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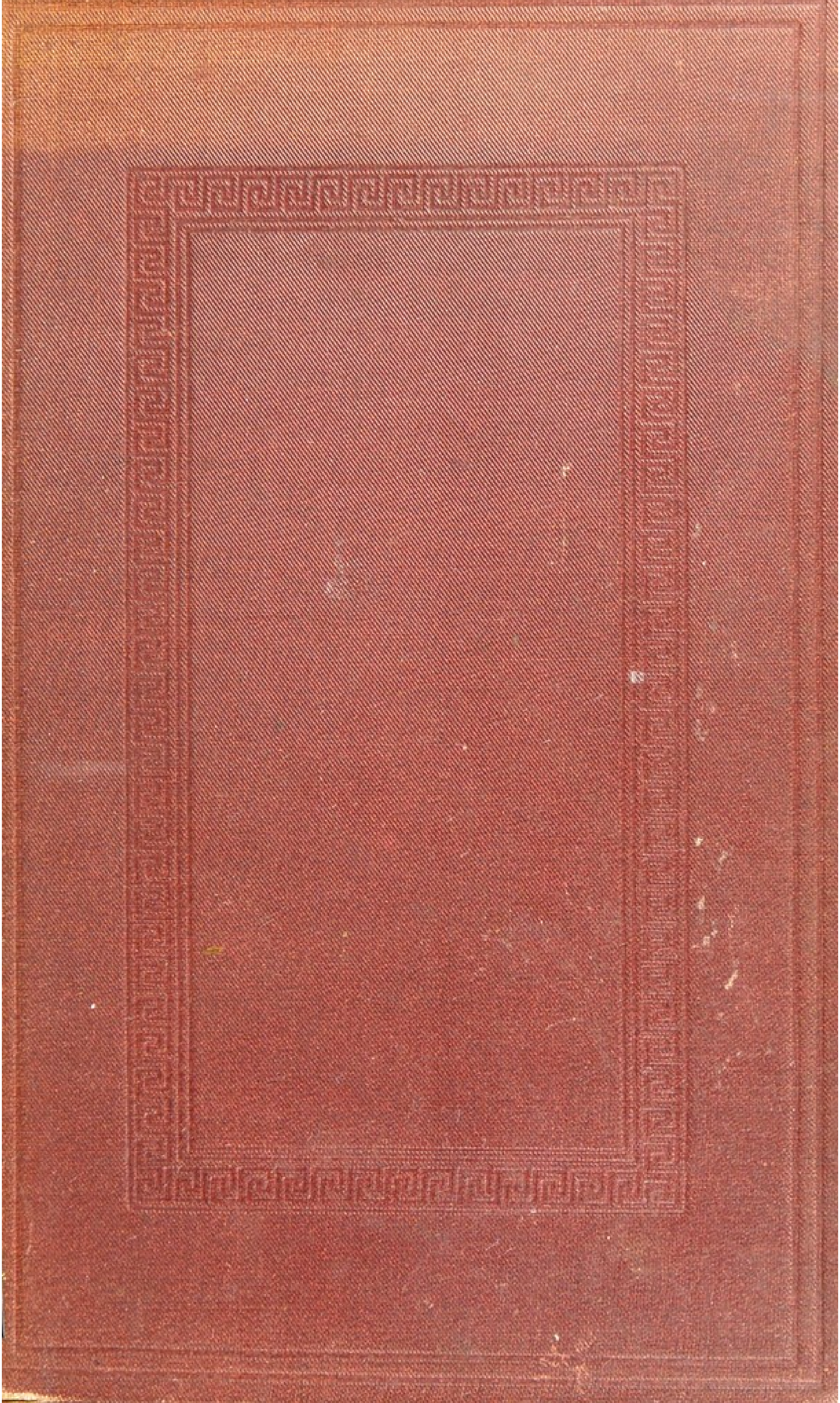

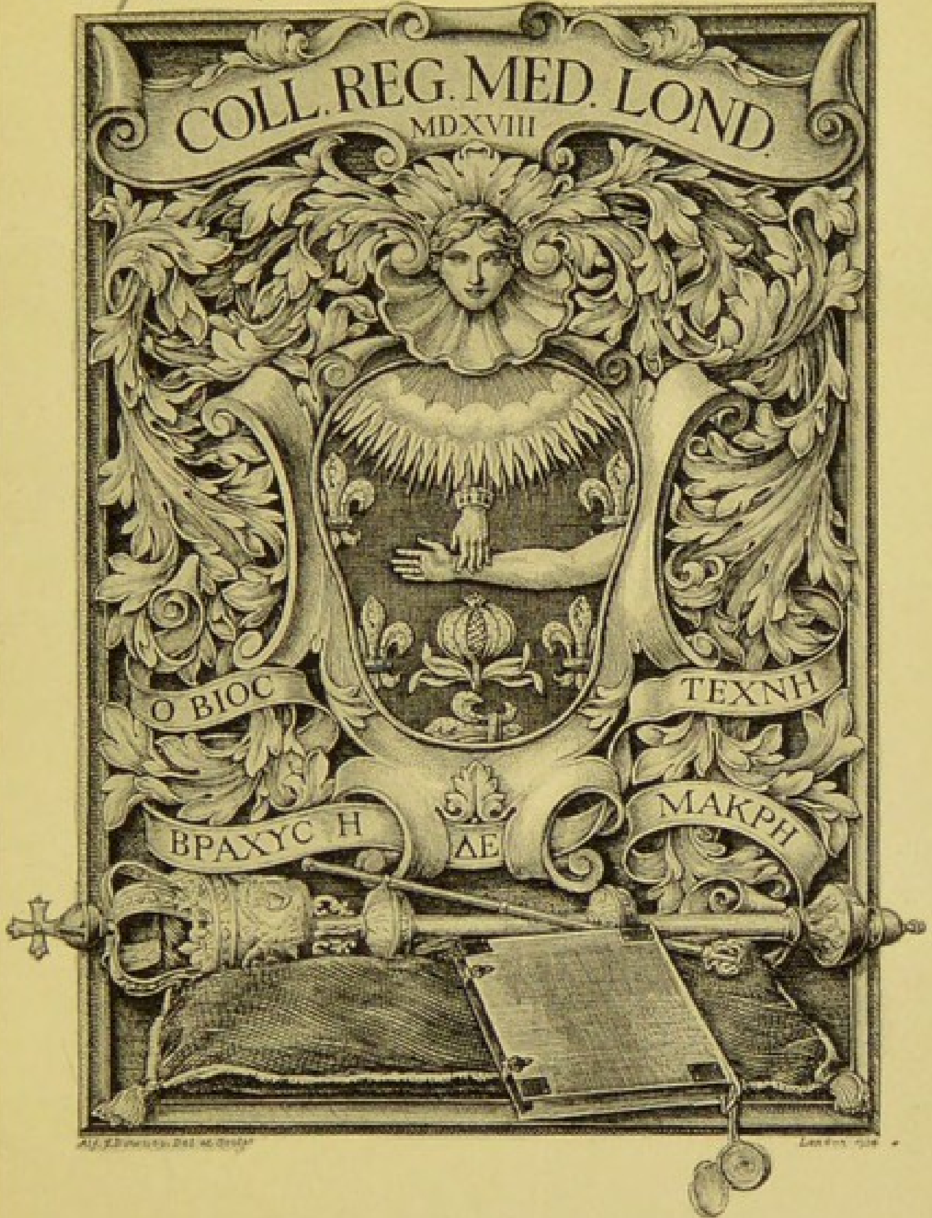
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ABSTRACTS OF LECTURES

DELIVERED AT

THE ROYAL INSTITUTION.

BY

WILLIAM ODLING, M.A., F.R.S.,

FULLERIAN PROFESSOR OF CHEMISTRY, 1868–~~1873.~~ 1876.

LONDON:
1874.
[1876]

CONTENTS.

Royal Institution of Great Britain.

WEEKLY EVENING MEETING,

Friday, May 22, 1868.

SIR HENRY HOLLAND, BART. M.D. D.C.L. F.R.S. President,
in the Chair.

WILLIAM ODLING, M.B. F.R.S.

On some Effects of the Heat of the Oxy-hydrogen Flame.

I.

CHEMICAL changes, whether of combination or decomposition, result in the production of new bodies which, under the conditions of the change, have for the most part a greater stability than the original bodies.

One evidence of this greater stability is afforded by the development of a quantity of heat—the heat of chemical action—from the produced bodies having a smaller potential heat than the original ones.

It results, both from reason and experiment, that in order to undo or reverse any definite chemical action, just so much heat must be directly or indirectly expended as was evolved by the original action.

For the same quantity of heat evolved, the resulting temperature varies with the mass and kind of matter heated, and with the rapid or gradual evolution of the heat.

When the evolution of heat is instantaneous, the resulting temperature may be calculated from the quantity of heat evolved, and the mass and specific heat, &c., of the matter heated.

By a unit of heat is meant the quantity of heat necessary to raise the temperature of one kilogramme of water one degree centigrade, or more accurately from 0° to 1°.

II.

Every 18 grammes of water is a combination of two 1-gramme proportions of hydrogen H, with one 16-gramme proportion of oxygen O; and, by the combination of two grammes of hydrogen with sixteen grammes of oxygen, there are developed 68 units of heat.

Of these 68 units of heat, however, little more than 57 units are really due to the chemical action,—nearly 11 units of heat being evolved by the contraction of the original mixed gas into two-thirds its volume of steam, and by the further condensation of the resulting steam into 18 cubic centimetres of water.

While the quantity of heat evolved by the combination of a given quantity of oxygen and hydrogen is invariable, the intensity of the heat may vary from a scarcely recognisable rise of temperature up to the highest temperature of the oxy-hydrogen blowpipe flame, capable of fusing platinum and silica.

A most remarkable effect of the intense temperature resulting from the combination of oxygen and hydrogen into water, is the partial decomposition of water into oxygen and hydrogen, discovered by Mr. Grove in 1846.

At this high temperature, hydrochloric acid and carbonic anhydride gases also undergo partial decomposition, into hydrogen and chlorine, and into carbonous oxide and oxygen respectively.

Upon what do these singular decompositions by heat, of bodies formed with great evolution of heat, depend; or with what class of chemical phenomena may they be associated?

III.

Under certain familiar conditions, chemical action seemingly takes place to its utmost possible extent in a single direction only, with production of a maximum amount of the substance that is formed with maximum evolution of heat.

For example, taking atomic proportions in grammes, the heat of formation of chloride of zinc, $ZnCl_2$, is 101 units, and the heat of formation of chloride of copper, $CuCl_2$, is 60·5 units. Hence, with chlorine in solution and excess of both copper and zinc, there is finally produced the maximum possible amount of chloride of zinc and no chloride of copper.

Again, an addition of sufficient zinc to solution of chloride of copper, there is complete combination of chlorine with zinc and complete separation of chlorine from copper, *i. e.* complete burning of the one metal and complete unburning of the other.

IV.

But under simpler though less familiar conditions, chemical action habitually takes place in more than one direction simultaneously, with production of correlative products in varying proportions.

Thus, with hydrogen and excess of both chlorine and oxygen, although the heat of formation of oxide of hydrogen H_2O is 57 units, and the heat of formation of chloride of hydrogen $2HCl$, is only 47·5 units, yet, in this case, the hydrogen does not combine with the oxygen to the exclusion of the chlorine, but divides itself between the oxygen and the chlorine in proportions which vary with the conditions of the experiment.

In accordance with this result it is found that, at the same red heat, excess of chlorine will effect the partial decomposition of water with extrusion of oxygen; and, conversely, that excess of oxygen will effect the partial decomposition of hydrochloric acid with extrusion of chlorine.

So that, beginning with the two chemical substances, water and chlorine, or beginning with the two chemical substances, hydrochloric and oxygen, or beginning with the three chemical substances, hydrogen, chlorine, and oxygen, there exist, at a full red heat, the four chemical substances, water, hydrochloric acid, chlorine, and oxygen; the proportions of the four substances depending certainly upon the relative quantities present of the elements concerned, and most probably also upon the temperature of the experiment.

Similarly, beginning with the one chemical substance, water (Grove), or beginning with the two chemical substances, oxygen and hydrogen (Bunsen), there always exist, at a sufficiently high temperature, the three chemical substances, water, oxygen, and hydrogen.

Although, by exposure to a red heat, the electrolytic mixture of oxygen and hydrogen gases becomes completely combined, or transformed into water, yet, as recently shown by Bunsen, at the high temperature of 2024 degrees, only one-half, and at the still higher temperature of 2844 degrees, only one-third of the mixture undergoes combination, the other one-half or two-thirds remaining in the state of mixed gas.

V.

Chemists are acquainted with many reciprocal actions comparable with those of chlorine upon water, and of oxygen upon hydrochloric acid, the most familiar instance being probably the decomposition of ignited oxide of iron by hydrogen with extrusion of iron, and the converse decomposition of oxide of hydrogen by ignited iron with extrusion of hydrogen.

Similarly, sodium will decompose the oxides of carbon, while carbon will decompose oxide of sodium; and just as a sufficient excess of chlorine may be made to effect the almost complete decomposition of a given quantity of water, so may a sufficient excess of carbon (or carbonous oxide) be made to effect the almost complete decomposition of a given quantity of sodium-oxide or zinc-oxide, as in the ordinary processes for obtaining the two metals; notwithstanding that, for an equal consumption of oxygen, the respective combination heats of sodium and zinc exceed by far the combination heat of carbon or carbonous oxide.

Again, although the combination heat of oxygen and carbonous oxide is 68 units, while that of oxygen and hydrogen is only 57 units, yet, as was shown by Bunsen many years ago, upon exploding a mixture of oxygen with a joint excess of carbonous oxide and hydrogen, the oxygen does not attach itself exclusively to the carbonous oxide, but divides itself between the carbonous oxide and hydrogen in a ratio determined by their relative proportions.

[W. O.]

Royal Institution of Great Britain.

WEEKLY EVENING MEETING,

Friday, June 4, 1869.

His Royal Highness the PRINCE OF WALES, K.G. Vice-Patron,
in the Chair.

WILLIAM ODLING, Esq. M.B. F.R.S.
FULLERIAN PROFESSOR OF CHEMISTRY, R.I.

On the Simplest Organic Compounds.

ALL the olefine hydrocarbons are found to have one and the same ultimate composition, or ratio of carbon to hydrogen.

$C_2 H_4$	Ethylene
$C_3 H_6$	Propylene
$C_4 H_8$	Butylene
$C_5 H_{10}$	Amylene
$C_x H_{2x}$	&c., &c.

But these hydrocarbons obviously differ in the complexity of their constitution. Some of them are gases, differing from one another in condensability; others of them are liquids, differing from one another in volatility; while others of them are solids, differing from one another in fusibility. The exact degree of complexity of each hydrocarbon is shown by its reactions. Thus the hydrogen of gaseous ethylene being experimentally divisible into four parts, and its carbon into two parts, there is deduced for it the formula C_2H_4; while the hydrogen of liquid amylene being experimentally divisible into ten parts, and its carbon into five parts, there is deduced for it the formula C_5H_{10}. Again, it is possible to extract from a given volume of ethylene gas and amylene vapour, four times and ten times respectively the actual weight of hydrogen obtainable from the same volume of hydrochloric acid gas; and also to extract therefrom two times and five times respectively the actual weight of carbon that is obtainable from the same volume of carbonic acid gas—these two gases, formulated as HCl and CO_2, containing within a given volume the smallest observed weights of hydrogen and of carbon respectively. The olefine hydrocarbons are said to be polymeric, and their different properties are satisfactorily referable to the different relative weights of their units or molecules. There exist many other series of polymeric bodies, that is of bodies having one and the same ultimate composition, but different molecular weights.

II.

Acetone, propion-aldehyd, and allyl-alcohol are entirely different substances, possessed of well-marked distinctive properties. Like the several olefines, they have the same ultimate composition as each other; but, unlike the several olefines, they have also the same molecular weight as each other, and are expressed by the same molecular formula C_3H_6O. In each of them the carbon is experimentally divisible into three parts, and the hydrogen into six parts, while the oxygen is indivisible; and it is possible to extract from any given volume of one of them exactly the same weights of carbon, hydrogen, and oxygen that are obtainable from the same gas-volume of each of the other two. These different bodies are said to be metameric, and their different properties are necessarily referable to a difference in the arrangement of their constituent elements.

III.

The existence of a determinate structural arrangement in chemical compounds is further demonstrated by a host of considerations; but the difficulty of making out the actual structure of individual compounds has hitherto proved insuperable. The facility of setting forth imaginary structure, however, is very great; and accordingly the presentation of imaginary for ascertained structure has been freely practised by chemists from the first introduction of chemical formulæ until now. But in what degree soever a determination of absolute chemical structure may hereafter be achieved, the possibility exists very generally, even at the present day, of determining relative chemical structure—of making out that in such and such a body the structural arrangement is similar to, or different from, that of some other and usually more simple body. Hence the importance of studying the structural analogies of the simplest organic bodies.

IV.

Marsh-gas is furnished by the decay of moist vegetable tissue, and in other ways. Chloride of methyl-gas is furnished by the action of hydrochloric acid upon narcotine, codeine, wood-spirit, &c. The ultimate composition of the two gases is expressed by the formulæ CH_4 and CH_3Cl respectively. Marsh-gas is transformable into methyl-chloride by the action of chlorine; and methyl-chloride into marsh-gas by the action of hydrogen. From this mutual metamorphosis, and from the parallelism of their properties, formations, and transformations, the two gases are inferred to have one and the same molecular structure, whatever that may be; and the same conclusion is applicable to the entire series of bodies formulated below:—

CH_4	Marsh-gas.
CH_3Cl	Methyl-chloride.
CH_2Cl_2	Methylen-dichloride.
$CHCl_3$	Chloroform.
CCl_4	Perchloride of carbon.

V.

Wood-spirit is usually furnished by the destructive distillation of wood, but is procurable from many other sources, and especially from essential oil of winter-green, by its decomposition with potash. The ultimate composition of wood-spirit is expressed by the formula CH_4O; and it is observable that the difference of ultimate composition between wood-spirit and methyl-chloride CH_3Cl, is the same as that between water H_2O, and hydrochloric acid HCl; as is shown more clearly by the following formulæ, in which the differential constituents of the two pairs of bodies are included in parentheses.

$$H(Cl) \;\text{.. ..}\; H(HO). \quad | \quad CH_3(Cl) \;\text{.. ..}\; CH_3(HO).$$

Further, the residue H of hydrochloric acid and residue CH_3 of methyl-chloride are transformable into water and wood-spirit respectively, and re-transformable from water and wood-spirit back to hydrochloric acid and methyl-chloride respectively, by precisely similar reactions.

From the mutual metamorphoses and parallel habitudes of the two bodies, methyl-chloride and wood-spirit, it is inferred that, with regard to their common residue CH_3, they have the same structure as one another; while, with regard to their differential constituents, (Cl) and (HO), their difference of structure is analogous to the difference between hydrochloric acid and water.

VI.

Hydrochloric acid HCl, and water H_2O, are the first and second terms of a series of bodies of which the third and fourth terms are constituted by ammonia H_3N, and marsh-gas H_4C respectively. Hence arises a question as to the existence of organic bodies bearing to methyl-chloride and wood-spirit the relation that ammonia and marsh-gas bear to hydrochloric acid and water.

VII.

Many years ago, methyl-amine was discovered by Wurtz. It is now known to occur as a product of the putrefaction of, and also of the action of alkalis upon, many animal substances. Its resemblance in properties to ammonia is most remarkable, and its differentiation therefrom somewhat difficult. Its ultimate composition is expressed by the formula CH_5N; whence it appears that the difference of ultimate composition between methyl-amine and wood-spirit and methyl-chloride is the same as that between ammonia and water and hydrochloric acid.

$$\begin{array}{lcl|lcl} HCl & \text{.. ..} & CH_3Cl & H(Cl) & \text{.. ..} & CH_3(Cl) \\ H_2O & \text{.. ..} & CH_4O & H(HO) & \text{.. ..} & CH_3(HO) \\ H_3N & \text{.. ..} & CH_5N & H(H_2N) & \text{.. ..} & CH_3(H_2N) \end{array}$$

Moreover, methyl-amine, wood-spirit, and methyl-chloride are mutually convertible, through exchanges of their differential constituents, by processes effecting similar mutual conversions of hydrochloric acid, water, and ammonia. From the mutual metamorphoses and parallel habitudes of the three bodies, it is inferred that, with regard to their common residue CH_3, they have the same structure as each other, while with regard to their differential constituents (Cl), (HO), and (H_2N), their difference of structure is similar to the difference between hydrochloric acid and water and ammonia.

VIII.

Wood-spirit or methyl-hydrate is producible by the action of methyl-chloride upon sodium-hydrate NaHO; and methyl-amine by the action of methyl-chloride upon sodium-amide NaH_2N. Similarly, methyl-methide is producible by the action of methyl-chloride upon sodium-methide NaH_3C. (Action of methyl-iodide upon zinc-methide.—Frankland and Kolbe.)

$$\begin{aligned} NaHO &+ CH_3Cl = CH_4O + NaCl \\ NaH_2N &+ CH_3Cl = CH_5N + NaCl \\ NaH_3C &+ CH_3Cl = CH_6C + NaCl \end{aligned}$$

This methyl-methide is now known to be identical with the hydrocarbon C_2H_6, producible by the indirect deoxidation of common alcohol C_2H_6O, and known as ethane or hydride of ethyl. Ethane $CH_3(H_3C)$, being susceptible of two distinct and similar sets of marsh-gas reactions, just as methyl-amine $CH_3(H_2N)$, is susceptible of one set of marsh-gas and one set of ammonia reactions—as before, an identity of structure between ethane and methyl-amine is inferred with respect to their common residue CH_3, and a difference of structure with respect to their differential constituents (H_3C) and (H_2N), parallel to the difference in structure between marsh-gas and ammonia.

IX.

The property of oxygen that is half-saturated by hydrogen, or of the water residue HO'', and the property of nitrogen that is two-thirds saturated by hydrogen, or of the ammonia residue H_2N''', to suffer an exchange for one proportion of chlorine or hydrogen, has been shown in the above, and might be shown in many other compounds. But oxygen, altogether unsaturated by hydrogen, has the additional property of being exchangeable for two proportions of chlorine or hydrogen; and nitrogen, altogether unsaturated by hydrogen, has the additional property of being exchangeable for three proportions of chlorine or hydrogen, as indicated by the succeeding formulæ for mercuric oxide and mercuric chloride, and for boric nitride and boric chloride respectively.

$$\begin{matrix} NaF' & \ldots & HgO'' & \ldots & BN''' \\ NaCl & \ldots & HgCl_2 & \ldots & BCl_3 \end{matrix}$$

Marsh-gas compounds, in which hydrogen or chlorine has been exchanged for half-saturated oxygen and two-thirds saturated nitrogen, have been already adduced in wood-spirit CH_4O, and methylamine CH_5N; and reference has also been made to the corresponding hydro-carbon CH_6C or C_2H_6. The question now arises as to the existence of marsh-gas compounds in which hydrogen or chlorine has been exchanged for else unsaturated oxygen and nitrogen, and of hydrocarbons corresponding to these compounds.

X.

Some few years back a curious oxidation product of wood-spirit was discovered by Hofmann. It is now called formic aldehyd, and its ultimate composition is expressed by the formula CH_2O. In respect of ultimate composition its relationship to the second marsh-gas chloride CH_2Cl_2 is obviously similar to that of mercuric oxide HgO, to mercuric chloride $HgCl_2$. Both formic aldehyd and methylen dichloride, however, are imperfectly studied compounds, and their actual metamorphoses are unknown. But in the case of many other aldehyds and corresponding organic dichlorides, the relationship of mutual metamorphosis is well established, whence it is believed to exist between these two compounds also. On this assumption formic aldehyd CH_2O'', and methylen dichloride CH_2Cl_2, are inferred to have one and the same structural arrangement in respect to their common residue CH_2, and a difference of structure in respect to their differential constituents O'' and Cl_2, similar to the difference between oxide and chloride of mercury for example.

XI.

Prussic-acid is a well-known organic compound producible by the action of water on bitter almond kernels, and in various other ways. Its ultimate composition being expressed by the formula CHN, the difference in ultimate composition between it and chloroform $CHCl_3$, is obviously similar to the difference in composition between nitride and chloride of boron, BN and BCl_3 respectively. Now chloroform is readily converted into prussic acid, and boric chloride into boric nitride, by the similar action of ammonia upon the two compounds, with exchange of Cl_3 for N''', thus :—

$$\begin{aligned} CHCl_3 + H_3N &= CHN + 3HCl \\ BCl_3 + H_3N &= BN + 3HCl. \end{aligned}$$

Prussic acid CHN''', and chloroform $CHCl_3$, are accordingly inferred to have one and the same structure in respect of their common residue CH, and a difference of structure in respect of their differential constituents N''' and Cl_3, parallel to the difference between nitride and chloride of boron for example.

XII.

Allowing for the different replaceable values of oxygen O″, and nitrogen N‴, the relationship of methyl-amine to prussic acid is comparable with that of formic aldehyd to wood-spirit:—

Wood-spirit	CH_4O	Formic aldehyd	CH_2O		
Methylamine	CH_5N		,,	Prussic acid	CHN
Ethane	CH_6C	Ethylene	CH_4C	Acetylene	CH_2C

Prussic acid and formic aldehyd are procurable from methylamine and wood-spirit respectively, by similar processes of dehydrogenation or oxidation; while methyl-amine actually, and wood-spirit analogically, are reproducible from prussic acid and formic aldehyd by the reverse process of hydrogenation. Now the difference in ultimate composition, between ethane and olefiant gas, or ethylene, is similar to that between wood-spirit and formic aldehyd: and the difference of ultimate composition, between the hydrocarbons ethane and acetylene, is similar to that between methyl-amine and prussic acid. Moreover ethane is convertible successively into ethylene and acetylene by oxidation; and acetylene is reconvertible into ethylene and ethane successively by hydrogenation.

XIII.

The experimental relationship of ethane, methyl-amine, and wood-spirit has been already considered. Formic aldehyd being a very imperfectly-studied compound, the relationship between it and ethylene is as yet analogical only; but the experimental relationship between acetylene and prussic acid has recently been established by Berthelot, who has shown that mixed acetylene and nitrogen are convertible into prussic acid, and that prussic acid is reconvertible into mixed acetylene and nitrogen, by the action of the electric spark.

$$CH_2C \text{ or } \overbrace{CH.HC + NN} = \overbrace{CHN + NHC}$$

XIV.

Just as the existence in methyl-chloride, in formic aldehyd, and in prussic acid of one marsh-gas residue, plus one hydrochloric acid residue Cl′, and one water residue O″, and one ammonia residue N‴, respectively, is inferable from the relationships and behaviour of the respective bodies—so is the existence alike in ethane, ethylene, and acetylene of two marsh-gas residues inferable from the relationships and behaviour of these respective bodies. As shown more especially by Kekulé, the individual marsh-gas residues of every hydrocarbon are found to be susceptible of changes exactly similar to those of marsh-gas itself, and resulting in the formation of similarly characterized bodies, as indicated below in the case of some ethane and ethylene derivatives.

Ethyl chloride	$C\,H_3 . C\,H_2\,(Cl)$	Vinyl-chloride	$C\,H_2 . C\,H\,(Cl)$
Alcohol . .	$C\,H_3 . C\,H_2\,(HO)$	Vinyl-alcohol	$C\,H_2 . C\,H\,(HO)$
Ethylamine	$C\,H_3 . C\,H_2\,(H_2N)$	Vinyl-amine	$C\,H_2 . C\,H\,(H_2N)$
Propane . .	$C\,H_3 . C\,H_2\,(H_3C)$	Propylene	$C\,H_2 . C\,H\,(H_3C)$

XV.

In any hydrocarbon or chlorhydrocarbon, the substitution of half-saturated oxygen HO'', for one proportion of hydrogen or chlorine, is productive of a compound either similar or dissimilar in its properties to common alcohol C_2H_6O or $CH_3.CH_2(HO)$. Hence, from an examination of the resulting product, and of its other modes of formation, an inference is deducible as to its genesis having resulted from a change effected in the marsh-gas residue CH_3 in the former case, and from a change effected in one or other of the marsh-gas residues CH_2 and CH in the latter case.

In any hydrocarbon or chlorhydrocarbon, the substitution of one proportion of oxygen O'', for two proportions of hydrogen or chlorine, is productive of a compound either similar or dissimilar in its properties to common aldehyd C_2H_4O or $CH_3.CHO''$. Hence, from an examination of the resulting product, and of its other modes of formation, an inference is deducible as to its genesis having resulted from a change effected in the marsh-gas residue CH_3 in the former case, and from a change effected in the marsh-gas residue CH_2 in the latter case.

The relative structure of the previously cited metameric compounds propion-aldehyd, acetone, and allyl-alcohol is thus ascertainable, and is expressed in the following structural formulæ :—

Hydrocarbon.	Metameric Derivatives.	
C_3H_8 or $CH_3 . CH_2 . CH_3$	$\left\{\begin{array}{l} CH_3 . CH_2 . CHO'' \\ CH_3 . CO . CH_3 \end{array}\right.$	Propion-aldehyd. .. Acetone.
C_3H_6 or $CH_2 . CH . CH_3$	$CH_2 . CH . CH_2(HO)$	Allyl-alcohol.

[W. O.]

Royal Institution of Great Britain.

WEEKLY EVENING MEETING,

Friday, January 28, 1870.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

WILLIAM ODLING, M.B. F.R.S.
FULLERIAN PROFESSOR OF CHEMISTRY, R.I.

On Professor Graham's Scientific Work.

THE simple story of Mr. Graham's life, though not without its measure of interest, and certainly not without its lessons, is referred to in the following pages only in illustration of the grander story of his work. Thomas Graham was born in Glasgow, on the 21st Dec., 1805. He entered as a student at the University of Glasgow, in 1819, with a view to becoming ultimately a Minister of the Established Church of Scotland. At that time, the University chair of Chemistry was filled by Dr. Thomas Thomson, a man of very considerable mark, and one of the most erudite and thoughtful chemists of his day. The chair of Natural Philosophy was also filled by a man of much learning, Dr. Meikleham, who appears to have taken a warm personal interest in the progress of his since distinguished pupil. Under these masters, Mr. Graham acquired a strong liking for experimental science, and a dislike to the profession chosen for him by his father; who, for a time at least, seems to have exerted the authority of a parent somewhat harshly, but quite unavailingly, to effect the fulfilment of his own earnest wishes in the matter.

After taking his degree of Master of Arts at Glasgow, in 1826, Mr. Graham worked for nearly two years in the laboratory of the University of Edinburgh, under Dr. Hope. He then returned to Glasgow; and, while supporting himself by teaching, at first mathematics and afterwards chemistry, yet found time to follow up the path of experimental inquiry, on which he had already entered.

His first original paper appeared in the 'Annals of Philosophy' for 1826, its author being at that time in his twenty-first year. It is interesting to note that the subject of this communication, "On the Absorption of Gases by Liquids," forms part and parcel of that large subject of spontaneous gas-movement with which Mr. Graham's name is now so inseparably associated; and that, in a paper communicated to the Royal Society just forty years later, he speaks of the liquefiability of gases by chemical means, in language almost identical with that used in this earliest of his published memoirs.

Having, in the interval, contributed several other papers to the scientific journals, in the year 1829, he published in the 'Quarterly Journal of Science'—the journal, that is to say, of the Royal Institution—the first of his papers relating specifically to the subject of gas-diffusion. It was entitled "A short Account of Experimental Researches on the Diffusion of Gases through each other, and their Separation by Mechanical Means." In the same year, he became Lecturer on Chemistry at the Mechanics' Institute, Glasgow; and in the next year, 1830, achieved the yet more decisive step of being appointed Professor of Chemistry at the Andersonian University. By this appointment he was relieved from anxiety on the score of living; and afforded, in a modest way, the means of carrying out his experimental work.

In 1831, he read, before the Royal Society of Edinburgh, a paper "On the Law of the Diffusion of Gases," for which the Keith prize of the Society was shortly afterwards awarded him. Although several of his earlier papers, and especially that on the Diffusion of Gases, published in the 'Quarterly Journal of Science,' had given evidence of considerable power, it was this paper—in which he established the now well-recognized law that the velocities of diffusion of different gases are inversely as the square roots of their specific gravities—that constituted the first of what may properly be considered his great contributions to the progress of chemical science.

In 1833, he communicated a paper, of scarcely less importance, to the Royal Society of London, entitled "Researches on the Arseniates, Phosphates, and Modifications of Phosphoric Acid." It afforded further evidence of Mr. Graham's quiet steady power of investigating phenomena, and of his skill in interpreting results; or rather of his skill in setting forth the results in all their simplicity, undistorted by the gloss of preconceived notions, so as to make them render up their own interpretation. It is difficult now-a-days to realize the independence of mind involved in Mr. Graham's simple interpretation of the facts, presented to him in this research, by the light of the facts themselves, irrespective of all traditional modes of viewing them. Their investigation let in a flood of light upon the chemistry of that day; and formed a starting-point from which many of our most recent advances may be directly traced. In this paper, Mr. Graham established the existence of two new, and, at that time, wholly unanticipated classes of bodies, namely, the class of polybasic acids and salts, and the class of so-called anhydro-acids and salts. The views of Graham on the polybasicity of phosphoric acid were soon afterwards applied by Liebig to tartaric acid, and by Gerhardt to polybasic acids in general, as we now recognize them. After a long interval, the idea of polybasicity was next extended to radicals and to metals by Williamson and myself successively; afterwards to alcohols by Wurtz, and to ammonias by Hofmann. The notion of anhydro-salts was extended by myself to the different classes of silicates; by Wurtz to the compounds intermediate between oxide of ethylene and glycol; and by other chemists to many different series of organic bodies.

The next most important of the researches, completed by Mr. Graham while at Glasgow, was the subject of a paper communicated to the Royal Society of Edinburgh, in 1835, "On Water as a Constituent of Salts," and of a second paper communicated to the Royal Society of London, in 1836, entitled "Inquiries respecting the Constitution of Salts, &c.," for which latter, a Royal medal of the Society was afterwards awarded. The subject of hydration had yielded him such a harvest of results in the case of phosphoric acid, that it was only natural he should wish to pursue the inquiry farther. Indeed, it is a curious illustration of the persistency of the man, that he never seems to have left out of sight the subjects of his early labours. Almost all his subsequent original work is but a development, in different directions, of his youthful researches on gas-diffusion and water of hydration; and so completely did he bridge over the space intervening between these widely remote subjects, that, with regard to several of his later investigations, it is difficult to say whether they are most directly traceable to his primitive work on the one subject or on the other.

In 1837, on the death of Dr. Edward Turner, Mr. Graham was appointed Professor of Chemistry at University College, London, then called the University of London. On his acceptance of this appointment, he began the publication of his well-known 'Elements of Chemistry,' which appeared in parts, at irregular intervals, between 1837 and 1841. Elementary works, written for the use of students, have necessarily much in common; but the treatise of Mr. Graham, while giving an admirably digested account of the most important individual substances, was specially distinguished by the character of the introductory chapters, devoted to Chemical Physics; wherein was set forth one of the most original and masterly statements of the first principles of chemistry that has ever been placed before the English student. "The Theory of the Voltaic Circle" had formed the subject of a paper communicated by Mr. Graham to the British Association in 1839; and the account of the working of the battery, given in his Elements of Chemistry, and based on the above paper, will long be regarded as a model of lucid scientific exposition.

