of two atoms of bi-carbureted hydrogen + 1 atom of chlorine gas. It has been called by Dr. Thomson, *chloric ether*; but a more appropriate name would be *hydro-chloride of carbon*.

When olefiant gas is mixed with eight or nine times its bulk of chlorine, and exposed to the sun's rays, at first the fluid hydro-chloride of carbon is formed, and this, by continuing the exposure, is changed into the crystalline compound of carbon and chlorine, discovered by Mr. Faraday, and already described as the *perchloride of carbon*.

When iodine and olefiant gas are exposed in a similar manner to the sun's rays, the two substances unite, and form colourless crystals. When the redundant iodine has been washed away by liquid potash, and the residue collected and dried, it is a solid white crystalline body, heavier than sulphuric acid; having a sweet taste and an aromatic smell; friable, and a nonconductor of electricity; fusible, and capable of being sublimed at a moderate heat without change; but decomposed by a strong heat. It is not readily combustible, but, when held in the flame of a spirit lamp, burns, diminishing the flame, and giving off abundance of iodine and some fumes of hydriodic acid. It is insoluble in water, and in acid and alkaline solutions; but dissolves in alcohol and in ether. It may be termed *hydriodide of carbon*, or *hydro-carburet of iodine*. (Faraday, Phil. Trans. 1821.) From a recent analysis by Mr. Faraday, it appears to consist of 1 atom of iodine + 2 atoms of olefiant gas. (Quarterly Journal, xiii. 429.)

**ART. 3.**—*On the Mixed Combustible Gases from Moist Charcoal, Alcohol, Ether, Coal, Oil, Tallow and Wax.*

The two gases, which have been just described under the names of carbureted and bi-carbureted hydrogen, appear to me to be the only compounds of those elements, that have as yet been proved to be distinct and well-characterized species; though it is extremely probable, as I have shown in the *Phil. Trans.* for 1820, that another gas exists, which was first observed by Mr. Dalton; is heavier and more combustible than olefiant gas; and contains a larger proportion of carbon. It is of mixtures of two or more of those three gases, with occasionally a proportion of carbonic oxide, that the almost infinite variety of aëriform products are constituted, which are obtainable by the exposure of moistened charcoal, of alcohol or ether, of oil, tallow, wax, or coal, to a heat a little above ignition. This view of the subject, at least, appears to me much more probable, than that they are so many distinct compounds of carbon and hydrogen, which, on this theory, would be capable of uniting in all possible proportions with each other.

Of these aëriform compounds, the gases from coal and from oil are of most importance, from their widely extended use in artificial illumination.

*Coal Gas.*—By submitting coal to distillation in an iron retort, besides a portion of tar and solution of carbonate of ammonia, which condense in a liquid form, a large quantity of permanent gas is evolved. This gas I have shown (*Phil. Trans.* 1808 and 1820) is extremely variable in composition and properties, not only when prepared from different coals, but from the same kind of coal under different circumstances. Within certain limits, the more quickly the heat is applied, the greater is the quantity, and the better the quality, of the gas obtained from coal; for too slow a heat expels the inflammable matter in the form of tar. The early products of gas are, also, the heaviest and most combustible, and there is a gradual decline in quality towards the close of the distillation, insomuch that the last products are inferior, by more than one half, to the first. The ge-

neral name of *coal gas* is, therefore, quite indefinite. It is, in fact, a mixture of the two varieties of carbureted hydrogen, with a third which remains to be more fully investigated, as well as with hydrogen gas, carbonic oxide, carbonic acid, nitrogen, and sulphureted hydrogen gases, in ever-varying proportions. To describe the methods of separating these gases from each other, would lead into minute details not suited to an elementary work, and I refer therefore to the papers which I have published in the *Phil. Trans.* for 1808 and 1820, and in the 3d. vol. 2d. Series, of the *Manchester Society's Memoirs, or Annals of Philosophy*, vol. xv.

Coal gas, as generally procured, has a very disagreeable odour, arising from sulphureted hydrogen, and, perhaps, a little sulphuret of carbon; but both these may be washed out of it by cream of lime, with (as I have shown) very little loss of illuminating power, and with an entire removal of all unpleasant smell either before or during burning. The best gas has the specific gravity .650 or upwards; and each volume consumes about  $2\frac{1}{4}$  volumes of oxygen and gives  $1\frac{1}{4}$  volume of carbonic acid; the last portions have a specific gravity as low as .340, and each volume consumes about 8-10ths of a volume of oxygen, and gives about 3-10ths of a volume of carbonic acid. In the best gas, chlorine, applied as directed page 416, detects from 13 to 20 per cent. of olefiant gas, and the remainder is almost pure carbureted hydrogen: but the last products contain little or no olefiant gas, much less carbureted hydrogen, and instead of these, a large proportion of hydrogen and carbonic oxide, both of which afford very little light by their combustion.

It is scarcely possible to assign the quantity of gas, which ought to be obtained from a given weight of coal, but it may be considered as an approach to a general average to state that 112lbs. of good coal are capable of giving from 450 to 500 cubic feet of gas of such quality, that half a cubic foot per hour is equivalent to a mould candle of six to the pound, burning during the same space of time.

*Oil Gas.*—In Nicholson's *Journal* for 1805, I have given an account of some experiments on the gas obtained by the destructive distillation of spermaceti oil, which showed that

of all the artificial gases, this, next to olefiant gas, consumes most oxygen, and is the best adapted to afford light. Since that time, an apparatus has been invented by Messrs. Taylor, of London, which has greatly facilitated the preparation of oil gas on a large scale, and this gas is now much used as a source of artificial light. The process consists in letting whale oil (the purity of which is not essential, since very inferior oil answers the purpose) fall by drops into an iron cylinder placed horizontally in a furnace, and ignited to a cherry redness. From each wine gallon of oil, about 100 cubic feet of gas may with care be obtained, of the specific gravity of more than .900, containing upwards of 40 per cent. of gas condensable by chlorine, and of which 100 volumes consume 260 volumes of oxygen, and yield 158 of carbonic acid. But of gas from Wigan cannel, when the whole product is mingled together, 100 measures do not saturate more than 155 of oxygen, and give 88 measures of carbonic acid. Oil gas, therefore, from this document, may be inferred to contain, in a given volume, twice the quantity of combustible matter that is present in the average of gas from cannel coal; and its illuminating power will be as 2 to 1. The experiments of Mr. Brande led him to conclude, that to produce the light of ten wax candles for one hour, there will be required

2600	cubical inches of olefiant gas
4875	..... oil gas.
13120	..... coal gas.

But it seems probable that the coal gas, employed in these experiments, was below the general standard, and that it is a fair average to consider 1 volume of oil gas as equivalent to 2 or at most  $2\frac{1}{2}$  volumes of gas from coal of good quality. This estimate agrees with the experience of the late Mr. Creighton, of Glasgow, author of the excellent article 'Gas Lights,' in the Supplement now publishing to the Encyclop. Britan. Oil gas he considers as superior, in an equal volume, to good average coal gas, in the proportion of only 2 to 1; and he has given the following Table of the comparative expense of lighting with these two gases, and with oil and tallow.



	<i>s.</i>	<i>d</i>
Valuing the quantity of light which 1 lb. of tallow gives in candles at .....	1	0
An equal quantity of light from sperm. oil consumed in an Argand's lamp, will cost .....	0	6½
Do. from whale oil gas .....	0	4½
Do. from coal gas .....	0	2¾

Twenty cubic feet of coal gas, or ten of oil gas, he considers as equivalent to a pound of tallow, and 5000 grains of good sperm. oil to 7000 of tallow, or 1lb. avoirdupois.

The advantages of oil gas over gas from coal are, that smaller distilling vessels are required; that gazometers and conduit pipes of half the capacity are sufficient; that no washing apparatus is necessary; that the trouble and expence of removing waste materials is avoided; and that the gas affords a much brighter light, and with a smaller production of heat, and also of water. When only a moderate quantity of light is required; when it is an object to save room or labour; and in countries where coal is dear, oil gas is entitled to a decided preference; but it cannot be brought into competition with coal gas, where coal is cheap, or where the establishments to be lighted are of very considerable magnitude, and of such a nature as to allow of their being freely ventilated.

Of the comparative value of different compounds of hydrogen and charcoal for the purpose of illumination, it still appears to me that the only accurate test is the one which I proposed in Nicholson's Journal for 1805, viz. the quantities of oxygen gas required to saturate equal volumes. If 100 measures, for instance, of one gas, require for perfect combustion 100 measures of oxygen, and 100 measures of another gas take 200 of oxygen, the value of the second will be double that of the first. Specific gravity, though a guide to a certain extent, is not a sufficient one, for the weight of a gas may be owing to a large proportion of carbonic oxide, which is capable of giving out only a very small quantity of light. Photometrical experiments, also, appear to me to require greater perfection in the instruments that have been invented for that purpose, before we can implicitly trust to results obtained by their means; but there can be no fallacy in the combustion of these gases by oxygen, if conducted with ordinary care,

and especially if, in each instance, an average be taken of two or three trials, which need not occupy more than a few minutes. Nor can it admit of a doubt that, other circumstances being equal, the brilliancy of light, evolved by the combustion of gases which are constituted of purely inflammable matter, will bear a proportion to their densities, perhaps even a greater proportion than one strictly arithmetical; because, while by the combustion of denser gases a higher temperature is produced, the cooling agencies remain the same. It is probable, therefore, that of two gases, composed of the same ingredients, that which has a double density will afford somewhat more than a double quantity of light.

ART. 4.—*On the Fire Damp of Coal Mines, and the Construction and Principle of the Safety-Lamp of Sir H. Davy.*

The fire-damp of coal mines, by an analysis of it which I published in 1806, was shown to be identical in composition with light carbureted hydrogen.\* This conclusion coincides with the subsequent results of Sir H. Davy, who has enlarged our knowledge of the chemical history of the fire-damp, by several important facts,† and has been led, by an ingenious and happy chain of reasoning, to a discovery most important to the interests of humanity. The most readily explosive mixture of fire-damp with common air he found to be one measure of the inflammable gas to seven or eight of air. The mixture was not capable of being set on fire by charcoal in a state of active combustion, nor by iron ignited to a red or even to a white heat, except when in a state of brilliant combustion; in which respects, the fire-damp differs from other combustible gases.

It was in attempting to measure the expansion, occasioned by the combustion of a mixture of fire-damp and air, that Sir H. Davy discovered a fact, which afterwards led him to the most novel and important results. An explosive mixture could not, he ascertained, be kindled in a glass tube so narrow as  $\frac{1}{4}$  of an inch diameter; and when two separate reservoirs of an explosive mixture were connected by a metallic tube,  $\frac{1}{2}$  of an inch diameter and  $1\frac{1}{2}$  inch in length, and one of the

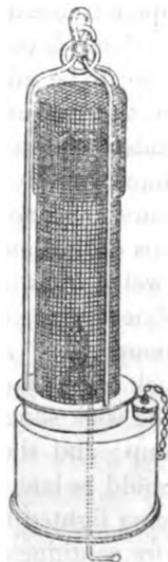
\* Nicholson's Journal, xix. 149.

† Phil. Trans. 1816.

portions of gas was set on fire, the explosion did not extend to the other. Fine wire sieves or wire gauze, interposed between two separate quantities of an explosive mixture, were also found to prevent the combustion of one portions from spreading to the other. A mixture of fire-damp and air, in explosive proportions, was deprived of its power of exploding, by the addition of about  $\frac{1}{7}$  its bulk of carbonic acid or nitrogen gas.

Reflection on these facts suggested to Sir H. Davy the possibility of constructing a lamp,\* in which the flame, by being supplied with only a limited quantity of air, might produce carbonic acid and nitrogen, in such proportion as to destroy the combustibility of explosive mixtures; and which might, also, by the nature of its apertures for giving admittance and exit to the air, be rendered incapable of spreading combustion to the surrounding atmosphere, supposing this to be an inflammable one.

This most desirable object was accomplished by the use of air-tight lanterns, supplied with air through tubes or canals of small diameter, or through apertures covered with wire gauze below the flame, and having a chimney at the upper part on a similar system, for carrying off the foul air. The apparatus was afterwards simplified by covering or surrounding the flame of a lamp or candle with a cylindrical wire sieve, having at least 625 apertures in a square inch. (See the sketch.) Within this cylinder, when the fire damp encompassing it is to the air as 1 to 12, the flame of the wick is seen surrounded by the feeble blue flame of the gas. When the proportion is as 1 to 5, 6, or 7, the cylinder is filled with the flame of the fire-damp; but though the wire gauze becomes red-hot, the exterior air, even when explosive, is not kindled. The lamp is therefore *safe* in the most dangerous atmospheres, and



\* A full history of the Safety Lamp, and of the chemical researches connected with it, has been published by Sir H. Davy, 8vo. printed for R. Hunter, 1818. In the Phil. Mag. l. 387, a document, also, may be found which fully establishes his claim to the priority of the invention.

has been used most extensively in the mines of Whitehaven, Newcastle, and other places, without the occurrence of a single failure or accident.

The effect of the safety-lamp depends on the cooling agency of the wire gauze, exerted on the portion of gas burning within the cylinder. Hence a lamp may be secure, where there is no current of an explosive mixture to occasion its being strongly heated; and yet not safe, when the current passes through it with great rapidity. But any atmosphere, however explosive, may be rendered harmless, by increasing the cooling surface; which may be done, either by diminishing the size of the apertures, or by increasing their depth, both of which are perfectly within the power of the manufacturer of the wire gauze.

When a small coil of platinum wire is hung above the wick of the lamp within the wire gauze cylinder, the metal continues to glow, long after the lamp is extinguished, and affords light enough to guide the miner in what would otherwise be impenetrable darkness. In this case, the combustion of the fire damp is continued so slowly, and at so low a temperature, as not to be adequate to that ignition of gaseous matter which constitutes flame, though it excites a temperature sufficient to render platinum wire luminous. A similar ignition of platinum wire, it has been found, may be supported for many hours, by surrounding the flame of a spirit lamp with small coils of that metal, not exceeding  $\frac{1}{100}$  of an inch in diameter. Twelve coils of this wire, twisted spirally round the tube of a tobacco-pipe, or round any thing that will render the coils about  $\frac{3}{8}$  of an inch in diameter, are to surround, six the wick of the lamp, and six to remain elevated above the wick. The wick should be small, and quite loose in the burner of the lamp; and the fibres of the cotton, surrounded by the coil, should be laid as straight as possible. When the lamp, after being lighted for a few moments, is blown out, the platinum wire continues to glow for several hours, as long as there is a supply of spirit of wine, and to give light enough to read by; and sometimes the heat produced is sufficient to re-ignite the lamp spontaneously.\*

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\* Thomson's Annals, vol. xi.

## SECTION III.

*Hydrogen with Phosphorus.—Phosphureted Hydrogen Gas.*

By heating solid phosphorous acid out of the contact of air, a large quantity of elastic fluid is generated, which may be collected by a proper apparatus, and has characteristic properties. According to Dr. Thomson, the same gas may also be formed by exposing bi-phosphureted hydrogen to the direct rays of the sun, which occasions the precipitation of part of the phosphorus.

It has a disagreeable smell, but is not so offensive as bi-phosphureted hydrogen. It does not burn spontaneously, when brought into contact with air, but detonates violently when heated with oxygen to about  $300^{\circ}$  Fahrenheit; or when a mixture of the two gases is rarefied by diminished pressure.\* It explodes in chlorine with a white flame. Water absorbs about  $\frac{1}{4}$  its volume. Its specific gravity was found by Sir H. Davy to be to that of hydrogen as 12 to 1, or to air as 0.87 to 1. He gave it the name of *hydro-phosphoric gas*, but he has since adopted that of phosphureted hydrogen. Dr. Thomson ascertained its specific gravity, air being 1, to be 0.9653, and he has proposed for it the name of *bi-hydroguret of phosphorus*. By a calculation founded on the proportion of its elements, its true specific gravity should be 0.9722.

Potassium doubles its volume, and the residue is pure hydrogen. Sulphur occasions the formation of sulphureted hydrogen, equal in volume to twice the original gas. Three parts of it in volume condense more than five of oxygen; or, according to Dr. Thomson, 1 volume requires 2 volumes of oxygen for complete combustion, one volume of which goes to the saturation of the hydrogen, and the remaining volume unites with the phosphorus. In this case phosphoric acid is formed. If only  $1\frac{1}{2}$  vol. of oxygen be used, phosphorous acid is produced. One in volume absorbs four of chlorine. It appears to be constituted of two atoms of hy-

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\* 6 Ann. de Chim. et Phys. 304.

drogen and one of phosphorus; and the hydrogen in it is condensed into half its bulk. In that case the weight of its atom will be  $2 + 12 = 14$ .

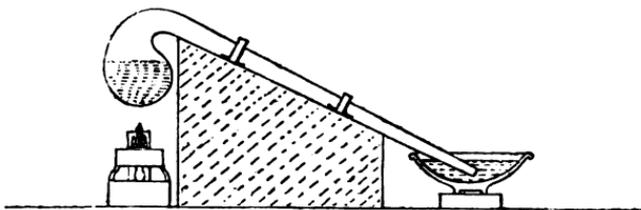
Its formation appears to be owing to the decomposition of water, the oxygen of which, with part of the phosphorous acid, forms phosphoric acid, while the hydrogen, dissolving the excess of phosphorus existing in another portion of phosphorous acid, composes the peculiar gas.

### *Bi-phosphureted Hydrogen Gas.*

I. This gas may be procured, by boiling, in a retort, a little phosphorus with a solution of pure potash, or by throwing into water, acidulated with muriatic acid, and contained in a retort or gas bottle, a few lumps of phosphuret of lime (see chap. ix. § 4); or, indeed, simply by the action of the latter compound upon water. The water is decomposed; its oxygen, uniting with the phosphorus, forms phosphoric acid, which combines with the alkali, while the hydrogen dissolves another portion of phosphorus, constituting bi-phosphureted hydrogen gas, or, as Dr. Thomson terms it, *hydroguret of phosphorus*. This gas may also be obtained, by putting into five parts of water half a part of phosphorus, cut into very small pieces, with one of finely granulated zinc, and adding three parts of strong sulphuric acid. This affords an amusing experiment. The gas is disengaged in small bubbles, which cover the whole surface of the fluid, and take fire on reaching the air; these are succeeded by others, and a well of fire is produced. (Davy.)

In preparing this gas from phosphorus and solution of potash, for exhibiting its spontaneous accension, both the body and neck of the retort should be entirely filled with the solution, which Dr. Coxe, of Philadelphia, recommends to be almost boiling hot. He employs a retort holding from half a pint to a pint; and after introducing both the phosphorus and the solution, fixes its neck on an inclined plane formed of a block of wood, the upper extremity of which is overhung by the body of the retort, while its mouth projects over the lower

end, and is dipped into a small bowl filled with a hot solution of potash, as represented in the figure. The gas, extricated



by the flame of a lamp, accumulates; and, forcing the alkaline solution down the neck, at length escapes, through the hot solution in the bowl, into the air, where it inflames. Should the heat slacken, and an absorption ensue, nothing passes into the retort but the hot solution of alkali from the bowl; and this, as the retort is secured from being displaced, does no harm. In this way, a torrent of gas may be kept up, as long as there remains sufficient of the solution in the retort; and all danger of breaking the retort is avoided.

II. The properties of this gas are the following:

(a) It takes fire immediately on coming into contact with the atmosphere. This may be shown by letting it escape into the air, as it issues from the retort, when a very beautiful appearance will ensue. A circular dense white smoke rises in the form of a horizontal ring, which enlarges its diameter as it ascends, and forms a kind of corona. The gas produces also a flash of light, when admitted into the best vacuum that can be made by an air pump.

(b) When mixed suddenly with oxygen gas, it detonates. One measure requires  $1\frac{1}{2}$  of oxygen for complete saturation; and the product is phosphoric acid. It may also be combined with an equal volume of oxygen, and the product is then phosphorous acid. This experiment should be made cautiously, and in small quantity. But in a tube only three-tenths of an inch in diameter, the mixture does not detonate.

(c) The same phenomenon ensues on mixing it with chlorine gas, or with nitrous oxide. Three volumes of chlorine are condensed by one of bi-phosphureted hydrogen; and the products are muriatic acid and per-chloride of phosphorus.

When 1 vol. of bi-phosphureted hydrogen is mixed with 3 of nitrous oxide, and an electric spark passed through the mixture, there remain after detonation 3 vols. of nitrogen. Hence the phosphureted hydrogen has in this case combined with  $1\frac{1}{3}$  volume of oxygen.

When fired with a similar proportion of nitrous gas, there remains only  $1\frac{1}{2}$  volume of nitrogen; and as nitrous gas contains half its bulk of oxygen, the bi-phosphureted hydrogen must have combined with  $1\frac{1}{2}$  volume of oxygen as before.

When mingled with any of these gases, it should be passed up by not more than a bubble or two at once.

(d) Sulphurous acid and bi-phosphureted hydrogen gases, when mingled together, mutually decompose each other.

(e) It deposits phosphorus, by standing, on the inner surface of the receiver, and loses its property of spontaneous accension, its volume remaining the same. It is, also, decomposed by electricity, without any change of volume.

(f) Its specific gravity is very variable. Sir H. Davy has obtained it, from phosphorus and alkaline lixivium, of all specific gravities from .400 to .700; Mr. Dalton states it at .850, air being 1.000, and Dr. Thomson at .902.2. The quantity absorbed by water is fixed by the former at  $\frac{1}{4}$  its bulk, and by the latter at  $\frac{1}{7}$ . Dr. Thomson makes it  $\frac{1}{5}$ .

(g) Two measures of the gas heated with potassium become three, and phosphuret of potassium is formed.

(h) When iodine is heated in bi-phosphureted hydrogen, iodide of phosphorus, and probably hydriodic acid, are formed.

From all that is known respecting this variety of phosphureted hydrogen, it may be inferred to consist of 1 atom of hydrogen + 1 atom of phosphorus; and the weight of its atom will be represented by 13.

We have, therefore, two compounds of phosphorus and hydrogen, viz.

Phosphureted hydr., or } = { 2 vols. of hydr. } condensed  
Bi-hydroguret of phosp. } = { 1 vol. of phosp. } into 1 vol.

Bi-phosphureted hydr., or } = { 1 vol. of hydr. } condensed  
Hydroguret of phosp. } = { 1 vol. of phosp. } into 1 vol.

And if the specific gravity of the vapour of phosphorus be



correctly assumed at 0.8328, and that of hydrogen at 0.0690, it is easy to estimate what should be the specific gravity of both those gases in a pure state. As the first gas consists of 1 atom of phosphorus + 2 of hydrogen; and the second of 1 of phosphorus + 1 of hydrogen, it must be admitted that the names bi-hydroguret, proposed by Dr. Thomson for the first, and hydroguret for the second, are more appropriate than those which have hitherto been in use.

The existence of different varieties of phosphureted hydrogen has, however, been denied by Mr. Dalton, whose experiments have led him to the conclusion, that the apparent diversities of composition are occasioned by the admixture of various proportions of free hydrogen and phosphureted hydrogen. These two gases admit, he finds, of separation by liquid chloride of lime, which absorbs the phosphureted hydrogen, and not simple hydrogen.

One volume of phosphureted hydrogen, in a pure state, requires, according to Dalton, two volumes of oxygen for saturation. When electrified *per se*, it is expanded one-third of its volume. It is absorbed by eight times its bulk of water. When two parts are mixed with five of nitrous gas, and an electric spark is passed through the mixture, a brilliant explosion takes place; and the results are phosphoric acid and water, and nitrogen gas, less in bulk by 2 or 3 per cent. than half the volume of the nitrous gas.\*



#### SECTION IV.

##### *Hydrogen with Sulphur.*

##### *Sulphureted Hydrogen Gas.*

SULPHURETED hydrogen gas, though known to Rouelle, was first investigated by Scheele in 1777; and afterwards by Bergman, Kirwan, Berthollet, Chaussier, Davy, and Gay Lussac and Thenard. It may be formed by repeatedly subliming sulphur in hydrogen gas; but this process is of little

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\* Thomson's Annals, xi. 7.

use, except to prove its nature by direct synthesis, for it is impossible thus to convert nearly the whole of any quantity of hydrogen into the compound gas. For the purposes of experiment, it may be procured by any one of the following methods; but the fifth is, perhaps, on the whole, the best.

1. By the action of diluted sulphuric acid on sulphuret of iron, prepared in the following manner. A bar of iron is to be heated to a white or welding heat in a smith's forge, and, in this state, is to be rubbed with a roll of sulphur. The metal and sulphur unite, and form a liquid compound, which falls down in drops. These soon congeal; and the compound must be preserved in a well-closed phial.

The sulphuret, prepared by melting iron filings with sulphur in a crucible, does not answer the purpose equally well, because the gas, which it affords, is mixed with a good deal of hydrogen gas.

2. Gay Lussac prepares sulphuret of iron, by introducing into a matrass two parts by weight of iron filings and one of flowers of sulphur. To these, water is added in sufficient quantity to give a thickish consistence; and the matrass is heated a little, to favour the combination, which is indicated by a copious disengagement of heat, and by the whole mass assuming a black colour. From this compound, sulphuric acid, diluted with four times its volume of water, separates sulphureted hydrogen in great abundance. It is better to prepare the compound when wanted, than to keep it ready made, because, unless very carefully preserved from contact with the air, it becomes less fit for the purpose of affording gas.\*

4. The sulphuret of potash, if prepared by boiling flowers of sulphur with liquid potash quite free from carbonic acid, gives pure sulphureted hydrogen, when acted upon by diluted sulphuric or muriatic acid.

5. To a mixture of powdered sulphuret of antimony (crude antimony of the shops) with 5 or 6 times its weight of muriatic acid (sp. gr. 1.160 or thereabouts) contained in a retort or gas bottle, apply the heat of a lamp. Sulphureted hydrogen will be disengaged in great abundance.

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\* Ann. de Chim. et Phys. vii. 314.

Whichever of these processes be followed, it is advisable, as the gas is absorbed quickly by standing over water, to receive it into bottles provided with glass stoppers, and after filling them entirely with the gas, to introduce the stopper.

II. Its properties are the following:

(a) Its smell is extremely offensive, resembling that of putrefying eggs, or of the washings of a gun barrel, to which indeed it imparts their offensive odour.

(b) It appears to be one of the most unrespirable of all the gases, for a small bird died immediately in air containing only  $\frac{1}{1500}$  of its volume of sulphureted hydrogen; a dog perished in air mingled with  $\frac{1}{800}$ ; and a horse in air containing  $\frac{1}{450}$ . (Thenard, i. 723.)

(c) It is inflammable, and burns either silently or with an explosion, according as it is previously mixed, or not, with oxygen gas or atmospheric air. During this combustion, water results from the union of the hydrogen with the oxygen, and sulphurous acid, with a little sulphuric acid, from that of the oxygen and sulphur. Two measures require three of oxygen gas, one measure of which saturates the hydrogen, and two the sulphur.

(d) It tarnishes silver, mercury, and other polished metals, and instantly blackens white paint and solution of acetate of lead. By direct experiments, I have found that one measure of this gas, mixed with 20,000 measures of hydrogen, or of carburated hydrogen, or common air, produces a sensible discoloration of white lead, or of oxide of bismuth, mixed with water and spread upon a piece of card. In this way we may ascertain the presence in coal gas of extremely small quantities of sulphureted hydrogen; and may even form a tolerable estimate of its proportion, when too minute to be otherwise measured, by comparing the shade of colour, with a series that has been prepared for the purpose, by exposing slips of card covered with white lead and water to mixtures of sulphureted hydrogen and common air in known proportions.

(e) Sulphureted hydrogen is absorbed by water, which takes up its own bulk, or according to Saussure twice and a half, or to Gay Lussac, three times, its bulk of the gas; but in order to obtain so considerable an absorption, the gas, submitted

to experiment, should be perfectly free from common hydrogen. Water thus saturated acquires the peculiar smell of the gas. It is this gas which gives to the Harrogate, and some other natural waters, their disagreeable odour. Liquid muriatic acid absorbs at least three times its volume of the gas; and sulphuric acid, diluted with an equal weight of water, once and a half its volume.

(f) Water, saturated with this gas, reddens the infusion of violets, in this respect producing the effect of an acid. From this and other properties, some of the German chemists have proposed for it the name of *hydrothionic acid*; and Gay Lussac has given it the very objectionable name of *hydro-sulphuric acid*, a term which would be much more properly applied to liquid sulphuric acid.

(g) Water impregnated with sulphureted hydrogen, when exposed to the atmosphere, becomes covered with a pellicle of sulphur. Sulphur is even deposited when the water is kept in well-closed bottles.

(h) On the addition of a few drops of nitric or nitrous acid to the watery solution, sulphur is instantly precipitated. In this case the oxygen of the acid combines with the hydrogen of the gas, and the sulphur is separated. The gas itself, also, is decomposed when transmitted through sulphuric, nitric, or arsenic acids.\*

(i) Sulphureted hydrogen is decomposed by mixture with chlorine, which seizes the hydrogen, and sulphur is precipitated. Vogel obtained, also, a liquid, analogous to the chloride of sulphur of Dr. Thomson. Iodine decomposes it, and hydriodic acid is formed.

(k) It is decomposed, also, when long kept in a state of mixture with atmospheric air, the oxygen of which combines with the hydrogen, and forms water, while the sulphur is precipitated.

(l) A succession of electric explosions throws down sulphur from it, and the volume of the gas remains unaltered. A similar effect is produced by passing it through an ignited porcelain tube, but it cannot in this way be entirely decomposed. Its

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\* Journ. of Science, &c. ii. 152.

elements are also disunited by exciting vivid ignition, by voltaic electricity, in platina wires surrounded by it; sulphur is deposited, and an equal volume of hydrogen remains.

(m) It is decomposed when passed over ignited charcoal, and is converted into carbureted hydrogen gas.

(n) Sulphureted hydrogen, both in the state of a gas and of watery impregnation, precipitates all metallic solutions, excepting those of iron, nickel, cobalt, manganese, titanium, and molybdenum.

(o) It is copiously absorbed by alkalies, and by all the earths, excepting alumina and zirconia. This property affords a ready method of ascertaining its purity, for if it be agitated with a solution of potash by means of the apparatus represented fig. 20 or 21, the unabsorbed residue will show the amount of the impurity, which is commonly hydrogen gas. Its alkaline and earthy combinations are termed hydro-sulphurets. It unites with an equal volume of ammoniacal gas, or, if transmitted through the watery solution of that gas, it is rapidly absorbed, and the compound, which is very useful as a chemical test, has a yellow colour and a strong smell of sulphureted hydrogen.

(p) When three volumes of sulphureted hydrogen gas, and two volumes of sulphurous acid gas, both dry, are mixed together over mercury, they are entirely condensed into a solid body, which adheres firmly to the inside of the vessel. This substance is of an orange yellow colour. Its taste is acid and hot, and it leaves a permanent impression on the mouth. When perfectly dry it does not change litmus paper; but reddens it immediately when moistened. Water, alcohol, nitric acid, and sulphuric acid, decompose it, and disengage sulphur. It does not precipitate the watery solution of barytes. It is decomposed at a moderate heat, and pure sulphur remains. Dr. Thomson, who discovered this compound, considers it as an acid, and terms it *hydro-sulphurous acid*. He states it to be constituted of 5 atoms of sulphur + 4 atoms of oxygen + 3 atoms of hydrogen. (Ann. of Phil. xii. 441.)

(q) When potassium or sodium is made to act on sulphureted hydrogen gas, a brilliant combustion takes place; a quantity of hydrogen gas is evolved, precisely equivalent to that which the same weight of metal would have separated

from water; the metal loses its lustre, and becomes greyish, or amber coloured, or reddish; and by the action of diluted muriatic acid, the whole of the sulphureted hydrogen is recovered. This experiment proves, that sulphureted hydrogen, and consequently sulphur, contain no oxygen; for, in that case, the potassium, having had its affinity for oxygen partly satisfied, would not, after being acted on by the gas, evolve the original quantity of sulphureted hydrogen from water. All that appears to take place, during the combustion, is the combination of the metal with sulphur, the liberation of hydrogen, and the formation of a sulphuret of potassium or sodium, which disengages from water exactly as much hydrogen, as would have been evolved by the metal in its separate state, and this hydrogen, while in a nascent state, re-dissolves the sulphur. The results of Sir H. Davy, which are somewhat different from these, are satisfactorily explained by Gay Lussac and Thenard.\*

(r) The specific gravity of sulphureted hydrogen gas has been variously stated. Mr. Kirwan found 100 cubic inches, at 60° Fahrenheit, and 30 inches barometer, to weigh 34.286 grains, which makes its specific gravity 1.124. Sir H. Davy states the weight of the same quantity at 36.5 grains, and its specific gravity, therefore, at 1.196. Gay Lussac and Thenard determined its specific gravity to be 1.1912 by experiment, or 1.1768 by calculation; and 100 cubic inches, according to the first of those two numbers, should weigh 36.33 grains.

The latest attempt to ascertain its specific gravity, is that of Dr. Thomson, the result of which was 1.1788, or, more correctly, he conceives, 1.180. Hence, 100 cubic inches (bar. 30, therm. 60°) would weigh 35.89 grains. To determine its composition, therefore, we have only to subtract the specific gravity of hydrogen from that of the compound gas, and the remainder will show the weight of the sulphur. Thus

Sp. grav. of sulphureted hydrogen gas.....	1.180
_____ of hydrogen gas .....	0.069
	1.111

\* Recherches, i. 202.

† 81 Ann. de Chim. 26.

It is constituted, therefore, of 1 volume of the vapour of sulphur = 1 atom (1.111) + 1 vol. of hydrogen gas = 1 atom (0.069.) But the numbers 0.069 and 1.111 are in the proportion very nearly of 1 to 16, which gives exactly the same relative weight for the ultimate particle of sulphur, as that deduced from the composition of sulphuric acid.

*Bi-sulphureted Hydrogen.*

This compound was discovered by Scheele, and afterwards examined by Berthollet (Ann. de Chim. tom. xxv.) It is obtained when hydro-sulphuret of potash (formed by boiling flowers of sulphur with liquid potash) is poured, by little and little, into muriatic acid. A very small portion only of gas escapes; and while the greater part of the sulphur separates, one portion of it combines with the sulphureted hydrogen; assumes the appearance of an oil; and is deposited at the bottom of the vessel. Or, dissolve sulphur in a boiling solution of pure potash; and into a phial, containing about  $\frac{1}{3}$ d its capacity of muriatic acid, of the specific gravity 1.07, pour about an equal bulk of the liquid compound. Cork the phial, and shake it; the hydrogureted sulphur gradually settles to the bottom in the form of a brown, viscid, semifluid mass. Its properties are the following:

1. Its taste and smell resemble those of putrid eggs, but are less offensive. Its precise specific gravity is unknown, but it is heavier than water, and descends through it. It is inflammable, and burns in the air with a smell of sulphurous acid.

2. If gently heated, sulphureted hydrogen gas exhales from it; the bi-sulphuret loses its fluidity; and a residue is left, consisting merely of sulphur.

3. It combines with alkalies and earths; and forms with them a class of substances called hydrogureted sulphurets.

4. It is constituted, according to Mr. Dalton, of two atoms of sulphur = 32, with one atom of hydrogen, and is represented by the number 33. It consists per cent. of

Sulphur . . . . .	96.75
Hydrogen . . . . .	3.25
	100.

There are, therefore, three distinct combinations of sulphur and its compounds with alkalies and earths. The first consist, simply, of sulphur, united with an alkaline or earthy base, and are properly called *sulphurets*. The second are composed of sulphureted hydrogen, united with a base, and are called *hydro-sulphurets*. The third contain bi-sulphureted hydrogen, attached to a base, and constitute *hydrogureted sulphurets*.

The pure sulphurets can exist, as such, only in a dry state; for the moment they begin to dissolve in water, a decomposition of that fluid commences; sulphureted hydrogen is formed; and of this a part is disengaged, while another part, uniting with an additional proportion of sulphur, composes bi-sulphureted hydrogen. This last, uniting with the base, forms an hydrogureted sulphuret. At the same time, it has been stated by Berthollet,\* sulphuric acid is composed, by the action of the sulphur on the oxygen of the water. This, however, Gay Lussac has shown, takes place only when the sulphuret has been formed at an unnecessary degree of heat, and that when carefully prepared, at a heat below redness, the solution of an alkaline sulphuret in water contains sulphurous and hypo-sulphurous acids, but no sulphuric acid.† The sulphurets, also, being partly changed, by solution, into hydrogureted sulphurets, the affusion of an acid throws down a quantity of sulphur. A distinguishing character, also, of solutions of this kind, is, that sulphur is precipitated by passing through them sulphureted hydrogen gas.

According to Proust, if red oxide of mercury be added to solutions of the kind which have just been described, the sulphureted hydrogen is removed, and what remains is a pure liquid sulphuret, from which acids precipitate sulphur only, without any effervescence.

II. The hydrogureted sulphurets are also formed by boiling, along with a sufficient quantity of water, the alkaline, or earthy base, with flowers of sulphur. Thus a solution of pure potash, pure soda, or of baryta or strontia, may be

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\* Ann. de Chim. xxv. 239, 269.

† 6 Ann. de Chim. et Phys. 322.



changed into an hydrogureted sulphuret. To prepare the compound with base of lime, the powdered earth, mixed with sulphur, may be boiled with a proper quantity of water, and the solution filtered or cleared by subsidence. One hundred grains of lime, or 134 of hydrate, dissolve about 215 of sulphur, and afford a liquid of 1.146 specific gravity.

Another method of forming, by a very simple process, the hydrogureted sulphurets, consists in digesting, in a gentle heat, a hydro-sulphuret with powdered sulphur, an additional portion of which is thus dissolved, while part of the sulphureted hydrogen escapes.

Hydrogureted sulphurets have the following properties :

1. They have a deep greenish yellow colour ; an acrid and intensely bitter taste ; and an excessively offensive smell.

2. They deposit sulphur when kept in close vessels ; become much more transparent and lighter coloured ; and less offensive to the smell.

3. They rapidly absorb oxygen from the atmosphere, and from oxygen gas. Hence their employment in eudiometry.\*

4. On the addition of dilute sulphuric, or muriatic, or of certain other acids, they are decomposed. Sulphureted hydrogen gas is evolved, and sulphur is precipitated.

5. When boiled in contact with filings of silver or of copper, and of those metals only, Vauquelin found that they lose their excess of sulphur, and become simple hydro-sulphurets.



## SECTION V.

### *Hydrogen with Selenium.—Selenureted Hydrogen Gas.*

BERZELIUS, by fusing together potassium and selenium, and adding water to the fused mass, obtained a hydro-selenuret of potash of a deep ale colour. By pouring diluted muriatic

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\* See page 289.

acid on the concentrated solution of this compound, a gas is disengaged, which has the following properties.\*

It has a smell resembling that of sulphureted hydrogen. It is absorbed to a considerable amount by water, which acquires no colour, but after some minutes becomes slightly opalescent, and deposits a little selenium. The solution has an hepatic taste, reddens litmus paper, and gives a permanent brown stain to the skin. Exposed to the air, it is gradually but completely decomposed. It precipitates all metallic solutions when neutral, even those of zinc and iron, generally of a brown or black colour.

This gas produces violent effects on the organs of respiration, and a sharp and painful sensation in the nose, which is followed by the loss, for a time, of the sense of smelling. A small bubble not larger than a pea, when let up into the nostrils, beside the immediate effects which have been described, produced a mucous discharge which continued 15 days.

To determine its composition, it was transmitted through a solution of acetate of silver, when a selenuret of silver was formed, from the known composition of which Berzelius deduces the composition of this gas to be

Selenium . . . . .	97.4	....	1 atom	....	41
Hydrogen . . . . .	2.6	....	1 do.	....	1
	100.				42

This determination of the equivalent of selenium does not essentially differ from that deducible from the composition of selenic acid.

Selenium agrees then with sulphur and with tellurium, in affording a weak acid when united with hydrogen; an acid which, in all three cases, forms salts with those oxides only whose radicals have a stronger affinity for oxygen than hydrogen has; while it reduces all other oxides, and forms compounds of their respective metals with selenium.

† Ann. of Phil. xiv. 100.

## SECTION VI.

*Nitrogen with Carbon.*ART. 1.—*Carburet of Nitrogen, or Cyanogen.*

CYANOGEN was discovered by Gay Lussac in 1815, in the course of his researches into the properties of the compound, then called *prussiate of mercury*. Its properties have since also been investigated by Vauquelin.

To obtain cyanogen, it is necessary first to boil fine powdered red oxide of mercury with twice its weight of prussian blue and a sufficient quantity of water. The compound is perfectly neutral, and crystallizes in long four-sided prisms truncated obliquely. It still, however, contains a little iron, which may be separated by digesting the liquor, before evaporation, with a little more of the oxide of mercury, and saturating the excess of this oxide with a little prussic acid, or even with a little diluted muriatic acid. The prussiate of mercury, thus obtained neutral and crystallized, must be carefully and completely dried at a temperature below that of boiling water, and then exposed to heat in a small glass retort, or in a tube closed at one extremity. It first blackens, then liquefies, and the cyanogen comes over in the form of a gas, which may be collected over mercury. In the retort there remains a charry matter of the colour of soot, and as light as lamp black.\*

1. Cyanogen is a true gas, or permanently elastic fluid. Its smell is strong, penetrating, and disagreeable. It burns with a bluish flame mixed with purple. Its specific gravity is to that of common air as 1.8064 to 1. Hence 100 cubic inches at 60° Fahr. weigh 55 grains.

2. Water at the temperature of 60° Fahr. absorbs almost  $4\frac{1}{2}$  times its volume, and pure alcohol 23 times its volume. The watery solution reddens litmus; this, however, is scarcely to be considered as an effect of cyanogen, but of the products

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\* Gay Lussac, *Ann. de Chim.* vol. xcv.; or Thomson's *Annals*, viii. 37.

to which it gives rise by the decomposition of water. (Vauquelin in Ann. of Phil. xiii. 430.)

3. When 100 measures of cyanogen are detonated, in a Volta's eudiometer, with 250 measures of oxygen gas, 200 measures of carbonic acid result, and 100 measures of nitrogen. There remain, also, 50 measures of oxygen gas uncondensed. From these data, it is calculated by Gay Lussac, that cyanogen is composed of two volumes of the vapour of charcoal and one volume of nitrogen, condensed into a single volume. Its density ought, therefore, to be  $0.9722 + 0.832 = 1.8042$ , a number not very remote from that obtained by experiment.

4. Analysis by more complicated methods affords the same result, coinciding with that in which cyanogen yields, by a decomposition effected by means of oxygen, twice its volume of carbonic acid and an equal volume of nitrogen. No water whatsoever is formed during its combustion, if the gas be perfectly free from prussic acid vapour, a sufficient proof of the absence of hydrogen from the composition of cyanogen.

5. Phosphorus, sulphur, and iodine, may be sublimed in it without producing any change; but when heated in contact with cyanide of mercury, compounds of those bodies with cyanogen are formed. (Davy, Journ. of Science, vol. i.)

6. The solutions of pure alkalis and alkaline earths absorb cyanogen; and the liquid obtained, when poured into a solution of black oxide of iron, affords prussian blue, but not without the addition of an acid. At the same time, carbonic acid gas escapes, in volume equivalent to the cyanogen absorbed, and there is a perceptible smell of prussic acid. These changes will be more evident from the following recapitulation:

$$1 \text{ vol. of } \left\{ \begin{array}{l} = 2 \text{ vol. char-} \\ \text{cyanogen} \left\{ \begin{array}{l} \text{coal and 1 vol.} \\ \text{nitrogen.} \end{array} \right. \end{array} \right\} 1 \text{ atom of } \left\{ \begin{array}{l} = 1 \text{ vol. oxygen} \\ \text{and 2 vol. hy-} \\ \text{water.} \quad \quad \quad \text{drogen.} \end{array} \right.$$

One volume of charcoal, uniting with one volume of oxygen, forms one volume of carbonic acid; the remaining volume of charcoal, uniting with half a volume of nitrogen and half a volume of hydrogen, composes prussic acid; and the residuary

half volume of nitrogen and  $1\frac{1}{2}$  volume of hydrogen compose together one volume of ammonia.

7. It will afterwards be shown, that when to two volumes of charcoal and one volume of nitrogen, together constituting cyanogen, one volume of hydrogen is joined, and the whole four volumes are condensed into two, we obtain *prussic* or *hydro-cyanic acid*. Cyanogen agrees then with chlorine and iodine, in being acidifiable by union with hydrogen. Hence its compounds with metallic bases have been called by Gay Lussac *cyanures*, as those of chlorine are called *chlorures*; but having elsewhere expressed a preference for the name of *chlorides*, I shall, from analogy, give to the compounds of cyanogen the name of *cyanides*.

ART. 2.—*Hydro-cyanic or Prussic Acid.*

From the *prussiate*, or more correctly *cyanide of mercury*, which has been already described, hydro-cyanic acid may be obtained by distillation with muriatic acid, taking care to employ a proportion of the latter which is not sufficient to saturate the metallic base of the salt. The neck of the retort must be prolonged, for about two feet, by a glass tube of at least half an inch bore placed horizontally, and containing in the  $\frac{1}{3}$ d next the retort, small pieces of white marble, in the other  $\frac{2}{3}$ ds fused chloride of calcium. To the end of this tube a small receiver must be luted, and be kept cool by a freezing mixture. Hydro-cyanic acid, along with muriatic acid and watery vapour, will be disengaged on gently heating the retort, the two last of which will be condensed by the materials in the tube, while the first, by successively heating the different parts of the tube, may be driven onwards to the receiver.

On repeating this process, Vauquelin found the product of hydro-cyanic acid so extremely small, that he was induced to seek for a better method of obtaining it. He succeeded by passing a current of sulphureted hydrogen gas, disengaged from sulphuret of iron and sulphuric acid, very slowly, through a glass tube slightly heated and filled with cyanide of mercury, its extremity ending in a receiver which was kept cool by a mixture of snow and salt. The process was

carried on till the smell of sulphureted hydrogen, which for a long time could not be perceived, was discovered in the receiver. The hydro-cyanic acid amounted in weight to  $\frac{1}{3}$ th the cyanide of mercury. To avoid any inconvenience from the process being carried too far, some carbonate of lead was placed at the end of the tube next the receiver, in order to absorb the sulphureted hydrogen that might pass undecomposed.

The hydro-cyanic acid is subject to spontaneous decomposition, and the more so the greater its state of concentration. For medical use, into which it has been of late years introduced, it may be obtained by dissolving 60 grains of cyanide of mercury in each ounce of water, and passing a current of sulphureted hydrogen gas through the solution, till the liquid contains a slight excess of it, which may be separated by a little carbonate of lead; after which the fluid may be filtered.

The process adopted at Apothecaries' Hall, London, is the following. One pound of cyanide of mercury is put into a tubulated retort with six pints of water and one pound of muriatic acid, sp. gr. 1.15; a capacious receiver is luted to the retort; and six pints are distilled over. The specific gravity of the product is 0.995; it must be preserved in bottles excluded from the light, and being subject to decomposition should not be long kept. (Brande's Manual, i. 140.) The specific gravity of the acid is considered by Dr. Ure as an inadequate test of its strength; and he recommends the following as a more simple method of analysis. "To 100 grains, or any other convenient quantity, of the acid, contained in a small vial, add, in succession, small quantities of the peroxide of mercury in fine powder, till it ceases to be dissolved on agitation. The weight of the oxide taken up, being divided by four, gives a quotient representing the quantity of real prussic acid present. By weighing out beforehand on a watch glass 40 or 50 grains of the peroxide, the residual weight of it shows at once the quantity expended." (Quarterly Journal, xiii. 312.)

Concentrated hydro-cyanic acid, prepared by the process of Gay Lussac or Vauquelin, is a limpid and colourless fluid.

It acts as a quick and virulent poison. It has a great tendency to decompose by keeping. Its taste is at first cool, but soon becomes hot and acrid. Though rectified from chalk, it still reddens litmus paper slightly. Its specific gravity at  $45^{\circ}$  Fahr. is .7058. It is highly volatile, and boils at  $79^{\circ}$  Fahr.; at  $68^{\circ}$  it supports a column of mercury of very nearly 15 inches; and it increases, five fold, the bulk of any gas with which it is mixed. It congeals at the temperature produced by snow and salt, and liquefies at  $5^{\circ}$  Fahr. A drop of it placed on paper becomes solid instantly, because the cold, produced by the evaporation of one portion, reduces the temperature of the remainder below its freezing point. Liquid hydro-cyanic acid forms prussian blue directly, both with iron and its oxide, and without the presence of either acid or alkali. The explanation of this fact will be given hereafter. It does not prove, as Vauquelin supposes, that prussian blue is a hydro-cyanate of iron.

Hydro-cyanic acid may also be collected in a gaseous form over mercury, by heating in a retort the crystallized ferrocyanate of potash with dilute sulphuric acid. This gas is absorbable by water and alcohol. It is speedily fatal when received into the lungs of small animals. At a temperature between  $86^{\circ}$  and  $95^{\circ}$  Fahr., the acid gas forms with oxygen gas a mixture which detonates on passing an electric spark. A quantity equal to 100 measures condense 125 measures of oxygen, and there result 100 measures of carbonic acid and 50 measures of nitrogen. But as the carbonic acid contains only its own volume of oxygen, there remain 25 measures of the latter gas which must have been converted into water by 50 measures of hydrogen existing in the prussic acid vapour. From these and other facts, Gay Lussac infers that it is composed of one volume of the vapour of charcoal, half a volume of hydrogen, and half a volume of nitrogen, condensed into one volume.