In 1841, the now flourishing Chemical Society of London was founded; and though Mr. Graham had been, at that time, but four years in London, such was the estimation in which he was held by his brother chemists, that he was unanimously chosen as the first President of the Society. The year 1844 is noticeable in another way. Wollaston and Davy had been dead for some years. Faraday's attention had been diverted from chemistry to those other branches of experimental inquiry in which his highest distinctions were achieved; and, by the death of Dalton in this year, Mr. Graham was left as the acknowledged first of English chemists, as the not unworthy successor to the position of Black, Priestley, Cavendish, Wollaston, Davy, and Dalton.

From the period of his appointment at University College, in 1837, Mr. Graham's time was fully occupied in teaching, in writing, in advising on chemical manufactures, in investigating fiscal and other questions for the Government, and in the publication of various scientific memoirs, several of them possessing a high degree of interest; but it was not till 1846 that he produced a research of any considerable magnitude. In that year he presented to the Royal Society the first part of a paper "On the Motion of Gases," the second part of which he supplied in 1849. For this research, Mr. Graham was awarded a second Royal Medal of the Society in 1850. The preliminary portion of the first part of the paper related to an experimental demonstration of the law of the effusion of gases, deduced from Toricelli's theorem on the efflux of liquids,—a demonstration that was achieved by Mr. Graham with much ingenuity, and without his encountering any formidable difficulty. But the greater portion of the first part, and whole of the second part, of this most laborious paper, were devoted to an investigation of the velocities of transpiration of different gases through capillary tubes; with a view to discover some general law by which their observed transpiration rates might be associated with one another. Again and again, with characteristic pertinacity, Mr. Graham returned to the investigation; but, although much valuable information of an entirely novel character was acquired —information having an important bearing on his subsequent work— the problem itself remained, and yet remains, unsolved. Why, for example, under an equal pressure, oxygen gas should pass through a capillary tube at a slower rate than any other gas is a matter that still awaits interpretation.

Near the end of the same year, 1849, Mr. Graham communicated, also to the Royal Society, a second less laborious, but in the novelty and interest of its results more successful, paper "On the Diffusion of Liquids." It was made the Bakerian lecture for 1850; and was supplemented by further observations communicated to the Society in 1850 and 1851. In his investigation of this subject, Mr. Graham applied to liquids the exact method of inquiry which he had applied to gases just twenty years before, in that earliest of his papers on the subject of gas-diffusion published in the 'Quarterly Journal of Science;' and he succeeded in placing the subject of liquid-diffusion on about the same footing as that to which he had raised the subject of gas-diffusion prior to the discovery of his numerical law.

In 1854, Mr. Graham communicated another paper to the Royal Society, "On Osmotic Force," a subject intimately connected with that of his last previous communication. This paper was also made the Bakerian lecture for the year; but, altogether, the conclusions arrived at were hardly in proportion to the very great labour expended on the inquiry. In the next year, 1855, just five-and-twenty years after his appointment at the Andersonian University, Mr. Graham was made Master of the Mint; and, as a consequence, resigned his Professorship at University College. During the next five years he published no original work.

Thus, at the beginning of the year 1861, Mr. Graham, then fifty-six years of age, had produced, in addition to many less important communications, five principal memoirs; three of them in the highest degree successful; the other two less successful in proportion to the expenditure of time and labour on them, but, nevertheless, of great originality and value. The most brilliant period, however, of his scientific career was to come. In the year 1861, and between then and his death in 1869, Mr. Graham communicated four elaborate papers to the Royal Society; three of them far exceeding in novelty, interest, and philosophic power anything that he had before produced; and the other of them, relating to a certain physical effect of that hydration of compounds, from the consideration of which his attention could never wholly be withdrawn. This least important paper, "On Liquid Transpiration in relation to Chemical Composition," was communicated to the Royal Society in 1861. Of the three greater papers, that "On Liquid-Diffusion applied to Analysis" was communicated also in 1861. For this paper more especially, as well as for his Bakerian lectures "On the Diffusion of Liquids" and "On Osmotic Force," Mr. Graham received, in 1862, the Copley Medal of the Royal Society; and, in the same year, was also awarded the Jecker Prize of the Institute of France. Following in quick succession, his paper "On the Molecular Mobility of Gases" was presented to the Royal Society in 1863; and that "On the Absorption and Dialytic Separation of Gases by Colloid Septa," in 1866. With regard to these three great papers, two of them were each supplemented by a communication to the Chemical Society; while the third was supplemented by four successive notes to the Royal Society, containing an account of further discoveries on the same subject, hardly less remarkable than those recorded in the original paper. The last of these supplementary notes was communicated on June 10th, 1869, but a few months before the death, on September 13th, of the indefatigable but physically broken-down man.

In considering Mr. Graham as a chemical philosopher and lawgiver we find him characterized by a pertinacity of purpose peculiarly his own. Wanting the more striking qualities by which his immediate predecessors, Davy, Dalton, and Faraday, were severally distinguished, he displayed a positive zeal for tedious quantitative work, and a wonderful keen-sightedness in seizing the points which his innumerable determinations of various kinds, conducted almost incessantly for a period of forty years, successively unfolded. His work itself was essentially that of detail, original in conception, simple in execution, laborious by its quantity, and brilliant in the marvellous results to which it led. As regards its simplicity of execution, scarcely any investigator of recent times has been less a friend to the instrument-maker than Mr. Graham. While availing himself, with much advantage, of appliances devised by Bunsen, Poisseuille, Sprengel, and others, all the apparatus introduced by himself was of the simplest character, and for the most part of laboratory construction.

Essentially inductive in his mode of thought, Mr. Graham developed his leading ideas, one after another, directly from experiment, scarcely, if at all, from the prevailing ideas of the time. As well observed by Dr. Angus Smith, "he seemed to feel his way by his work." His records of work are usually, in a manner almost characteristic, preceded each by a statement of the interpretation or conclusion which he formed; but the records themselves are expressed in the most unbiassed matter-of-fact language. Singularly cautious in drawing his conclusions, he announces them from the first with boldness, making no attempt to convince, but leaving the reader to adopt them or not as he pleases. Accordingly, in giving an account of his various researches, Mr. Graham rarely, if ever, deals with argument; but he states succinctly the experiments he has made, the conclusions he has himself drawn, and not unfrequently the almost daring speculations and generalizations on which he has ventured. Some of these speculations, on the constitution of matter, are reproduced in his own words farther on.

Mr. Graham was elected a Fellow of the Royal Society in 1837; Corresponding Member of the Institute of France in 1847; and Doctor of Civil Law of Oxford in 1855.

The remaining pages of this abstract are devoted to an account of his principal discoveries,—the generalizations they suggested to him, and the relations in which they stood to precedent knowledge.

I.

Modifications of Phosphoric Acid.—At the date of Mr. Graham's investigation of this subject, when oxy-salts were usually represented as compounds of anhydrous base with anhydrous acid, the point of greatest importance, with regard to each class of salts, was held to be the ratio borne by the oxygen of the base to the oxygen of the acid. Thus, in the carbonates, this ratio was as 1 to 2; in the sulphates, as 1 to 3; and in the nitrates, as 1 to 5. But with regard to the phosphates, taking common phosphate of soda as a type of phosphates in general, there was a difficulty. Dr. Thomson maintained that, in this salt, the ratio of the oxygen of the base to the oxygen of the acid was as 1 to 2; and his view was substantially supported by Sir Humphry Davy. Berzelius contended, however, that the ratio was as 1 to $2\frac{1}{2}$, or, to avoid the use of fractions, as 2 to 5; but, notwithstanding the excellence of the Swedish chemist's proof, and its corroboration by the researches of others, the simpler and, as it seemed, more harmonious view of Dr. Thomson prevailed very generally in this country. Anyhow, those phosphates in which the oxygen ratio was the same as that in phosphate of soda were taken as the neutral salts. But phosphate of soda was found to have the peculiar and quite inexplicable property of reacting with nitrate of silver to throw down, as a yellow precipitate, a phosphate of silver, in which the proportion of metallic base exceeded that in the original phosphate of soda,—the precipitation of the basic salt being accompanied correlatively by the formation of a strongly acid liquid. According to Berzelius, the ratio of the oxygen of the base to that of the acid, in this yellow precipitate, was as 3 to 5.

In 1821, Mitscherlich, then working in Berzelius's laboratory, obtained, by treating ordinary phosphate of soda with aqueous phosphoric acid, a new crystallizable phosphate of soda, in which the ratio of acid to base was twice as great as that in the ordinary phosphate. This new salt, which had a strongly acid reaction to test paper, he called the bi-phosphate of soda. He observed that it was a hydrated salt; and that while the ratio, in it, of the oxygen of the base to the oxygen of the acid was as 1 to 5, the ratio of the oxygen of the base to the oxygen of the water was as 1 to 2.

In 1827, Mr. Graham's fellow-townsman, and predecessor at the Mechanics' Institute, Dr. Clark, discovered another new phosphate of soda, in which the ratio of the oxygen of the base to the oxygen of the acid was identical with that in the ordinary phosphate, namely, as 2 to 5. But whereas the ordinary phosphate crystallized with 25 proportions of water, the new phosphate crystallized with only 10; and whereas the ordinary phosphate gave a yellow precipitate with nitrate of silver and a strongly acid supernatant liquid, the new phosphate gave a chalk-white precipitate with nitrate of silver and a perfectly neutral supernatant liquid. This new phosphate, being formed by heating the common phosphate to redness, was accordingly designated the pyrophosphate. By dissolution in water and evaporation of the liquid, it could be obtained in the 10-hydrated crystalline state; and by desiccation at a sand-bath heat, the crystalline salt could be again rendered anhydrous. With regard to the 25 proportions of water belonging to the ordinary salt, Dr. Clark noticed that 24 proportions could be driven off by a sand-bath heat, and that this moderate heat did not alter the nature of the salt. He found that the 25th proportion of water, however, could only be driven off by a full red heat; and that, simultaneously with its expulsion, the change in the nature of the salt was effected. But he carefully guarded himself against being supposed to think that the change in properties of the salt was consequent upon an elimination of its water. The driving off of water from salts being, as he justly remarked, a common effect of heat, he regarded this effect as a concomitant only of the peculiar effect of heat in altering the nature of the phosphate.

Other anomalies with regard to phosphoric acid and the phosphates were also known to chemists; and, on referring now to standard chemical works written before the year 1833, the whole subject of the phosphates will be seen to be in the greatest confusion. It was in this year that Mr. Graham communicated his paper, entitled "Researches on the Arseniates, Phosphates, and Modifications of Phosphoric Acid," to the Royal Society.*

In the course of these researches he established the existence of a class of soluble sub-phosphates analogous to the yellow insoluble phosphate of silver; and he showed, with great clearness, that in the three classes of phosphates, namely, the sub-phosphates, the common phosphates, and the bi-phosphates, the ratio borne to the oxygen of the acid by the other oxygen of the salt is the same, namely, as 3 to 5; only that, in the three classes of salts, the non-acid oxygen is divided between different proportions of metallic base and water, thus:

Sub-phosphate of soda	$3NaO.PO_5$.
Common phosphate of soda	$HO.2NaO.PO_5$.
Bi-phosphate of soda	$2HO.NaO.PO_5$.

He further pointed out that, to these three series of salts, there corresponded a definite phosphate of water, or,

Hydrated phosphoric acid	$3HO.PO_5$.

Compounds of one and the same anhydrous acid with one and the same anhydrous base, in different proportions, had long been known; but it was thus that Mr. Graham first established the notion of poly-basic compounds,—the notion of a class of hydrated acids having more than one proportion of water replaceable by metallic oxide, and that successively, so as to furnish more and more basic salts, all preserving, as we should now say, the same type.

Mr. Graham further showed that Dr. Clark's pyrophosphate of soda, like the common phosphate, yielded an acid-salt or bi-phosphate; and that these two compounds were related to a hydrated phosphoric acid, differing in composition and properties from the above-mentioned hydrate, and yielding, after neutralization with alkali, a white instead of a yellow precipitate with nitrate of silver. This series of compounds he expressed by the following formulæ:

Clark's pyrophosphate of soda	$2NaO.PO_5$.
Acid or bi-pyrophosphate of soda	$HO.NaO.PO_5$.
Hydrated pyrophosphoric acid	$2HO.PO_5$.

Lastly, Mr. Graham showed that when the bi-phosphate or bi-pyrophosphate of soda was ignited, there was left a new variety of phosphate, which he called the metaphosphate, having the same proportions of soda and anhydrous phosphoric acid as the original compound, but differing from it in several properties, more particularly in its inability to furnish any acid salt. From this new phosphate he obtained the corresponding hydrated acid, and found it to be identical with that variety of phosphoric acid then, and still, known as glacial phosphoric acid; which had previously been noticed to possess

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* 'Phil. Trans.,' 1833, p. 253.

the distinctive property of causing a precipitate in solutions of albumen. This salt and acid he represented as follows:—

Metaphosphate of soda	$NaO.PO_5$.
Metaphosphoric acid	$HO.PO_5$.

Speaking of the acid obtainable from, and by its neutralization reconverted into, the phosphate, pyrophosphate, and metaphosphate of soda respectively, Mr. Graham remarked:—"The acid, when separated from the base, will possess and retain for some time the characters of its peculiar modification. . . . . But I suspect that the modifications of phosphoric acid, when in what we would call a free state, are still in combination with their usual proportion of base, and that that base is water. Thus the three modifications of phosphoric evidence may be composed as follows:—

Phosphoric acid	$3HO.PO_5$
Pyrophosphoric acid	$2HO.PO_5$
Metaphosphoric acid	$HO.PO_5$;

or they are respectively a triphosphate, a biphosphate, and phosphate of water." These remarks he followed up by analytical evidence, showing the existence of the three hydrates, each in its isolated state.

Just as in his demonstration of the relationship to one another of sub-phosphate of soda, phosphate of soda, bi-phosphate of soda, and common phosphoric acid, Mr. Graham originated the notion of polybasic compounds, so, in his demonstration of the nature of the pyrophosphates and metaphosphates, as bodies differing from the normal compounds by an abstraction of water or metallic base, did he originate the notion of anhydro-compounds—so did he discover, for the first time, an instance of that relationship between bodies which is now known to prevail most extensively among products of organic as well as of mineral origin.

The different properties manifested by phosphoric acid, in its different reputedly isomeric states, having been shown by Mr. Graham to be dependent on a difference of hydration, that is to say on a difference of chemical composition, he was inclined to view the difference of properties observed in the case of other reputedly isomeric bodies as being also dependent on a difference of composition, the difference occasionally consisting in the presence of some minute disregarded impurity. Accordingly, he communicated to the Royal Society of Edinburgh in 1834,* a paper "On Phosphuretted Hydrogen," in which he showed that the spontaneously inflammable and non-spontaneously inflammable varieties of the gas "are not isomeric bodies, but that the peculiarities of the spontaneously inflammable species depend upon the presence of adventitious matter," removable in various ways,

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* 'Edin. Roy. Soc. Trans.,' xiii., 1836, p. 88.

and existing but in very minute proportion.[*] He further showed that the vapour of some acid of nitrogen, apparently "nitrous acid, is capable of rendering phosphuretted hydrogen spontaneously inflammable when present to the extent of *one ten-thousandth part* of the volume of the gas." In connection with this research, may be mentioned Mr. Graham's earlier experiments on the influence of minute impurities in modifying the chemical behaviour of different substances. In some "Observations on the Oxidation of Phosphorus," published in the 'Quarterly Journal of Science,'[†] for 1829, he showed that the presence of $\frac{1}{450}$ of olefiant gas, and even $\frac{1}{4400}$, by volume, of turpentine vapour, in air under ordinary pressure, rendered it incapable of effecting the slow oxidation of phosphorus. He also observed and recorded the influence upon the oxidation of phosphorus of various additions of gas and vapour to air, under different circumstances of pressure and temperature.

II.

Hydration of Compounds.—In the earliest of Mr. Graham's published memoirs, that "On the Absorption of Gases by Liquids,"[‡] he contended that the dissolution of gases in water, at any rate of the more soluble gases, is a chemical phenomenon, depending on their essential property of liquefiability being brought into play by their reaction with the solvent, that is to say by their hydration. The results of some further work on the same subject he published under the title of "Experiments on the Absorption of Vapours by Liquids."[§]

In 1827, he gave to the Royal Society of Edinburgh "An Account of the Formation of Alcoholates, definite Compounds of Salts and Alcohol analogous to the Hydrates."[||] In this paper, after a description of some experiments on the desiccation of alcohol, he showed that anhydrous chloride of calcium, nitrate of lime, nitrate of magnesia, chloride of zinc, and chloride of manganese have the property of uniting with alcohol, as with water, to form definite compounds. The crystalline compound with chloride of zinc, for instance, containing 15 per cent. of alcohol, he represented by the formula $ZnCl.\ 2\,C_2H_3O$; corresponding to the modern formula $ZnCl_2.\ 2C_2H_6O$.

In 1835, Mr. Graham communicated a paper, also to the Royal Society of Edinburgh, "On Water as a Constituent of Salts."[¶] In this paper he showed more particularly that the so-called magnesian sulphates, crystallizing usually with 7, 6, or 5 proportions of water, gave up all but the last proportion of water at a moderate heat, but retained this last proportion with great tenacity. The comparatively stable mono-hydrated salts, — monohydrated sulphate of zinc, for

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[*] It was afterwards isolated by P. Thenard.

[†] 'Quart. Journ. Sci.,' ii., 1829, p. 83.

[‡] Thomson, 'Ann. Phil.,' xii., 1826, p. 69.

[§] 'Edin. Journ. Sci.,' viii., 1828, p. 326.

[||] 'Edin. Roy. Soc. Trans.,' xi., 1837, p. 175.

[¶] Ibid., xiii., 1836, p. 297.

instance, $ZnO.SO_3.HO$,—he regarded as the analogues of crystallizable sulphuric acid $HO.SO_3.HO$. He showed further that the firmly-retained water of sulphate of zinc, for instance, differed from the firmly-retained water of phosphate of soda, in not being basic, or replaceable, that is to say, by metallic oxide. He conceived, however, that in the double sulphates, potassio-sulphate of zinc, for instance, $ZnO.SO_3$, $KO.SO_3$, the water of the compound, $ZnO.SO_3.HO$, was replaced by alkali-sulphate, and he accordingly designated the water of this last, and of similar compounds, by the name of saline or constitutional water.

In the following year, 1836, Mr. Graham communicated to the Royal Society of London an elaborate paper, entitled "Inquiries respecting the Constitution of Salts, of Oxalates, Nitrates, Phosphates, Sulphates, and Chlorides." * In it are recorded careful analyses of very many salts, more particularly in respect to their water of hydration; with remarks upon the greater or less tenacity with which the water is retained in different instances. In this paper he put forward the notion that truly basic salts are nevertheless neutral in constitution; and that the excess of metallic base does not stand in the relation of a base to the anhydrous acid, but as a representative of the water of hydration of the neutral salt. He illustrated this position by a comparison of the definite hydrate of nitric acid with other hydrated nitrates, thus:

Hydrated nitric acid, sp. gr. 1·42	$HO.NO_5.3\,HO$
Hydrated nitrate of zinc	$ZnO.NO_5.3\,HO$
Hydrated nitrate of copper	$CuO.NO_5.3\,HO$
Basic nitrate of copper	$HO.NO_5.3\,CuO$

He contended that, in the last cupric salt, it is the water and not the oxide of copper which acts as a base; and, in support of this view, he remarked that if the water of the salt were water of hydration simply, it ought, in presence of so large an excess of metallic base, to be very readily expelled by heat; whereas it is actually inexpulsable by any heat whatever, short of that effecting an entire decomposition of the salt. Again, he pointed out that when the strongest nitric acid $HO.NO_5$, is added, in no matter what excess, to oxide of copper, the basic salt is alone produced, apparently by a direct addition of the oxide of copper to the nitrate of water.

In 1841, Mr. Graham gave to the Chemical Society "An Account of Experiments on the Heat disengaged in Combination." † These experiments included numerous determinations of the heat evolved in the hydration of salts, and more particularly of the sulphates, including sulphate of water, or hydrated sulphuric acid. Starting from oil of vitriol $HO.SO_3$, he found that each successive addition of a proportion of water HO, evolved an additional, but successively

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* 'Phil. Trans.,' 1837, p. 47.

† 'Chem. Soc. Mem.,' i., p. 106.

smaller and smaller increment of heat; and that, even after the addition of fifty proportions of water to the acid, the further addition of water was yet followed by a perceptible development of heat.

The relation of ether to alcohol being regarded as that of an oxide to its hydrate, and expressed by the formulæ C_4H_5O, and $C_4H_5O.HO$, the conversion of alcohol into ether became a matter of dehydration; and, accordingly, could not escape the examination of Mr. Graham, who, in 1850, presented to the Chemical Society some "Observations on Etherification."* The process of manufacture consisting in the distillation of a mixture of alcohol with sulphuric acid, and being attended by an intermediate production of sulphate of ether or sulphethylic acid, the substitution of ether for the basic water of sulphuric acid at one temperature, and the reverse substitution of water for the basic ether of sulphethylic acid at a higher temperature, had been represented as depending on the augmented elasticity of the ether vapour at the higher temperature. Mr. Graham showed, however, that ether could be very readily formed by heating the mixture of sulphuric acid and alcohol in sealed tubes—that is, under conditions in which the augmentation of volatility due to heat was *pari passu* counterbalanced by the diminution of volatility due to pressure. Altogether, Mr. Graham supported the contact theory of ether formation, as opposed to the then received reaction theory; but several of his experiments afforded clear, though indeed supererogatory, support to the reaction theory soon afterwards introduced by Williamson.

In addition to the memoirs cited above, the question of hydration formed an express or incidental subject of many other of Mr. Graham's investigations. It is noteworthy that, for him, osmosis became a mechanical effect of the hydration of the septum; that the interest attaching to liquid-transpiration was the alteration in rate of passage consequent on an altered hydration of the liquid; that the dialytic difference between crystalloids and colloids depended on the dehydration of the dialytic membrane by the former class of bodies only; and similarly in many other instances.

III.

Movements of Liquids under Pressure. Transpiration.—That the velocities with which different liquids, under the same pressure, issue from a hole in the side or bottom of a vessel should be inversely as the square roots of their respective specific gravities is a proposition deducible from well-known mechanical principles. As demonstrated, however, by Dr. Poiseuille, this law is not applicable to the case of liquids issuing under pressure through capillary tubes. In addition to determining experimentally the laws of the passage of the same liquid—that the velocity is directly as the pressure, inversely as the length of the capillary, and directly as the fourth power of the diameter; and that it is accelerated by elevation of temperature—

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* 'Chem. Soc. Journ.,' iii., p. 24.

Dr. Poiseuille further showed that the rate of passage of different liquids through capillary tubes is for the most part a special property of the particular liquids; and that while the rate of passage of water, for instance, is scarcely affected by the presence of certain salts in solution, it is materially accelerated by the presence of chlorides and nitrates of potassium and ammonium, and materially retarded by the presence of alkalies. He also showed that while the rate of passage of absolute alcohol is much below that of water, the rate of passage of alcohol diluted with water in such proportion as to form the hydrate, $H_6C_2O.3Aq$, is not only much below that of alcohol, but also below that of any other mixture of alcohol and water.

Some time after Dr. Poiseuille's death, Mr. Graham, starting from this last observation, took up the inquiry. Giving to the phenomenon itself the name of "transpiration," which he had previously applied to the similar passage of gases through capillary tubes, he communicated his results to the Royal Society in a paper "On Liquid Transpiration in relation to Chemical Composition."* The method he followed in his experiments was precisely that of Dr. Poiseuille, and the principal results at which he arrived are the following:—

1. That dilution with water does not effect a *pari passu* alteration in the transpiration velocity of certain liquids; but that dilution up to a certain point, corresponding to the formation of a definite hydrate, not unfrequently retards the transpiration velocity (or increases the transpiration time) to a maximum, from which the retardation gradually diminishes with further dilution. This is well seen in the following table, giving the transpiration times of certain liquids in their undiluted state, and also the maximum transpiration times observed with the same liquids when diluted with a regularly increasing quantity of water, the particular dilution causing the maximum retardation corresponding in every case to the production of a definite hydrate.

		Transpiration Times.		
Water	H_2O ..	1·000	1·000	x Aq.
Sulphuric acid ..	H_2SO_4 ..	21·651	23·771	H_2SO_4 . Aq.
Nitric acid	HNO_3 ..	·990	2·103	2 HNO_3.3 Aq.
Acetic acid	$H_4C_2O_2$ ..	1·280	2·704	$H_4C_2O_2$ .2 Aq.
Alcohol	H_6C_2O ..	1·195	2·787	H_6C_2O.3 Aq.
Wood-spirit	$H_4C\,O$ ..	·630	1·802	$H_4C\,O$.3 Aq.
Acetone	H_6C_3O ..	·401	1·604	H_6C_3O.6 Aq.

2. That the transpiration times of homologous liquids increase regularly with the complexity of the several molecules constituting terms of the same series—certain first terms of the different series,

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* 'Phil. Trans.,' 1861, p. 373.

however, presenting some anomalies, as was indeed to be expected. The transpiration times of the fatty ethers are given below in illustration. Similar results were obtained with the series of fatty acids and their corresponding alcohols.

			Transpiration Times.
	Water	H_2O ..	1·000
Ethers	Formic	$H_6C_3O_2$ ..	·511
	Acetic	$H_8C_4O_2$ ..	·553
	Butyric	$H_{12}C_6O_2$ ..	·750
	Valeric	$H_{14}C_7O_2$ ..	·827

In this paper, Mr. Graham also recorded the results of two very full series of determinations of the transpiration rates of water at different temperatures between 0° and 70°; and of two similar series of experiments made with alcohol. The transpiration velocity of water was found to increase uniformly from 0·559 at 0° to 1·000 at 20°, and thence to 2·350 at 70°; and correlatively the transpiration times were found to decrease in the same proportion. The results obtained with alcohol were precisely similar.

IV.

Diffusion of Liquids.—Mr. Graham's early study of the spontaneous movements of gases, so as to mix with one another, naturally led him to investigate the similarly occurring movements of liquids. His results formed the subject of two papers communicated to the Royal Society, one in 1849 "On the Diffusion of Liquids,"* and the other in 1861 "On Liquid Diffusion applied to Analysis."† In the series of experiments, described in the first of these papers and in two supplementary communications, an open wide-mouthed vial, filled with a solution of some salt or other substance, was placed in a jar of water; when, in course of time, a portion of the dissolved salt, described as the diffusate, passed gradually from the vial into the external water. By experimenting in this manner, the amounts of diffusate yielded by different substances were found to vary greatly. Thus, under precisely the same conditions, common salt yielded twice as large a diffusate as Epsom salt, and this latter twice as large a diffusate as gum-arabic. Every substance examined was in this way found to have its own rate of diffusibility in the same liquid medium—the rate varying with the nature of the medium—whether water or alcohol, for instance. It is noticeable that the method of vial-diffusion resorted to in these experiments, is exactly similar to that employed by Mr. Graham in

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* 'Phil. Trans.,' 1850, pp. 1, 805; 1851, p. 483.

† Ibid., 1861, p. 183.

his earliest experiments on the diffusion of gases, published in the 'Quarterly Journal of Science' for 1829.

In the series of experiments recorded in the paper "On Liquid Diffusion applied to Analysis," the solution of the salt to be diffused, instead of being placed in a vial, was conveyed by means of a pipette to the bottom of a jar of water; when, in course of time, the dissolved salt gradually rose from the bottom, through the superincumbent water, to a height or extent proportional to its diffusibility. The results of this method of jar-diffusion were found to bear out generally those attained by the method of vial-diffusion; while they further showed the absolute rate or velocity of the diffusive movement. Thus, during a fourteen days' aqueous diffusion from ten per cent. solutions of gum-arabic, Epsom salt, and common salt respectively, the gum-arabic rose only through $\frac{7}{14}$ths of the superincumbent water, or to a height of 55·5 millimètres; the Epsom salt rose through the whole $\frac{14}{14}$ths of superincumbent water, or to a height of 111 millimètres; and the common salt not only rose to the top, but would have risen much higher, seeing that the uppermost or fourteenth stratum of water, into which it had diffused, contained about fifteen times as much salt as was contained in the uppermost or fourteenth stratum of water into which the Epsom salt had diffused.

But of all the results obtained, the most interesting, from their bearing on various natural phenomena, were those on the partial separation of different compounds from one another, brought about by their unequal diffusibility. Thus, with a solution of equal weights of common salt and gum-arabic placed in the diffusion-vial, for every 100 milligrammes of salt not more than 22·5 milligrammes of gum were found to pass into the external water; or a separation of the salt from the gum, to this large extent, took place spontaneously by the excess of its own proper diffusive movement. Again, when a solution, containing five per cent. of common salt and five per cent. of Glauber's salt, was submitted for seven days to the process of jar-diffusion, the upper half, or $\frac{7}{14}$ths, of superincumbent water was found to contain 380 milligrammes of common salt and only 53 grammes of Glauber's salt; or the ratio of common salt to Glauber's salt in the upper half of the liquid was as 100 to 14, the ratio in the original stratum of solution being as 100 to 100. And not only a partial separation of mixed salts, but even a partial decomposition of chemical compounds was found to result from the process of liquid diffusion. Thus the double sulphate of potassium and hydrogen, when submitted to diffusion, underwent partial decomposition into the more diffusible sulphate of hydrogen and the less diffusible sulphate of potassium; and, similarly, ordinary alum, a double sulphate of aluminum and potassium, underwent partial decomposition into the more diffusible sulphate of potassium, and the less diffusible sulphate of aluminum. Strictly speaking, perhaps, the decomposition of the original salts was not caused by, but only made evident by, the difference in diffusibility of the products.

As a general result of his experiments, Mr. Graham inferred that liquid diffusibility is not associated in any definite way with chemical composition or molecular weight. Thus he found the complex organic bodies picric acid and sugar to have much the same diffusive rates as common salt and Epsom salt respectively. Isomorphous compounds, however, proved for the most part to be equi-diffusive; although the groups of equi-diffusive substances habitually comprehended other than those which were isomorphous.

Observing further that, in many cases, the diffusion-rates of different equi-diffusive groups stood to one another in some simple numerical relation, Mr. Graham remarked that, "In liquid diffusion we no longer deal with chemical equivalents or the Daltonian atoms; but with masses even more simply related to each other by weight." We may suppose that the chemical atoms "group together in such numbers as to form new and larger molecules of equal weights for different substances, or . . . . . of weights which appear to have a simple relation to each other;" and he inferred that the relative weights of these new molecules would be inversely as the square roots of the observed diffusion rates of the substances—that is inversely as the squares of their diffusion times. Thus the squares of the times of equal diffusion of hydrate, nitrate, and sulphate of potassium being 3, 6, and 12, the densities of their diffusion molecules would be as the reciprocals of these numbers, or as 4, 2, and 1.

Lastly, in comparing highly diffusive substances on the one hand, with feebly diffusive substances on the other, one broad dissimilarity became apparent, namely, that highly diffusible substances affected the crystalline state, while feebly diffusive substances were amorphous, and characterized, in particular, by a capability of forming gelatinous hydrates. Hence the distinction established by Mr. Graham between highly diffusive bodies, or *crystalloids*, and feebly diffusive bodies, or *colloids*. Compounds capable of existing both in the crystalline and gelatinous states he found to be possessed of two distinct diffusive rates corresponding respectively each to each.

V.

Dialysis and Osmose.—The subject of dialysis was included in the paper "On Liquid Diffusion applied to Analysis," referred to in the preceding section; and some further results were communicated, in 1864, to the Chemical Society, in a paper "On the Properties of Silicic Acid, and other analogous Colloidal Substances." *

In the course of his experiments on diffusion, Mr. Graham made the curious discovery that highly diffusible crystalloid bodies were able to diffuse readily, not only into free water, but also into water that was already in a low form of combination, as in the substance of a soft solid, such as jelly or membrane. Common salt, for instance, was

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* 'Chem. Soc. Journ.,' xvii., p. 318.

found to diffuse into a semi-solid mass of jelly, almost as easily and as extensively as into a similar bulk of free water; but the introduction of a gelatinous substance, though not interfering in any appreciable degree with the diffusion of a crystalloid, was found to arrest almost entirely the diffusion of a colloid. The colloid, of but little tendency to diffuse into free water, proved quite incapable of diffusing into water that was already in a state of combination, however feeble. Hence, although the partial separation of a highly diffusible from a feebly diffusible substance might be effected by the process of free diffusion into water, a much better result was obtained by allowing the diffusion to take place into, or through, the combined water of a soft solid such as a piece of membrane or parchment-paper. In the process of dialysis, then, crystalloid and colloid bodies, existing in solution together, are separated from one another by pouring the mixed solution into a shallow tray of membrane or parchment-paper, and letting the tray rest on the surface of a considerable excess of water, once or twice renewed. By this means the crystalloid, in process of time, diffuses completely away through the membranous septum into the free water; but the colloid, being quite incapable of permeating the membrane, however thin, is retained completely on the tray, unable to reach the free water on the other side.

By means of the process of dialysis, Mr. Graham succeeded in obtaining various colloid organic substances, such as tannin, albumen, gum, caramel, &c., in a very pure state; some of them, indeed, in a state of purity exceeding any in which they had before been met with. But the most curious results were obtained with different mineral substances, usually thrown down from their dissolved salts in the state of gelatinous or colloid precipitates. Most of these precipitates being soluble in some or other crystalloid liquid, on submitting the so-produced solutions to dialysis, the crystalloid constituents diffuse away, leaving the colloid substances in pure aqueous solution. By proceeding in this manner, Mr. Graham was able to obtain certain hydrated forms of silica, ferric oxide, alumina, chrome, prussian blue, stannic acid, titanic acid, tungstic acid, molybdic acid, &c., &c., in the state of aqueous solution,—these bodies having never before been obtained in solution, save in presence of strongly acid or alkaline compounds serving to dissolve them. Altogether, the production of these colloid solutions of substances, such as silica and alumina—in their crystalline state, as quartz and corundum, completely insoluble—threw an entirely new light upon the conditions of aqueous solution.

The colloidal solutions, obtained as above, of substances usually crystalline, were found to be exceedingly unstable. Either spontaneously, or on the addition of some or other crystalloid reagent, even in very minute quantity, they pectized or became converted into solid jellies. Hence Mr. Graham was led to speak of two colloidal states; the peptous, or dissolved, and the pectous, or gelatinized. In addition to their power of gelatinizing, their mutability, their non-crystalline habit, and their low diffusibility, substances in the colloid state were found to be further characterized by their chemical inertness and by their high combining weights. Thus the saturating power of colloid silica was only about $\frac{1}{36}$th of that of the ordinary acid.

In his supplementary paper communicated to the Chemical Society, Mr. Graham showed how the pectous forms of different mineral colloids could, in many cases, be reconverted into their peptous forms. He further showed how the water of different peptous and pectous colloids could be mechanically displaced by other liquids, as alcohol, glycerine, sulphuric acid, &c. To the different classes of compounds, so formed, he gave distinctive names. Thus, the alcoholic solution and jelly, of silicic acid for instance, he designated as the alcosol and alcogel respectively.

Closely associated with the passage of different liquids through membranes is the action, known as endosmose, discovered by Dutrochet. Mr. Graham's principal results on this subject are recorded in a very elaborate paper "On Osmotic Force," communicated to the Royal Society in 1854;[*] but a few further results, and a statement of his final views, are contained in the paper, referred to immediately above, "On Liquid Diffusion applied to Analysis." When the solution of a saline or other compound is separated from an adjacent mass of water by a membranous septum, a greater or less quantity of the water very commonly passes through the septum into the solution; and if the solution be contained in a vessel of suitable construction, having a broad membranous base and a narrow upright stem, the water, in some cases, flows into the vessel through the membrane, with a force sufficient to raise and sustain a column of 20 inches or more of liquid in the stem. The problem is to account for this flow; which, with acid fluids more particularly, takes place in the reverse direction—*i. e.* from the solution into the water.

In the course of his experiments, Mr. Graham examined the osmotic movement produced with liquids of most diverse character; employing osmometers of animal membrane, albuminated calico, and baked earthenware. His results were, moreover, observed and recorded in very great detail. As an illustration of these results, it may be mentioned that with 1 per cent. solutions in the membranous osmometer, the liquid rose in the stem 2 millimètres in the case of common salt, 20 millimètres with chloride of calcium, 88 millimètres with chloride of nickel, 121 millimètres with chloride of mercury, 289 millimètres with proto-chloride of tin, 351 millimètres with chloride of copper, and 540 millimètres with chloride of aluminum. Mr. Graham showed, further, in opposition to the views of Dutrochet, that the velocity of the osmotic flow was not proportional to the quantity of salt or other substance originally contained in the solution; and that the flow did not depend on capillarity, as Dutrochet had inferred; or yet on diffusion, as some of his own experiments

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[*] 'Phil. Trans.,' 1854, p. 177.

might be thought to indicate. Eventually he was led to the conclusion that osmose was essentially dependent on a chemical action, taking place between one or other of the separated liquids and the material of the septum. He appears to have held somewhat different views of the nature of this chemical action at different times; and not to have considered it as being in all cases of the same character.

The following extracts, expressing his latest views on the subject, are taken from the conclusion of his paper, "On Liquid Diffusion applied to Analysis."

"It now appears to me that the water movement in osmose is an affair of hydration and of de-hydration in the substance of the membrane, or other colloid septum, and that the diffusion of the saline solution placed within the osmometer has little or nothing to do with the osmotic result otherwise than as it affects the state of hydration of the septum. . . . . . Placed in pure water, such colloids (as animal membrane) are hydrated to a higher degree than they are in neutral saline solutions. Hence the equilibrium of hydration is different on the two sides of the membrane of an osmometer. The outer surface of the membrane being in contact with pure water, tends to hydrate itself in a higher degree than the inner surface does, the latter surface being supposed to be in contact with a saline solution. When the full hydration of the outer surface extends through the thickness of the membrane, and reaches the inner surface, it there receives a check. The degree of hydration is lowered, and water must be given up by the inner layer of the membrane, and it forms the osmose. . . . . . Far from promoting this separation of water, the diffusion of the salt throughout the substance of the membrane appears to impede osmose by equalizing the condition as to saline matter of the membrane through its whole thickness. The advantage which colloidal solutions have in inducing osmose, appears to depend in part upon the low diffusibility of such solutions, and their want of power to penetrate the colloidal septum."

VI.

Movements of Gases under Pressure. Effusion and Transpiration.— The mechanical law of the passage of different gases under the same pressure through a mere perforation, as of the passage of different liquids, being that the velocities are inversely as the square roots of the specific gravities, Mr. Graham subjected this law to an experimental verification, and made known his results in a paper communicated to the Royal Society in 1846. The mode of experimenting was as follows:—A jar standing on the plate of an air-pump was kept vacuous by continued exhaustion, and a measured quantity of gas allowed to find its way into the jar through a minute aperture in a thin metallic plate. The admission of 60 cubic inches of dry air into the vacuous, or nearly vacuous jar, being arranged to take place in about 1000 seconds, the times of passage of the same volume of air were found not to vary from each other by more than two or three seconds in successive experiments.

Operating with different gases, the relative times of passage, or of "effusion," as it was denominated by Mr. Graham, proved to be approximatively identical with the square roots of the specific gravities of the several gases; or, in other words, their velocities of effusion were shown experimentally to be inversely as the square roots of their specific gravities. The rate of effusion of a mixed gas corresponded in most cases with the calculated mean rate of its constituents; but the rates of effusion of the light gases, marsh gas and hydrogen, were very disproportionately retarded by the admixture with them, even to a small extent, of the heavier gases, oxygen and nitrogen.

Passing from the study of the effusion of gases through a perforated plate, Mr. Graham next submitted their "transpiration" through a capillary tube to a similarly conducted experimental inquiry. His results were communicated to the Royal Society in two very elaborate papers, "On the Motion of Gases," Parts I. and II.,* the first part containing also his above-described results on the effusion of gases. With a very short capillary, the relative rates of passage of different gases were found to approximate to their relative rates of effusion; but with every elongation of the capillary, a constantly-increasing deviation from these rates was observed—the increase of the deviation, however, becoming less and less considerable with each successive increment of elongation, until, when the tube had acquired a certain length in proportion to its diameter, a maximum deviation of the relative rates of passage of the different gases from their relative rates of effusion was arrived at. These ultimate rates of passage, unaffected in relation to each other by further elongation of the capillary, constitute the true transpiration velocities of the different gases, as distinguished from their velocities of effusion. Of all the gases experimented on, oxygen was found to have the longest transpiration time, or slowest transpiration velocity. In the following Table its time of transpiration is taken as unity, and the times of a few other gases compared therewith. In other columns are given the specific gravities of the same gases, referred to the specific gravity of air as unity; and the square roots of their specific gravities, which also express their relative times of effusion.

	Specific Gravity.	$\sqrt{\text{Specific Gravity.}}$	Transpiration Time.
Hydrogen	·069	·263	·437
Marsh gas ..	·559	·747	·551
Nitrogen	·971	·985	·877
Oxygen	1·105	1·051	1·000
Carbonic gas ..	1·529	1·236	·730

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* 'Phil. Trans.,' 1846, p. 573; 1849, p. 349.

That gas transpiration has no direct relation to gas specific gravity is shown by the transpiration times of oxygen and nitrogen exceeding the transpiration times both of the much lighter hydrogen and marsh gas, and of the much heavier carbonic gas. Again, ammonia, olefiant gas, and cyanogen, with the different specific gravities ·590, ·978, and 1·806 respectively, have the almost identical transpiration times ·511, ·505, and ·506; or, approximatively, half the transpiration time of oxygen, 1·000. Nevertheless the transpiration times of oxygen and nitrogen are directly as their specific gravities; and further, the specific gravities of nitrogen, carbonic oxide, and nitric oxide being ·971, ·968, and 1·039, their transpiration times are ·877, ·874, and ·876 respectively. But then olefiant gas, with the same specific gravity ·978, has the much shorter transpiration time ·505; and similarly in other cases. Altogether the discordance between transpiration and specific gravity is of greater frequency than the accordance; but still the circumstance of gases having the same, or about the same, specific gravity, having also the same, or about the same, rate of transpiration, is of too frequent occurrence to be merely accidental.

As a rule, the observed transpiration rate of a mixture of gases corresponded with the calculated mean rate of its constituents; but the transpiration rates of the light gases, hydrogen and marsh gas, were found to be disproportionately retarded to a greater extent even than their effusion rates by the admixture with them of heavier gases. Further, by employing mixtures of gas and vapour, Mr. Graham extended his inquiry so as to include a determination of the transpiration times of several vapours; the results being calculated on the assumption that the observed transpiration time of the mixture was the mean of the transpiration times of the permanent gas and of the coercible vapour experimented on. In this way the transpiration time of ether vapour, sp. gr. 2·586, was shown to be identical with that of hydrogen gas, sp. gr. 0·069; and the transpiration time of carbonic sulphide vapour, sp. gr. 2·645, identical with that of sulphuretted hydrogen gas, sp. gr. 1·191.

With respect to gas transpiration in general, the rates of transpiration of different gases were found to be independent of the nature of the material of the capillary; apparently from the capillary, of what material soever, becoming lined with a film of gas, with which alone the current of gas could come in contact; so that the friction was purely intestine, and suggestive of a sort of viscosity in the gas itself. The rate of passage was further shown to be inversely as the length of the capillary; and directly, in some high but undetermined ratio, as its diameter. Lastly, the rate of "effusion" of a given volume of any particular gas being independent of pressure and temperature, the rate of transpiration of a given volume of any particular gas was observed to vary directly with its variation of density, whether the result of alteration of pressure or of temperature; 100 cubic inches of dense air, for example, transpiring more rapidly than 100 cubic inches of tenuous air, in proportion to the excess of density.

Speaking of the importance and fundamental nature of the physical properties manifested by bodies in the gaseous state, and of the extent of his own inquiries on gas-transpiration, Mr. Graham observed,—"It was under this impression that I devoted an amount of time and attention to that class of constants (transpiration-velocities) which might otherwise appear disproportionate to their value and the importance of the subject. As the results, too, were entirely novel, and wholly unprovided for in the received view of the gaseous constitution, of which indeed they prove the incompleteness, it was the more necessary to verify each fact with the greatest care."

VII.

Diffusion of Gases.—In 1801, Dalton, in an essay "On the Constitution of mixed Gases, and particularly of the Atmosphere," propounded the now celebrated view that "where two elastic fluids denoted by A and B are mixed together, there is no mutual repulsion amongst their particles; that is, the particles of A do not repel those of B, as they do one another; consequently the pressure or whole weight upon any one particle arises solely from those of its own kind." During the act of admixture, "the particles of A meeting with no repulsion from those of B . . . . would instantaneously recede from each other as far as possible under the circumstances, and consequently arrange themselves just as in a void space." At the beginning of 1803, in a supplementary paper "On the tendency of Elastic Fluids to Diffusion through each other," he made known the remarkable action of intermixture which takes place, even in opposition to the influence of gravity, when any two gases are allowed to communicate with each other. Thus, in a particular experiment, he showed that when a vial of hydrogen is connected with a vial of carbonic gas by means of a narrow piece of tubing, so that the vial of light hydrogen may be inverted over the other vial of heavy carbonic gas, the heavy carbonic gas actually ascends through the light hydrogen, and the light hydrogen descends through the heavy carbonic gas until the uniform admixture of the two gases with each other is effected. The subject was afterwards investigated by Berthelot, who, in a series of experiments performed with great care, while opposing Dalton's theoretical conclusions, corroborated his results; and indicated further the high diffusiveness of hydrogen. Here it was that Mr. Graham took up the inquiry. The first of his papers relating directly to the subject of gas-diffusion appeared in the 'Quarterly Journal of Science' for 1829, under the title, "A short Account of Experimental Researches on the Diffusion of Gases through each other, and their Separation by Mechanical Means."* The mode of proceeding adopted in these researches was as follows:—Each gas experimented on was allowed to diffuse from a horizontally placed bottle through a narrow tube,

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* 'Quart. Journ. Sci.,' ii., 1829, p. 83.

directed either upwards or downwards according as the gas was heavier or lighter than air, so that the diffusion always had to take place in opposition to the influence of gravity. The result was that equal volumes of different gases escaped in very unequal times, the rapidity of the escape having an inverse relation to the specific gravity of the gas. Thus hydrogen was found to escape four or five times more quickly than the twenty-two times heavier carbonic gas. Again, with a mixture of two gases, the lightest or most diffusible of the two was found to leave the bottle in largest proportion, so that a sort of mechanical separation of gases could be effected by means of their unequal diffusibility. Most of these last results were obtained by allowing the gaseous mixture to diffuse into a limited atmosphere of some other gas or vapour, capable of subsequent removal by absorption or condensation.

But these methods of operating, by free or adiaphragmatic diffusion, were soon abandoned by Mr. Graham for the more practicable method of diffusion through porous septa. Once again, however, many years afterwards, in a paper "On the Molecular Mobility of Gases," to be more fully considered presently, Mr. Graham made some additional and very curious observations on the free diffusion of hydrogen and carbonic gas into surrounding air, showing the absolute velocities of the molecular movements in each of the two cases. A glass cylinder, ·57 mètre high, had the lowest tenth of its height filled with carbonic gas. Then, after different intervals of time, the uppermost tenth of air in the cylinder was drawn off and examined. In five minutes the carbonic gas in this upper tenth of air amounted to ·04, and in seven minutes to 1·02 per cent.; or 1 per cent. of carbonic gas had diffused to the distance of half-a-mètre in seven minutes, being at the rate of 73 millimètres per minute. Now, the conditions of this movement always prevail in the air of the atmosphere, and, using the words of Mr. Graham, "it is certainly most remarkable that in perfectly still air its molecules should spontaneously alter their position, and move to a distance of half-a-mètre in any direction in the course of five or six minutes." By similar experiments made with an inverted cylinder, 1 per cent. of hydrogen was found to diffuse downwards at the rate of 350 millimètres per minute, or about five times as rapidly as the carbonic gas diffused upwards.

With regard to Mr. Graham's experiments on the diffusion of gases through porous septa, his earliest results on this subject were communicated to the Royal Society of Edinburgh, in a paper "On the Law of the Diffusion of Gases," already referred to as the first-born of what may be considered his great papers.* Prior even to Dalton's above-mentioned experiments on free diffusion, Dr. Priestley, when transmitting different gases through stoneware tubes surrounded by burning fuel, perceived that the tubes were porous; and that not only was

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* 'Edin. Roy. Soc. Trans.,' xii., 1834, p. 222.

there an escape of the gas, under pressure, from within the tube outwards to the fire, but that there was also a penetration of the exterior gases of the fire into the tube, notwithstanding the superior pressure of the current of gas passing through the tube.

Mr. Graham, however, appears to have had his attention originally directed to the study of the transmission of gases through porous diaphragms by the curious observation and experiments of Döbereiner, who, having occasion to collect and store some quantities of hydrogen over water, accidentally made use of a fissured jar, and was surprised to find that the water of the pneumatic trough rose in this jar to the height of an inch and a half in twelve hours, and to not far short of three inches in twenty-four hours. Having assured himself of the constancy of the phenomenon, Döbereiner attributed it to capillary action, conceiving hydrogen to be alone attractable by, and, on account of the assumed minuteness of its atoms, admissible through the fissure. In repeating Döbereiner's experiments, however, Mr. Graham soon observed that the escape of hydrogen outwards was always accompanied by a penetration of air inwards, the volume of air finding an entrance through the fissure amounting to about one-fourth of the volume of hydrogen making its escape; or the fissure proved permeable to the grosser air as well as to the finer hydrogen. Having arrived at this point, he replaced the fissured jar by an instrument admitting of much greater experimental precision. For the jar itself he substituted a piece of glass tube about half-an-inch in diameter and from eight to fourteen inches long, and for the fissure in the jar he substituted a plate of stucco serving to close one end of the tube. Operating with a diffusion-tube of this kind standing in a jar of water, it was found, as in Dalton's experiments, that the two gases, say external air and internal hydrogen, exhibited a powerful tendency to intermix or change places with each other; but more than this, it was found that the air did not exchange with its own volume of hydrogen, but instead with 3·8 times its volume. Using the word diffusion-volume to express the bulks of different gases exchanging thus with one another by the process of diffusion, the diffusion-volume of hydrogen would be 3·8, that of air being taken as 1. Similarly, it was ascertained that every gas has a diffusion-volume which is peculiar to itself, and is indeed inversely as the square root of its specific gravity; and since the unequal diffusion volumes of different gases are consequences of their unequal diffusion velocities, it follows that the relative velocities at which different gases diffuse into one another, by virtue of their own inherent mobility, are identical with those at which they effuse under pressure into a vacuum—a result quite in accordance with, and indeed deducible from, Dalton's aphorism. But although the relative rates of effusion and diffusion are alike, it is important, wrote Mr. Graham, in the later paper already quoted from, "to observe that the phenomena of effusion and diffusion are distinct and essentially different in their nature. The effusion movement affects masses of gas, the diffusion movement affects molecules; and a gas is usually carried by the former kind of impulse with a velocity many thousand times as great as is demonstrated by the latter." *

Thus the result arrived at by Mr. Graham, in his original paper, was the enunciation of the now well-recognized law of the diffusion of gases; but, some thirty years afterwards, he again subjected the phenomena of gas-diffusion to an elaborate experimental investigation,—going over the old and penetrating into new ground with an activity by no means impaired, and with intellectual powers largely expanded by increase of years. His results were communicated to the Royal Society of London, in a paper "On the Molecular Mobility of Gases," † and it is impossible to read this and his original paper "On the Law of the Diffusion of Gases" together, without being struck by the great advance in philosophic grasp and breadth of view which had become developed in the long interval between the publication of the two memoirs. These later experiments on gas-diffusion were made principally with septa of compressed graphite; and it will be well to preface their consideration by Mr. Graham's own introductory remarks. He observes:—

"The pores of artificial graphite appear to be really so minute, that a gas *in mass* cannot penetrate the plate at all. It seems that molecules only can pass; and they may be supposed to pass wholly unimpeded by friction, for the smallest pores that can be imagined to exist in the graphite must be tunnels in magnitude to the ultimate atoms of a gaseous body. The sole motive agency appears to be that intestine movement of molecules which is now generally recognized as an essential property of the gaseous condition of matter.

"According to the physical hypothesis now generally received, a gas is represented as consisting of solid and perfectly elastic spherical particles or atoms, which move in all directions, and are animated with different degrees of velocity in different gases. Confined in a vessel, the moving particles are constantly impinging against its sides and occasionally against each other, and this contact takes place without any loss of motion, owing to the perfect elasticity of the particles. If the containing vessel be porous, like a diffusiometer, then gas is projected through the open channels, by the atomic motion described, and escapes. Simultaneously the external air is carried inwards in the same manner, and takes the place of the gas which leaves the vessel. To this atomic or molecular movement is due the elastic force, with the power to resist compression, possessed by gases. The molecular movement is accelerated by heat and retarded by cold, the tension of the gas being increased in the first instance and diminished in the second. Even when the same gas is present both within and without the vessel, or is in contact with both sides of our porous plate, the movement is sustained without abatement—molecules con-

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* The motions of effusion under pressure, and of spontaneous diffusion, would appear to be alike traceable to the elasticity of the gas itself, exerted under the conditions to which it is exposed at the time.

† 'Phil. Trans.,' 1863, p. 385.

tinuing to enter and leave the vessel in equal number, although nothing of the kind is indicated by change of volume or otherwise. If the gases in communication be different, but possess sensibly the same specific gravity and molecular velocity, as nitrogen and carbonic oxide do, an interchange of molecules also takes place without any change in volume. With gases opposed of unequal density and molecular velocity, the permeation ceases of course to be equal in both directions."

One set of novel experiments recorded in the later paper, from which the above remarks are extracted, had reference to the diffusion of single gases through porous septa, into a vacuous or partially vacuous space. The diffusion-tube was substantially the same as that formerly employed, except in the circumstance of its being closed by a plate of compressed graphite instead of by stucco, and in the further circumstance of the tube itself being in some cases so far lengthened and otherwise modified as to admit of the production within it of a barometric vacuum of comparatively large dimensions. The mode of experimenting was as follows:—The short tubes, when employed, were filled with mercury, and inverted in a mercurial trough. Then, by means of a very simple arrangement, the gas under examination was allowed to sweep over the surface of, and diffuse through, the graphite plate, so as to depress the mercury within the tube until it stood at a height of 100 millimètres only,—that is, until the external pressure exceeded the internal pressure by 100 millimètres only. Matters being in this state, the experiment consisted in observing the number of seconds required for the admission through the graphite septum, into the graduated tube, of a given volume of gas—the mercury in the tube being kept throughout at the constant height of 100 millimètres, by a gradual lifting up of the tube, effected by a mechanical arrangement originally devised and employed by Professor Bunsen. The long tubes were filled with mercury in a different manner; but the conduct of the experiments made with them differed only from that of the experiments made with the short tubes, in that the level of mercury in the long tubes was maintained throughout at or near to the barometric height, so that the external gas diffused into the tube under full atmospheric pressure. Experimenting in this way, the relative times of permeation of equal volumes of different gases were found to be almost identical with the square roots

	Times of Equal Diffusion.	Square Roots of Specific Gravities.
Oxygen	1·0	1·0
Air	·9501	·9507
Carbonic gas ..	1·1860	1·1760
Hydrogen	·2505	·2502

of the specific gravities of the respective gases, as shown in the preceding Table.

These results are of great value from the simplicity and constancy of the conditions under which they were obtained, and from their close accordance with the induced law. By allowing the diffusion to take place into a complete or partial vacuum, instead of into an atmosphere of other gas, the results were not complicated with those of interdiffusion; and by employing a thin plate of highly-compressed graphite, instead of a comparatively thick plug of more porous stucco, the results were not complicated with those of transpiration, as happened in some otherwise admirable experiments of Professor Bunsen, which led that distinguished investigator to question at one time the accuracy of Mr. Graham's law.

The absence of any transpiration of gas through the graphite wafer was made evident by the want of any approximation, in the rates of passage, to the characteristic rates of transpiration; and was consequent on the impermeability of the exceedingly minute pores of the graphite to any enforced bodily transmission of gas through them. It may be as well to state this conclusion in Mr. Graham's own words:—

"The movement of gases through the graphite plate appears to be solely due to their own proper molecular motion, quite unaided by transpiration. It seems to be the simplest possible exhibition of the molecular or diffusive movement of gases. This pure result is to be ascribed to the wonderfully fine (minute) porosity of the graphite. The interstitial spaces appear to be sufficiently small to extinguish capillary transpiration entirely. The graphite plate is a pneumatic sieve which stops all gaseous matter in mass, and permits molecules only to pass."

By similarly conducted experiments, a determination was also made of the difference of rate, if any, at which hydrogen diffuses through a graphite plate into a vacuum and into atmospheric air. Thus, in one minute of time, the following quantities of hydrogen passed through the graphite plate, in the two cases respectively:—

1·289 cubic centimètre into a vacuum.
1·243 cubic centimètre into air.

These numbers indicate a close approach to equality in the velocities of passage into a vacuum and into a space of other gas,—a yet closer equality being probably attainable by a modified form of experimenting.

The diffusion of hydrogen into air, as in the above-referred-to experiment, is of course accompanied by a diffusion of air into hydrogen, which had to be allowed for in calculating out the above result. Moreover, Mr. Graham made a special repetition of his early experiments on interdiffusion, operating with dry instead of moist gas, substituting mercury for water in the diffusion-tube, maintaining a constant pressure by Bunsen's mechanism instead of by a pitcher of water, and using a wafer of graphite instead of a plug of stucco as the porous diaphragm. The theoretical exchange of hydrogen for air being 3·8 volumes for 1, and that of hydrogen for oxygen being 4·0 volumes for 1, the exchanging volumes actually found were 3·876 and 4·124 respectively.

Referring to the approximatively equally rapid passage of hydrogen into a vacuous and an aerial space, Mr. Graham remarks as follows on the subject of interdiffusion:—

"In fine, there can be little doubt left on the mind that the permeation through the graphite plate into a vacuum, and the diffusion into a gaseous atmosphere, through the same plate, are due to the same inherent mobility of the gaseous molecule. They are the exhibition of this movement in different circumstances. In interdiffusion we have two gases moved simultaneously through the passages in opposite directions, each gas under the influence of its own inherent force; while with gas on one side of the plate, and a vacuum on the other side, we have a single gas moving in one direction only. The latter case may be assimilated to the former if the vacuum be supposed to represent an infinitely light gas. It will not involve any error, therefore, to speak of both movements as gaseous diffusion,—the diffusion of gas into gas (double diffusion) in the one case, and the diffusion of gas into a vacuum (single diffusion) in the other. The inherent molecular mobility may also be justly spoken of as the diffusibility or diffusive force of gases.

"The diffusive mobility of the gaseous molecule is a property of matter, fundamental in its nature, and the source of many others. The rate of diffusibility of any gas has been said to be regulated by its specific gravity, the velocity of diffusion having been observed to vary inversely as the square root of the density of the gas. This is true, but not in the sense of the diffusibility being determined or *caused* by specific gravity. The physical basis is the molecular mobility. The degree of motion which the molecule possesses regulates the volume which the gas assumes, and is obviously one, if not the only, determining cause of the peculiar specific gravity which the gas enjoys. If it were possible to increase in a permanent manner the molecular motion of a gas, its specific gravity would be altered, and it would become a lighter gas. With the density is also associated the equivalent weight of a gaseous element, according to the doctrine of equal combining volumes."

In addition to the above two sets of experiments, on the diffusion of a single gas into a vacuum and on the diffusion of one gas into another, a third set of experiments was made on the diffusion of one gas away from another; or on the partial separation of mixed gases by the process of atmolysis. The experiments on this subject were conducted in several different ways, but the most striking results were obtained with what Mr. Graham named his tube atmolyser. This instrument consists of one or more lengths of ordinary tobacco-pipe (conveying the current of mixed gas), surrounded by a glass tube maintained in a more or less vacuous state by exhaustion with an air-pump. The most diffusible constituent of the mixed gas passing away in largest proportion through the porous material of the tobacco-pipe, the least diffusible constituent becomes concentrated in the residue of gas passing along, and finally delivered by the pipe. By this simple contrivance, the proportion of oxygen in ordinary air, transmitted by the tobacco-pipe, was increased from below 21 up to 24·5 per cent., as a result of the small superior diffusive velocity of nitrogen 1·01, over that of oxygen 0·95.

In experiments made with the far more unequally diffusive gases oxygen and hydrogen, mixed in equal volumes, the proportion of oxygen transmitted by the tobacco-pipe was increased from the original 50 per cent., to 90, and even in some cases to 95 per cent. Electrolytic gas, consisting of 33·3 per cent. oxygen and 66·6 per cent. hydrogen, was slowly transmitted through a single tobacco-pipe, in some experiments enclosed in a vacuum, in others exposed to the air. In the vacuum experiments the transmitted gas was found to consist of 90·7 per cent. oxygen and 9·3 per cent. hydrogen. In the air experiments, the transmitted gas was found to consist of 40·4 per cent. oxygen, 5·5 per cent. hydrogen, and 54·1 per cent. air. In both cases it had lost its explosive character, and acquired the property of re-inflaming a glowing splinter.

This paper of Mr. Graham's "On the Molecular Mobility of Gases" was supplemented by a communication made to the Chemical Society, in 1864, entitled "Speculative Ideas respecting the Constitution of Matter,"* from which the following extracts are taken:—

"It is conceivable that the various kinds of matter, now recognized as different elementary substances, may possess one and the same ultimate or atomic molecule existing in different conditions of movement. The essential unity of matter is an hypothesis in harmony with the equal action of gravity upon all bodies. We know the anxiety with which this point was investigated by Newton, and the care he took to ascertain that every kind of substance, 'metals, stones, woods, grain, salts, animal substances,' &c., are similarly accelerated in falling, and are therefore equally heavy.

"In the condition of gas, matter is deprived of numerous and varying properties, with which it appears invested when in the form of a liquid or solid. The gas exhibits only a few grand and simple features. These again may all be dependent upon atomic or molecular mobility. Let us imagine one kind of substance only to exist—ponderable matter; and further, that matter is divisible into ultimate atoms, uniform in size and weight. We shall then have one substance and a common atom. With the atom at rest the uniformity of matter would be perfect. But the atom possesses always more or less motion, due, it must be assumed, to a primordial impulse. This motion gives rise to volume. The more rapid the movement the greater the space

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* 'Chem. Soc. Journ.,' xvii., p. 368.

occupied by the atom, somewhat as the orbit of a planet widens with the degree of projectile velocity. Matter is thus made to differ only in being lighter or denser matter. The specific motion of an atom being inalienable, light matter is no longer convertible into heavy matter. In short, matter of different density forms different substances—different inconvertible elements, as they have been considered.

"But further, these more and less mobile, or light and heavy forms of matter, have a singular relation connected with equality of volume. Equal volumes of two of them can coalesce together, unite their movement, and form a new atomic group, retaining the whole, the half, or some simple proportion of the original movement and consequent volume. This is chemical combination. It is directly an affair of volume, and only indirectly connected with weight. Combining weights are different, because the densities, atomic and molecular, are different. The volume of combination is uniform, but the fluids measured vary in density. This fixed combining measure—the *metron* of simple substances—weighs 1 for hydrogen, 16 for oxygen, and so on with the other 'elements.'

"To the preceding statements respecting atomic and molecular mobility, it remains to be added that the hypothesis admits of another expression. As in the theory of light we have the alternative hypotheses of emission and undulation, so in molecular mobility the motion may be assumed to reside either in separate atoms and molecules, or in a fluid medium caused to undulate. A special rate of vibration or pulsation originally imparted to a portion of the fluid medium enlivens that portion of matter with an individual existence, and constitutes it a distinct substance or element.

"Lastly, molecular or diffusive mobility has an obvious bearing upon the communication of heat to gases by contact with liquid or solid surfaces. The impact of the gaseous molecule, upon a surface possessing a different temperature, appears to be the condition for the transference of heat, or the heat movement, from one to the other. The more rapid the molecular movement of the gas, the more frequent the contact with consequent communication of heat. Hence, probably, the great cooling power of hydrogen gas as compared with air or oxygen. The gases named have the same specific heat for equal volumes, but a hot object placed in hydrogen is really *touched* 3·8 times more frequently than it would be if placed in air, and 4 times more frequently than it would be if placed in an atmosphere of oxygen gas. Dalton had already ascribed this peculiarity of hydrogen to the high 'mobility' of that gas. The same molecular property of hydrogen recommends the application of that gas in the air-engine, where the object is to alternately heat and cool a confined volume of gas with rapidity."

VIII.

Passage of Gases through Colloid Septa.—In 1830, Dr. Mitchell, of Philadelphia, discovered a power in gases to penetrate thin sheet india-rubber; and, noticing the comparatively rapid transmission of carbonic gas through the rubber, associated this observation with the further one that a solid piece of india-rubber is capable of absorbing its own volume of carbonic gas, when left in contact with excess of the gas for a sufficient length of time. By means of a suitable arrangement, Dr. Mitchell found that various gases passed spontaneously through a caoutchouc membrane into an atmosphere of ordinary air with different degrees of velocity—that as much of ammonia gas was transmitted in 1 minute as of carbonic gas in 5½ minutes, as of hydrogen in 37½ minutes, and as of oxygen in 113 minutes. Soon after their publication, these results were ably commented on and extended by Dr. Draper, of New York; and, altogether, they attracted considerable attention in scientific circles. One of Mr. Graham's earliest observations—having reference to the spontaneous passage of carbonic gas into a moist bladder of air, so as ultimately to burst the bladder—had obviously a very close connection with Dr. Mitchell's results, and received from Mr. Graham in 1829 the same explanation that in 1866 he gave to his own india-rubber experiments, the account of which he communicated to the Royal Society in a paper "On the Absorption and Dialytic Separation of Gases by Colloid Septa." * In his experiments on the penetration of different gases, through septa of india-rubber, into a vacuum, Mr. Graham employed a tube considerably exceeding in length the barometric column, open at one end and closed at the other by a thin film of caoutchouc stretched over a plate of highly porous stucco. On filling this tube with mercury, and inverting it into a cup of mercury, a Torricellian vacuum was left at the top, into which the external air, or any external gas experimented on, gradually found its way by passage through the caoutchouc film, so as to cause a depression of the mercurial column. By experiments made in this manner, it was found that different gases penetrated the rubber, and entered the vacuous space with the following relative velocities, differing widely from the velocities of diffusion and transpiration of the same gases given in the other two columns of the table:—

	Rates of Passage through Caoutchouc.	Transpiration Velocities.	Diffusion Velocities.
Nitrogen	1·00	1·14	1·01
Marsh gas ..	2·15	1·81	1·34
Oxygen	2·55	1·00	·95
Hydrogen	5·50	2·29	3·80
Carbonic gas ..	13·58	1·37	·81

Bearing in mind the partial separation of gases from one another attainable by reason of their unequal diffusive velocities, the pos-

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* 'Phil. Trans.,' 1866, p. 399.

sibility of effecting a similar separation of gases by reason of their unequal velocities of transmission through india-rubber was easily to be foreseen. For example, atmospheric air consisting of 20·8 volumes of oxygen and 79·2 volumes of nitrogen, and the transmission velocities of these two gases being respectively 2·55 and 1·0, it follows that the air transmitted through india-rubber into a vacuum should consist of 40 per cent. oxygen and 60 per cent. nitrogen, thus:—

$$\left.\begin{array}{llrcl} \text{Oxygen} & .. & 20{\cdot}8 \times 2{\cdot}55 & = & 53{\cdot}04 \\ \text{Nitrogen} & .. & 79{\cdot}2 \times 1{\cdot}0 & = & 79{\cdot}20 \\ \hline & & & & 132{\cdot}24 \end{array}\right\} \text{ or } \left\{\begin{array}{r} 40 \\ 60 \\ \hline 100 \end{array}\right.$$

In subjecting this conclusion to the test of experiment, Mr. Graham availed himself of Dr. Sprengel's then newly-invented mercurial pump or exhauster, an instrument which also stood him in good stead in his subsequent work, and to which he freely acknowledged his obligations. By a slight alteration in the pump, as originally constructed, Mr. Graham made it serve not only for its original purpose of creating and maintaining an almost perfect vacuum, but also for delivering *pari passu* any gas penetrating into the vacuum through its caoutchouc or other walls.

The caoutchouc films employed in these experiments were of various kinds; but the most readily practicable and, on the whole, successful results, were obtained with india-rubber varnished silk made up into a flat bag, exposing on each side about 0·25 metre squared of surface. The interior of such a bag being in communication with the Sprengel pump, the constituents of the external air were gradually sucked through the walls of the bag and delivered by the turned-up fall-tube of the pump. On examining the delivered gas, it was found to contain on the average 41·6 per cent. of oxygen; and accordingly, to have the property of re-inflaming a glowing splinter. Thus, by the simple suction of atmospheric air through a caoutchouc film, the remarkable result was arrived at of nearly doubling the proportion of oxygen in the volume of air sucked through. Unfortunately for the practical application of the process, the entire volume of air sucked through proved to be very small, about 2·25 cubic centimètres per minute, per square mètre of surface, at 20° C. At 60° C., however, the passage of air through the rubber was almost exactly three times as rapid as at 20°.