When potassium is heated in hydro-cyanic vapour, it evolves hydrogen gas equal to half the volume of the vapour. The other elements of the gas unite with the potassium. Thus the hydro-cyanic acid is resolved into hydrogen and cyanogen, which last, uniting with the potassium, forms a cyanide of that metal. As hydro-cyanic acid is constituted of equal volumes of those two gases, united without condensation, the

specific gravity of the acid gas ought to be the mean of those of its component, viz. 0.9360 very nearly. This differs very little from the result of experiments, viz. 0.9476. Its constituents, therefore, are by weight,

Cyanogen .....	100
Hydrogen .....	3.846

or two atoms of charcoal = 12, + 1 of nitrogen = 14, + 1 of hydrogen; and its equivalent number is 27.

The salts formed by the union of this acid with salifiable bases are called *hydro-cyanates*, but they are not permanent, and have no useful properties. They are decomposed by the weakest acids, such as the carbonic.

*Hydro-cyanate of ammonia* crystallizes in cubes or in very small prisms. Its volatility is such that at a temperature of 72° Fahr. its vapour supports a column of upwards of 15 inches of mercury; and at 97° Fahr. it is equal to the pressure of the atmosphere. Dr. Thomson finds that when prussian blue is exposed to a red heat in a copper tube, and the products received over mercury, the glass receiver is coated with transparent crystals of this salt. The solution of this salt precipitates several metallic solutions not affected by hydro-cyanic acid, which, according to Scheele, acts only on nitrates of silver and mercury, and on carbonate of iron. (Ann. of Phil. xv. 394.)

#### ART. 3.—*Chloro-cyanic Acid.*

Chloro-cyanic acid was discovered by Berthollet, who found that hydro-cyanic acid, by absorbing chlorine, acquires new properties, and no longer forms a blue precipitate with the solutions of iron. Supposing it to result from the union of oxygen with the prussic acid, he gave to the new compound the name of *oxy-prussic acid*. The nature of this combination has since been investigated by Gay Lussac. To prepare it, a current of chlorine gas may be passed through a solution of hydro-cyanic acid in water, till the liquid discolours the solution of indigo in sulphuric acid. By agitating this liquid with mercury, and by distilling at a gentle heat, an elastic fluid is formed. This, however, is not pure chloro-cyanic acid, for at temperatures from 60° to 70° Fahr., and



under common pressures, that acid can only exist as a liquid. It is a mixture of carbonic acid and chloro-cyanic acids, in proportions not yet determined.

The mixture of carbonic and chloro-cyanic acids is colourless; it has a very penetrating smell, and excites a flow of tears; its density, determined by calculation, is 2.123, air being 1. It reddens litmus, is not inflammable, and does not detonate by passing an electric spark through a mixture of the gas, with twice its volume of hydrogen or of oxygen; but with a mixture of the two, it burns vividly, with the production of a blueish white flame and of an extremely dense white vapour, which has the smell of nitrous gas and the taste of a mercurial salt.

When potassium is heated in the mixed gases, the chloro-cyanic acid is entirely decomposed; the chlorine and cyanogen are absorbed; and the carbonic acid mingled with it undergoes a decomposition more or less complete.

The watery solution of the mixed acids does not precipitate either barytic water or nitrate of silver; but from the latter it produces, after being mixed with potash and then with nitric acid, a precipitate of chloride of silver.

Alcaline solutions absorb it rapidly, but do not destroy its odour, except when they are in excess. These compounds, on the addition of acids, are decomposed; a brisk effervescence arises in consequence of the escape of carbonic acid, water and chloro-cyanic acids are reciprocally decomposed, and muriatic acid and ammonia are generated.

A characteristic property of this acid is, that with the intervention of potash, it forms green precipitates from solutions in which the iron is oxidized to a minimum. The experiment only succeeds when we first add the chloro-cyanic acid to the metallic solution, then a little alkali, and finally a small portion of acid.

According to the analysis of Gay Lussac, this acid is constituted of

1 vol. of gaseous carbon	}	condensed into 1 volume.
$\frac{1}{2}$ a volume of nitrogen . .		
$\frac{1}{3}$ ————— chlorine . .		

In other words 1 vol. of chlorine and 1 vol. of cyanogen produce by combining 2 vols. of chloro-cyanic acid. Hence its density should be the mean of those of its components.

ART. 4.—*Of Sulpho-cyanic Acid.*

This acid was discovered by Mr. Porrett, to whom we are indebted for a number of curious and interesting experiments on all the acids having cyanogen for their base. He gave it the name of *sulphureted chyazic acid*, the term chyazic being compounded of the first letter of carbon, the first syllables of hydrogen and azote, with the usual termination signifying an acid. He considered it as a compound of sulphur with hydrocyanic acid, but since the researches of Gay Lussac, it may rather be regarded as a compound of sulphur with cyanogen.

The original process of Mr. Porrett is somewhat complicated and tedious. The following method was contrived by Grotthus, and improved by Vogcl. Mix equal weights of pulverised ferro-cyanate (commonly called prussiate) of potash and flowers of sulphur, and expose the mixture in a flask to a heat sufficient to melt the sulphur, keeping it melted for several hours. When cold, reduce the mass to powder, and digest it in water enough to take up every thing soluble. Filter the liquor, and drop into it a sufficient quantity of potash to precipitate any iron that may be held in solution. The liquid, thus prepared, is a solution of sulpho-cyanate of potash in water, and the acid ingredient may be obtained, mixed with water, by distilling it with sulphuric acid.

Sulpho-cyanic acid, thus obtained, is a transparent liquid, colourless, or with a slight pinkish hue, with an odour as strong as, and somewhat resembling, that of acetic acid. The strongest obtained by Mr. Porrett had the specific gravity 1.022. It dissolves a little more sulphur at a boiling temperature; but most of this is separated again on cooling. In this state it throws down oxide of silver from the nitrate of a dark colour; but otherwise the precipitate is white.

Sulpho-cyanic acid boils at  $216\frac{1}{2}^{\circ}$ ; and at  $54\frac{1}{2}^{\circ}$  crystallizes in six-sided prisms. When thrown into a red hot platinum crucible, sulphur is disengaged, and a blue flame is produced.

It is partially decomposed by being transmitted through a red-hot porcelain tube; and if brought into contact with ignited iron turnings, sulphuret of iron is formed, and hydro-cyanic acid and sulphureted hydrogen disengaged.

By a sufficient quantity of chlorine, the whole of the sulphur is converted into sulphuric acid, and hydro-cyanic acid is disengaged. Iodine produces a similar effect.

With protoxide of copper, it affords a white insoluble sulpho-cyanate. From the analysis of this salt, Mr. Porrett drew his inference respecting the composition of the acid, which he conceived to consist of one third by weight of the elements of hydro-cyanic acid, and two thirds of sulphur. According to Dr. Thomson (System, 6th edit. ii. 306.) it is constituted of

2 atoms of sulphur .....	32
2 atoms of charcoal .....	12
1 atom of nitrogen .....	14
1 atom of hydrogen .....	1
	—

Hence its equivalent number is ..... 57

It is capable of uniting with salifiable bases, and composes a genus of salts called *sulpho-cyanates*. Many of these have been investigated by Mr. Porrett.

#### ART. 5. — *Ferro-cyanic Acid.*

The ferro-cyanic acid may be prepared by the following process: dissolve in cold water any quantity of the salt called triple prussiate (ferro-cyanate) of baryta, and for every ten grains so dissolved add a quantity of sulphuric acid equivalent to 2.53 grains of real acid; stir the mixture; and set it aside for some time. The baryta and sulphuric acid are precipitated in combination; and the ferro-cyanic acid may be decanted for use. Its characters are the following:

It has a pale lemon yellow colour; has no smell; and is not poisonous in small quantities. It is decomposed by a gentle heat, or by exposure to a strong light, in which case hydro-cyanic acid is formed, and also white triple prussiate of

iron, which, by absorbing oxygen, becomes prussian blue. With alkalies, earths, and metallic oxides, it forms directly the salts called *triple prussiates*. It displaces acetic acid from all its combinations, and also detaches, from other acids, those bases, with which it is susceptible of forming compounds that are insoluble in acids. Being decomposable by heat, it can never be obtained by distillation. In that case, hydro-cyanic acid and hydro-cyanate of iron are formed. Mr. Porrett has also pointed out a method of obtaining ferro-cyanic acid in a crystallized form. Dissolve 58 grains of crystallized tartaric acid in alcohol, and 50 grains of ferro-cyanate of potash in as little warm water as possible. Mix the two liquids. Bi-tartrate of potash is precipitated, and the ferro-cyanic acid remains in solution. By spontaneous evaporation, it crystallizes in small yellow cubes, which, on exposure to the light, lose their regular shape, are decomposed, and become coated with prussian blue. It appears, therefore, that the balance of affinities preserving this acid is very soon disturbed, and its elements easily thrown into new arrangements.

We are indebted to Mr. Porrett for the view, which is most commonly taken, of the nature of the acid entering into the composition of the salts formerly called *prussiates*, or *triple prussiates*. It had generally been supposed that the protoxide of iron, which is always present in these salts, acted the part of a base, with which (as well as with the alkali or earth in the triple compounds) the prussic acid was supposed to be united. Mr. Porrett, however, has rendered it more probable that the oxide is really an element of the acid, and not a base; for he finds that when triple prussiate of soda in solution is exposed to galvanic electricity, the oxide of iron is carried, along with the elements of the prussic acid, to the positive pole, whereas, if it had existed as a base, it would have been determined to the negative pole. He proposed for it the name of *ferrureted chyazic acid*; but I prefer that of ferro-cyanic, which, not necessarily excluding hydrogen from its composition, is still consistent with the new view arising out of Mr. Porrett's researches. This view explains why the iron in triple prussiates (ferro-cyanates) is not discover-

able by the most delicate tests, for it can no more be affected by them, than sulphur can be indicated by its appropriate tests when existing in sulphuric acid.

The precise constitution of ferro-cyanic acid, however, does not appear to have been as yet satisfactorily made out; nor even is it absolutely certain that it contains hydrogen as an essential element. It is possible that it may be a compound, not of hydro-cyanic acid, but of cyanogen, with protoxide of iron: Or the compounds called triple prussiates may be hydro-cyanates with a double base. The greater permanency of these salts than of mere hydro-cyanates, may, as observed by Gay Lussac and Berzelius, (who admit the facts of Mr. Porrett, but dissent from his conclusions) be analogous to what happens in some other cases. Thus alumina, when associated with potash, enters into more energetic union with sulphuric acid, than singly by itself.

According to the latest analysis by Mr. Porrett, ferro-cyanic acid consists of 1 atom of hydro-cyanic acid + 2 atoms of charcoal + 1 atom of metallic iron. M. Robiquet, on the other hand, regards it as compounded of the elements of hydro-cyanic acid and of cyanide of iron, in the same manner as we may conceive alcohol to be formed of water and bi-carbureted hydrogen. (Ann. de Ch. et Phys. xvii. 197.) Berzelius has been led to adopt the opinion, that ferro-cyanic acid is merely a hydro-cyanate of protoxide of iron with excess of acid. In the present state of the enquiry, it seems impossible to determine which of these is the correct view; and a further appeal to experiment must be made, before we can decide respecting the true nature of the ferro-cyanic acid. Its present name may, therefore, be considered as only provisionally adopted, till its constitution is more accurately known.

#### *Nitrogen and Phosphorus.*

The only instance of the combination of nitrogen with phosphorus, is that presented by the solution of a minute portion of phosphorus in the nitrogen gas, remaining after the combustion of that inflammable substance in atmospheric air. By this solution, the nitrogen gas gains an increase of volume of about  $\frac{1}{10}$  th, but is not distinguished by any interesting

properties, and may perhaps indeed be considered rather as a mixture of the vapour of phosphorus with nitrogen gas, than as a true chemical compound.

No combination is known of nitrogen with sulphur or selenium.

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## SECTION VII.

### *Compounds of Phosphorus.*

#### ART. 1.—*Phosphuret of Sulphur.*

PHOSPHORUS is capable of uniting with sulphur in various proportions; but it is probable that the most energetic compound will be obtained by taking the two substances in quantities, indicated by the weights of their atoms, viz. 16 parts of sulphur to 12 of phosphorus. The process requires some caution, to prevent accidents by the explosion of the melted substances; and it is advisable not to operate on more than from 60 to 80 grains of the materials taken together. The combination may be effected either under water or not. In the first case, the phosphorus and sulphur may be put together into a tube containing water, the temperature of which should not exceed from  $140^{\circ}$  to  $160^{\circ}$  Fahr., and the tube may be agitated till the combination has taken place. In the second case, into a tube 4 or 5 inches long, and from 4-10ths to 8-10ths of an inch wide, the phosphorus may be put first, and, when fused by the heat of a lamp, the sulphur may be added at intervals in small fragments. In both cases, sulphureted hydrogen is evolved at the moment of combination.

The phosphuret of sulphur is much more fusible than phosphorus itself, its melting point being about  $41^{\circ}$  Fahr. Hence it is fluid at the average temperature of the atmosphere. It has a reddish brown colour when fresh prepared, but this may be removed by shaking it with a solution of ammonia, and leaving it some hours under that liquid. At common temperatures, it does not act at all on water, nor does it decompose water rapidly even at  $212^{\circ}$  Fahr. A compound, pre-

pared by Mr. Faraday from 5 of sulphur and 7 of phosphorus, did not become solid at 20° Fahr. and was perfectly fluid at 32°. On remaining some weeks under water, it deposited crystals of pure sulphur, and a compound remained that was not so fusible as the original one.\*

ART. 2.—*Phosphuret of Selenium.*

Selenium is speedily dissolved by melted phosphorus, and, if added to saturation, a very fusible compound results, which, when cold, has a dark brown colour, much lustre, and a vitreous fracture. When this compound is digested in water, selenureted hydrogen is formed, which, dissolving in the water, communicates to it a peculiar hepatic odour. The proportions of its constituents are unknown.

SECTION VIII.

*Compounds of Sulphur.*

THE compounds of sulphur with hydrogen having been already described, the only ones that remain are those which sulphur forms with carbon and with selenium.

ART. 1.—*Sulphuret of Carbon, or Alcohol of Sulphur.*

There has been much controversy respecting the nature of this compound; and several contradictory statements have been given of its composition. It was discovered by Lampadius in 1796, and was considered by him as consisting of sulphur and hydrogen. Clément and Desormes were led, by their researches, to deny the presence of the latter element; and to conclude that it is a compound of sulphur and charcoal only. This inference was afterwards controverted by Vauquelin and by Berthollet, jun.; and the experiments of Cluzel also were supposed by their author to be favourable to

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\* Quarterly Journal, iv. 361. See also Pelletier, Ann. de Chim. iv. 10; and Accum and Briggs, Nicholson's Journal, vi. and vii.

the opinion, that it contains hydrogen.\* In a report, however, on the Memoir of Cluzel, MM. Berthollet, sen. Thenard, and Vauquelin, described a set of experiments made by the last mentioned chemist, which led them to believe that the alcohol of sulphur is a true binary compound of sulphur and charcoal only;† and this inference has been proved to be correct, by the subsequent investigation of Berzelius and Marcet.‡

To prepare this substance, a coated earthen tube, of about one inch and a half in diameter, partly filled with small pieces of charcoal, well prepared and quite free from moisture, may be disposed in a furnace, as represented fig. 40, c c, one end being placed higher than the other. To this end may be adapted a glass tube, open at both ends, containing small bits of sulphur; and to the other end, by means of an adapter, is to be fixed a curved tube, passed into water contained in a two-necked bottle. The part of the tube, containing the charcoal, may then be made red-hot; and, when this happens, the bits of sulphur are to be pushed forwards, one by one, by means of a wire, carefully excluding air. As soon as the sulphur comes into contact with the charcoal, bubbles of gas will be produced in great abundance, and a vapour will appear, which will condense, under the water in the bottle, into a liquid, of which, in the course of a day, about half a pint may be procured. This liquid may be purified by redistilling it at a very gentle heat, not exceeding 100° or 110° Fahrenheit; and some dry chloride of calcium may be put into the retort, in order to obtain the fluid perfectly free from water. The liquid which comes over is quite pure, and some sulphur remains in the retort. It may also be obtained by distilling a mixture of ten parts of finely pulverized and perfect charcoal with 50 of native bi-sulphuret of iron, from an earthen retort, into a receiver surrounded by ice or snow. One part of sulphuret of carbon will be obtained from these materials.

The alcohol of sulphur has the following properties:

1. It is eminently transparent, and perfectly colourless.

\* *Ann. de Chim.* lxxiv. 73.

† *Ann. de Chim.* lxxviii. 252.

‡ *Phil. Trans.* 1819.



Sometimes, immediately after distillation, the oily liquid appears a little opaque and milky; but the next day it is found to have become completely limpid. It has an acrid, pungent, and somewhat aromatic taste; its smell is nauseous and fetid, though differing from that of sulphureted hydrogen.

2. Its specific gravity is 1.272; its refractive power, as ascertained by Dr. Wollaston, is 1.645. Its expansive force (at 30 inches barometer, and  $59\frac{1}{2}^{\circ}$  Fahrenheit) is equal to the pressure of 7.36 inches of mercury; so that air, to which it is admitted, will dilate about one-fourth of its volume. It boils briskly under the common atmospheric pressure, at a temperature of  $105^{\circ}$  or  $110^{\circ}$  Fahrenheit. It does not congeal, even at a temperature so low as  $60^{\circ}$  below 0 of Fahrenheit.

3. It is highly inflammable, and takes fire at a temperature scarcely exceeding that at which mercury boils. Its flame is bluish, and it emits copious fumes of sulphurous acid. If a long glass tube, open at both ends, be held over the flame, care being taken to keep the tube quite cool, no moisture whatever is deposited on its inner surface, a sufficient proof of the absence of hydrogen.

4. It is decomposed by contact with chlorine, and chloride of sulphur is obtained.

5. The oily liquid readily dissolves in alcohol and ether, though not in all proportions, and these solutions are decomposed by the addition of water. It readily incorporates with fixed and volatile oils, and rapidly dissolves camphor. It is not soluble in water, but when shaken with it separates again on standing.

6. In its liquid state, it suffers no change on being heated with potassium; but potassium, when heated in its vapour, becomes ignited, and emits a reddish flame. The residue, when washed with water, affords sulphuret of potash and charcoal.

7. It does not tarnish mercury or its amalgams, nor silver, unless it contain more sulphur than is essential to its constitution.

8. The alkalis dissolve it entirely, but very slowly. Of the acids, none exert any sensible action on it.

9. When transmitted over ignited copper or iron turnings, alcohol of sulphur is decomposed, the metal combining both

with charcoal and sulphur; and a rose-coloured fluid is obtained, differing in its sensible qualities from the original liquid, and apparently consisting of the same elements in different proportions. It is decomposed also when brought into contact with ignited per-oxide of iron; sulphuret of iron is formed; and sulphurous and carbonic acids are produced, and may be separated from each other by borax, which absorbs the former only. In this way it may be analyzed, and its proportions calculated.

The proportions of the elements of sulphuret of carbon are deduced by Berthollet, Thenard, and Vauquelin, to be from 14 to 15 parts of charcoal, and from 85 to 86 of sulphur, in 100. This statement of its composition nearly agrees with that determined by Drs. Berzelius and Marcet; *viz.*

Sulphur.....	84.83 ... or ...	100.
Carbon .....	15.17 .....	17.89
	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
	100.	117.89

The above-mentioned numbers establish the proportion of the elements of this compound to be two atoms of sulphur = 32 to one of carbon = 6, and its equivalent number to be 38.

The sulphuret of carbon was found by Berzelius to be capable of uniting with alkaline and earthy bases, and of forming compounds which may be called *Carbo-Sulphurets*. But their properties, and the proportion of their elements, require further investigation.

In a subsequent memoir in the same volume of the Philosophical Transactions, Dr. Marcet describes the extraordinary power of alcohol of sulphur, in producing cold. The bulb of a thermometer being covered with fine lint, and moistened with a few drops of the liquor, the mercury sinks rapidly from 60° to 0; and under the exhausted receiver of an air-pump (the valves of which must, for this purpose, be made of metal, and not of silk) it falls from + 70°, to 70° or even 80° below 0, so that by this process mercury may readily be frozen. It has been found, also, by Mr. Murray, that when a few drops of this liquid are poured on the surface of a glass of water, the temperature of which is 32° Fahr., plumose branches

of ice dart from the sulphuret to the bottom of the vessel, and the whole water is suddenly frozen. At the same time, the sulphuret becomes volatilized; and the spiculæ of ice beautifully exhibit the colours of the solar spectrum. (Ann. of Philos. iii. N. S.)

By the action of a mixture of fuming muriatic acid on sulphuret of carbon, Berzelius obtained a solid white crystalline body, resembling camphor, and possessing some remarkable properties. Its analysis afforded

Muriatic acid.....	48.74
Sulphurous acid .....	29.63
Carbonic acid (and loss).....	21.63
	100.

It appears, therefore, to consist of two atoms of muriatic acid, one of sulphurous acid, and one of carbonic acid.

#### *Sulphuret of Selenium.*

One part of selenium, melted with 100 parts of sulphur, imparts to the sulphur a dirty yellow colour; but the only method of obtaining a sulphuret of selenium of determinate composition is to precipitate a solution of selenic acid by sulphureted hydrogen gas, and to wash the precipitate with a little muriatic acid. A deep orange coloured compound is formed, in which 100 parts by weight of selenium are united with 60.75 sulphur. It is attacked with difficulty by nitric acid, but more readily by nitro-muriatic. It is soluble in the fixed caustic alkalis, as well as in alkaline hydrosulphurets, and gives a solution of a deep orange colour. When heated in the air, it burns at first with the odour of sulphurous acid, then with that of horse-radish.\*

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\* Berzelius, Ann. of Phil. xiv. 109.

## CHAPTER IX.

### OF METALS.

#### *Of the General Properties of Metals.*

THE metals constitute a class of bodies, which are not more interesting from their application to the common arts of life, than from the facts which they contribute to the general principles of chemical science. Only seven or eight were known to the ancients; but the class has been increased to more than five times that number, within the last century. The following appear to have a sufficient claim to be considered as distinct metals.

TABLE OF METALS.

Names of Metals.	Discovered by	Date.	
1. Gold .....	} Known since the remotest antiquity.		
2. Silver .....			
3. Iron .....			
4. Copper .....			
5. Mercury .....			
6. Lead .....			
7. Tin .....			
8. Zinc .....	Known to Paracelsus, who died .....	1541	
9. Bismuth .....	Described by Agricola .....	1520	
10. Antimony ..	Described by Basil Valentine, 15th centy.		
11. Arsenic .....	} Brandt .....	1783	
12. Cobalt .....			
13. Platinum ..			Wood, Assay Master, Jamaica .....
14. Nickel .....	Cronstedt .....	1751	
15. Manganese	Gahn and Scheele .....	1774	
16. Tungsten ..	M.M. Delhuyart .....	1781	
17. Tellurium ..	Muller .....	1782	
18. Molybdenum	Ditto and Hielm .....	1782	

Names of Metals.	Discovered by	Date.
19. Titanium ..	Gregor .....	1781
20. Uranium ..	Klaproth .....	1789
21. Chromium..	Vauquelin .....	1797
22. Columbium	Hatchett .....	1802
23. Palladium ..	} Dr. Wollaston .....	1803
24. Rhodium ...		
25. Iridium ....	Descostils and Tennant .....	1803
26. Osmium ....	Tennant .....	1803
27. Cerium ....	Hisinger and Berzelius .....	1804
28. Potassium ..	} Sir H. Davy .....	1807
29. Sodium ....		
30. Barium ....		
31. Strontium ..		
32. Calcium....		
33. Lithium....	Arfwedson .....	1818
34. Cadmium ..	Stromeyer .....	1818

The foregoing table comprehends only 34 out of 41 of the bodies at present acknowledged as metals. The remaining seven, all of very recent date, viz. magnesium, glucinum, yttrium, aluminum, thorium, zirconium, and silicium, have not yet been exhibited in a separate form, and are arranged among the metals from analogy; chiefly because the earths, in which they exist, present a striking resemblance, as to their properties, to the oxides of ascertained metals.

Of a class comprehending so many individuals, it is not easy to offer a general description; but it will be found that the metals are all characterised by one or more of the following properties.

1. With the exception of the newly discovered bases of the alkalis and earths, they are distinguished by a high degree of specific gravity, the lightest of the other metals (tellurium) being considerably heavier than the most ponderous of the earths.

The following table exhibits the specific gravity of several metals in the order of their densities.

*Table of the Specific Gravities of Metals ; water at 60° Fahr.  
being 1.*

		Authority.
Platinum	20.98	Brisson.
Gold	19.257	Ditto.
Tungsten	17.6	D'Elhuyart.
Mercury	13.568	Brisson.
Palladium	11.3 to 11.8	Wollaston.
Lead	11.352	Brisson.
Silver	10.474	Ditto.
Bismuth	9.822	Ditto.
Cobalt	8.538	Haüy.
Uranium	9.000	Bucholz.
Copper	8.895	Hatchett.
Cadmium	8.604	Stromeyer.
Arsenic	8.308	Bergmann.
Nickel	8.279	Richter.
Iron	7.788	Brisson.
Molybdenum	7.400	Hielm.
Tin	7.291	Brisson.
Zinc	6.861 to 7.1	Ditto.
Manganese	6.850	Bergmann.
Antimony	6.702	Brisson.
Tellurium	6.115	Klaproth.
Sodium	0.972	{ Gay Lussac and Thenard.
Potassium	0.865	

The metals, are, perhaps, the only solid bodies, whose specific gravity is affected by mechanical means, or, in other words, whose particles can be brought permanently into a state of nearer approximation by compression. In consequence of this property, several of the metals undergo material changes in their specific gravity, by the mechanical operations of rolling, hammering, &c. It may be questioned, whether the metals are heavier than other bodies, in consequence of the greater specific gravity of their individual atoms, or from a greater number of atoms being aggregated into a given volume. The former, however, is most probably the

case, though it must be acknowledged that their specific gravity is by no means *exactly* proportional to the weight of their atoms.

2. They are opaque, at least in the state in which they generally occur to our observation. Gold, however, beat into leaves  $\frac{1}{280000}$ th of an inch in thickness, transmits a faint greenish light, when held between the eye and the direct rays of the sun.

3. They possess various degrees of lustre, and it is of so peculiar a kind, that it has been termed by mineralogists the *metallic lustre*, and referred to as a known standard in the description of other minerals. Some of the metals possess this property in so remarkable a degree, as to be applicable to highly ornamental purposes. Polished steel takes place of all the metals in the perfection of its lustre; but some of the class (as cobalt and nickel) appear to be susceptible of it in only a small degree.

4. The metals are excellent *reflectors*, not only of light but of caloric; and hence they are the best materials for the composition of burning mirrors. From the experiments of Mr. Leslie, they appear to possess this property in the following order, the highest number denoting the greatest reflecting power.

Brass .....	100
Silver .....	90
Tinfoil .....	85
Planished block tin .....	80
Steel .....	70
Lead .....	60
Tinfoil softened by mercury .....	50

In general the reflecting power was found, by Mr. Leslie, to be proportionate to the degree of polish, and to be impaired by every thing that diminished this quality. A tin reflector, for example, had its reflecting power diminished nine-tenths by being rubbed with sand paper.

5. Metallic bodies are, of all others, the best conductors of electricity. When their surface is extensive enough to convey away the electricity which seeks a passage, no change is produced in them; but when insufficient, the electric fluid pene-

trates into them, heats them, and sometimes fuses and even volatilizes them. In this state of vapour, they burn more or less vividly, and with differently coloured flames; zinc with a white flame mixed with blue and red; tin, bluish white; lead, bluish or purple; and silver, green.

Their properties as *electro-motors* have already been described in the chapter on the chemical agencies of electricity and galvanism.

6. The metals are also excellent *conductors of caloric*. The degrees, in which different metals possess this property, will be found enumerated in the chapter on caloric.

7. The metals are all *fusible*, provided a due degree of heat be applied, which, for some, is very moderate, and for others extremely intense. Mercury is the only metal that exists constantly in a fluid state at the temperature of our climate. Potassium, sodium, tin, bismuth, lead, tellurium, arsenic, zinc, antimony, and cadmium, all melt at a temperature below that of visible redness, and in the order set down, the most fusible being placed first. Silver, copper, gold, cobalt, iron, manganese, nickel, and palladium, all require a red heat. Molybdenum, uranium, tungsten, and chromium, are almost infusible, and cannot be obtained by the heat of a forge in compact buttons, but fuse under the oxygen and hydrogen blow-pipe. Titanium, cerium, osmium, iridium, rhodium, platinum, and columbium, are infusible by the forge, but yield to the powers of the oxygen and hydrogen blow-pipe.

8. One of the most useful properties of the metals is their *malleability*, or capacity of being extended by the blows of a hammer. In this quality, gold takes place of all the rest. The gold leaf, which is sold in books, is so extremely thin, that less than five grains cover a surface of about  $272\frac{1}{2}$  square inches; and the thickness of each leaf does not exceed  $\frac{1}{100000}$ th part of an inch. All the metals, however, are not malleable. Gold, platinum, silver, palladium, mercury (in its frozen state), copper, iron, lead, tin, zinc, and nickel,\* are the only ones to which this property belongs. The rest, on account of their brittleness, were formerly called *semi-metals*. But since, even in these, a diminishing progression of mal-

\* Nickel on the authority of Richter.



leability may be observed, the distinction, though retained in common language, is very properly rejected from chemical and mineralogical systems.

9. All the metals, that have been described as malleable, (with the exception, perhaps, of nickel) are also ductile, or may be formed into wire. Iron, though so hard a metal, may be drawn into wire not thicker than a human hair. A grain of gold, it has been asserted by Boerrhaave, has been extended into wire of the length of 500 feet; but even this has been surpassed by Dr. Wollaston; for, by surrounding the gold with silver, he has been able to extend it, so that 700 feet weighed only 1 grain, which gives a thickness of only  $\frac{1}{35000}$  of an inch. The coating of silver was afterwards removed by nitric acid, which has no action on gold. Silver too is extremely ductile; so also are platinum, iron, copper, zinc, tin, lead, nickel, palladium, and cadmium, in the order set down; and this property belongs to even some of the compound metals, especially to brass, which may be drawn into wire of great fineness. It may be observed, however, that the most ductile metals are not always the most malleable; iron, for instance, though extremely ductile, cannot be beaten into very thin laminæ.

10. Wires of the same diameter, but of different metals, are found to be capable of sustaining very different weights. This arises from their variable *tenacity*, which is estimated by gradually adding weights till the wire is broken. From the experiments of Guyton Morveau, the following are the utmost weights, which wires of 0.787 of an English line in diameter can support without breaking.

		lbs. decr. avoird. parts.
A wire of iron	supports	549.250
———— copper	————	302.278
———— platinum	————	274.320
———— silver	————	187.137
———— gold	————	150.753
———— zinc	————	109.540
———— tin	————	34.630
———— lead	————	27.621*

\* 71 Ann. de Chim. 182.

The tenacity of tin is greatly inferior to that of gold; and lead has still less tenacity than tin, and even than some sorts of wood.

11. Some of the malleable and ductile metals have, also, a high degree of *elasticity*. This property fits them for being applied to the mechanical purpose of springs. Steel and iron are, in this respect, superior to all other metals. Upon the properties of elasticity and hardness, appears also to depend that of *fitness for exciting sound*, for whatever renders metals harder and more elastic, increases also their sonorousness. Thus bell metal is more remarkable for those properties, than either tin or copper, which are its constituents.

12. The *structure or texture* of several of the metals appears to be *crystalline*. That of iron, developed by the action of solvents, has been shown by Mr. Daniel to be fibrous. Bismuth and antimony have a lamellated texture; nickel presents a fracture between fibrous and foliated; and steel is granular. Several of the metals, when melted and cooled under favorable circumstances, form regular crystals. Thus bismuth, melted in a crucible, and suffered to cool, becomes covered with a crust, and when this is pierced, and the fluid beneath allowed to flow out, the cavity is found studded with beautifully regular cubic crystals. Arsenic crystallizes in regular tetrahedrons, and titanium in long slender filaments or prisms.

Beside the circumstances of agreement in their physical qualities, which have been enumerated, the metals resemble each other, also, in their chemical properties. Some of these resemblances it may be proper to state, for the purpose of avoiding unnecessary repetitions.

The metals, so far as we know at present, are simple or elementary bodies, and are completely incapable of being converted into each other. They were formerly, indeed, considered, but on very insufficient evidence, to be composed of a combustible base, peculiar to each metal, united with a general principle of inflammability, which received the name of *phlogiston*. When the metals are exposed to a strong heat, the first change which is produced in them is that they melt, or run into fusion. This effect takes place, in the different metals, at very

different temperatures. Some of them may be made to boil, and are actually converted into vapour, at a heat considerably below redness; while others require a very intense heat for their fusion. By a sufficient elevation of temperature, it is probable, however, that they would all be volatilized; for platinum itself, which does not melt at a less heat than  $170^{\circ}$  of Wedgwood, has been observed to boil, when placed in the focus of a powerful burning lens.\* In some of the metals, no farther change is produced by the application of heat with the free access of air; and they return, on cooling, to their former condition. But other metals undergo a very remarkable change. Their cohesion, lustre, malleability, tenacity, and all the properties that have been described as characteristic of them, are destroyed. Though their *absolute* weight is increased, yet they become *specifically* lighter, and they are distinguished by a new train of properties which were not observed in the metals themselves.

These changes have been very differently explained, at different periods in the history of chemical science. On the theory of phlogiston, they were accounted for by assuming that the metals, during the process of exposure to air at a high temperature, abandon their phlogiston, which, it was supposed, unites with the air and renders it *phlogisticated*, and consequently unfit for supporting the combustion of other inflammable bodies. The hypothesis, however, could no longer be maintained, when it was proved that the metals, so far from losing weight, become heavier after calcination.

The theory, which is now almost universally admitted, as best explaining the phenomena in question, though suggested by the hints furnished by preceding discoveries, was first reduced to a systematic and consistent form by Lavoisier. The metals, according to the views of that philosopher, are simple bodies, and undergo the changes that have already been described, in consequence of the absorption of oxygen from the air. Hence, while the metallic body becomes heavier, the air, in which the process is performed, should sustain a proportional diminution of weight. That this is the fact, admits of being

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\* Annales de Chimie, lxi. 92.

demonstrated; and still more readily and satisfactorily, if we employ oxygen gas instead of common air. A certain quantity of oxygen gas, (or the whole indeed, under favourable circumstances) disappears; and the increase of weight in the metal is found, on examination, to be precisely equivalent to that of the gas which has been condensed. In some cases, we can even go farther, and separate the oxygen from the metal by the mere application of heat, the oxygen being recovered in the state of gas, and the metal returning to a metallic form. More satisfactory evidence than this could scarcely be required of the nature of the change which takes place; and it may be admitted, therefore, as an established truth, that metals lose their metallic properties, in consequence of their combination with oxygen. The process has been called by Lavoisier, *oxidation*, and the result of it an *oxide*. For the former term, however, Mr. Chevenix, influenced by reasons which are stated in his work on chemical nomenclature, has proposed to substitute that of *oxidizement*. In the following pages, I shall employ both these expressions indiscriminately.

The phenomena and results of the oxidizement of metals are not the same in all cases, but differ very considerably with respect to different metals.

1. Some metals are oxidized by mere exposure to atmospheric air at the ordinary temperature, and even to air which has been deprived of its hygrometric water. Arsenic, manganese, and the new metals discovered by Sir H. Davy, are perhaps the only ones which have been proved to possess this property. Potassium, indeed, has been stated by Thénard to be the only metal that is acted upon by perfectly dry oxygen gas. Others, it is true, as lead and copper, are changed by the action of the air, but extremely slowly, and not without the conjoined operation of moisture.

2. Other metals absorb oxygen from the atmosphere, but not without a considerable increase of their temperature. Iron, zinc, copper, tin, &c. when heated to redness, lose their metallic lustre, and are slowly converted into variously coloured oxides. In some instances, the process is accompanied with so abundant an extrication of light and heat, as to exhibit a vivid inflammation. This happens, chiefly, with some of the

volatile metals. Arsenic and zinc, for example, when projected into a red-hot crucible, emit a brilliant flame. In other metals, the process is unaccompanied by any remarkable phenomena, and is known to have taken place only by its results.

To convert the metals into oxides, there is a *degree* of heat, which is peculiar to each metal, and even to different oxides of the same metal. Mercury, for example, is oxidized, at a degree of heat which produces no change on iron; and lead at one degree of temperature becomes minium, at another massicot.

3. With the exception of mercury, the metals, which have been called *perfect* (comprehending, also, gold, platinum, silver, and palladium,) are not oxidized, even by the combined operations of air and of an increased temperature. Gold, silver, and other metals of this kind, may be kept for many days in fusion, without undergoing any change. That they have an affinity, however, for oxygen, and are even capable of taking it from atmospheric air, is proved by the effect of an electrical or galvanic battery. By the former, the wires of the perfect metals are, at the same moment, dispersed into smoke and oxidized; and by transmitting a powerful discharge, through any of the perfect metals beaten into thin leaves, the metal burns with a remarkable degree of splendour.

4. All metals that are oxidized by atmospherical air, are still more readily oxidized by oxygen gas. In many cases a metal, which undergoes this change slowly and invisibly by the action of air, takes fire in oxygen gas, and exhibits a bright inflammation. For example, it has already been shown, that iron wire may be entirely and vividly consumed in oxygen gas.

These are the most simple cases of metallic oxidizement. In order that the changes, which have been described, may take place, it is only necessary that there should exist a stronger affinity between oxygen and the metal, than between the oxygen and light (and perhaps the electricity) which constitute the gas; and fusion, and other modes of promoting the oxidation of metals, are probably efficient by overcoming the cohesive attraction of the metallic particles. In certain cases,

the phenomena become more complicated, and the metal acquires oxygen by the decomposition of some other compound, in which that element is present. Of these sources of oxygen, the most important, if not the only ones, are water, the acids, and other oxides; or compounds containing one or more of these substances.

I. Water gives up its oxygen to those metals only, which manifest a powerful affinity for that basis, and, generally speaking, to those which are most efficient in decomposing atmospherical air. The metallic bases of the alkalis and earths decompose it with a rapidity which amounts to actual inflammation; but, in general, the change is slow at common temperatures. Iron filings, for example, when moistened with water, and confined in an inverted jar over mercury, become very gradually oxidized, and evolve hydrogen gas. But water, brought into contact with red-hot iron, is rapidly decomposed, and hydrogen gas is disengaged in torrents.

Water, it is observed by Gay Lussac, has the power of bringing all metals, on which it is capable of acting alone, to the same degree of oxidation as when assisted by the action of acids, sometimes to a higher degree, but never to an inferior one. Thus water by itself oxidizes tin to the *maximum*, and iron and potassium to the *medium*; but mingled with acids, it oxidates iron and tin to the *minimum* only.

II. All those acids in which oxygen has been proved to exist, and especially those which Dr. Thomson has called *supporters of combustion*, and the neutral salts containing them, are efficient means of oxidizing the metals. In general, the less strong the affinity of the acid base for oxygen, the more rapidly is the metal oxidized. Those acids, that have not been proved to contain oxygen, are remarkably inert in their action on metals; and the same inactivity belongs to other acids, in which the oxygen and base are held combined by a powerful affinity. Thus, concentrated sulphuric acid, at the temperature of the atmosphere, scarcely attacks any of the metals; because the oxygen and sulphur, of which it consists, forcibly attract each other. On the other hand, the nitric and nitromuriatic acids, in which there exists a large quantity of loosely

combined oxygen, readily abandon a part of it, and act on the metals with considerable energy. Even the perfect metals are oxidized by the last acid; and thus we obtain proof that the resistance, which the perfect metals show to the action of oxygen gas, is not owing to their want of affinity for that basis, but to the predominance of other opposing forces.

Some of the acids, which do not, in their concentrated state, act upon metals, acquire the power of oxidizing them when diluted with water. This is true of the sulphuric and muriatic acids, to either of which, when concentrated, we may apply iron or zinc, without any change ensuing. But on adding water, the metal disappears, and hydrogen gas is abundantly evolved. Now it is a principle, to which no exception has yet been discovered, that a metal cannot, in its perfectly metallic state, unite with any acid. In order to be dissolved, it must first be brought into the state of an oxide; and in the case which has been just now stated, no substance, capable of furnishing oxygen, is in contact with the iron except water. As an additional proof that water is, in this instance, the source of the oxygen, it has been ascertained that no portion of the acid is decomposed; but that the same quantity of acid exists in combination with oxide of iron, as was originally submitted to experiment.

By measuring the quantity of hydrogen gas, evolved in experiments of this kind, it is easy to calculate how much oxygen the metal has acquired; for every 100 cubic inches of hydrogen gas indicate the transference to the metal of 16.9 grains of oxygen. Equal weights of different metals evolve different quantities of hydrogen gas, in consequence of their combining with different quantities of oxygen. If 100 grains of one metal, for example, in order to become soluble in sulphuric acid, require 20 grains of oxygen, and another only 10 grains, the former in an equal weight will disengage twice as much hydrogen gas as the latter. The same metal, also, in different states, may evolve different quantities of hydrogen. If, for example, the metal be already a little oxidized, it will set at liberty less hydrogen than if it were perfectly metallized. On this principle, the different proportions of real metal in several varieties of iron and steel have been investigated, the

most perfectly metallized iron yielding, of course, the most hydrogen gas.

The phenomena, observed during the solution of a metal, and those attending the solution of its oxide, in the same acid, are essentially different. For the most part, a metal is dissolved with effervescence, an appearance always occasioned by the escape of gas. Iron, it has already been stated, effervesces strongly during its solution in diluted sulphuric acid; but the black oxide of that metal is taken up silently, and without any discharge of gas.

III. The metals may be oxidized by the transfer of oxygen from other metallic oxides. Thus, when iron filings are distilled with the red oxide of mercury, the oxygen passes to the iron, and the mercury is *revived*, or appears in a metallic state. In a similar manner, the oxides, held in solution by acids, are decomposed by immersing, in the solution, other metals. When copper, for example, is immersed in a solution of nitrate of mercury (consisting of oxide of mercury and nitric acid) the latter metal is deprived of its oxygen by the former, and appears on the surface of the copper in a revived state. The nitrate of copper, which is thus produced, is precipitated by iron, which has a stronger affinity than copper for oxygen. A variety of similar examples might be given, in which the precipitating metal takes oxygen from that which is precipitated. In cases of this sort, it must be confessed that the comparative affinities of the acid for the oxides of the two metals may have some share in the effect, but much less than the affinities of oxygen separately considered. The precipitated metal, also, is seldom quite pure, but almost always contains a portion of the metal, which has caused the precipitation.

From an attentive examination of facts of this kind, Lavoisier has deduced the proportion of oxygen necessary to the solution of different metals, according to this analogy: *As the quantity of the PRECIPITANT is to that of the PRECIPITATED metal, so is the quantity of oxygen necessary for the solution of the precipitated to that necessary for the solution of the precipitant.* For example, it has been found by experiment that 135 grains of mercury are necessary for the precipitation of 100 grains of silver from the nitric acid. It is evident, then,



that 135 grains of mercury require, to become soluble in nitric acid, the same quantity of oxygen as 100 grains of silver; and, therefore, as 100 to 135, so is the quantity necessary to render soluble 100 grains of mercury, to that necessary for the solution of 100 grains of silver. Now eight grains of oxygen are necessary to the solution of 100 grains of mercury; and therefore 10.8 grains must be required for the solution of 100 grains of silver. By an extension of the same experiments to other metals, Lavoisier formed a table of the quantity of oxygen necessary for the solution of all the metals; but I omit giving it in this place, because subsequent discoveries have pointed out several inaccuracies, with respect to individual oxides.

Such are the principal means of effecting the oxidation of metals. Different individuals of the class, it has already been stated, combine with different proportions of oxygen; and it has been conceived by M. Frere de Montizon, that a relation exists between the specific gravity of the metals, and the quantity of oxygen, with which they are capable of uniting, the oxygen being either a multiple or submultiple of the density.\* Thus the specific gravity of manganese being 7, the oxygen of the protoxide is by experiment 28.1, which is very nearly a multiple of the density by 4. The law, however, cannot be considered as generally established. If it were to hold good universally, it would indicate the existence of a relation between the density of metals and the weight of their atoms.

The same metal, it may be added, is susceptible of different degrees or stages of oxidation. Iron, for example, when united with oxygen in the proportion of 29.5 grains or thereabouts, to 100 grains of metal, composes a *black* oxide; and with 43.5 parts of oxygen to 100 of metal it constitutes a *red* oxide. These different oxides of the same metal have not only different colours, but each of them is characterized by a distinct train of chemical properties, and especially by different habitudes with respect to the acids. Thus the black oxide of iron readily unites with muriatic and sulphuric acids; but the red oxide

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\* Ann. de Chim. et Phys. vii. 7. Thomson's Ann. xii. 8.

less easily. The salts with base of the protoxide of iron afford a white precipitate with triple prussiate of potash; and none at all with the gallic acid, or with sulphureted hydrogen. But the salts, in which the iron is at the maximum of oxidation, give a deep-blue compound with the triple prussiate, and a black one with the gallic acid.

It is an interesting question, whether the same metal is capable of uniting with oxygen, in all proportions between the maximum and minimum, or whether it does not rather combine with that principle in a few proportions only, between which there are no intermediate compounds. Are there, for example, only two oxides of mercury, the *black*, consisting of 100 parts of metal united with four of oxygen; and the *red*, composed of the same quantity of metal and eight parts of oxygen? The determination of this point requires more precise and multiplied appeals to experiment, than have hitherto been made, before it can be laid down as a principle, from which there is no exception, that every metal unites with oxygen only in a few definite proportions. But in a great variety of cases, where the question has been accurately investigated, different oxides of the same metal have been proved to contain oxygen, in proportions which are simple multiples or divisors of each other, and in no others; and the fact will probably be established with respect to all other oxides. It is by no means necessary, however, that the possible number of oxides of any one metal should be limited, as Proust has supposed, to two; for it is perfectly consistent with the atomic hypothesis that there may be three, four, or even a greater number of oxides of each.

It had been long known that of different oxides of the same metal, the one which contains a larger proportion of oxygen is capable of saturating more acid, than the one which contains less. This was ascertained by Proust, with respect to the two muriates of copper, as appears from the following statement, which still holds true, if we consider the salts as in a state of solution, or as true *muriates*, and not *chlorides*.

The green muriate consists of { 100 copper.  
24.57 oxygen.  
69.16 acid.

The white muriate of  $\left\{ \begin{array}{l} 100 \text{ copper.} \\ 12.28 \text{ oxygen.} \\ 41.59 \text{ acid.} \end{array} \right.$

The same law appears, also, from the experiments of Sir H. Davy, to apply to the oxides of potassium and sodium. To this principle, an important addition has been proposed by Gay Lussac,\* and supported by a variety of illustrations; viz. *that the quantity of acid, which different metals require for saturation, is in direct proportion to the quantity of oxygen in their oxides.* Let us suppose, for example, that of any two metals, A combines with twice as much oxygen as B; then, a given weight of the oxide of A will neutralise twice as much of any given acid as an equal weight of the oxide of B.

The solubility of the metallic salts in water, it has been observed by Gay Lussac, bears a proportion to the quantity of oxygen in the oxides; and consequently to the quantity of acid with which that oxide is combined. Salts, in which the metal is at the minimum of oxidation, are generally those which are most insoluble. This is the fact with respect to the salts of lead, silver, and mercury; for these are metals which, at the minimum of oxidizement, take very little oxygen, and consequently very little acid. A similar law seems applicable to the compounds of chlorine, for corrosive sublimate, which contains the largest proportion of that element, is much more soluble than calomel.

It has been deduced by Berzelius † as a general principle, from the comparison of a great number of facts; that in all neutral salts, the oxygen of the acid is a multiplication of that of the base by some entire number. The law, he apprehends, may be expressed more generally in the following terms: *When two oxidated substances enter into a neutral combination, the oxygen of that, which in a galvanic circle, would be attracted to the positive pole, is a multiplication, by an entire number, of the oxygen of that, which would be deposited at the negative pole.* For example, 279 parts of protoxide of lead contain 19.95 parts of oxygen, and saturate 100 parts of sulphuric acid, which contain 59.85 parts of oxygen. Now the oxygen

\* Mémoires d'Arcueil, n. 159; or 37 Phil. Mag. 1808.

† 18 Ann. de Chim. 127.

of the oxide  $19.95 \times 3 = 59.85$ , which is precisely the oxygen of the acid. The same coincidence holds good in a variety of other instances. The composition of a metallic oxide may, therefore, be deduced if we know the quantity of any acid, also of known constitution, which is required to neutralize it,— a method of investigation which may be resorted to with advantage, when the composition of an oxide cannot be directly proved by analysis or synthesis.

There is a certain state of oxidation, peculiar to the different metals, in which they are most readily acted upon by the several acids. Iron and manganese, for example, at the maximum of oxidization, are altogether insoluble in nitric acid; but readily dissolve in it, when combined with a smaller proportion of oxygen. Even when once brought into combination with that acid, the oxide, by attracting a further quantity of oxygen from the atmosphere, or from any other source, is separated in the state of an insoluble precipitate, which, however, does not consist of pure oxide, but of the oxide, with a certain proportion of acid. This explains the change, which is produced in solutions of iron, by keeping them exposed to air. The oxides of iron and manganese, saturated with oxygen, are soluble, however, in the less oxygenated acids; for example, in the sulphurous or nitrous, which first deprive the oxide of part of its oxygen, and then dissolve the less saturated oxide.