Instead of allowing the gases experimented on to pass through the india-rubber into a vacuous space, they were in some cases allowed to pass into a space already occupied with a different gas, somewhat as in Dr. Mitchell's original experiments; but the conditions of the action were then more complex. The constituent gases of atmospheric air, for instance, pass through an india-rubber septum into a space containing carbonic gas at the relative velocities with which they enter a vacuous space; but throughout the experiment, not only are oxygen and nitrogen continually entering the space, but carbonic gas is continually, and very rapidly, escaping from it. Eventually, by the rapid escape of carbonic gas, the proportion or pressure of oxygen in the internal space comes to exceed that in the external air; whereupon a reverse transmission, through the india-rubber, of the excess of oxygen into the external air, at once begins. But by stopping the operation at an early stage, and then absorbing the carbonic gas with caustic alkali, a residue of hyperoxygenized air was left, capable, in some cases, of re-inflaming a glowing splinter, and containing as much as 37·1 volumes of oxygen to 62·9 volumes of nitrogen.

The interpretation, given by their discoverer to the above results, was in accordance with his slowly developed views on the relations of gases and liquids to each other and to soft solids. Having satisfied himself that the merest film of india-rubber is quite devoid of porosity, and that oxygen is at least twice as absorbable by india-rubber as by water at ordinary temperature (the absorbability of its own volume of carbonic gas by india-rubber, as by water, having been noticed by Dr. Mitchell), Mr. Graham came to view the entire phenomenon as having a very complex character,—as consisting in a dissolution of the gas in the soft india-rubber; in a diffusion of the liquefied gas, as a liquid, through the thickness of the india-rubber; in an evaporation of the liquefied gas from the internal surface of the india-rubber; and lastly in a diffusion of the evaporated gas into the internal space. Thus, in reference to the remarks of Drs. Mitchell and Draper, he writes—"These early speculations lose much of their fitness from not taking into account the two considerations already alluded to, which appear to be essential to the full comprehension of the phenomenon—namely, that gases undergo liquefaction when absorbed by liquids and such colloid substances as india-rubber, and that their transmission through liquid and colloid septa is then effected by the agency of liquid and not gaseous diffusion. Indeed, the complete suspension of the gaseous function during the transit through colloid membrane cannot be kept too much in view." Mr. Graham seems thus to have recognized at least three distinct modes of gas transmission through a solid or semi-solid septum:—

1st. By a sufficient degree of pressure gases might be forced bodily, *i. e.* in masses, through the minute channels of a porous septum; or, in other words, might pass through such a septum by *transpiration*, of course in the direction only of the preponderating total pressure.

2nd. As the channels of a porous septum became more and more minute, their resistance to the bodily transmission of gas would become greater and greater, and the quantity of gas forced through them less and less, until at length the septum would be absolutely impermeable to transpiration under the particular pressure. But such a septum, of which the individual capillary channels were so small as to offer a frictional resistance to the passage of gas greater than the available pressure could overcome, might nevertheless present a considerable aggregate of interspace through which the *diffusion* proper of gases, consequent on their innate molecular mobility, could take place freely in both directions.

3rd. A septum might be quite free from pores, of any kind or degree of minuteness, and so far be absolutely impermeable to the transmission of gas in the form of gas; but it might nevertheless permit a considerable transmission of certain gases by reason of their prior solution or *liquefaction* in the substance of the septum. And whereas the mere passage of gas, by transpiration or diffusion through a porous septum, would take place in thorough independence of the nature of the material of the septum, in this last considered action, the transmission would take place by virtue of a sort of chemical affinity between the gas and the material of the septum—the selective absorption of the gas by the septum being a necessary antecedent of its transmission; whence it might be said the gas was transmitted because it was first absorbed. Of course in certain transmissions two, or all three, modes of action might come into play simultaneously.

IX.

Occlusion of Gases by Metals.—The experiments of Deville and Troost having made known the curious fact of the permeability of ignited homogeneous platinum and ignited homogeneous iron to hydrogen gas, and given some indication also of the permeability of ignited iron to carbonic oxide gas, Mr. Graham, in 1866, corroborated the results of the French chemists in reference to platinum; but, modifying their method by letting the hydrogen pass into a space kept vacuous by the Sprengel pump, instead of into an atmosphere of other gas, assimilated the process to that which he had employed in his india-rubber experiments. The results he obtained were communicated to the Royal Society, partly in the paper already referred to "On the Absorption and Separation of Gases by Colloid Septa," and partly in four supplementary notices published in the Proceedings of the Society.* In carrying out the investigation forming the subject of these several communications, Mr. Graham had the advantage of being admirably seconded by his assistant, Mr. W. Chandler Roberts, whose able and zealous co-operation he repeatedly acknowledged in the warmest terms.

In the course of experiments made on the transmission of gases through ignited metallic septa, a particular platinum tube, being rendered vacuous, was found at all temperatures below redness to be quite impermeable to hydrogen; whereas at a red heat, it transmitted 100 cubic centimètres of hydrogen in half-an-hour—the quantities of oxygen, nitrogen, marsh-gas, and carbonic gas, transmitted under the same conditions, not amounting to ·01 cubic centimètre each in half-an-hour. It was ascertained further that, with an ignited vacuous tube of platinum surrounded by a current of ordinary coal gas (a variable

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* 'Roy. Soc. Proc.,' xv., p. 502; xvi., p. 422; xvii., p. 212, p. 500.

mixture of gases containing on the average about 45 per cent. of marsh-gas, 40 per cent. of hydrogen, and 15 per cent. of other gases and vapours), a transmission of pure hydrogen alone took place through the heated metal. This property of selective transmission, manifested by platinum, was so far analogous to the property of selective transmission manifested by india-rubber, that whereas a septum of india-rubber transmitted the nitrogen of the air in a much smaller ratio than the oxygen, the septum of ignited platinum transmitted the other constituents of coal gas in an infinitely smaller ratio than the hydrogen. Hence the knowledge, of the absorption by india-rubber of the gases which it most freely transmitted, suggested to Mr. Graham an inquiry as to the possible absorption of hydrogen gas by platinum. Accordingly platinum, in different forms, was heated to redness, and then allowed to cool slowly in a continuous current of hydrogen. The metal so treated, and after its free exposure to the air, was placed in a porcelain tube, which was next made vacuous by the Sprengel pump. During the production and maintenance of the vacuum, no hydrogen was extracted from the metal at ordinary temperatures; or even during an hour's exposure to the temperature of 220°; or yet at a heat falling just short of redness. But at a dull red-heat and upwards, a quantity of hydrogen gas was given off amounting in volume, measured cold, to as much, in some cases, as 5·5 times the volume of the platinum. Thus was opened out to Mr. Graham the subject of his last, and probably greatest discovery—the occlusion of gases by metals. Very many metals were examined in their relations to different gases, but the most interesting results were those obtained with platinum as above described; and those obtained with silver, with iron, and above all, with palladium.

The characteristic property of silver, heated and cooled in different atmospheres, proved to be its capability of absorbing and retaining, in some cases, as much as seven times its volume of oxygen—its absorption of hydrogen falling short of a single volume. Some silver leaf, heated and cooled in ordinary air, and subsequently heated in a vacuum, gave off a mixture of oxygen and nitrogen gases containing 85 per cent. of oxygen, or more than four times the proportion contained in the original air. This remarkable property of solid silver to effect the permanent occlusion of oxygen gas, must be distinguished from the not less remarkable and doubtless associated property of melted silver to effect the temporary absorption of a yet larger volume of the same gas; which, on the solidification of the metal, is discharged with the well-known phenomenon of spitting.

Iron, though tolerably absorptive of hydrogen, was found to be specially characterized by its absorption of carbonic oxide. What may be called the natural gas of wrought iron, or the gas derived from the forge in which it was heated, proved to consist chiefly of carbonic oxide, and, in different experiments, was found to range from 7 to 12·5 times the volume of the metal; so that, in the course of its preparation, iron would appear to occlude upwards of seven times its volume of carbonic oxide, and to carry this gas about with it ever after. The absorbability of carbonic oxide by iron has an obviously important bearing on the theory of steel production by cementation. This process would appear to consist in an absorption of carbonic oxide gas into the substance of the iron, and in a subsequent decomposition of the absorbed gas into carbon entering into combination with the metal, so as to effect its acieration, and carbonic gas discharged from the surface of the metal, so as to produce the well-known appearance of blistering. Nor is this the only, or even the chief point of interest that was made out with regard to iron; for the study of the behaviour of telluric manufactured iron naturally led Mr. Graham to the examination of sidereal native iron, that is to say, the iron of meteorites, and with the following result. A portion of meteoric iron, from the Lenarto fall, when heated in vacuo, gave off 2·85 times its volume of natural gas, of which the preponderating constituent, to the extent of 85·7 per cent. of the total quantity, consisted not of carbonic oxide, but of hydrogen, the carbonic oxide amounting to only 4·5 per cent., and the remaining 9·8 per cent. consisting of nitrogen. The inference that the meteorite had been, at some time or other, ignited in an atmosphere having hydrogen as its prevailing constituent, seems irresistible; and judging from the volume of gas yielded by the iron, the hydrogen atmosphere in which it was ignited must, in all probability, have been a highly condensed one; the charge of hydrogen extracted being fully five times as great as it was found possible to impart to ordinary iron artificially.

But it was with palladium that Mr. Graham obtained his most extraordinary results. This metal he found to have the property of transmitting hydrogen with extreme facility, even at temperatures very far short of redness. Coincidently, at temperatures even below those requisite for transmission, palladium was found capable of absorbing many hundred times its volume of hydrogen. Thus a piece of palladium foil maintained at a temperature of 90°–97° for three hours, and then allowed to cool down during an hour and a half, while surrounded by a continuous current of hydrogen gas, gave off, on being afterwards heated in vacuo, 643 times its volume of the gas, measured cold; and even at ordinary temperatures, it absorbed 376 times its volume of the gas, provided it had first been recently ignited in vacuo. In another experiment, palladium sponge, heated to 200° in a current of hydrogen and allowed to cool slowly therein, afterwards yielded 686 times its volume of the gas; while a piece of electrolytically deposited palladium heated only to 100° in hydrogen, afterwards yielded, upon ignition in vacuo, no less than 982 times its volume of the gas. The lowness of the temperature at which, under favourable circumstances, the absorption of hydrogen by palladium could thus be effected, soon suggested other means of bringing about the result. For example, a piece of palladium foil was placed in contact with a quantity of zinc undergoing solution in dilute sulphuric acid; and, on subsequent examination, was found to have absorbed 173 times its volume of hydrogen. Again, palladium, in the forms of wire and foil, was made to act as the negative pole of a Bunsen's battery effecting the electrolysis of acidulated water; and in this manner was found to absorb from 800 to 950 times its volume of hydrogen in different experiments.

Palladium being thus chargeable with hydrogen in three different ways, namely, by being heated and cooled in an atmosphere of the gas; by being placed in contact with zinc dissolving in acid, *i. e.* with hydrogen in the act of evolution; and, lastly, by being made the negative electrode of a battery,—correlatively, the charged metal could be freed from its occluded hydrogen by exposing it to an increase of temperature in air or vacuo; by acting on it with different feebly oxidizing mixtures; and by making it the positive electrode of a battery.

The palladium, when charged to its maximum, was frequently found to give off a small proportion of its hydrogen, though with extreme slowness, at ordinary temperatures, both into the atmosphere and into a vacuum. But not until the temperature approached 100° was there any appreciable gas-evolution; which, above that point, took place with a facility increasing with the temperature, so as to be both rapid and complete at about 300°. Since, however, the transmission of hydrogen through heated palladium is a phenomenon of simultaneous absorption and evolution, it follows that the property of palladium to absorb hydrogen does not cease at 300°, or indeed at close upon the melting-point of gold,—the highest temperature at which Mr. Graham's experiments on transmission were conducted; but whereas the maximum absorption of hydrogen by palladium takes place at comparatively low temperatures, the velocity of transmission was observed to increase, in a rapid ratio, with the increase of temperature, indefinitely.

As regards the removal of hydrogen from palladium by oxygenants, the gas of the charged metal was found to manifest all the chemical activity of hydrogen in the nascent state. Thus it reduced corrosive sublimate to calomel, combined directly with free iodine, converted ferrid- into ferro-cyanides, destroyed the colour of permanganates, &c. Moreover, the spongy metal, charged with hydrogen and exposed to the air, was apt to become suddenly hot, and so completely discharged, by a spontaneous aërial oxidation of its absorbed gas into water; while the hydrogen of a piece of charged palladium wire was often capable of being set fire to, and of burning continuously along the wire.

Lastly, the reversal of the position of the palladium plate in the decomposing cell of the battery afforded a most ready means of completely extracting its hydrogen. Indeed, for some time after the reversal, while hydrogen was being freely evolved from the negative pole, no oxygen was observable on the surface of the palladium plate, now made the positive pole, through its rapid oxygenation of the absorbed hydrogen.

As regards the extent of the absorption of hydrogen by palladium, it was found, as already indicated, to vary considerably with the physical state of the metal, whether fused, hammered, spongy, or electrolytically deposited, for example. In one case, previously referred to, a specimen of electrolytically deposited palladium, heated to 100°, and then slowly cooled in a continuous current of hydrogen, was found to occlude 982·14 times its volume of the gas, measured cold. In this case, the actual weight of palladium experimented with, was 1·0020 gramme, and the weight of hydrogen absorbed ·0073 gramme, being in the ratio of 99·277 per cent. of palladium and 0·723 per cent. of hydrogen. The atomic weight of hydrogen being 1, and that of palladium 106·5, it is observable that the ratio of the weights of the constituents of the charged metal, hydrogen and palladium, approximates to the ratios of their atomic weights.

In another experiment some palladium wire, drawn from a piece of the fused metal, was charged electrolytically with 935·67 times its volume of hydrogen. Some idea of these enormous absorptions of hydrogen may be formed by remembering that water at mean temperature absorbs only 782·7 times its volume of that most absorbable of the common gases, ammonia.

A point of interest with regard to the different quantities of hydrogen absorbable by palladium in its different states, is the gradual diminution in the absorptive power of any particular specimen of the metal, with each successive charge and discharge of gas, in whatever way effected—the absorptive power, however, being partially restorable by subjecting the metal to a welding heat.

The density of palladium charged with eight or nine hundred times its volume of hydrogen is perceptibly lowered. Owing, however, to a continuous formation of bubbles of hydrogen on the surface of the charged metal when immersed in water, there is a difficulty in taking its exact density by comparing its respective weights in air and water with one another. There is also a difficulty in determining the density by direct measurement of the charged palladium when in the form of wire; owing to the curious property of the wire, on being discharged, of not merely returning to its original volume, but of undergoing a considerable and permanent additional retraction. But in the case of certain alloys of platinum, silver, and gold with excess of palladium, while the absorptive power of the constituent palladium is still manifested, the excess of retraction on discharge of the wires does not occur; and the specific gravities deducible from the mere increase in length of wires of these alloys, are found to accord approximatively with those deducible from the increase in length of the pure palladium wire, not above its original length, but above the length to which it retracts on discharge of its absorbed gas. It would thus appear that, simultaneously with its absorption of hydrogen, the pure palladium wire, unstably stretched by the process of drawing, suffers two opposite actions; that is to say, it undergoes a process of shortening by assuming a more stable condition of cohesion, and a process of lengthening by the addition to it of other matter—the lengthening due to the additional matter being the excess of the length of the charged above that of the discharged wire. In a particular experiment illustrative of this peculiarity, a new platinum wire took up a full charge of hydrogen electrolytically, namely, 956·3 volumes, and increased in length from 609·585 to 619·354 millimètres. With the expulsion of the hydrogen afterwards, the wire was permanently shortened to 600·115 millimètres. The sum of the two changes taken together amounts to 19·239 millimètres, and represents the true increase in the length of the wire due to the addition of hydrogen. It corresponds to a linear expansion of 3·205 in 100, or to a cubical expansion of 9·827 in 100. The original volume of the wire being ·126 cubic centimètre, the volume of the condensed hydrogen would accordingly be ·01238 cubic centimètre. Then as the charged wire, on being heated in vacuo, evolved 120·5 cubic centimètres of hydrogen gas, weighing ·0108 gramme, the density of the absorbed hydrogen would be

$$\frac{\cdot01080}{\cdot01238} = \cdot872.$$

Calculated from the mere increase in length of the charged wire above that of the wire originally, the density of the absorbed hydrogen would be 1·708. The following Table gives the densities of condensed hydrogen in different experiments made with palladium wire, in which the excess of retraction on discharge was allowed for as above; and also the densities observed in experiments made with palladium alloys in which the contraction on discharge took place to the original lengths of the wires only.

When united with	Density of Condensed Hydrogen.
Palladium	0·854 to 0·872
Palladium and platinum	0·7401 „ 0·7545
Palladium and gold	0·711 „ 0·715
Palladium and silver	0·727 „ 0·742

Whether the absorption of hydrogen by palladium, alloyed or not with another metal, was large or small, the density of the occluded hydrogen was found to be substantially the same. That the excessive retraction of the palladium wire on the discharge of its absorbed hydrogen is not a mere effect of heat was shown by the charged wire undergoing a similar retraction when discharged electrolytically instead of by ignition in vacuo; and also by the original wire not undergoing any sensible retraction as a result of annealing. That the retraction is merely in length was shown by the absence of any difference in specific gravity between the original and the discharged wire. Very curiously, the shortening of the wire, by successive chargings and dischargings of hydrogen, would seem to be interminable. Thus the following expansions of a particular wire, caused by variable charges of hydrogen, were followed, on expelling the hydrogen, by the contractions recorded in the other column.

	Elongation in Millimètres.	Retraction in Millimètres.
1st Experiment	9·77	9·70
2nd ,, ...	5·765	6·20
3rd ,, ...	2·36	3·14
4th ,, ...	3·482	4·95
		23·99

The palladium wire, which originally measured 609·144 millimètres, thus suffered, by four successive chargings and dischargings of hydrogen, an ultimate contraction of 23·99 millimètres, or a reduction of its original length to the extent of nearly 4 per cent., each increment of contraction below the original length usually exceeding the previous increment of elongation above the original length of the wire. The alternate expansion and contraction of palladium by its occlusion and evolution of hydrogen is ingeniously shown by a contrivance of Mr. Roberts', in which a slip of palladium foil, varnished on one side, is made to curl and uncurl itself, as it becomes alternately the negative and positive electrode of a battery, or is alternately charged and discharged of hydrogen on its free surface.

That hydrogen is the vapour of a highly volatile metal has frequently been maintained on chemical grounds; and from a consideration of the physical properties of his hydrogenized palladium, Mr. Graham was led to regard it as a true alloy of palladium with hydrogen, or rather hydrogenium, in which the volatility of the latter metal was restrained by the fixity of the former, and of which the metallic aspect was equally due to both of its constituents. Although, indeed, the occlusion of upwards of 900 times its volume of hydrogen was found to lower the tenacity and electric conductivity of palladium appreciably, still the hydrogenized palladium remained possessed of a most characteristically metallic tenacity and conductivity. Thus, the tenacity of the original wire being taken as 100, the tenacity of the fully charged wire was found to be 81·29; and the electric conductivity of the original wire being 8·10, that of the hydrogenized wire was found to be 5·99. In further support of the conclusion arrived at by Mr. Graham, as to the metallic condition of the hydrogen occluded in palladium, he adduced his singular discovery of its being possessed of magnetic properties, more decided than those of palladium itself, a metal which Mr. Faraday had shown to be "feebly but truly magnetic." Operating with an electro-magnet of very moderate strength, Mr. Graham found that while an oblong fragment of electrolytically deposited palladium was deflected from the equatorial by 10° only, the same fragment of metal, charged with 604·6 times its volume of hydrogen, was deflected through 48°. Thus did Mr. Graham supplement the idea of hydrogen as an invisible incondensable gas, by the idea of hydrogen as an opaque, lustrous, white metal, having a specific gravity between 0·7 and 0·8, a well-marked tenacity and conductivity, and a very decided magnetism.

[W. O.]

Royal Institution of Great Britain.

WEEKLY EVENING MEETING,

Friday, June 10, 1870.

Sir Henry Holland, Bart. M.P. D.C.L. F.R.S. President,
in the Chair.

William Odling, M.B. F.R.S.

FULLERIAN PROFESSOR OF CHEMISTRY, ROYAL INSTITUTION,

On the Ammonia Compounds of Platinum.

For nearly a century past ammonia gas, discovered by Priestley in 1774, has been a subject of extreme interest to chemists. This ammonia gas, H_3N, is especially characterized by its property of uniting directly with hydrochloric acid gas, HCl, to form a solid deposit of sal-ammoniac, or hydrochloride of ammonia, $H_3N.HCl$.

In several important particulars, sal-ammoniac presents a remarkable similarity of behaviour to chloride of potassium; and, by linking together the hydrogen of its acid with its ammonia so as to form the grouping $H_3N.H$ or H_4N, it may be regarded as the chloride of a composite metal ammonium, just as potassium chloride is the chloride of the simple metal potassium; thus:—

$$(H_3N.H)Cl \qquad\qquad KCl$$

Ordinarily, when potassium chloride is subjected to the action of a weak current, no potassium, but only potash, makes its appearance at the negative pole; but if the negative pole be constituted of a drop of mercury, the electrolytically-liberated potassium remains dissolved in the mercury as potassium-amalgam K_xHg_y. Similarly, when solution of sal-ammoniac is subjected to electrolysis, the negative pole being constituted of mercury, there is produced a bulky amalgam of ammonium $(H_3N.H)_xHg_y$; which, however, when no longer under the influence of the current, speedily breaks up into ammonia, hydrogen, and mercury. Ammonium-amalgam may further be produced on a large scale by the action of potassium-amalgam or sodium-amalgam on sal-ammoniac solution, thus:—

$$x(H_3N.H)Cl \;+\; K_xHg_y \;=\; xKCl \;+\; (H_3N.H)_xHg_y$$

Another characteristic property of ammonia gas is its extreme solubility in water. By its dissolution it furnishes a liquid having many of the properties of aqueous potash, as, for example, the properties of affecting test-paper, of neutralizing acids, and of precipitating metallic salts. And just as sal-ammoniac may be regarded as a chloride of ammonium, analogous to chloride of potassium, so may aqueous ammonia be regarded as a hydrate of ammonium analogous to hydrate of potassium, thus :—

$$(H_3N.H)HO \qquad KHO$$

But whereas chloride of ammonium, analogous to chloride of potassium, constitutes a definite body,—hydrate of ammonium, analogous to hydrate of potassium, has an inferential existence only. It is inferred to exist in solution from the reactions of the solution; but, under all attempts at extraction, it breaks up into ammonia gas and water, thus :—

$$(H_3N.H)HO \text{ or } H_3N.H_2O = H_3N + H_2O$$

But by far the most interesting circumstance with regard to ammonia is its property, so remarkably developed by Hofmann, of serving as a type from which compounds of the most varied character are derivable by substitution. Just, for example, as the hydrocarbon residue, or radical, ethyl C_2H_5, can replace the hydrogen of hydrochloric acid to form ethylic chloride $C_2H_5.Cl$, so can it also replace the hydrogen of ammonia to form ethylamine $C_2H_5.H_2N$. This ethylamine constitutes a very volatile liquid, vaporizing considerably even at ordinary temperatures. Its vapour closely resembles ammonia gas, but is distinguishable therefrom by its ready inflammability. Like ammonia, ethylamine combines directly with hydrochloric acid to form ethylamine sal-ammoniac, or hydrochloride of ethylamine $C_2H_5\,H_2N.HCl$. Like ammonia, also, ethylamine is extremely soluble in water; and its solution, like that of ammonia, behaves in many respects as a definite hydrate $C_2H_5\,H_2N.H_2O$, not obtainable, however, in the isolated state, but, like hydrate of ammonia, known only in the state of solution.

There exist, moreover, derivatives of ammonia in which a portion of its hydrogen is replaced, not by a monad, but by a diad residue or radical. Just, for example, as diad ethylene, C_2H_4, replaces the hydrogen of two units of hydrochloric acid to form ethylenic chloride, $C_2H_4.Cl_2$, so can it also replace, in part, the hydrogen of two units of ammonia to form ethylenamine, $C_2H_4(H_2N)_2$ or $(C_2H_4)''H_4N_2$. This double ammonia unites with *two* units of hydrochloric acid to form the definite hydrochloride, $C_2H_4(H_2N)_2.2HCl$, and with *two* units of water to form the equally definite, stable, isolable, volatile, crystallizable hydrate $C_2H_4(H_2N)_2.2H_2O$.

The hydrochloride and non-isolable hydrate of ethylamine being compared with the chloride and hydrate of the monad alkali-metal potassium, the hydrochloride and isolable hydrate of ethylenamine are similarly comparable with the chloride and hydrate of the diad alkali-metal barium, thus :—

$K'Cl$	$\{C_2H_5(H_2N)H\}'Cl$	$Ba''Cl_2$	$\{C_2H_4(H_2N)_2\}''Cl_2$
$K'HO$	$\{C_2H_5(H_2N)H\}'HO$	$Ba''(HO)_2$	$\{C_2H_2(H_2N)_2\}''(HO)_2$

And hydrate of ethylenamine agrees with hydrate of barium, as well in being a powerfully alkaline base, as in being de-hydrateable, not by the action of heat, but by indirect methods only.

Through the further researches of Hofmann, chemists are acquainted with ammonias and di-ammonias, in which, not only one-third, but two-thirds and three-thirds of the hydrogen are replaced by monad ethyl and diad ethylene respectively. With regard to these compounds, both in their properties and in the nature of the hydrochlorides and hydrates which they furnish, di- and tri-ethylamine correspond very closely to ethylamine—di- and tri-ethylenamine very closely to ethylenamine.

	Ethylamines.	Ethylenamines.
Mono-	$(C_2H_5)'H_2N$	$(C_2H_4)''H_4N_2$
Di-	$(C_2H_5)'_2HN$	$(C_2H_4)''_2H_2N_2$
Tri-	$(C_2H_5)'_3N$	$(C_2H_4)''_3N_2$

Although, in this way, the principal developments and ultimate establishment of the idea of ammonia as a type have resulted from investigations in organic chemistry, the idea itself appears to have originated in the first instance from investigations made in mineral chemistry; and especially from the investigation of compounds formed by the reaction of certain metallic salts and ammonia. Graham, indeed, had early represented certain compounds of metallic chlorides with ammonia as being metallicized sal-ammoniacs; but the notion of ammonia as a trihydric type, susceptible of three successive degrees of substitution, was first enunciated by Laurent, and was employed by that most original chemist to explain, among other matters, the constitution of different ammoniated compounds of platinum, discovered by Magnus, Gros, and Reiset successively. These compounds he represented as being salts of derived ammonias, in which different proportions of the hydrogen of ammonia were replaced by platinum.

Platinum is a moderately hard, pewter-coloured metal, possessed of many singular properties. It was first recognized as a distinct metal by Wood, an assayer of Jamaica, in 1741. The mode of working it was discovered and practised by Wollaston early in the present century, and described by him in the 'Philosophical Transactions' for 1829. Platinum is especially characterized by its high specific gravity; by its low conductivity, dilateability, and specific heat; by its high ductility and tenacity; by its facile divisibility and reducibility; by its curious absorptivity of certain gases, more especially hydrogen; by its difficult attackability by chemical agents; and by its infusibility at the highest furnace heats. And by each of these several properties, except perhaps its high specific gravity, is it suited to some special application in the arts.

Chemically, platinum is characterized by its high atomic weight, 197; and by its formation of two well-defined chlorides,—a perchloride, also known as platinic chloride, expressed by the formula $Pt''''Cl_4$, and a protochloride, also known as platinous chloride, expressed by the formula $Pt''Cl_2$. Platinic chloride occurs in crystalline, dark orange masses, freely soluble in water. Platinous chloride forms an olive-brown amorphous powder, quite insoluble in water, but dissolving in hydrochloric acid to form an ochre-coloured liquid. In 1828, the late Professor Magnus, by supersaturating this liquid with ammonia, obtained a remarkable compound, containing the elements of platinous chloride and ammonia, and presenting itself as a dull green, usually crystalline, precipitate. This notable green precipitate has formed the subject of frequent investigation from then till now; and different views of its constitution, from time to time, have been put forward. But no one of these views has received a sufficiently general acceptance to warrant the designation of the compound in accordance therewith; so that, from the period of its discovery down to the present day, it has ever borne the honoured name of its discoverer, and been known as the green salt of Magnus.

Some time after, Gros, in 1838, by treating the salt of Magnus with nitric acid, obtained a peculiar series of pale yellow, or colourless, platin-ammonia compounds. Next, in 1840–44 *et seq.*, Reiset and Peyrone, by acting on the salt of Magnus, or on platinous chloride itself, with ammonia, obtained, independently of each other, two additional series of compounds, having relations of metamorphosis both with one another and with the foregoing series of Gros. Then, in 1846, Raewsky, by acting on the salt of Magnus with nitric acid, obtained yet another series of compounds, differing from those furnished to Gros by the same reagent.

But the formulæ, attributed by Raewsky to the salts which he had just discovered, were inconsistent both with Laurent's view of ammonia as a type, and with other views of chemical constitution which those illustrious fellow-workers Laurent and Gerhardt shared in common. Accordingly, Gerhardt, in 1848, subjected Raewsky's formulæ,—notwithstanding their corroboration by a Committee of the Academy,—to a most trenchant criticism; and after supplementing his criticism by laboratory research, published in 1850, his celebrated memoir "On the Ammoniacal Compounds of Platinum." In this memoir he established the existence of another, entirely new, series of platin-ammonia compounds; he showed, by experiment, the simple relationship in which the salts of Raewsky stand to the salts of Gros; and he set forth a complete, self-consistent scheme of viewing the several series of platin-ammonia compounds in their relations to ammonia and to one another.

Since the publication of Gerhardt's memoir, further important contributions to the knowledge of platin-ammonia compounds have been made by different chemists, especially by Buckton, Hadow, and Thomsen. But neither before nor since has any complete general scheme of the constitution of this class of bodies been put forward. Nevertheless the scheme of Gerhardt, though always treated with respect, has never met with general acceptation, and nowadays, at any rate, is open to very serious objections.*

The attention of the writer having of late been directed to the study of these compounds, he has succeeded in differentiating the simplest of the platinum sal-ammoniacs from several allied and isomeric bodies with which it had before been confounded; and in obtaining from it the corresponding hydrated base of the series. He has also obtained some reactions of interest with bodies belonging to the more complex series; and, as a general result of his inquiries, has ventured to put forward a new scheme of regarding the entire group of bodies. This scheme is based on the recognition of two principal facts or propositions:—

1°. The different platin-ammonia compounds are produced in the first instance from platinous chloride $PtCl''_2$; and just as the platinum of this compound possesses the property of taking up two additional proportions of chlorine so as to furnish the platinic compound Cl_2PtCl_2 or $Pt''''Cl_4$, so also does the platinum of the different ammoniated bodies obtained from platinous chloride possess the property of taking up two proportions of chlorine, or its equivalent of other negative radical, so as to furnish platinic compounds corresponding to the original platinous compounds respectively. Hence the division of platin-ammonia compounds into the two classes of platinous and platinic; the compounds of the former, differing in constitution from those of the latter class, just as platinic differs from platinous chloride, by a direct fixation of chlorine.

2°. The monad residue or radical amidogen H_2N, is capable of becoming the monad radical ammon-amidogen $H_2N.H_3N$ or H_5N_2, just as the monad radical methyl H_3C, is capable of becoming the monad radical methylen-methyl or ethyl $H_3C.H_2C$ or H_5C_2.† Viewing sal-ammoniac $H_3N.HCl$ as the analogue of methylic chloride $H_2C\,HCl$, the difference is noticeable, that while the ammonia both of sal-ammoniac and ammon-amidogen is easily separable, the methylen both of methylic chloride and methylen-methyl is inseparable from the remaining constituents of the respective compounds. Hence the distinction between the two classes of amic and ammon-amic platinum compounds, the latter differing from the former by an actual addition of diad ammonia, much as ethylic differ from methylic compounds by a virtual addition of diad methylen. The parallelism is indicated in the under-written formulæ for methylic chloride and ethylic chloride, sal-ammoniac and ammonio-chloride of silver, respectively:—

$$H_2C\,HCl \qquad \left.\begin{matrix}H_2C\\H_2C\end{matrix}\right\}\begin{matrix}H\\Cl\end{matrix} \qquad \Bigg| \qquad H_3N\,.\,HCl \qquad \left.\begin{matrix}H_3N\\H_3N\end{matrix}\right\}\begin{matrix}Ag\\Cl\end{matrix}$$

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* Gerhardt's own base platinamine, for instance, is represented by the certainly improbable formula $pt_2\,HN$ or $Pt''HN$, and its hydrochloride by the yet more improbable formula $pt_2\,HN.2HCl$; in which the unit of a mon-ammonia is represented as combined with two units of hydrochloric acid, and by which the entire chlorine of the salt is represented as fulfilling one and the same function.

† 'Phil. Mag.,' 1869, p. 459.

The group of platin-ammonia compounds is thus divisible into the two classes of platinous and platinic; and each of these again into the two classes of amic and ammon-amic compounds. To these four classes must yet be added a fifth sub-class of di-platinic compounds, including the nitrate-chloride of Raewsky and the subsequently-discovered nitrate of Gerhardt and chloride of Hadow. The scheme of the constitution of the entire group, in accordance with the writer's views, is exhibited in the accompanying table of the principal chloride, hydrate, nitrate and nitrite compounds.

PLATINUM BASES AND SALTS.

PROPOSED SCHEME.

Platosamine.	*Amo-platosamine* (Reiset's).
$Pt''(H_2N)_2 . 2HCl$	$Pt''(H_5N_2)_2 . 2HCl . Aq.$
$Pt''(H_2N)_2 . 2H(HO)$	$Pt''(H_5N_2)_2 . 2H(HO)$
$Pt''(H_2N)_2 . 2H(NO_3)$	$Pt''(H_5N_2)_2 . 2H(NO_3)$
Platinamine (Gerhardt's).	*Amo-platinamine* (Gros').
$Cl_2 Pt''''(H_2N)_2 . 2HCl$	$Cl_2 Pt''''(H_5N_2)_2 . 2HCl$
$Cl_2 Pt''''(H_2N)_2 . 2H(HO)$?	$Cl_2 Pt''''(H_5N_2)_2 . 2H(NO_3)$
$(HO)_2 Pt''''(H_2N)_2 . 2H(HO)$	$(HO)_2 Pt''''(H_5N_2)_2 . 2H(NO_3)$
$O Pt''''(H_2N)_2 . 2H(NO_3) . 3Aq.$?	$(NO_2)_2 Pt''''(H_5N_2)_2 . 2H(NO_3)$
$(NO_3)_2 Pt''''(H_2N)_2 . 2H(NO_3)$	$(NO_2)_2 Pt''''(H_5N_2)_2 . 2HCl$
Amo-diplatinamine (Raewsky's, &c.).	$Cl_2O Pt_2''''(H_5N_2)_4 . 4HCl$ $Cl_2O Pt_2''''(H_5N_2)_4 . 4HNO_3 . Aq.$ $(NO_3)_2O Pt_2''''(H_5N_2)_4 . 4HNO_3 . Aq.$

Platosamine.