Every acid, with a few exceptions, is capable of uniting with each individual of the classes of alkalis, earths, and metallic oxides. In these compounds, the separate qualities of the component principles are in many instances no longer apparent, and hence they have been called *neutral salts*. In every salt, then, there are present two distinct ingredients. The acid, of whatever kind it may be, has been denominated, by Lavoisier, the *salifying principle*; and the body, with which the acid is combined, whether an alkali, an earth, or an oxide of any of the common metals, the *salifiable base*, or simply *the base*. The salts, formed by an individual acid with all the different bases, may be considered as a genus or class; and may be distinguished by a generic name, expressive, in part, of their composition. This generic name is taken from that of the acid. The combination of sulphuric acid, for instance, with

any base, is called a *sulphat* or *sulphate*; of phosphoric acid a *phosphate*; and so of the rest. The name of the individual salt is derived from that of the base. Thus we have the *sulphat of potash*, the *sulphat of soda*, &c. But sulphur, phosphorus, and other bodies, it has already been observed, are susceptible of different degrees or stages of oxygenation; and afford, in these different stages, acids which are characterized by a peculiar train of properties. The compounds, also, which result from the union of two different acids, having the same combustible base, with alkalis and earths, are altogether different from each other. The salt, for example, which sulphuric acid affords with potash, is wholly unlike that which results from the combination of sulphurous acid with the same base. It was necessary, therefore, to distinguish the compounds of the more oxygenated from those of the less oxygenated acid; and this has been done by changing the termination from *ate* to *ite*. Thus the salts, formed with sulphurous and phosphorous acids, are called sulphites and phosphites: as sulphite of potash, phosphite of soda, &c.

An important law has been deduced, by Berzelius, respecting the combination of acids with bases, *viz.* that the quantities of different bases, required to saturate a given quantity of any acid, all contain the same quantity of oxygen. For example, 100 parts of sulphuric acid are saturated by a quantity of any base, containing 20 parts of oxygen; and 100 parts of muriatic acid by a quantity of base, which holds in combination 30.49 parts of oxygen. These proportions do not seem to be changed by varying the state of oxygenation of the acid; for sulphites absorb oxygen to become sulphates, and still remain neutral; the phosphites, when changed into phosphates, give up phosphorus, and continue neutral. It would appear, therefore, that the proportion between the oxygen of the acid, and that of the base, is regulated by the proportion of the combustible ingredients of the acid and base to each other. In sulphurets, for example, the metal and sulphur are in such proportion, that when both are oxygenated, the oxide, resulting from the one, precisely saturates the acid, resulting from the other. These facts strongly confirm the atomic theory, and cannot, indeed, be explained by any other.

Hitherto, we have considered the compounds of acids with their respective bases only in the state of neutral compounds, in which neither the acid, nor the base predominates. But we have several instances, in which a neutral compound is susceptible of uniting with an additional quantity of acid or of base, and thus of acquiring an entirely new set of properties. Potash and tartaric acid, for example, when united in the proportions which neutralize each other, compose an extremely soluble salt, which has no action on vegetable colours; but with a double proportion of acid, a salt is formed, which requires a large quantity of water for solution, has an acid taste, and instantly reddens vegetable blue colours.

To distinguish this and other similar salts, the epithet *acidulous* was first proposed; but, for the sake of brevity, it has now become customary to prefix the Latin preposition *super*. Thus we have the *super-tartrate* of potash; the *super-sulphate* of potash; &c. On the contrary, when the base is predominant, we denote the deficiency of acid by the preposition *sub*, as *sub-carbonate* of potash, *sub-borate* of soda, &c. In the instance of the compounds of oxalic acid with potash, Dr. Wollaston has employed the words *binoxalate* and *quadraxalate*, to express the proportions in which the acid unites with the base; and this method of nomenclature has been extended to other salts, formed by the union of an acid and base in different proportions. There are several cases, however, in which it is extremely difficult to decide, whether a salt is to be classed among neutral, or among *sub* or *super* salts.\*

There are a few instances of salts with compound bases; and in cases of this kind, it is customary to annex, to the generic name, those of both the bases. Thus, for example, we have the *tartrate* of potash and soda, the *phosphate* of ammonia and magnesia, or, as it is sometimes called, *ammoniaco-magnesian phosphate*.

In no part of chemistry is the advantage of the new nomenclature more sensibly experienced, than in the class of neutral salts; for the number of these compounds is susceptible of

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\* See the remarks of Berzelius, *Ann. de Chim.* lxxix. 284, and lxxxii. 225.

being multiplied to an immense extent. If the knowledge of the name did not lead to that of the compound, scarcely any memory would be adequate to retain them. But by changing the arbitrary titles, formerly assigned to them, for names expressive of their composition, we are furnished with a kind of artificial memory, which renders their recollection perfectly easy. Thus for the terms butter of antimony, sugar of lead, and Glauber's salt, are now substituted the more appropriate epithets of chloride of antimony, acetate of lead, and sulphate of soda.

Beside the class of acids, which are the best solvents of the metals, alkaline solutions act upon metallic substances. The water which holds the alkali in solution, is decomposed; its hydrogen is disengaged, and its oxygen transferred to the metal; and the oxide, thus produced, is taken up by the alkaline liquor. The oxides ready formed, are also, in several cases, dissolved by liquid alkalis. When a pure alkali is added to a metallic solution, the metal is precipitated in the state of an oxide; but the precipitate is seldom quite free from alkali, and the metallic oxide, in a few instances, instead of appearing in a separate form, is dissolved by the alkali. When alkaline carbonates are employed instead of pure alkalis, for the precipitation of metallic solutions, the oxide combines with carbonic acid, and appears in the state of a metallic carbonate.

The compounds of ammonia with metallic oxides are of more importance than those of the other alkalis, and have obtained the generic name of AMMONIURETS. They may be formed, either by acting on the metals with liquid ammonia, the water in which is decomposed, and furnishes a metallic oxide, which unites with the alkali; or they may be produced, by exposing the oxides to ammoniacal gas, at the temperature of the atmosphere. At least fifteen oxides, or rather hydrated oxides, may be brought into combination with ammonia, viz. oxide of zinc; deutoxide of arsenic; both the oxides of copper; oxide of silver; tritoxide and tetroxide of antimony; oxide of tellurium; protoxides of nickel, cobalt, and iron; peroxide of tin; deutoxide of mercury; and deutoxides of gold and platinum.

The ammoniurets are decomposed by a strong heat; the oxygen of the oxide uniting with the hydrogen of the alkali, and the azote of the latter being set free. In some cases, as in that of ammoniuret of gold, this decomposition is attended with a loud explosion.

The oxides, existing in metallic solutions, are decomposed by inflammable substances. Light only is sufficient for the decomposition of some of them. Hydrogen gas, charcoal, sulphur, phosphorus, and the compounds of hydrogen with the last three bodies, when brought into contact with the solutions of perfect metals at common temperatures, attract the oxygen from the metal, and occasion its precipitation in a metallic form. In this way, several beautiful appearances may be produced, which will be described in treating of the individual metals.

The oxides themselves are decomposed when exposed to a strong heat in contact with hydrogen, charcoal, or phosphorus. The two first, or substances containing them, are chiefly employed for the decomposition of those oxides, which occur as natural productions. The oxide, mixed with a portion of inflammable matter, is exposed to an intense heat; and, in order to obtain the metal in a coherent mass, and not in the small grains which would otherwise be formed, some substance is generally added, which is capable of being melted, and of allowing the metal to subside through it. Substances of this kind are called *fluxes*, and the process is termed the *revival* or *reduction* of the metal.

If only one oxide had existed of each metal, it would have been easy, by applying the general principles of chemical nomenclature, to have distinguished them by names sufficiently expressive of their composition. But as the metals severally are susceptible of several stages of oxidizement, it is difficult to find terms, which shall sufficiently express the characteristic distinctions of the several oxides of the same metal. The existence of only two oxides would have greatly simplified their nomenclature; for, in that case, we might have applied the term *oxide* to the metal fully saturated with oxygen, and of *oxidule* to the compound at an inferior stage of oxidizement, as has been done by several of the French chemists. In the present state of the science, however, this nomenclature is



inadmissible; and the specific name has been derived from some external character, chiefly from that of colour. Thus we have the black and red oxides of iron; and the black and red oxides of mercury. In most instances, the denominations, which have been proposed by Dr. Thomson for the metallic oxides, may be advantageously adopted. When there are several oxides of the same metal, he has proposed the terms *protoxide*, *deutoxide*, *tritoxide*, &c. signifying that the metal is in its first, second, or third stage of oxidizement. Or if two oxides only of any metal are known, he suggests the appellation of *protoxide* for that at the minimum, and of *peroxide* for that at the maximum of oxidation.

A similar difficulty has been experienced, also, with respect to the neutral salts with metallic bases; for when different oxides of the same metal combine with a given acid, the resulting salts require to be distinguished by appropriate names. This has sometimes been done by prefixing the word oxygenized (or for brevity oxy-) to the salt containing the most highly oxidized metal; as the sulphate and oxy-sulphate of iron. The latter term, however, is improper; because, in strictness, it can only be applied to the compounds of oxy-sulphuric acid (an acid not yet proved to exist) with different bases; whereas what was meant to be expressed is merely a compound of ordinary sulphuric acid, with iron in its highest state of oxidizement. If the principle, assumed by Gay Lussac, should be confirmed by farther investigation (*viz.* that the acid in metallic salts is proportional to the oxygen in the oxides), it will be more easy to derive a specific name from the proportion of acid than from that of oxygen. Thus we shall have the sulphate and per-sulphate of iron. But till greater precision is acquired in our knowledge of this class of bodies, it may be well to continue to derive the specific name of the salt from some obvious quality; as the *green* and *red sulphates of iron*, the *white* and *green muriates of copper*, &c.

The following Table exhibits, at one view, the composition of most of the metallic oxides.

*Table showing the Proportions of Oxygen with which Metals combine.*

Metals.	No. of Oxide.	Colour of Oxide.	100 of Metal take Oxygen.	Authority.	Equivalent number of the Metal.	Equivalent number of the Oxide.
Potassium	1	White	20	Gay Lussac and Thenard.	40	48
	2	Orange	60			
Sodium	1	White	34	Ditto.	24	32
	2	Orange	57			
Lithium		White	72+	Gmelin.	11	19
Calcium		White	39.4	Berzelius.	20	28
Barium	1	White	11.4	Ditto.	70	78
	2	Grey	28.			
Strontium		White	18.3		44	52
Magnesium		White	66.6	Thomson.	12	20
Glucinum	1	White	44.4	Ditto.	18	26
Yttrium		White	25	Ditto.	89	40
Aluminum		White	80	Ditto.	10?	18?
Thorium		White				
Zirconium		White	23.78?	Ditto.	33.5?	41.5?
Silicium		White	117.88	Berzelius.	8	18
Manganese	1	Green	31.25	Forchammer.	28?	
	2	Brown	42.04			
	3	Black	62.50			
Zinc	1	White	24.41	Gay Lussac.	23	41
Iron	1	Black	29.5	Berzelius.	28?	36
	2	Red	44.25			
Tin	1	Grey	19.5	Gay Lussac.	59	67
	2	White	27.1			
Cadmium		Brownish yellow	14.332	Stromyer.	56	64
Arsenic	1	White	31.57	Thomson.	38?	
	2	Ditto (acid)	52.63			
Molybdenum	1	Brown	16.6	Thomson.	47	53
	2	Blue	33.3			
	3	White (acid)	52.7			
Chromium	1	Green			28?	36?
	2	Brown				
	3	Red (acid)	87.72			

Table continued.

Metals.	No of Oxide.	Colour of Oxide.	100 of Metal take Oxygen.	Authorities.	Equivalent number of the Metal.	Equivalent number of the Oxide.
Tungsten	1	Black	16.6	Bucholz.	96	112
	2	Yellow	25.			
Columbium		White	5.5	Berzelius.	144?	152
Antimony	1	Dull white	18.2	Berzelius.	44	52
	2	White (acid)	27.3	Ditto.		
	3	Yellow (acid)	36.4	Ditto.		
Uranium	1	Black	6.4	Schoubert.	125?	133
	2	Yellow	9.6			
Cerium	1	White	17.41	Hisinger.	46	54
	2	Fawn	26.115	Ditto.		
Cobalt	1	Blue	27.3	Roehoff.	30	38
	2	Black	40.93	Ditto.		
Titanium	1	Blue				
	2	Red				
	3	White				
Bismuth		Yellowish	11.275	Lagerhjelm.	71	78
Copper	1	Red	12.5	Proust and Berzelius.	64	72
	2	Black	25.			
Tellurium	1	Yellowish	94.8	Berzelius.	38?	
Nickel	1	Ash grey	27.25	Roehoff.	30	39
	2	Black	40.98	Ditto.		
Lead	1	Yellow	7.72	Berzelius.	104	112
	2	Red	11.08	Ditto.		
	3	Puce	15.60	Ditto.		
Mercury	1	Black	4	Thenard.	200	208
	2	Red	8	Ditto.		
Silver	1	Olive	7.272	Berzelius.	110	118
Gold	1	Brown black	10.61	Oberkampf.	80?	88
Platinum	1	Black	8.287	Berzelius.	96.5?	100.5?
	2	Iron grey	11.9	E. Davy.		
	3		16.38	Berzelius.		
Palladium	1		14.285	Ditto.		
Rhodium	1		6.71	Ditto.	56	64
	2		13.42	Ditto.		
	3		20.13	Ditto.		
Iridium	1	Blue		Tennant.		
	2	Red		Ditto.		

Many of the metallic oxides have an attraction for water, which they manifest by being soluble in it, or by reducing it to a solid or gelatinous form. The soluble oxides are potassa, soda, baryta, strontia, and lime; the deutoxide of arsenic, and the oxide of osmium. There are a few others, which are soluble in a very small degree only, not exceeding one thousandth of the weight of the water, viz. oxide of molybdenum, deutoxide of mercury, tritoxide and tetroxide of antimony.

The compounds of oxides and water, in which the water exists in a condensed state, are termed **HYDRATES**, or **HYDRO-OXIDES**, or **HYDROXURES**. The hydrates of potash, soda, strontia, and baryta, retain the water which constitutes them such, at the temperature of ignition, and it can only, indeed, be expelled by bodies that have a stronger affinity for the alkali or earth. The hydrates of the remaining earths are decomposed by the heat of ignition. The hydrated oxides of the common metals are obtained, by adding a solution of pure potash, soda, or ammonia, to the solution of the oxide in sulphuric, muriatic, or nitric acid. The precipitate, washed repeatedly with water, is to be collected on a filter; and, if dried, the heat employed must be as gentle as possible; for a slight elevation of temperature is sufficient to expel the whole water, and to leave only an oxide.

The hydrated oxides are, for the most part, much more soluble in acids than the oxides. According to Berzelius, they are definite compounds, in such proportions, that the oxygen of the water is equal in weight to that of the oxide. It is, however, probable that each metallic oxide is capable of uniting with water in several definite proportions, the greater of which are multiples of the less.

Besides the important class of compounds, which result from the union of metals with oxygen, the metals are capable, also, of entering into combination with chlorine, iodine, hydrogen, carbon, phosphorus, and sulphur. They afford, also, by uniting with each other, an interesting class of compounds called *metallic alloys*.

I. All the metals are capable of uniting with chlorine. The very malleable metals, such as gold, silver, &c. which can

be reduced to extremely thin leaves, are best applied to the gas in that state; others, as iron, zinc, copper, &c. may be introduced in the state of fine filings. The best proportion of the filings is about 40 grains of each metal to 40 cubic inches of the gas; and into the bottom of the receiver a little dry sand may be poured, to prevent it from being broken. The temperature of the gas, in order that the experiment may succeed perfectly, should not be below 70° Fahr.

The most readily oxidized metals burn with the greatest brilliancy. Metallic antimony emits a very brilliant white flame, and throws out sparks. Arsenic exhibits a fine green or blue flame, attended with sparks and a dense white smoke; bismuth a blueish flame; zinc a white flame and sparks; tin, a blueish white light; lead, a clear white flame; copper, a red and slowly spreading light; and iron a bright red light.

The results of combustion in these instances are compounds of chlorine with the different metals, which appear to be maintained by a very powerful affinity, for chlorine is capable of expelling the whole of the oxygen from any metallic oxide, and taking its place. Even those metals, that are most distinguished by their affinity for oxygen, abandon it when their oxides are heated in contact with chlorine; and oxygen gas is in that case disengaged. The same metal is capable also of uniting with different proportions of chlorine, which, so far as has been yet ascertained, are definite, and in no case exceed two proportions to one of metal. Hence it was proposed by Sir H. Davy, in fixing the nomenclature of these compounds, to designate those containing the least chlorine by the termination *ane* added to the Latin name of the metal, as *cuprane* for that of copper; and those containing most chlorine by the termination *anea*, as *cupranea*. This nomenclature, however, has not been generally adopted; but the compounds of chlorine with metals are now either called *chlorures*, or (which appears to me to be preferable from analogy with the similar compounds of oxygen) *chlorides*. When more than one compound exists of chlorine with any metal, that at the minimum may be called *proto-chloride*, and the others *deuto-chloride*, *perchloride*, &c.

The metallic chlorides may also be formed, by exposing certain metals to muriatic acid gas at high temperatures. In this case, the muriatic acid is decomposed; its hydrogen is liberated; and its chlorine combines with the metal. Diluted muriatic acid acting on certain metals (iron for example) occasions the decomposition of water; hydrogen is evolved; and an oxide is formed, which unites with the muriatic acid and constitutes a true muriate. When this muriate is first evaporated to dryness, and then strongly heated, the oxygen of the metallic oxide unites with the hydrogen of the acid and forms water, which escapes, and there remains a true *chloride*, or compound of the metal with chlorine. Again, the chlorides may be formed by double elective affinity; thus sulphate of mercury, exposed to heat with chloride of sodium, gives chloride of mercury and sulphate of soda; the oxygen and sulphuric acid passing from the mercury to the sodium, and the chlorine from the sodium to the mercury.

The compounds of chlorine with metals have been ably investigated by Dr. John Davy, and it is chiefly his results that have furnished materials for the following Table, in which the equivalent of chlorine is taken at 36. The first column contains the name of the chloride; the second the equivalent of the metal deduced from its oxide or from some other compound; the third the proportion of chlorine; and the fourth the equivalent of the metal, deduced from the lowest proportion, in which it has actually been found to unite with chlorine. In most instances, the numbers in the first and last columns will be found very nearly to coincide. When the difference is trifling, it may be imputed to errors unavoidable in analyses of this kind; but when very considerable, as in the case of arsenic, the disagreement shows the necessity of more accurate experiments either on the oxide, the chloride, or on both.

*Table of the Principal Compounds of Metals with Chlorine.*

Name of chloride.	Equiv. of metal.	Proportion of chlorine.	Equiv. of metal deduced from the chloride.
Chloride of Potassium....	40	36	40
----- Sodium .....	24	36	24
----- Calcium .....	20	36	20
----- Barium.....	70	36	70
----- Strontium....		36	44
----- Magnesium ..	12	36	12
----- Manganese...	28	36	28
----- Zinc .....	33	36	33
----- Iron, 1st....	28	36	28
----- 2d.....		72	
----- Tin, 1st.....	59	36	59
----- 2d.....		72	
----- Arsenic. ....	38?	72	23.46
----- Antimony....	44	36	44.21
----- Bismuth. ....	71	36	71.05
----- Copper, 1st..	64	36	66.05
----- 2d...		72	
----- Lead.....	104	36	103.52
----- Mercury, 1st..	200	36	204.17
----- 2d..		72	
----- Silver .....	110	36	110.14
----- Gold.....	?	36	104.23

II. All the metals unite with IODINE, and form compounds which have been called *iodes*, *iodures*, or *iodides*. The last term is to be preferred, on account of the analogy of the compounds denoted by it with *oxides* and *chlorides*. The iodides all decompose water, the hydrogen of which forms hydriodic acid with the iodine, while its oxygen is transferred to the metal, and the acid produced combines with the metallic oxide.

III. THE COMPOUNDS OF METALS WITH HYDROGEN are neither numerous nor of much importance. When water is decomposed by certain metals, at the same time that the oxygen combines with one portion, the hydrogen, which is disengaged in the state of gas, takes up a portion of metal.

This is the case, in a very small degree, with iron; still more with zinc; and most remarkably with potassium, arsenic, and tellurium, all of which afford compounds with hydrogen, having distinctly characteristic properties.

IV. THE COMBINATIONS OF METALLIC BODIES WITH SULPHUR have been divided by Vauquelin \* into three classes, *viz.* 1st, the compounds of metals with sulphur, which alone are with propriety called *sulphurets*; 2dly, the compounds of sulphur with metallic oxides, termed *sulphureted oxides*; and 3dly, those of sulphureted hydrogen with metallic oxides, which may be called *hydro-sulphureted oxides*.

1. All the metals, with the exception of gold, zinc, and tin, are, in their metallic state, susceptible of combination with sulphur. In order to effect their union, it is sufficient that one of the bodies be brought into a fluid state; and as sulphur is readily fusible, a very moderate heat only is required for the purpose. Thus a mixture of 45 parts of iron filings with 15 of sulphur, or of 40 parts of copper filings with 15 of sulphur, when heated in a glass tube, combines, the moment the fusion of the sulphur is accomplished. The phenomena are very remarkable, consisting in a sudden and bright glow, like that of intense ignition. During combination, however dry the materials may have been, it appears from the experiments of Mr. Clayfield † that a quantity of elastic fluid is extricated, amounting to nine or ten times the bulk of the mixture, and consisting of sulphureted hydrogen and sulphurous acid. The former, probably, arises from the sulphur, and the latter from the metallic filings, which may have been partially oxidized by the process of washing and drying.

In these compounds, the properties of the metals cease to be apparent; for the sulphurets are brittle; have colours different from those of the metals; and, when artificially formed, are destitute of lustre. The quantity of sulphur, with which different metals are capable of uniting, varies for each metal.

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\* Annales de Chimie, xxxvii. 57.

† Note to Sir H. Davy's paper on alkalis. (Philosophical Transactions, 1808.)



The same metal, also, in some instances, combines with different quantities of sulphur, and affords compounds, characterized by a distinct train of properties. Thus the compound of 100 parts of iron with  $58\frac{1}{2}$  of sulphur is brittle and of a dark grey colour; has little or no lustre; and is attracted by the magnet. But 100 parts of iron with 117 of sulphur form a yellow compact compound; of sufficient hardness to strike fire with steel; and having so much lustre, as to have been often mistaken by the ignorant for gold. When different sulphurets of the same metal exist, the sulphur, in those which contain the larger proportion, is an exact simple multiple of the sulphur in those which contain the less.

The following Table exhibits the composition of several of the metallic sulphurets, so far as they are yet known. In several, it is probable the numbers are incorrect, because they do not stand the test of a comparison with the oxides; for as the equivalent of sulphur is precisely double that of oxygen, the quantities of sulphur, that unite with metals, should be multiples by two of the oxygen in the corresponding oxides.

*Table of Sulphurets.*

<u>100 Parts of</u>	<u>Unite with Sulphur.</u>	<u>Authority.</u>
Gold.....	24.39 .....	Berzelius.
Platinum 1st .....	19.04 .....	E. Davy.
——.. 2d .....	28.21 .....	Ditto.
——.. 3d .....	38.8 .....	Ditto.
Palladium.....	24.0 .....	Vauquelin.
Silver .....	14.9 .....	Ditto.
Copper .....	25.6 .....	Ditto.
Iron.....1st .....	58.75 .....	Ditto.
—— .....	117. ....	Ditto.
Tin..... 1st .....	27.234 .....	Dr. John Davy.
—— .....	54.5 .....	Ditto.
Lead ...1st.....	15.384 .....	Berzelius.
——.....2d .....	30.76 .....	Ditto.
Nickel... 1st .....	51.5 .....	E. Davy.
—— .....	77. ....	Ditto.

*Table of Sulphurets, continued.*

<u>100 Parts of</u>	<u>Unite with Sulphur.</u>	<u>Authority.</u>
Zinc .....	48.84 .....	Dr. Thomson.
Bismuth..1st .....	22.52 .....	Lagerhjelm.
———— 2d .....	45. ....	Vauquelin.
Antimony .....	37.25 .....	Berzelius.
Arsenic ..1st .....	33.3 .....	.....
———— .. 2d .....	75. ....	.....
Cobalt .....	39.8 .....	Proust.
Molybdenum .....	67. ....	.....

Metallic sulphurets can only be partially decomposed by heat: and though this assertion appears to be contradicted by the effect of roasting these compounds; yet it is to be considered that the metals, when heated with the contact of air, absorb oxygen, and thus lose their affinity for sulphur. The sulphuret of one metal may, in many instances, be decomposed by another metal. Thus when sulphuret of mercury is distilled with a proper proportion of iron filings, the sulphur passes to the iron, and the mercury comes over in a metallic state.

Concentrated sulphuric acid, with the assistance of heat, acts upon metallic sulphurets, and is converted into sulphurous acid, which, being volatile, escapes.\* Metals which, in their separate state, were dissolved by dilute sulphuric acid, continue sensible to its action, after being combined with sulphur. When dilute sulphuric acid, however, acts on such compounds, instead of hydrogen gas simply, we obtain sulphureted hydrogen. It is chiefly the compounds with the minimum of sulphur, that produce this effect; for the *super-sulphurets*, or those containing a farther proportion of sulphur, resist the action of this solvent.

Concentrated muriatic acid has no effect on sulphurets; but the diluted acid acts like the diluted sulphuric. Nitric acid is decomposed by the metallic sulphurets; nitrous gas is disengaged; and sulphur is precipitated.† In this case, though

\* Berthollet, *Annales de Chimie*, xxv. 256.      † Vauquelin, *loc. cit.* 65.

all nitric acid contains water, yet sulphureted hydrogen is not formed, because the acid yields its oxygen more easily than the water.

Sulphurets, composed of metals which powerfully attract oxygen, and the oxides of which have moreover an affinity for sulphuric acid, absorb oxygen from the atmosphere, and pass to the state of *sulphates*. In this way most of the sulphate of iron is formed, which occurs in commerce. But if the metal has either a strong affinity for sulphur, or a weak one for oxygen, then the conversion into a sulphate does not happen, as in the sulphurets of copper, antimony, and mercury.\* The sulphuret of iron containing a full proportion of sulphur resists, also, the conjoined action of air and moisture.

2. In general, the metals have a stronger affinity than their oxides for sulphur; and several of the oxides, when heated with sulphur, are decomposed, their oxygen being separated in the state of sulphurous acid, and a true metallic sulphuret remaining. This appears to be the case, in part at least, even with the oxides of metals which powerfully attract oxygen, such as potassa, soda, &c. But there are a few cases, in which certain metals are incapable of combining with sulphur, till they are brought into the state of oxides. These are chiefly zinc, mercury, and manganese, the compounds of which with sulphur may be called *sulphureted oxides*.† Other metals, also, are capable of affording similar compounds; but in general their affinity for sulphur diminishes, in proportion to the quantity of oxygen which they hold in combination.

Sulphureted oxides act on acids, somewhat differently from the mere sulphurets. If the metal be only oxidized at its minimum, they yield sulphureted hydrogen with diluted muriatic and sulphuric acids, and nitrous gas with nitric acid. But in their perfectly oxidized state, the oxides dissolve without effervescence, and the sulphur remains unaltered.

3. Sulphureted hydrogen enters into combination with a few of the metals, with mercury and silver for example; but

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\* Berthollet, loc. cit. 256.

† Vauquelin asserts, however, (Ann. de Chim. et Phys. v. 6,) that the oxides of manganese and iron are decomposed by sulphur, and that true metallic sulphurets are formed.

it unites, in general, more readily and permanently with their oxides. From such compounds, the sulphureted hydrogen is detached in a gaseous state by some concentrated acids, which seize the metallic oxide. Most of the sulphureted oxides, also, undergo, in process of time, spontaneous decomposition, in consequence of the union of the hydrogen and oxygen which they contain, and which, by combination, form water. When this happens, the oxide is partly reduced, and the sulphur unites with the deoxidized metal. Hence the same sulphureted oxide varies in composition, according to the period which has elapsed since its preparation.

When we precipitate a metallic solution by sulphureted hydrogen alone, or by its compounds with alkalies, we obtain either a metallic sulphuret or a hydro-sulphuret. In the first case, the hydrogen of the sulphureted hydrogen takes all the oxygen of the oxide; and the sulphur forms a true sulphuret with the reduced metal. In the second case, the sulphureted hydrogen unites directly with the oxide, without decomposing it, and its proportion is such that the hydrogen is sufficient to saturate all the oxygen of the oxide. The quantity of hydrogen, then, which is destroyed, or may be destroyed, depends on the state of oxidizement of the metal, and so also does the quantity of sulphur. Now if metals, as appears probable, are susceptible of oxidation in only a few determinate degrees, it follows that by precipitations of this kind, we may obtain metallic sulphurets with fixed proportions, which may be easily calculated from the known quantity of oxygen in the oxide, and the known composition of sulphureted hydrogen.\* Thus the law of fixed proportions will be extended to the compounds of metals with sulphur; and another step will be made towards establishing the important general principle in chemical philosophy, which has been so ably illustrated, in other cases, by Mr. Dalton.

4. Hydrogureted sulphurets of metals and their oxides may be obtained by precipitating metallic solutions with the hydrogureted sulphurets of alkalies. In sulphureted oxides, it has been observed by Berzelius,† the oxygen of the oxide

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\* Gay Lussac, Mémoires d'Arcueil, ii. 175. † 29 Ann. de Chim. 200.

is to the hydrogen of the sulphureted hydrogen, precisely in the proportion necessary to constitute water. The oxides of all those metals, he adds, which have for oxygen a greater affinity than hydrogen has, may unite with sulphureted hydrogen. In the compounds, thus produced, the metal, sulphur, hydrogen, and oxygen, exist in such proportions, that the oxygen is precisely sufficient to change the sulphur into acid, the metal into protoxide, and the hydrogen into water. But if the affinity of the metal for oxygen be inferior to that of hydrogen, the oxide is then reduced, and water and a sulphuret are generated. Thus the alkalis, the earths, and protoxides of zinc and manganese, afford, with sulphureted hydrogen, saline combinations; but the oxides of lead and copper are decomposed by it.

It had been generally supposed that metals, which have a great affinity for oxygen, and which decompose water (as manganese, iron, zinc, uranium, nickel, cobalt, &c.) are not precipitated from their solutions by sulphureted hydrogen, except with the concurrence of double affinities. Gay Lussac, however, has shown\* that the compounds of these metals with the weaker acids (as the acetic, tartaric, and oxalic) are decomposed by sulphureted hydrogen, and produce hydrosulphurets of the respective metals. When a still weaker solvent of the metal is employed, the decomposition is more easily effected. Thus the ammoniurets of iron, nickel, &c. are entirely decomposed by that gas; and this furnishes an excellent process for obtaining pure hydrosulphurets; for the alkaline hydrosulphurets, commonly employed for this purpose, are almost always contaminated with sulphur. Those metals, which are not precipitable by sulphureted hydrogen, become so, when acetate of potash is added to their solutions.

V. Several metals have an affinity for phosphorus, and form a class of compounds called METALLIC PHOSPHURETS. The best method of effecting this combination is to expose the metals to heat, in contact with phosphoric acid and charcoal. The charcoal deprives the phosphorus of oxygen; and the

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\* 80 Ann. de Chim. 995.

de-oxygenized phosphorus unites with the metal. Metals, however, that have a strong affinity for oxygen, decompose the phosphoric acid, and unite with its base, without the intervention of charcoal. The metallic phosphurets have not hitherto been applied to any useful purpose; and it is sufficient, therefore, to refer to the description of them by Pelletier, in the first and thirteenth volumes of the *Annales de Chimie*.

VI. The compounds of metals with carbon are called **CARBURETS**. That of iron and carbon, the properties of which vary according to the proportion of the two ingredients, is the only one of importance. It will be described in its proper place.

VII. The metals are, for the most part, capable of uniting with each other. For this purpose, they require to be brought into a state of fusion; and, even when melted, considerable care is necessary to form a permanent compound. If one metal is considerably heavier than the other, it is apt to sink to the bottom of the fluid mass. Nothing can show this in a more striking manner, than a fact which has been stated by Mr. Hatchett. He found that when gold, which has been melted with a proportion of copper or other metals, is cast into bars, the moulds for which are placed vertically, the lower part of the bar contains more gold in proportion than the upper part.

There are a few of the metals that do not unite by being fused together. This is the case with lead and iron; but even in such cases we are scarcely, perhaps, entitled to deny all affinity; for some of the metals, which were formerly thought incapable of combination, have been made to combine by circuitous processes. This is the fact with respect to iron and mercury.\*

In the new nomenclature, the word **ALLOY** is retained as a general term for all combinations of metals with each other; and the specific name is derived from that of the metal, which prevails in the compound. Thus in the *alloy of gold with silver*, the gold is to be understood as being in greatest pro-

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\* Aikin, in *Philosophical Magazine*.

portion; in the *alloy of silver with gold*, the silver is the principal ingredient. The compounds of mercury with other metals, at a very early period of chemistry, were called **AMALGAMS**, and as the name does not lead to any erroneous notions, it may still be retained to denote this sort of alloy.

The metals in general have been supposed capable of uniting with each other in unlimited proportions; but a careful examination of those alloys, which are characterized by peculiar properties, and adapted to specific uses, has shown that such compounds are definite, and fall within the general laws of the atomic system. This proposition has been ably maintained by Berzelius, as well as by Dalton. Potassium, the former observes, gives with mercury two crystallized compounds, one of which contains twice as much potassium as the other. The *arbor Dianæ* is a definite compound of silver and mercury. When zinc and copper are distilled together, a certain quantity of zinc comes over, but the rest cannot be raised by heat. From a fused mixture of antimony, iron, and copper with much tin, metallic crystals separate on cooling, containing fixed proportions of the component metals. Whenever, indeed, the new compound has an opportunity of separating from the fused mass, it appears to be formed in established proportions.

By combination with each other, the metals undergo a considerable change of properties, and acquire new ones, not observable in the separate metals.

1. The *specific gravity* of an alloy is seldom the mean of those of its component parts. Thus an alloy of silver with copper or tin, or one of silver or gold with lead, has a greater than the mean specific gravity. An alloy, also, of silver with mercury, though the former metal is specifically lighter than the latter, possesses so much acquired density as to sink in quicksilver. In other cases, on the contrary, the specific gravity of the compound falls short of the mean of that of its components, or there appears to be a degree of dilatation, as in the alloys of gold with copper, iron, or tin. To estimate exactly, however, either the increase or diminution of density, requires an attention to several circumstances.\*

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\* See Aikin's Dictionary, article Alloy.

2. The *ductility* and *malleability* of metals is generally changed by being alloyed together; and, for the most part, these qualities are impaired. Even two metals, which separately are both malleable and ductile, may be rendered brittle by combination. This is very remarkably the case with an alloy of gold and lead, the latter of which, even in the trivial proportion of half a grain to an ounce of gold, renders the alloy quite destitute of tenacity; and an alloy of platinum, copper, and zinc, though eminently ductile and malleable, is rendered brittle by a quantity of iron not exceeding half a grain in four ounces of the alloy.\* In such cases, it has been supposed that a true chemical union does not take place, and that the newly added metal is merely mechanically interposed between the particles of the other, the cohesion of which it thus impairs. This explanation, however, can scarcely be admitted as satisfactory; and, among other arguments in proof of the existence of chemical union, it may be remarked, that gold is rendered brittle by being kept in fusion in the vicinity of melted tin, the vapour of which it seems capable of attracting.

3. The *hardness* of metals is varied by combination. Gold, by combination with a small quantity of copper, and silver by a minute proportion of the same metal, acquire such an increase of hardness, that these additions are always made to gold or silver which is to be exposed to wear. By a small addition of gold, iron is said to gain so much hardness, as to be even superior to steel for the fabrication of cutting instruments.

4. *Change of colour* is a common effect of the combination of metals with each other. Arsenic, for example, which resembles steel, and copper, which has a red colour, afford by their union a compound which has nearly the whiteness of silver.

5. The *fusibility* of compound metals is different from what might have been inferred from that of their components. Platinum, for example, is rendered easily fusible by arsenic, and a compound of lead, tin, and bismuth, melts at a temper-

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\* Journ. of Science, iii. 179.



ature below that of boiling water, though the most fusible of the three (tin) requires for its fusion a much higher degree of heat than  $212^{\circ}$ . This is the principle of *solders*.

6. Metals have their *volatility* increased, by being combined with other metals which are more volatile than themselves. Gold, separately, requires an intense heat for its volatilization; but when an amalgam of gold with mercury is distilled, a quantity of gold passes over with the quicksilver.

7. By chemical union with each other, the metals have their *tendency to combine with oxygen* considerably increased, partly in consequence of the diminution of their cohesion, but in some cases, in consequence of their forming a galvanic combination. Lead, when amalgamated with mercury, is oxidized by merely shaking the compound with water. Lead and tin, melted together, acquire such an increase of affinity for oxygen, that, at the moment of combination, they actually inflame. By the oxidation of either ingredient in any of these alloys, the compound is destroyed. The oxide of lead, for example, separates from mercury in the form of a black powder. Hence, also, a pellicle of oxide is generally observed on the surface of melted solders, which is renewed as soon as it is removed.

8. The solubility of metals in acids is modified by their combination with each other. When gold is alloyed with a small proportion of silver, the latter metal is protected from the action of the nitric acid, and in order to render it soluble in that acid, it is necessary to raise its proportion to one fourth the weight of the alloy, which constitutes the process of *quartation*. In a similar manner, in order to render tin capable of being entirely dissolved out of an alloy of that metal with antimony, it is necessary that it should constitute 20 parts out of 21 of the alloy; in which case the tin is wholly dissolved by boiling with muriatic acid, and the antimony is left untouched.\*

From a comparison of the resemblances among metals, both as to physical and chemical properties, several arrangements

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\* Chaudet, Ann. de Chim. et Phys. iii. 382.

of them have been formed into smaller classes. The circumstance on which a subordinate division of the metals is perhaps best founded, is the nature of their relation to oxygen. Without creating more of these subdivisions than are absolutely necessary, it appears to me that they may be conveniently arranged under the following heads:—

**CLASS I. METALS, THAT AFFORD OXIDES, WHICH CANNOT BE REDUCED TO A METALLIC FORM WITHOUT THE ADDITION OF COMBUSTIBLE MATTER.**

**CLASS II. METALS, THE OXIDES OF WHICH ARE DECOMPOSED BY HEAT ONLY.**

**I. THE FIRST CLASS, which have been termed *base metals*, to distinguish them from the *noble* or *perfect*, may be again sub-divided as follows:—**

1. *Metals that are either known from experiment, or believed from analogy, to absorb oxygen at high degrees of heat, and to decompose water at common temperatures.* The metals that have been actually ascertained to produce these effects, are six, viz.

Potassium,  
Sodium,  
Lithium,  
Calcium,  
Barium, and  
Strontium.

There is a striking resemblance, also, between the properties of the oxides of these metals. Those of potassium, sodium, and lithium, are readily soluble in water; have a peculiar acrid taste; change certain blue vegetable colours to green, and some yellow ones to brown; neutralize acids, forming salts which, for the most part, are easily soluble; and, from these similarities, have been classed together under the name of **ALKALIS**. With these oxides, those of calcium, barium, and strontium agree so nearly, that they also might, without any impropriety, be called alkalis; but, being themselves, as well as several of their neutral compounds with acids, less readily soluble in water, they have been termed, perhaps without sufficient reason, **ALKALINE EARTHS**.

The metals, belonging to this sub-division, which are as yet distinctly known to us only when in combination, but which are presumed from analogy to have a similar relation to oxygen and water, with those already enumerated, are the seven following :

Magnesium,  
Glucinum,  
Yttrium,  
Aluminum,  
Thorinum,  
Zirconium, and  
Silicium.

The oxides of these seven metals are sparingly soluble in water; have little or no taste; do not afford solutions in water which are capable of acting on vegetable blue or brown colours; but (silica excepted) unite with acids, and form neutral salts. They have been hitherto termed EARTHS, or EARTHS PROPER; though the grounds of their distinction from other metallic oxides are constantly becoming more limited. It has been questioned whether one of these bodies, silica, does not, as to its powers of combination, exhibit rather the qualities of an acid; and whether its base, which some writers have called silicon, can properly be arranged among metals.

2. *The second sub-division includes those metals, which absorb oxygen from atmospheric air at high temperatures; and decompose water, but not under a red heat. They are five in number, viz.*

Manganese,  
Zinc,  
Iron,  
Tin, and  
Cadmium.

The last of these is associated with the others, from the agreement of its general properties with those of tin.

3. *Metals of the third sub-division are capable, like the foregoing, of absorbing oxygen at high temperatures, but not of de-*

*composing water at any temperature.* There are no less than fourteen which answer to this description ; viz.

Arsenic,  
Molybdenum,  
Chromium,  
Tungsten,  
Columbium,  
Antimony,  
Uranium,  
Cerium,  
Cobalt,  
Titanium,  
Bismuth,  
Copper,  
Tellurium, and  
Lead.

Of these metals, the first five are distinctly acidifiable ; and the nine others are oxidizable only.

II. THE SECOND CLASS OF METALS, the oxides of which are reducible by heat, without the addition of combustible matter, are nine in number ; viz.

Mercury,  
Silver,  
Gold,  
Platinum,  
Palladium,  
Rhodium,  
Iridium,  
Osmium, and  
Nickel.

The three first have been long classed together under the name of *noble or perfect metals* ; and the remaining ones have been associated with them, as they have been successively discovered. Nickel, which was for some time placed among the imperfect metals, was removed a few years since into this class, after a more accurate investigation of its relation to oxygen.

## CLASS I.

METALS, WHOSE OXIDES ARE NOT REDUCIBLE BY HEAT,  
WITHOUT THE ADDITION OF COMBUSTIBLE MATTER.

### DIVISION I.

METALS THAT ABSORB OXYGEN FROM ATMOSPHERIC AIR, AND  
DECOMPOSE WATER AT COMMON TEMPERATURES.

#### SECTION I.

##### *Of Potassium.*

THIS metal was discovered by Sir H. Davy in 1807, and was obtained from a substance which will be described in this section, under the name of potassa. To this discovery and many others of a similar kind, that distinguished philosopher was led by a train of inductive reasoning, which is not surpassed by any investigation in the history of the physical sciences.

From the facts which have been stated in a former section, respecting the powers of electrical decomposition, it appeared to be a natural inference, that the same powers, applied in a state of the highest possible intensity, might disunite the elements of some bodies, which had resisted all other instruments of analysis. If potassa, for example, were an oxide, composed of oxygen united to an inflammable base, it seemed probable, that when subjected to the action of opposite electricities, the oxygen would be attracted by the positive wire and repelled by the negative. At the same time, the reverse process might be expected to take place with respect to the combustible base, the appearance of which might be looked for at the negative pole.

In his first experiments, suggested by these views, Sir H. Davy failed to effect the decomposition of potassa, owing to his employing the alkali in a state of aqueous solution, and to the consequent expenditure of the electrical energy in the mere

decomposition of water. In his next trials, the alkali was liquefied by heat in a platinum dish, the outer surface of which, immediately under the alkali, was connected with the zinc or positive end of a battery consisting of 100 pairs of plates, each six inches square. In this state, the potassa was touched with a platinum wire proceeding from the copper or negative end of the battery; when instantly a most intense light was exhibited at the negative wire, and a column of flame arose from the point of contact, evidently owing to the development of combustible matter. The results of the experiment could not, however, be collected, but were consumed immediately on being formed.

The chief difficulty in subjecting potassa to electrical action is, that in a perfectly dry state it is a complete non-conductor of electricity. When rendered, however, in the least degree moist by breathing on it, it readily undergoes fusion and decomposition, by the application of strong electrical powers. For this purpose, a piece of potassa, weighing from 60 to 70 grains, may be placed on a small insulated plate of platinum, and may be connected, in the way already described, with the opposite end of a powerful electrical battery, containing not less than 100 pairs of six inch plates. On establishing the connection, the potassa will fuse at both places where it is in contact with the platinum. A violent effervescence will be seen at the upper surface, arising, as Sir H. Davy has ascertained, from the escape of oxygen gas. At the lower or negative surface, no gas will be liberated; but small bubbles will appear, having a high metallic lustre, and being precisely similar in visible characters to quicksilver. Some of these globules burn with an explosion and bright flame; while others are merely tarnished, and are protected from farther change by a white film, which forms on their surface.\*

This production of metallic globules is entirely independent of the action of the atmosphere; for Sir H. Davy found that they may be produced *in vacuo*.

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\* For the repetition of this experiment, very useful practical directions may be found in a paper by Mr. Singer.—Nicholson's Journal, xxiv. 174. The potassa, submitted to electrical action, must of course be in the state of solid hydrate.

To preserve this new substance, it is necessary to immerse it immediately in pure naphtha, a fluid which will be described in a subsequent part of the work. If exposed to the atmosphere, it is rapidly converted back again into the state of pure potassa. To prevent its oxidation still more effectually, Mr. Pepys has proposed to produce it under naphtha; and has contrived an ingenious apparatus for this purpose, which is described in the 31st volume of the Philosophical Magazine, page 241.

Nothing then can be more satisfactory than the evidence furnished by these experiments, of the nature of one of the fixed alkalis. By the powerful agency of opposite electricities, it is resolved into oxygen and a peculiar base.\* This base, like other combustible bodies, is repelled by positively electrified surfaces, and attracted by negative ones; and hence its own natural state of electricity must necessarily be positive. Again, by uniting with oxygen, it is once more changed into alkali, either slowly at ordinary temperatures; or with heat and light, at high temperatures. We have the evidence, therefore, both of analysis and synthesis, that potassa is a compound of oxygen with a peculiar inflammable basis.

In assigning to this newly discovered substance a fit place among the objects of chemistry, Sir H. Davy was induced to class it among the metals, because it agrees with them in opacity, lustre, malleability, conducting powers as to heat and electricity, and in its qualities of chemical combination. The only property, which can be urged against this arrangement, is its extreme levity, which even exceeds that of water. But when we compare the differences which exist among the metals themselves, this will scarcely be considered as a valid objection. Tellurium, for example, which no chemist hesitates to consider as a metal, is only about six times heavier than the base of potassa, while it is four times lighter than platinum;

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\* The proportions of oxygen and base in each will be stated at the end of the articles Potassium and Sodium.

thus forming a sort of link between the old metals and the bases of the alkalis.

In giving names, therefore, to the alkaline bases, Sir H. Davy has adopted that termination, which, by common consent, has been applied to other newly discovered metals, and which, though originally Latin, is now naturalized in our language. The base of potassa he has called POTASSIUM, and the base of soda SODIUM; and these names have met with universal acceptance among chemical philosophers.

*Process for preparing Potassium.*

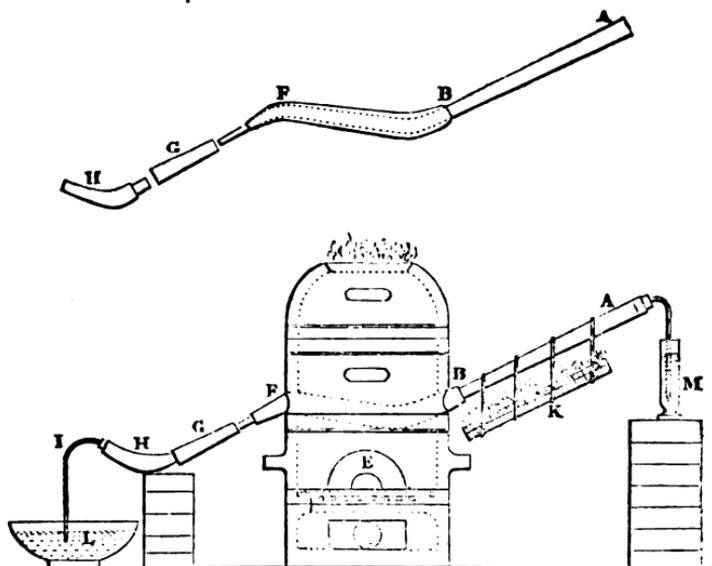
It is not, however, by electrical means only that the decomposition of potassa has been accomplished. Soon after Sir H. Davy's discoveries were known at Paris, Messrs. Gay Lussac and Thenard\* succeeded in their attempts to decompose both the fixed alkalis, without the aid of a Voltaic apparatus, merely by the intervention of chemical affinities. Their process, though it affords the alkaline bases of less purity, yields them in much larger quantity than the electrical analysis, *viz.* to the amount of nearly 400 grains by one operation. It consists in bringing the alkalis into contact with intensely heated iron, which, at this temperature, attracts oxygen more strongly than the alkaline base retains it.

The apparatus, used for obtaining potassium, has a general resemblance to that which is employed for decomposing water by means of iron. It consists of a gun-barrel curved as in the annexed sketch, which is copied from Thenard's *Traité de Chimie*. At one end the barrel is drawn out to rather a smaller diameter; and, before being used, it is to be covered between B and F with a lute of infusible clay, which should be suffered to dry thoroughly. Into the barrel between F and B, clean iron turnings are to be introduced, and between A and B pieces of solid hydrate of potassa. A tube of safety is to be luted to the end A, and is to be immersed in mercury in the

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\* *Annales de Chimie*, lxx. 325; or *Mémoires d'Arcueil*, ii. 499.





glass vessel M. To the smaller end of the barrel, a short piece of copper tube, G, is accurately ground, and to this last a small copper receiver, H, destined to collect the potassium, is fitted by grinding. To the other end of H, a tube of safety, I, is to be luted, and made to dip into mercury contained in the vessel L, but to a less depth than the safety tube M.