The hydrochloride is obtainable by direct action of platinous chloride $Pt''Cl_2$, on ammonia, just as ethylenamine hydrochloride is obtainable by direct action of ethylenic chloride $(C_2H_4)''Cl_2$, on ammonia; and, in both reactions, the two compounds are each accompanied by various other products. The parallelism, in constitution and properties, of the two compounds and of their corresponding hydrates is complete:—

$$\begin{array}{ll} Pt''(H_2N)_2 . 2HCl & C_2H_4(H_2N)_2 . 2HCl \\ Pt''(H_2N)_2 . 2H_2O & C_2H_4(H_2N)_2 . 2H_2O \end{array}$$

Hydrochloride of platosamine, in its pure state, has a dull, very pale, primrose colour, approaching almost to white. It is very insoluble in cold, considerably more soluble in hot water.* From its concentrated hot solution it is usually deposited as a flocculent-looking, though really crystalline, or partly crystalline, precipitate; and by slow cooling of the solution, it may be obtained wholly in the form of distinct needles. The base is obtained from the hydrochloride, through the intervention of the sulphate, by decomposing the latter with baryta water. It is extremely soluble in water, and readily crystallizable. It furnishes a solution manifesting a strongly alkaline reaction, liberating ammonia from its salts, neutralizing acids, absorbing carbonic acid from the air, and decomposing metallic salts—the precipitates thrown down being, however, for the most part double compounds.

The base and other soluble platosamine compounds are characterized by giving with hydrochloric acid a precipitate of the hydrochloride, which, when formed in this way, is almost always yellow and crystalline. All platosamine compounds, including the hydrochloride, exhibit the platinous property of absorbing chlorine, and hence of decolourizing a mixture of hydrochloric acid and permanganate, to yield platinamine compounds; and they all, including the hydrochloride, dissolve in gently-heated ammonia, to yield their corresponding amo-platosamine compounds.

Amo-platosamine.

The hydrochloride of this series, unlike that of the preceding, is freely soluble in water. It is a beautiful salt, crystallizing usually in a mass of interlaced lengthy needles. It is made by dissolving platinous chloride, salt of Magnus, or the above platosamine hydrochloride, in aqueous ammonia at a gentle heat. The hydrated base is obtained from it, as is the preceding hydrated base from the preceding hydrochloride. The so-produced hydrate corresponds in its general properties with the above hydrate of platosamine, than which, however, it is far more powerfully alkaline. From different metallic salts it throws down the respective metallic hydrates.

Amo-platosamine salts, like those of platosamine, exhibit the platinous property of decolourizing a mixture of hydrochloric acid and permanganate, of directly absorbing chlorine or bromine, and also of directly absorbing nitric peroxide, to furnish amo-platinic compounds.† The resulting amo-platinic chloro-chloride occurs as a pale yellow, the nitro-chloride as a pale green, and the nitro-nitrate as a pale blue precipitate. Amo-platosamine is further distinguished from platosamine by the free solubility of its hydrochloride, and by the reaction of this salt with platinous chloride solution to throw down the green salt of Magnus.

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* The orange-yellow, scaly, far more soluble hydrochloride, obtained by dissolving salt of Magnus in sulphate of ammonia solution, is a distinct compound.

† The reaction of amo-platosamine compounds with nitric peroxide was discovered by Hadow, but received from him a different interpretation.

Platinic Compounds.

The most characteristic of the salts of platinamine is the chloride $Cl_2Pt''''(H_2N)_2 . 2HCl$. It is best made by addition of permanganate, in very slight excess, to a hot solution of platosamine hydrochloride, acidified with hydrochloric acid. It is a beautiful bright yellow salt, dissolving sparingly in cold, moderately, though, on account of its density, somewhat slowly, in boiling water; and crystallizing readily on cooling in isolated octohedrons or square plates. It reacts with excess of ammonia, at a gentle heat, to form the insoluble chloride of amo-platinamine. Its chlorine, like that of the amo-platinic chloride, is evidently in two different conditions of attackability by reagents, such as alkalis and silver salts. The hydrate of platinamine is obtained from the hydrate-nitrate, by means of ammonia, as a neutral, almost insoluble, bright yellow, crystalline precipitate.

The best known salt of amo-platinamine is the chloro-nitrate $Cl_2Pt''''(N_2H_5)_2 . 2HNO_3$, obtained by treating the salt of Magnus, or preferably the hydrochloride of amo-platosamine, with nitric acid. It is moderately soluble in water, and crystallizes therefrom in brilliant white flat prisms. Its chlorine is not immediately recognizable by nitrate of silver; and is only partially precipitable thereby, even after long boiling. Its solution yields, with ammonium chloride and sodium sulphate, crystalline white precipitates of the chloro-chloride and chloro-sulphate respectively.

The most familiar salt of amo-diplatinamine is the chloroxy-nitrate $Cl_2OPt_2''''(H_5N_2)_4 . 4HNO_3 . Aq$. It is best made by boiling the chloro-nitrate or chloro-chloride of amo-platinamine with nitric acid and nitrate of silver. It presents considerable resemblance to the chloro-nitrate of amo-platinamine, but its solution is not disturbed either by sulphate of sodium or chloride of ammonium. It yields moreover, with platinous chloride solution, a moss-like coppery precipitate which is highly characteristic (Hadow).

[W. O.]

From the PHILOSOPHICAL MAGAZINE for December 1869.

NOTE ON A THEORY

OF

CONDENSED AMMONIA COMPOUNDS.

BY

WILLIAM ODLING, M.B., F.R.S.

THE unit of ammonia, NH^3, has the well-known property of combining with the unit of hydrochloric acid, HCl, to form a unit of the more complex body sal-ammoniac, HCl,NH^3.

Hypothetical methylene being regarded as the analogue of ammonia, chloride of methyle will be the hydrochloride of methylene, corresponding to sal-ammoniac or hydrochloride of ammonia,

$$HCl,CH^2, \quad HCl,NH^3.$$

But this chloride of methyle or hydrochloride of methylene is known to be the first term of a series of compounds, the earlier terms of which are formulated below. In a parallel column are written the formulæ of what, if they existed, would form a similar series of sal-ammoniac compounds:—

Chloride of methyle	$HCl, C\,H^2$	$HCl, N\,H^3$
,, ethyle	HCl, C^2H^4	HCl, N^2H^6
,, propyle	HCl, C^3H^6	HCl, N^3H^9
,, butyle	HCl, C^4H^8	HCl, N^4H^{12}
,, amyle	HCl, C^5H^{10}	HCl, N^5H^{15}
	&c.	&c.

Substituting an equivalent of metallic chloride for chloride of hydrogen in the sal-ammoniac series, we have the following compounds, all of which, and many like them, are fairly well known:—

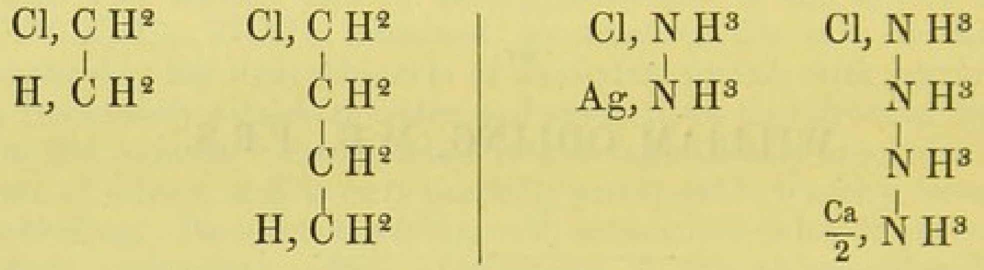
$$\frac{\mathrm{Zn}}{2}\mathrm{Cl,\ N\ H^3},$$

$$\mathrm{AgCl,\ N^2\,H^6},$$

$$\frac{\mathrm{Cu}}{2}\mathrm{Cl,\ N^3\,H^9},$$

$$\frac{\mathrm{Ca}}{2}\mathrm{Cl,\ N^4\,H^{12}}.$$

Chemists who express the composition of the chlorides of ethyle and butyle as underneath, may express the composition of the ammoniated chlorides of silver and calcium in a similar fashion; thus—



$$\begin{array}{rl|rl} \mathrm{Cl,\ C\,H^2} & \mathrm{Cl,\ C\,H^2} & \mathrm{Cl,\ N\,H^3} & \mathrm{Cl,\ N\,H^3} \\ \vert\quad & \vert\quad & \vert\quad & \vert\quad \\ \mathrm{H,\ C\,H^2} & \mathrm{C\,H^2} & \mathrm{Ag,\ N\,H^3} & \mathrm{N\,H^3} \\ & \vert\quad & & \vert\quad \\ & \mathrm{C\,H^2} & & \mathrm{N\,H^3} \\ & \vert\quad & & \vert\quad \\ & \mathrm{H,\ C\,H^2} & & \frac{\mathrm{Ca}}{2},\ \mathrm{N\,H^3} \end{array}$$

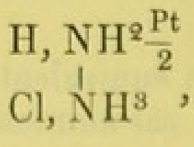
The polyammoniated salts are all more or less unstable. It is observable, however, that the diammonia compounds are habitually less unstable than their more highly ammoniated congeners, and coincidently that in the diammonia compounds alone is it possible for each unit of ammonia to be combined directly with a constituent of the hydrochloric acid or of its representative metallic chloride.

The superior stability of diammonia compounds is especially recognizable in the case of the best-characterized metal-ammonia bases, such as platinamine and platosamine. In the salts which these and such like bases form with hydrochloric acid, a portion of the hydrogen of the ammonia, instead of the hydrogen of the hydrochloric acid, would appear to be replaced by its equivalent of metal.

Still employing the equivalent method of notation, hydrochloride of platosamine (the yellow salt) would be represented thus:

$$\mathrm{HCl,\ NH^2}\frac{\mathrm{Pt}}{2}.$$

This salt very readily absorbs another unit of ammonia, and thereby forms the hydrochloride of diplatosamine,



$$\mathrm{HCl,\ N^2\,H^5}\frac{\mathrm{Pt}}{2},\quad \text{or}\quad \begin{array}{l} \mathrm{H,\ NH^2}\frac{\mathrm{Pt}}{2} \\ \quad\ \vert \\ \mathrm{Cl,\ NH^3} \end{array},$$

from which, as is well known, ammonia is not liberable by treatment of the salt with potash, or by its desiccation at upwards of 100°. The base $N^2H^5\frac{Pt}{2}$, though not procurable in the free state, as upon the above view of the cause of its stability it scarcely should be, is yet transferable from one salt to another by double decomposition with almost as much facility as ammonia itself.

What I conceive to be the constitution of the different platinous and platinic ammonia compounds in relation to each other, is indicated in the last chapter of my 'Outlines of Chemistry,' just published.

It is observable that in no stable metallicized ammonia hydrochloride is the number of nitrogen atoms more than double the number of chlorine atoms in the salt. Thus the empirical formulæ of the purpuro-cobaltic and luteo-cobaltic chlorides are $Co^2Cl^6, 10NH^3$, and $Co^2Cl^6, 12NH^3$ respectively. These expressions are of course easily translatable into forms harmonizing with the above suggested view of the constitution of condensed ammonia compounds.

Royal Institution of Great Britain.

WEEKLY EVENING MEETING,

Friday, January 27, 1871.

Sir Henry Holland, Bart. M.D. D.C.L. F.R.S. President, in the Chair.

William Odling, M.B. F.R.S.
FULLERIAN PROFESSOR OF CHEMISTRY, ROYAL INSTITUTION,

On Improvements in the Manufacture of Chlorine.

Chlorine gas was first obtained in 1774 by the Swedish chemist, Scheele, as a product of the action of muriatic acid—or marine acid, as it was then called—on the black earthy mineral manganese. In accordance with the theoretical notions of the day, Scheele gave to his newly-discovered aerial substance the name dephlogisticated marine acid, which, translated into the language of the new Lavoisierian school, became soon afterwards oxy-muriatic acid. Its assumed constitution, and relationship to muriatic acid are indicated below.

$$\begin{array}{ll}
\multicolumn{2}{c}{\overbrace{\text{Hydrogen} \qquad\qquad\qquad\qquad\qquad \text{Chlorine.}}^{\text{Muriatic acid.}}} \\
\underbrace{\text{Hydrogen} + \text{Oxygen.}}_{\text{Water.}} & \underbrace{\overbrace{\text{Murium} + \text{Oxygen.}}}_{\text{Hypothetic dry muriatic acid.}}
\end{array}$$

But Davy, in 1810, showed that muriatic acid gas is a substance wholly free from water, and a definite compound of Scheele's gas with hydrogen. He showed further that Scheele's gas, the so-called oxy-muriatic acid, was not only incapable of furnishing oxygen under any circumstance whatever; but that, so far as experience went, it was altogether undecomposable. Being thus an undecompounded and apparently undecomposable substance, he proposed to regard it as an element, and to designate it, from its yellowish-green colour, by the name chlorine, which it has ever since borne. After considerable opposition, especially on the part of Berzelius, who subsequently, however, became a convert, the view of Davy at length prevailed, and has ever since held its ground, not indeed without occasional challenging from time to time. Thus Schönbein, in several of his letters to Faraday, maintained very strongly the superior truthfulness of the original view; and still more recently Brodie has represented the comparable units of hydrogen H_2, muriatic acid HCl, and chlorine Cl_2, by the symbols α, $\alpha\chi$, and $\alpha\chi^2$, implying that the units of muriatic acid and chlorine differ from the unit of hydrogen by a combination of the matter of α with the matter of χ and with the matter of χ^2, respectively. But whatever may hereafter prove to be its real nature, chlorine has hitherto proved undecomposable, and is accordingly regarded by the generality of chemists as an element.

Coincident with the discovery of chlorine itself was the discovery of its most characteristic property, that of bleaching vegetable colours. The petals and leaves of plants, infusions of their several colouring matters, as well as fabrics dyed with the several colouring matters, were found to be rapidly bleached when treated either with chlorine gas, or with a solution of the gas in water. From the rapid action of the gas and its solution on pronounced vegetable colours, Berthollet in 1785 conceived the notion that chlorine in one form or other might be used with advantage commercially for the bleaching of calicoes and linens, theretofore always bleached by a tedious exposure to air and sunlight. The processes devised by Berthollet for carrying out the new method of bleaching were introduced into Scotland in 1787, and soon afterwards became extensively employed. Woven fabrics were bleached by immersion in chlorine water, and paper-pulp more especially by exposure to chlorine gas.

The bleaching action of chlorine takes place only in presence of water or moisture, and is dependent on the property of chlorine under suitable circumstances to decompose water, by uniting with its hydrogen to form muriatic acid, and so setting free its oxygen, by which the bleaching is really effected. Thus when chlorine, blue indigo, and water are present together, the opposite tendencies of the chlorine to take hydrogen, and of the indigo to take oxygen from the water, are satisfied by the production of chloride of hydrogen or muriatic acid on the one hand, and of oxide of indigo or isatin on the other, this isatin being a soluble orange-red non-tinctorial body:

$$Cl_2 + H_2O + C_8H_5NO = 2\,HCl + C_8H_5NO_2.$$

Thus bleaching by the action of chlorine, like bleaching by exposure to air, is really an act of oxidation.

But the action of chlorine on vegetable fabrics is not confined to that of bleaching their attached colouring matter; the fibre of the fabric is itself liable to be attacked both by the free chlorine and the muriatic acid to which it gives origin. Hence it became important to find a substitute for the free chlorine which should have, like it, the property of liberating nascent oxygen so as to bleach, but should not have, at any rate in the same degree, the property of corrosiveness so as to destroy. Such a substitute is offered in the familiar compound known as bleaching powder, introduced into commerce by the Messrs. Tennant, of Glasgow, in the year 1799. This substance is made by exposing slaked lime to an atmosphere of chlorine gas. The chlorine enters into combination with the lime of the slaked lime, to furnish a product which in practice contains some 35 per cent. of its weight of chlorine, and consists of a definite compound of lime with its own weight of chlorine, plus a variable excess of slaked lime unacted upon:

$$CaO \, . \, H_2O + Cl_2 = CaOCl_2 + H_2O.$$

Bleaching powder occurs as a dry white pulverulent solid, having a characteristic smell, allied to but not identical with that of weak chlorine. It dissolves considerably in water to form a yellow-tinted liquid, known as bleaching liquor, having a marked alkaline reaction from the presence in it of excess of lime. Coloured goods immersed for a longer or shorter time in bleaching liquor of greater or less strength and temperature, gradually have their colouring constituents destroyed or oxidated, the bleaching salt $CaOCl_2$, losing its oxygen, and becoming changed into chloride of calcium, $CaCl_2$. It is observable that the bleaching or liberation of nascent oxygen from bleaching powder is much slower than the bleaching or liberation of nascent oxygen by means of free chlorine; to such an extent, indeed, that for many purposes bleaching powder would be quite inapplicable, were it not for the property it has of liberating chlorine on acidification, whereby a still indirect but yet almost immediate oxidation is effected. Ten grains of bleaching powder, for instance, mixed with a little sulphuric or muriatic acid, will evolve some four cubic inches of chlorine gas:

$$CaOCl_2 + H_2SO_4 = H_2O + Cl_2 + Ca''SO_4.$$

The superior activity of the chlorine liberated by acidification of bleaching liquor to the original bleaching liquor, is taken advantage of commercially. Brown linens, for example, are first steeped in weak bleaching liquor with little apparent result, and then "soured" by immersion in dilute acid, whereby an immediate more or less complete bleaching is effected. Again, in what is known as the "discharge style" patterns or designs are printed with a mixture of gum and tartaric or other acid, upon a red or blue ground, and the printed fabric passed through a solution of bleach. The red or blue ground withstands the feebler action of the bleach, but the acid printed pattern becomes completely decolorized by the chlorine set free locally, as a result of the action of the acid upon the bleach. It is to this facility of management and capability of being used in different ways that the great utility of bleaching powder and its consequent enormous consumption are due. The amount of bleaching powder made annually in Great Britain and Ireland at the present time is estimated at 75,000 tons, representing at the price of ten pounds a ton, a value of three-quarters of a million sterling.

Bleaching powder being formed by exposing slaked lime to an atmosphere of chlorine, the manufacture of bleaching powder involves the production of chlorine. Indeed, chlorine is produced at chemical works almost exclusively for the manufacture of bleaching powder, and of one other product, namely, chlorate of potash. This latter is made to the extent of about 750 tons per annum, having at the price of one hundred and five pounds per ton, a value of nearly 80,000*l.* sterling.

The original reaction upon one another of muriatic acid and peroxide of manganese, by which Scheele was led to the discovery of chlorine, is the basis of the manufacturing process which has ever since been almost exclusively followed. The action consists essentially in the excessive oxygen of the peroxide taking away the hydrogen of the muriatic acid and so setting its chlorine free. Peroxide of manganese, more often called simply manganese, is one of that very limited class of native mineral substances containing an excess of oxygen ; the only other similarly peroxidized substance abundant in nature being nitre, in its two forms of East Indian or potash-nitre, and Chilian or soda-nitre. Now, when muriatic acid instead of being acted on by manganese is acted on by nitre, or by the nitric acid, formerly known as spirit of nitre, produced therefrom, the excessive oxygen of the nitre takes away hydrogen from the muriatic acid and sets its chlorine free. Thus by addition of nitric acid or nitre to aqueous muriatic acid a solution of chlorine is produced, recognizable in various ways, and especially by its power of dissolving gold leaf. Now, although nitre or nitric acid is a much more expensive oxygenant than manganese it was conceived that nitric acid might nevertheless be substituted with advantage for manganese, from the circumstance that after it had given up its excessive oxygen so as to liberate the chlorine of the muriatic acid, its deoxidized residue could readily acquire fresh oxygen from the atmosphere, and so reproduce nitric acid, to be used as an oxygenant over and over again indefinitely ; and, indeed, the nitric method of producing chlorine has for some time past been to a limited extent in actual use.

With regard to manganese, however, until recently no means have been known of causing its deoxidized residue to re-acquire oxygen from the air, and so become in a condition to serve again for the liberation of chlorine. From time to time, more particularly by Messrs. Tennant and Mr. Wm. Gossage, attempts have been made in this direction, some of them so far successful as to achieve a limited adoption ; and at length a process of reviving the spent manganese residue by effecting its aerial oxidation, has proved a decided commercial success. This process, introduced by Mr. Walter Weldon, has the incidental advantage of doing away with the discharge of the extremely corrosive manganese liquor into streams and watercourses, whereby great damage was frequently occasioned. It consists substantially in neutralizing with chalk, the acid liquor left by the action of the muriatic acid on the manganese, and then pumping air through the neutralized liquor mixed with excess of lime. The original acid liquor is substantially a solution of chloride of manganese with perchloride of iron, chloride of aluminum, chloride of calcium, and the excess of chloride of hydrogen, or muriatic acid, employed. By neutralization of the acid liquor with chalk, the iron of the perchloride of iron is precipitated, and a pale pink manganous solution left. By treatment of this solution with milk of lime, an almost white precipitate, consisting of hydrated protoxide of manganese with excess of hydrate of lime, is thrown down. Then by blowing air through the resulting thin sludge, raised to the temperature of 140°–160° F. by injection of steam, oxygen is rapidly absorbed, and the sludge rendered of a deep black colour. By subsidence the now black sludge yields a dense deposit, from which the supernatant clear liquid is run off. Finally, the deposit in its moist condition, and containing in every cubic foot about four pounds weight of peroxide of manganese, is acted upon by muriatic acid in the chlorine stills, and the resulting acid liquid treated over again in the same way, and so on indefinitely.

Already the Weldon process of manganese restoration is employed and about to be employed at many large works, to such an extent that before very long one-half of the entire quantity of bleaching powder produced in the kingdom may be expected to be made with chlorine generated by means of the restored manganese. It is noteworthy that the original pale precipitate of hydrated protoxide of manganese undergoes oxidation very imperfectly save in presence of a considerable excess of lime, and that the black product finally obtained is not simply peroxide of manganese MnO_2, but a compound of the peroxide with lime, of composition varying in different instances between that indicated by the respective formulæ $CaO.MnO_2$ and $CaO.2MnO_2$, a small portion of the lime CaO being usually replaced by its equivalent of protoxide of manganese MnO. Some idea of the rapidity of oxidation effected under favourable circumstances may be gathered from the following result. Of the entire quantity of oxygen contained in 175,000 cubic feet of air blown into the sludge within five hours, 14·8 per cent., equal to rather more than four hundredweights, was absorbed in the production of twenty-two hundredweights of manganese peroxide MnO_2. It is obvious that where Weldon's process is carried out, what happens is this :—The original peroxide of manganese first oxidizes a quantity of muriatic acid, and sets free its chlorine. Then the spent manganese is caused to acquire a fresh dose of oxygen from the air, and is used to oxidize a fresh quantity of muriatic acid, and so on continuously. Thus, except during the first use of the manganese, the muriatic acid is really oxidized by the oxygen of the air, the manganese serving only as a carrier. Latterly, Mr. H. Deacon, of the Widnes Alkali Works, has conceived the idea of dispensing with the carrier—that is the manganese—altogether. It has been known for some time that when muriatic acid vapour mixed with air is passed through heated tubes, the oxygen of the air effects a partial oxidation of the muriatic acid, setting free its chlorine; but the reaction is not sufficiently complete to render the process commercially available. Mr. Deacon however has ascertained that when a mixture of air and muriatic acid vapour, heated to about 700° F., is passed over a mass of brickwork that has been steeped in solution of sulphate of copper and afterwards dried, an almost complete decomposition of the muriatic acid is effected. The copper salt certainly takes part in the reaction as an intermediary, but in the end is quite unaffected, the sole obvious result being that the chlorine of the muriatic acid is set free by the oxygen of the air, with a rapidity which seems to leave nothing to be desired. The nature of the intermediary action exerted by the copper-salt, so ingeniously made serviceable by Mr. Deacon, has not been clearly ascertained. It would appear, however, that by two simultaneous reactions taking place continuously throughout the process, chloride of copper is ever being alternately formed and decomposed; it being remembered that chloride of copper gives off a portion of its chlorine with much facility, even by heat alone. The extreme result would probably be somewhat as follows:

$$\begin{aligned} CuCl_2 + O &= CuO + Cl_2 \\ CuO + 2\,HCl &= CuCl_2 + H_2O \end{aligned}$$

Although this new process has not yet been worked on a manufacturing scale, considerable experience has been acquired with regard to it, and the difficulties to which it at first seemed liable have been successfully provided against. One inevitable difficulty arising from the diluted state of the produced chlorine, has proved to be less serious than was anticipated. This state of dilution is at all times considerable; for the chlorine being generated by the action of atmospheric oxygen on muriatic acid, every volume of chlorine produced even in an absolutely perfect working of the process, must be necessarily diluted with twice its volume of atmospheric nitrogen. Nevertheless, according to Mr. Deacon's experience, the diluted state in which the chlorine is always obtained, has not been found to interfere with its application to the manufacture either of chlorate of potash or bleaching powder. The requisite plant for carrying out the invention on a large scale is now being erected at Messrs. Gaskell and Deacon's works.

For experimental purposes the new process of continuous chlorine production may be performed with oxygen instead of air. It then manifests a striking reverse relationship to a process of continuous oxygen production, in which oxide of cobalt acts as a permanent intermediary. In the one experiment the gas goes in oxygen and comes out chlorine, muriatic acid being decomposed and water formed. In the other experiment the gas goes in chlorine and comes out oxygen, water being decomposed and muriatic acid formed. In the presence of slaked lime to arrest the muriatic acid, this last reaction takes place readily and completely below the boiling point of water.

[W. O.]

Royal Institution of Great Britain.

WEEKLY EVENING MEETING,

Friday, April 28, 1871.

Sir Henry Holland, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

William Odling, M.B. F.R.S.
FULLERIAN PROFESSOR OF CHEMISTRY, ROYAL INSTITUTION.

On the Revived Theory of Phlogiston.

> *Observationem, quam produco, bono jure mihi vindico. . . . Materia hæc ignescens, in omnibus tribus regnis, una eademque existit. Unde, ut e vegetabili in animale, abundantissime transmigrat, ita ex utrolibet horum, in mineralia et ipsa metalla, promptissime omnium transfertur.*—Stahlii, Experimenta, Observationes, Animadversiones, CCC, Numero.

In 1781–83, Cavendish showed that when inflammable air or hydrogen, and dephlogisticated air or oxygen, are exploded together in certain proportions, "almost the whole of the inflammable and dephlogisticated air is converted into pure water," or as he elsewhere expresses it, "is turned into water."

On June 24, 1783, the experiment of Cavendish was repeated on a larger scale and in a somewhat different form by Lavoisier, who not only confirmed the synthesis of the English chemist, but drew from it the conclusion—at first strongly contested, then rapidly acknowledged, and since never called into question—"that water consists of inflammable air united to dephlogisticated air," or that it is a compound of hydrogen and oxygen.

This conclusion, so opposite to his own preconception on the matter, Lavoisier subsequently confirmed by an analysis of water. He found that iron, heated to redness and exposed to the action of water-vapour, became changed by an abstraction of oxygen from the water, into the self-same oxide of iron procurable by burning the metal in oxygen gas,—the other constituent of the water, namely, its hydrogen, being freely liberated.

With the demonstration by Lavoisier of the composition of water began the triumph of that antiphlogistic theory, which he had conceived, in a necessarily imperfect form, so far back as 1772, or before the discovery of oxygen, and had brought to completion by the aid of every successive step in pneumatic chemistry, achieved by himself or by others.

In 1785, the relationship to one another of hydrogen and water being then conclusively established, Berthollet declared himself a convert to the new theory of combustion put forward by his countryman. Fourcroy next gave in his adhesion; and soon afterwards De Morveau, invited to Paris expressly to be reasoned with by Lavoisier, succumbed to the reasons set before him. The four chemists then associated themselves together, and in spite of a strong though short-lived opposition both in England and Germany, succeeded in obtaining for *La Chimie Française* an all but universal recognition.

The principal articles of the new or antiphlogistic theory of combustion propounded by Lavoisier are as follows:—That combustible bodies in burning yield products of various kinds,—solid in the case of phosphorus and the metals, liquid in the case of hydrogen, gaseous in the case of carbon and sulphur. That in every case the weight of the products formed by the burning is greater than the weight of the combustible burnt. That the increase of weight is due to an addition of matter furnished to the combustible by the air in which its burning takes place. That bodies of which the weights are made up of the weights of two or more distinct kinds of matter are of necessity compound; whereas bodies of which the weights cannot be shown to be made up of the weights of two or more distinct kinds of matter are in effect simple or elementary. That inasmuch as the weights of the products furnished by the burning of different combustibles are made up of the weights of the combustible burnt and of the oxygen consumed in the burning, these products are compound bodies—oxides in fact of the substances burnt. That inasmuch as given weights of many combustibles, as of hydrogen, sulphur, phosphorus, carbon, and the metals, are not apparently made up of the weights of two or more distinct kinds of matter, these particular combustibles are in effect elementary; as for the same reason is the oxygen with which in the act of burning they enter into combination. And, lastly, that combustion or burning consists in nothing else than in the union of combustible matter, simple or compound, with the empyreal matter, oxygen—the act of union being somehow attended by an evolution of light and heat. And except that it would be necessary nowadays to explain how in certain cases of combustion, the combustible enters into union not with oxygen, but with some analogue of oxygen, the above precise statement might equally well have been made by Lavoisier in 1785, or be made by one of ourselves at the present day.

Lavoisier's theory of combustion being known as the antiphlogistic theory, the question arises, What was the phlogistic theory to which it was opposed, and which it succeeded so completely in displacing? This phlogistic theory was founded and elaborated at the close of the seventeenth century by two German physicians, Becher and Stahl. Having exercised a scarcely disputed authority over men's minds until the notorious defection in 1785, it preserved for some years longer a resolute though tortuous existence, and was to the last defended and approved by our own Priestley and Cavendish—who died, the former in 1804, and the latter in 1810.

The importance attached to the refutation of this theory may be judged of from the circumstance that after the early experiments of Lavoisier on the composition and decomposition of water had been successfully repeated by a committee of the French Academy in 1790, a congratulatory meeting was held in Paris, at which Madame Lavoisier, attired as a priestess, burned on an altar Stahl's celebrated *Fundamenta Chemiæ Dogmaticæ et Experimentalis*, solemn music playing a requiem the while. And the sort of estimation in which the Stahlian doctrines have since been held by chemists is fairly illustrated by a criticism of Sir J. Herschel, who, speaking of the phlogistic theory of chemistry, says that it "impeded the progress of the science, as far as a science of experiment can be impeded by a false theory, ... by involving the subject in a mist of visionary and hypothetical causes in place of the true acting principles." Possibly, however, this much-abused theory may yet prove to contain an element of permanent vitality and truth; anyhow the study of this earliest and most enduring of chemical theories can never be wholly devoid of interest to chemists.

To appreciate the merit of the phlogistic theory it is necessary to bear in mind the period of its announcement. Its originator, Beccher, was born in 1625, and died a middle-aged but worn-out man in 1682, a few years before the publication of the 'Principia.' His more fortunate disciple, Stahl, who was born in 1660 and died in 1734, in his seventy-fifth year, though afforded a possibility of knowing, seems equally with Beccher to have remained throughout his long career indifferent to the Newtonian principle that the weight of a body is proportionate to its quantity of matter—that loss of weight implies of necessity abstraction of matter, and increase of weight addition of matter. Whether or not the founders of the phlogistic theory conceived that change of matter in the way of kind, might equally with its change in point of quantity, be associated with an alteration in weight—and it must not be forgotten what pains Newton thought it necessary to take in order to show the contrary—certain it is they attached very little importance to the changes of weight manifested by bodies undergoing the metamorphosis of combustion. It might be that when combustible charcoal was burned the weight of incombustible residue was less than the original weight of charcoal—it might be that when combustible lead was burned the weight of incombustible residue was greater than the original weight of metal—this was far too trifling an unlikeness to stand in the way of the paramount likeness presented by the two bodies. For the lead and charcoal had the common property of manifesting the wonderful energy of fire; they could alike suffer a loss of light and heat—that is, of phlogiston—by the deprivation of which they were alike changed into greater or less weights of inert incombustible residue.

And not only were these primitive students of the philosophy of combustion unconscious of the fact and meaning of the relationship in weight subsisting between the consuming and the consumed body, but they were altogether ignorant of the part played by the air in the phenomena which they so boldly and successfully attempted to explain. Torricelli's invention of the barometer and Guericke's invention of the air-pump were both indeed made during Beccher's early boyhood; but years had to elapse before the consequent idea of the materiality of air could be domiciled, as it were, in human understandings. And not until more than a century after Torricelli's discovery of the weight of air,—not, indeed, until the time of the great pneumatic chemists Black, and Cavendish, and Priestley, and Scheele, was it ever imagined that the aerial state, like the solid or liquid state, was a state common to many distinct kinds of matter; and that the weight or substance of a rigid solid might be largely contributed to by the weight or substance of some constituent having its independent existence in the aerial or gaseous form. The notion that 100 lbs. of smithy-scales might consist of 73 lbs. of iron and 27 lbs. of a particular kind of air, and that 100 lbs. of marble might consist of 56 lbs. of lime and 44 lbs. of another kind of air, was a notion utterly foreign to the older philosophy. Air, it was allowed, might be rendered mephitic by one kind of contamination, and sulphurous by another, and inflammable by a third; it might even be absorbed in, and so add to the weight of, a porous solid, as water is absorbable by sand; but still air was ever indisputably air, essentially alike and unalterable in its mechanical and chemical oneness. This familiar conception had to be overcome, and the utterly strange notion of the largely aerial constitution of solid matter to be established in its stead, by the early pneumatic chemists, Black, and Cavendish, and Bergmann, before the deficiencies rather than positive errors of the phlogistic theory could be perceived.

But long ere the foundation of modern chemistry had thus been laid, in 1756, by Black's discovery of fixed air or carbonic acid as a constituent of mild alkalis and limestone, those old German doctors, Beccher and Stahl, though ignorant of the nature of air and neglectful of the import of gravity, had yet found something to say about the chemistry of combustion worthy of being defended a century afterwards by men like Priestley and Cavendish,—worthy, it is believed, of being recognized nearly two centuries afterwards as the expression of a fundamental doctrine in chemical and cosmical philosophy. They pointed out, for example, that the different and seemingly unlike processes of burning, smouldering, calcining, rusting, and decaying, by which combustible is changed into incombustible matter, have a community of character; that combustible bodies possess in common a power or energy capable of being elicited and used, whereas incombustible bodies are devoid of any such energy or power; and lastly, that the energy pertaining to combustible bodies is the same in all of them, and capable of being transferred from the combustible body which has it to an incombustible body which has it not, rendering the body that was energetic and combustible inert and incombustible, and the body that was inert and incombustible energetic and combustible—and further rendering some particular body combustible over and over again. That this is a fair representation of the views held by phlogistic chemists is readily recognizable by a study of chemical works written before the outbreak of the antipholgistic revolution. After Lavoisier's challenge, the advocates of phlogiston, striving to make it account for a novel order of facts with which it had little or nothing to do, were driven to the most incongruous of positions; for while Priestley wrote of inert nitrogen as phlogisticated air, Kirwan and others regarded inflammable hydrogen as being phlogiston itself in the isolated state. Very different is the view of phlogiston to be gathered from the writings of Dr. Watson, for example, who was appointed Professor of Chemistry at Cambridge in 1764, became Regius Professor of Divinity in 1771, and Bishop of Llandaff in 1782. This cultivated divine, indifferent it is true to the novel questions by which in less placid regions men's minds were so deeply stirred, amused the leisure of his dignified University life by writing scholarly accounts of the chemistry it had formerly been his province to teach; and in the first volume of his well-known 'Chemical Essays,' published in 1781, the following excellent account of phlogiston is to be found:—

"Notwithstanding all that perhaps can be said upon this subject, I am sensible the reader will still be ready to ask, *What is Phlogiston?* You do not surely expect that chemistry should be able to present you with a handful of phlogiston, separate from an inflammable body; you may just as reasonably demand a handful of magnetism, gravity, or electricity to be extracted from a magnetic, weighty, or electric body. There are powers in nature which cannot otherwise become the objects of sense, than by the effects they produce; and of this kind is phlogiston. But the following experiments will tend to render this perplexed subject somewhat more clear.