A strong heat is now to be raised in the furnace, and, while this is doing, the part of the barrel containing the potassa, as well as the end F, and the attached copper tube and receiver, should be kept cool by wet cloths. If gas now issues abundantly through the safety tube I, the junctures may be concluded to be tight. When the barrel has become white hot, the potassa may be melted by burning charcoal contained in a moveable cage K. It will then flow upon the intensely ignited iron turnings, and a large quantity of hydrogen gas, holding some potassium in solution, will issue through the safety tube, I. The cage may now be removed for a short time; and, when the production of gas slackens, it may be restored to its place. These operations may be repeated alternately till no more gas is evolved; after which the heat in the furnace should be made

as intense as possible, in order to drive off some of the potassium which strongly adheres to the iron turnings. If the escape of gas through I should at any time cease during the operation, and take place through M, this will probably be owing to a lodgment of potassium at the end, F, of the barrel, from which it may be melted into the copper receiver, by holding a little red-hot charcoal under the part where it has condensed. The principal difficulty, in the process of decomposing potassa, is to excite sufficient heat without melting the gun-barrel; and to this object the attention of the operator must be carefully directed, throughout the whole manipulation.

At the close of the operation, as soon as the vessels G and H are sufficiently cool, they are to be removed, then filled with naphtha, emptied again, and quickly stopped with corks. As a portion of potassium generally remains in the end F, the barrel should also be plugged by an iron stopper provided for the purpose. When sufficiently cold it may be removed from the furnace, and a little naphtha be passed through it. The potassium must be detached in as large pieces as possible from the barrel, and from the copper receiver, and be kept under rectified naphtha in a well-stopped vial.

When the iron turnings are very clean, the potash very dry and pure, and the whole apparatus free from foreign matters, the metal produced differs very little from that obtained by a Voltaic battery. Its lustre, ductility, and malleability are similar. Its point of fusion and specific gravity, however, are a little higher; for it requires nearly  $130^{\circ}$  Fahr. to render it perfectly fluid, and is to water as 796 to 1000 at  $60^{\circ}$  Fahrenheit. This Sir H. Davy ascribes to contamination with a minute proportion of iron. The affinities, indeed, by which the decomposition is produced, he supposes to be those of iron for oxygen, of iron for potassium, and of potassium for hydrogen.

Charcoal, it has been asserted by Curaudau,\* may be employed, also, for the decomposition of the alkalies. To ensure

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\* Nicholson's Journal, xxiv. 37.

success in the process, great attention, it appears, is necessary to the manipulations, which are fully described in the memoir of the inventor. The fact sufficiently explains an observation of Professor Woodhouse.\* A mixture of half a pound of soot and two ounces of pearlash was exposed, for two hours, in a covered crucible to an intense heat. When the mixture became cold it was emptied upon a plate, and a small quantity of water poured upon it, when it immediately took fire. This could only be owing to the conversion of part of the potassa into potassium.

*Properties of Potassium.*

I. The base of potassa, at 70° Fahrenheit, exists in small globules, which possess the metallic lustre, opacity, and general appearance of mercury; so that when a globule of mercury is placed near one of potassium the eye can discover no difference between them. At this temperature, however, the metal is only imperfectly fluid; but, when gradually heated, it becomes more and more fluid; and at 150° Fahr. its fluidity is so perfect, that several globules may easily be made to run into one.

By reducing its temperature, potassium becomes, at 50° Fahrenheit, a soft and malleable solid, which has the lustre of polished silver. It is soft enough, indeed, to be moulded by the fingers like wax, but should be covered by a film of naphtha to prevent it from taking fire. At about the freezing point of water, it becomes hard and brittle, and exhibits, when broken, a crystallized texture, which, in the microscope, seems composed of beautiful facets of a perfect whiteness and high metallic splendor.

To be converted into vapour, it requires a temperature approaching that of a red heat; and, when the experiment is conducted under proper circumstances, it is found unaltered after distillation.

II. Potassium is a perfect conductor both of electricity and of heat.

III. Its specific gravity at 60° Fahrenheit, making some allowance for unavoidable errors in the experiment, is, accord-

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\* Nicholson's Journal, xxi. 290.

ing to Gay Lussac and Thenard, 0.865. Bucholz states it at 0.876, and Sir H. Davy, in general terms, at between .8 and .9, water being considered as 1.

IV. At the temperature of the atmosphere, potassium acts on oxygen gas, even when the gas is deprived of its hygrometrical moisture; but to produce its full effect it is necessary that it should be in thin flattened pieces, as it soon becomes covered with a coating of oxide which protects the mass beneath from further action. If heated nearly to redness, or to its point of vaporization, it burns with a brilliant white flame and a very intense heat.

V. Potassium appears to be susceptible of different degrees or stages of oxidizement. Istly, By heating it to a point, below what is necessary for its inflammation, either in common air or oxygen gas; or (which is still better), by confining it, for some days, in an empty phial loosely corked, a substance is formed of a bluish grey colour, softer than wax, and readily fusible. This substance takes fire in oxygen gas, or even common air, at about 70° Fahrenheit, and acts on water, giving out hydrogen, but in less quantity than is extricated by potassium. It is now, however, generally considered not as a distinct oxide, but a mixture of that which is next to be described with metallic potassium.

2. The true *protoxide of potassium* is best obtained by the action of potassium on water. This is attended with some striking phenomena. When potassium is thrown upon water exposed to the atmosphere, or when it is brought into contact with a drop of water, it decomposes the water with great violence; an instantaneous explosion is produced with a vehement flame; and a solution of pure potassa is the result. The hydrogen gas, which is disengaged, appears to dissolve a portion of potassium; for, on escaping into the air, it forms a white ring of smoke, gradually enlarging as it ascends, like the bluish phosphureted hydrogen gas.

When water is made to act on the base of potassa, atmospheric air being excluded, there is much heat and noise, but no luminous appearance; and the gas evolved is pure hydrogen. Each grain of potassium, by acting on water, detaches about 1.06 cubic inch of hydrogen gas.

If a globule of the base of potassa be placed on ice, it instantly burns with a bright flame, and a deep hole is made in the ice, filled with a fluid which is found to be a solution of potassa.

The production of alkali, by the action of water on potassium, is most satisfactorily shown, by dropping a globule of the metal upon moistened paper, which has been tinged with turmeric. At the moment when the globule comes into contact with the paper, it burns, and moves rapidly, as if in search of moisture, leaving behind it a deep reddish brown trace, and acting upon the paper exactly like dry caustic potassa. So strong, indeed, is the affinity of potassium for oxygen, that it discovers and decomposes the small quantities of water contained in alcohol and ether, even when carefully purified, and disengages, from both these fluids, hydrogen gas.

On naphtha, colourless and recently distilled, potassium has very little power of action; but in naphtha, which has been exposed to the air, it soon oxidates, and alkali is formed. This unites with the naphtha into a brown soap, that collects round the globules.

*Potassa.—Hydrate of Potassa.—Peroxide.*

It was important to determine the proportions, in which potassium and oxygen unite when potassa is regenerated. This Sir H. Davy investigated by two different processes. The one consisted in ascertaining how much oxygen gas is absorbed by a known weight of potassium: the other, how much hydrogen is disengaged from water by that metal; and dividing the evolved hydrogen gas by 2, he learned the quantity of oxygen which had been abstracted from the water. By the united evidence of these methods of investigation, he determined that 75 parts of potassium, to become potassa, absorb 15 parts by weight of oxygen, a result which coincides very nearly with that of Gay Lussac and Thenard, who found that 100 of potassium combine with 19.945, or, in whole numbers, with 20 of oxygen. Hence potassa contains

Potassium .....	83.34
Oxygen .....	16.66
	<hr/>
	100.

And  $15 : 75 :: 8 : 40$  : potassa, therefore, is constituted of 1 atom of potassium = 40, + 1 atom of oxygen = 8; and its representative number is 48.

This, however, applies to potassa, only when perfectly pure, and free from water. In this state it is white, extremely caustic, turns the syrup of violets green; is fusible a little above a red heat; is deliquescent, and therefore very soluble in water; when heated in oxygen gas absorbs a farther proportion of oxygen, and from the state of protoxide passes to that of the orange-coloured *peroxide*.

The precise nature of the orange-coloured compound was first explained, and its properties examined, by Gay Lussac and Thenard. It is fusible at a lower heat than hydrate of potassa, and crystallizes in laminæ by cooling. When thrown into water, oxygen gas is evolved, and it passes to the state of protoxide. The same change occurs by exposing it on a platinum tray, coated with fused chloride of potassium, to a heat considerably above that at which it was produced. It is constituted of 1 atom of potassium = 40, + 3 atoms of oxygen = 24, and its representative number is 64.

Potassa, as generally obtained by chemical operations, is not the pure protoxide, but is intimately united with a certain proportion of water. The credit of this discovery is due to Darcet, who has established his claim to it very satisfactorily. The solid hydrate of potassa appears to be constituted of an atom of protoxide = 48, + an atom of water = 9, and its equivalent number, therefore, is 57. Hence 100 parts of hydrate of potassa will contain very nearly

Protoxide of potassium .....	84
Water.....	16
	<hr style="width: 100px; margin: 0 auto;"/>
	100

*Hydrate of potassa* may be prepared as follows. Dissolve any quantity of American or Dantzic pearlash in twice its weight of boiling water; or, if the alkali be required particularly pure, substitute carbonate of potassa, which has been prepared by burning a mixture of one part of pure nitre with two of super-tartrate of potassa. Add this solution to an equal weight of fresh burned quick lime, first slaked to a fine powder, and then diffused through water sufficient to render the mix-

ture quite fluid. Boil these ingredients in an iron kettle, and continue stirring for half an hour. Then separate the liquid alkali, either by subsidence, or by straining through calico, and boil it to dryness in a silver dish. Put the dry mass into a bottle, and pour upon it as much pure alcohol as is necessary to dissolve all that is soluble in that fluid. Then decant the alcoholic solution of potassa, and distil off the alcohol, in an alembic of pure silver fitted with a glass head. (See pl. I. fig. 2.) Pour the alkali, when in fusion, upon a silver dish, and, as soon as cold, break it into pieces, and preserve it in well-stopped vials. If the whole of the alcohol be not thus separated, the hydrate of potassa will shoot, on cooling, into regular crystals. For common purposes, it is sufficient to boil down the watery solution, and to fuse the residue; and thus prepared, especially when procured from nitre and tartar, it is sufficiently pure for affording potassium. In all accurate experiments, however, it is necessary to employ hydrate of potassa which has been purified by alcohol.

From the electro-chemical researches of Sir H. Davy, it appears that potassa is not completely deprived of carbonic acid by any process hitherto employed for its preparation. It is probable that the method suggested by Darcet, of removing the last portions of carbonic acid from the alkaline solution, after the action of quicklime, by adding solution of barytes, would be found effectual. The potassa is apt, during the concentration in the alembic, to act upon the alcohol, and disengage a portion of charcoal; and to dissolve, also, a minute quantity of silver.

The solution of hydrate of potassa has, when concentrated, an intensely acrid taste, and destroys the texture of animal and vegetable substances. It changes the colour of the violet to green; neutralizes acids without effervescing with them; renders oils miscible with water; and dissolves resins. Hence it is powerfully detergent.

It is often of importance to know the quantity of real potassa contained in solutions of different specific gravities. For this purpose, the following Table has been constructed by Mr. Dalton. The first of the liquid compounds is that containing 1 atom of potassa + 2 atoms of water.

*Table of the Quantity of Real Potassa in watery Solutions of different Specific Gravities.*

Atoms of pot. water.	Potassa per cent. by weight.	Potassa per cent. by measure.	Specific Gravity.	Congeeing point.	Boiling point.
1 + 0	100	240	2.4	unknown.	unknown.
1 + 1	84	185	2.2	1000°	red heat.
1 + 2	72.4	145	2.0	500°	600°
1 + 3	63.6	119	1.88	340°	420°
1 + 4	56.8	101	1.78	220°	360°
1 + 5	51.2	86	1.68	150°	320°
1 + 6	46.7	75	1.60	100°	290°
1 + 7	42.9	65	1.52	70°	276°
1 + 8	39.6	58	1.47	50°	265°
1 + 9	36.8	53	1.44	40°	255°
1 + 10	34.4	49	1.42		246°
	32.4	45	1.39		240°
	29.4	40	1.36		234°
	26.3	35	1.33		229°
	23.4	30	1.28		224°
	19.5	25	1.23		220°
	16.2	20	1.19		218°
	13	15	1.15		215°
	9.5	10	1.11		214°
	4.7	5	1.06		213°

#### *Chloride of Potassium.*

When potassium is heated in chlorine gas, it burns much more vividly than in oxygen; each grain absorbs 1.1 cubic inches of the gas, and a neutral compound is formed, which is a true chloride of potassium. The same compound is formed by heating potassium in muriatic acid gas, for in this case the gas is decomposed into chlorine, which unites with the metal, and hydrogen, which is liberated in a gaseous state. It may also be procured by dissolving either hydrate or carbonate of potassa in muriatic acid, and evaporating the solution to perfect dryness. In the first instance, muriate of potassa is formed, which, by the subsequent application of heat, is converted into chloride of potassium; the hydrogen of the muriatic acid uniting with the oxygen of the potassa, and forming water which is volatilized.



According to Sir H. Davy, chloride of potassium is constituted of 75 potassium + 67 chlorine, proportions which nearly agree with those stated by Gay Lussac, viz. 111.31 potassium + 100 chlorine. Hence it is composed of 1 atom of potassium, = 40, + 1 atom of chlorine = 36, and its equivalent number is 76. One hundred grains, according to Berzelius, when dissolved in water, and decomposed by nitrate of silver, yield 192.4 of fused chloride of silver, formerly called *luna cornea*.

When chloride of potassium is dissolved in water, a double elective affinity is supposed to operate; water is decomposed; its hydrogen, uniting with the chlorine, composes muriatic acid; and the oxygen of the water, being transferred to the potassium, constitutes potassa. The acid and alkali together form muriate of potassa. By evaporating the solution, crystals are again obtained of chloride of potassium. These crystals are cubical, have a bitter disagreeable taste; undergo little change when exposed to the air; and when suddenly heated to redness decrepitate, with a very trifling loss of weight, arising from the escape of a little water. They are soluble in three times their weight of water at 60° Fahr. and in a rather less proportion of boiling water.

Considered as muriate of potassa (in which state this salt must always exist when in watery solution), it may be regarded as constituted of an atom of muriatic acid 37, and an atom of potassa 48, and its representative number is 85. Under this view, it is constituted of

Acid .....	36.57
Potassa .....	63.43
	<hr style="width: 100px; margin: 0 auto;"/>
	100.

#### *Iodide of Potassium.*

This compound may be formed, by heating potassium in a tube of green glass with an excess of iodine. At the moment of combination light appears, which, being seen through the vapour of iodine, has a purple hue.

Iodide of potassium enters into fusion, and is volatilized at a heat below redness. It dissolves readily in water, which,

during solution, it decomposes, forming a neutral hydriodate of potassa. It is constituted of 1 atom of potassium = 40, + 1 atom of iodine = 125, and its representative number is 165; 100 of potassium are combined, therefore, with 319 of iodine

*Potassium with Simple Acidifiable Bodies.*

*With hydrogen*, it forms two compounds, the one gaseous, the other solid. The first results from the action of potassium on water, the hydrogen of which, while in a nascent state, dissolves a portion of the metal. It may, also, as appears from Sir H. Davy's experiments, be formed, directly, by heating the metal in hydrogen gas. A large portion of potassium is thus dissolved; but the greater part precipitates on cooling.

This gas is spontaneously inflammable in the atmosphere; burns with a very brilliant light, which is purple at the edges; and throws off dense vapours of potassa. It loses its inflammability by keeping; is heavier than hydrogen gas; and is very dilatable by electricity. Besides the gas, which is spontaneously combustible, there is also, according to Sementini, another compound of potassium and hydrogen, which is not possessed of this property, and probably contains a less proportion of the combustible metal.

Gay Lussac and Thenard\* have succeeded, also, in forming a solid compound of potassium and hydrogen. The process consists in heating the metal in hydrogen gas; and the only difficulty is to regulate the heat, for a high temperature decomposes the compound. The flame of a spirit lamp, applied to potassium, in a retort filled with hydrogen gas, occasions an absorption of the gas, and the formation of a solid *hydruret of potassium*.

The colour of this substance is grey; it is destitute of metallic lustre; and is infusible. It is not inflammable, either in air or in oxygen gas at common temperatures, but burns vividly at a high one. When strongly heated in a close vessel, it is totally decomposed; all the hydrogen it contains is liberated in the state of gas; and the potassium remains. When

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\* *Recherches*, i. 176.

brought into contact with heated mercury, hydrogen gas is evolved, and an amalgam of potassium and mercury is produced.

Nitrogen gas has not, at any temperature, any action on potassium.

*Potassium with Sulphur.*—When sulphate of potassa is decomposed by hydrogen gas or by charcoal at a red heat, the residue is a compound of sulphur and potassium. It is difficult to obtain it perfectly pure, for it acts both on glass and on platinum. When prepared in glass, it has a pale cinnamon colour, and a crystalline fracture; fuses at a heat below redness; and then becomes dark and opaque. It attracts moisture from the air, and dissolves into a yellowish fluid, which, when diluted with water, becomes colourless. This appears to be a sulphuret of the first degree of sulphuration.

By fusing sub-carbonate of potassa with double its weight of sulphur, out of the contact of air, a sulphuret of potassium is formed in which 100 of the metal are united with 207.7 of sulphur, which is equivalent to 10 atoms. Varying the proportions, Berzelius, to whom we owe these facts, obtained sulphurets which he regards as compounds of 1 atom of potassium with 2, 4, 6, 7, 8, 9, and 10 atoms of sulphur.\*

When potassium is fused with sulphur, in a vessel filled with the vapour of naphtha, a rapid combination ensues, accompanied with heat and light, and a disengagement of sulphureted hydrogen. The result is a grey *sulphuret of potassium* not unlike artificial sulphuret of iron. Its formation and properties have been investigated by Vauquelin.†

The *phosphuret of potassium* may be formed by fusing potassium with phosphorus under naphtha. It requires for its fusion a stronger heat than either of its constituents. It is of the colour of lead; and, when spread out, has a lustre similar to polished lead. By exposure to the air, or by rapid combustion, it forms phosphate of potassa. Besides this, there is, also, a chocolate coloured compound of potassium and phos-

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\* Annals of Phil. N.S. iv. 284.

† Ann. de Chim. et Phys. vi. 22.

phorus; so that it is probable these two bodies unite in different proportions, the lead coloured compound consisting of 2 atoms of metal + 1 of phosphorus; and the chocolate of 1 atom of metal + 1 of phosphorus.

*Compounds of Potassium with Metals.*

*With mercury*, potassium gives some extraordinary and beautiful results. The combination is very rapid, and is effected by merely bringing the two metals into contact at the temperature of the atmosphere. The amalgam, in which the potassium is in least proportion, seems to consist of about 1 part in weight of basis and 70 of mercury. It is very soft and malleable; but by increasing the proportion of potassium we augment, in a proportional degree, the solidity and brittleness of the compound.

The compound of mercury and potassium may be obtained by an easy and simple process, first pointed out by Berzelius. Mercury, to the depth of a line, is put into a glass capsule, two inches in diameter, with a flat bottom. On this a solution of pure potassa is poured; an iron wire connects the mercury with the negative pole of a galvanic arrangement, which needs not contain more than 20 pairs of plates; and a spiral platina wire, from the positive pole, is immersed in the solution, and kept within about a line from the surface of the mercury. In six hours, the effect is observable, and in 24 is very distinct; for, in that time, more than 1200 grains of mercury will be rendered solid by combination with potassium. Unfortunately, this combination cannot be so decomposed, as to obtain the potassium in a separate state.

In this state of division, potassium appears to have its affinity for oxygen considerably increased. By a few minutes' exposure to the air, potassa is formed which deliquesces, and the mercury is left pure and unaltered. When a globule is thrown into water, it produces a rapid decomposition and a hissing noise; potassa is regenerated; pure hydrogen disengaged; and the mercury remains free.

The fluid amalgam of potassium and mercury dissolves all

the metals; and in this state of union, mercury even acquires the power of acting on platina.

Potassium unites, also, with gold, silver, and copper; and, when the compounds are thrown into water, this fluid is decomposed, potassa is formed, and the metals are separated unaltered. When the reduction of an ore has been accomplished by the use of fluxes containing potassa, M. Vauquelin has shown that the revived metal contains a greater or less proportion of potassium, which modifies its properties. By exposure to the air, or by the action of water, this impurity may be removed.\*

Potassium reduces all the metallic oxides when heated with them, even of those metals which most powerfully attract oxygen, such as oxides of iron. In consequence of this property, it decomposes and corrodes flint and green glass by a very gentle heat; potassa is generated with the oxygen taken from the metal, which dissolves the glass, and exposes a new surface. At a red heat even the purest glass, formed merely of potassa and silex, is acted upon. The alkali in the glass seems to give up a part of its oxygen to the potassium, and an oxide of potassium results, with a less proportion of oxygen than is necessary to constitute potassa. The silica, also, it is probable, is partly de-oxidized.

#### *Salts of Potassa.*

##### *Chlorate (Hyper-oxy-muriate) of Potassa.*

This salt was discovered by Berthollet. It may be formed either by the direct mixture of liquid chloric acid with solution of potassa or carbonate of potassa;—or by passing chlorine gas, as it proceeds from the mixture of muriate of soda, sulphuric acid, and manganese, through a solution of caustic potassa. This may be done by means of Woulfe's apparatus, using only one three-necked bottle in addition to the balloon. The tube, which is immersed in the alkaline solution, should be at least half an inch in diameter, to prevent its being choked up by any crystals that may form. The solution, when saturated with the gas, may be gently evaporated,

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\* Ann. de Chim. et Phys. vii. 33.

and the first products only of crystals are to be reserved for use; for the subsequent products consist of common muriate of potassa only.

When obtained by the absorption of chlorine by solution of potassa, the changes which take place admit of being explained as follows. Part of the chlorine may be employed in decomposing the water of the alkaline solution, forming, with its hydrogen, common muriatic acid, while another portion of chlorine unites with the oxygen thus set at liberty;—or the change may consist in the decomposition of potassa, the oxygen of one portion of which may be transferred to another portion, while the chlorine is partly expended in decomposing water and forming muriate of potassa, and partly in forming a triple compound of chlorine, oxygen, and per-oxide of potassium. In this view, chlorate of potassa is constituted of 1 atom of potassium weighing 40, 1 atom of chlorine = 36, and 6 atoms of oxygen = 48; and its equivalent number is the sum of these, viz. 124.

Even by the advocates of the simple nature of chlorine, two different views have been taken of this class of salts. By Gay Lussac, the chlorates are considered as compounds of chloric acid with alkaline and earthy bases; by Sir H. Davy, they are regarded as triple compounds of one atom of chlorine, one atom of metallic base, and six atoms of oxygen. But chloric acid being, as is deducible from the experiments of Gay Lussac, compounded of five atoms of oxygen with one atom of chlorine; there is no difference as to the facts, whatever there may be as to their explanation. This will appear from the following comparative statement.

According to Davy,

Chlorates consist of  $\left\{ \begin{array}{l} 1 \text{ atom of metallic base} \\ 1 \text{ atom of chlorine} \\ 6 \text{ atoms of oxygen.} \end{array} \right.$

According to Gay Lussac,

Chlorates are composed of  $\left\{ \begin{array}{l} 1 \text{ atom of base,} \\ \text{consisting of} \\ 1 \text{ atom of chloric acid} \end{array} \right. \left\{ \begin{array}{l} 1 \text{ atom metal} \\ 1 \text{ atom oxygen.} \\ 5 \text{ atom oxygen} \\ 1 \text{ atom chlorine.} \end{array} \right.$

It will easily be perceived, on examining these statements,

that the same proportions of elements are assigned by both philosophers to the chlorates, and that the only difference is as to the manner in which those elements are arranged.

The chlorate of potassa has the following qualities :

(a) It has the form of shining hexaedra lamiæ, or rhomboidal plates.

(b) One part of the salt requires 17 of cold water for solution, but five parts of hot water take up two of the salt.

(c) It is not decomposed by exposure to the direct rays of the sun, either in a crystallized or dissolved state.

(d) When chlorate of potassa is submitted to distillation in a coated glass retort, it first fuses, and, on a farther increase of temperature, yields oxygen gas of great purity. A hundred grains of the salt afford 75 cubic inches of gas (= about  $25\frac{1}{2}$  grains of gas), containing not more than three per cent. of nitrogen gas. Berzelius, from the same quantity, obtained a much larger product of gas, viz. 39.15 grains = 112 or 114 cubic inches.\* And Gay Lussac found that 100 grains give 38.88 grains of oxygen, and 61.12 of chloride of potassium, containing 28.93 chlorine and 32.19 potassium. The residue of this distillation, Vauquelin asserts,† is sensibly alkaline; from whence it should appear that the capacity of saturation is less in chlorine than in chloric acid.

(e) The chlorate of potassa has no power of discharging vegetable colours; but the addition of a little sulphuric acid, by setting chlorine at liberty, develops this property.

(f) The salt is decomposed by the stronger acids, as the sulphuric and nitric. This may be proved by dropping a few grains of the salt into a little concentrated sulphuric acid. A strong smell will arise, and, if the quantities be sufficiently large, an explosion will ensue. The experiment should, therefore, be attempted with caution. When this mixture is made at the bottom of a deep vessel, the vessel is filled with euchlorine gas, which inflames sulphuric ether, alcohol, or oil of turpentine, when poured into it; and also camphor, resin, tallow, elastic gum, &c. (Davy.)—By the action of sulphuric

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\* Ann. de Chim. et Phys. t. 175.

† Ibid. xcvi. 101.

acid, regulated as already described, peculiar gaseous compounds result.

Muriatic acid, as has already been stated, disengages chlorine, and the addition of a few grains of the salt to an ounce measure of the acid, imparts to it the property of discharging vegetable colours.

(g) Chlorate of potassa exerts powerful effects on inflammable bodies.

1. Rub two grains into powder in a mortar, and add one grain of sulphur. Mix them very accurately, by gentle trituration, and then, having collected the mixture to one part of the mortar, press the pestle down upon it suddenly, and forcibly. A loud detonation will ensue.—Or, if the mixed ingredients be wrapped in some strong paper, and then struck with a hammer, a still louder report will be produced.

2. Mix five grains of the salt with half the quantity of powdered charcoal in a similar manner. On triturating the mixture strongly, it will inflame, especially with the addition of a grain or two of sulphur, but not with much noise.

3. Mix a small quantity of sugar with half its weight of the salt, and on the mixture pour a little strong sulphuric acid.\* A sudden and vehement inflammation will be produced. This experiment, as well as the following, requires caution.

4. To one grain of the powdered salt, in a mortar, add about half a grain of phosphorus. The phosphorus will detonate, on the gentlest triture, with a very loud report. The hand should be covered with a glove in making this experiment, and care should be taken that the phosphorus, in an inflamed state, does not fly into the eyes.—Phosphorus may also be inflamed under the surface of water by means of this salt. Put into a wine glass, one part of phosphorus with two of the salt; fill it nearly with water, and pour in, by means of a glass tube, reaching to the bottom, three or four parts of sulphuric acid. The phosphorus takes fire, and burns vividly

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\* A mixture of this kind is the basis of the matches, now generally used for the purpose of procuring instantaneous light. The bottle, into which they are dipped, contains concentrated sulphuric acid, which is prevented from escaping by a quantity of finely spun glass or the fibres of amianthus.



under the water. This experiment too requires caution, lest the inflamed phosphorus should be thrown into the eyes. (Davy.) Oil may also be thus inflamed on the surface of water, the experiment being made with the omission of the phosphorus, and the substitution of a little olive or linseed oil.

5. Chlorate of potassa may be substituted for nitre in the preparation of gunpowder, but the mixture of the ingredients requires extreme circumspection, on account of their liability to explode by trituration. It may be proper also to state, that this salt should not be kept mixed with sulphur in considerable quantity, such mixtures having been known to detonate spontaneously.

#### *Per-chlorate of Potassa.*

This salt may be formed by mixing one part of powdered chlorate of potassa with three of sulphuric acid, and exposing the mixture to heat till it turns white, when we obtain a mixture of bi-sulphate and per-chlorate of potassa. The former, being much more soluble than the latter in cold water, their separation may be effected by solution and crystallization.

Per-chlorate of potassa does not change vegetable colours. It requires more than 50 times its weight of water at  $60^{\circ}$  for solution; and crystallizes by evaporation in lengthened octohedrons. Distilled at  $280^{\circ}$  Fahr. with an equal weight of sulphuric acid, it yields per-chloric acid. When heated *per se* to  $412^{\circ}$ , oxygen is evolved and chloride of potassium remains. It is constituted of 1 atom of per-chloric acid = 86, + 1 atom of potassa = 45, and its representative number is therefore 131.

#### *Iodate and Hydriodate of Potassa.*

Both these salts are formed by agitating iodine with a solution of potassa; water is decomposed, and gives origin to a very soluble hydriodate and a difficultly soluble iodate. The latter may be purified by being washed first with a little water, and afterwards with alcohol sp. gr. .820, which removes the hydriodate. The iodate remains in small white and granular crystals.

When projected on red-hot coals, iodate of potassa burns like saltpetre; 100 parts heated in a retort give 22.59 oxygen

gas, and 77.41 iodide of potassium. It requires for solution  $13\frac{1}{2}$  parts of water at  $60^{\circ}$  Fahr. It is constituted of 22.246 potassa and 77.754 iodic acid.

*Hydriodate of Potassa* is deliquescent, and consequently very soluble. It is constituted of 100 hydriodic acid + 37.426 potassa. By crystallization, or simple desiccation, it is changed into iodide of potassium, which is easily fused and volatilized without change at a red heat.

#### *Nitrate of Potassa.*

A direct synthetic proof of the composition of this salt may be obtained by saturating nitric acid with potassa, either pure or in a carbonated state. The solution, on evaporation, yields crystals of nitrate of potassa, or nitre.

For the purposes of experiment, however, the nitrate of potassa, which may be purchased in the shops under the name of nitre or saltpetre, and which is an abundant product of nature, may be employed on account of its greater cheapness. The nitre, which is met with as an article of commerce, is brought to this country, chiefly from the East Indies. When it arrives it is a very impure salt, containing, besides other substances, a considerable proportion of muriate of soda. In this state it is called rough nitre. For the purposes of chemistry, it requires to be purified by solution in water and re-crystallization; and it then obtains the name of refined nitre, or refined saltpetre.

This salt has the following properties:

(a) It crystallizes in prismatic octahedrons, generally constituting six-sided prisms, terminated by two-sided summits.

The composition of nitrate of potassa has been differently stated:

	Acid.	Base.
100 parts, according to Kirwan, contain	45.92	.. 54.08
————— Richter	46.7	.. 53.3
————— Berard	51.36	.. 48.64
————— Wollaston	53.33	.. 46.67
————— Ure	53.	.. 47.
————— Thomson	54.34	.. 45.66

Taking the result, adopted by Dr. Wollaston in fixing

its number on the scale of equivalents, we shall find reason to believe that it is constituted of 1 atom of nitric acid = 54, + 1 atom of potassa = 48; and its equivalent therefore is 102. But as the atom of acid contains 5 atoms of oxygen and 1 of nitrogen, and the atom of potassa 1 of oxygen and 1 of potassium, we find in all six atoms of oxygen, weighing 48, in each atom of nitrate of potassa.

(b) For solution, it requires seven times its weight of water at 60° of Fahrenheit; and boiling water takes up its own weight. This is the degree of solubility assigned by Bergman; but La Grange asserts, that, at the ordinary temperature, nitrate of potassa requires only three or four times its weight of water for solution; and half its weight of boiling water.\* With the addition of common salt it becomes considerably more soluble.

(c) By the application of a moderate heat it fuses, and being cast in moulds, forms what is called Sal Prunelle. After fusion, Sir H. Davy found that it still yielded water, when distilled with boracic acid, though Berzelius asserts that nitre contains essentially no water.

(d) If a red-heat be applied, nitrate of potassa is decomposed in consequence of the destruction of its acid. By distilling it in an earthen retort, or in a gun-barrel, oxygen gas may be obtained in great abundance, one pound of nitre yielding about 12,000 cubic inches, of sufficient purity for common experiments, but not for purposes of accuracy.

(e) Nitrate of potassa, that has been made red-hot, seems to contain an acid less highly oxygenated than the nitric acid, and having a weaker affinity for alkalis. For if acetic acid be poured on nitre that has been thus treated, the nitrous acid is expelled in red fumes, whereas common nitre is not at all affected by acetic acid.

(f) Nitrate of potassa is rapidly decomposed by charcoal in a high temperature. This may be shown, by mixing two parts of powdered nitre with one of powdered charcoal, and setting fire to the mixture in an iron vessel under a chimney.—The products of this combustion, which, may be collected by

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\*Manual, 1st edition, i. 243.

a proper apparatus, are carbonic acid and nitrogen gases. Part of the carbonic acid also remains attached to the residuary alkali, and may be obtained from it on adding a stronger acid. This residue was termed, by the old chemists, *chylus* of nitre.

(g) Nitrate of potassa is also decomposed by sulphur, and with different results, according to the temperature and proportions employed.

1. Mix powdered nitre and sulphur, and throw the mixture, by a little at a time, into a red-hot crucible. The sulphur will unite with the oxygen of the nitric acid, and form sulphuric acid; which, combining with the potassa, will afford sulphate of potassa. The production of the latter salt will be proved by dissolving the mass remaining in the crucible, and crystallizing it, when a salt will be obtained exhibiting the characters of the sulphate.

2. Mix a portion of sulphur with one sixth or one eighth its weight of nitrate of potassa; put the mixture into a tin cup, and raise it, by a proper stand (fig. 25), a few inches above the surface of water, contained in a flat shallow dish. Set fire to the mixture, and cover it with a bell-shaped receiver. In this case, also, sulphuric acid will be formed; but it will not combine, as before, with the alkali of the nitre, which alkali is present in sufficient quantity to absorb only a part of the acid produced. The greater part of the acid will be condensed on the inner surface of the glass bell, and by the water, which will thus become intensely acid. The operation may be repeated three or four times, using the same portion of water. When the water is partly expelled, by evaporation in a glass dish, concentrated sulphuric acid remains.

(h) A mixture of three parts of powdered nitre, two of carbonate of potassa, or common salt of tartar, and one part of sulphur, all accurately mixed together, forms the *fulminating powder*, which explodes with a loud noise, when laid on an iron heated below redness.

(i) A mixture of five parts of powdered nitre, one part of sulphur, and one of powdered charcoal, composes *gunpowder*. The materials are first very finely powdered separately, then mixed up together, and beaten with a wooden pestle, a suffi-

cient quantity of water being added to prevent an explosion. The mixture is afterwards granulated, by passing through sieves, and dried very cautiously.\*

*Carbonate of Potassa.*

*Carbonate or Sub-carbonate.*—The simplest mode of showing the absorption of carbonic acid by potassa, is the following: Fill a common phial with carbonic acid gas over water; and when full, stop it by applying the thumb. Then invert the bottle in a solution of pure potassa contained in a cup, and rather exceeding in quantity what is sufficient to fill the bottle. The solution will rise into the bottle, and if the gas be pure, will fill it entirely. Pour out the alkaline liquor, fill the bottle with water, and again displace it by the gas. Proceed as before, and repeat the process several times. It will be found, that the solution will condense many times its bulk of the gas; whereas water combines only with its own volume.

This experiment may be made, in a much more striking manner, over mercury, by passing into a jar, about three fourths filled with this gas, a comparatively small bulk of a solution of pure potassa, which will condense the whole of a large quantity of the gas. If dry hydrate of potassa be substituted in this experiment, no change will ensue; which proves that solution is essential to action of alkalis on this gas. A solution of potassa, which has condensed all the carbonic acid it is capable of absorbing, when evaporated to dryness, affords *sub-carbonate*, or, more properly, *carbonate of potassa*.

The composition of this salt is differently stated by chemical writers, *viz.*

	Acid.	Base.
According to Dalton 100 grains consist of	31.10	.68.9
————— Dulong . . . . .	30.70	.69.30
————— Dr. Wollaston . . . . .	31.71	.68.29
————— Vauquelin . . . . .	33.	.67.†
————— Berard . . . . .	29.79	.70.21

The proportions of 31.71 to 68.29 agree very nearly with the notion, that the carbonate of potassa is constituted of an

\* On the preparation of gunpowder, and the theory of its detonation, consult Nicholson's Journal, xxiii. 277.

† Ann. de Chim. et Phys. v. 25.

atom of carbonic acid, weighing 22, and an atom of potassa, weighing 48; and that the weight of its atom is 70. The affinity of carbonic acid for potassa, though apparently feeble, is in reality very strong; since it has the power of expelling from potassa the whole of the water, which that alkali contains in the state of a hydrate; for dry carbonate of potassa contains no water.

The solution of carbonate of potassa will be found to have a much milder taste than the pure alkali, and no longer to destroy the texture of woollen cloth; but it still turns to green the blue infusion of vegetables. In the pure alkaline solution, no remarkable change ensued on mixing it with diluted sulphuric acid; but if that, or almost any other acid, be now added, a violent effervescence will ensue, arising from the escape of the gas that had been previously absorbed. If the mixture be made in a gas bottle, the gas, that is evolved, may be collected, and will be found to exhibit every character of carbonic acid.

For experimental purposes, carbonate of potassa may be obtained from crystals of tartar (bi-tartrate of potassa) calcined in a crucible; then lixiviated with water; and evaporated to dryness. By this treatment, the salt yields about one third its weight of dry carbonate. Or the tartar may be mixed with about an eighth of purified nitrate of potassa, and wrapped up in paper in the form of cones, which may be placed on an iron dish, and set on fire. The residuary mass is to be lixiviated, and evaporated as before directed. Or purified nitrate of potassa may be mixed with a fourth of its weight of powdered charcoal, and projected into a red-hot crucible, the contents of which are to be poured, when in fusion, into an iron dish. The carbonate, thus obtained, amounts to rather less than one half the nitre which has been employed. Even when thus prepared, it is apt to contain some impurities, consisting chiefly of a minute proportion of sulphate and muriate of potassa, with a little silica, from which it is extremely difficult entirely to free it. That which is procured from burnt tartar may be made to crystallize, in which state it contains 20.60 per cent. of water.

In this state of union with carbonic acid, potassa generally occurs in the arts. The potash and pearlash of commerce, are in fact carbonates of potassa, of different degrees of pu-

ality. The quantity of carbonic acid, contained in these alkalis, may be learned by a very simple experiment. Put one or two hundred grains of the alkali into a Florence flask, and add a few ounce-measures of water. Take also a phial filled with dilute sulphuric acid, and place this, as well as the flask, in one scale. Balance the two, by putting weights into the opposite scale, and, when the equilibrium is attained, pour gradually the acid into the flask of alkali, till an effervescence no longer ensues. When this has ceased, the scale containing the weights will be found to preponderate. This shows that the alkali, by combination with an acid, loses considerably of its weight; and the exact amount of the loss may be ascertained, by adding weights to the scale containing the flask and phial, till the balance is restored.

Carbonate of potassa dissolves very readily in water, which, at the ordinary temperature, takes up more than its own weight.—Hence, when an alkali, which should consist almost entirely of carbonate of potassa, is adulterated, as very often happens, with substances of little solubility, the fraud may be detected by trying how much of one ounce will dissolve in two or three ounce-measures of water. In this way I have detected an adulteration of one third its weight of sulphate of potassa. There are certain substances of ready solubility, however, which may be used in adulterating pearl-ashes, as common salt for example; and, when this is done, we must have recourse to an acid test for the means of discovery. The best, that can be employed for this purpose, is sulphuric acid of sp. gr. 1.141. Of this, 355 grains are equivalent to the saturation of 100 grains of carbonate of potassa. Dissolving, therefore, that quantity of the carbonate in water, and gradually adding the test, so as to produce neutralization, we learn, by the quantity of acid expended, the quantity of real carbonate which has been acted upon; for as 355 to 100, so is the weight of the test which has been used to the number required.

The strongest solution of this salt that can be obtained has the specific gravity 1.54, and contains 48.8 per cent. by weight of carbonate, or eight atoms of water to one of salt.

Carbonate of potassa, when exposed to the atmosphere, attracts so much moisture, as to pass rapidly to a liquid state.

This change is termed *deliquescence*. All the water thus absorbed is expelled again by a heat of 280°.

When submitted, in a crucible, to a high temperature, it fuses; but none of its carbonic acid is expelled.

*Bi carbonate of Potassa.*

Carbonate of potassa, in the state which has been already described, is far from being completely saturated with acid. This sufficiently appears from its strongly alkaline taste. It may be much more highly charged with carbonic acid, by exposing a solution of one part of the carbonate in three of water to streams of carbonic acid gas, in a Nooth's machine, or other apparatus; or by the process to be hereafter described. When a solution of alkali, after this treatment, is very slowly evaporated, it forms regular crystals. According to Dr. Wollaston,\* the quantity of acid in the bi-carbonate is exactly double that in the carbonate. This he proves by disengaging the carbonic acid from each, by a stronger acid, such as the sulphuric, when one part of the bi-carbonate, considered apart from its water of crystallization, is found to give twice as much carbonic acid as the sub-salt. Berthollet† obtained 189 grains of carbonic acid from 500 of this salt; and, as nearly as possible, the same quantity from 1000 grains of the salt, reduced by calcination to the state of carbonate. Berard found, that 100 parts of potassa are fully saturated by 85.86 carbonic acid.‡ The following Table exhibits the composition of the bi-carbonate, as stated by him, by Vauquelin, and by Dr. Wollaston. One hundred grains contain,

	Acid.	Base.	Water.
According to Berard . . . . .	42.01	48.92	9.07
Dr. Wollaston ..	43.9	47.1	9.0
Vauquelin . . . . .	47.	46.	7.

The atomic constitution, deducible from these proportions, is one atom of potassa, = 48, two atoms of carbonic acid, = 44, and one atom of water, = 9, in all 101, which last is its representative number.

\* Philosophical Transactions, 1808.

† Mem. d'Arcueil, ii. 470.

‡ 71 Ann. de Chim. 42.



The BI-CARBONATE OF POTASSA differs from the carbonate in the following particulars:—

1. In the greater mildness of its taste. Though still alkaline, yet it may be applied to the tongue, or taken into the stomach, without exciting any of that burning sensation, which is occasioned by the carbonate.

2. It is unchanged by exposure to the atmosphere.

3. It assumes the shape of regular crystals. The form of these crystals is a four-sided prism, with dihedral triangular summits, the facets of which correspond with the solid angles of the prism.

4. It requires, for solution, four times its weight of water at 60°; and, while dissolving, absorbs caloric. Boiling water dissolves five-sixths of its weight; but, during this solution, the salt is partly decomposed, as is manifested by the escape of carbonic acid gas. The quantity thus separated amounts, according to Berthollet, to about  $\frac{1}{10}$ th the weight of the salt.

5. By calcination in a low red heat, the portion of carbonic acid, which imparts to this salt its characteristic properties, and all the water, are expelled, and the salt returns to the state of carbonate.

(k) Bi-carbonate of potassa, in all its forms, is decomposed by the stronger acids; as the sulphuric, nitric, and muriatic, which unite with the alkali, and set the gas at liberty. This may be shown by pouring, on the carbonate contained in a gas bottle, any of the acids, and collecting the gas by a proper apparatus.

The sub-borate of Potassa is a salt which is little known. It may be formed by the direct combination of liquid hydrate of potassa with boracic acid.

#### *Phosphite, Phosphate, &c. of Potassa.*

*Hypo-phosphite of Potassa* may be formed by the direct combination of its ingredients. It is a deliquescent salt, readily soluble in water, and in alcohol. When heated in a glass tube, bi-phosphureted hydrogen is disengaged; phosphorus is deposited on the inside of the tube; and a yellowish residue is left of phosphate of potassa.

*Phosphite of Potassa* is a neutral salt, not crystallizable,

deliquescent, and very soluble in water, but not in alcohol. When heated, a yellow residue is left, which, with acids, gives a little phosphureted hydrogen.

*Phosphate of Potassa* is a salt which is neutral only when in solution, for, on attempting to crystallize it, an acid salt separates, and there remains an uncrystallizable *magma*, with an excess of alkali.

This phosphate has little taste. By the action of heat it undergoes the igneous fusion. It is not decomposed by lime, unless when the lime is added in considerable excess, and then a compound is formed of phosphoric acid with potassa and lime. The vegetable grains belonging to the *cerealia* contain a small quantity of this salt. It is believed to be a compound of 1 atom of phosphoric acid + 1 atom of potassa.

*Sub-phosphate of Potassa* may be obtained by evaporating the uncrystallizable portion of the foregoing solution, or by fusing phosphate and hydrate of potassa together in a platinum crucible. It is insoluble in cold, and very sparingly soluble in hot water. It is probably constituted of 2 atoms of potassa, and 1 atom of acid.

*Bi-phosphate of Potassa* has been very little examined. All that is known is, that of the compounds of potassa with phosphoric acid, this is the only one which is susceptible of crystallization.

*Sulphuret, Hydro-Sulphuret, Hydrogureted Sulphuret, Hypo-sulphite, and Sulphite of Potassa.*

*Sulphuret of Potassa* (or the compound hitherto so called) may be formed by fusing together in a covered crucible, at a heat below redness, six parts of sulphur with eight of dry carbonate of potassa. The fused mass is to be poured upon a smooth stone; and, when cold, preserved in a well-closed vial. It has a reddish brown or liver colour, from whence it has been called *hepar*, or *liver of sulphur*. In the humid way, a pure sulphuret cannot be produced, for other products are also generated, which remain in the solution.

It had been doubted, whether in the fusion of dry potassa with sulphur, a mere combination of those two bodies takes place; or whether the alkali is not rather deoxidized, and

sulphuret of potassium a part, at least, of the product. The latter has been lately shown by Berzelius to be the true rationale of the process; and he has proved that potassium is capable of uniting with sulphur in several different proportions.\* Vauquelin, also, had long ago observed that during the fusion of potassa with sulphur, a considerable quantity of sulphureted hydrogen gas is evolved, and that sulphuric acid is formed, which, uniting with the base, composes sulphate of potassa. But the production of sulphuric acid, Gay Lussac ascertained, takes place only at high temperatures; for when that degree of heat was used, which was barely sufficient for the purpose, the sulphuret, dissolved in water, gave no trace of sulphuric acid, but abounded with hypo-sulphurous acid. The latter acid must, however, have been generated by the decomposition of the water employed for the solution of the fused mass; for it is incapable of being formed, or even of existing, at high temperatures. It should appear, therefore, that sulphuret of potassium can only exist, strictly speaking, in a solid form, for the act of solution causes the immediate formation of new products.

Sulphuret of potassa has, when moistened, a disagreeable smell, and an offensive taste. It is very soluble in water, and the solution blackens the skin, and turns syrup of violets green, like an alkali. All acids, even the weakest, precipitate sulphur from it, and the stronger acids, when previously diluted, occasion a disengagement of sulphureted hydrogen gas. The solution absorbs oxygen gas, and has been employed in eudiometry. According to Vauquelin 100 of potassa unite with 111.5 of sulphur. Berzelius finds that 100 parts of the carbonate absorb 93.9 parts of sulphur.

*Hydro-sulphuret of potassa* may be formed by transmitting a current of sulphureted hydrogen gas through liquid hydrate of potassa, which acquires a yellow colour, and an offensive smell. It forms large transparent crystals, not unlike those of sulphate of soda, but having the shape of four-sided prisms acuminate with four planes, or of six-sided prisms acuminate with six planes. It is deliquescent, and runs into a thick syrupy liquor, which gives a green colour to the skin.

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\* Annals of Phil. iv. 284.

It dissolves readily in water and alcohol, with a production of cold. On adding any diluted acid, abundance of sulphureted hydrogen is disengaged, but no sulphur is deposited. Vauquelin found that its solution in water might be evaporated to dryness without decomposing the hydro-sulphuret; for on heating the residuum, mixed with sulphur in a retort, sulphureted hydrogen was copiously evolved.

*Hydrogureted sulphuret of potassa* may be formed by boiling flowers of sulphur in liquid hydrate of potassa, or by digesting sulphur with the liquid hydro-sulphuret. The resulting product may be considered as a compound of bi-sulphureted hydrogen with potassa, in proportions not yet ascertained. By mere solution in water, the sulphuret of potassa is partly changed into this substance. According to Proust, red oxide of mercury, digested with hydrogureted sulphurets, removes the sulphureted hydrogen, and what remains is a pure liquid sulphuret.

*Hypo-sulphite of Potassa*.—This salt is best formed by exposing the hydrogureted sulphuret to the atmosphere, till it has lost its colour, after which, on evaporation, it crystallizes in the form of fine needles; or by decomposing hydro-sulphuret, or hydrogureted sulphuret of potassa by sulphurous acid. The salt has a taste, at first not unlike that of nitre, succeeded by bitterness, and it is deliquescent. When carefully dried, it takes fire on raising the heat, and burns somewhat like tinder, but with a feeble blue flame. It dissolves chloride of silver, even when very dilute, with great readiness.

*Sulphite of Potassa* may be formed by passing sulphurous acid into a saturated solution of carbonate of potassa, till all effervescence ceases. The solution becomes warm, and crystallizes on cooling in rhomboidal plates, or in small needles diverging from a common centre, which have sometimes a yellowish tinge. It has a pungent and sulphurous taste, and is soluble in an equal weight of cold, or in a less proportion of boiling water. At the temperature of 300° Fahr. it loses only about 2 per cent.; but when more strongly heated, the salt is decomposed, and suffers a loss of about 22 per cent. of which 15 are sulphurous acid, 5 sulphur, and 2 water. When thrown into a red hot crucible, a blue flame arises from it. Its solu-

tion, exposed to the air, slowly attracts oxygen, and is converted into sulphate of potassa. From Dr. Thomson's analysis, it is constituted in 100 parts, of 2 water + 54.5 base + 43.5 acid; or 100 of sulphurous acid unite with 150 of potash.

*Sulphate and Bi-sulphate of Potassa.*

*Sulphate of Potassa.*—This salt may be formed by saturating the carbonate of potassa with sulphuric acid, and crystallizing the solution. It is a refuse product, also, of several chemical operations. Its properties are the following:

(a) It crystallizes in small six-sided prisms, terminated by six-sided pyramids with triangular faces. Its specific gravity, according to Hassenfratz, is 2.0473.

(b) It has a bitter taste.

(c) It decrepitates when thrown on a red hot iron, or on red-hot coals, and is volatilized by a strong heat, first running into fusion. By a low red heat it loses very little of its weight, not more than one and a half or two per cent. Indeed it does not essentially contain any water.

(d) Water, at 60° of Fahrenheit, takes up only one sixteenth of its weight; but boiling water dissolves one fifth, or by continuing the application of heat even one fourth.

(e) The composition of this salt is determined by the quantity of sulphate of barytes, which its solution affords when decomposed by any barytic salt. From 100 parts of the ignited salt, dissolved in water, Dr. Marcet obtained 132 of sulphate of barytes, Berzelius 134.68, and Mr. R. Phillips, 136.7. Hence the composition of the salt (reckoning the acid in sulphate of barytes at 33.5 per cent.) is,

	Acid.	Base.
According to Dr. Marcet . . . .	44.22 . . . . .	55.78
———— Mr. Phillips . . . .	45.79 . . . . .	54.21
———— Bucholz . . . . .	46.21 . . . . .	53.79
———— Dalton . . . . .	44.70 . . . . .	55.30
———— Berard . . . . .	42.76 . . . . .	57.24
———— Berzelius . . . . .	45.0 . . . . .	55.0
———— Dr. Ure . . . . .	45.5 . . . . .	54.5

Estimating the weight of the atom of sulphuric acid at 40 and that of potassa at 48, the numbers last stated (viz. 45.5

acid, and 54.5 base in 100 of the salt) appear to be nearest the truth. There can be no doubt, however, that the salt is constituted of 1 atom of acid + 1 atom of base, without any water as an essential ingredient.

(f) Sulphate of potassa is decomposed, at high temperatures, by charcoal. Mix any quantity of the salt with one fifth of its weight of charcoal finely powdered, and expose the mixture, in a crucible, to a strong heat. The carbon will unite with the oxygen of the sulphuric acid, and will escape in the state of a gas. What remains is a compound, hereafter to be described, of sulphur and potassa, or more probably of sulphur and potassium.\* No change is effected in sulphate of potassa by fusion with sulphur, which sublimes unaltered.†

#### *Bi-sulphate of Potassa.*

When to a saturated solution of sulphate of potassa in boiling water, we add an excess of sulphuric acid, the first crystals, which are formed, contain a considerable excess of sulphuric acid, not less in the whole, according to Berthollet,‡ than 55.8 per cent. By continuing to evaporate the solution, we obtain successive quantities of crystals, which hold less and less acid in combination. Thus the second set, according to the same chemist, contain only 49.5 per cent. of acid; and he was therefore of opinion, that sulphuric acid and potassa are capable of uniting in all proportions. It is much more agreeable, however, to analogy to believe, that in this, as in all other energetic combinations, the proportions are limited. The bi-sulphate, or super-sulphate, has been shown by Dr. Wollaston to contain just twice as much acid as the sulphate. It is constituted, therefore, of one atom of base with two atoms of acid, or of 48 base + 80 acid; and its composition may be contrasted with that of the sulphate as follows:

	Bi-sulphate.	Sulphate.
Potassa . . . . .	37.5 .. 100	54.5 .. 100
Sulphuric acid . . .	62.5 .. 167	45.5 .. 83.5
	100	183.5
	267	100

\* Vauquelin, Ann. de Chim. et Phys. v. 31.

† Ibid. p. 20.

‡ Mémoires d'Arcueil, ii. 480.

The bisulphate has an intensely sour taste, and a powerful action on blue vegetable colours. One part is soluble in two of water at 60°, and in less than an equal weight at 212°. It is insoluble in alcohol.

*Hypo-sulphate of Potassa* is a salt of which little is known. It crystallizes in cylindroidal prisms, terminated by a plane perpendicular to their axis. (Ann. of Phil. xiv. 355.)

*Seleniates of Potassa*.—Selenic acid is capable of uniting with potassa in three different proportions, and of composing either a seleniate, bi-seleniate, or quadri-seleniate; but as these salts are not of much importance, I refer for their description to Berzelius's paper in the 9th vol. of Ann. de Chim. et Physique, p. 257.

*Cyanide of Potassa*.—Cyanogen is absorbed by liquid hydrate of potassa, and a solution is obtained, which has scarcely any colour unless the cyanogen is in excess, when it becomes brown, and apparently carbonaceous. This solution affords prussian blue when added to an acid solution of iron, carbonic acid escaping, and a smell of hydro-cyanic acid being at the same time perceptible. The volume of carbonic acid produced, it has been shown by Gay Lussac, is precisely equal to that of the cyanogen absorbed, and he has rendered it extremely probable that hydro-cyanic acid and ammonia are at the same time generated.

*Hydro-cyanate of Potassa* may be formed by the mixture of hydro-cyanic acid, and liquid hydrate of potassa. It is very soluble, is alkaline to the taste, and turns syrup of violets green. It is decomposed by the weaker acids, even by the carbonic. With salts having protoxide of iron for a base, it gives a precipitate which is at first orange-coloured, and afterwards, by exposure to the air, changes successively to green and to deep blue. From solutions containing peroxide of iron, it causes a pale blue precipitate, the colour of which becomes deeper by exposure to air. When calcined, the acid ingredient abandons its hydrogen, and the salt becomes a *cyanide of potassa*.

*Ferro-cyanate of Potassa*.—When the salt just described is digested in a state of solution with protoxide of iron, a portion of the oxide is dissolved, the solution becomes yellow, and, on adding more hydro-cyanic acid, is rendered neutral, crystal-

izable, and capable of resisting decomposition by weak acids. But the same compound may be better formed by digesting prussian blue in fine powder with liquid hydrate of potassa. The common prussian blue of commerce should first be heated with an equal weight of sulphuric acid, which has been diluted with five or six parts of water, and then be washed with a large quantity of distilled water. This will remove the alumine which it always contains. After being thus purified, it may be added to the hydrate of potassa, as long as that liquor continues alkaline. The filtered liquor, when evaporated and cooled, deposits crystals, which are quadrangular prisms. These may be purified by a second crystallization.

The ferro-cyanate (formerly called triple prussiate) of potassa is a transparent salt, often in fine large crystals, of a lemon yellow colour, and free from taste and smell. Its specific gravity is 1.833. Water at 60° Fahr. dissolves nearly one-third of its weight, and boiling water nearly an equal weight. When heated, it loses 13 per cent. and becomes white, but does not run into fusion, or undergo decomposition. Submitted to a still higher temperature in a retort, it is decomposed, and yields hydro-cyanic acid and ammonia, besides carbonic acid, carbonic oxide, and carbureted hydrogen; and a residue is left, composed of charcoal, metallic iron, and potassa, which last is still united with more or less cyanogen. (See Robiquet, *Ann. de Ch. et Phys.* xvii. 205.)

Diluted acids have little action on ferro-cyanate of potassa, except with the aid of heat, and then the sulphuric, muriatic, and even the acetic acid disengage a certain quantity of hydro-cyanic acid, and occasion a white precipitate, the nature of which is not understood. Red oxide of mercury, digested with a solution of the salt, decomposes it, and gives rise to the formation of cyanide of mercury, and to the disengagement of free alkali, and of peroxide of iron attached to a little acid.

The solution of ferro-cyanate of potassa is not precipitated by alkalis, or by alkaline salts, but is decomposed by some of the earthy, and by almost all the metallic salts. The following Table by M. Thenard shows the colours of the precipitates, thrown down from various solutions, both by the ferro-cyanate, and hydro-cyanate of potassa.



*Table of the Colours of Precipitates from Metallic Solutions.*

From solutions of salts of	By ferro-cyanate of potassa.	By hydro-cyanate of potassa.
Manganese .....	White .....	Yellow.
Iron (protoxide) ....	White .....	Orange.
— (deutoxide) ....	Pale blue .....	Blueish green.
— (tritoxide) ....	Deep blue .....	Scarcely any.
Tin .....	White .....	White.
Zinc .....	Ditto .....	Ditto.
Cadmium .....	Ditto .....	Ditto.
Antimony .....	Ditto .....	Ditto.
Uranium .....	Blood red .....	Yellowish white.
Cerium .....	White .....	
Cobalt .....	Grass green ....	Cinnamon.
Titanium .....	Reddish brown ..	
Bismuth .....	White .....	White.
Copper (protoxide)	Ditto .....	Ditto.
— (deutoxide)	Deep brown ....	Yellow.
Nickel .....	Apple green ....	Yellowish white.
Lead .....	White .....	
Mercury (deutoxide)	Ditto .....	Yellow.
Silver .....	White, changing to blue.	White, soluble in an excess of hydro- cyanate.
Palladium .....	Olive .....	
Platinum .....	Yellow .....	
Gold .....	White .....	White, becoming yellow.

The ferro-cyanate of potassa has been analyzed with great care by Berzelius. He decomposed it by heating it with peroxide of copper, and obtained carbonic acid and azotic gases, in the proportions in which they are evolved by the decomposition of cyanogen, viz. 2 volumes of the former and one of the latter. Hence he considers it as a cyanide, and not a prussiate, and deduces its composition to be two atoms of cyanide of potassium + 1 atom of cyanide of iron. This cyanide, in common with all those in which the metal is strongly

electro-positive, as those of sodium, barium, &c. he believes to continue such, even after solution in water; while the cyanides with weaker bases, such as those of ammonia, and many of the metallic oxides, become, on the contrary, hydro-cyanates.

Mr. Porrett, on the other hand, states the composition of ferro-cyanate of potassa as follows:

Potassa ..	40.34 .....	= 1 atom	} forming one atom of ferro-cyanic acid.
Iron ....	11.76 .....	= $\frac{1}{2}$ ditto	
Carbon ..	20.17 .....	= 4 ditto	
Azote ...	11.76 .....	= 1 ditto	
Hydrogen .	.84 .....	= 1 ditto	
Water ..	15.13 .....	= 2 ditto.	
	<hr/>		
	100.*		

## SECTION II.

### *Sodium.*

SODIUM was discovered in 1808 by Sir. H. Davy. It is procured by a process exactly resembling that employed in preparing potassium, with this difference, that hydrate of soda must be substituted for that of potassa. In its external characters and chemical properties it bears a near resemblance to potassium, and it is chiefly by examining the results of its action, that we discover its differences from the latter metal.

I. Sodium, at common temperatures, exists in a solid form. It is white, opaque, and, when examined under a thin film of naphtha, has the lustre and general appearance of silver. It is exceedingly malleable, and much softer than any of the common metallic substances. When pressed upon by a platinum blade with a small force, it spreads into thin leaves; and a globule of  $\frac{1}{10}$ th or  $\frac{1}{4}$ th of an inch in diameter is easily spread over a surface of a quarter of an inch. This property is not diminished, by cooling it to 32° Fahrenheit. Several

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\* Ann. of Phil. xiv. 398.

globules, also, may, by strong pressure, be forced into one; so that the property of *welding*, which belongs to platinum and iron at a high degree of heat only, is possessed by this substance at common temperatures.

II. It is lighter than water. As near as can be determined, its specific gravity is as 0.972 to 1.

III. It is much less fusible than the base of potassa. At 120° Fahrenheit, it begins to lose its cohesion, and it is a perfect fluid at 180° or 190°. Hence it readily fuses under heated naphtha.

IV. Its point of vaporization has not been ascertained; but it remains fixed, in a state of ignition, at the point of fusion of plate glass.

V. When SODIUM is exposed to the atmosphere, it immediately tarnishes, and by degrees becomes covered with a white crust of soda, which deliquesces more slowly than that formed on potassium. It is not changed, however, by air that has been artificially dried.

VI. It combines with oxygen, slowly and without luminous appearance, at all common temperatures. When heated to its fusing point, the combination becomes more rapid; but no light is emitted till it becomes nearly red hot. The flame, which it then produces, is white, and it sends forth bright sparks, exhibiting a very beautiful effect. In common air, it burns with a similar colour to charcoal, but with much greater splendour.

VII. When thrown into water, it produces a violent effervescence and a loud hissing noise; it combines with the oxygen of the water to form soda; and hydrogen gas is evolved, which does not, however, as in the case of potassium, hold any of the alkaline base in solution. Neither can sodium be made to dissolve in hydrogen gas, by being heated in contact with it.

When thrown into hot water, the decomposition is more violent, and in this case a few scintillations are generally observed at the surface of the fluid; but this is owing to small particles of the base, which are ejected from the water, sufficiently heated to burn in passing through the atmosphere.

VIII. Its action on alcohol, ether, volatile oils, and acids,

is similar to that of potassium; but with nitric acid a vivid inflammation is produced.

IX. Sodium appears to be susceptible of different degrees of oxidation. 1st. When it is fused with dry soda, a portion of oxygen takes place between the alkali and the metal. A deep brown fluid is produced, which becomes a dark grey solid on cooling. This substance is capable of attracting oxygen from the atmosphere, and of decomposing water, by which it is again converted into soda. The same oxide of sodium is formed, by fusing this metal in tubes of plate glass.

It is of a greyish colour, destitute of lustre, brittle, and gives hydrogen when acted on by water, but less than an equal weight of sodium. It may, however, be doubted, whether this is a compound of sodium and oxygen, or merely a mixture of the metal with soda.

2d. The next oxide of sodium is *soda*. It may be formed by burning sodium in a quantity of air, containing just oxygen enough to convert the metal into alkali. It is of a grey colour; of a vitreous fracture; and requires a strong red heat for its fusion. This, indeed, may be considered as the true protoxide of sodium, constituted, according to Gay Lussac and Thenard, of 100 metal + 33.995 oxygen; or, according to Berzelius, of 100 of the former + 34.372 of the latter. Taking the oxygen at 34, the number representing sodium will be 23.5, for  $34 : 100 :: 8 : 23.5$ ; or, in round numbers, it may be taken at 24.

When the protoxide is brought into contact with water, it absorbs it with great heat, and cannot be again separated from it, except by some substance which it attracts still more powerfully. Even after fusion, the soda is still a hydrate, containing 1 atom of protoxide =  $32 + 1$  atom of water = 9, together 41. Hydrate of soda contains, therefore,  $22\frac{1}{4}$  per cent. of water, which considerably exceeds the proportion in the similar compound of potassa.

The following table by Mr. Dalton shows the proportion of real soda, free from water, in solutions of different specific gravities. The first liquid compound is that which consists of 1 atom of soda + 2 atoms of water.

*Table of the Quantity of Real Soda in watery Solutions of different Specific Gravities.*

Atoms of Soda Water.	Soda per cent. by weight.	Soda per cent. by measure.	Specific Gravity.	Congeeing point.	Boiling point.
1 + 0	100	230?	2.30?	1000°	unknown.
1 + 1	77.8	156	2.	500°	red hot.
1 + 2	63.6	118	1.85	250°	600°
1 + 3	93.8	93	1.72	150°	400°
1 + 4	46.6	76	1.63	80°	300°
1 + 5	41.2	64	1.56		280°
1 + 6	36.8	55	1.50		265°
	34	50	1.47		255°
	31	45	1.44		248°
	29	40	1.40		242°
	26	35	1.36		235°
	23	30	1.32		228°
	19	25	1.29		224°
	16	20	1.23		220°
	13	15	1.18		217°
	9	10	1.12		214°
	4.7	5	1.06		213°

3d. The peroxide of sodium may be formed, by burning the metal with an excess of oxygen. It is of a deep orange colour, very fusible, and a non-conductor of electricity. When acted on by water, its excess of oxygen escapes, and it becomes soda. It deflagrates with most combustible bodies. It appears to be constituted of 2 atoms of sodium = 48, with 3 atoms of oxygen = 24, and its equivalent number is therefore 72.

#### *Chloride of Sodium.*

Sodium burns in chlorine gas, and is converted into a white substance having a penetrating taste. The same compound may be formed by heating sodium strongly in muriatic acid gas; the hydrogen of which is liberated, while the chlorine combines with the metal. Or it may be formed by saturating carbonate or hydrate of soda with muriatic acid, and evaporating the liquid, which yields chloride of sodium in a solid form. This chloride, also, is an abundant produce

of nature, being that well-known substance, common salt, which is become a necessary ingredient in the food of man, and is of essential utility in several of the arts. For purposes of experiment, the common salt may be employed, which is to be found in the shops. This may be purified, by adding to a solution of it in water a solution of carbonate of soda, as long as any milkiness ensues; filtering the solution, and evaporating it till it crystallizes.

II. Its qualities are as follow :

1. It crystallizes in solid regular cubes, or, by hasty evaporation, in hollow quadrangular pyramids, which, when the salt is pure, are but little changed by exposure to the air. The common salt of the shops, however, being impure, acquires an increase of weight, in consequence of the absorption of moisture. The various forms under which it appears, of stoved salt, fishery salt, bay salt, &c. arise from modifications in the size and compactness of the grain, rather than from any essential difference of chemical composition, as I have shown in a memoir published in the Phil. Trans. for 1810.

2. It requires, for solution, twice and a half its weight of water, at 60° of Fahrenheit, and hot water takes up very little more. Hence its solution crystallizes, not like that of nitre, by cooling, but by evaporation.

3. When heated gradually, it fuses, and forms, when cold, a solid compact mass.

4. If suddenly heated, as by throwing it on red-hot coals, it decrepitates. It does not, however, after being dried at the temperature of boiling water, lose by ignition more than two or three parts of water *per cent.* and essentially it contains no water.

5. It is not decomposed when ignited in contact with inflammable substances, except with potassium, which sets at liberty half its weight of sodium.

6. When mixed with powdered charcoal or sulphur, and fused in a crucible, it does not undergo any decomposition or essential change.

7. It is decomposed by the carbonate of potassa, the alkali of which combines with the muriatic acid of the salt, and the carbonic acid is transferred to the soda.—Hence we obtain

muriate of potassa and carbonate of soda. A process for effecting this decomposition, on a large scale, is described by Westrumb, in Crell's Journal, English translation, ii. 127.

8. It is decomposed by the sulphuric acid in the mode already described. Nitric acid also separates the muriatic acid.

When chloride of sodium is dissolved in water, it passes, by the decomposition of that fluid, to the state of muriate of soda, and it is this salt, and not the chloride of sodium (which last can only exist in a solid form) that is the ingredient of sea water and other solutions of common salt. Muriate of soda is composed, in 100 grains,

	Acid.	Base.
According to Darcet . . . . of . . . .	49.27	50.73
———— Berard . . . . — . . . .	43.	57.
———— Dr. Marcet — . . . .	46.	54.
———— Berzelius . . — . . . .	46.56	53.44

From 100 grains of transparent rock salt, dissolved in water, and precipitated by nitrate of silver, I obtained 242 of luna cornea; Dr. Marcet, from 100 grains of pure artificial muriate of soda, fused before solution, obtained 241.6; Berzelius 244.6; and Rose, 243.4. Now 100 grains of luna cornea may be stated, in round numbers, to denote 19 grains of real muriatic acid, so that it is easy, from this datum, to calculate the composition of common salt, or of any muriatic salt, which has been decomposed by nitrate of silver.

When, again, we expel the water from a solution of common salt, we re-obtain the chloride of sodium, so that muriate of soda can have no existence except in a fluid state. Chloride of sodium, as it exists in fused common salt, is constituted of an atom of sodium, weighing 24, with an atom of chlorine weighing 36, and its equivalent is 60. It consists, then, of

Sodium . . . . .	40.5	100	68
Chlorine . . . . .	59.5	147	100
	<u>100.</u>	<u>247</u>	<u>168</u>

Dr. Wollaston assumes its constitution to be either 39.64 sodium + 60.36 chlorine; or, on the old theory of muriatic acid, he admits its composition as stated by Berzelius.

### *Sodium and Iodine.*

The action of *sodium* and *iodine* on each other is so analogous to that of potassium and iodine, that it is unnecessary to describe it. Iodide of sodium is obtained, and this compound, when made to act on water, forms both iodate and hydriodate of soda.

No combination is yet known of sodium and *hydrogen*.

On *azotic gas* sodium appears to have no action, but when heated in ammoniacal gas, hydrogen is disengaged, and a nitret of sodium is formed, which has an olive green colour, is fusible at a low heat, and, according to the experiments of Gay Lussac and Thenard, is composed of 100 parts of sodium and 11.728 nitrogen.

### *Phosphuret and Sulphuret of Sodium.*

There is scarcely any difference between the visible phenomena attending the action of the base of soda, and that of potassa on sulphur, phosphorus, and the metals. The sulphuret of sodium has a deep grey colour; the phosphuret resembles lead.

### *Amalgam of Sodium and Mercury.*

Added to mercury in the proportion of  $\frac{1}{16}$ th, sodium renders that metal a fixed solid of the colour of silver, and the combination is attended with a considerable degree of heat. This amalgam seems, like that of potassium, to form triple compounds with other metals, and even with iron and platinum, which remain united with the mercury, when it is deprived of the new metal by the action of air.

### *Salts of Soda.*

*Chlorate of Soda.*—This salt may be obtained, by following the process already described, with the substitution of pure soda for potassa; or by adding chloric acid to carbonate of soda, till the effervescence ceases. It is exceedingly difficult, however, to obtain it pure, by the first process, because it nearly agrees in solubility, with the common muriate of soda; and the second method is therefore preferable. It is soluble in three parts of cold water, and in rather less of hot, and is slightly deliquescent. It is soluble also in alcohol; but so also, according to M. Chevenix, is the chloride. It crystallizes



in cubes, or in rhomboids approaching the cube in form. In the mouth it produces a sensation of cold, and a taste scarcely to be discriminated from that of muriate of soda. In other properties it agrees with the similar salt with base of potassa.

*Iodate and Hydriodate of Soda.*—Both these salts are obtained by agitating iodine with liquid hydrate of soda. The iodate has the form of small grains which have a cubical shape contain no water of crystallization; and when heated yield oxygen gas, a little iodine, and an iodide of sodium. They contain 84.1 iodic acid and 15.9 soda.

Hydriodate of soda crystallizes in flattened rhomboidal prisms, which are deliquescent, and contain much water of crystallization. By a sufficient heat it is converted into iodide of sodium: of this iodide, 100 parts of water at 60° Fahr. dissolves 173 parts, and, when strongly heated, it becomes slightly alkaline, and is volatilized. The hydriodate of soda is composed of 100 parts hydriodic acid, and 24.728 soda.

*Nitrate of Soda.*—This salt may be formed by saturating carbonate of soda with nitric acid, or by distilling common salt with three fourths its weight of nitric acid. When the former process is adopted, the solution must be evaporated, till a pellicle appears on its surface, and then allowed to cool. Crystals will be produced, having the shape of rhomboids, or rhomboidal prisms.

These crystals have a taste like that of saltpetre, but more intense. They are soluble in three parts of water, at 60°, and in less than an equal weight of boiling water. They attract moisture from the atmosphere. In other respects, they agree with the nitrate of potassa. The only use of nitrate of soda is, perhaps, that which has been suggested by Proust, who has found it to be more economical in the making of fire-works than nitrate of potassa.\* It consists, according to Dalton, of 57.6 acid = 42.4 base, but these proportions do not exactly agree with those which ought to be its ingredients, if constituted of an atom of base + 1 atom of acid, and if free from water, as asserted by M. Longchamp.

#### *Carbonate of Soda.*

There are two distinct compounds of carbonic acid and

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\* Nicholson's Journal, xv, 262. See also 6 Ann. de Chim. et Phys. 206.

soda, the one containing precisely half as much carbonic acid as the other.

The first, called sometimes the *sub-carbonate*, a name, however, which is less appropriate in this case than that of *carbonate*, is obtained by carefully re-crystallizing the soda of commerce. When required of great purity, it is best prepared from pure acetate of soda, which is decomposed at a red heat, and converted into carbonate of soda and charcoal, the former of which is separable by water. The primitive crystal of this salt is an octohedron, with a rhombic base of  $60^\circ$  and  $120^\circ$ , the planes of which meet, at the summit, at  $104^\circ$ , and, at the base, at  $76^\circ$ . This crystal varies by becoming coniciform, and also by the replacement of the solid angle of the summits by planes parallel to the base, affording the decahedral variety, which is most common. These crystals have the following properties.

1. When heated to  $150^\circ$  Fahrenheit, they fuse; boil violently, if the heat be raised; and leave a dry white powder. What escapes is water only; and it forms, according to Berard, 62.69 per cent. of the weight of the salt; to Kirwan, 64; Dalton, 63; and D'Arcet, 63.6. The crystals, also, lose their water by exposure to the atmosphere, or *effloresce*.

2. If the fused salt be kept boiling in a retort, Mr. Dalton finds that it deposits a hard, small-grained salt, which contains only 46 per cent. of water; the clear liquid has the specific gravity of 1.35; and, on cooling, concretes into a fragile icy mass. The first compound, Mr. Dalton estimates to consist of 1 atom of carbonate, and 10 of water; the second of 1 atom of salt, and 5 of water; and the third of 1 atom of salt, and 15 of water.

3. Water at  $60^\circ$  takes up half its weight of the sub-carbonate; and boiling water dissolves rather more than its own weight. The strongest solution, that can be preserved at the temperature of the atmosphere, has the specific gravity 1.26; but even this is liable to partial crystallization.

4. If 100 grains of the salt be slowly added to a quantity of diluted sulphuric acid, more than sufficient for neutralization, and of known weight, the loss of weight will show the quantity of carbonic acid contained in 100 grains. From experiments of this kind, joined with others on its loss by fusion, Berard deduces its composition to be

Acid . . . .	13.98	. . . .	100	. . . .	60
Base . . . .	23.33	. . . .	166	. . . .	100
Water ..	62.69				
	<hr/>				
	100.				

Independently of the water of crystallization, its composition has been differently stated, viz. 100 grains contain,

	Acid.	Base.
According to Berard . . . . .	37.50	.. 62.50
<hr/> Dulong . . . . .	40.09	.. 59.91
<hr/> Dalton . . . . .	40.40	.. 59.60
<hr/> Klaproth . . . . .	42.	.. 58.
<hr/> Kirwan . . . . .	40.10	.. 59.90

On the supposition that dry carbonate of soda is constituted of 1 atom of acid = 22, + 1 atom of base = 32, its equivalent number will be 54, and it will consist of

Acid . . . . .	41.23	. . . . .	100.	. . . . .	70.15
Base . . . . .	58.77	. . . . .	142.54	. . . . .	100.
	<hr/>			<hr/>	
	100.		242.54		170.15

And the crystallized salt will be constituted of one atom of dry carbonate = 54, + 7 atoms of water = 63, and its equivalent number will be 117. This gives for its composition, in 100 grains, 37.13 carbonate + 62.87 water, agreeing in this respect very nearly with the experimental result of Berard. One hundred grains of the dry salt require for neutralization 460 grains of sulphuric acid of density 1.141; and hence the quantity of dry carbonate in the soda of commerce may be learned, by ascertaining the proportion of sulphuric acid of that strength which 100 grains of any sample require for saturation.

When a solution of the carbonate of soda is saturated, by passing through it a stream of carbonic acid gas, or when a solution of 100 parts of the salt are heated with one of 14 parts of carbonate of ammonia, we obtain by evaporation an indistinctly crystallized salt, which is the *bi-carbonate of soda*. The taste of this salt is much milder than that of the carbonate; and it requires a much larger quantity of water for solution. It appears to be constituted of 1 atom of soda = 32, + 2

atoms of carbonic acid = 44, and its equivalent number is 76; or it is composed of

Acid .....	58.4 .....	100. ....	140.30
Base .....	41.6 .....	71.27 .....	100.
	100.	171.27	140.30

But, according to Berard, 100 grains contain 20.2 grs. of water, which would indicate that each atom of the anhydrous salt is united with 2 atoms of water. The composition of the crystals then must be 1 atom of the dry salt = 76, + 2 atoms of water = 18, giving in all 94, for the equivalent number of the bi-carbonate in crystals. By exposure to a red heat, the whole of the water, and one half of the carbonic acid, are expelled, and the salt is reduced to the state of simple carbonate.

*Sesqui-carbonate.*—A native carbonate of soda, found near Fezzan in Africa, and there called *trona*, has been analyzed by Mr. R. Phillips. He finds it to be a compound intermediate between the carbonate and bi-carbonate, or to be constituted of 3 atoms of acid + 2 of soda, or of  $1\frac{1}{2}$  atoms of acid = 33, + 1 of soda = 32, together 65. Hence he has given it the name of *sesqui-carbonate of soda*. (Journ. of Science, &c. vii. 298.)

#### *Sub-borate of Soda.*

This salt is imported in a crude state from India under the name of *tincal*, which, when purified, becomes the *refined borax* of the shops. It crystallizes in prisms with six irregular sides; effloresces in the air; fuses when ignited; then loses its water of crystallization, and is changed into a white powder, which, on increasing the heat, leaves a transparent mass called *glass of borax*, a substance of great use in experiments with the blowpipe. The crystallized salt dissolves in 20 parts of water at 60°, and in six parts of boiling water. According to Gmelin, whose analysis of this and other borates is published in the 9th vol. of the Annals of Philosophy, it consists of

Boracic acid .....	35.6 .....	100	100
Soda .....	17.8 .....	50	
Water .....	46.6		

100.

*Phosphite and Phosphate of Soda.*

*Phosphite of Soda* has not been examined. *Hypo-phosphite of soda* is very soluble in water and alcohol. Little else is known respecting it. (See Ann. de Ch. et Phys. ii. 142.)

*Phosphate of Soda* may be obtained by saturating with carbonate of soda the phosphoric acid obtained from bones (see p. 365), and evaporating the filtered liquor till a pellicle appears. On cooling, crystals are formed which are rhomboidal prisms, the acute angles  $60^\circ$ , and the obtuse angles  $120^\circ$ , terminated by a three sided pyramid. The salt is soluble in four parts of water at  $60^\circ$  Fahr. or in twice its weight of water at  $212^\circ$ . It contains always an excess of base, and effloresces when exposed to the atmosphere. By a strong heat it loses 62 per cent. of water, and the residuum is fusible into an enamel. The dry salt is constituted\* of

Phosphoric acid .....	53.48	100.
Soda .....	46.52	87.
	100.	

Hence the crystals consist of

Phosphoric acid .....	20.33	
Soda .....	17.67	
Water .....	62.	
	100.	

Mr. Dalton considers the salt above described as a *bi-phosphate*, and constituted of 46 phosphoric acid + 28 soda, or of two atoms of acid and one of base. To render it neutral by colour tests, he finds that the acid must be doubled, or that the neutral phosphate is in fact a *quadri-phosphate*. The simple phosphate, consisting of one atom of acid and one of base, may be formed by adding as much more caustic soda to the bi-phosphate as it already contains. The new salt is much more soluble than the bi-phosphate, and crystallizes in very fine needles. This salt Mr. Dalton recommends as the proper re-agent in chemical analysis.†

\* Berzelius Ann. de Chim. et Phys. ii. 164. † Manch. Memoirs, N.S. iii. 11.

*Sulphuret, Hydro-Sulphuret, Hydrogureted Sulphuret, Hypo-sulphite, and Sulphite of Soda.*

The sulphuret and hydrogureted sulphuret of soda are so analogous to the similar compounds with base of potassa, that it is unnecessary to add any thing respecting them.

*Hydro-sulphuret of soda* derives its chief importance from being produced, along with the carbonate, in several processes, by which soda is obtained from the sulphate.\* When first formed, it is transparent, colourless, and crystallizes in four sided prisms acuminated by four planes. It has an acrid and alkaline taste, which soon changes to a strong bitter. Its solution is colourless, but tinges the skin and paper green. With acids it effervesces briskly, sulphureted hydrogen escapes, and no sulphur is deposited, unless chlorine or nitric acid be added, which attract the hydrogen and throw down sulphur.

To distinguish this hydro-sulphuret from that of potassa, which it closely resembles, Vauquelin proposes to add a solution of alumine in sulphuric acid. This occasions a crystallization of alum with the latter, but not with the hydro-sulphuret of soda.

*Sulphite of soda* forms white and transparent crystals, which are four sided prisms with two broad sides and two narrow ones, terminated by dihedral summits. It has a cool sulphurous taste, is soluble in four parts of cold or in less than its weight of boiling water. By exposure to the air, it effloresces, and is changed into a sulphate. It is constituted, according to Dr. Thomson, of

Acid .....	24.5
Soda .....	24.5
Water .....	51.

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100.

*Hypo-sulphite of soda* may be prepared in the same way as the analogous salt of potassa. When the solution is evaporated to a syrupy consistence, it crystallizes in silky tufts, radiat-

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\* Ann. de Chim. lxiv. 59.

ing from a centre, and rendering the liquid solid. It is deliquescent, and its taste is intensely bitter and nauseous. When heated, it first fuses, then dries into a white mass, and at length takes fire and burns with a bright yellow flame. It is insoluble in alcohol. It has the property of rapidly dissolving the chloride of silver, when newly precipitated.

*Sulphate of Soda.*

(a) This salt forms regular octahedral crystals, of a prismatic or cuneiform figure; the two terminating pyramids of which are truncated near their basis.

(b) It has a more bitter taste than the preceding sulphate, and dissolves more easily in the mouth.

(c) It melts and swells upon a heated iron, in consequence of the loss of its water of crystallization, and a white powder is left, amounting to only about 36 parts from 100 of the original salt, or 43.2 according to Bucholz.

(d) By exposure to the atmosphere, it effloresces, and loses weight, and with so much quickness, that it is difficult to ascertain precisely its water of crystallization. Berzelius states it at 56 per cent, which agrees with my experience.

(e) It is very soluble in water, three parts of which, at 60° of temperature, dissolve one of the salt; and boiling water dissolves its own weight.

(f) Its composition is inferred from the quantity of sulphates of barytes, obtained by decomposing the solution of a known weight of this salt by any barytic salt. Bucholz, from 1000 grains of the crystallized salt (= 432 deprived of water) obtained 698 of sulphate of barytes; and Berzelius, from 5 parts of the dry salt, precipitated 8.16 of sulphate of barytes. His experiment, to have corresponded with that of Bucholz, should have given 8.12. Assuming the acid in sulphate of barytes to be 33.5 per cent., 100 parts of dry sulphate of soda (giving 161.3 of the barytic sulphate) must consist of

Base . . . . .	46 . . . . .	100
Acid . . . . .	54 . . . . .	117.5

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100

2 N 2

Mr. Dalton's numbers are 54.8 acid + 45.2 base; Dr. Wollaston's 56 + 44; Dr. Ure's 55.55 + 44.45; and those of Berzelius 55.76 + 44.24. The proportion of 56 to 44 is most consistent with the notion that this salt is constituted of 1 atom of acid + 1 of base; for 40 : 32 :: 56 : 44. Hence its equivalent number is 72; and, adding 10 atoms of water (90), we obtain 162 for the equivalent of the crystallized salt, which must be composed of

Acid . . . . .	24.66
Soda . . . . .	19.34
Water . . . . .	56.
	100.

*Bisulphate of soda* may be formed by adding sulphuric acid to a hot solution of sulphate of soda. Large rhomboidal crystals are formed, which are soluble in twice their weight of water at 60°; effloresce by exposure to the air; and when heated lose their excess of acid.

*Seleniates of soda*.—Selenic acid unites with soda in three different proportions, each of which constitutes a distinct salt, but they have no particularly interesting properties.

*Hydro-cyanate of soda*, like all the other salts of this class, is alkaline, and is decomposed by mere exposure to the atmosphere.

*Ferro-cyanate of soda* is of a yellow colour, and forms four sided prisms, terminated by dihedral summits, which effloresce in the air, and lose  $37\frac{1}{2}$  per cent. of their weight. At 55° Fahr. they dissolve in  $4\frac{1}{2}$  times their weight of water, but require much less boiling water, from which they separate on cooling. They are soluble in alcohol.

### SECTION III.

#### *Lithium.*

THE discovery of lithia, the source of this new metal, which dates only from the commencement of 1818, is due to the



skill and sagacity of M. Arfvredson, a pupil of Berzelius. In the analysis of a mineral called *Petalite* (first distinguished as a new species by M. D'Andrada, who found it in the mine of Uto, in Sweden), about 3 per cent. of an alkali was obtained, which M. Arfvredson at first supposed to be soda. On more accurate examination, however, the new substance displayed properties entirely distinct from those of either soda or potassa, especially in possessing the power of neutralizing a much greater quantity of the different acids than either of those alkalis; in which respect it even surpassed magnesia. To distinguish it from the two other fixed alkalis, both of vegetable origin, it received the name of *lithion*, (from *λιθιος*, *lapideus*;) and this term, to suit the analogy of the other alkalis, was afterwards converted into *lithia* or *lithina*.

The proportion of lithia in petalite has since been found to be 5 per cent.: and from some very pure pieces of that mineral, Vauquelin has extracted even 7 per cent. M. Arfvredson has discovered it, to the amount of 8 per cent. in *triphane* or *spodumene*, a mineral which is not so scarce as petalite; and, to the extent of 4 per cent. in *crystallized lepidolite*. The simplest process for obtaining it consists in fusing the mineral, finely pulverized, with three times its weight of carbonate of potassa; dissolving the fused mass in muriatic acid; evaporating to dryness; and digesting in alcohol, which takes up scarcely any thing but a compound of the new earth with muriatic acid. By evaporating a second time to dryness, and again dissolving in alcohol, the muriate of lithia is obtained pure. This muriate may be decomposed by digestion with carbonate of silver; and the solution of the carbonate, being decomposed by lime or by barytes, yields a solution of pure lithia, which may be evaporated to dryness out of contact with the air, from which it rapidly imbibes carbonic acid.

M. Arfvredson decomposed petalite by the following method. He strongly calcined, for an hour and a half, the finely powdered mineral with four times its weight of pure carbonate of barytes; digested the product with an excess of muriatic acid, which, leaving the silica undissolved, took up the baryta, alumina, &c.; precipitated the baryta by sulphuric acid, and

the alumina by carbonate of ammonia; and then, evaporating to dryness the residuary liquor, and raising the heat so as to expel the ammoniacal salts, a saline residue was left, which was dissolved by water, with the exception of a small quantity of sulphate of lime. It was a neutral salt, consisting of the new substance in combination with sulphuric acid. The sulphate was decomposed by acetate of barytes, and the acetate of lithia, thus obtained, was converted by calcination into carbonate of lithia.\* For carbonate of barytes, Vauquelin and Gmelin† advantageously substituted the nitrate.

Pure lithia is very soluble in water, and, like the other alkalis, has an acrid, caustic taste. Like them also, it changes vegetable blue colours to green. When heated in contact with platinum, it fuses, and then acts on the metal. That it agrees with the other alkalis in containing a metallic base, has been proved by Sir H. Davy, who applied the power of a galvanic battery to a portion of the carbonate, fused in a platinum capsule. On rendering the platinum positive, and bringing a negative wire to the surface of the fused carbonate, the alkali was decomposed with bright scintillations: but the reduced metal burned again so rapidly, that it was only observed to be of a white colour and very similar to sodium. Gmelin was not more successful in attempting to obtain the base of lithia separate, for, as fast as it was formed, it was again converted into an oxide. From analogy, this base has received the name of *lithium*. The proportion, in which this metal unites with oxygen, has, of course, not been determined by direct experiment; but it has been deduced by Vauquelin, from an analysis of the sulphate of lithia, and the application of the law, that the proportion between the oxygen of sulphuric acid and that of the bases which it saturates is as 3 to 1, to be as follows:

Lithium . . . . .	56.50	....	100	....	130
Oxygen . . . . .	43.50	....	77	....	100
			100.		

Arfvedson's estimate scarcely differs from this; but Gmelin

\* Ann. de Chim. et Phys. x. 86.

† Ann. of Philos. xv. 341.

deduces the composition of lithia to be 58.05 metal + 41.95 oxygen; and if this be correct, and lithia be constituted of an atom of each of its ingredients, lithium will be represented by 11, and lithia by that number + 8 = 19.

*Chloride of lithium* may be obtained by evaporating the muriate of lithia to dryness, and fusing the residue. It is white and semi-transparent, extremely deliquescent, soluble in alcohol, is decomposed when strongly heated in the open air, when it parts with chlorine, absorbs oxygen, and becomes highly alkaline. It is very difficultly crystallizable, and tinges the flame of alcohol red. In all these respects, it presents striking differences from potassa and soda.

With *sulphur*, lithia affords a very soluble yellow compound, which is decomposed by acids, with the same phenomena as the alkaline sulphurets, and, from the abundance of the precipitate, appears to contain a large proportion of sulphur.

*Sulphate of lithia* crystallizes in small prisms of a shining white colour. It is more fusible and soluble than sulphate of potassa, and has a saline, not a bitter, taste. It is constituted of

Sulphuric acid	.....	69.20
Lithia	.....	30.80
		100.

*Bi-sulphate of lithia* is produced by adding an excess of sulphuric acid to the neutral sulphate. It is more fusible and less soluble in water than the sulphate.

*Nitrate of lithia* is very soluble, and by evaporation crystallizes sometimes in regular rhomboids, sometimes in needles. It is extremely fusible; and at the instant when it has cooled, it attracts moisture from the air, and becomes fluid. The *muriate* is not crystallizable, but a crust appears on the surface of its solution during evaporation.

*Carbonate of lithia* is efflorescent in the air, and is sparingly soluble, requiring about 100 times its weight of cold water. It consists of 54.46 acid + 45.54 base. The watery solution effervesces with acids; changes vegetable blue colours to green; decomposes solutions of alumine and magnesia, and of

the metals; is rendered caustic by lime; disengages ammonia from its combinations; and does not precipitate the muriate of platinum. The dry carbonate, when fused on platinum, acts as powerfully on that metal as the alkaline nitrates.

*Phosphate of lithia* is formed by adding phosphate of ammonia with excess of base to sulphate of lithia, when an insoluble phosphate of lithia falls down. By this property it may be separated from potassa and soda. There exists also a *Li-phosphate of lithia*.

Lithia, then, is sufficiently distinguishable both from potassa and soda, by its difficult solubility in water; by affording deliquescent salts with muriatic and nitric acids; and, still more, by its higher capacity of saturation. It agrees with soda in not being precipitated by tartaric acid or muriate of platina; but the salts of lithia, when their concentrated solutions are mixed with one of carbonate of soda, deposit carbonate of lithia.

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#### SECTION IV.

##### *Calcium.*

To obtain calcium, a paste may be moulded, either of pure lime, or of sulphate of lime and water, into the shape of a small capsule, which may be placed on a metallic dish. Into this capsule mercury may be poured, and connected with the negative extremity of a galvanic apparatus of sufficient power, while the positive wire of the same pile is made to touch the under surface of the metallic plate. When the contact has been continued sufficiently long, an amalgam of mercury and calcium is obtained, which may be put into a small retort, along with naphtha enough to cover it. The retort is then to be connected with a tubulated receiver, the tubulure of which is only loosely stopped with a cork. On applying heat, the naphtha first comes over; then the mercury; and the calcium remains, surrounded by an atmosphere of vapour of naphtha. As the vessels cool, it would be desirable, and would not be difficult, to fill them with nitrogen gas, to prevent the oxidation of the calcium.

At present our knowledge of calcium in a pure state is very imperfect. In the instance in which Sir H. Davy succeeded to the greatest extent in distilling the quicksilver from the amalgam, the tube unfortunately broke while warm, and at the moment when the air entered, the metal, which had the colour and lustre of silver, took fire, and burned with an intense white light into lime. Berzelius obtained an amalgam of mercury and calcium, by electrifying lime liquor in contact with mercury, and on this amalgam water was made to act. From the quantity of lime thus produced, he estimates its composition to be

Calcium . . . . .	71.73	. . . . .	100.
Oxygen . . . . .	28.27	. . . . .	39.4
	—————		
	100.		

And  $39.4 : 100 :: 8 : 20.3$ , which last number is the equivalent of calcium; and  $20 + 8 = 28$  may be regarded as representing very nearly the atom of lime.

#### *Lime.*

The external characters of lime may be exhibited in common quicklime, such as is employed for the purposes of building or agriculture. In the same state, it is generally pure enough for demonstrating its chemical properties; but, when used for purposes of the latter kind, it should be fresh burnt from the kiln. For accurate experiments, it should be prepared by calcining in a crucible, for several hours, Carara or Parian marble, or carbonate of lime, which has been precipitated by carbonate of ammonia from the muriate, and perfectlyedulcorated by abundance of distilled water. Its specific gravity is 2.3. It requires for its fusion the intense heat of voltaic electricity, or of the oxy-hydrogen blow-pipe. It is not volatile.

#### *Relation of lime to water.*

(a) Lime absorbs water very rapidly, and with considerable heat and noise. This may be shown by sprinkling a little water on some dry quicklime; when the lime will become extremely hot, and fall into powder, which has been called *dry*

*hydrate of lime.* In this compound, the lime is to the water, according to Mr. Dalton, as 23 to 8; according to Davy, as 55 to 17; and to Berzelius, as 100 to 32.1, which last numbers, being as nearly as possible in the proportion of the weights of the atoms of lime and water (viz. 28 to 9), are probably the correct ones. It is, therefore, strictly a *proto-hydrate*. Some care is necessary in its preparation, lest more water should be added, than is essential to its constitution. It affords a very convenient form of keeping lime, for occasional use in a laboratory; for the hydrate may safely be preserved in glass bottles, which are almost constantly broken by the earth, if inclosed in its perfectly dry state. The hydrate of lime differs from those of baryta and strontia, in retaining its water much less forcibly; for the whole of it may be expelled by a strong red heat; and pure and absolutely dry lime remains.

The degree of heat, produced by the combination of lime with water, is supposed by Mr. Dalton to be not less than  $800^{\circ}$ , and is sufficient to set fire to some inflammable bodies; and when a large quantity of lime is suddenly slaked in a dark place, even light, according to Pelletier, is sometimes evolved. The caloric, which is thus set at liberty, is doubtless that contained in the water, and essential to its fluidity. By combination with lime, water passes to a solid state, and probably even to a state of much greater solidity than that of ice. Hence, during this change, it evolves more caloric than during conversion into ice; and hence even ice itself, when mixed with quicklime, in the proportion of one to two, enters into a combination which has its temperature raised to  $212^{\circ}$ . When a sufficient quantity of water has been added to reduce lime into a thin liquid, this is called *milk* or *cream of lime*; but this can scarcely be regarded as a definite compound.

Lime, though not of itself volatile, is, in some manner, perhaps mechanically, carried up by the vapour of water employed in slaking it. When a piece of moistened paper, stained with the juice of the violet, is held in the steam, which arises from lime suddenly slaked, its colour is changed from blue to green. Hence the smell which is perceived during the slaking of lime.

(b) Lime absorbs moisture from the atmosphere, and falls gra-

dually into powder, containing pure lime and water, in the proportion nearly of 100 to 32; or it becomes a true proto-hydrate.

(c) Lime is very sparingly soluble in water, *viz.* in the proportion of about 1 to 700; according to Thomson, 1 to 758; to Davy, 1 to 450; and to Dalton, at 60° Fahrenheit, 1 to 778. From a wine pint of lime water prepared at 60° Fahr. Mr. R. Phillips precipitated by carbonate of ammonia 17.3 grains of carbonate, equivalent to 9.7 of lime. And as a wine pint of this lime water weighs about 7300 grains, it follows that water at 60° Fahr. takes up about  $\frac{1}{752}$  of its weight of that earth. The experiments of Mr. Dalton tend to establish a curious fact respecting the solubility of lime, *v.z.* that it dissolves more plentifully in cold than in hot water. He has given the following table, the first column of which expresses the temperature of the water; the second, the number of grains of water, required to take up one grain of lime; and the third, the number required to dissolve one grain of hydrate of lime.

Temperature	Grains of water that dissolve 1 gr. of lime.	Grains of water that dissolve 1 gr. of hydrate.
60° .....	778 .....	584
130° .....	972 .....	720
212° .....	1270 .....	952

At the freezing point, or nearly so, Mr. Dalton thinks it probable that water would take up nearly twice as much lime, as is dissolved by boiling water. This inference has been confirmed by Mr. R. Phillips, who, after satisfying himself of the correctness of Mr. Dalton's statement of the composition of lime water prepared at 212°, determined by experiment that water at or near 32° Fahr. dissolves  $\frac{1}{350}$  of its weight of lime, or as nearly double as possible. He found also that the solution prepared at this temperature, when heated to ebullition in a glass vessel, from which a long tube issued to allow the escape of steam, and to prevent the access of carbonic acid, deposited small white particles of lime. These separated in such quantity, that though only  $\frac{1}{12}$ th of the solution was evaporated, the proportion of lime was reduced to  $\frac{1}{5000}$ . The cause of this crystallization Mr. Phillips supposes to be the influence

of heat in increasing the aggregative affinity of the lime; but it is probable that the heat may also operate in diminishing the affinity of water for lime. (See Ann. of Phil. N. S. i. 107.)