"If you take a piece of *sulphur* and set it on fire, it will burn entirely away, without leaving any ashes or yielding any soot. During the burning of the sulphur, a copious vapour, powerfully affecting the organs of sight and smell, is dispersed. Means have been invented for collecting this vapour, and it is found to be a very strong acid. The acid thus procured from the burning of sulphur, is incapable of being either burned by itself, or of contributing towards the support of fire in other bodies: the sulphur, from which it was procured was capable of both: there is a remarkable difference, then, between the acid procured from the sulphur, and the sulphur itself. The acid cannot be the only constituent part of sulphur; it is evident that *something* else must have entered into its composition, by which it was rendered capable of combustion. This something is, from its most remarkable property, that of rendering a body combustible, properly enough denominated the food of fire, the *inflammable principle, the phlogiston*. . . . . This inflammable principle, or phlogiston, is not one thing in animals, another in vegetables, another in minerals; it is absolutely the same in them all. . . . . This identity of phlogiston may be proved from a variety of decisive experiments; I will select a few, which may at the same time confirm what has been advanced concerning the constituent parts of sulphur.

"From the analysis or decomposition of sulphur effected by burning, we have concluded that the constituent parts of sulphur are two—an *acid* which may be collected, and an *inflammable principle* which is dispersed. If the reader has yet acquired any real taste for chemical truths, he will wish to see this analysis confirmed by synthesis; that is, in common language, he will wish to see sulphur actually made by combining its acid with an inflammable principle. It seldom happens that chemists can reproduce the original bodies, though they combine together all the principles into which they have analyzed them; . . . . in the instance, however, before us, the reproduction of the original substance will be found complete.

"As the inflammable principle cannot be obtained in a palpable form separate from all other bodies, the only method by which we can attempt to unite it with the acid of sulphur must be by presenting to that acid some substance in which it is contained. Charcoal is such a substance; and by distilling powdered charcoal and the acid of sulphur together, we can produce a true yellow sulphur, in nowise to be distinguished from common sulphur. This sulphur is formed from the union of the acid with the phlogiston of the charcoal; and the charcoal may by this means be so entirely robbed of its phlogiston, that it will be reduced to ashes, as if it had been burned. . . . .

"I will in this place, by way of further illustration of the term phlogiston, add a word or two concerning the necessity of its union with a metallic earth, in order to constitute a metal. Lead, it has been observed, when melted in a strong fire, burns away like rotten wood; all its properties as a metal are destroyed, and it is reduced to ashes. If you expose the ashes of lead to a strong fire, they will melt; but the melted substance will not be a *metal*, it will be a yellow or orange-coloured *glass*. If you pound the glass, and mix it with charcoal dust, or if you mix the ashes of the lead with charcoal dust, and expose either mixture to a melting heat, you will obtain, not a *glass*, but a *metal*, in weight, colour, consistency, and every other property the same as lead. The ashes of lead melted *without* charcoal become *glass;* the ashes of lead melted *with* charcoal become a *metal*. The charcoal, then, must have communicated *something* to the ashes of lead, by which they are changed from a glass to a metal. Charcoal consists of but two things—of ashes and of phlogiston; the ashes of charcoal, though united with the ashes of lead, would only produce glass; it must therefore be the other constituent part of charcoal, or phlogiston, which is communicated to the ashes of lead, and by an union with which the ashes are restored to their metallic form. The ashes of lead can never be restored to their metallic form without their being united with *some* matter containing phlogiston, and they may be reduced to their metallic form by being united with *any* substance containing phlogiston in a proper state, whether that substance be derived from the animal, vegetable, or mineral kingdom; and thence we conclude not only that phlogiston is a necessary part of a metal, but that phlogiston has an identity belonging to it, from whatever substance in nature it be extracted. And this assertion still becomes more general, if we may believe that metallic ashes have been reduced to their metallic form, both by the solar rays and the electrical fire."

The foregoing account by Dr. Watson is almost a translation from Stahl's '*Zymotechnica Fundamentalis, simulque experimentum novum sulphur verum arte producendi*,' in which he establishes what may be called the permanency of chemical substance—that metallic lead is reproducible from the ashes of lead, *sulphur verum* from the acid of sulphur. And, whether or not taking note of the oxidations and deoxidations effected, how little differently, even at the present day, would the actions referred to be described and explained. Is it not our habit to say that charcoal and sulphur and lead are bodies possessing potential chemical energy, that is phlogiston; that in the act of burning, their energy which was potential becomes kinetic or dynamical, and is dissipated in the form of light and heat; that the products of their burning (including the gaseous product now known to be furnished by the burning of charcoal) are substances devoid of chemical energy, that is, of phlogiston; that when the acid substance furnished by burning sulphur is heated with charcoal, some energy of the unburnt charcoal is transferred to the burnt sulphur, just as some energy of a raised weight may be transferred to a fallen one, whereby the burnt sulphur is unburnt, provided with energy, and enabled to burn again, and the fallen weight is lifted up, provided with energy, and enabled to fall again; that the potential chemical energy of metallic lead did not originate in the lead, but is energy or phlogiston transferred thereto from the charcoal by which it was smelted; and lastly, that the chemical energy of the charcoal itself, its capability of burning, its power of doing work, in one word its phlogiston, is merely a portion of energy appropriated directly from the solar rays?

If this be a correct interpretation of the phlogistic doctrine, it is evident that the Stahlians, though ignorant of much that has since become known, were nevertheless cognisant of much that became afterwards forgotten. For most of what has since become known, mankind are indebted to the surpassing genius of Lavoisier; but the truth which he established, alike with that which he subverted, is now recognizable as a partial truth only; and the merit of his generalization is now perceived to consist in its addition to—its demerit to consist in its supersession of—the not less grand generalization established by his scarcely remembered predecessors. This being so, the relationship to one another of the Stahlian and Lavoisierian theories of combustion furnishes an apt illustration of the general truth set forth by a great modern writer, that "in the human mind, one-sidedness has always been the rule, and many-sidedness the exception. Hence, even in revolutions of opinion, one part of the truth usually sets while another rises. Even progress, which ought to superadd, for the most part only substitutes one partial and incomplete truth for another; improvement consisting chiefly in this, that the new fragment of truth is more wanted, more adapted to the needs of the time, than that which it displaces."

The partial truth contributed by Lavoisier was indeed more wanted, more adapted to the needs of the time, than the partial truth which it displaced. To him chemists are indebted for their present conception of material *elements;* and especially for their knowledge of the part played by the air in the phenomena of combustion, whereby oxygenated *compounds* are produced. The phlogistians, indeed, were not unaware of the necessity of air to combustion, but being ignorant of the nature of air were necessarily ignorant of the function which it fulfilled. To burn and to throw off phlogiston being with them synonymous expressions, the air was conceived to act by somehow or other enabling the combustible to throw its phlogiston off; and a current of air was conceived to promote combustion by enabling the combustible to throw its phlogiston off more easily. Moreover, contact of air was not essential to combustion, provided there was present instead some substance, such as nitre, which equally with, or even more effectively than air, could enable the combustible to discharge itself of phlogiston. But while the phlogistians, on the one hand, were unaware that the burnt product differed from the original combustible otherwise than as ice differs from water, by loss of energy; Lavoisier, on the other hand, disregarded the notion of energy, and showed that the burnt product included not only the stuff of the combustible, but also the stuff of the oxygen it had absorbed in the burning. But, as well observed by Dr. Crum-Brown, we now know "that no compound contains the substances from which it was produced, but that it contains them *minus* something. We now know what this something is, and can give it the more appropriate name of potential energy; but there can be no doubt that this is what the chemists of the seventeenth century meant when they spoke of phlogiston."

Accordingly, the phlogistic and antiphlogistic views are in reality complementary and not, as suggested by their names and usually maintained, antagonistic to one another. It has been said, for example, that according to Stahl, the product of combustion is simple, and the combustible a compound of the product with imaginary phlogiston—which is false; whereas, according to Lavoisier, the combustible is simple, and the product a compound of the combustible with actual oxygen—which is true. But in this case, as in so many others, everything turns upon the use of the same word in a different sense at different periods of time. When Lavoisier spoke of red lead as being metallic lead combined with oxygen, he meant that the matter or stuff of the red lead consisted of the matter or stuff of lead *plus* the matter or stuff of oxygen. But when the Stahlians spoke of metallic lead being burnt lead combined with phlogiston, they had the same sort of idea of combination in this instance, as others have expressed by saying that the weight of a body is compounded of its matter and its gravity; or that steam is a compound of water and heat; or, to use a yet more Lavoisierian expression, that oxygen gas itself is a compound of the basis of oxygen with caloric. It is not, then, that the one statement, Stahlian or Lavoisierian, is false and the other true, but that both of them are distorted, because incomplete. Chemists nowadays are both Stahlian and Lavoisierian in their notions; or have regard both to energy and matter. But Lavoisierian ideas still interfere very little with our use of the Stahlian language. While we acknowledge that in the act of burning the combustible and the oxygen take equal part, just as in the act of falling the weight and the earth take equal part, yet in our common language we alike disregard the abundant atmosphere and abundant earth as being necessarily understood, and speak only of the energy of the combustible and of the weight, which burn and fall respectively. Whatever may be the fault of language, however, chemists do not omit to superpose the Lavoisierian on the Stahlian notion. They recognize fully that it is by the union of the combustible with oxygen that phlogiston is dissipated in the form of heat; and further, that phlogiston can only be restored to the burnt combustible on condition of separating the combustible from the oxygen with which it has united; just as energy of position can only be restored to a fallen weight on condition of separating it to a distance from the surface from which it has fallen.

That Stahl and his followers regarded phlogiston as a material substance, if they did so regard it, should interfere no more with our recognition of the merit due to their doctrine, than the circumstance of Black and Lavoisier regarding caloric as a material substance, if they did so regard it, should interfere with our recognition of the merit due to the doctrine of latent heat. But though defining phlogiston as the principle or matter of fire, it is not at all clear that the phlogistians considered this matter of fire as constituting a real body or ponderable substance; but rather that they thought and spoke of it as many philosophers nowadays think and speak of the electric fluid and luminiferous ether. The nondescript character, properly ascribable to phlogiston, is indicated by the following quotation taken from Macquer's 'Elemens de Chymie Theorique:' 1749. It must not, of course, be forgotten that the popular impression as to phlogiston having been conceived by its advocates as a material substance having a negative weight or levity, is erroneous; and is based on an innovation that was introduced during the struggling decadence of the phlogistic theory, and advocated more particularly by Lavoisier's subsequent colleague, Guyton de Morveau, in his 'Dissertation sur le Phlogistique, considéré comme Corps grave, et par rapport aux changemens de pesanteur qu'il produit dans les corps auxquels il est uni:' 1762. Macquer writes as follows:—

"La matière du soleil, ou de la lumière, le phlogistique, le feu, le soufre principe, la matière inflammable, sont tous les noms par lesquels on a coutume de désigner l'élément du Feu. Mais il paroît qu'on n'a pas fait une distinction assez exacte . . . . du nom qu'il mérite véritablement lorsqu'il entre effectivement comme principe dans la composition d'un corps, ou bien lorsqu'il est seul et dans son état naturel. Si on l'envisage sous cette dernière vue, le nom de Feu, de matière du soleil, de la lumière et de la chaleur, lui convient particulièrement. Pour lors, c'est une substance que l'on peut considérer comme composée de particules infiniment petites, qui sont agitées par un mouvement très rapide et continuel, par conséquent essentiellement fluide. Cette substance, dont le soleil est comme le réservoir général, s'en émane perpétuellement, et est répandue universellement dans tous les corps que nous connoissons ; mais non pas comme principe ou essentielle à leur mixtion, puisqu'on peut les en priver, du moins en grande partie, sans qu'ils souffrent pour cela la moindre décomposition. . . . . Cependant les phénomènes que présentent les matières inflammables lorsqu'elles brulent, nous indiquent qu'elles contiennent réellement la matière du Feu comme un de leurs principes. . . . . Examinons donc les propriétés de ce feu fixé, et devenu principe des corps. C'est lui auquel nous donnerons particulièrement le nom de matière inflammable, du soufre principe, ou de Phlogistique, pour le distinguer du Feu pur."

Again, much the same thing is to be found in Baumé's 'Manuel de Chymie:' 1765 ; as for example :—

"Nous considérons le feu sous deux états différens. Lorsqu'il est pur, isolé, et qu'il ne fait partie d'aucun composé . . . . Lorsqu'il est combiné avec d'autres substances, et qu'il fait un des principes constituans des corps composés . . . . On n'est pas certain si le feu est pesant. Il y a des expériences pour et contre. . . . .

"Pendant la combustion des substances, le feu combiné se reduit en feu élémentaire, et se dissipe à mesure. Le célébre Boerhaave n'est cependant pas de ce sentiment ; il dit que si cela étoit, la quantité de feu élémentaire devroit augmenter à l'infini dans la nature. . . . . Mais il est facile de répondre à cette objection, en disant comme on est en droit de le présumer, que le feu élémentaire, dégagé des corps, se combine à mesure avec d'autres substances, et qu'il perd toutes ses propriétés de feu libre, en devenant principe constituent des corps, dans la composition desquels il entre. . . . . Le principe dont nous entendons parler ici, est celui que Stahl a nommé *phlogistique*."

In interpreting the above and other phlogistic writings by the light of modern doctrine, it is not meant to attribute to their several authors the precise notion of energy that now prevails. It is contended only that the phlogistians had, in their time, possession of a real truth in nature which, altogether lost sight of in the intermediate period, has since crystallized out in a definite form. "I trust," said Beccher, "that I have got hold of my pitcher by the right handle." And what he and his followers got hold of and retained so tenaciously, though it may be shiftingly and ignorantly, we now hold to knowingly, definitely, and quantitatively, as part and parcel of the grandest generalization in science that has ever yet been established.

[W. O.]

Royal Institution of Great Britain.

WEEKLY EVENING MEETING,

Friday, June 7, 1872.

Sir Henry Holland, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

Professor Odling, F.R.S.

On the History of Ozone.

The most important points in the history of ozone are the following: I. Its recognition as a distinct variety of matter or substance, by Schönbein in 1840. II. An inquiry into its nature, made by Marignac in 1845, whereby it was established that the action of ozone on various substances results simply in their oxidation. III. The evidence of different kinds, accumulated by many observers during a period extending from 1845 to 1863, that the matter of ozone is identical with the matter of oxygen. IV. The demonstration by Andrews and Tait in 1860, that ozone is a condensed form of oxygen. V. The recognition by Andrews and Tait in 1860, and interpretation by the speaker in 1861, of the singular fact that, in certain cases, the removal of its constituent ozone from a mixture of ozone and oxygen is unattended by any alteration in the volume of the gas, notwithstanding the considerable oxidation effected by it. VI. The study of the quantitative reactions of ozone by Brodie in 1872; and his establishment of the relationship of ozone to ordinary oxygen, in corroboration of some less exact results obtained by Soret in 1865, as also of a suggestion made by the speaker in 1861.

I.

Ozone was discovered by Schönbein, in 1840, when experimenting with the then newly-invented battery of Sir Wm. Grove,—an instrument still recognized as yielding a current superior, in respect of joint quantity and intensity, to the current yielded by any other electromotor available for general use. Ozone was recognized by Schönbein successively, as a minute constituent of the oxygen gas resulting from the electrolysis of water effected by a current of high tension; as a minute constituent of air or oxygen through which electric discharges have taken place; and as a minute constituent of air in which moist phosphorus has been undergoing slow oxidation. To Schönbein then is due the great merit of recognizing ozone as a distinct form of matter, having an identity of its own by whatsoever means prepared—

as also the merit of discovering the most important means for the production of ozone, and of establishing its principal properties and reactions.

The general properties of ozone are those of an active oxygenant. Thus, like chlorine and peroxide of nitrogen, it bleaches colouring matters, corrodes fabrics, tarnishes or otherwise attacks metals, and liberates iodine from iodide of potassium. Its special properties are its characteristic pungent odour, its destructibility by a moderate heat, and its non-manifestation of any acidulous reaction.

II.

The nature of ozone was at first the subject of much speculation, Schönbein inclining to the view that it was a new elementary body, and a component of nitrogen. But in 1845, Marignac, in a series of most exact experiments, made partly in association with De la Rive, brought the question as to the nature of ozone within a very narrow compass. The experiments of these investigators, in which they established, among other points, that by exposure to the action of ozone, moist silver was converted simply into oxide of silver, and iodide of potassium into its oxidized form of iodate of potash, were susceptible only of one or other of two interpretations—either the interpretation which they themselves put on their results, that the matter of ozone is identical with the matter of oxygen—or, else the interpretation put on their results by Schönbein, that ozone is constituted of oxygen plus the elements of water, or in other words, that it is a peroxide of hydrogen. For a long time, experiment seemed quite incompetent to decide between these two views—opposite conclusions being arrived at almost alternately by the different investigators engaged on the inquiry. Corroboration, however, if any were needed, of the fact that ozone is really formed from oxygen itself with or without water, and not from any trace of nitrogen or other foreign matter that might possibly be present, was afforded by a remarkable experiment conducted by Fremy and Becquerel in 1853, being, indeed, the first recorded quantitative experiment made with ozone. By passing a long series of electric discharges through a given volume of oxygen standing over an aqueous solution of iodide of potassium, Messrs. Fremy and Becquerel succeeded in causing the whole of this oxygen to assume the form of ozone; as was shown by its ultimate complete absorption by the solution, with correlative liberation of iodine from the dissolved iodide of potassium.

The difficulty experienced in those early days of making out the real nature of ozone—of ascertaining whether it is a form of oxygen or a peroxide of hydrogen—depended mainly on the very small degree to which it was then possible to charge air or oxygen with the ozone to be examined, and on the necessity for the exclusive employment in the investigation of apparatus in which neither metal nor organic matter was present for the ozone to react with. The apparatus had consequently to be constructed entirely of glass, and all the junctions to be made before the blow-pipe or by grinding. Now-a-days, by improvements in the methods of conducting the processes of electrization and electrolysis, it is possible to charge oxygen with ozone in very considerable proportion; while by means of paraffin, a substance on which ozone is without recognizable action, junctions of the glass apparatus employed may be made and unmade with the greatest facility.

III.

Assuming the ozone furnished by the three principal processes for its production to be one and the same substance, it was not until the year 1863 that the absolute freedom of ozone from any proportion of hydrogen was so definitely established as not to allow of any further question. In this year, Soret showed that although ozonized oxygen obtained by electrolysis, after having been desiccated as thoroughly as possible, frequently yielded some water as a product of its decomposition by heat, yet that when certain precautions were taken, and certain sources of error in the production and collection of the electrolytic oxygen were recognized and avoided, a uniformly negative result was obtained, and not a trace of moisture or other compound of hydrogen resulted from the decomposition by heat of the ozone present in the oxygen.

This conclusion of Soret's was confirmatory both of the previous result of Andrews with regard also to electrolytically obtained ozone, and of the yet earlier result of Schönbein himself with regard to the ozone obtained by the slow oxidation of moist phosphorus. For in opposition to the view enunciated first by himself, and in seeming discrepancy with the undoubted fact that for the production of ozone by means of phosphorus the presence of moisture is essential, Schönbein, in 1849, showed by repeated experiment, that when ordinary air in quantities of several hundred litres, ozonized as strongly as possible by its passage over moist phosphorus, was transmitted first through a desiccating tube, then through a tube heated to 400°, so as to effect the destruction of the ozone present, and finally through another desiccating tube to absorb any moisture that might result from the destruction of the ozone, this last desiccating tube did not show, by an increase of weight or other change, any absorption of moisture whatever, notwithstanding the largeness of the absolute quantity of ozone destroyed in the experiment. From this time forth, Schönbein abandoned the notion of hydrogen being a constituent of ozone; and while making a valid distinction between his own view and that of Marignac and De la Rive, admitted with them that the matter of ozone is identical with the matter of oxygen. These last-named investigators, in their research already referred to (1845), showed that perfectly dry oxygen, submitted to the influence of electric discharges, experienced an alteration of character, whereby it acquired the property of liberating iodine from moist iodide of potassium,—a result afterwards confirmed by Fremy and Becquerel. But they did not regard this alteration of character as due to the formation in small proportion of a new substance within the mass of oxygen, but rather to the assumption by the mass of oxygen of a peculiar electric condition. Moreover, the fact of dry oxygen being capable of some modification by the action of electric discharges, coupled with the fact of the inability of the so modified oxygen to act upon iodide of potassium save in the presence of water, was not inconsistent with the notion of this modified oxygen having to unite with water in order to produce a compound identical with the ozone obtained immediately from moist or watery reagents. That the effect of electrical discharges, and more particularly of the silent discharge, on perfectly dry oxygen, is really to convert a small proportion of this oxygen into ozone identical with that furnished by electrolysis, and capable of acting upon certain substances, as mercury and iodine, when in the dry state, and on certain other substances, as iodide of potassium and metallic silver, only when in the moist state, was first put beyond question by Andrews and Tait, in a research next to be considered.

IV.

In the spring of 1860, Dr. Andrews and Prof. Tait made a joint communication to the Royal Society on the volumetric relations of ozone. The primary object of this research was to ascertain whether any, and if so what, alteration of volume took place in the conversion of a given quantity of oxygen into ozone. They thus attacked the problem from an entirely new point of view, and, with admirably directed pains and skill, succeeded in making probably the most important contribution hitherto made to an exact knowledge of the nature of the ozone. In their experiments, a quantity of perfectly pure and dry oxygen, contained in a straight glass tube with a pressure-gauge appendix, was ozonized by means of the silent electric discharge passed through the gas for some time. Coincidently with the passage of the silent discharge through it, the quantity of gas contained in the glass tube was observed to undergo a marked contraction in volume. This contraction proceeded at first rapidly, but afterwards more slowly, till it attained a limit which, in one of their experiments, was estimated at one-twelfth the original volume of the gas. And as whenever the gas, contracted in this manner, was examined, it was found to be proportionately ozonic, the general fact was established that the production of ozone from ordinary oxygen is attended with a contraction in volume. The converse result was also obtained. It was found that when oxygen, contracted by the passage of the electric discharge, was exposed for a short time to the temperature of 270°–300°, it was restored to its original volume. And as whenever the gas, re-expanded in this manner, was examined, it was found to be free from ozone, the general fact was established that the conversion of ozone into ordinary oxygen is attended with an expansion in volume. And this alternate contraction of a given quantity of oxygen by exposure to prolonged electrization, with production of ozone, and re-expansion of the gas to its original volume by exposure to a temporary heat, with destruction of ozone, could be repeated an indefinite number of times. Now the only possible conclusion to be drawn from these experiments would appear to be that, the matter of ozone being identical with the matter of oxygen, ozone is oxygen in a denser form,—that is to say, in the form of a more complex unit. Some years afterwards, this conclusion was confirmed in a very interesting manner by Professor Tyndall, in the case of ozone obtained electrolytically. He found that the absorptivity for radiant heat of electrolytically obtained oxygen, when rich in ozone, was upwards of a hundred times greater than that of ordinary oxygen—a result indicating ozone to have a more complex molecular constitution, and consequently a greater density, than ordinary oxygen. Moreover, after this same electrolytically obtained and richly ozonic oxygen had been subjected to the action of heat, so as to have its ozonic character destroyed, it then exhibited merely the absorptivity for heat of ordinary oxygen,—the observed absorptivity not going at all beyond that of ordinary oxygen, as would have been the case if the ozone originally present in the electrolytic gas had been decomposed into ordinary oxygen and aqueous vapour.

Referring to the statement already made, that in Messrs. Andrews and Tait's experiments, the oxygen gas, more or less contracted by the electric discharge, was found to be proportionately ozonic, this point was ascertained in the following way:—A small thin glass bulb, containing a solution of iodide of potassium, was introduced into the oxygen-holding tube, prior to its being filled with the gas; which, after having been more or less contracted by the process of electrization, was next submitted to the action of the solution, released on the breaking, effected by concussion, of the small bulb wherein it was contained. And on estimating the quantity of iodine set free from the iodide of potassium solution by its reaction with the contracted gas, it was found to be the exact chemical equivalent of a weight of oxygen equal in volume to the amount of contraction which the original gas had experienced during the process of electrization; so that if in the process of electrization, there had been one, two, or three cubic centimètres of contraction, the quantity of iodine liberated was chemically equivalent to the weight of one, two, or three cubic centimètres of oxygen; whence it results that to ascertain the iodine-titre of the ozonized gas is to learn the contraction of the original gas effected by its electrization, or the correlative expansion of the electrized gas effected by its exposure to heat. In the case also of electrolytically obtained ozonized oxygen, it was shown firstly by Andrews and Tait, and subsequently by Soret, that the iodine-titre of the gas is the measure of its expansion by heat, consequent on the conversion of its constituent ozone into ordinary oxygen.

V.

It has just been remarked that in the action of the contracted gas on iodide of potassium solution, there is absorbed by the reagent, with equivalent liberation of iodine, a weight of oxygen corresponding to a volume equal to that of the original contraction; but very curiously, the absorption by the reagent of this weight of oxygen from the contracted gas was found by Messrs. Andrews and Tait not to produce any further contraction or alteration of its volume; or the weight of oxygen which acted on the iodide of potassium solution appeared to occupy no part of the volume of the contracted gas, its removal from the contracted gas by means of the reagent not effecting any alteration in that volume. Since this remarkable result was first announced by Messrs. Andrews and Tait in 1860, it has been abundantly confirmed by von Babo and Claus, by Soret, and by Sir Benjamin Brodie—the modes of experimenting adopted in the original investigation of Andrews and Tait and in the three subsequent investigations, being all different from one another. And moreover, not only has the fact been established by the four several investigations with regard to iodide of potassium, but by one or other of the investigations with regard also to iodine, to mercurous salts, to ferrous salts, to arsenites, and to ferrocyanides. So that, when a given volume of ozonized oxygen is allowed to act upon these different oxidizable bodies, the oxidation effected by the ozone present in the gas is found to be unattended by any diminution in the volume of the gas. An interpretation of this singular result was put forward by the speaker soon after the publication of Messrs. Andrews and Tait's experiments, to the following effect: Ozone being proved to be a condensed form of oxygen, it is clear that any volume of ozone will contain a greater weight of the matter of oxygen than is contained in the same volume of ordinary oxygen. And since in the action of ozone upon iodide of potassium, the volume of the reacting gas does not undergo any alteration, it is obvious that the oxidation effected must be effected by only so much of the matter of oxygen contained in the volume of ozone, as is in excess of the matter of oxygen contained in the same volume of ordinary oxygen. This interpretation, so far as it went, was considered to be demanded by Messrs. Andrews and Tait's experiments, as the only satisfactory explanation of them. With regard to the weight of the matter of oxygen contained in a given volume of ozone, in excess of the weight of the matter of oxygen contained in the same volume of ordinary oxygen, no data whatever existed to show what this weight really is. But relying upon the fact that the weight of oxygen contained in a standard volume of free oxygen is composed of two simple weights of the matter of oxygen, it was conjectured that the weight of oxygen contained in a standard volume of ozone might not improbably be constituted by an introduction into the standard volume of ordinary oxygen of another simple weight of oxygen—equal volumes of ozone, free oxygen, and nitric oxide, for example, being expressible by the comparable formulæ O_3, O_2, and NO respectively. In accordance with this supposition, the action of ozonized gas upon iodide of potassium, &c., is explicable as follows:—The ozone which acts is decomposed into a weight of free oxygen equal in volume to the volume of the ozone, and into another weight of absorbed oxygen, assumed to be one-half of the former weight. The suggestion as to the standard volume of ozone being constituted thus of three simple weights of the matter of oxygen, was admittedly not a necessary deduction from the then known facts, which were indeed equally consistent with its being constituted of four, five, or six such weights; it was only the suggestion of the simplest possible constitution for ozone that was consistent with the facts.

A few years afterwards, in 1865–66, the probability of this being the real constitution of ozone was much strengthened by the results of some experiments conducted by Soret. Operating by a process very simple and ingenious, but scarcely calculated to afford precise results, Soret found that when electrolytically obtained ozonized oxygen was allowed to act upon oil of turpentine, the absorption of the ozone by the turpentine was attended by a diminution in the volume of the gas equal approximatively to twice the initial contraction,—as inferred, of course, from the iodine-titre of the ozonized gas, or from its permanent expansion after exposure to a temporary heat. Supposing the final diminution effected by the turpentine to have been exactly twice the initial contraction, inferred from the iodine-titre, it is clear, that while the original gas would have suffered altogether a diminution of three volumes, the ozonized gas would have suffered a diminution of only two volumes. Or there would have been ultimately abstracted from the original uncontracted gas three volumes of the matter of oxygen, occupying in the contracted or ozonized gas, submitted to the action of the turpentine, only the bulk of two volumes. But as a mean result of Soret's first set of five experiments, the final diminution effected by the turpentine was 2·40 times the original contraction; while, as a mean result of his second set of seven experiments, the final diminution was 1·81 times the original contraction. Assuming, however, ozone to have the constitution expressed by the symbol O_3, its specific gravity, and consequently its diffusion-velocity, would approximate closely to the specific gravity and diffusion-velocity of carbonic acid gas, CO_2; and in 1867, Soret, in corroboration of his previous absorption results, satisfied himself that the diffusion-velocity of ozone really does approximate very closely to that of carbonic acid.

VI.

During the last few years, the quantitative reactions of ozone have been made the subject of an elaborate study by Sir Benjamin Brodie, whose results constitute indeed "a body of exact information as to the chemical properties of ozone, through which it may be hoped that this important question will be finally removed from the domain of arbitrary speculation and brought within the precincts of science." In Brodie's experiments, a quantity of pure perfectly dry oxygen, after having been submitted to electrization by its passage through a modified form of Siemens' induction tube, carefully maintained at a low temperature, was collected in an oil of vitriol gas-holder, to the amount of four or five thousand cubic centimètres. From the store of ozonized gas thus collected, which was found to maintain its proportion of ozone without appreciable deterioration for some hours, portion after portion was allowed to pass into a pipette of about 250 c.c. capacity, by displacement of the oil of vitriol originally filling it; and successive equal volumes of the store of ozonized gas so measured off, were submitted one after another to the action of the same or of different reagents, by the passage of each pipetteful of gas through a small bulb-tube containing the reagent in solution. The gas, freed from all ozone by its passage through the reagent, was next received into a mercurial measuring cylinder, in which it was expanded to a definite volume; and then, by reading off the pressure at which it occupied this volume, its proper volume was ascertained. Finally, the difference between the capacity of the pipette and the volume obtained in the mercurial cylinder showed the volume of the gas absorbed by the reagent,—the weight of this gas being determined directly or indirectly by titrations of the reagent. Of course, very many points of detail in the construction and use of the apparatus had to be attended to, in order to ensure trustworthy results; but, both in its principle and general working, the process is exceedingly simple. One essential novelty consists in the application of that very useful instrument, the pipette, to the purposes of gas analysis; and by its aid, results having a degree of accuracy far greater than those furnished by any previous method of ozone investigation, were found to be obtainable with both speed and facility.

Operating, then, with the apparatus just described, Brodie has succeeded in establishing three perfectly definite classes of ozone-reactions,—the first of them including the instances previously made known by Andrews and Tait. In this first class of reactions, of which there are several distinct varieties, the absorption or decomposition of the ozone present in a mixture of ozone and oxygen, is unattended by any diminution in the volume of the gas; or a volume of ozone O^{2+x}, is resolved into an equal volume of free oxygen, and an indefinite weight of other oxygen, either absorbed or set free. This class of reactions accordingly does not afford any information as to the value of x, or, in other words, as to the relationship of the formula O^{2+x} to the formula O^2.

$$\overbrace{O^{2+x} \;=\; O^2}^{\text{Unit-volumes.}} \;+\; x\,O \text{ absorbed.}$$

In a second class of reactions, the absorption or decomposition of the ozone present in a mixture of ozone and oxygen, is attended with a diminution in the volume of the gas, equal to half the volume that the weight of oxygen absorbed would occupy in the free state. In this class of reactions, then, one of but two occurrences must happen: either the ozone present in the mixture of gases, is absorbed wholly without decomposition, in which case the density of ozone must be twice that of ordinary oxygen, and the formula O^{2+x} become O^4; or the ozone present in the mixture, is decomposed into half its volume of oxygen liberated, and into a quantity of oxygen, corresponding to its entire volume, absorbed; in which case the density of ozone must be one-and-a-half that of ordinary oxygen, and the formula O^{2+x} become O^3.

$$\left.\begin{array}{rcl} \overbrace{O^{2+x} \;=\; \text{nil}}^{\text{Unit-volumes.}} & + & 4\,O \\ 2\,(O^{2+x}) \;=\; O^2 & + & 4\,O \end{array}\right\}\text{absorbed.}$$

In a third class of reactions, the absorption or decomposition of the ozone present in a mixture of ozone and oxygen, is attended with a diminution in volume of the gas, equal to two-thirds the volume that the weight of oxygen absorbed would occupy in the free state; or the weight of the gas absorbed is to the weight of an equal volume of oxygen as 3 to 2. But consistently with this class of reactions, the density of ozone must necessarily be one-and-a-half times that of ordinary oxygen, and the formula O^{2+x} must become O^3.

$$\overbrace{(O^{2+x}) \;=\; \text{nil}}^{\text{Unit-volumes.}} + 3\,O.$$

This last and most important class of reactions, by which the formula of ozone as O^3, is put beyond question, was established by a long series of experiments, made chiefly with a neutral or but slightly alkaline solution of hyposulphite of soda, and in a few cases with oil of turpentine. As a result, the ratio of the entire diminution in volume suffered by the original oxygen, to the diminution in volume of the electrized or contracted oxygen effected by the reagent, was found to be, as a mean of twenty-seven concordant experiments made with the hyposulphite, 3·02 to 2·02; and as a mean of eight concordant experiments made with the turpentine, also as 3·02 to 2·02. But neither with the hyposulphite nor with the turpentine, could the weight of oxygen absorbed by the reagent be determined, otherwise than by a calculation from the alteration in volume of the gas. A direct determination, however, was effected in the case of a few experiments made with protochloride of tin, under conditions carefully considered and regulated so as to ensure a trustworthy result. And it was found, in these few experiments, that the weight of the matter of oxygen absorbed from the ozonized gas by the tin-salt, was almost exactly three times the weight of the matter of oxygen absorbed from the same gas by iodide of potassium, —the volume occupied by the weight of oxygen absorbed by the tin-salt being almost exactly twice the volume proper to the weight of oxygen absorbed by the iodide of potassium.