The watery solution of lime has an acrid disagreeable taste, turns vegetable blues to green, and unites with oil, forming an imperfect soap. To prepare the solution, lime is to be slaked to a thin paste, and a sufficient quantity of water afterwards added. The mixture is to be stirred repeatedly, the lime allowed to settle, and the clear liquor decanted for use. It must be preserved in closely stopped vessels, for reasons which will be stated in the chapter on carbonic acid.

(d) When lime water is freely exposed to the atmosphere, the lime is precipitated from it in the state of a carbonate; and it is, therefore, not possible to obtain crystals of pure lime, by evaporating lime water in the common way. Its crystallization, however, has been effected by Gay Lussac, by inclosing a vessel of lime water, and another of concentrated sulphuric acid, under the same glass receiver.\* The evaporation of the water goes on quickly, especially when the sulphuric acid is occasionally renewed, and small transparent crystals are obtained in regular hexahedrons, cut perpendicularly to their axes. They remain transparent when exposed to the air for a few days, and are then changed into carbonate of lime. By ignition in a glass tube, their water of crystallization is expelled, and they are proved to consist of

Lime . . . . .	76.26	. . . . .	100.
Water . . . . .	23.74	. . . . .	31.14
			100.

These crystals agree, therefore, very nearly in composition with the proto-hydrate, which is obtained by exposing quicklime to a damp atmosphere. This, if the atom of water be taken at 9, and the atom of lime at 28, will make that of the hydrate 37.

#### *Peroxide of Calcium.*

When oxygen gas is passed over ignited quicklime, the

\* Ann. de Chim. et Phys. i. 334.



gas is absorbed, and a peroxide of calcium is obtained; the exact composition of which has not been determined. A similar peroxide, united with water, is formed also, according to Thenard, when lime is brought into contact with the oxygenated water, discovered by that chemist.

*Chloride of Calcium and Muriate of Lime.*

When lime is heated in chlorine gas, oxygen is evolved, and a chloride of calcium is formed. The same compound is obtained by saturating muriatic acid with carbonate of lime, and evaporating to dryness, and fusing the residue. In this case the muriatic acid is decomposed; its hydrogen, uniting with the oxygen of the lime, escapes in the state of water; and the chlorine unites with the calcium. The chloride and the muriate are, therefore, mutually convertible by adding or expelling water. One hundred grains of carbonate of lime afford, according to Berzelius, 109.6 of fused chloride of calcium, containing, as appears from calculation, 69.6 chlorine, and 40 of the metal, which numbers are as nearly as possible in the proportion of 36 to 20, the equivalents of chlorine and calcium. Hence the representative number of chloride of calcium is  $36 + 20 = 56$ ; or it consists of

Chlorine .....	64
Calcium .....	36
	100

When chloride of calcium is exposed to the atmosphere, it deliquesces very rapidly. It is of course, therefore, soluble in a very small quantity of water, and it forms a solution of a thick oily consistence, and of a bitter acrid taste. This solution, which is strictly muriate of lime, deposits crystals, if exposed to the temperature of  $32^{\circ}$  Fahr. These crystals, when mixed with fresh fallen snow, produce a degree of cold sufficient to freeze quicksilver, as already stated in the chapter on caloric. They contain, according to Berzelius,

Muriatic acid .....	24.69
Lime . . . . .	25.71
Water .....	49.60
	100.

It is probable, however, that this determination is not correct, for if the acid and lime be in atomic proportion, they ought to exist in this salt in the proportions of 37 to 28, which numbers represent the weight of their atoms; whereas the ingredients of muriate of lime, as stated by Berzelius, are nearly in equal weights.

*Iodide of calcium* is obtained by evaporating to dryness the hydriodate of lime, and strongly heating the residue. It is a white fusible compound.

#### *Salts, &c. with Base of Lime.*

*Chloride of Lime.*—When chlorine gas is brought into contact with proto-hydrate of lime, which has been passed through a fine sieve, the gas is absorbed with rapidity, and with the evolution of much heat. It is necessary, indeed, either to pass the current of gas very slowly, or to surround the vessel containing the lime with cold water, and occasionally also to change the surface of the lime by stirring it. When the hydrate has taken all the gas that it is capable of absorbing, there remains a dry white powder, of considerable importance, from its extensive use in the art of bleaching, and known in commerce by the names of *bleaching powder*, or *oxymuriate of lime*.

This substance, to which the name of *sub-chloride of lime*, or *sub-chloride of hydrated lime*, is more appropriate, has a faint odour of chlorine, and a penetrating taste. When agitated with water, a portion is dissolved, varying in different specimens. The solution of a sort of fair commercial quality, when a wine gallon of water had been made to act upon a pound of the salt, I found had the specific gravity of 1.035. A large residue of undissolved matter is always left, which consists for the most part of hydrate of lime, not entirely free, however, from chlorine, the smell of which is evolved from it on adding an acid. The solution in water always contains an excess of lime, and does not actively discharge vegetable colours, till some acid is added to disengage the lime from the chlorine.

Chloride of lime exposed to heat is decomposed; a small portion of chlorine gas and some water first come over; and

on raising the heat to upwards of  $600^{\circ}$ , oxygen gas is evolved, by the action of the chlorine upon the calcium, which is the base of the lime. For every 50 cubic inches of oxygen that are obtained, we may reckon that 100 cubic inches of chlorine ( $= 76\frac{1}{4}$  grains) have united with calcium. The chloride of lime is thus converted by heat into chloride of calcium. A similar change appears to take place by long keeping at ordinary temperatures; for the salt gradually loses its bleaching power. When fresh prepared, it does not essentially contain any chloride of calcium, or muriate of lime; but in a specimen which had been kept about five years, Mr. Dalton found 30 per cent. of that salt, the chloride of lime being proportionally diminished.

The composition of sub-chloride of lime was first attentively examined by Mr. Dalton.\* A specimen formed by exposing the proto-hydrate of lime to chlorine gas, till it would absorb no more, he found to be constituted of

Chlorine .....	23
Lime .....	38
Water .....	39
	100

These numbers, indeed, do not exactly agree with any atomic proportions; but if altered a little, as follows, to correct defects in the analysis, which are within the limits of possible error, the constitution of the salt would cease to be anomalous; *viz.*

Chlorine ....	24.36	.... = 1 atom	....	36
Lime .....	38.54	.... = 2 atoms	....	56
Water .....	37.10	.... = 6 atoms	....	54
	100.			146

Each atom of lime appears, therefore, to have been united with 3 atoms of water, or to have been in the state of trihydrate. These proportions of chlorine and lime are such as to constitute a true *sub-chloride*, as Mr. Dalton names it; or *sub-bichloride*, as it has been called by Dr. Thomson.

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\* Ann. of Phil. i. 15, and ii. 6.

When water was made to act upon the sub-chloride, Mr. Dalton found that one-half of the whole lime was deposited. The atom of chlorine, therefore, was, in the solution, engaged by an atom of base, constituting a true *chloride of lime*. This compound is probably not capable of existing long in solution, for when the liquid is boiled to dryness, chloride of calcium is the product, giving muriate of lime by solution in water.

In this view of the constitution of chloride of lime, Dr. Thomson\* and M. Welter† for the most part agree; except that they assign, to the dry salt, proportions of water differing from those of Mr. Dalton. Both of them admit that a partition of the base is effected by solution, and that, in the liquid, the existing compound contains an atom of each of its elements.

The assay of sub-chloride of lime, in order to ascertain its commercial value, has been effected in several ways. Mr. Dalton first proposed detaching the gas from a given weight either of the dry or liquid compound, over mercury in a graduated tube, by means of an acid. A portion of the chlorine is retained by the liquid, which may be estimated at twice its volume; but no sensible error is, it seems, occasioned by the action of the chlorine on the mercury. He afterwards announced what he considers as an improved method, *viz.* the successive addition of a solution of the chloride to a solution of green sulphate of iron (sp. gr. 1.149) till the smell of chlorine is developed. This method, however, I consider as greatly inferior to that of liberating the chlorine by an acid. To effect this, without the aid of a mercurial trough, Dr. Ure has contrived an instrument described in the *Quarterly Journal*, xiii. 21. For the purposes of the artist, I believe, however, the most practicable method will be found to be the test of solution of indigo in sulphuric acid. It may be of such strength that 1600 parts of the liquor contain one of indigo. Of this solution 100 cubic inches of chlorine =  $76\frac{1}{4}$  grains, destroy the colour of 1159.5 cubic inches, or 10 grains of chlorine discharge the colour of 152 cubic inches of the solution. It is desirable to dilute the solution of chloride, so that its volume may be nearly one-half

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\* Ann. of Phil. xv. 401.

† Ann. de Ch. et Phys. vii. 383.

that of the colour test; to pour the former into the latter slowly and at intervals, stirring the mixture well after each addition; and in making several comparative experiments to take care that the quality of the test, and the manner of proceeding, shall be the same in all. It cannot, however, be pretended that this test possesses the scientific accuracy attainable by the admeasurement of the disengaged chlorine, which alone is to be depended upon, when a precise analysis is required.

*Chlorate of lime* may be formed by acting on carbonate of lime with chloric acid. A deliquescent compound is obtained, of a sharp and bitter taste, soluble in alcohol, and giving oxygen gas when heated. It is constituted, according to Che-né-ix, of 55.2 acid + 28.3 lime + 16.5 water.

*Iodate of lime* requires for solution several hundred times its weight of water. When exposed to a strong heat, it is decomposed, oxygen and iodine are given off; and the base remains.

*Hydriodate of lime* is deliquescent, crystallizable, enters into fusion at a heat a little below redness, and is converted into iodide of calcium in close vessels; but when heated with the free access of air, much of the iodine is separated, and a sub-iodide of calcium remains.

#### *Nitrate of lime.*

This salt is found abundantly in the cement of old buildings, which have been long inhabited. To prepare it artificially, nitric acid, diluted with five or six parts of water, may be saturated with carbonate of lime, 63 parts of which are decomposed by 90.23 of nitric acid of density 1.5, and give 103.05 of dry nitrate of lime.\* When this solution is boiled down to the consistence of syrup, and exposed in a cool place, long prismatic crystals are formed, resembling, in their disposition, bundles of needles diverging from a common centre. These crystals are readily soluble in water, of which, at 60°, they require two parts, and boiling water dissolves an equal weight. They deliquesce speedily, when exposed to

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\* Phillips, *Journal of Science*, v. 167.

the air; and are decomposed at the temperature of ignition. Exclusive of water, it contains,

	Acid.	Base.
According to Dalton . . . . .	61.3	38.7
————— Phillips . . . . .	65.6	34.4

When a solution of nitrate of lime is evaporated to dryness in an earthen vessel, then fused for five or ten minutes in a crucible, and poured, while in fusion, into an iron pot previously heated, the congealed mass forms *Baldwin's phosphorus*. It must be broken into pieces, and preserved in a well-stopped phial. These pieces, after having been exposed to the sun for a few hours, emit in the dark a beautiful white light, affording one variety of solar phosphorus.

#### *Carbonate of Lime.*

Lime has a strong attraction for *carbonic acid*, but not when perfectly dry; for if a piece of dry quicklime be passed into a jar of carbonic acid gas over mercury, no absorption whatever ensues. But if a bottle, filled with carbonic acid gas, be inverted over a mixture of lime and water of the consistence of cream, a rapid absorption will be observed, especially if the bottle be agitated: or if a jar or bottle, filled with carbonic acid, be brought over a vessel of lime water, on agitating the vessel, a rapid diminution will ensue, and the lime water will become milky. When a shallow vessel of lime water is exposed to the air, a white crust forms on the surface, and this, if broken, falls to the bottom, and is succeeded by another, till the whole of the lime is precipitated from the solution. This is owing to the absorption of carbonic acid gas from the air by the lime, which is thus rendered insoluble in water. Dry lime, also, when exposed to the atmosphere, first acquires moisture, and, having become a hydrate, next absorbs carbonic acid. In a sufficient space of time, all the characters distinguishing it as lime disappear, and it acquires the property of effervescing with acids. The strong affinity of lime for carbonic acid enables it to take this acid from other substances. Thus carbonates of alkalis are decomposed by lime. Slake a given quantity of lime into a paste

with water, and add half its weight of carbonate of potassa or soda. Boil the mixture, for half an hour, in an iron kettle, and separate the liquid part by filtration or by subsidence. The carbonic acid combines with the lime, and the alkali is obtained in a state of solution perfectly free from carbonic acid. This is the ordinary mode of depriving the alkalis of carbonic acid.

Carbonate of lime is a most abundant product of nature. In the forms of lime-stone, marble, and chalk, it constitutes extensive strata, and it is the basis also of calcareous spar and stalactites. Carrara marble of perfect whiteness, or, for common purposes, chalk, may be employed to exhibit its properties.

The carbonic acid existing in carbonate of lime is expelled by a strong red heat. If distilled in an earthen retort, carbonic acid gas is obtained, and lime remains in the retort in a pure or caustic state. By this process carbonate of lime loses about 45 per cent.

The experiments of Sir James Hall have proved, that when the escape of the carbonic acid is prevented by strong pressure, carbonate of lime is fusible in a heat of about  $22^{\circ}$  of Wedgwood's pyrometer.\* And Mr. Bucholz has lately fused this substance, by the sudden application of a violent heat, without additional compression.†

Carbonate of lime is decomposed by almost all acids. This will appear if upon chalk or marble contained in a gas bottle diluted sulphuric or muriatic acid be poured. A violent effervescence will ensue, owing to the escape of carbonic acid gas, which may be collected over water or mercury. By a little modification of the experiment, the quantity of carbonic acid expelled from the carbonate may be correctly ascertained. Let 100 grains of the carbonate be put into a Florence flask, with an ounce or two of water; place this in the scale of a balance; and in the same scale, but in a separate bottle, about half an ounce of muriatic acid. Add the muriatic acid to the carbonate as long as any effervescence is produced, and then blow out that part of the disengaged carbonic acid, which

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\* Nicholson's Journal, xiii. xiv.

† Ibid, xvii. 229.

remains in the flask, by a pair of bellows. Ascertain, by adding weights to the opposite scale, how much has been lost; suppose it to be 43.5 grains; this shows the quantity of carbonic acid disengaged. Calcine another 100 grains in a covered crucible. It will lose rather more of its weight; because, besides its carbonic acid, all the water is expelled which it may contain. Let this loss be stated at 45 grains; the former loss deducted from this (45 - 43.5), or 1.5 grains, shows the quantity of water in 100 of the carbonate. The proportion, however, thus discovered, is so small that it may be considered as an accidental ingredient. Independently of water it is constituted,

	Acid.	Base.
According to Dr. Wollaston, of . . . .	43.7	56.3
----- Berzelius of. . . . .	43.6	56.4

The proportions of 1 atom of lime = 28, + 1 atom of acid = 22, would require that it should consist of

Acid . . . . .	43.86	. . . .	100	. . . .	78
Lime . . . . .	56.14	. . . .	128	. . . .	100
100.					

Carbonate of lime, though scarcely dissolved by pure water, is soluble in water saturated with carbonic acid. The most striking method of showing this is the following: Add to a jar, about one-fourth filled with lime water, a very small quantity of water saturated with carbonic acid. An immediate milkiness will ensue, because the carbonic acid forms with the lime an insoluble carbonate. Add gradually more and more of the water, impregnated with carbonic acid, shaking the vessel as these additions are made. At last the precipitate will be completely re-dissolved. Hence it appears that lime, with a certain proportion of carbonic acid, is insoluble, and, with a still larger, again becomes soluble in water. By heating the solution of lime in carbonic acid, we do not, as in the case of alkaline solutions, obtain a bi-carbonate of lime, which is a salt still unknown; but the lime is thrown down in the state of simple carbonate, and the excess of carbonic acid escapes into the atmosphere.



*Borate of lime* may be formed by adding a solution of boracic acid to lime water. The resulting compound is a white tasteless powder, which dissolves very sparingly in water.

*Fluate of lime.*—There is a natural product, well known in Derbyshire, and other parts of the world, under the name of *fluor spar*, which is worked into a variety of ornaments. It most commonly, when crystallized, occurs in cubes, but its primitive form is an octohedron. Its specific gravity is 3.15. It is perfectly tasteless and insoluble in water. When thrown in powder upon a plate of iron heated below redness in a dark place, it emits a phosphorescent light. Concentrated sulphuric acid occasions an effervescence by expelling fluoric acid gas. Berzelius considers it as a compound of 100 fluoric acid + 258.9 lime:\* In strictness, however, it is to be regarded as a *fluoride of calcium*, and its composition is probably 100 fluorine + 131.25 calcium.

*Phosphuret of lime is prepared as follows:*—Take a glass tube, about 12 inches long, and one-third of an inch diameter, sealed hermetically at one end. Let this tube be coated with clay, except within about half an inch of the sealed end. Put first into it a drachm or two of phosphorus, cut into small pieces, and then fill the tube with small bits of fresh burnt lime, of the size of split peas. Stop the mouth of the tube loosely with a little paper, in order to prevent the free access of air.—Next, heat to redness that part of the tube which is coated with clay, by means of a chafing-dish of red-hot charcoal; and, when the lime may be supposed to be ignited, apply heat to the part containing the phosphorus, so as to sublime it, and to bring the vapour of it into contact with the heated lime. The lime and phosphorus will unite, and will afford a compound of a reddish-brown colour.

If the carbonate of lime be substituted for pure lime, the carbonic acid is decomposed. Its carbon is set at liberty, and appears in the state of charcoal; while its oxygen unites with the phosphorus; and the phosphoric acid, thus produced, forms phosphate of lime. In this process, discovered by the late Mr. Tennant, carbonic acid is decomposed by the con-

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\* Ann. of Ph. xv. 282.

spirating affinities of phosphorus for oxygen, and of lime for phosphoric acid, though the former affinity only would be inadequate to produce the effect.

The phosphuret of lime has the remarkable property of decomposing water at the common temperature of the atmosphere ; and the water afterwards contains phosphite, or hypophosphite, not phosphate, of lime.\* Drop a small piece of it into a wine-glass of water, and in a short time bubbles of phosphureted hydrogen gas will be produced ; which, rising to the surface, will take fire, and explode. If the phosphuret of lime be not perfectly fresh, it may be proper to warm the water to which it is added.

Into an ale-glass put one part of phosphuret of lime, in pieces about the size of a pea (not in powder), and add to it half a part of chlorate of potassa. Fill the glass with water, and put into it a funnel, with a long pipe, or narrow glass tube, reaching to the bottom. Through this pour three or four parts of strong sulphuric acid, which will decompose the chlorate ; and, the phosphuret also decomposing the water at the same time, flashes of fire dart from the surface of the fluid, and the bottom of the vessel is illuminated by a beautiful green light. (Davy).

*Phosphite and hypo-phosphite of lime* have not been particularly examined.

*Phosphate of lime* derives importance from its being the principal ingredient of animal bones, of which it constitutes about 86 per cent. It may be obtained by dissolving bones, which have been well calcined and then pulverized, in dilute muriatic acid, and precipitating the solution with pure ammonia. The precipitate, when sufficientlyedulcorated, is *phosphate of lime*, an insipid white powder, insoluble in water, but soluble in diluted nitric, muriatic, and acetic acids, and again precipitable, unaltered, from those acids by caustic ammonia. At a high temperature, it fuses into an opaque white enamel. It is constituted, according to Mr. Dalton's experiments, of 49 acid + 51 lime, proportions which authorize us to consider

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\* Gay Lussac, 85 Ann. de Chim. 206, and Ann. de Chim. et Phys. vi. 328.

phosphate of lime as consisting of 1 atom of acid = 28, + 1 atom of base = 28, the compound atom being 56.

*Bi-phosphate of lime* may be formed by digesting phosphate of lime with a quantity of phosphoric acid equivalent to that already engaged in the salt. The solution has an acid, and somewhat harsh and disagreeable taste. It does not crystallize, but forms, when evaporated, a white mass, which attracts moisture from the air. Before the blow-pipe it melts into a transparent glass, insoluble in water.

*Tri-phosphate of lime.*—This salt, according to Mr. Dalton, may be formed by adding pure phosphoric acid to lime water, till a commencement of precipitation appears, when the solution must be cleared by a drop or two of acid. If the solution be evaporated to dryness at a moderate heat, and then dissolved in water again, simple phosphate of lime remains, and a quadri-phosphate exists in the solution.

*Quadri-phosphate of lime.*—If 100 parts of phosphate of lime be digested for 24 hours with 87 parts of sulphuric acid, diluted with a sufficient quantity of water, and be then filtered, the liquid which passes through contains the whole of the phosphoric acid, with only one-fourth of the lime which existed in the original salt, the remaining  $\frac{3}{4}$ ths having formed an insoluble compound with the sulphuric acid. The dissolved salt is, therefore, a compound of 1 atom of lime = 28, + 4 atoms of acid = 112. When evaporated, it forms, on cooling, pearly scales, which have an acid taste, and dissolve readily in water, giving a solution of the sp. gr. 1.44. When dried and fused in a crucible, a transparent glass is obtained, commonly called *glacial phosphoric acid*, and employed chiefly in the production of phosphorus.

*Octo-phosphate of lime.*—Mr. Dalton is of opinion that a compound of 8 atoms of acid and 1 atom of lime is the true result of the process described under the last head; and that a compound of as many as 12 atoms of acid with one of lime may exist, forming a *dodecaphosphate*.

*Sulphuret of lime* may be formed by heating, in a covered crucible, one part of sulphur and two of lime. This compound can exist as such, only when in a solid state, for water

decomposes it, and sulphureted hydrogen results from its action.

*Hydro-sulphuret of lime* is obtained by transmitting a current of sulphureted hydrogen gas through water in which lime is kept mechanically suspended. It is crystallizable, and the crystals are colourless and readily soluble in water.

*Hydrogureted sulphuret of lime* is formed whenever the sulphuret is dissolved in water, or by boiling together three parts of hydrate of lime, one of sulphur, and ten of water. The compound has a deep orange colour, and derives importance from its use as an eudiometrical test. From the experiments of Vauquelin, it seems probable that it is subject to a variety in its proportions, and to corresponding differences in its properties. (Ann. de Chim. et Phys. vi. 39.)

Mr. Herschell, by boiling 3 parts of hydrate of lime with one of sulphur and 20 of water, and allowing the solution to cool on the sediment, obtained crystals, which, when dried by sulphuric acid under an exhausted receiver, had the shape of quadrilateral prisms somewhat elongated with dihedral summits. They dissolved sparingly in cold water; the solution had only the sp. gr. of 1.0105, was yellow, and had an acrid sulphurous taste. The crystals are constituted of 2 atoms of lime, two of sulphur, + one of hydrogen, (forming bisulphureted hydrogen,) and four of water. When these crystals are ground with sulphurous acid, its smell disappears, and hyposulphite of lime is formed.

*Hypo-sulphite of lime.*—By passing a current of sulphurous acid gas through a solution of the hydrogureted sulphuret of lime, the whole of the acid gas is converted into hyposulphurous acid. When this solution is boiled down to a certain degree of consistence, sulphur and sulphite of lime separate abundantly. The solution, evaporated at a temperature not exceeding 130° or at most 140° Fahr., and filtered while hot, yields on cooling large and very beautiful crystals, which affect a variety of complicated forms.

These crystals are *hypo-sulphite of lime*. They are very soluble in water, which, at 37° Fahr. dissolves nearly its own weight, during which the thermometer falls to 31°. The

specific gravity of the solution, saturated at 50°, is 1.300. The crystals are not altered by exposure to air of the usual humidity; but when dried by sulphuric acid *in vacuo*, or at 100° Fahr. in the air, they become covered with a white efflorescence, which destroys their lustre without altering their figure. They are insoluble in alcohol of sp. gr. 0.823, which precipitates them from their watery solution. By an analysis very carefully and skilfully conducted, Mr. Herschell found them to be composed of

	Atoms.	
Hypo-sulphurous acid . . . .	36.71	= 2 = 48
Lime . . . . .	21.71	= 1 = 28
Water . . . . .	41.58	= 6 = 54
	100.	130.

Or they consist (exclusive of water) of two atoms of acid united with one of base, the acid being composed of oxygen and sulphur atom to atom. (Edinburgh Phil. Journ. i. 17.) In strictness, therefore, this salt is a *bin-hyposulphite*.

*Sulphite of lime* may be obtained by passing a current of sulphurous acid through water in which carbonate of lime is kept mechanically suspended. If the sulphurous acid be in excess, the resulting salt is soluble, and its solution, when evaporated, crystallizes on cooling in six-sided prisms, terminated by long six-sided pyramids. It is at first almost tasteless, but when kept in the mouth has a sulphureous flavour. It requires for solution about 800 parts of water. By exposure to the air, the surface of the crystals is changed into sulphate of lime, and the same conversion is rapidly effected by heating it. It is constituted of

Acid . . . . .	54.29
Lime . . . . .	45.71
	100.

#### *Sulphate of Lime.*

Sulphate of lime may be formed, by adding to the carbonate a sufficient quantity of sulphuric acid; and by gently calcining the residue, to expel the redundancy of the latter

**acid.** It is also found native, in great abundance, under the names of gypsum, plaster of Paris, &c.

It has the following properties :

1. It is insipid and free from smell.
2. It is difficultly soluble, requiring 500 times its weight of cold water, or 450 of hot water.
3. It is fusible by a moderate heat. When sulphate of lime, which has been dried at 160° Fahrenheit, is exposed to a low red-heat, 100 grains lose 22 according to Berzelius, or 21 according to Bucholz, consisting entirely of water. After calcination, it absorbs water rapidly, and forms a good cement.
4. It is decomposed by alkaline carbonates, a double exchange of principles ensuing. Hence the milkiness which ensues on adding carbonate of potassa to many spring waters; the carbonate of lime, which is generated, being less soluble than the sulphate. Hence, also, hard waters, which always contain sulphate of lime in solution, curdle soap, the alkali of which is detached by the sulphuric acid, and the oil is set at liberty.
5. It is decomposed by ignition with charcoal, which separates the oxygen of the sulphuric acid, and leaves a combination of lime with sulphur.

By dissolving 100 grains of calcined sulphate of lime in boiling distilled water, and adding muriate of barytes, I obtained a precipitate, which, when well washed, dried, and calcined in a low red-heat, weighed 175.9. Hence 100 parts of calcined sulphate of lime must contain very nearly

	Acid.	Base.
According to the above experiment . . . .	59	. . . 41
———— Thomson and Berzelius ..	58	. . . 42
———— Klaproth . . . . .	57.63	. . . 42.37
———— Dalton . . . . .	58.60	. . . 41.40

It consists, therefore, of an atom of lime = 28, united with an atom of acid, = 40, and its equivalent number is 68.

*Seleniate of lime.*—Selenic acid is capable of uniting with lime in two different proportions, forming a seleniate and a

biseleniate; but these salts have no particularly interesting properties.

*Ferro-cyanate of lime.*—This compound, which is useful as a test of iron, may be formed by adding powdered prussian blue to lime water, till the lime no longer alters paper stained with turmeric. If this effect be still slightly produced, a little more prussian blue may be added, and the mixture boiled a short time and filtered. The filtered liquor has a greenish yellow colour, and an unpleasant bitterish taste. Its specific gravity is 1.005. When evaporated, it yields small crystalline grains, which dissolve sparingly in water, and are insoluble in alcohol.



## SECTION V.

### *Barium.*

BARIUM was obtained by Sir H. Davy by distilling its amalgam, which had been formed in the following manner. A quantity of native carbonate of baryta was made into a paste with water, and placed on a tray of platinum; a cavity was made in the paste to receive a globule of mercury, which was rendered negative, at the same time that the platinum was made positive by means of a Voltaic battery, containing about 100 double plates. In a short time, an amalgam was formed consisting of mercury and barium. This amalgam was introduced into a little tube made of glass free from lead, which was bent into the shape of a retort, then filled with the vapour of naphtha, and hermetically sealed. Heat was then applied to the tube, till all the mercury was driven off.

The residuum of this distillation was a dark grey metal, with a lustre inferior to that of cast iron. At the ordinary temperature of the air it remained a solid; but became fluid at a heat below redness. It did not rise in vapour, till heated nearly to redness, and then acted violently upon the glass.

When exposed to the air, this substance rapidly tarnished, and fell into a white powder, which was baryta. When this

process was conducted in a small portion of air, the oxygen was absorbed; and the nitrogen remained unaltered. A portion of it thrown into water acted upon it with great violence, and sank to the bottom, producing baryta, and evolving hydrogen gas.

The quantities obtained were too minute for an examination either of its physical or chemical qualities. It sank rapidly in water, and even in sulphuric acid, though surrounded by globules of hydrogen equal to two or three times its volume. Hence it is probable that it cannot be less than four or five times as heavy as water. It was flattened by pressure, but required considerable force for this effect.

The proportion of the components of baryta Sir H. Davy deduces to be 89.7 barium and 10.3 oxygen per cent. The determination of Berzelius nearly agrees with this, *viz.*

Barium.....	89.52 .....	100.00
Oxygen .....	10.48 .....	11.69
	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
	100.	111.69

If then the protoxide of barium be, as is most probable, composed of an atom of the metal united with an atom of oxygen, the atom of barium will be represented by 69.6, for 10.3 : 89.7 :: 8 : 69.6. In round numbers 70 may be taken as the equivalent of barium and 78 of baryta.

*Baryta* may be obtained for experimental purposes from the nitrate or carbonate of that earth in the manner which will presently be described. It exhibits, when pure, the following properties.

1. Baryta, in a pure form, has a sharp caustic taste; changes vegetable blue colours to green; and serves as the intermedium between oil and water. In these respects, it bears a strong resemblance to alkalis.

2. When exposed to the flame of the blow-pipe on charcoal, it melts; boils violently; and forms small globules, which sink into the charcoal. After being kept in fusion in a crucible during ten minutes, it still, according to Berthollet, contains 9 per cent. of water; from theory it should contain 10.59 per cent. This, however, is true only of barytes which has



been obtained from the carbonate, by a process to be described hereafter. Baryta, procured by decomposing the nitrate of that earth, is not fusible, and appears to contain little if any water.\*

3. If a small quantity of water be added to recently prepared baryta, it is absorbed with great rapidity; prodigious heat is excited; and the water is completely solidified, a sort of hard cement being obtained. A little more water converts this mass into a light bulky powder; and, when completely covered with water, the baryta is dissolved. Boiling water should be employed for this purpose; unless sufficient temperature has been produced, by the sudden addition of the whole quantity necessary for solution.

4. When the solution, prepared with boiling water, is allowed to cool slowly, it shoots into regular crystals. These have the form of flattened hexagonal prisms, having two broad sides, with two intervening narrow ones; and terminated, at each end, by a quadrangular pyramid. They lose, according to Bucholz, half their weight of water in a red heat; the baryta then continues fused, and parts with no more water, though still combined with the proportion above stated. Mr. Dalton, from his experiments, infers that the crystals contain 30 baryta and 70 water per cent., which would make them consist of 1 atom of baryta + 20 atoms of water.

5. The crystals are so soluble, as to be taken up, when heated, merely by their own water of crystallization. When exposed to a stronger heat, they swell, foam, and leave a dry white powder, amounting to about 47 parts from 100 of the crystals. This again combines with water with great heat and violence. At 60° of Fahrenheit, an ounce measure of water dissolves only 25 grains of the crystals, *i. e.* they require for solution,  $17\frac{1}{2}$  times their weight of water. Exposed to the atmosphere, they effloresce, and become pulverulent.

6. When added to spirit of wine, and heated in a spoon over a lamp, they communicate a yellowish colour to its flame.

7. The specific gravity of this earth, according to Fourcroy, is 4; but Hassenfratz states it at only 2.374. The

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\* Nicholson's Journal, xxiii. 281.

former account, however, is the more probable. All its combinations have considerable specific gravity; and hence its name is derived, *viz.* from the Greek word βαρύς, signifying heavy.

8. Baryta does not unite with any of the alkalies.

#### *Peroxide of Barium.*

Barium has been shown, by Gay Lussac and Thenard, to be capable of uniting with an additional atom of oxygen to that contained in baryta; for when that earth, prepared from the nitrate, was ignited in oxygen gas, the gas was rapidly absorbed, and a grey compound was formed, glazed on its outer surface. This compound may be called *dentoxide* or *peroxide of barium*; and it appears to be constituted of one atom of the metal = 70, + 2 atoms of oxygen = 16, together 86. To prepare the peroxide, Thenard recommends that the nitrate of baryta be ignited in a retort of white porcelain (one of Wedgwood's ware is well adapted to the purpose) till oxygen gas ceases to be evolved. The product, hastily broken into fragments about the size of a hazle nut, is to be put into a well-luted green glass tube, which is to be placed horizontally in a furnace, and heated to dull redness. A current of oxygen gas, dried by having first been passed over quicklime, is then to be transmitted through the tube, and continued 10 or 15 minutes. The gas is rapidly absorbed, and a greyish white substance obtained, which is the *peroxide*, the compound employed by Thenard in giving an additional proportion of oxygen to water. (See page 262.)

#### *Chloride of Barium.*

Chloride of barium may be formed by heating pure baryta in chlorine gas, each measure of which disengages half a measure of oxygen gas from that earth. Or when baryta is heated in muriatic acid gas, the gas disappears, and the chloride, which is produced, becomes red hot. But for purposes of experiment, this salt is best prepared, by dissolving either the artificial or native carbonate in muriatic acid much diluted; or, if neither of these can be had, the sulphuret. The iron and lead, which are occasionally dissolved, along with the baryta,

may be separated by the addition of a small quantity of liquid ammonia, or by boiling and stirring the solution in contact with a little lime; or, which is still better, by solution of baryta in water. When filtered and evaporated, the solution yields regular crystals, which have most commonly the shape of tables, bevelled at the edges, or of eight-sided pyramids, applied base to base. These crystals dissolve in five parts of water, at 60°, or in a still smaller quantity of boiling water; and also in alcohol. They are not altered by exposure to the atmosphere; nor are they decomposed, except partially, by a high temperature. The sulphuric acid separates the muriatic; and the salt is also decomposed by alkaline carbonates and sulphates.

Fifty grains of chloride of barium first ignited, and then dissolved and precipitated by nitrate of silver, give, according to Berzelius 68 grs. of luna cornea. The dry salt Sir H. Davy considers as a compound of 1 atom of barium = 70 + 1 atom of chlorine = 36; hence its representative number is 106, and it consists of

Chlorine .....	34
Barium .....	66
	100

Muriate of baryta, formed by the action of water on the chloride, must therefore be constituted of 1 atom of muriatic acid = 37, + 1 atom of baryta = 78, and its equivalent must be 115. Hence it should consist, when crystallized, of

Acid .....	27.82 = 1 atom
Baryta .....	58.47 = 1 atom
Water .....	13.71 = 2 atoms
	100.

These numbers do not exactly agree with the experimental results of Aikin and Berzelius, which state its composition as follows:

	Acid.	Base.	Water.
According to Mr. Aikin ....	22.93	62.47	14.6
————— Berzelius. ....	23.35	61.85	14.8

The analysis, therefore, requires to be attentively repeated.

*Chlorate of Baryta.*—To prepare this salt, chlorine gas must be received into a warm solution of baryta in water, till the baryta is saturated. The solution is to be filtered, and boiled with phosphate of silver, which decomposes the common muriate of baryta, and at the same time composes two insoluble salts, phosphate of baryta, and chloride of silver. Vauquelin finds the addition of acetic acid recommended by Chenevix, objectionable, and that the compounds of chloric acid are liable, if acetic acid has been employed, to detonate violently when heated. To judge when enough of the phosphate of silver has been used, add to a portion of the filtered liquor, a few drops of nitrate of silver, which, in that case, ought not to disturb its transparency. If too much phosphate of silver has been used, a drop or two of muriatic acid will discover it, and, in that case, the cautious addition must be made of some of the original solution, set apart for the purpose, to which no phosphate of silver has been added. It is from solution of chlorate of baryta, thus carefully prepared, that chloric acid is obtained by the intervention of sulphuric acid, as described page 219.

Chlorate of baryta has the form of four-sided prisms; its taste is pungent and austere; it requires for solution about four times its weight of water, at 50° Fahrenheit; and its solution, when pure, is not precipitated either by nitrate of silver or muriatic acid. By a red heat, it loses 39 per cent., and the residue is alkaline. From calculation it should consist, besides water, of

1 atom of baryta . . . . .	78.	. . . .	50.6
1 do. of chloric acid. . . . .	76.	. . . .	49.4
	<hr style="width: 50px; margin: 0 auto;"/>		<hr style="width: 50px; margin: 0 auto;"/>
	154.		100.

*Iodide of barium* may be formed by evaporating and igniting the hydriodate of baryta. The hydrogen of the acid unites with the oxygen of the earth, and the iodine with its metallic base.

*Hydriodate of baryta* is extremely soluble in water, and rather deliquescent. It crystallizes in very small prisms, which are decomposed by mere exposure to the atmosphere into

water, a salt with excess of iodine, and carbonate of baryta. When ignited in close vessels, it is converted into iodide of barium. It is constituted of 100 acid + 60.62 baryta.

*Iodate of baryta* is an extremely insoluble salt. It may be formed by adding iodine to solution of baryta, from which the iodate precipitates in the state of a white powder, and may beedulcorated by washing with distilled water. When strongly heated, oxygen and iodine are evolved from it, and baryta remains. It consists of 100 acid + 46.34 base.

*Nitrate of Baryta.*

Nitrate of baryta may be prepared, by dissolving either the artificial or native carbonate in nitric acid, diluted with eight or ten parts of water. If the artificial carbonate be employed, it should be previously well washed with distilled water, till the washings cease to precipitate nitrate of silver. A solution of nitrate of baryta, mixed with one of nitrate of silver, should continue perfectly transparent. On evaporation, it yields regular octahedrons, often adhering to each other in the form of stars; and sometimes it is obtained in small brilliant plates. It requires for solution 12 times its weight of water at 60°, and three or four parts of boiling water. It is not altered by exposure to the air. In a red-heat, its acid is decomposed, and the earth remains pure. This furnishes another method of procuring pure baryta; but the heat must not be carried too far, otherwise the baryta is apt to vitrify with the crucible. The residue, on the addition of water, dissolves with great heat and noise, and the solution, on cooling, yields crystals of pure baryta.

Nitrate of baryta consists of

	Acid.	Base.
According to Clément and Desormes..	40	60
————— Mr. Jas. Thomson.....	40.7	59.3
————— Berzelius. ....	41.54	58.46

If a compound of 1 atom of acid + 1 atom of base, it should consist of

Baryta .....	78.	58.94
Nitric acid .....	54.	41.06
	132.	100.

### Carbonate of Baryta.

Pure baryta has a very powerful affinity for carbonic acid, as may be shown by exposing a solution of the earth in water to the atmosphere. It will soon be covered with a thin white pellicle; which, when broken, will fall to the bottom of the vessel, and be succeeded by another. This may be continued, till the whole of the baryta is separated. The effect arises from the absorption of carbonic acid, which forms with baryta a compound, *viz.* carbonate of baryta, much less soluble than the pure earth. Or if the air from the lungs be blown by means of a quill, or glass tube, through a solution of baryta, the solution will immediately become milky, in consequence of the production of an insoluble carbonate. The same effect will be produced by mingling, with a solution of pure baryta, a little water impregnated with carbonic acid. In this case, also, an immediate precipitation of carbonate of baryta will ensue.

Baryta has so strong an affinity for carbonic acid, as even to take it from other bodies. If to a solution of a small portion of carbonate of potassa, of soda, or of ammonia, we add the solution of baryta, the earth will detach the carbonic acid from the alkali, and will fall down in the state of a carbonate. By adding a sufficient quantity of a solution of baryta in hot water, the whole of the carbonic acid may thus be removed from a carbonated alkali; and the alkali will remain perfectly pure.

Carbonate of baryta has the following properties:

1. It is nearly insoluble in water, which, at  $60^{\circ}$ , does not take up more than  $\frac{1}{4300}$  part, or, when boiling, about  $\frac{1}{3100}$ . Water impregnated with carbonic acid dissolves  $\frac{1}{810}$ th.

2. Carbonate of baryta is perfectly tasteless, and does not alter vegetable blue colours. It acts nevertheless as a violent poison.

3. The combination of carbonic acid with baryta may either be produced artificially, as in the manner already described, and by other processes, to be detailed in the sequel, in which case it is termed, the *artificial carbonate*: or it may be procured, ready formed as a natural product, and is then called the *native carbonate*. The largest quantity, hitherto discovered,

is in a mine, now no longer worked, at Anglezark, near Chorley, in Lancashire, but it is also found in several other places.

The following table shows the experimental results of its analysis by various chemists.

	Carb. acid.	Baryta.
Analysis of Mr. Aikin .....	21.67	78.33
———— Thomson .....	21.75	78.25
———— Klaproth and Rose .....	22.00	78.00
———— Bucholz .....	21.00	79.00
———— Berzelius* .....	21.60	78.40
———— Dr. Wollaston (from theory)	22.09	77.91

Carbonate of baryta appears then to be constituted of 1 atom of base and 1 atom of acid. Hence it ought to consist of

Baryta.....	78.	100
Carbonic acid.....	22.	28.54
	100.	128.54

When 100 grains of the carbonate are dissolved in nitric acid, and precipitated by a sulphate, they afford, according to Berzelius, 118.6 or 119 grains of sulphate of baryta.

5. Carbonate of baryta is decomposed by an intense heat; its carbonic acid being expelled; and the baryta remaining pure. The artificial carbonate is most readily decomposed; but the native one is generally employed for obtaining pure baryta, because it may be had in considerable quantity. The process, which I have found to answer best, is nearly that of Pelletier. Let the native carbonate be powdered, and passed through a fine sieve. Work it up with about an equal bulk of wheaten flour into a ball, adding a sufficient quantity of water. Fill a crucible of proper size, about one third its height, with powdered charcoal; place the ball on this; and surround and cover it with the same powder, so as to prevent its coming into contact with the sides of the crucible. Lute on a cover; and expose it, for two hours, to the most violent heat that can be raised in a wind furnace. Let the ball be removed when cold. On the addition of water, it will evolve great heat, and the baryta will be dissolved. The filtered solu-

\* 78 Ann. de Chim. 49.

tion, on cooling, will shoot into the beautiful crystals already described p. 573.

6. Carbonate of baryta is decomposed by the sulphuric, nitric, muriatic, and various other acids, which detach the carbonic acid, and combine with the earth.

*Borate of baryta* is an insoluble white powder, which has not been particularly examined.

*Phosphite of baryta* may be obtained by adding muriate of baryta to phosphite of ammonia. No immediate precipitation ensues, but in 24 hours the glass is covered with a crust of phosphite of baryta, which may be edulcorated by water. According to Berzelius it is constituted of

Phosphorous acid.....	24.31
Baryta .....	67.24
Water.....	8.45

100.

This analysis renders it probable that its true constitution is 1 atom of acid = 20, + 1 atom of base = 78, + 1 atom of water = 9, and that its equivalent number is the sum of these 107.

*Hypo-phosphite of baryta* is a very soluble salt, crystallizable with difficulty. (Dulong, Ann. de Chim. et Phys. ii. 142.)

*Phosphate of baryta.* Phosphoric acid and baryta combine in various proportions.

The first or *neutral phosphate of baryta* is formed by mixing solutions of muriate of baryta and phosphate of soda. An insoluble precipitate is obtained, which, when edulcorated and dried, contains according to Berzelius,

Phosphoric acid .....	31.8	....	100.00
Baryta .....	68.2	....	214.46

100.

But if, as is probable, the phosphate consists of 1 atom of acid + 1 atom of base, it ought to be composed of

Phosphoric acid....	28.	....	26.62	....	100.
Baryta.....	78.	....	73.38	....	280.

106.

100.



By dissolving phosphate of baryta in phosphoric acid, and evaporating the clear solution, Berzelius obtained white crystals, which had an acid taste, and reddened vegetable blues. They are probably constituted of 2 atoms of acid = 56 + 1 atom of base = 78, together 134; and may therefore be considered as the *bi-phosphate*.

When a solution of these crystals is poured into alcohol, a bulky precipitate falls, which is white and tasteless. It appears to be constituted of 2 atoms of base and 3 of acid, or 1 of the former and  $1\frac{1}{2}$  of the latter, and hence may be called a *sesqui-phosphate*.

Besides the above compounds, Berzelius has described two sub-phosphates of baryta. (Ann. of Phil. xv. 277.)

*Sulphite of baryta* may be formed by mixing sulphite of potassa and muriate of baryta. An insoluble compound is formed of

Acid . . . . .	29.26	. . . . .	100
Base . . . . .	70.74	. . . . .	241.7
	<hr style="width: 50px; margin: 0 auto;"/>		
	100.		

*Hypo-sulphite of baryta* may be obtained by adding muriate of baryta to a concentrated solution of hypo-sulphite of lime. It forms a white shining scaly powder, slightly soluble in water. According to Mr. Herschell, who alone has described it, it is a compound of 2 atoms of hypo-sulphurous acid = 48, + 1 atom of base = 78, and its equivalent number therefore is 126.

*Sulphate of Baryta.*

Baryta has a more powerful affinity than any other base for sulphuric acid, and its combination with that acid may therefore be effected with great facility, either by dropping the watery solution of baryta into diluted sulphuric acid, or into the solution of any of the alkaline sulphates. The new compound is extremely difficult of solution, requiring at least 43,000 times its weight of water, and it is not sensibly more soluble in hot than in cold water. In sulphuric acid, when concentrated and heated, it dissolves, but is again precipitated on pouring the solution into water.

It is owing to these properties that baryta and several of its salts are so much employed as tests of sulphuric acid, and as

means of separating that acid from its combinations. By collecting the precipitate, first well edulcorated, then drying, igniting, and weighing it, and allowing 34 per cent. (a number which I have been decided to adopt, since the foregoing sheets were printed) of its weight for real sulphuric acid, we learn the quantity of acid in any sulphate. This estimate is founded, not only on the theoretical constitution of the salt, viz. 1 atom of acid + 1 atom of base, but on the coincidence of this with the best analyses. The following Table exhibits the experimental results of several chemists. Sulphate of baryta contains,

	Base.	Acid.
According to Klaproth .....	66.55	33.45
———— Mr. A. Aikin* ...	66.04	33.96
———— Mr. J. Thomson †.	66.96	33.04
———— Berthollet ‡.....	66.50	33.50
———— Berzelius § .....	65.69	34.31

Its composition, deduced from the atomic weight of its ingredients, is as follows :

Baryta.....	78	65.91	100
Sulphuric acid....	40	34.09	51.7
	118.	100.	

Sulphate of baryta is decomposed by alkaline carbonates, either by fusing a mixture of one part of the finely powdered sulphate with three of carbonate of potassa or soda, or by boiling together the pulverized sulphate and a solution of carbonate of potassa. Respecting this decomposition some curious facts have been ascertained by Dulong and by Mr. R. Phillips. When sulphate of baryta is boiled, for two hours, in contact with precisely its equivalent quantity of carbonate of potassa, (that is, with the quantity which ought, from theory, to produce entire decomposition), only one fourth of the sulphate of baryta is converted into carbonate. Reversing the process, and boiling together equivalent quantities of carbonate of baryta and sulphate of potassa (the mutual decomposition of which could not have been expected from the established order of affinities) it was found that, out of 85

\* Nicholson's Journal, xxii. 301.

† Ibid. xxiii. 174.

‡ Memoires d'Arcueil, ii.

§ 79 Ann. de Chim. 138.

parts of carbonate of baryta, 57 had been changed into sulphate. It is obvious, therefore, that the entire decomposition of sulphate of baryta by carbonate of potassa can never be expected, so long as the carbonate of baryta, formed by the mutual action of these two salts, remains in contact with the sulphate of potassa generated at the same time; for this will re-convert the carbonate of baryta into sulphate. Nor will any quantity of carbonate of potassa, that can be employed, be adequate to the entire decomposition of the sulphate of baryta.

By this process carbonate of baryta may, however, be procured in sufficient quantity for the purpose of preparing the pure earth, and its various salts, when the native carbonate cannot be had in sufficient abundance. The sulphate is found, in considerable masses, accompanying lead ore, in Derbyshire and other parts of England, where it is known by the names of cawk, ponderous spar, &c. The native sulphate is extremely heavy, having the specific gravity of 4.7. It occurs either in amorphous masses, or crystallized in a variety of forms, its primitive figure being a rhomboidal prism, the angles of which are  $101^{\circ} 42'$  and  $78^{\circ} 18'$ . When applied to the purpose of obtaining the carbonate of baryta, it is to be finely powdered, mixed with three or four times its weight of carbonate of potassa, and boiled with a proper quantity of water for a considerable time, in an iron kettle, stirring it, and breaking down the hard lumps, into which it is apt to run, by an iron pestle. It is then to be washed with boiling water, as long as this acquires any taste. On the addition of dilute muriatic acid, a violent effervescence will ensue, and a considerable portion of the earth, probably along with some metals, will be dissolved. To the saturated solution, add solution of pure baryta in water, as long as it disturbs the transparency of the liquor. This will throw down any metals that may be present; and the excess of baryta may afterwards be precipitated in the state of a carbonate, by a stream of carbonic acid. Decompose the muriatic solution by any alkaline carbonate; let the precipitated earth be well washed with distilled water; and if the pure baryta is to be obtained from it, let it be treated as directed page 579.

Sulphate of baryta is also decomposed when strongly ignited with one sixth of its weight of powdered charcoal,

which abstracts the oxygen of the sulphuric acid, and leaves a combination of sulphur and baryta. From this, the baryta may be removed by muriatic acid, as already directed, and the muriatic solution be decomposed by carbonate of potassa.

The sulphate of baryta, when decomposed by charcoal, affords one variety of solar phosphorus. This phosphorus has been called, from the place where the sulphate is found from which it was first prepared, the *Bolognian phosphorus*. The native sulphate, powdered after being ignited, and finely sifted, is to be formed into a paste with mucilage of gum arabic, and divided into cylinders or pieces of one fourth of an inch in thickness. These, after being dried in a moderate heat, are to be exposed to the temperature of a wind furnace, placed in the midst of the charcoal. When the fuel is half consumed, it must be replenished, and suffered to burn out. The pieces will be found, retaining their original shapes, among the ashes, from which they may be separated by the blast of a pair of bellows. They must be preserved in a well-stopped phial.

This kind of phosphorus, after being exposed a few minutes to the sun's rays, shines in the dark sufficiently to render visible the dial of a watch. This property is lost by repeated use, in consequence of the oxygenation of the sulphur; but it may be restored by a second calcination.

*Seleniate of baryta*.—Selenic acid is capable of uniting with baryta in two proportions. The neutral salt, which is insoluble, consists of 100 acid + 197.7 base; the *bi-seleniate*, which crystallizes in round transparent grains, and is soluble in water, is composed of 100 acid + 68 base.

*Ferro-cyanate of baryta* may be formed by adding prussian blue to a heated solution of baryta in water, till it ceases to be discoloured. The filtered solution deposits yellowish crystals, which have the figure of rhomboidal prisms, and are soluble in 1920 parts of cold, or 100 parts of boiling water. They dissolve in nitric and muriatic acids. Mr. Porrett, who has analyzed them, states them to consist of

Acid . . . . .	34.31
Base . . . . .	49.10
Water . . . . .	16.59

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100.

Hence this salt must be constituted of 1 atom of acid = 54, + 1 atom of base = 78, + 2 atoms of water = 18, and its equivalent number will be 150.

SECTION VI.

*Of Strontium.*

STRONTIUM may be procured by exactly the same process as barium, substituting the native carbonate of strontia for that of baryta. It was first obtained by Sir H. Davy in 1808, but in very minute quantities. It resembles barium, has not a very high lustre, is difficultly fusible, and not volatile. It is converted into strontia by exposure to air, or by contact with water.

*Strontia.*

According to Stromeyer, 100 of strontium combine with 18.107 of oxygen, which numbers are in the proportion very nearly of 44 to 8.\* Dr. Thomson, from his experiments, deduces 65 for the weight of the atom of strontia, oxygen being 10, corresponding with 52 when hydrogen is taken as unity; and from this, deducting 8, we again obtain 44 for the atom of strontium.† With this result, that of Berzelius agrees so nearly, that it will probably be near the truth to consider strontia as represented by 52 and its base by 44. Hence strontia will consist of

Strontium .....	84.54	....	100
Oxygen .....	15.46	....	18.3
			100.

*Properties of Strontia.*

Strontia (so called from Strontian in Scotland, where it was first discovered in combination with carbonic acid) may be prepared either by subjecting the carbonate to a strong heat in

\* Ann. de Chim. et Phys. iii. 397.

†: Ann. of Phil. xv. 5.

a crucible, or by igniting the nitrate in a porcelain retort or other close vessel. A grey substance remains, which becomes very hot on the affusion of water; and when more water is added, and heat applied, a considerable proportion of the earth is dissolved. On cooling, the solution deposits regular crystals: but the shape of these differs considerably from that of barytic crystals. The crystals of strontia are thin quadrangular plates, sometimes square, oftener parallelograms; not exceeding in length, and not reaching in breadth, a quarter of an inch. Sometimes their edges are plain, but they oftener consist of two facets, meeting together, and forming an angle like the roof of a house. They adhere to each other in such a manner as to form a thin plate, of an inch or more in length, and half an inch in breadth. Sometimes they assume a cubic form.

These crystals undergo, by the action of heat, much the same changes as those of baryta; and leave only about 32 per cent. of the dry earth. One part of the crystals requires about  $51\frac{1}{2}$  of water at the temperature of  $60^{\circ}$  for solution, but boiling water takes up half its weight. Mr. Dalton supposes the crystals to consist of 1 atom of strontia and 12 atoms of water.

Boiling alcohol, with the addition of these crystals, burns with a blood red flame.

Strontia does not combine with alkalis. Baryta has no affinity for it; for no precipitation ensues, on mixing the watery solutions of the two earths.

From the preceding enumeration of its characters, it appears that strontia differs from baryta in the form of its crystals, which contain also more combined water, and are less soluble than those of baryta; and also in affording, with alcohol, a flame of different colour. These distinctions were deduced by Dr. Hope, from his excellent series of experiments on the two earths.\* Other circumstances of distinction, derived from the properties of their respective salts, will be stated hereafter.

*Chloride of Strontium* may be formed either by heating

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\* Ediub. Trans. vol. iv.

strontia in chlorine gas, which disengages oxygen; or by dissolving carbonate of strontia in muriatic acid, and evaporating to dryness. The product is a compound, according to Dr. Thomson, of 55 strontium to 45 chlorine, which are as nearly as possible in the proportion of 44 to 36, numbers agreeing with the weights of their respective atoms. When the chloride is converted into a muriate by the action of water, the resulting compound must, therefore, consist of 52 strontia + 37 acid. Hence we have the composition of these two salts as follows:

Chloride of strontium	{	Strontium . . . . .	55.04
		Chlorine . . . . .	44.96
			100.
Muriate of strontia.	{	Strontia . . . . .	53.4
		Acid. . . . .	41.6
			100.

*Muriate of strontia* crystallizes in long slender hexagonal prisms, which are soluble in two parts of water at 60°, and to almost any amount in boiling water. In a very moist atmosphere, they deliquesce. They dissolve in alcohol, and impart to it the property of burning with a blood-red flame.

*Chlorate of strontia* may be obtained by the direct action of chloric acid on carbonate of strontia. It is a deliquescent salt, having an astringent taste, and communicating to the flame of alcohol a fine purple tint.

*Hydriodate of strontia* is extremely soluble, and crystallizes in very slender prisms. Heated a little below redness in a close vessel, it is transformed into *iodide of strontium*.

*Iodate of strontia* is an insoluble compound, requiring some hundred parts of water for solution. At a red heat it is decomposed into oxygen, iodine, and strontia.

*Nitrate of strontia*. This salt may be obtained in the same manner as the nitrate of baryta. Its crystals are dissolved by their own weight of water at 60°, or by little more than half their weight of boiling water. When applied to the wick of a candle, or added to boiling alcohol, they communicate to the flame a deep blood-red colour. They are decomposed by

a high temperature, and afford pure strontia. Exclusive of water, the salt consists, according to Richter, of 51.4 acid + 48.6 base; or, according to Stromeyer, of 50.62 acid + 49.38 base. The proportions deducible from the weights of the atoms of its ingredients are 51 acid + 49 base.

*Carbonate of strontia.* The relation of strontia to carbonic acid resembles, very nearly, that of baryta; and all the experiments, directed to be made with the solution of the latter earth, may be repeated with that of strontia, which will exhibit similar appearances.

The carbonate of strontia requires for solution 1536 parts of boiling water. It is found native, but containing a little carbonate of lime, at Strontian in Argyleshire; and may, also, be prepared by artificial processes, which will be afterwards described. From this carbonate pure strontia may be obtained, by treating it in the same manner as was directed for the calcination of carbonate of baryta. (See p. 579.)

The artificial carbonate, according to Stromeyer,\* does not essentially contain any water. It consists of

Strontia .....	70.313	or	100
Carbonic acid.....	29.687	..	42.22
	100.		

These scarcely differ from its theoretical proportions, *viz.* 1 atom of strontia = 52.0 + 1 atom of carbonic acid = 22, together 74; or 70.09 + 29.91 = 100.

*Borate of strontia* is described by Dr. Hope as a white powder, soluble in about 130 parts of boiling water, and changing syrup of violets to green.

*Phosphite of strontia* has not been examined.

*Hypo-phosphite of strontia* is a very soluble salt, which is with difficulty made to crystallize.

*Phosphate of strontia* may be formed, by mixing solutions of muriate of strontia and phosphate of soda. It is tasteless, insoluble in water, but soluble in an excess of phosphoric acid; fusible by the blow-pipe into a white enamel; and de-

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\* Ann. de Chim. et Phys. iii. 396.



composable only by sulphuric acid. It consists, according to Stromeyer, of

Acid .....	36.565
Base .....	63.435
	<hr style="width: 100px; margin: 0 auto;"/>
	100.

If a true binary compound, it should consist of very nearly 65 base + 35 acid.

*Sulphuret of strontia* may be formed either by fusing in a green glass tube three parts of dry strontia with one of sulphur, or by strongly igniting the sulphate with one-seventh or one-eighth its weight of charcoal. By solution it is converted into hydro-sulphuret and hydrogureted sulphuret of strontia. These are separable from each other, if the solution be evaporated with the exclusion of air, for the hydro-sulphuret forms crystals which have a white silky lustre, while the hydrogureted sulphuret remains in solution.

*Sulphite of strontia* is not known.

*Hypo-sulphite of strontia.* Mr. Herschell formed this salt by passing a current of sulphurous acid through hydrogureted sulphuret of strontia. It has a bitter taste; dissolves in about 14 times its weight of water; is insoluble in alcohol; dissolves chloride of silver with great facility; and when heated *per se* becomes white, and then burns with a faint flame.

*Sulphate of strontia.* This salt resembles, very nearly, the sulphate of baryta. It may be formed in a similar manner, by pouring a solution of the pure earth into diluted sulphuric acid, or into the solution of an alkaline sulphate; for strontia has a stronger affinity than any of the alkalis for sulphuric acid. It is soluble in 3840 parts of boiling water.

The sulphate of strontia is also found native in considerable quantities; chiefly at Aust Passage, and at other places in the neighbourhood of Bristol. As the native carbonate is rather scarce, this compound may be advantageously employed for procuring artificial carbonate of strontia. The process is precisely similar to that already described for decomposing the sulphate of baryta. (Page 582.)

According to a considerable majority of the chemists who have analyzed it, sulphate of strontia consists of

Acid .....	42	.....	100
Strontia .....	58	.....	138
	—————		
	100		238

From these numbers its equivalent has been deduced by Dr. Wollaston. But Vauquelin has stated, that it is composed of 46 acid and 54 base, and Stromeyer of 43 acid and 57 base. The theoretical constitution of 1 atom of acid + 1 of base, would require it to consist of 43.60 acid + 56.40 base.

*Seleniate of strontia.* The *neutral seleniate* is white and insoluble; the *biseleniate* dissolves with difficulty even at a boiling temperature.

*Ferro-cyanate of strontia* is a salt which dissolves in less than four parts of cold water, but has not been made to crystallize. It is not deliquescent.

## SECTION VII.

### *Of Magnesium.*

The *base of magnesia*, for which Sir H. Davy has proposed the term *magnesium*, is very imperfectly known. In the attempts to distil its amalgams, the metal seemed to act upon the glass, even before the whole of the quicksilver was distilled from it. In one experiment, in which the process was stopped, before the mercury was entirely driven off, it appeared as a solid, having the same whiteness and lustre as the other metals of the earths. It sank rapidly in water, though surrounded by globules of gas, and produced magnesia. In the air, it quickly changed, falling into a white powder, which proved to be magnesia. This earth Berzelius states, in round numbers, to consist of 38 or 39 per cent. oxygen, and 61 or 62 magnesium. This would make the weight of its atom 15.5, and that of magnesia 23.5. Dr. Thomson's experiments (Ann. of Phil. N. S. vol. i. p. 5) give 20 for the equi-

valent of magnesia, from which if 8 be subtracted, there results 12 for the atom of magnesium. Perhaps it will be sufficiently near the truth to consider it as represented by that number.

*Magnesia.*

Magnesia possesses the properties of an alkali, but in a considerably less degree than any of the foregoing earths. Its characters are as follow :

When perfectly pure, it is entirely destitute of taste and smell. Its specific gravity is between 2 and 3.

No heat is excited by the affusion of water, and only a very small proportion is dissolved, not exceeding 1-5142d of its weight at 60°, or 1-36000th at 212°, according to Dr. Fyfe's experiments. Magnesia appears, however, to have an affinity for water; for when moistened, and afterwards dried, its weight is found increased in the proportion of 118 to 100. When precipitated also by pure potassa or soda from any of its salts, it falls down in union with water as a *hydrate*, which, when dried by a very gentle heat, forms transparent masses. In this state, according to Davy, it contains about  $\frac{1}{3}$  of its weight of water; but, according to Berzelius, 100 parts of magnesia combine with 142 to 144 of water. None of these proportions exactly agree with the atomic weights of water and magnesia; though the numbers of Berzelius approach very nearly to those of a compound of 3 atoms of water (27) with one of magnesia (20.) It is probable, indeed, that magnesia and water unite in several proportions. The native hydrate, analyzed by Dr. Fyfe, contained 69.75 base + 30.25 water.\* If these numbers be altered to 68.5 of the former + 31.5 of the latter, they will agree with the proportion of one atom of magnesia to one atom of water, constituting the *proto-hydrate*.

Magnesia reddens turmeric and changes to green the blue colour of the violet; but water which has been agitated with magnesia, when filtered through paper, does not produce similar effects. In these respects magnesia differs from lime, and approaches to those earths which are destitute of decidedly alkaline qualities.

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\* Ann. of Phil. N. S. i. 396.

Magnesia is not dissolved by liquid alkalis, nor by alkaline earths; and, in the dry way, it has no affinity for baryta or strontia.

Magnesia is by no means a rare production of nature, for though very seldom found in a state approaching to purity, yet it enters largely into some rocks that compose extensive formations, such as serpentine, magnesian lime-stone, steatite, &c.; and in combination with sulphuric and muriatic acids it forms a large proportion of the ingredients of sea water. Its principal use is in medicine, for hitherto it has not been extensively applied to any of the practical arts.

*Chloride of magnesium* may be formed by passing chlorine gas over pure magnesia. This compound is little known.

*Chloride of magnesia* may be prepared by passing chlorine gas into water, in which magnesia is kept mechanically suspended, or by the mixture of solutions of chloride of lime and sulphate of magnesia. It has not yet been accurately investigated. It is of use in some of the processes of bleaching.

*Chlorate of magnesia* is also little known.

*Muriate of magnesia* is a deliquescent and very soluble salt; of an intensely bitter taste; soluble in alcohol; and decomposed by a red heat which expels the muriatic acid. From the weight of its elements it ought to consist of

Magnesia . . . . .	20. . . . .	35.71 . . . .	100
Muriatic acid . . . . .	37. . . . .	64.29 . . . .	186
	—	—	
	57.	100.	

It constitutes about one eighth of the solid ingredients of sea water, in which as I showed (Phil. Trans. 1810), and as Dr. Marcet has also lately observed (Phil. Trans. 1822), it is free from any admixture of muriate of lime.

*A triple muriate of potassa and magnesia* was obtained by Dr. Marcet in rhombic crystals from the bittern of sea water; but the constitution of this salt was found to be so delicate, that it was liable to be separated into muriate of potassa and muriate of magnesia by water alone, and was with certainty decomposed by alcohol, which took up the magnesian muriate only. (Phil. Trans. 1822, p. 456.)

*Hydriodate of magnesia* is deliquescent, and abandons its acid when heated.

When *iodine* is heated along with magnesia and water, both hydriodate and iodate of magnesia are formed. By concentrating the solution, both salts are partly decomposed; and a flocculent iodide of magnesia is formed, resembling kermes in its appearance, which, when heated, loses part of its iodine, and is changed into a sub-iodide.

### *Nitrate of Magnesia.*

This compound may be prepared, by dissolving carbonate of magnesia in diluted nitric acid. The solution, when evaporated, yields crystals in the shape of prisms, with four oblique faces truncated at their summits. Most commonly, however, it forms a shapeless mass, consisting of an immense number of small needle-shaped crystals, crossing each other irregularly. These crystals deliquiate in the air, and are soluble in half their weight of water. When exposed to the heat of ignition, they fuse; a few bubbles of oxygen gas first escape; and the nitric acid then passes undecomposed. The salt contains, exclusive of water, according to Dalton, 69 acid + 31 base; but if constituted of an atom of each of its ingredients, it ought to be composed of 73.19 acid + 26.81 base.

*Ammonia-nitrate of magnesia* may be obtained by mixing the solutions of nitrate of ammonia and nitrate of magnesia, and evaporating the solution. The crystals are prisms, which are soluble in about 11 parts of water at 60°, and are less deliquescent than either of the component salts.

### *Carbonate of Magnesia.*

Pure magnesia does not attract carbonic acid with nearly the same intensity as lime. Hence magnesia may be exposed to the air, without any important change in its properties, or much increase of weight, unless the exposure be long continued, when it first becomes a hydrate by absorbing water, and then attracts carbonic acid from the atmosphere. The carbonate of magnesia, used in medicine, and for experimental purposes, is prepared by a process to be described in speaking

of the sulphate. In this state, however, it is not entirely saturated with carbonic acid. Its composition varies, as it has been precipitated with or without heat. If the former, it contains, according to Bucholz, 42 base, 35 acid, 23 per cent. water; if prepared from cold solutions of carbonate of soda and sulphate of magnesia, it consists of 33 base, 32 acid, and 35 water. Mr. Dalton states it to be composed of 43 base, 40 acid, and 17 water. Berzelius is of opinion that it is a compound of three atoms of carbonate of magnesia with one atom of the hydrate of the same earth;\* and if, as appears to me probable, this be the correct view of its composition, it will consist of

$$\begin{array}{r}
 3 \text{ atoms of carbonate } 42 \times 3 = 126 \dots\dots 72.77 \\
 1 \text{ atom of tri-hydrate } 20 + 27 = 47 \dots\dots 27.23 \\
 \hline
 173 \qquad \qquad \qquad 100.
 \end{array}$$

Or, of

Magnesia in the carbonate . . . .	34.34	}	45.82
Ditto in the hydrate . . . . .	11.48		
Carbonic acid . . . . .	38.42		
Water . . . . .	15.76		
			100.

The true carbonate of magnesia, consisting of 1 atom of acid + 1 atom of base, though it has not yet been formed artificially, is found as a natural product, and, being entirely without water, it may be called the *anhydrous carbonate of magnesia*. A specimen of this mineral from the East Indies, I have analyzed and described in the *Annals of Phil. N. S. i. 252*.

The saturated carbonate of magnesia (as it has generally been considered), may be obtained, by passing streams of carbonic acid gas through water, in which common magnesia is kept mechanically suspended, or by adding a very dilute solution of carbonate of soda, highly charged with carbonic acid under pressure, to a dilute solution of sulphate of magnesia. No immediate precipitation ensues, but, after a few days, congeries of crystals will be found adhering to the inner

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\* Thomson's *Annals*, xii. 30.

surface of the glass vessel. Some of these I analyzed several years ago, and showed them to consist of, base 29, acid 30, water 41. Berzelius, from the examination of a specimen probably purer than mine, deduced its proportions to be, base 29.583, acid 31.503, water 38.914.\* There can be little doubt that its true constitution is as follows, and that it is a carbonate and not, as has been supposed, a *bi-carbonate*, a salt which, in fact, has not yet been proved to exist, *viz.*

1 atom of magnesia . . . . .	20	....	28.60
1 atom carbonic acid . . . . .	22	....	32.
3 atoms water . . . . .	27	....	39.40
	69		100.

Water at 60° dissolves only 1-2493d of its weight, and, at the boiling temperature, 1-9000th part, of common carbonate of magnesia. (Edinb. Journ. v. 305.) The addition of almost any acid to the carbonate expels its carbonic acid, and a compound remains of magnesia with the new acid which has been added. The affinity of carbonic acid for magnesia appears, indeed, to be feeble, for it is expelled by a very moderate heat, much inferior to that required for the decomposition of carbonate of lime. The residue is pure magnesia, which, for medicinal and chemical uses, is always prepared by the calcination of the carbonate, and hence its name of *calcined magnesia*.

Carbonate of magnesia precipitates lime from lime water, a carbonate of the latter earth being formed in consequence of its greater affinity for carbonic acid.

*Carbonate of Magnesia and Potassa.*—Berzelius has described a salt with double base, which may be formed by mixing bi-carbonate of potassa in excess with muriate of magnesia.† No precipitate appears, but in a few days the salt arranges itself in crystalline groups on the sides of the vessel. It consists of

Potassa . . . . .	18.28
Magnesia . . . . .	15.99
Carbonic acid . . . . .	34.49
Water . . . . .	31.24
	100.

\* Edinb. Phil. Journ. i. 73.

† Ibid. ii. 67.

*Borate of magnesia* may be formed by dissolving magnesia in boracic acid. It precipitates in small irregular crystals, sparingly soluble in water, but soluble in acetic acid. A natural compound of boracic acid and magnesia, with a proportion of lime, is found near Luneburg in Germany, and known by the name of *boracite*.

*Phosphate of magnesia* may be formed either directly by dissolving carbonate of magnesia in phosphoric acid, or by mixing solutions of sulphate of magnesia and phosphate of soda. No immediate change ensues, but, after a few hours, large transparent crystals of phosphate of magnesia make their appearance in the solution. The crystals require 15 parts of cold water, but a smaller proportion of boiling water, for solution. They effloresce in the air, and, when heated, leave a dry powder which is fusible into a transparent glass.

*Ammonia-phosphate of magnesia* may be prepared by mixing solutions of phosphate of ammonia and phosphate of magnesia, or any other soluble salt with base of that earth. It falls down in the form of a white insoluble powder; but, in certain varieties of urinary calculi, it is found lining cavities of the concretions, in a distinctly crystallized form, and it is deposited in crystals on the sides of vessels in which urine is long kept. It is tasteless, scarcely soluble in water, readily soluble in dilute acids, and is decomposed by heat, leaving phosphate of magnesia only. According to Fourcroy, it contains equal weights of phosphate of ammonia, phosphate of magnesia, and water.

*Sulphuret of Magnesia*.—It does not appear that magnesia forms a permanent union with sulphur, for, when heated together, the latter sublimes.

*Hydro-sulphuret of Magnesia*.—This earth is soluble in water impregnated with sulphureted hydrogen, but the properties of the compound have not been investigated. The same may be said of the hydrogureted sulphuret.

*Sulphite of magnesia* may be prepared by saturating carbonate of magnesia with sulphurous acid; but the sulphite, which is first formed, is insoluble till an excess of acid is added, when it dissolves, and may be crystallized by slow evaporation. It is soluble in 20 parts of cold water, but hot water takes up a



larger portion, and deposits it again on cooling. The crystals effloresce in the air, and are slowly changed into sulphate.

*Hypo-sulphite of magnesia* may be obtained by boiling a solution of sulphite of magnesia with flowers of sulphur. The salt crystallizes when the solution has cooled. It is intensely bitter, and readily soluble in water, but is not deliquescent. When heated, it burns with a blue flame, and, by a sufficient continuance of the heat, the whole of the acid is expelled, and magnesia remains.

#### *Sulphate of Magnesia.*

When highly concentrated sulphuric acid is suddenly added to fresh prepared and pure magnesia, very great heat and vapour are excited, and are accompanied frequently with an extrication of light; an appearance first observed by Westrumb. But if the carbonate of magnesia be added to diluted sulphuric acid, the carbonic acid is expelled, and a solution of sulphate of magnesia is formed, which crystallizes on evaporation and cooling. Crystals of sulphate of magnesia may also be procured in the shops, under the name of Epsom salt.

These crystals have the following properties:

1. They have the form of small quadrangular prisms, surmounted by quadrangular pyramids with dihedral summits. They undergo no change by exposure to the atmosphere.

2. At the temperature of 60°, this salt is soluble in an equal weight of cold water, and in three-fourths its weight of boiling water, which thus receives an addition of one-fourth of its bulk.

3. When exposed to a low red-heat, it undergoes the watery fusion, but is not volatilized. It loses, however, rather more than one-half its weight, which is water of crystallization, and, according to Berzelius, a very minute portion of acid escapes.

The crystallized salt is composed\* of

Dry sulphate of magnesia . . . .	48.57	}	or	{	60
Water . . . . .	51.43				63
	100.00				123

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\* Gay Lussac, *Ann. de Ch. & Phys.* xiii. 308.

or of 1 atom of anhydrous salt, and 7 atoms of water. The dry salt is constituted of

1 atom of magnesia . . . . .	20	....	33.04	....	100
1 atom sulphuric acid . . . . .	40	....	66.96	....	202
			<hr/>		
	60		100.		

And the crystals contain,

Magnesia . . . . .	16.
Sulphuric acid . . . . .	32.57
Water . . . . .	51.43
	<hr/>
	100.

4. Its solution is precipitated by carbonates of potassa and of soda; but not by carbonate of ammonia, unless heat is applied. The carbonate of magnesia of the shops is prepared by mixing together concentrated and hot solutions of carbonate of potassa and sulphate of magnesia. The sulphate of potassa, thus formed, is removed by copious washing with water, and the carbonate of magnesia is then dried. The proportions employed are filtered solutions of 4 parts of the crystallized sulphate, and 3 of the carbonate of potassa. One hundred parts of the desiccated sulphate give about 71 of carbonate of magnesia, or about 33 of the pure earth.

When solution of pure ammonia is added to that of sulphate of magnesia, part of the earth is precipitated. The rest remains in solution, and, by evaporation, a triple salt is formed, consisting of sulphuric acid, magnesia, and ammonia, and called *ammoniaco-magnesian sulphate*.

A compound *Sulphate of Magnesia and Soda* has been described by Dr. Murray, in a note to his paper on the Analysis of Sea Water.\* It crystallizes in rhombs truncated on the angles and edges; is soluble in rather more than three times its weight of water at 60° Fahrenheit; is permanent in the air; and does not fuse, but decrepitates on applying heat. It is composed of

\* Edinb. Trans.

Sulphate of magnesia .....	32
Sulphate of soda .....	39
Water of crystallization .....	29

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 100

*Sulphate of potassa and magnesia* was composed by Link by saturating bi-sulphate of potassa with magnesia. The taste of this triple salt is bitter; in solubility it nearly agrees with sulphate of potassa; its crystals are rhomboidal, and consist of about 3 parts sulphate of potassa, and 4 sulphate of magnesia. It has been found by Dr. Marcet to be an ingredient of sea water. (Phil. Trans. 1822, p. 455.)

*Seleniate of Magnesia*.—Selenic acid unites with magnesia in two proportions, forming a seleniate and a bi-seleniate, but the compounds have no particularly interesting properties.

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## SECTION VIII.

### *Glucinum.*

WE have no experimental knowledge of the base of glucina. When obtained, its proper denomination will be *glucinum*. The general fact of its existence is proved by igniting glucina with potassium, which is thus changed into potassa.

### *Glucina.*

This earth was discovered by Vauquelin, in the year 1798. He obtained it from the aqua marina or beryl, a precious stone of a green colour, and very considerable hardness, which is found crystallized in Siberia. Glucina has since been detected in the emerald of Peru, and in the gadolinite. The following process may be employed to separate it from the beryl:

Let the stone, reduced to a fine powder, be fused with three times its weight of pure potassa. To the fused mass add a quantity of water, and afterwards diluted muriatic acid; which last will effect a complete solution. Evaporate the solution to dryness, re-dissolve the dry mass, and add carbo-

nate of potassa so long as any precipitation ensues. Dissolve the precipitate in sulphuric acid; add a little sulphate of potassa; and, on evaporation, crystals of alum will be obtained. By this process the alumina is detached. The residuary liquor, which yields no more crystals, contains the glucina, and a small portion of alumina. Add a solution of carbonate of ammonia to excess; this will throw down the alumina, and the glucina will remain dissolved by the superabundant carbonate. When this solution is evaporated to dryness, and moderately heated, the alkaline carbonate is expelled, and a carbonate of glucina remains, in the proportion of 16 parts from every 100 parts of the stone.

Glucina has the following properties:

1. It is a fine white and soft powder, resembling alumina in its sensible properties; and, like that earth, adhering to the tongue. Its specific gravity is 2.97.

2. It has no action on blue vegetable colours.

3. It does not harden, or contract, like alumina, by heat; and is infusible.

4. It is insoluble in water, but forms with it a ductile paste.

5. It is soluble in liquid potassa and soda, but not in the solution of pure ammonia. In these respects it agrees with alumina.

6. Glucina is soluble in carbonate of ammonia; a property distinguishing it from alumina.

7. It appears, like alumina, to have an affinity for colouring matter.

8. With the different acids it forms combinations, which have a sweet and rather astringent taste. Hence its name has been derived from *γλυκος*, signifying sweet.

9. It is not precipitated by triple prussiate of potassa.

## SECTION IX.

### *Yttrium.*

THE base of yttria has not yet been exhibited in a separate form; but the presence of oxygen in yttria is established by

its converting potassium into potassa, when ignited with that metal.

*Yttria, or Ittria.*

This earth was discovered in 1794, by Professor Gadolin, in a stone from Ytterby in Sweden; and its title to the character of a peculiar earth rests, also, on the unquestionable authority of Klaproth and Vauquelin, both of whom have made it the subject of experiment. The following process for obtaining it, is described by Vauquelin in the 36th volume of the *Annales de Chimie*, p. 150.

Fuse the pulverized stone (called Gadolinite) in the manner already described, with twice its weight of potassa; wash the mass with boiling distilled water, and filter. The filtered solution, which has a beautiful green colour, yields, during evaporation, a black precipitate of oxide of manganese. When this has ceased to appear, allow the liquor to stand; decant the clear part, and saturate with nitric acid. Let the insoluble part be, also, digested with extremely dilute nitric acid, which will take up the soluble earths only, and will leave, undissolved, the silica and oxide of iron. Let the two portions be mingled together, and evaporated to dryness; then re-dissolved and filtered; by which means any remains of silica and oxide of iron are separated. To obtain the yttria from the nitric solution, it would be sufficient, if no other earth were present, to precipitate it by carbonate of ammonia; but small portions of lime, and of oxide of manganese, are still present along with it. The first is separated by a few drops of carbonate of potassa; and the manganese, by the cautious addition of hydro-sulphuret of potassa. The yttria is then to be precipitated by pure ammonia, washed abundantly with water, and dried. It amounts to about 35 per cent. of the stone.

Yttria has the following properties:

1. It is perfectly white; but it is difficult to preserve it free from a slight tinge of colour, owing to its contamination with oxide of manganese.

2. It has neither taste nor smell; and it is smooth to the touch, like alumina.

3. It is insoluble in water, and infusible except by an intense heat.

4. It is very ponderous; its specific gravity being 4.842.

5. It is not attacked by pure alkalis; and, in this respect, it differs from glucina and alumina, both of which are abundantly soluble in fixed alkalis.

6. Like glucina, it is soluble in carbonate of ammonia, but five or six times less so than that earth; or, in other words, of equal quantities of glucina and yttria, the latter requires for solution five or six times more of the carbonate of ammonia than the former.

7. It is soluble in most acids; and is precipitated by pure alkalis, by baryta, and by lime.

8. From these solutions it is also precipitated by the oxalic acid, and by oxalate of ammonia, in a state resembling fresh precipitated muriate of silver. Prussiate of potassa throws it down in small white grains passing in a short time to pearl grey; phosphate of soda in a white gelatinous form; and infusion of galls in brown flocculi.

9. Yttria, which has been a long time exposed to the action of fire, gives out chlorine gas, when dissolved in common muriatic acid; thus manifesting one property of a metallic oxide.\*



## SECTION X.

### *Aluminum.*

THE experiments of Sir H. Davy afford a strong presumption that alumina is a metallic oxide; but its base, *aluminum*, has not been yet obtained in such a state as to make its properties an object of investigation. Yet alloys have been formed, which give sufficient evidence of its existence; and the presence of oxygen in alumina is proved, by its changing potassium into potassa, when ignited with that metal.

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\* Nicholson's Journal, xviii. 77.

*Alumina.*

*Alumina may be obtained* free from other earths, but still combined with carbonic acid, by precipitating a solution of alum in water by the bi-carbonate of potassa. To secure its complete purification from sulphuric acid, Guyton advises that the precipitate be re-dissolved in nitric acid, that nitrate of baryta be cautiously added to the solution, till it no longer occasions milkiness, and that the alumina be afterwards precipitated, or separated from the nitric acid by heat.\* Electro-chemical analysis, however, in this, as in many other instances, shows the imperfection of the common methods of separating bodies from each other; for the most carefully prepared alumina yields the metals of soda and potassa, when negatively electrified in contact with mercury.† Berzelius, also, found that when alumina is precipitated either from the sulphate or nitrate, it is contaminated with those acids; but not with the muriatic, when thrown down from the muriate of alumina by ammonia. Gay Lussac recommends the preparation of alumina by exposing that kind of alum which has ammonia for its base, first to a gentle heat to expel the water of crystallization, and afterwards to a red heat, which leaves the alumina pure.‡

Alumina has the following properties:

1. It is destitute of taste and smell.
2. When moistened with water, it forms a cohesive and ductile mass, susceptible of being kneaded into a regular form. It is not soluble in water; but retains a considerable quantity, and is, indeed, a hydrate, containing, when dried at the temperature of the atmosphere, almost half its weight of water. Even after ignition, alumina has such an affinity for moisture, that it can hardly be placed on the scale of a balance, without acquiring weight. Berzelius found that 100 parts, after being ignited, gained  $15\frac{1}{2}$  from a dry atmosphere, and 33 from a humid one. For full saturation, 100 grains of alumina, he ascertained, require  $5\frac{1}{2}$  of water.§
3. Alumina does not affect blue vegetable colours.

\* Ann. de Chim. xxxii. 64.

† Ann. de Chim. et Phys. v. 101.

‡ Davy, Phil. Trans. 1808.

§ 82 Ann. de Chim. 14.

4. It is dissolved by the liquid fixed alkalis, and is precipitated by acids unchanged. In ammonia, it is very sparingly soluble. It is not soluble in alkaline carbonates.

5. Baryta and strontia combine with alumina, both by fusion and in the humid way. In the first case, the result is a greenish or bluish coloured mass. In the second two compounds are formed. The first, containing an excess of alumina, is in the state of an insoluble powder; the other, having an excess of the alkaline earth, remains in solution. Alumina may be united, by fusion, with the fixed alkalis, and with most of the earths.

6. Alumina, as will be afterwards shown, has a strong affinity for colouring matter.

7. Alumina has the property of shrinking considerably in bulk, when exposed to heat, and its contraction is in proportion to the intensity of the heat applied. On this property is founded the *pyrometer of Wedgwood*, which measures high degrees of heat, by the amount of the contraction of regularly shaped pieces of china clay. The pieces of clay are small cylinders, half an inch in diameter, flattened on the under surface, and baked in a low red heat. The contraction of these pieces is measured, by putting them between two fixed rulers of brass or porcelain, twenty-four inches long, half an inch distant from each other at one end, and three tenths of an inch at the other. The rulers are divided into 240 equal parts, called degrees, which commence at the wider end; and each of which is equal to  $130^{\circ}$  of Fahrenheit. When the clay piece is fixed in its place, before exposure to heat, it is stationary at the first degree, which indicates about  $1077^{\circ}$  of Fahrenheit. After being strongly heated, in a small case which defends it from the fuel, its bulk is diminished, and it slides down, between the converging rulers, till stopped by their approach. The number on the graduated scale, opposite to the upper end of the piece, indicates the degree of heat to which it has been exposed. In the Appendix, rules may be found for reducing the degrees of Wedgwood's pyrometer to those of Fahrenheit's thermometer. It is proper, however, to remark that this instrument is a much less accurate measurer of heat than was long supposed; since the contraction



of clay is influenced not merely by the degree of heat to which it is exposed, but by the mode of its application.

*Equivalent of Alumina.*

From indirect experiments, Sir H. Davy several years ago derived 24 as the number representing alumina, from which, deducting one atom of oxygen = 8, we obtain 16 for the equivalent of aluminum. The number for the equivalent of alumina, deduced by Gay Lussac,\* is 21.611, oxygen being 10, = 17.28, when hydrogen is taken as the decimal unit. Dr. Thomson,† from recent experiments, concludes it to be 2.25, oxygen being 1, = 18 when hydrogen is made unity. The former determination would reduce the atom of aluminum to 9.28, and Dr. Thomson's to 10, the atom of oxygen being considered as 8. Mr. R. Phillips is of opinion‡ that the atom of alumina is correctly expressed by 27, and Mr. Brande (*Quarterly Journ.* xiv. 50) fixes it at 26. Differences so considerable as these sufficiently show that we are not prepared to assign the true weight of the atom of alumina, but that the subject is still open to further investigation.

Alumina forms a very large proportion of the rocks and strata that compose this globe. It is the chief ingredient of all the varieties of clay, and gives them the property of tenacity and ductility, or of being capable of being moulded into the shapes of vessels which are rendered hard and durable by the subsequent application of heat. Bricks, tiles, and all the varieties of pottery and porcelain, are chiefly formed of alumina, with variable proportions of silica and other earths. It imparts to soils, when present in due proportion, the quality of being sufficiently retentive of moisture; for a soil may be too open and light to be fertile, as well as too stiff from the excess of its aluminous ingredient. It is remarkable, also, that alumina, nearly pure, composes some of the hardest minerals, such as the corundum, which is hard enough to be employed in polishing diamonds.

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\* *Ann. de Ch. et Ph.* xvi. 36.

† *Ann. of Phil.* N. S. iii. 168.

‡ *Ibid.*, iv. 283.

*Salts of Alumina.*

*Alumina with Chlorine.*—No substance (Sir H. Davy observes) exists, that can be considered as a true compound of alumina and chlorine.

*Muriate of Alumina* may be formed by dissolving fresh precipitated alumina in muriatic acid, but the acid is always in excess. It is scarcely possible to obtain this salt in crystals, for by evaporation it becomes a thick jelly. It is extremely soluble in water, and when dried deliquesces. At a high temperature it abandons its acid.

*Nitrate of Alumina* may be formed in the same manner as the last-mentioned compound. The solution, which is always acid, crystallizes in thin ductile plates. The crystals are extremely soluble, and are deliquescent. At a high temperature they are decomposed. Potassa throws down alumina from the solution, but, if added in excess, re-dissolves the precipitate.

*Alum.—Sulphate of Alumina.*

Alum and sulphate of alumina are often confounded together under the same name; but alum, as will afterwards appear, is not merely a combination of this earth with sulphuric acid; but is a triple salt, composed either of sulphuric acid, alumina, and potassa; or of sulphuric acid, alumina, and ammonia. It has the following characters:

(a) It has a sweetish astringent taste. Its specific gravity is 1.71.

(b) It dissolves in water, five parts of which, at 60°, take up one of the salt, but hot water dissolves about three-fourths of its weight.

(c) This solution reddens vegetable blue colours; which proves the acid to be in excess.

(d) When mixed with a solution of carbonate of potassa, an effervescence is produced by the uncombined acid, which also prevents the first portions of alkali, that are added to a solution of sulphate of alumina, from occasioning any precipitate.

(e) On a farther addition of alkali, the alumina is precipitated.

(f) Alum, when heated, swells up, loses its regular form, and becomes a dry spongy mass, called burnt alum; but, according to Vauquelin, the whole of its acid cannot be expelled by heat.

Considerable differences exist in the statements which have been given by different analysts, of the composition of alum, as will appear from the following table:

100 parts contain.	Acid.	Alumina.	Potassa.	Water.
According to Vauquelin . . . . .	30.52	10.50	10.40	48.58
————— Dalton . . . . .	33.	12.	9.	46.
————— R. Phillips . . . . .	34.94	11.18	10.33	43.55
————— Berzelius . . . . .	34.23	10.86	9.81	46.
Do. corrected by Thomson	33.82	10.86	9.90	45.
————— Dr. Thomson . . . . .	32.85	11.99	9.85	46.21

Some of these differences may be accounted for by the circumstance, that in estimating the sulphuric acid, the composition of sulphate of baryta has been differently calculated. When welledulcorated, dried, and ignited, the barytic sulphate should be assumed to contain, in every 100 grains, 34 grains of real sulphuric acid.

Different views also have been taken of the state of combination in which the potassa and sulphuric acid exist in alum. Mr. R. Phillips considers the constitution of alum to be as follows, a slight alteration of his experimental results being made to accommodate them to atomic proportions.

- 1 atom of bi-sulphate of potassa,
- 2 atoms of sulphate of alumina,
- 22 atoms of water.

Dr. Thomson, however, does not admit that bi-sulphate of potassa exists in alum, and contends that it is constituted of

- 1 atom of sulphate of potassa,
- 3 atoms of sulphate of alumina,
- 25 atoms of water.\*

If the number representing alumina were ascertained, it would be easy to determine which of these two views is most

\* Ann. of Phil. N.S. iii. 168.

consistent with the atomic doctrine; but till this has been done, the subject must remain involved in some obscurity.

*Ammoniacal alum* has been examined by Riffault,\* who found it to consist of

1 atom of sulphate of ammonia,  
3 atoms of sulphate of alumina,  
24 atoms of water.

In this species of alum M. Riffault concludes that 11.906 of alumina are united with 26.979 of sulphuric acid, the remaining 9.063 of the acid being combined with 3.898 of ammonia.

In the Quarterly Journal (viii. 386) an alum containing soda as its alkaline base, is described. It appears to be constituted of 51.2 water, 32.14 sulphuric acid, 10 alumina, and 6.32 soda, or of

2 atoms of sulphate of alumina,  
1 atom of bi-sulphate of soda,  
28 atoms of water.

In vol. xiii. p. 276 of the same Journal, Dr. Ure assigns nearly the same proportions to a soda alum examined by him.

*Magnesia*, also, it appears, is capable of furnishing a base to alum; but, like the last species, it has not yet been applied to any useful purpose.

A neutral sulphate of alumina was obtained by Berzelius, by the following process. He decomposed alum by ammonia; washed the precipitate, and redissolved it in sulphuric acid. To the liquor, after evaporation, he added alcohol, which threw down a sulphate nearly neutral, and rendered perfectly so, by being washed with farther portions of alcohol. Gay Lussac has also given the following process, communicated to him by Descotils, for preparing a neutral sulphate of alumina. On alum with base of ammonia, boil nitro-muriatic acid, till all the ammonia is destroyed, and evaporate to dryness to expel all the nitric and muriatic acids. The ammonia is decomposed by the chlorine, which results from the mutual action of those two acids, and the alumina remains in

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\* Ann. de Chim. et Phys. ix. 106.

combination with sulphuric acid only. The saturated solution of this salt in water is an excellent test to discover potassa; for a drop or two, added to a solution of that alkali, or of any of its salts, immediately causes a precipitation of alum.\* It is most probably constituted of 1 atom of acid + 1 atom of base.

The sub-sulphate of alumina and potassa has been analyzed by M. Riffault (Ann. de Ch. et Phys. xvi. 355), and found to consist of

Sulphuric acid .....	35.495
Alumina .....	39.654
Potassa .....	10.021
Water .....	14.830
	100.

This corresponds very nearly with 3 atoms of acid, 8 of alumina, 1 of potassa, and 4 of water. A native sub-sulphate of alumina has also been examined by Stromeyer, and ascertained to be composed of 30 alumina, 24 sulphuric acid, and 45 water.

(h) Alum is decomposed by charcoal, which combines with the oxygen of the sulphuric acid, and leaves the sulphur attached to the alumina. A combination of alumina, sulphur, and charcoal, forms the *pyrophorus of Homberg*. To prepare this, equal parts of powdered alum and brown sugar are melted over the fire, and are kept stirring till reduced to dryness. The mixture, when cold, is to be finely powdered, and introduced into a common phial, coated with clay, to which a glass tube, open at each end, is to be luted, to allow the escape of the gases that are produced. The phial must then be set in the fire, surrounded by sand, in a crucible. Gas will issue from the open end of the tube, and may be inflamed by a lighted paper. When this ceases to escape, the crucible may be removed from the fire, and a little moist clay pressed down upon the open end of the tube, to prevent the access of air to the contents of the phial. When cold, the tube may be removed, and a cork substituted in its place. The principal difficulty in the process is to stop it precisely at the period,

\* Ann. de Chim. et Phys. vi. 201.

when the pyrophorus is formed ; for if the heat be continued longer, the preparation will be spoiled.

The pyrophorus thus formed is a black and light powder, which instantly takes fire when poured out of the bottle into the air, and inflames suddenly in oxygen gas. Sulphate of potassa appears to be essential to its production, and hence the sulphuret of potassa is a necessary ingredient. From the discoveries of Sir H. Davy, it appears not improbable that this pyrophorus may contain sulphuret of potassium. The principal part of the phenomena, however, is owing to the combustion of an extremely light and finely divided charcoal.

The remaining salts of alumina have no properties sufficiently important to entitle them to a separate description.



## SECTION XI.

### *Thorinum.*

NOTHING is known of the metallic base of this earth, and it is only from analogy that it is supposed to be constituted of such a base united with oxygen.

### *Thorina.*

I. While analyzing some minerals from the neighbourhood of Fahlun in Sweden, Professor Berzelius found in them a new earth, which he had also extracted, in the summer of 1815, from a species of gadolinite. In these it was combined with the fluete of cerium and yttria. The pulverized mineral was first treated with concentrated sulphuric acid, which decomposed the greater part of it, and expelled the fluoric acid. From this solution, sulphate of potassa precipitated the oxide of cerium, and caustic ammonia afterwards occasioned a farther precipitate. This, dissolved by long digestion in muriatic acid, consisted of the muriates of yttria and of the new earth. It was evaporated to dryness, in order to expel the excess of acid, and water poured over it to dissolve the muriate of yttria. The residue was subjected to the action of muriatic acid, and the solution accurately saturated by caustic

ammonia. On adding water, and applying a boiling heat, a white gelatinous precipitate fell, which was collected on a filter. The liquor, that passed through the filter, was again saturated with pure ammonia, and heated to ebullition, which occasioned a fresh precipitation of the same earth. This, when washed, and gently dried, is the substance in question.

II. 1. This earth, when dried, is perfectly white; it absorbs carbonic acid, and dissolves with effervescence in acids. After calcination, its white colour remains unimpaired; but if the heat has been strong, it is rendered less easily soluble in acids. The neutral solutions of it have a purely astringent taste, which is neither sweet, nor saline, nor bitter, nor metallic, a property in which it differs from all the earths except zirconia.

2. When dissolved in a slight excess of sulphuric acid, and subjected to evaporation, it yields transparent crystals, which are not altered by exposure to the air, and have a sweet astringent taste.

3. It dissolves readily in nitric and muriatic acids, but does not afford crystallizable salts. When precipitated by pure alkalis, it absorbs carbonic acid from the air with avidity; and the alkaline carbonates throw it down, in combination with the whole of their carbonic acid. It is precipitated by the oxalate, tartrate, and benzoate of ammonia. Succinate of ammonia occasions a precipitate, which is immediately redissolved; and ferro-prussiate of potassa throws down a white precipitate, which is soluble in muriatic acid.

4. It is not soluble, even when fresh precipitated and at a boiling temperature, by the pure alkalis. The alkaline carbonates dissolve it, but much more sparingly than any other earth on which they are capable of acting.

5. It is not reducible, when strongly heated in contact with charcoal. Before the blow-pipe it cannot be brought into fusion. With borax or phosphate of soda, it fuses into a transparent glass, but is infusible with soda.

Messrs. Gahn and Berzelius having been accustomed to speak of this earth under the name of Thorina (from Thor, a Scandinavian Deity), we may distinguish it by this name, till a more appropriate one shall be pointed out.

Thorina differs from the other earths in the following properties: From *alumina* and *glucina*, by its insolubility in liquid potash; from *yttria*, by its solutions being purely astringent to the taste, without any sweetness, and by the property of being precipitated at a boiling heat, except when prevented by too great an excess of acid. It differs from *zirconia* in the following respects: 1st, Because, after being ignited, it is still soluble in acids. 2d, It is not precipitated by sulphate of potassa, which throws down zirconia, even from solutions containing a considerable excess of acid. 3d, Thorina is precipitated by oxalate of ammonia, which is not the case with zirconia. 4th, Its combination with sulphuric acid crystallizes readily, while sulphate of zirconia forms, when pure and dried, a gelatinous transparent mass, without any trace of crystallization.



## SECTION XII.

### *Zirconium.*

THE base of zirconia, or *zirconium*, is still unknown, though investigated by Sir H. Davy in the same manner as the bases of other earths. When potassium was brought into contact with ignited zirconia, potassa was formed, and dark metallic particles were diffused through the alkali.

### *Zirconia.*

I. This earth was discovered by Klaproth in the year 1789, in a precious stone from the island of Ceylon, called Jargon or Zircon, and has since been detected in the hyacinth.

MM. Dubois and Silveira have described the method of obtaining zirconia from zircons as follows: powder the zircons very fine, mix them with two parts of pure potassa; and heat them red hot in a silver crucible for an hour. Treat the substance obtained with distilled water, pour it on a filter, and wash the insoluble part well; it will be a compound of zirconia, silica, potassa, and oxide of iron. Dissolve it in muriatic acid, and evaporate to dryness, to separate the silica. Redissolve the muriates of zirconia and iron in water; and to



separate the zirconia which adheres to the silex, wash it with weak muriatic acid, and add it to the solution. Filter the fluid, and precipitate the zirconia and iron by pure ammonia; wash the precipitates well, and then treat the hydrates with oxalic acid, boiling them well together, that the acid may act on the iron, retaining it in solution while an insoluble oxalate of zirconia is formed. It is then to be filtered, and the oxalate washed, until no iron can be detected in the water which passes through. The earthy oxalate is, when dry, of an opaline colour; after being well washed, it is to be decomposed by heat in a platinum crucible.