Independently of the importance attaching to the actual determination of the density of ozone, Sir B. Brodie's result has a further interest for chemists, which it would be difficult to exaggerate. The principal of the elementary bodies, known to chemists in the gaseous or vaporous state, are hydrogen, chlorine and its congeners, oxygen, sulphur, nitrogen, phosphorus, arsenic, mercury, and cadmium. Now it is a fact that the weight of phosphorus or arsenic contained in any volume of phosphorus or arsenic vapour, is four times the weight of phosphorus or arsenic contained in the same volume of phosphoretted or arsenetted hydrogen, and of a host of other phosphoretted or arsenetted gases or vapours. It is also a fact that the weight of hydrogen, chlorine, oxygen, or nitrogen contained in any volume of each of these elementary gases, is twice the weight of hydrogen, chlorine, oxygen, or nitrogen contained in the same volume of a variety of hydrogenous, chlorinous, oxygenous, or nitrogenous compound gases. It is also a fact that the weight of mercury or cadmium contained in any volume of the vapour of either element, is identical with the weight of the element contained in the same volume of the vapour of all its hitherto examined volatile compounds. But now a variety of oxygen is shown to exist, the weight of any given volume of which is three times the weight of oxygen contained in the same volume of the simplest of oxygenous compounds respectively, thus:—

$$\overbrace{\begin{array}{cccc} P_4 & O_3 & O_2 & Hg \\ PCl_3 & CO & NO & HgCl_2 . \end{array}}^{\text{Unit-volumes.}}$$

The question, then, naturally arises, how long will it be before another variety of oxygen is recognized, the weight of any given volume of which, like that of a given volume of phosphorus vapour, shall furnish the weight of the element contained in four such volumes of its several simplest compounds? And again, how long will it be before yet another variety of oxygen is recognized, the weight of any given volume of which, like that of any given volume of mercury vapour, shall furnish but the weight of the element contained in the same volume of its several simplest compounds? There is the strongest indirect reason for believing in the existence of such a unitary oxygen. For in its reactions, oxygen behaves as a sort of more active electro-negative counterpart of electro-positive mercury Hg; and like mercury Hg, and unlike hydrogen H_2, and chlorine Cl_2, it enjoys the property of adding itself to a pre-formed unit of substance by an indivisible proportion.

[W. O.]

Royal Institution of Great Britain.

WEEKLY EVENING MEETING,

Friday, June 6, 1873.

Sir Henry Holland, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

Professor Odling, M.A. F.R.S.

On Evaporation and Diffusion.

Of the circumstances on which the rate of evaporation of the same volatile substance chiefly depends, one very influential circumstance, namely, the nature of the atmosphere into which the vapour proceeds and distributes itself, does not appear to have been made the subject of careful examination. There is, however, one familiar experiment on the subject; and it consists in passing up a little ether into two equal volumes, one of hydrogen and the other of air, contained in similar cylinders standing over water. Evaporation of the ether takes place in both cases; though far more rapidly into the hydrogen than into the air, as shown by the far more rapid expansion of the hydrogenous than of the aerial space, from the addition to it of the ether-vapour. This experiment is usually cited in illustration of the greater rapidity at which ether-vapour diffuses itself into an atmosphere of light hydrogen than into an atmosphere of comparatively heavy air. It is doubtful, however, whether the explanation in this precise form is strictly correct, the diffusive mobility of any gas or vapour being a property altogether special to itself, irrespective of extraneous conditions. Thus, in a particular experiment, Mr. Graham found that while the quantity of hydrogen which in one minute of time passed through a graphite plate into a vacuum was 1·289 c. c., the quantity of hydrogen which in the same time passed through the same graphite plate into the surrounding air was 1·243 c. c., or almost exactly the same.

A novel experiment on the influence due to the nature of the contiguous atmosphere upon the rapidity of the process of evaporation, consists in introducing into each of two similar tall cylinder bottles a sealed glass bulb containing a little iodine. The one cylinder being filled with hydrogen, and the other with air, and each having suspended from its mouth a piece of starched paper or cloth, the bulbs are then broken by concussion of the containing cylinders. But, in this case, the test paper or cloth suspended in the cylinder of air becomes affected by the iodine considerably before that suspended in the cylinder of hydrogen; or, contrary to what happens with ether, the iodine *appears* to volatilize more quickly in the comparatively heavy air than in the much lighter hydrogen. Similarly, if some weak aqueous ammonia contained in a sealed glass bulb be set free in a tall bottle of hydrogen, and also in a tall bottle of air, a piece of turmeric paper suspended from the stopper of each bottle becomes affected by the ammonia vapour more quickly in the bottle of air than in the bottle of hydrogen.

Water may be taken as the type of a volatile substance, and the nature of the process of evaporation be conveniently studied in relation thereto. Now, in a hermetically-closed vessel exhausted of air, but partly filled with water, the matter of the water exists in two states—a portion of it in the liquid state, and another portion in the aerial, or vaporous, or evaporated state; and, with excess of liquid water present, the quantity of vaporous water that can exist in an otherwise vacuous space, or the density of the vapour filling the space, is found to vary solely with the temperature. Thus 100 cubic inches of space will contain at 58° C., 3 grains of vaporous water; at 100° C., 15 grains; at 144° C., 58 grains, and so on; or the densities of the vapour of water at these different temperatures are as the numbers, 3, 15, and 58, respectively. Now, the quantity of water-vapour that can exist at any particular temperature in a volume of otherwise vacuous space, is almost identical—it used to be considered absolutely identical,—with the quantity of vapour that can exist in the same volume of space already occupied by air. In other words, a cubic inch of water-vapour, and a cubic inch of air saturated with water-vapour, contain the same weight of the matter of water. Hence it is found that with continuous increase of temperature, a greater and greater quantity of liquid water ceases to be liquid and becomes vaporous, or is, in other words, evaporated into the adjoining space, whether vacuous or aerial; and conversely with decrease of temperature, a greater and greater quantity of vaporous water ceases to be vaporous, and is deposited in the liquid state. Thus, upon cooling a globe of transparent warm moist air, it is at once filled with an opaque mist, which, left to itself, soon becomes deposited in the form of drops; but which may be readily made to disappear or re-vapourize by gently heating the globe. The deposition of dew on cold surfaces brought into a warm moist room is familiar to all.

The tension or spring of water-vapour varies with the quantity of vapour filling the space—that is, with the density of the vapour, and consequently with its temperature. Thus the tension is equal at 15° C., to a pressure of 13 millimètres of mercury; at 60° C., to a pressure of 149 millimètres; at 100° C., to a pressure of 760 millimètres; at 144° C., to a pressure of 3040 millimètres. At the temperature of 100° C., the tension of the vapour of water being equal to a pressure of 760 millimètres of mercury, balances the tension or pressure of the atmosphere, as measured by the height of the barometric column. Hence on continuing to heat water already at the temperature of 100°, it boils, or is converted into vapour, having a tension equal to that of the atmosphere. And so with a less or greater external pressure, water boils at a lower or higher temperature—in each case at the particular temperature whereat the elastic force of the water-vapour balances the particular external pressure. Under a pressure of 149 millimètres, for instance, water boils at 60° C.; under a pressure of 3040 millimètres, it boils at 144° C. The occurrence, then, of ebullition at some particular point of temperature may be viewed as a mere accident of the process of evaporation—a more and more rapid evaporation, with production of vapour of higher and higher density and elasticity, proceeding continuously with the continuous increase of temperature, although, indeed, at a far more rapid rate than the rate of increase of temperature.

In the conversion of liquid water into water-vapour, heat is absorbed. It was at one time considered that the quantity of heat absorbed was independent of the temperature and correlative tension of the vapour yielded, and that it varied only with the quantity yielded. It was held, for example, that in the conversion, say, of a gramme of liquid water into a gramme of water-vapour—whether of tenuous vapour at a low temperature, or of dense vapour at a high temperature—the same quantity of heat was absorbed. This rule, though now known to be only approximatively true, is nevertheless sufficiently true to allow of the amount of cold, or absorption of heat, resulting from any evaporation, being taken as an indication or measure of the amount of that evaporation. The depression of temperature caused by the evaporation of water, is familiarly shown in the use of the wet-bulb hygrometer. This instrument consisting simply of a couple of thermometers, one of which has its bulb kept continuously moist, the difference in way of deficit between the temperature manifested by this wet-bulb thermometer and the temperature manifested by the other thermometer, is a measure of the amount of water evaporating from the surface of the moistened bulb.

What is true of liquid water and of water-vapour is true, in principle, of other volatile liquids and of their several vapours. At any given temperature some of these bodies volatilize much more rapidly, others of them much less rapidly, than one another, and than water; and in the process of their evaporation some of them absorb a much greater amount of heat than others, though for the same weight of vapour formed no one of them is known to absorb so large an amount of heat as water. Disulphide of carbon, ether, and alcohol, are familiar examples of bodies more volatile than water; aniline, mercury, and molten silver, of bodies less volatile. It is well known that water when required pure is distilled—that is to say, it is first vaporized by heat and then re-liquefied by cold; and silver when required absolutely pure is sometimes submitted to the same process of distillation. Evaporation is, moreover, a property not only of liquid, but also of solid bodies, as of sal-ammoniac, iodine, camphor, ice and snow, solid carbonic acid, &c. Many of the phenomena of evaporation can be illustrated more conveniently with other volatile substances than with water. Thus the cooling produced by evaporation may be strikingly illustrated by means of ether, and still more strikingly by means of some liquefied gas, as liquefied sulphurous or nitrous oxide.

The necessary influence of some conditions on the rate of evaporation is obvious. Evaporation being a direct result of the absorption of heat, and the higher the temperature the greater the quantity of vapour capable of existing in a given space, it is found that at higher and higher temperatures water evaporates or dries up more and more rapidly, in proportion approximatively to the increasing density of the vapour at higher and higher temperatures. Wet linen, for example, is habitually dried by being hung before the fire or placed in heated chambers or ovens.

Similarly with regard to the influence of the extent of liquid surface on the rate of evaporation, it is found that the evaporation of a given weight of liquid water takes place more rapidly when the water is spread out in a wide dish than when it is contained in a narrow tube, in proportion to the greater extent of surface from which the evaporation can take place in the one case than in the other. Thus, while half a pint of water in a tumbler will remain for an almost indefinite time without becoming dried up, half a pint of water absorbed in a thick towel exposing on its two sides more than a dozen square feet of surface, will become dried up in the course of twenty-four hours.

Again, the influence exerted by the greater or less dryness of the adjacent space, whether or not aerial, upon the evaporation of water is obvious. Into a space already saturated with vapour no further evaporation whatever can take place; and other conditions being alike, the drier the space the greater the amount of evaporation that can take place with it, and the more rapid the process of evaporation. In the laboratory, moist substances are made dry by allowing the water from them to evaporate into spaces kept artificially dry by means of desiccating agents, such as oil of vitriol, quicklime, chloride of calcium, &c., which absorb the water-vapour from the space as fast as it is produced therein. Moreover, evaporation proceeding into any space, vacuous or aerial, until the space is saturated with water-vapour, and more rapidly in proportion to the removal from saturation of the space, it is obvious that, other conditions being equal, evaporation proceeds more rapidly into a large space requiring for its saturation a considerable weight of water-vapour than into a small space capable of being saturated by a minute quantity of the vapour.

The influence of the extent of aerial space into which a vapour can distribute itself upon the rate of formation of the vapour, leads to a consideration of the effect of the movement of the contiguous air upon the rate of evaporation from a given surface. With an absolutely quiescent atmosphere, the layer of atmosphere in immediate contact with the surface of evaporating liquid must become quickly saturated with vapour; and but for some spontaneous means of removal of the vapour itself, or of the air saturated with it, from the surface of the liquid, all further evaporation would be arrested. The nature of these spontaneous means of removal will be considered presently; but the influence of the artificial removal of the more or less saturated air from the surface of the evaporating liquid can be easily manifested. Thus on allowing a strong current of air to play upon a surface of ether contained in a thin glass vessel standing on a stratum of water, the stratum of water becomes quickly frozen by reason of the heat abstracted from it, in the rapid production of ether-vapour which takes place in the current of air. For whereas with the ether in the vessel left to itself, the interior of the vessel soon becomes saturated with ether-vapour, and further evaporation with correlative cooling effect is almost arrested; with a current of air blown on to the surface of the ether, the liquid ether is in continuous contact with a fresh unsaturated atmosphere, into which it continues to evaporate with rapidity.

In connection with the above influences, it is observable that the evaporation of water from growing plants is favoured by the three conditions of extent of leaf surface, movement of the more or less dry atmosphere, and heat of the summer sun. An early and very striking experiment on the extent of this evaporation was made by Dr. Stephen Hales in 1724, and is recorded in his 'Vegetable Statics.' He found that with a healthy full-grown sunflower more than a yard high, planted when young in a suitable pot, the evaporation from the plant itself amounted on the average to 20 ounces in a twelve hours' day, the maximum quantity being 30 ounces. Some very interesting and exact modern experiments on this subject were conducted in 1850 by Mr. Lawes at Rothamstead. As an example of the results obtained, he found that a plant of barley, during a period of 172 days' growth, in which it acquired 419 grains of dry organic, and 46 grains of dry mineral matter, evaporated not less than 120,000 grains, or upwards of 17 lbs. of water; so that for every grain of dry matter, organic and mineral, fixed by the plant during its period of growth, 257 grains of water were absorbed and evaporated.

A most important condition affecting the rate of evaporation is the pressure on the surface of the volatile substance. Into a vacuum indeed, where there is no pressure, evaporation is practically instantaneous. Thus on letting up a little water, alcohol, or ether into the vacuum of a barometer, the mercury is at once depressed to the maximum extent producible by the tension of the particular vapour at the particular temperature. Again, on breaking a sealed bulb of iodine, within and at the lower end of a long sealed vacuous tube, a piece of starch-paper at the upper end of the tube is almost immediately affected by the iodine vapour. Further, the cooling consequent on the rapid evaporation of ether, ammonia, &c., into a vacuum, is taken advantage of in the construction of several well-known freezing machines. Again, in Leslie's celebrated experiment, the evaporation even of water into a vacuous space, from which the water-vapour is removed by some desiccant as fast as produced, takes place with such rapidity and correlative absorption of heat, as to effect the freezing of the residual water from which the evaporation is proceeding. The same result is effected in Wollaston's cryophorus, the water-vapour in this case not being absorbed by oil of vitriol or other desiccant, but being simply condensed by cold applied to the other and distant bulb of the twice bent vacuous tube. Moreover, it was long ago shown by Daniel that evaporation of water into the same dry atmosphere takes place at a rate inversely proportioned to the pressure of the atmosphere. Thus in a particular set of experiments, the pressures of the air being 30·4, 15·2, and 7·6 inches of mercury, the quantities of water evaporated in half an hour were found to be 1·24, 2·97, and 5·68 grains respectively.

That the nature of the atmosphere into which a vapour can distribute itself has an important influence on the rate of formation of the vapour may be manifested by several experiments, in addition to those shown at the beginning of the lecture. Thus with a couple of thin glasses standing on a stratum of water, and containing each some rectified wood-spirit, if the one portion of spirit be blown upon by a strong current of hydrogen, and the other portion by a strong current of air, the stratum of water underlying the glass of spirit blown upon by the hydrogen, will alone become frozen, by reason of the excessive vaporization of, and heat-absorption by, the spirit in contact with the atmosphere of hydrogen. Again, a series of experiments has recently been made by the speaker on the relative rates of evaporation of water into limited atmospheres of hydrogen, air, and carbonic acid respectively, alike kept dry by contact with a large surface of oil of vitriol. In these experiments, the evaporation was found to take place most rapidly in hydrogen, and least rapidly in carbonic acid; and as a mean of seven tolerably concordant results, the ratio of the rate of evaporation in hydrogen to the rate of evaporation in air, under the particular conditions of the experiment, was found to be as 2·68 : 1.

The influence of the particular contiguous atmosphere on the rate of evaporation of any particular liquid may be, and probably is, of a very complex nature. There are, however, two easily intelligible ways in which the particular atmosphere may act by virtue of its specific gravity. Thus a lighter or heavier gas or vapour ascends or descends bodily through another at a rate proportionate to the difference in their specific gravities, a very slight difference sufficing to bring about an upward or downward current of considerable activity. This upward or downward movement is well shown by introducing first heavy ether-vapour, and then light coal-gas, through a lateral opening made at about the middle of the length of a tall somewhat wide perpendicular glass tube, open at both ends; when it will be found that the ether-vapour, descending by reason of its heaviness, can only be inflamed at the bottom of the tube, while the coal-gas, ascending by reason of its lightness, can only be inflamed at the top. Now, the specific gravities of hydrogen, aqueous vapour, and air at the same temperature, being to one another as the numbers 1, 9, and 14·5 respectively, it is obvious that whereas hydrogen saturated with water-vapour is heavier than dry hydrogen, air saturated with water-vapour is lighter than dry air. Accordingly, with a surface of water exposed to an atmosphere of originally dry hydrogen, the hydrogen in actual contact with the water will not, by becoming moist, acquire a tendency to rise up through the dry hydrogen, and so be removed from the surface of the liquid; whereas, with a surface of water exposed to an atmosphere of originally dry air, the air in actual contact with the water will, by becoming moist, acquire a tendency to rise up through the dry air, and so become removed from the surface of the liquid. And having regard to this influence alone, water when occupying an inferior position, should evaporate more rapidly into air than into hydrogen. It must be borne in mind that any given volume of moist air or gas is the sum of the volume of its constituent water-vapour, and of the volume of its constituent dry air or gas; and that the tension of the moist air or gas is the sum of the tension of its constituent water-vapour, and of the tension of its constituent dry air or gas, actually or virtually expanded by the addition to it of a certain volume of water-vapour. So that with water boiling in a deep open vessel, there may exist in close proximity to each other, almost pure water-vapour, different mixtures of water-vapour and air, and comparatively dry air, all having alike a tension of 760 millimètres of mercury.

But independently of their bodily movements in the form of currents, gases and vapours distribute themselves among one another by a proper molecular movement of diffusion—the relative diffusive mobilities of different gases or vapours being inversely as the square roots of their several specific gravities. Accordingly, with equal surfaces of water exposed respectively to an atmosphere of hydrogen and to an atmosphere of air, the vapour produced from the surface of the water is interpenetrated and distributed through the contiguous space with greater rapidity by the highly-diffusive hydrogen than by the feebly-diffusive air, in proportion to their relative diffusion-velocities, 3·8 and 1·0 respectively. And it is, doubtless, to the more rapid diffusion of hydrogen than of air into the vapour as formed, and the consequent more rapid supply to the liquid of an unsaturated atmosphere into which it can evaporate, that the more rapid evaporation of water, ether, and wood-spirit into an atmosphere of hydrogen than into an atmosphere of air, as in the experiments, for instance, already shown and described, is substantially due.

[W. O.]

Royal Institution of Great Britain.

NOTES
OF
PROFESSOR ODLING'S JUVENILE LECTURES,
CHRISTMAS, 1870–71.

BURNING AND UNBURNING.

Lecture I.—*Tuesday, December* 27, 1870.

Burning in Air.

1. Our grandfathers used to strike a light, or obtain sparks, with flint and steel. Charred rag, known as tinder, is easily set on fire by sparks. Then brimstone, at the tip of a wooden match, is set on fire by the burning tinder, and the wood of the match set on fire by the burning brimstone or sulphur.

2. To strike a light, nowadays, we use a lucifer-match. The phosphorous composition, at the end of the match, takes fire when drawn across a piece of sand-paper or other rough surface, and the wood of the match is set on fire by the burning phosphorus.

3. With our burning match we can set light to a gas-jet, a lamp, a candle, or a fire. The gas-jet, lamp, candle, and fire do not begin burning of themselves. They require first to be set light to.

4. Many substances do not burn even when set light to. We cannot set a silver spoon or a piece of brick on fire.

5. The act of burning is called *combustion.* Substances capable of burning are called combustible, and substances incapable of burning, incombustible. Combustibles, when set fire to, usually go on burning, diminish in quantity, and at last disappear.

6. What becomes of the scuttlefuls of coals, the pounds of candles, the gallons of oil, and the cubic feet of gas continually being burnt or consumed? Or, one thing at a time, what happens when a candle is burnt?

7. An ordinary sperm-candle, being set light to, continues to burn. It diminishes in length about one inch an hour, and it loses in weight about two grains a minute.

8. The burning of the candle takes place in the air of the room, and the presence of air is necessary to enable the burning to go on. On cutting off the supply of air, the flame of the candle is at once extinguished, and its burning ceases.

9. A candle cannot be set a-light, or inflamed, in a space from which the air has been removed by an air-pump. Contact of air with the candle is necessary for it both to become lighted and to continue burning.

10. The candle burns in ordinary atmospherical air. But there exist several kinds of air quite distinct from ordinary air ; and in some of these other kinds of air, a candle will not burn, any more than it will in a space not containing air at all.

11. Hence the burning of a candle in ordinary air would seem to be an event in which both the candle and the air are concerned.

12. When ordinary atmospheric air is shaken up with a chemical substance called pyrogallate of potash, one-fifth part of the bulk of air taken disappears, being absorbed by the pyrogallate.

13. The properties of the residual four-fifths of air are quite different from those of the original air. In the residual air, a candle will not burn and an animal cannot breathe. Hence this residual air is sometimes called non-vital air or *azote*.

14. The candle being unable to burn in the four-fifths of air left of the pyrogallate, its burning in ordinary air would seem to consist in a something taking place between it and the one-fifth of air absorbed by the pyrogallate.

15. This is really the case. A lighted candle, introduced into a closed vessel of air, burns for a little time, then goes out, and a portion of the original bulk of air is found to have disappeared. But the quantity of air unabsorbable by pyrogallate of potash is the same as at first; it is only some of that constituent of the air absorbable by the pyrogallate which has disappeared, or been removed by the burning candle.

16. The one-fifth of ordinary air absorbable by pyrogallate of potash—that is the one-fifth necessary alike for the burning of combustibles and the breathing of animals—may be obtained apart, by first absorbing it into, and then evolving it from, some substance by which it is absorbable.

17. Quicksilver or mercury is a suitable substance for the purpose. When this metal is heated for a long time in air, it absorbs one-fifth of the original bulk of air, and the remaining four-fifths are found to consist of non-vital air or azote.

18. By the absorption which it has effected, the mercury is converted into red scales of mercury-rust; and when this rust is more strongly heated, it changes back into metallic mercury and into the volume of air absorbed by the mercury from the original air.

19. The one- fifth of ordinary air, slowly absorbed by heated mercury and quickly evolved by more strongly heated mercury-rust, has the property of causing a glowing splinter to burst into flame.

From its being necessary to the processes of burning and breathing it was originally called vital air.

20. Ordinary atmospheric air, then, is a mixture of about one measure of vital air with four measures of non-vital air or azote. Vital air is, nowadays, called oxygen, from its being a constituent of many acids. Non-vital air is called nitrogen, from its being a constituent of nitre.

21. A candle and different combustibles, which burn quietly in air or much-diluted oxygen, burn very fiercely in pure oxygen. In the act of burning, whether in air or oxygen, the stuff of the candle unites with oxygen to form products which are invisible or gaseous, like air itself.

22. One of these products is steam, or the vapour of water. A sperm-candle weighing $2\frac{3}{4}$ ounces, yields by its combustion about $3\frac{1}{4}$ ounces of water. Water is an oxide of hydrogen,—burnt hydrogen in fact. Hence hydrogen is shown to be a constituent of the candle, by reason of the candle yielding burnt hydrogen, or water, as a product of its burning.

23. Another product of the burning candle is carbonic gas. Carbonic gas is an oxide of carbon,—burnt carbon in fact. Hence carbon is shown to be a constituent of the candle, by reason of the candle yielding burnt carbon, or carbonic gas, as a product of its burning.

24. In the act of burning in air, the weight of sperm becomes less and less until the candle is burnt out. But the weight of the products formed by the burning, becomes more and more,—the weight of oxygen consumed being constantly added to the weight of sperm consumed.

25. All ordinary combustibles, coal, wood, oil, and gas, consist mainly of carbon and hydrogen. By burning in air or oxygen, they yield burnt carbon or oxide of carbon, and burnt hydrogen or oxide of hydrogen, as products of their burning.

26. Other combustibles, such as sulphur and phosphorus, when burning in air or oxygen, yield burnt sulphur or oxide of sulphur, and burnt phosphorus or oxide of phosphorus respectively. The oxide of sulphur, obtained by burning sulphur, is an invisible gas. The oxide of phosphorus, obtained by burning phosphorus, is a white solid.

27. The burning then of different substances, in air or oxygen, consists in a combination of the different substances with oxygen to form oxydized products; and this act of combination is attended by an evolution of light and heat.

LECTURE II.—*Thursday, December* 29, 1870.

BURNING WITH FLAME.

28. Coal gas and hydrogen gas, when set fire to, immediately take fire, and go on burning. Spirit of wine also, when set fire to, seems to inflame immediately. But sperm-oil, in a cup, will not take fire at all; while sperm-oil, absorbed in a wick, will take fire and burn with flame, only after an instant or so.

29. Ether is a liquid boiling at about the temperature of the body, and giving off much vapour at the temperature of the air. On bringing a lighted taper near to ether, the heavy vapour or gas of the ether inflames at some distance from the surface of the liquid.

30. To make spirit of wine or alcohol vaporize appreciably, a rather higher temperature is required. On bringing a lighted taper near to hot alcohol, the vapour of the alcohol inflames at some distance from the surface of the liquid.

31. On bringing a lighted taper almost in contact with cold alcohol, the heat of the burning taper causes a small portion of the alcohol to vaporize, and the produced vapour then inflames. In continuing to burn, the heat of the burning alcohol-vapour vaporizes some more alcohol; and throughout, it is the vaporous or gaseous alcohol, and not the liquid alcohol, that burns with flame.

32. The most dangerous variety of paraffin oil, or rather paraffin spirit, behaves like ether. A somewhat safer variety behaves like alcohol. A perfectly safe paraffin oil does not inflame until heated considerably. When sufficiently heated, all paraffin oil gives off vapour, and this vapour it is that burns with flame.

33. With paraffin oil absorbed in a wick, the portion of the oil brought into contact with a lighted taper applied to the wick, becomes vaporized by the heat of the taper, the produced gas or vapour takes fire, and the continually produced gas or vapour continues to burn with flame.

34. Colza oil and sperm oil, unless absorbed in a wick, do not take fire when simply brought into contact with flame. Tallow, stearine, spermaceti, paraffin, and wax, burnt in the form of candles, become melted at a gentle heat; but the melted substances do not take fire when brought into contact with flame. All these substances, however, when more strongly heated, give off gas or vapour, and the produced gas or vapour readily takes fire and burns with flame.

35. On bringing a lighted taper into contact with the wick of a lamp or candle, the oil or melted wax is first so far heated as to give off gas or vapour; and this vapour it is which takes fire and burns with flame. Afterwards, gas or vapour is continually produced by the heat of the lamp-, or candle- flame; and, as it is produced, continues to burn with flame.

36. Hence the flames, not only of coal-gas and hydrogen gas, but of a spirit lamp, a paraffin lamp, an oil lamp, a candle, and indeed all flames whatever, are really gas flames. Flame is the burning of a gas or vapour.

37. Substances like iron and charcoal, that do not volatilize or vaporize, may burn very brilliantly, but not with flame.

38. The conical form of ordinary flame is dependent on the ascending current of heated, and therefore lighter air; and may be altered by interfering with the current.

39. True flame takes place only where the oxygenous air and the combustible gas come into contact and combine with each other. Outside of an ordinary flame is the air; inside the flame is combustible gas; between the two is a conical stratum of true flame.

40. Flame being thus hollow, the interior of a flame is comparatively cool. Wood placed in the interior of a flame does not char; metal placed in the interior of a flame does not become ignited.

41. Combustibles, or substances capable of burning in air, do not burn in the interior of a conical flame. Even a piece of lighted phosphorus is extinguished, when thrust into the centre of a large hollow flame.

42. In an ordinary flame, the combustible gas is surrounded by the oxygen-supplying air; and the gas is said to burn. But we can arrange instead to have the air inside and the gas outside; when the air should be said to burn. Air from the mouth of a person may be made to burn in an atmosphere of ordinary coal-gas.

43. Just as a piece of coal, or other carbonaceous solid, burns in oxygenous air, so may an oxygenous solid, such as nitre, be burnt in carbonaceous coal-gas. The combustion takes place where the solid, carbonaceous or oxygenous, comes into contact with the air or gas, oxygenous or carbonaceous.

44. With oxygenous air and a combustible gas completely mixed, the flame is quasi-solid, or continuous throughout, and usually explosive. The occasional explosions, of fire-damp in mines and of coal-gas in houses, result from the sudden combustions of mixtures of fire-damp with air and of coal-gas with air respectively.

45. The burning of a mixture of oxygenous with combustible solid, as of nitre with coal-dust, also takes place throughout the mass, and is independent of the presence of air. Gunpowder, which is a mixture of oxygenous nitre with combustible charcoal and sulphur, can burn in the closed chamber of a gun, likewise under water, and in a space from which the air has been removed by an air-pump.

46. Some chemical compounds, as gun-cotton, contain both an oxygenous and a combustible constituent. They burn throughout their mass, like gunpowder, independently of the presence of air.

LECTURE III.—*Saturday, December* 31, 1870.

CONTINUOUS BURNING.

47. In the combustions or burnings hitherto spoken of, some combustible substance or other has entered into combination with some form or other of oxygen,—with pure oxygen gas, or with the diluted oxygen of the air, or with the oxygen of some chemical compound, as nitre. And, at one time, combustion or burning was thought to consist in, and to be confined to, the combination of substances with oxygen.

48. But hydrogen burns in, or with, chlorine to produce chloride of hydrogen or muriatic acid, just as it burns in, or with, oxygen to produce oxide of hydrogen or water. Again, copper burns in sulphur vapour to form sulphide of copper; phosphorus, in iodine vapour to form iodide of phosphorus.

49. And, in general, combustion, or burning, is only an evidence of intense chemical action; and takes place whenever different substances, whether or not containing oxygen, enter into combination with sufficient energy.

50. The intense chemical action constituting combustion is usually set up, in the first instance, by the application of fire or heat. In some cases, the influence of a strong light is equally effective. Thus, a mixture of chlorine and hydrogen gases undergoes an explosive combustion on exposure to sunlight.

51. In many cases, a degree of heat far below that of redness is competent to set up combustion. Thus, the moderate degree of heat produced by the friction of a lucifer-match on rough paper suffices to bring about the combustion of its phosphorus.

52. In some cases, bodies enter into active combination with each other, and take fire, upon being brought into contact with each other, at ordinary atmospheric temperatures. Bodies taking fire on exposure to air, at the ordinary temperature of the air, are said to be spontaneously combustible.

53. In other cases, a very high temperature is necessary to bring about combustion or intense chemical combination. As a rule, bodies enter actively into combination with each other only at a somewhat elevated temperature; and, within certain limits, more actively in proportion to the elevation of temperature.

54. A piece of red-hot pumice removed from the fire, quickly becomes cold. It gives up heat to the air in contact with it, and further radiates heat in every direction. Similarly, all heated bodies have a tendency to become cold by dissipating their heat.

55. A piece of red-hot charcoal removed from the fire, dissipates heat as much as a piece of red-hot pumice ; but it does not become cold. It goes on burning; and the amount of heat evolved by its burning compensates for the heat which it loses by dissipation.

56. All heated bodies having a tendency to become cold, and combustible bodies requiring, as a rule, to be strongly heated in order to burn, it is obvious that for their burning to go on, the temperature necessary for their burning must be maintained by heat being supplied to them somehow or other.

57. It has been shown that bodies entering into combination with each other, give out more or less heat—the heat of combination, or heat of burning. And bodies continue to burn, only when the amount of heat given out by their burning is sufficient to maintain them at the temperature necessary for their burning.

58. The continued mutual burning of a combustible gas and an oxygenous gas is often prevented or arrested by the admixture of either with a third inactive gas,—through the inactive gas carrying off so much of the heat produced by the burning as to prevent the temperature necessary for burning being maintained. In such a case, continuous burning may be effected by a continuous application of external heat.

59. Again, the heat evolved by the combination of strongly ignited carbon with hydrogen, is insufficient to maintain the temperature necessary for the combination. But the continuous combination, or burning, of the two substances can be effected, by keeping the carbon strongly ignited by an electric current.

60. Conversely, the burning of mixed coal-gas and air may be arrested, by carrying off the heat of their combination by a mesh of metal, and so cooling them down to below their burning temperature.

61. The action of the Davy safety-lamp depends on the property of metal gauze to arrest the burning or flaming of a mixture of gas and air, by cooling down the mixture to below its inflaming or exploding point.

62. In the case of bodies capable of taking fire when brought into contact with each other at the ordinary temperature of the air (*vide* 52), combustion may often be prevented by first cooling them down to considerably below the ordinary temperature of the air.

LECTURE IV.—*Tuesday, January 3rd*, 1871.

TEMPERATURE OF BURNING.

63. By means of charcoal, burning in the oxygen of the air to produce carbonic gas, a temperature varying from that of dull redness only, up to that at which even wrought iron fuses, may be attained.

64. Again, a temperature falling below that of redness or exceeding that attainable by any other chemical means, may result from the combination of hydrogen with oxygen to produce water.

65. And, in general, very different degrees of temperature are producible by one and the same chemical action.

66. When metallic sodium is thrown on to a dish of cold water, violent chemical action, attended by an evolution of much heat, is manifested; but inflammation does not occur,—the elevation of temperature necessary for inflammation being prevented by the cooling influence of the mass of cold water.

67. But when metallic sodium is brought into contact with a drop or so of cold water, or with a larger quantity of hot water, inflammation immediately occurs,—the rise of temperature being no longer opposed by the same extent of cooling influence.

68. And, in general, the temperature resulting from a particular chemical action, varies with the kind, quantity, and condition of the matter by which the heat of the chemical action is appropriated.

69. While the temperature produced by the slow oxidation of hydrogen into water, effected by a ball of platinized clay, falls short of redness, the temperature producible by the rapid oxidation of hydrogen into water surpasses that of a white heat (*vide* 64).

70. Or the temperature resulting from a particular chemical action, varies with the amount of that action taking place within a given space and time,—varies, that is to say, with the rapidity or intensity of the chemical action.

71. The rapidity or intensity of a particular chemical action depends largely upon the extent and intimacy of contact of the reacting bodies. In the combination of a solid body with a gas, extent of contact may be attained by finely dividing the solid or by compressing the gas.

72. The rapidity of ordinary combustion, and degree of temperature resulting from the combustion, may be greatly increased by employing a blast of air; still more by employing a blast of hot air; still more by employing a blast of oxygen instead of air.

73. When burnt in a blast or current of air, the combustible comes, within a given time, into contact with a greater amount of oxygen with which to combine,—whereby a greater amount of combination is effected within the time.