When thus obtained, zirconia is perfectly pure, but is not soluble by acids. To render it so, it must be re-acted on by potassa as before, and then washed until the alkali is removed. Afterwards dissolve it in muriatic acid, and precipitate by ammonia. The hydrate thrown down, when well washed, is perfectly pure and easily soluble in acids. (Ann. of Phil. New Series, i. 74.)

II. Zirconia has the following properties:

1. It has the form of a fine white powder, which, when rubbed between the fingers, has somewhat of the harsh feel of silica. It is entirely destitute of taste and smell. Its specific gravity exceeds 4.

2. It is insoluble in water; yet it appears to have some affinity for that fluid, for it retains, when slowly dried after precipitation, one third its weight, and assumes a yellow colour and slight transparency, like that of gum arabic.

3. It is insoluble in pure liquid alkalis; nor does it even combine with them by fusion; but it is soluble in alkaline carbonates.

4. Exposed to a strong heat, zirconia fuses, assumes a light grey colour; and such hardness, on cooling, as to strike fire with steel, and to scratch glass, or even rock crystal.

5. Its action on other earths has not been fully investigated.

6. It dissolves readily in acids. Its solution in muriatic acid, when sufficiently heated, becomes milk white, and runs in some measure into a jelly, especially if concentrated to a certain point by evaporation.

7. From the muriatic solution of zirconia, oxalic acid throws down a white precipitate, which is re-dissolved by an excess of the acid.

8. It is precipitated from its acid solutions, by the neutral succinates and benzoates, in copious white bulky flocks, which are again readily dissolved by an excess of succinic acid. It is also thrown down from its solutions by tartaric acid, malic acid, and tartrate of potassa.

9. From a sufficiently neutral solution of zirconia, ferrocyanate of potassa throws down a greenish blue precipitate, which, on adding muriatic acid, becomes more blue, but after some time changes into celadon green.

10. Hydrosulphuret of ammonia produces, in the muriatic solution of zirconia, a dark olive or blackish green precipitate in very loose flocks. This precipitate may be washed with water without changing colour; but, when exposed to sunshine, it becomes white.

Professor Pfaff has remarked that in most of their properties there is a striking resemblance between zirconia and oxide of titanium. The only re-agent, which acts in a strikingly different manner upon solutions of oxide of titanium and zirconia, is tincture of galls, which, from the common solution of oxide of titanium, throws down a reddish brown precipitate, whereas from solution of zirconia it occasions a deposition of yellow flocks. (Ann. of Phil. xiii. 83.)

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### SECTION XIII.

#### *Silicium.*

IN his attempts to obtain the base of silica, or *silicium*, in a state of perfect separation, Sir H. Davy was unsuccessful; but the results of his experiments leave little room to doubt that this earth is, like the rest, compounded of oxygen with a peculiar base.

Berzelius has since decomposed silica, by fusing it with charcoal and iron in a blast furnace. He obtained an alloy

of iron and *silicium*, which, by the action of a diluted acid, gave more hydrogen than the same weight of iron.\* This process was successfully repeated by Stromeyer, and the properties of the different alloys investigated. He recommends the fusion of 7 parts of iron, 5 of silica, and from  $\frac{1}{4}$  to  $\frac{1}{10}$ ths of a part of soot. From the results of acting on the alloy by dilute acids, Berzelius infers silica to consist of

Silicium . . . . .	45.92 . . . . .	100
Oxygen . . . . .	54.08 . . . . .	117.38
	100.	217.38

And Sir H. Davy deduces the proportions to be 31 of metal to 30 oxygen. These numbers, however, can be considered in no other light than as approximations. The base of silica Sir H. Davy believes not to be a metal, but a substance most resembling *boron*; and, like it, bearing an analogy to charcoal, sulphur, and phosphorus. In the present imperfect state of our knowledge of *silicium*, it would be premature to assign the weight of its atom. If silica be a protoxide, its equivalent will be 16, and that of *silicium*, or *silieon*, as it is called by Dr. Thomson, will be represented by 8; but these numbers must be considered as open to correction.

### *Silica.*

I. Siliceous earth, or silica, may be obtained tolerably pure from flints by the following process:—Procure some common gun-flints, and calcine them in a crucible in a low red heat. By this treatment they will become brittle, and easily reducible to powder. Mix them, when pulverized, with three or four times their weight of carbonate of potassa, and let the mixture be fused in a strong red heat, in a crucible. The materials must bear only a small proportion to the capacity of the crucible; and the heat must at first be very moderate, and slowly increased. Even with this precaution, the mass, on entering into fusion, will be apt to overflow; and must be

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\* 81 Ann. Ch. 179. See also his account of an attempt to analyze silica, in 40 Phil. Mag. 201.

pressed down as it rises by an iron rod. When this effervescence has ceased, let the heat be considerably raised, so that the materials may be in perfect fusion during half an hour, and pour the melted mass on a copper or iron dish. We shall thus obtain a compound of alkali and siliceous earth. Dissolve this in water, filter the solution, and pour it into diluted sulphuric or muriatic acid. An immediate precipitation will ensue, and, as long as this continues, add fresh portions of the solution. In precipitating the alkaline solution of silica, more acid must be used than is sufficient to engage the alkali; and the alkaline liquor must be added to the acid, and not the reverse; for, in the latter case, the precipitate will be glass, and not silica. Let the precipitate subside, pour off the liquor that floats above it, and wash the sediment with hot water, till it comes off tasteless. Then dry it.

Silica, obtained by this process, though pure enough for the following experiments, may still contain a portion of alumina. To separate the latter earth, boil the precipitate with diluted sulphuric acid, to which a little sulphate of potassa may be added. The alumina will thus be dissolved; and, the silica may be freed from the solution of alum by repeated washings with water. Even silica, however, that has been most carefully washed, still gives traces of potassa on the application of electro-chemical powers. (Davy.) According to Mr. Brande, silica may be obtained of sufficient purity for most purposes by heating rock-crystal to redness, quenching it in water, and then reducing it to fine powder.

II. Siliceous earth, as thus obtained, has the following qualities:

(a) It is perfectly white and tasteless. It is infusible by the intense heat of Voltaic electricity;\* but was melted by Dr. Clarke with the oxygen and hydrogen blow-pipe. To a certain degree it appears to be volatile, for a filamentous substance, collected from iron furnaces, and resembling amianthus, was found by Vauquelin to be pure silica.

(b) When mixed with water, it does not form a cohesive mass like alumina, but has a dry and harsh feel to the fingers.

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\* Phil. Trans. 1815, p. 370.

It retains, when fresh precipitated, about 26 per cent. of water, after being dried at 70° Fahrenheit. But, according to Berzelius, this water is not chemically combined.

(c) It is insoluble in water. Yet when fresh precipitated, water has the property of retaining in solution about one thousandth of its weight.\* That silica, however, is dissolved in water by processes of nature, can scarcely be doubted, when it is considered, that it is found, in considerable quantities, in a crystallized form.

(d) It is not acted on by any acid, except the fluoric. Sulphuric acid, according to Dalton, after expelling the fluoric acid from fluate of lime, does not unite with the silica. But though the earth itself is not dissolved by acids, yet when first combined with an alkali, it unites with several acids, forming triple salts.† When fresh precipitated, however, Dr. Marcet asserts, that it is sparingly soluble in most acids; and, for this reason, he recommends, in analysis, to precipitate silica by muriate of ammonia, which does not, like the acids, re-dissolve it.

(e) When prepared in the foregoing manner, and very minutely divided, silica is taken up by a solution of pure potassa, or of soda, but not by ammonia. In the aggregated state of flints, however, it is perfectly insoluble in this way by alkaline solutions; an excellent illustration of the principle that a very minute division of solid bodies, by presenting a greater surface to the action of fluids, facilitates solution. .

(f) When mixed with an equal weight of carbonate of potassa, and exposed to a strong heat in a furnace, it forms a glass, insoluble in water, and identical in all its properties with the glass commonly manufactured. It is owing to the siliceous earth which it contains, that glass is decomposed by the fluoric acid. Glass, however, has occasionally other ingredients, besides the two that have been mentioned, the object of which admixtures is to adapt it to particular purposes. *Flint glass* is formed of fine siliceous sand, pearlash, litharge, or minium, a little nitre, and a small quantity of manganese;

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\* See Klaproth's Contributions, i. 399, 400. † 81. Ann. de Chim. 239.

*crowns glass for windows*, of soda, fine siliceous sand, lime, and fragments of glass; *green bottle glass*, of sand, kelp, pearlash, clay, and fragments of glass; and *plate glass*, of fine sand, soda, lime, manganese, oxide of cobalt, and fragments of glass. *Pastes, or artificial gems*, are only another variety of glass, into the composition of which borax generally enters, the colour being given by various metallic oxides.\*

(g) With a larger proportion of alkali, as three or four parts to one of silica, this earth affords a compound, called, by Dr. Black, *silicated alkali*. This compound, formed by the process which has been just described, is soluble in water, and affords a good example of the total change of the properties of bodies by chemical union; for, in a separate state, no substance whatever is more difficult of solution than silica. The solution of silicated alkali was formerly termed *liquor silicum*, or *liquor of flints*. Acids seize the alkali, and precipitate the silica, which is even separated by mere exposure to the atmosphere, in consequence of the absorption of carbonic acid by the alkali.

(h) Baryta or strontia, and silica, combine together, in a manner similar to the union of this earth with alkalis; but the combination has not been applied to any useful purpose.

(i) When a solution of silica in potassa is mingled with one of baryta, of strontia, or of lime in water, or of alumina in alkali, a precipitation ensues. Hence silica may be inferred to have an affinity for all these earths, in the humid way. The composition of these precipitates is stated by Mr. Dalton in his System, p. 541.

In consequence of its possessing a stronger affinity for alkalis and earths than for acids, as well as from its other habitudes, silica has been thought to present a closer analogy with acids than with earths, and in a chemical arrangement to be more properly placed in the former class than in the latter. On the other hand, as it is deficient in some of the characters which have hitherto been deemed essential to acid-

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\* See Guyton, Ann. de Chim. vol. lxxiii. and Aikin's Dictionary of Chemistry, art. Glass, for an excellent account of the several varieties of glass.

ity, I have not thought it expedient to remove it from the place which it has hitherto held in chemical arrangements.

Silica is a very abundant product of nature. It constitutes a principal ingredient of several rocks that form extensive mountain masses, such as granite; it composes a large proportion of the sand found in the beds of rivers, and on the sea shore; and it enters largely into several minerals of rarer occurrence, as rock-crystal, quartz, flint, chalcedony, carnelian, opal, &c. It constitutes an essential ingredient of fertile soils, and renders them porous and open to the transmission of moisture. In the arts, its most important application is to the manufacture of glass, and a certain proportion is of use in the composition of porcelain; for absolutely pure clay, without an admixture of siliceous earth, would shrink too much to be fit for the uses of the potter.

#### *Silicated Fluoric Acid.*

Silicated fluoric acid gas may be prepared by pouring on finely powdered fluor spar, mixed with half its weight of pulverized glass, an equal weight of strong sulphuric acid. It may be received over mercury in glass vessels, the transparency of which it does not impair.

1. The specific gravity of this gas is very high, 100 cubic inches of it weighing 110.78 grains. By causing a known volume of it to be absorbed by liquid ammonia, Dr. John Davy separated the silica, which he found to weigh 61.4 per cent. of the weight of the gas. When absorbed by water, much of the silica is deposited, and it retains only 54.5 per cent. of that earth in combination. To this liquid, Dr. Davy gave the name of *sub-silicated fluoric acid*.

2. Water absorbs about 263 volumes of the gas, and the solution may be kept in glass vessels without corroding them.

3. It condenses twice its volume, and no other proportion, of ammoniacal gas, forming a dry white salt, which is slightly acid, deposits silica by solution in water, and, when its concentrated solution is boiled in glass vessels, powerfully corrodes them. By adding an excess of liquid ammonia, the whole of

the silica is precipitated, and a pure fluato of ammonia is obtained.

4. The effects of heating potassium in silici-fluoric gas have already been described in the chapter on Fluorine.



# APPENDIX.

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## DESCRIPTION OF THE COPPER PLATES.

[To facilitate the reference to the Plates, they are placed at the end of the Second Volume.]

### PLATE I,

FIG. 1. (a) *A plain retort*, the neck of which is shown introduced a proper length into the mouth of a *plain receiver* b. These may be made of any size, from the capacity of a few drachms to that of several gallons, and either of white or green glass. The latter material has the advantage, when solids are distilled, of being much less fusible than flint glass.

FIG. 2. *A glass alembic*; a the body, and b the head, which are ground so as to fit accurately, and may be separated when necessary. The head b is so shaped, that any liquid, which may be condensed, collects into a channel, and is carried by the pipe c into the receiver.

FIG. 3. *A separator*, for separating liquids of different specific gravities. It is furnished with a ground stopper at a, and a glass stop-cock at b. The vessel is filled with the liquids that are to be separated (oil and water for example), which are allowed to stand till the lighter has completely risen to the top. The stopper a is then removed, and the cock b opened, through which the heavier liquid descends; the cock being shut, as soon as the lighter one is about to flow out.

FIG. 4. A glass vessel, termed a *mattress*, useful for effecting the solution of bodies, which require heat before they can be dissolved, or long continued digestion. The upper extremity of the long neck generally remains cool, and allows the vessel and its contents to be shaken occasionally.

consistent with the atomic doctrine; but till this has been done, the subject must remain involved in some obscurity.

*Ammoniacal alum* has been examined by Riffault,\* who found it to consist of

1 atom of sulphate of ammonia,  
3 atoms of sulphate of alumina,  
24 atoms of water.

In this species of alum M. Riffault concludes that 11.906 of alumina are united with 26.979 of sulphuric acid, the remaining 9.063 of the acid being combined with 3.898 of ammonia.

In the Quarterly Journal (viii. 386) an alum containing soda as its alkaline base, is described. It appears to be constituted of 51.2 water, 32.14 sulphuric acid, 10 alumina, and 6.32 soda, or of

2 atoms of sulphate of alumina,  
1 atom of bi-sulphate of soda,  
28 atoms of water.

In vol. xiii. p. 276 of the same Journal, Dr. Ure assigns nearly the same proportions to a soda alum examined by him.

*Magnesia*, also, it appears, is capable of furnishing a base to alum; but, like the last species, it has not yet been applied to any useful purpose.

A neutral sulphate of alumina was obtained by Berzelius, by the following process. He decomposed alum by ammonia; washed the precipitate, and redissolved it in sulphuric acid. To the liquor, after evaporation, he added alcohol, which threw down a sulphate nearly neutral, and rendered perfectly so, by being washed with farther portions of alcohol. Gay Lussac has also given the following process, communicated to him by Descotils, for preparing a neutral sulphate of alumina. On alum with base of ammonia, boil nitro-muriatic acid, till all the ammonia is destroyed, and evaporate to dryness to expel all the nitric and muriatic acids. The ammonia is decomposed by the chlorine, which results from the mutual action of those two acids, and the alumina remains in

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\* Ann. de Chim. et Phys. ix. 106.

combination with sulphuric acid only. The saturated solution of this salt in water is an excellent test to discover potassa; for a drop or two, added to a solution of that alkali, or of any of its salts, immediately causes a precipitation of alum.\* It is most probably constituted of 1 atom of acid + 1 atom of base.

The sub-sulphate of alumina and potassa has been analyzed by M. Riffault (Ann. de Ch. et Phys. xvi. 355), and found to consist of

Sulphuric acid .....	35.495
Alumina .....	39.654
Potassa .....	10.021
Water .....	14.830
	100.

This corresponds very nearly with 3 atoms of acid, 8 of alumina, 1 of potassa, and 4 of water. A native sub-sulphate of alumina has also been examined by Stromeyer, and ascertained to be composed of 30 alumina, 24 sulphuric acid, and 45 water.

(h) Alum is decomposed by charcoal, which combines with the oxygen of the sulphuric acid, and leaves the sulphur attached to the alumina. A combination of alumina, sulphur, and charcoal, forms the *pyrophorus of Homberg*. To prepare this, equal parts of powdered alum and brown sugar are melted over the fire, and are kept stirring till reduced to dryness. The mixture, when cold, is to be finely powdered, and introduced into a common phial, coated with clay, to which a glass tube, open at each end, is to be luted, to allow the escape of the gases that are produced. The phial must then be set in the fire, surrounded by sand, in a crucible. Gas will issue from the open end of the tube, and may be inflamed by a lighted paper. When this ceases to escape, the crucible may be removed from the fire, and a little moist clay pressed down upon the open end of the tube, to prevent the access of air to the contents of the phial. When cold, the tube may be removed, and a cork substituted in its place. The principal difficulty in the process is to stop it precisely at the period,

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\* Ann. de Chim. et Phys. vi. 201.

FIG. 5. A glass bottle with a very thin bottom, and a projecting ring round the neck for suspending it over a lamp. These are useful for effecting *solutions* on a small scale.

FIG. 6. An apparatus contrived by Mr. Pepys, for *ascertaining the quantity of carbonic acid discharged from any substance by the addition of an acid*. It consists of a bottle closed by a ground stopper. This stopper is perforated, and forms the lower part of a tube, which is twisted into the shape of a still-worm. In this worm, any water, that escapes along with the gas, is condensed, and falls down again into the bottle. The loss of weight is determined at the close of the effervescence.

FIG. 7. Mr. Leslie's *differential thermometer* described, vol. i. p. 93.

FIG. 8. (a) *An air thermometer*, for ascertaining the temperature of liquids. It consists of a bottle, partly filled with any coloured liquid, and partly with air, a glass tube of small bore, open at both ends, being either cemented or hermetically sealed into the bottle, so that its lower extremity may nearly touch the bottom of the bottle. The expansion of the included air, on the application of heat, drives the coloured liquid up the tube, and to an extent which may be measured by the application of a scale. The fig. *b* is another variety of the same instrument, described vol. i. p. 92.

FIG. 9. The original *air thermometer of Sanctorio*; see vol. i. p. 91.

FIG. 10. A bent funnel for introducing liquids into retorts, without soiling their necks.

FIG. 11. *An adopter*. The wider end admits the neck of a retort; and the narrower is passed into the mouth of a receiver.

FIG. 12. A section of an evaporating dish of Wedgwood's ware. Under this figure, is a representation, 12 *a*, of a small brass prong with a wooden or other handle, for holding an evaporating glass over a lamp.

FIG. 13. (a) *A tubulated retort* luted to (b) *a quilled receiver*, the pipe of which enters the neck of a bottle (c) supported by a block of wood.

FIG. 14. Different forms of jars for precipitations, with lips for conveniently decanting the fluid from the precipitate.

FIG. 15. A tube, blown in the middle into a ball, for dropping liquids. The ball is filled by the action of the mouth applied to the upper orifice, while the lower one is immersed in the liquid; or by immersing the ball and tube with its point downwards, in the liquid intended to be introduced. The finger is then applied to the upper orifice, and, on cautiously removing it, the liquid is expelled in drops.

FIG. 16. *A bottle for ascertaining the specific gravity of liquids.* When filled up to a mark on the neck, with distilled water of a given temperature, it should hold exactly an even number of grains; and a series of such bottles holding respectively 200, 300, 500, 800, and 1000 grains will be found extremely useful. The quantity, which it is found to contain, of any other liquid of the same temperature, shows at once the specific gravity of the latter. For example, if it hold 1000 grains of water, and 1849 of sulphuric acid, the specific gravity of the latter is to that of water as 1849 to 1000.

## PLATE II.

FIG. 17. An apparatus for procuring gases, without the possibility of their escaping into the room during the process, a circumstance which is of importance, when the gas has an unpleasant smell or deleterious properties. Suppose that sulphureted hydrogen gas is to be obtained from sulphuret of antimony and diluted sulphuric acid. The sulphuret, in coarse powder, is put into the body of the gas bottle *c*, with a proper quantity of water. The acid holder *a* is filled with diluted acid, the cock *b* being shut, and is then fixed into the tubulure of the gas bottle, to which it is accurately adapted by grinding. The bent tube *d* being made to terminate under a receiver filled with, and inverted in water, the perforated cock *b* is gradually opened, in consequence of which the acid descends into the gas bottle; and acts on the sulphuret of antimony. If it be found necessary to renew the acid, without disturbing the apparatus, this may be done as follows. The cock *b* being shut, the stopper, which closes the acid holder, may be removed, and fresh acid be poured in, through the aperture. This may be repeated as often as is found necessary. The acid holder may be advantageously adapted to a retort for certain distillations, such as that of muriatic acid. The

shape, also, of the vessel *c* may be occasionally varied, as convenience may require. When, for example, it is shaped like the bottom part of a Nooth's machine (to be seen in almost every glass shop), it stands much more firmly on a table for use.

FIG. 18. A plain gas bottle with *sigmoid* tube, the end, which is received into the bottle, having a ground stopper accurately fitted to the neck. For ordinary purposes (such as obtaining hydrogen gas from diluted sulphuric acid and iron filings) this apparatus answers perfectly well, and is much less costly than that represented by fig. 17. It is frequently made with a tubulure and glass stopper, and is then called a tubulated gas bottle.

FIG. 19. *A gas funnel*, useful in transferring any gas, from a wide-mouthed vessel into a jar of narrower diameter, or into a bottle. When employed for this purpose, it is held inverted, as shown by the figure, the pipe being admitted into the aperture of the bottle or jar, which is filled with and inverted in water, and the gas is then made to pass into it in bubbles.

FIG. 20. *Dr. Hope's Eudiometer*. The manner of using it has already been described, vol. i. p. 289.

FIG. 21. A modification of Dr. Hope's Eudiometer described, vol. i. p. 290.

FIG. 22. *A gas receiver*, into the neck of which is cemented a brass cap, with a female screw for receiving a stop-cock. The vessel *b* is a glass flask, which may be made to communicate with the interior of the jar *a*, by opening the two air cocks. Supposing that the weight of any gas is to be ascertained, the flask *b* is exhausted, by screwing it on the transfer of an air-pump; and, if great accuracy be required, it is proper to measure the degree of exhaustion by a fit gage. Let the flask be weighed when exhausted; then screw it upon the top of the receiver containing the gas which is to be weighed; and open the communication, observing, by using a graduated jar, how much gas has been admitted. Suppose this to be 50 cubic inches. By weighing the flask again when full, we determine the weight of 50 cubic inches of the gas under examination. The experiment should be made when the temperature of the room is 60°, and when the barometer stands at 30 inches (see vol. i. p. 19).

FIG. 23. *A plain air-jar for receiving gases, with a ground stopper.*

FIG. 24. *An eudiometer for trying the purity of a mixture of gases containing oxygen gas, by means of nitrous gas. The process has already been described, vol. i. p. 308. The instrument should be accompanied with a phial, holding, when completely full, precisely a cubic inch.*

FIG. 25. *A wire stand, with a leaden foot, for the purpose of raising, above the surface of water within a jar, any substance which is to be exposed to the action of a gas.*

FIG. 25. (a) *A bottle and tube for directing a small stream or a few drops of water on any object. The method of using it is described, vol. i. page 11.*

FIG. 25. (b) *A bottle with an elongated stopper, by means of which a single drop of any liquid can be taken up, and allowed to fall into any fluid under examination.*

FIG. 26. *An apparatus for showing that caloric exists in gases in a latent form. The application of it has been already described, vol. i. p. 136.*

FIG. 27. *An apparatus for drying precipitates by steam, described, vol. i. p. 12.*

FIG. 28. *A graduated tube for ascertaining the strength of acids and alkalis, and for various other useful purposes.*

FIG. 29, a and b. *Tubes for exploding mixtures of hydrogen and other inflammable gases with oxygen gas, commonly termed the Eudiometer of Volta; see vol. i. p. 236.*

### PLATE III.

FIG. 30. *The common form of a Woulfe's apparatus. In this figure the retort a is represented plain, but it is better to employ a tubulated one. The use of this apparatus has already been described, vol. i. p. 7.*

FIG. 31. *A modification of the apparatus, which has been already described. In this figure, the mercurial trough is shown with a jar standing inverted in it, for the purpose of receiving any gas that may escape condensation by water.*

FIG. 32. *Mr. Pepys's improvement of Woulfe's apparatus described, vol. i. p. 8.*

## PLATE IV.

FIGS. 33 and 34. Cuthbertson's apparatus, for exhibiting the composition of water, with the substitution of gazometers for the receivers originally employed by him. The apparatus has been described, vol. i. p. 246. FIG. 33 is an enlarged view of the conical brass piece, which is cemented into the bottom of the receiver, and through which the gases are transmitted.

FIG. 35. A gazometer of the most simple and common construction; see vol. i. p. 16.

FIG. 36. A gas holder, described, vol. i. p. 17.

FIG. 37. A galvanic trough; see vol. p. i. 167. The tube *b* shows the arrangement for decomposing water. The upper wire may be hermetically sealed into the tube, and the lower one passed through a cork, which should have a small slit cut in it, to allow the water to escape in drops as the gas is produced.

FIG. 38. The manner in which a candle may be burned in oxygen gas; see vol. i. p. 207.

FIG. 39. The combustion of iron wire in oxygen gas, vol. i. p. 208.

FIG. 40. Apparatus for decomposing water over red-hot iron or charcoal; see vol. i. p. 250.

FIG. 41. An apparatus for showing the diminution effected in the volume of hydrogen and oxygen gases by their slow combustion; see vol. i. p. 237.

FIG. 42. A very simple and cheap contrivance for freezing quicksilver by muriate of lime and snow. The outer vessel of wood may be twelve and a half inches square, and seven inches deep. It should have a wooden cover, rabbeted in, and furnished with a handle. Within this is placed a tin vessel *b b*, standing on feet which are one and a half inch high, and having a projection at the top, half an inch broad, and an inch deep, on which rests a shallow tin pan *c c*. Within the second vessel is a third *d*, made of untinned iron, and supported by feet two inches high. This vessel is four inches square, and is intended to contain the mercury. When the apparatus is used, a mixture of muriate of lime and snow



is put into the outer vessel *a a*, so as completely to surround the middle vessel *b b*. Into the latter, the vessel *d*, containing the quicksilver to be frozen, previously cooled down by a freezing mixture, is put; and this is immediately surrounded by a mixture of snow and muriate of lime, previously cooled to 0° Fahrenheit, by an artificial mixture of snow and common salt. The pan *c c* is also filled with these materials, and the wooden cover is then put into its place. The vessels are now left till the quicksilver is frozen. A more elegant, but more expensive apparatus, by Mr. Pepys, intended for the same purpose, is figured in an early volume of the Philosophical Magazine.

FIG. 43. A wire stand, consisting of an interior circle, and three straight pieces of wire proceeding from it in the same plane. Its use is noticed, vol. i. p. 209.

FIG. 44. Sir. H. Davy's apparatus for the analysis of soils.

## PLATE V.

FIG. 45. Pictet's arrangement of an apparatus for showing the radiation of caloric, unaccompanied by light; see vol. i. p. 102.

FIG. 46. An oval copper boiler, (referred to, vol. i. p. 129) for exhibiting the most important facts respecting latent caloric. The size of its different parts (except the width, which is 4 inches) may be learned from the scale affixed to the plate, which is abundantly sufficient to enable any intelligent workman to construct the apparatus. The collar joint and stuffing box, however, it is indispensably necessary to describe, especially as the former article of apparatus is generally constructed on a bad plan.

FIG. 47 is a section upon a larger scale, of the collar joint at *b* (fig. 46), made for the convenience of screwing together long or crooked metal tubes, without turning them round: *a* is a section of the end of one of the tubes, and *b* that of the other which is to be attached to it; *c* is a collar which turns loose upon the shoulder of *a*, and screws upon *b*. By screwing this collar upon *b*, the end *e e* of the tube *a* is brought to press upon the part *d d* of the tube *b*, without

turning round either of those tubes. If upon *d* be laid a ring of linen cloth soaked in boiled linseed oil, the joint, when screwed up (if tolerably well made), will be impervious to steam as well as to water or air. The projection at *d* is for preserving the ring of cloth from being displaced, and for guiding the ends of both tubes, so as to meet properly.

FIG. 48 is a section of a socket, for fixing the stem of a thermometer into a boiler or a digester, where there is much heat and pressure; *b* is a socket fixed on the outside of the boiler or digester, having a hole through it large enough to admit the bulb of the thermometer; *a* is a plug which screws into *b*, having a hole through its centre large enough to admit only the stem of the thermometer; *c c* is a loose round plate, concave on the upper side, having a hole through its centre just sufficient also to admit the stem of the thermometer. When the instrument is to be inserted, the plug *a*, and the plate *c*, must both be taken out of the socket. The bulb is then passed through it. The plate *c* is next slipped over the stem, and dropped into its place. Some flax, soaked in linseed-oil, must next be wrapped round the stem, so as nearly to fill the socket. The plug *a* must then be screwed in, till the flax be compressed so as to make the whole sufficiently tight. The opposite surfaces of the plate *c*, and the plug *a* are made concave, for the purpose of compressing the flax round the stem of the thermometer. The gage represented above the cock *c* at the top of the boiler is adapted to show the density of the steam, by its effect on a portion of air confined by mercury; for the volume of the air will of course be inversely as the compressing force. The bent part of this gage and small ball are of iron, and the straight part only where the mercury is to be seen through, should be of glass.

## PLATE VI.

FIGS. 49, 50, 51. Sections of crucibles.

FIG. 52. A muffle; see vol. i. p. 5.

FIG. 53. Stands for raising the crucible above the bars of the grate; *a* one adapted to Mr. Aikin's blast furnace; *b* one of the common form.

FIG. 54. A skittle-shaped crucible.

FIG. 55. Mr. Aikin's portable blast furnace. It is composed of three parts, all made out of the common thin black-lead melting pots, sold in London for the use of the goldsmiths. The lower piece *c* is the bottom of one of these pots, cut off so low as only to leave a cavity of about an inch, and ground smooth above and below. The outside diameter over the top is five and a half inches. The middle piece, or fire-place *a*, is a larger portion of a similar pot, with a cavity about six inches deep, and measuring seven and a half inches over the top, outside diameter, and perforated with six blast holes at the bottom. These two pots are all that are essentially necessary to the furnace for most operations; but when it is wished to heap up fuel above the top of a crucible contained within, and especially to protect the eyes from the intolerable glare of the fire when in full heat, an upper pot *b* is added, of the same dimensions as the middle one, and with a large opening in the side, cut to allow the exit of the smoke and flame. It has also an iron stem, with a wooden handle (an old chisel answers the purpose very well) for removing it occasionally.

The bellows, which are double (*d*), are firmly fixed, by a little contrivance which will take off and on, to a heavy stool, as represented in the plate; and their handle should be lengthened so as to make them work easier to the hand. To increase their force on particular occasions, a plate of lead may be firmly tied on the wood of the upper flap. The nozzle is received into a hole in the pot *c*, which conducts the blast into its cavity. From hence the air passes into the fire-place *a*, though six holes of the size of a large gimlet, drilled at equal distances through the bottom of the pot; and all converging in an inward direction, so that if prolonged, they would meet about the centre of the upper part of the fire. Fig. 56 shows the distribution of these holes in the bottom. The large central hole is intended to receive the stand *a*, fig. 53, which serves for supporting the crucible.

No luting is necessary in using this furnace, so that it may be set up and taken down immediately. Coke or common

cinders, taken from the fire when the coal just ceases to blaze, sifted from the dust, and broken into very small pieces, forms the best fuel for higher heats. The fire may be kindled at first by a few lighted cinders, and a small quantity of wood-charcoal.

The heat which this little furnace will afford is so intense, that its power was, at first, discovered accidentally by the fusion of a thick piece of cast iron. The utmost heat procured by it was  $167^{\circ}$  of Wedgwood's pyrometer piece, which was withdrawn from a Hessian crucible, when actually sinking down in a state of porcellanous fusion. A steady heat of  $155^{\circ}$  or  $160^{\circ}$  may be depended on if the fire be properly managed, and the bellows worked with vigour.\*

By a letter from Mr. Aikin, I have learned, also, a convenient way of exhibiting, in a lecture, and performing at other times, the process of cupellation, by means of this furnace. It consists in causing a portion of the blast to be diverted from the fuel, and to pass through a crucible in which the cupel is placed. This arrangement supplies air; and the whole may be seen by a sloping tube, run through the cover of the crucible. Fig. 57 shows the furnace when used for this purpose; *a a* the furnace; *b* the perforated stopper for the central blast; *c c* a portion of earthen tube, through which the air passes, and is heated during this transit; *e* a piece of soft brick perforated to admit the earthen tube *f*, which may be kept open for inspecting the process. No luting is required, except to join *f* to *e*.

It may be proper to add that Mr. Aikin has lately (1823) made considerable improvements in this useful little furnace, which may be had, thus altered, of Mr. Knight in Foster-lane. The principal one is the enlargement of the air chamber *c*. In using the furnace, Mr. Aikin has found that its power is greater when the pipe of the bellows is not actually introduced into the opening leading to the air chamber, but kept at the distance of from one to two inches. He prefers, also, a straight tube of communication between the bellows and the air chamber, in preference to one bent as shown in the figure.

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\* See Philosophical Magazine, vol. xvii. p. 166.

FIG. 58. Knight's portable furnace,\* composed of strong iron plate lined with fire lute, the inside diameter six inches: *a* shows the grate; *b* the ash pit door; *d* the door of the fire-place when used as a sand heat; *e e* two holes opposite to each other for transmitting a tube; *g* an opening for a retort neck, when used for distilling with the naked fire.

FIG. 59. A different view of the same furnace; *a* the grate; *c* the register to the ash pit; *f* a small door, with a contrivance for supporting a muffle. The other letters correspond with the explanation of the preceding figure.

For this furnace the proper fuel, when it is used as a wind furnace, is wood-charcoal, either alone, or with the admixture of a small proportion of coke. For distillation with a sand heat, charcoal, with a little pit coal, may be employed.

## PLATE VII.

FIG. 60 represents a fixed furnace, which I find very useful, because it may either be employed as a wind furnace or for distillation with a sand heat. Its total height outside is thirty-three inches, and the outside square is eighteen inches, or two bricks laid lengthwise. The thickness of the sides of the furnace is the breadth of a brick, or four and a half inches; but whenever there is room, it is better to make them nine inches in thickness. From the top of the furnace to the grate, which is moveable, and supported by two bearers, the height is thirteen inches; and at *c* is a double Rumford door; or in preference, a hole closed by a moveable earthen stopper for introducing fuel. The ash pit should have a register door. The chimney is four inches wide by three high, and may either be furnished with a damper or not. On the top of the furnace a cast-iron ring is fixed, ten inches inside diameter, three inches broad, and half an inch thick. It is secured in its place by three iron pins, passing through three equidistant holes in the ring, and bent at the distance of nine inches at a right angle. These serve the purpose of binding the ring firmly into the brick-work. The sand pots are of dif-

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\* This furnace is also described in vol. i. p. 2, 3.

ferent sizes; and a variety of them may be made to fit the same ring, by varying the breadth of their rims, as shown fig. 71. The bricks should be cemented together, at least for the inner half of their breadth, by loam, or by a mixture of Stourbridge clay, with two or three parts sand, and a proper quantity of water.

When this is used as a wind furnace, the opening in the side is to be closed by its stopper; or, if a Rumford door be employed, it must be defended from the fuel by a fire tile. The fuel (coke) is introduced at the top, which is occasionally covered by a fire tile. When distillation with a sand heat is performed, the sand pot rests on the iron ring, and the fuel, which may be common pit coal, is added through the opening in the side. It may be proper to state, that, in order to receive a sand pot of as large a size as possible, the upper course of bricks should be bevelled within the furnace; and the width at the top may exceed a little that at the grate.

The best Stourbridge or Newcastle-on-Tyne fire-bricks are necessary in constructing this and the following furnaces.

FIG. 61 is a longitudinal section of a wind furnace, invented by Mr. Knight, with an additional chamber for applying the waste heat to useful purposes: *a* the internal cavity, which is square, for containing the fuel and the crucible: *b* the flue passing into a hot chamber *c*; an appendage particularly useful for drying luted crucibles, or bringing them to a proper temperature for the furnace; for roasting ores and various other purposes: *d* the flue connecting it with the vertical chimney *e*; which, to produce a strong heat, should never be less than thirty or forty feet high: *f f* covers, consisting of twelve-inch Welsh tiles, with handles: *g* the stoke hole, through which no more of the fire is seen than what appears between the grate and the bearing bar *h*. This space is left for the double purpose of raking the fire, and occasionally taking out the bars: *k* the ash pit, which is sunk below the level of the ground, and is covered, where it projects at *l*, by an iron grating.

The best situation for this furnace, is an angle of the laboratory, the chimney being in the corner, as represented in the

sketch. By this arrangement, the operator is spared the disagreeable necessity of scorching his legs, by standing opposite the stoke hole, while the backs of his legs are exposed to a current of cold air rushing to the furnace.

FIGS. 62 and 63 are different views of a furnace invented by Mr. Knight, and convertible to various purposes.

The inside of this furnace is nine inches square, and sixteen inches deep from the top to the grate. The face of the opening at *g* rises at an angle, which makes the back part five inches higher than the front. This contrivance enables us completely to cover a large retort with fuel, without obstructing the passage of the air, and also relieves partly the weight of the cover, when it requires to be moved. The walls of the furnace are at least a brick and a half thick, and as much more as local convenience will allow. By sinking the ash pit below the level of the ground, at *i*, the height of the furnace needs not exceed eighteen inches, which renders the management of the fuel much more easy, and subjects the face and hands less to the action of the heat. The ash pit *a*, must be at least eighteen inches deep, below the surface of the ground, and more if convenient. It must have an opening, projecting from it three or four feet, to be covered with boards, and with an iron grating next the furnace. This preserves the legs of the operator from the action of the fire.

The grate *b* is formed of separate bars, each of a triangular shape, three-fourths of an inch apart, and resting on two bearers. In the front of the furnace, an iron bar is to be placed to support the brick-work, and to leave an opening, through which the bars may occasionally be drawn out, and the fire raked and cleared of the slag. The chimney *e* is two and a half inches from the top, and four and a half wide by two and a half high.

To fit this furnace for occasional distillation with the naked fire, an opening *d*, fig. 62, is left on one side, which is filled up, when not wanted, by five pieces of soft fire-brick, cut to a proper shape, and secured by a clay lute. It is proper, also, to be provided with other pieces, having arched openings for transmitting the neck of a retort. One of these pieces may have a round hole for occasionally transmitting a tube, and

a corresponding hole, *h*, fig. 63, must then be made in the opposite side of the furnace, to be closed, when not wanted, with a stopper.

FIGS. 64 and 65 represent a sand heat, for containing flat evaporating vessels; the depth from back to front two feet; the width, agreeably to the scale, six feet. At the front is a rim four inches deep, consisting of a piece of iron plate, which is fastened at each end into the wall. The floor or bottom *e e*, is formed of cast-iron plates, which rest upon each other in corresponding rabbets. The advantage of several small plates, over one large one, is the cheapness and facility, with which they are replaced, if cracked by the heat, an accident of not unfrequent occurrence. The joints are secured by a fire lute, which effectually prevents the sand from falling through. The fire place is shown by *b*; at the bottom it has a grate ten inches long, by eight wide. The flame and smoke circulate first through the flue, *c*, and then through the returning flue, *d*, which conveys the smoke to the chimney *g*. In constructing the flue beneath the grate, a row of bricks, set edgeways, answers the purpose, and serves also to support the inner edge of the plates.

It is advisable to cover the sand heat with a sloping roof, which may be formed of lath and plaster, and supported by side walls. The lowest part of the roof may be foremost and about three feet above the edge of the iron plates. It is, also, necessary to have an air flue, nearly at the top of the back wall, under the dome or roof, to be closed occasionally by a door. This must open into the chimney, in which case it serves the purpose of carrying off noxious vapours.

## PLATE VIII.

FIGS. 66, 67, 68, are the section and plans of a reverberatory furnace for experimental purposes. In this furnace, the fuel is contained in an interior fire-place; and the substance, to be submitted to the action of heat, is placed on the floor of another chamber, situated between the front one and the chimney. The flame of the fuel passes into the second compartment; by the form of which it is concentrated upon the



substance exposed to heat, which is not confined in a separate vessel or crucible, but placed on the floor of the furnace. When reduced to a state of fusion, the melted mass is allowed to flow out through a tap-hole at *h*. The dimensions of this furnace it is scarcely possible to state, as they vary so considerably in different parts of it; but they may be ascertained by referring to the figures, and by the application of the scale. In all three figures *a* represents the ash pit; *b* the grate composed of moveable bars; *c* the door at which the fuel is introduced; *d* a door in the side of the chamber, for the purpose of inspecting the process; *e* the floor of the furnace which descends, and is gradually contracted towards the back part; *f* another door for introducing and stirring the materials; *g* the back part of the furnace, immediately under the chimney; *h* the tap-hole; *i* the chimney.

FIGS. 69 and 70, exhibit a cupelling or *enamelling furnace*. The form of this should be an oblong square; its dimensions being regulated by that of the muffle, which should go home, to the back, its front edge lodging on the mouth of the furnace. On each side of the muffle, two inches and a half must be left, to let the fuel pass readily underneath, where there should also be a similar space. A stoke hole must be left on the other side, but the situation of the view will not admit its being shown. Before the muffle, is a projecting ledge or shelf, shown at *e*, which is intended to support any thing that is to be put into the muffle. Two twelve-inch tiles, worked in along with the bricks, will answer this purpose. In both figures, *a* shows the ash pit; *c* the grate; *d* the muffle; *e* the opening for introducing the muffle; *f* the chimney, and *g* the cover.

FIG. 71. Sand pots with rims of different sizes.

FIGS. 72, 73. Dr. Black's portable furnace, made of sheet iron lined with fire clay. Its dimensions, as they vary in almost every part, will best be learned from the scale; *a* the fire place; *b* the chimney; *c* the ash pit; *d* the door of the ash pit; *e* a register for regulating the quantity of air admitted to pass through the fuel.

FIG. 74. Mr. Chenevix's wind furnace. This is rudely sketched in Nicholson's Journal, from which the more accurate figure in plate viii. is taken. This furnace Mr. Chenevix

describes as follows: "I have constructed a wind furnace, which, in some respects, is preferable to the usual form. The sides, instead of being perpendicular, are inverted; so that the hollow space is pyramidal. At the bottom the space is twelve inches square, and at the top only eight. The perpendicular height is seventeen inches, from the top to the grate. This form unites the following advantages. 1. A large surface is exposed to the air, which, having an easy entrance, rushes through the fuel with great rapidity. 2. The inclined sides act as reverberators. 3. The fuel falls of itself, and is always close to the grate."

In the figure, *a* represents the grate; *c c* are two bricks which can be let in at pleasure, to diminish the capacity: *b* is another grate which can be placed on the bricks *c c*, for occasional purposes: *d d* are bricks, which can be placed on the grate *b*, to diminish the capacity of this part of the furnace; *e* the cover. Both set of bricks should be ground to the slope of the furnace.

In the construction of every furnace, which is intended to produce a strong heat, lime or mortar should be avoided, and the bricks should be set in loam, or Stourbridge clay, worked up with water and sand, inserting occasionally pieces of sheet iron, bent twice in opposite directions at right angles. The furnace should be allowed to remain some weeks, after setting up, before it is used; and before raising a strong heat, a gentle fire should be sometimes kindled in it, the strength of which may be gradually increased. When a strong blast is expected, it is necessary to bind the brick-work together, externally, by strong iron bars and plates, kept in their places by screws. The chimney should be nine inches wide, and raised to as great a height as circumstances will admit.

The coke of pit coal is the only fuel fitted for exciting an intense heat, and should be used in all cases, except in the reverberatory, and in distillations with the sand bath, when pit coal may be employed. The charcoal of wood is adapted principally to portable furnaces.

## PLATE IX.

FIG. 75. The galvanic battery called *couronne de tasses*, described vol. i. p. 168.

FIG. 76. Apparatus for obtaining the elements of water in separate tubes; see vol. i. p. 177.

FIG. 77. The pile of Volta; see vol. i. p. 167. The tube annexed to the pile is for the purpose of showing the decomposition of water; see vol. i. p. 176.

FIG. 78. Section of a galvanic trough, to explain the theory of the excitation of galvanic electricity; see vol. i. p. 188.

FIG. 79. Apparatus for obtaining oxygen and hydrogen gases, from separate quantities of water not in contact with each other; see vol. i. p. 177.

FIG. 80. Two agate cups connected by moistened amianthus; see vol. i. 178.

FIG. 81. Two gold cones similarly connected, p. 179.

FIG. 82. Agate cups similarly connected with an intermediate vessel *i*; see vol. i. p. 180.

FIG. 83. Apparatus for procuring potassium from potassa and iron filings. A better apparatus for this purpose is represented by the wood cut, vol. i. p. 501.

FIG. 84. Apparatus for firing gases by electricity, or submitting them to electrical discharges, vol. i. p. 19.

FIG. 85. Pepys's improved gas-holder: *a* a small iron rectort placed in the fire with a jointed conducting tube *b*, which is admitted into the vessel at *c*. This is shown on a larger scale in a different part of the plate. The letter *d* is placed on the body of the reservoir, and near the central pipe, which descends from the cistern *e* to nearly the bottom of the vessel. At *f* a glass tube is fixed, which shows the height of the water within the vessel. When a jar is intended to be filled with gas from the reservoir, it is placed, filled with water and inverted, in the cistern *e*. The cocks 1 and 2 being opened, the water descends through the pipe attached to the latter, and the gas rises through the cock 1. By raising the cistern *e* to a greater elevation, any degree of pressure may be obtained; and a blow-pipe may be screwed on the cock at the left side of the vessel.

## PLATE X.

FIGS. 1, 2, 3. Views of Mr. Newman's *Mercurio-pneu-*

*matic trough*, combined with a mercurial gazometer. The same letters refer to all three figures.

FIG. 1, is a front view; fig. 2, a section; and fig. 3, a view looking down from above into the cavity of the trough. A, the glass bell of the gazometer, shown about half full of gas; B, the exterior vessel of the gazometer. In fig. 1, the central solid part, which fills the cavity of the bell when depressed as far as it will go, is shown by dotted lines, as also is a small iron tube, on which the letter B stands. This tube conveys the gases from the small bell-shaped vessel E, in which they are first received, into the receiver A of the gazometer. In fig. 2, this tube is marked *bb*, and may be seen rising a little above the mercury, which is thus prevented from falling into it. In fig. 3, the termination of this pipe is marked by a circle, close to the letter C.

D, fig. 1. one of the sides of the cistern for containing mercury, at G the cistern has a semi-cylindrical cavity seen more distinctly in fig. 2. F is a small tube opening into the gazometer, and also under one of the small holes *iii*, fig. 3. By means of this tube, a small portion of gas may, at any time, be transferred from the gazometer into a narrow test tube or other vessel. H is a deep circular cavity, or well, into which a long tube or jar may be occasionally immersed, when it is necessary to have the mercury at the same level within and without. I is a receiver into which gas is supposed to be passing from a retort heated by the spirit lamp N. This lamp, by means of a pillar and socket, may be raised or lowered at pleasure, and is secured at any desired height by a spring. K, a Volta's Eudiometer secured by an upright pillar L, in which is a spring to diminish the recoil on firing any gases. This is moveable, and is fixed when wanted to the side of the trough by the screws M. O O, a sheet iron tray, intended to collect any mercury that may be spilled out of the trough.

FIGS. 4, 5, 6, 7. The *compound blowpipe for compressed oxygen and hydrogen gases*, with the addition of a safety tube for preventing explosions. A, the barrel of the condensing syringe. B, the handle of the piston. C, a cock for closing occasionally the communication with a bladder filled with the mixed gases. D, a cock between the syringe, and the square

copper box into which the gases are condensed. This box is marked E. F, a perforated metal cap fitted by a screw to the top of the box, and containing a pile of circular discs of wire gauze, seen in fig. 5, such as is used for the safety lamps. G, a cock to prevent occasionally the escape of the condensed gases. H, a ball and socket joint, by means of which the jet I, of which there should be two or three of different sizes, can be turned in any direction.

The addition to the apparatus for preventing explosions is represented in fig. 5, within the copper box. The letter *d* is placed on a piece of brass tube closed at the bottom, and fixed air tight into the box. Into the bottom of this, is fixed a small pipe *a a*, covered at the upper extremity *a* by a piece of wire gauze, and opening into the brass tube by two or four holes. A circular flat valve, lined with silk or leather, which may be seen in the sketch, covers these holes, and prevents the passage of any thing backwards from the brass tube into the box E.

When the instrument is to be used, the common air should be exhausted from the box E, by means of the syringe, the box then filled with the gases; after which water or oil should be poured into the brass tube (the cap F being supposed removed) to about *e*. The gases may then be condensed into the box, and by their own elastic force will pass through the tube, the fluid, and the various screens of wire gauze, and will issue out at the jet. When the inflammation, by the use of a large jet, passes backwards, it is generally arrested by the discs of wire gauze; but if it pass these, it kindles only the gases in the brass tube, and does no harm; and the valve prevents the fluid from being propelled into the box.

END OF THE FIRST VOLUME.