74. The temperature produced by burning a body in heated air is higher than the temperature produced by burning the same body in cold air, because, among other reasons, the total amount of heat produced by the burning is imparted to bodies, including the nitrogen of the air, already at a high instead of a low temperature.

75. The temperature produced by burning a body in oxygen is higher than the temperature produced by burning the same body in air—partly because, in the former case, the burning body has in contact with it, at each instant of time, four times as much oxygen with which to combine, whereby a greater amount of combination is effected within the time.

76. Partly also, as well as for other reasons, because, in the former case, the heat evolved by the combination is shared only between the two combining substances and the product of their combination, instead of being shared by the nitrogen of the air in addition.

77. The degree of resulting temperature varying with the intensity of the chemical action,—within certain limits, the intensity of the chemical action varies with the degree of temperature at which it takes place (*vide* 53).

78. So that while chemical action leads to elevation of temperature, elevation of temperature mostly leads to increase of chemical action, and this again to further elevation of temperature.

79. Accordingly, a slow chemical action, attended with but little rise of temperature, may develop into a rapid chemical action attended with considerable rise of temperature,—or develop even into active combustion.

80. The metals lead and iron are capable of being obtained in the state of minute spongy particles, which take fire almost immediately on coming into contact with the air.

81. In both instances, the spongy particles of metal absorb the oxygen of the air, begin to combine with this oxygen, thereby get their temperature raised, thereby combine more rapidly with oxygen, thereby are rendered red-hot and enter into active combustion.

LECTURE V.—*Thursday, January* 5, 1871.

HEAT OF BURNING.

82. If a gallon and a pint of boiling-hot water be each poured upon a sufficiency of crushed ice, eight times as much ice will be found to be melted by the gallon as by the pint of hot water.

83. Hence, although the gallon of boiling water and the pint of boiling water have the same temperature, the pint of boiling water can impart to the ice but one-eighth as much heat as can the gallon.

84. An ounce weight of iron, heated to redness and then immersed in a pint of cold water, will render the pint of water less hot than will a pound weight of iron heated to the boiling-point of water and similarly immersed in a pint of cold water.

85. Hence, although the ounce weight of iron heated to redness, is much hotter than the pound weight of iron heated to the boiling-point of water, the pound weight of iron at the lower, can impart a greater quantity of heat to water than can the ounce weight of iron at the higher temperature.

86. Accordingly, to know the mere temperature, or intensity of heat of a body, is not to know the quantity of heat which it contains or is capable of imparting.

87. A degree of temperature, on the centigrade scale, is the $\frac{1}{100}$ part of the difference of temperature between the melting-point of ice and the boiling-point of water. Instruments used for measuring temperature are called thermometers.

88. A degree of heat, or unit of heat, is the quantity of heat necessary to raise the temperature of 1 litre of water 1 degree centigrade (or 2 lbs. of water 2 degrees Fahrenheit, very nearly). Instruments used for measuring heat are called calorimeters.

89. The heat of a given combustion is determined by effecting the combustion in a calorimeter,—that is, under such conditions that the entire heat evolved in the process shall be imparted to a known weight of water, the increased temperature of which can be afterwards noted.

90. Common experience tends to show that the quantity of heat evolved by the burning of a definite weight of combustible, as coal, for example, is limited and approximatively uniform.

91. Accurate experiment confirms and defines the conclusion of common experience. An equal quantity of heat, or the same number of units of heat, is always found to be evolved on burning equal weights of the same combustible.

92. In the combustion of one gramme of hydrogen to furnish nine grammes of water, there are always evolved 34 units of heat,—sufficient heat to raise the temperature of a litre of water 34 degrees.

93. In the combustion of one gramme of carbon to furnish rather more than three and a half grammes of carbonic gas, there are always evolved 8 units of heat,—sufficient heat to raise the temperature of a litre of water 8 degrees.

94. Whereas, then, the temperature resulting from a given chemical change or reaction can vary to an unlimited extent, it is demonstrable, in various ways, that the heat evolved by a given chemical change or reaction is invariable.

95. The reactions taking place between bodies at low temperatures are often different from the reactions taking place between the same bodies at high temperatures. Thus alcohol reacts with oxygen at a comparatively low temperature to produce acetic acid,—at a high temperature to produce carbonic gas and water.

96. But where, as in the combination of hydrogen with oxygen, the reaction at high and low temperatures is the same, the quantity of heat evolved may be shown to be the same, notwithstanding the differences of temperature manifested.

UNBURNING.

97. Hydrogen burns in chlorine to produce chloride of hydrogen or muriatic acid gas, HCl; and sodium or natrium also burns in chlorine to produce chloride of sodium or common salt, $NaCl$. But sodium can also burn in muriatic acid gas, HCl, to produce the same chloride of sodium, $NaCl$, and set free hydrogen, H.

98. The sodium, whether burnt in chlorine or in muriatic acid, is changed into the same burnt product, chloride of sodium or common salt. It has become burnt out, and has so lost the power of burning.

99. But in the latter case, the burning of the sodium has been attended by an unburning of hydrogen. From having been burnt out, the hydrogen has become unburnt, and rendered capable of being burnt over again.

100. The original burning of the hydrogen may be compared with the falling of a small weight from the ceiling to the floor. The unburning of the hydrogen may be compared with the raising of the same small weight from the floor to the ceiling, whence it can fall again,—its raising up being effected by the falling down of a heavier weight, to which it is attached by a cord passing over a pulley.

101 *a*. Metallic copper burns in oxygen gas to produce black oxide of copper. It becomes burnt out, and thereby loses its capability of burning.

„ *b*. When hydrogen gas is passed over gently-heated black oxide of copper, the combustible hydrogen becomes burnt into incombustible water, and the copper of the incombustible copper-oxide becomes unburnt into combustible metallic copper.

101 *c*. When metallic zinc is heated to redness in a current of water-vapour or steam, the combustible zinc becomes burnt into incombustible zinc-oxide, and the hydrogen of the incombustible water-vapour becomes unburnt into combustible hydrogen.

102 *a*. Metallic arsenic burns in air or oxygen, with conversion into arsenious oxide or white arsenic.

„ *b*. When carbon or charcoal is heated with arsenious oxide, the combustible charcoal becomes burnt into incombustible carbonic gas, and the arsenic of the incombustible arsenious oxide becomes unburnt into combustible metallic arsenic.

„ *c*. When metallic sodium is strongly heated in carbonic gas, the combustible sodium becomes burnt into incombustible soda, and the carbon of the incombustible carbonic gas becomes unburnt into black combustible charcoal.

103. In the first series of experiments (101), burnt copper is unburnt by hydrogen, and burnt hydrogen unburnt by zinc. In the second series of experiments (102), burnt arsenic is unburnt by charcoal, and burnt charcoal unburnt by sodium.

LECTURE VI.—*Saturday, January 7th*, 1871.

UNBURNING.

104. At a high temperature, metallic zinc burns in air or oxygen, to produce a white powder, oxide of zinc. This oxide of zinc dissolves readily in acetic acid—the acid of vinegar—to form a crystallizable salt, acetate of zinc.

105. Melted lead burns in air or oxygen to produce a yellow powder, oxide of lead. This oxide of lead dissolves readily in acetic acid to form the salt, acetate of lead, better known as sugar of lead.

106. Metallic lead does not dissolve appreciably in acetic acid. But when a current of air or oxygen is blown through a mixture of lead shavings and acetic acid, oxide of lead is simultaneously produced by the oxygen and dissolved by the acid.

107. When a piece of metallic zinc is suspended in acetate of lead solution, the zinc gradually disappears, becoming dissolved as acetate of zinc; while metallic lead is deposited in the form of a lead tree.

108. This action may be regarded as a de-oxidation by zinc, of lead-oxide dissolved in acetic acid,—the produced zinc-oxide, like the original lead-oxide, being retained in solution by the acid.

109. The retention in solution of the produced zinc-oxide, of however much importance in itself, being unimportant to the subject before us, may be dismissed from our present consideration. It suffices to observe that in the production of the dissolved zinc-oxide from the dissolved lead-oxide, the zinc has become oxidized or burnt, and the lead of the lead-oxide unburnt.

110. Just as metallic zinc dissolves in acetate of lead solution with separation of metallic lead, so does it dissolve in acetate of hydrogen solution, or in sulphate of hydrogen solution, with liberation of hydrogen gas.

111. The dissolving of metallic zinc in sulphate of hydrogen solution, *i.e.* in aqueous sulphuric acid, may be regarded as an oxidation of zinc at the expense of hydrogen,—the produced zinc-oxide, however, being retained in solution by the acid under the form of sulphate of zinc.

112. Disregarding the retention in solution of the produced zinc-oxide, what has happened is this: the originally un-oxidized zinc has become oxidized or burnt, and the originally oxidized hydrogen has become de-oxidized or unburnt. Or, so to speak, the falling of the heavy weight has effected the raising up of the lighter one.

113. When sixty-five grammes of zinc are burnt in oxygen or air, and the resulting oxide of zinc is dissolved in aqueous sulphuric acid, there are evolved 104 units of heat. But when sixty-five grammes of zinc are dissolved at once in aqueous sulphuric acid, there are evolved only 36 units of heat; or 68 units of heat fail to make their appearance.

114. But the dissolving or burning of the sixty-five grammes of zinc in acid, has been accompanied by an unburning of two grammes of hydrogen; and if this unburnt hydrogen be set fire to, it will, in the course of its re-burning, evolve exactly the 68 units of heat missing.

115. So that whether the zinc is burnt by itself in air or oxygen, or whether the burning of the zinc is associated with the unburning of hydrogen which is itself afterwards burnt, the heat evolved by the burning amounts in each case to the same number of units.

116. The actual manifestation of heat by the zinc in burning, has been diminished by the capability of manifesting heat acquired by the hydrogen in unburning; just as the manifestation of active motion by the larger weight in falling, is diminished by the capability of manifesting such motion acquired by the smaller weight in being lifted up.

117. Further, when the liberated hydrogen burns, it manifests a portion of the heat-evolving power belonging originally to the zinc; just as when the smaller weight falls, it manifests a portion of the power of falling belonging originally to the larger weight,—not,

indeed, manifested by the larger weight in its fall, but transferred from it to the smaller weight lifted up.

118. When metallic zinc dissolves in aqueous sulphuric acid, or sulphate of hydrogen, the quantity of heat evolved by the burning of the dissolved zinc, in excess of that absorbed, so to speak, in the unburning of the liberated hydrogen, is manifested by the rise in temperature of the acid liquid and of the metallic zinc immersed in it; but it may be manifested in other ways.

119. If a plate of zinc dissolving in acid be connected, by means of a thick copper wire, with a plate of platinum also immersed in the acid, the heat-evolving power possessed by the zinc undergoing oxidation, in excess of the heat-evolving power acquired by the hydrogen undergoing de-oxidation, is still manifested by the rise in temperature of the acid liquid and of the metals immersed in it.

120. But if the two plates of metal immersed in the acid, be connected by a thin platinum wire, a portion of the excessive or available heat of the oxidizing zinc fails to be manifested in the acid liquid; but instead, an equivalent of this missing portion is then manifested in the platinum wire, to such an extent indeed that the wire becomes visibly red hot.

121. A series of properly connected pairs of plates of zinc and platinum, immersed in a series of jars of acid, constitutes a voltaic battery. With a sufficiently powerful battery, so much of the available heat-evolving power of the oxidizing zinc as is not manifested in the jars or cells of the battery, may be manifested in the intense ignition or even fusion of a considerable length of platinum wire.

122. It may also be manifested in the intense ignition of two points of charcoal,—in the production, that is to say, of the well-known electric light.

123. It may also be manifested indirectly in the decomposition or unburning of water into its constituent gases, hydrogen and oxygen. In this case, however, that portion of the available heat of the oxidizing zinc, not manifested in the battery-cells, fails to appear at all, and seems to be permanently wanting.

124. But on setting fire to the constituent gases of the unburnt water, the quantity of heat evolved in their reburning to reproduce water, is the exact supplement of heat due to the zinc oxidized in the battery, that failed to make its appearance when the water was unburnt or decomposed.

125. So that the power acquired by the hydrogen unburnt, to reburn and evolve heat in burning, is consequent on the non-manifestation of just that amount short of its proper complement of heat, by the zinc burnt in the battery.

126. When water is made to boil, and the resulting steam or vapour of water is subjected to intense heat, a small portion of the

strongly heated water-vapour is unburnt or decomposed into its constituent gases.

127. In this case also, it would appear that the direct heat to which the water-vapour is subjected, suffers a diminution in quantity by exactly the quantity capable of being afterwards evolved on setting fire to, and so re-burning the liberated gases.

128. And, in general, the quantity of heat manifested in any act of burning is the exact equivalent of a quantity of heat that failed to make its due appearance, or that positively disappeared, in some previous act of unburning, or other analogous act;—just, indeed, as the motive action of a falling weight is the equivalent of a previous reverse action, of some kind or other, whereby the weight was lifted up.

129. Under exposure to the sun's rays, the wood of a growing tree is gradually formed by a partial or incomplete unburning of carbonic gas and water,—into oxygen gas discharged into the atmosphere, and partially de-oxidized carbon and hydrogen transformed into woody tissue; and this act of unburning is attended necessarily by a disappearance of solar heat.

130. On burning the so-formed woody tissue in the oxygen of the air, into carbonic gas and water, the quantity of heat evolved in the act of burning, is the equivalent of the quantity of solar heat absorbed in the previous act of unburning carbonic gas and water, by which the wood was constituted.

131. Thus, the genial heat produced by burning a log of wood on a Christmas fire, is merely a restoration of the sun's heat that disappeared when the tree, furnishing the log of wood, was grown,—no matter how many years ago.

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ADDRESS

TO THE

SECTION OF

CHEMISTRY AND MINERALOGY

AT THE OPENING OF THE THIRTY-FOURTH MEETING OF THE BRITISH ASSOCIATION, IN BATH, SEPTEMBER 15, 1864.

BY

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,

SECRETARY TO THE CHEMICAL SOCIETY, LECTURER ON CHEMISTRY AT
ST. BARTHOLOMEW'S HOSPITAL,

AT the Leeds Meeting of the British Association in 1858, Sir John Herschel, the then President of the Chemical Section, opened its proceedings with an introductory address of singular interest, and thereby established a precedent which, with a solitary exception, has been uniformly adopted by successive occupants of the position which I have now the honour to hold. Following in his footsteps, *longo intervallo,* I in my turn now venture upon a few words of introduction to the proper business that we have in hand. In the first place, I may congratulate the Section upon the presence among us of so many distinguished chemists, including several of my more immediate predecessors. I need scarcely express the personal gratification I feel at meeting them here, nor say how much their presence relieves me from the feeling of responsibility and self-mistrust with which I undertook the honourable office so kindly entrusted to me by the Committee, feeling now that, upon any occasion of difficulty, I shall have them to apply to for counsel and assistance.

After the great diversity, or rather antagonism, of opinion which has existed for the last dozen years or so, I am almost bound to take a somewhat prominent notice of the substantial agreement which now prevails among English chemists as to the combining proportions of the elementary bodies and the molecular weights of their most important compounds. The present unanimity of opinion on this fundamental subject among those who have given it their attention is, I conceive, greater than has ever been the case since Dalton published his 'New System of Chemical Philosophy,' more than half a century ago. As yet, indeed, the unanimity of practice falls considerably short of the unanimity of belief; but, even in this direction, great progress is being made, to which the publication of Miller's 'Elements of Chemistry,' Watts's 'Dictionary of Chemistry,' and Hofmann's 'Jury Report on the Chemical Products in the Great Exhibition,' will doubtless give a yet stronger impetus. As was well observed by Dr. Miller at a previous Meeting of this Association, "Chemistry is not merely a science; it is also an art, which has introduced its nomenclature and its notation into our manufactories, and in some measure even into our daily life." Hence the great difficulty of effecting a speedy change in chemical usages alike so time-honoured and intimately ramified with the affairs of our everyday existence. I propose, by your permission, to make a few remarks upon the history of this chemical reformation, more especially in connexion with certain points which one or two of its acknowledged leaders have scarcely, I think, correctly estimated.

From the time when Dalton first introduced the expression "atomic weight," up to the year 1842, when Gerhardt announced his views upon the molecular constitution of water, there does not appear to have been any marked difference of opinion among chemists as to the combining proportions of the principal elements. That 1 part by weight of hydrogen, united with 36 parts by weight of chlorine to form a single molecule of hydrochloric acid, and with 8 parts by weight of oxygen to form a single molecule of water, was the notion both of Berzelius and Gmelin, who may be taken as representatives of the two chief Continental schools of theoretic chemistry. Indeed, no doubts seem to have been entertained in their time as to the combining proportions of the three elements. Using the hydrogen scale of numbers, both chemists represented the combining proportion of hydrogen as 1, that of chlorine as 36, and that of oxygen as 8. Both, moreover, represented the molecular weight of hydrochloric acid as 37, and the molecular weight of water as 9. It is true that Berzelius professedly regarded the single combining proportions of hydrogen and chlorine as consisting each of two physical atoms; but, since the two atoms of hydrogen, for instance, which constituted the one combining proportion of hydrogen, were chemically inseparable from one another, they were really tantamount to one atom only of hydrogen, and, in point of fact, were always employed by Berzelius as representing the single chemical atom of hydrogen, or its smallest actual combining proportion. Distinguishing thus between the physical atom and the combining proportion, Berzelius's recognition of the truth, that equal volumes of the elementary gases contain an equal number of atoms, was utterly barren. But, identifying the physical atom with the combining proportion, Gerhardt's recognition, or rather establishment, of the broader truth, that equal volumes of all gases, elementary and compound, contain the same number of atoms, has been in the highest degree prolific. From Gerhardt's division of volatile bodies into a majority whose recognized molecules corresponded respectively with four volumes of vapour, and a minority whose recognized molecules corresponded respectively with but two volumes, and from his proposal, in conjunction with Laurent, to double the molecular weights of these last, so as to make the molecules of all volatile bodies, simple and compound, correspond each with four volumes of vapour, must, I conceive, be traced the development by himself and others of the matured views on chemical philosophy which now prevail. With every respect for my predecessor in this chair, and for the accomplished author of the 'Leçons de Philosophie Chimique,' from neither of whom do I ever venture to differ without fear and trembling, I cannot join with them in regarding the initiation of Gerhardt's system as an imperfect return, and its remarkable maturation in these recent days as a more complete return to the notions of Berzelius. Although, indeed, the elementary weights now employed, with the exception of those for some half-dozen metals, are identical with the atomic weights of Berzelius, yet so unlike are they to his combining weights that fully four-fifths of all known compounds have to be expressed by formulæ entirely different from his—namely, all those bodies, with but very few exceptions, into which hydrogen, fluorine, chlorine, bromine, iodine, nitrogen, phosphorus, arsenic, boron, and the metals lithium, sodium, potassium, silver, and gold, enter as constituents. Fully admitting that the new system of atomic weights, as it now exists, is the joint product of many minds—fully admitting that it owes its present general acceptance chiefly to the introduction of the water type by Williamson during Gerhardt's lifetime, and the recognition of diatomic metals by Wurtz and Cannizzaro, after his decease—and fully admitting, moreover, that some of Gerhardt's steps in the development of his unitary system were decidedly, though perhaps excusably, retrograde, I yet look upon him, not I trust with the fond admiration of the pupil, but with the calm judgment of the chemist, as being the great founder of that modern chemical philosophy in the general spread of which I have already ventured to congratulate the Members of the Section. Prior to the time of Gerhardt, the selection of molecular weights for different bodies, elementary and compound, had been almost a matter of hazard. Relying conjointly upon physical and chemical phenomena, he first established definite principles of selection, by pointing out the considerations upon which the determination of atomic weights must logically depend. Relying upon these principles, he established his classification of the non-metallic elements into monhydrides, represented by chlorine; dihydrides, represented by oxygen; trihydrides, represented by nitrogen, &c.; and, relying upon the same principles, but with a greatly increased knowledge of phenomena, later chemists have given to his method a development and unity, more especially as regards the metallic elements, which have secured for the new system the impregnable and acknowledged position which it at present occupies. The comparative unanimity which prevailed before the time of Gerhardt was the unanimity of submission to authority; but the greater unanimity which now prevails is the unanimity of conviction consequent upon an intermediate period of solitary insurrection, general disturbance, and ultimate triumph.

Bearing in mind how much the origin of the new system by Gerhardt, and its completion by his colleagues and disciples, are due to a correct appreciation of the harmony subsisting between chemical and physical relations, we cannot but give a hearty welcome to any large exposition of mixed chemico-physical phenomena; and, whether or not we agree with all his conclusions, there can be but one opinion as to the obligation chemists are under to Professor Kopp, of Giessen, for the great addition he has recently made to our knowledge and means of obtaining a further knowledge of what has hitherto been but a very limited subject—namely, specific heat.

The agreement of chemists as to the elemental atomic weights is tantamount to an agreement among them as to the relative quantities of the different kinds of matter which shall be represented by the different elemental symbols; and this brings me to the subject of chemical notation. At one time many chemists, even of considerable eminence, believed and taught that Gerhardt's reformation had reference mainly to notation, and not to the association and interpretation of phenomena, and it became rather a fashion among them to declaim against the puerilities of notational questions. That the idea is of far greater importance than the mode of expressing it, is an obvious truism; nevertheless, the mode of expression has an importance of its own, as facilitating the spread of the idea, and more especially its development and procreation. It has been well asked, in what position would the science of arithmetic have been but for the substitution of Arabic for Roman numerals, the notation in which value is expressed by the change in position for that in which it is expressed mainly by the repetition of a few simple signs? It is unfortunately too true that chemical notation is at present in anything but a satisfactory state. The much-used sign of addition is, I conceive, about the last one would deliberately select to represent the fine idea of chemical combination, which seems allied rather, I should say, to an interpenetration than to a coarse apposition of atoms. The placing of symbols in contiguity, or simply introducing a point between them, as indicative of a sort of multiplication or involution of the one atom into the other, is, I think, far preferable; but here, as pointed out by Sir John Herschel, we violate the ordinary algebraic understanding, which assigns very different numerical values to the expressions XY and $X+Y$ respectively. I know, indeed, that one among us has been engaged for some years past in conceiving and working out a new and strictly philosophical system of chemical notation by means of actual formulæ, instead of mere symbols; and I am sure that I only express the general wish of the Section when I ask Sir Benjamin Brodie not to postpone the publication of his views for a longer time than is absolutely necessary for their sufficient elaboration. In any case, however, the symbolic notation at present employed, with more or less modification of detail, must continue to have its peculiar uses as an instrument of interpretation; and hence the importance of our endeavouring to render it more precise in meaning and consistent in its application. Many of its incongruities belong to the very lowest order of convention; such, for example, as the custom of distinguishing between the representation of so-called mineral and organic compounds, one particular sequence of symbols being habitually employed in representing the compounds of carbon, and an entirely different sequence of symbols in representing the more or less analogous compounds of all other elements. Now that organic and mineral chemistry are properly regarded as forming one continuous whole, a conclusion to which Kolbe's researches on sulphuretted organic bodies have largely contributed, it is high time that such relics of the ancient superstition that organic and mineral chemistry were essentially different from one another should be done away with.

Although, during the past year, the direct advance of that crucial organic chemistry, the synthesis of natural organic bodies, has not been striking, yet, on the other hand, its indirect advance has, I submit, been very considerable. Several of the artificially produced organic compounds, at first thought to be identical with those of natural origin, have proved to be, as is well known, not identical, but only isomeric therewith. Hence, *reculer pour mieux sauter*, chemists have been stepping back a little to examine more intimately the constitution both of natural organic bodies and of their artificial isomers. The synthetic power having been attained of putting the bricks together in almost any desired way, it is yet necessary, in order to construct some particular biological edifice, first to learn the way in which its constituent bricks have been naturally put together. We accordingly find the study of isomerism, or, what comes to the same thing, the study of the intimate constitution of bodies, assuming an importance never before accorded to it. Isomerism is, in fact, the chemical problem of the day, and concurrently with its rapidly advancing solution, through the varied endeavours of many workers, will be the advance in rational organic synthesis. It is curious to note the oscillations of opinion in reference to this subject. Twenty years ago the molecular constitution of bodies was perceived by a special instinct, simultaneously with, or even prior to, the establishment of their molecular weights. Then came an interval of scepticism, when the intimate constitution of bodies was maintained to be not only unknown, but unknowable. Now we have a period of temperate reaction, not recognizing the desired knowledge as unattainable, but only as difficult of attainment. And in this, as in many other instances, we find evidence of the healthier state of mind in which, now more perhaps than ever, the first principles of chemical philosophy are explored. Speculation, indeed, is not less rife and scarcely less esteemed than formerly, but is now seldom or never mistaken for ascertained truth. Scepticism, indeed, still prevails—not, however, the sterile scepticism of resignation, but the fertile scepticism which aspires to greater and greater certainty of knowledge. Chemical science is advancing, I believe, not only more rapidly, but upon a surer basis than heretofore; and, while with every advance, the prospect widens before our eyes, so that we become almost alarmed at contemplating what those who come after us will have to learn, we console ourselves with the determination that their labour of unlearning shall be as little as possible—far less, we hope, than what we in our time have had to experience.

Royal Institution of Great Britain.

WEEKLY EVENING MEETING,

Friday, March 3, 1876.

George Busk, Esq. F.R.S. Treasurer and Vice-President, in the Chair.

Professor Odling, M.A. F.R.S. M.R.I.

The Paraffins and their Alcohols.

I. Hydrocarbons in General.

Olefiant gas, turpentine spirit, and the beautiful crystalline body naphthalene are familiar examples occurring in the gaseous, liquid, and solid states respectively, of a particular class of combustible substances; and although usually burning imperfectly, that is with a smoky flame, they are alike capable of complete combustion, that is of complete oxidation, by the oxygen of the air.

Instead, however, of burning these substances directly in the air, metallic copper may first be burnt or oxidized in the air, and the combustible substance be then heated with the resulting oxide of copper. In this way, the previously burnt copper becomes unburnt, and the combustible substance completely burnt by the oxygen which it acquires from the oxidized copper,—this oxygen having been originally acquired by the copper from the air in the process of its own oxidation or burning.

Pure hydrogen by being burnt in the air or with oxide of copper furnishes only water, and pure carbon by being completely burnt in the air or with oxide of copper furnishes only carbonic acid,—water and carbonic acid being the burnt or fully oxidized forms of hydrogen and of carbon respectively.

Now olefiant gas, turpentine spirit, and solid naphthalene are alike shown to be constituted of hydrogen and carbon by the circumstance of their alike yielding as products of their burning, water or burnt hydrogen and carbonic acid or burnt carbon.

That they have no other constituents than hydrogen and carbon is shown negatively, by the impossibility of recognizing in them the presence of any other constituent; and positively, by weighing the amounts of water and carbonic acid produced by their burning,—a process of great ease and exactitude when their burning is effected by means of oxide of copper.

For instance, from a gramme of any one of these substances, burnt with oxide of copper, there are produced a weight of water corresponding to a certain quantity of hydrogen and a weight of carbonic acid corresponding to a certain quantity of carbon,—these quantities of hydrogen and carbon taken together amounting to exactly one gramme.

Accordingly, olefiant gas, turpentine, and naphthalene, belong alike to the class of hydrocarbons,—that is, of compounds constituted solely of carbon and hydrogen.

Now while chemists are acquainted with only two compounds of hydrogen and oxygen with each other—namely, water and peroxide of hydrogen; and with only two compounds of carbon and oxygen with each other, namely, half burnt carbon or carbonous oxide, and fully burnt carbon or carbonic acid gas,—the known compounds of carbon and hydrogen with each other may be counted by hundreds.

These hundreds of hydrocarbons differ much from one another in many ways; and especially in their behaviour when submitted to active chemical agents. With the majority of hydrocarbons, exposed under suitable conditions to the action of chlorine for instance, chlorine is absorbed and a compound of the original hydrocarbon with chlorine obtained.

Thus in the special case of olefiant gas, the compound so obtained is an oily liquid, which may not only be shown by analysis to have the composition of olefiant gas plus chlorine, but which, when heated with metallic magnesium for instance, breaks up into its constituent olefiant gas and chlorine—the latter appearing in this case as chloride of magnesium, a compound producible directly by heating the metal in chlorine gas.

And the majority of known hydrocarbons agree with olefiant gas in this respect, namely, that they have the property of uniting directly with chlorine and its analogues; with the compounds formed by the union of chlorine and its analogues with hydrogen; and even, in many cases, under suitable conditions, with hydrogen itself.

The combination of these hydrocarbons with hydrogen is, however, usually effected indirectly. Olefiant gas, for instance, is first combined with chlorine Cl_2, or hydriodic acid HI, and the halogen of the resulting compound then simultaneously withdrawn and replaced by hydrogen, acting in the nascent state.

II. Paraffins in General.

But certain hydrocarbons are distinguished from the generality by being altogether devoid of this property of entering into combination; and inasmuch as they are further very difficultly attackable in any way by chemical agents, they are called paraffins, or bodies deficient in chemical activity.

Hydrocarbons of this inactive chemical habit are some of them solid, some of them liquid, whether spirituous or oily, and some of them gaseous. The best known of the gaseous paraffins is marsh-gas,—the inflammable gas of coal-mines, and most abundant constituent of ordinary coal-gas. Of the liquid paraffins, the most dense varieties are used as lubricating oils; the intermediate varieties as burning oils, their use in this way being unattended with danger or even offensive smell; while the lightest and most volatile varieties constitute benzoline, a liquid of many uses in the arts, but exceedingly dangerous as a fuel for lamps. The solid paraffins including the curious mineral ozokerite are, as is well known, used largely in the manufacture of candles.

Now it is found by analysis that the proportion by weight of constituent hydrogen in the paraffins, solid, liquid, and gaseous, is larger than the proportion by weight of hydrogen met with in hydrocarbons of any other class; and that it varies from 14·5 per cent. in the most dense solid to 25·0 per cent. in the lightest gas, the proportion increasing regularly with the volatility of the paraffin.

Moreover hydrocarbons, not belonging to the paraffin class, become converted into paraffins by their direct or indirect fixation of additional hydrogen. Thus the compound formed by adding hydrogen to olefiant gas, in exchange for the iodine of the hydriodide of olefiant gas, constitutes the paraffin known as ethane.

The paraffins being then the most highly hydrogenized of hydrocarbons, and the halogens and halogen acids when got to combine with certain other hydrocarbons, occupying but the place of the excessive hydrogen of corresponding paraffins, the inability of the paraffins to enter into combination with hydrogen or its representatives would appear to depend upon their being already saturated with hydrogen; and accordingly they are often spoken of as saturated hydrocarbons.

A very simple relationship, in respect of composition, is found to subsist between the different paraffins one with another. In each and all of them, gaseous, liquid, or solid, the number of their proportions of hydrogen is found to exceed by two proportions, twice the number of their proportions of carbon; or they are each and all of them expressible by the general formula C_nH_{2n+2}.

Two liquid paraffins, for instance, met with in benzoline or paraffin-spirit, boiling the one at 99°, the other at 124°, have received the names of heptane and octane, and are expressed by the formulæ C_7H_{16}, and C_8H_{18} respectively; not, however, as a mere result of analysis, which indeed shows very little difference between them—the one consisting of 84 per cent. carbon and 16 per cent. hydrogen, the other of 84·2 per cent. carbon and 15·8 per cent. hydrogen.

The mode, however, in which the above and similar formulæ are arrived at is very simple. If chloroform or prussic acid, for example, be converted into vapour, it is found that the volume of vapour (reduced to standard temperature and pressure) which contains one gramme by weight of hydrogen, is 22·4 litres; and, further, that this same volume contains also twelve grammes by weight of carbon.

And taking the vapours of a variety of hydrogen compounds, whether or not carbonous also, it is found that 22·4 litres of such a vapour always contain, within the limits of experimental error, either one gramme or two, three, four, five, or six, &c., &c., grammes of hydrogen. Similarly, taking the vapours of a variety of carbon compounds, whether or not hydrogenous also, it is found, even more exactly, that 22·4 litres of such a vapour contain either twelve grammes, or twenty-four, thirty-six, forty-eight, &c., &c., grammes of carbon.

In the case of heptane C_7H_{16}, for instance, it is found that 22·4 litres of its vapour contain sixteen grammes of hydrogen, and eighty-four grammes of carbon; or 16 times as much hydrogen and 7 times as much carbon as are contained in 22·4 litres of the vapour of chloroform $CHCl_3$, or of prussic acid CHN. Whereas in the case of octane C_8H_{18}, 22·4 litres of its vapour are found to contain eighteen grammes of hydrogen and ninety-six grammes of carbon, or 18 times as much hydrogen and 8 times as much carbon as are found in 22·4 litres of the vapour of chloroform or prussic acid.

Moreover, in heptane, it is found possible to form definite new compounds by replacing its hydrogen in the proportion of one or more sixteenths of the whole, but not in the proportion of one or more eighteenths; whereas, in octane, it is found possible to replace its hydrogen in the proportion of one or more eighteenths of the whole, but not in the proportion of one or more sixteenths.

Again from certain similar derivatives of heptane and octane respectively, it is possible to remove by one and the same process exactly one-seventh of the entire carbon in the case of heptane C_7H_{16}, and exactly one-eighth of the entire carbon in the case of octane C_8H_{18}; showing the carbon of the two paraffins to be divisible into sevenths and into eighths respectively.

Other evidence leading to the same conclusion may be adduced; so that altogether the synoptic formulæ, as they are called, of the different paraffins, are the expressions of well-ascertained facts with regard to them.

III. Isomeric Paraffins.

But there is something of yet further interest to be made out with respect to the paraffins. Thus while the formulæ CH_4, C_2H_6, and C_3H_8, apply each of them, so far as is known, to a single paraffin only, the formula C_4H_{10} applies to two distinct compounds, the formula C_5H_{12} to three distinct compounds, the formula C_6H_{14} to five distinct compounds, the formula C_7H_{16} to eight distinct compounds, and so on.

Considering the case of the fourth paraffin more particularly, there are two perfectly distinct gases, or highly volatile liquids known, of composition expressible by the formula C_4H_{10}; the least volatile of them, or normal butane, boiling at 1° above the freezing point, and the most volatile, known as isobutane, boiling at 15° below the freezing point. Yet not only do equal weights of the two bodies contain exactly the same weights of hydrogen and of carbon respectively, but equal volumes of the vapours of the two bodies also contain the same weights of hydrogen and of carbon respectively. Moreover, the hydrogen of both of them is replaceable in tenths, and the carbon of both of them in fourths.

And the similar derivatives, obtainable from the two butanes by similar processes, present corresponding differences in their properties. Thus the butyric acid obtainable from normal butane is of sp. gr. 981, boils at 163°, and yields a calcium salt which, crystallizing with but one proportion of water, is singular in being more soluble in cold than in hot water; while the butyric acid obtainable from isobutane by exactly the same process, having the same composition and expressed by the same formula $C_4H_8O_2$, has a sp. gr. 959, boils at 154°, is more readily oxidizable than, though into the same products as the other acid, and yields a calcium salt crystallizing with five proportions of water, less soluble than the other salt and observing the usual rule of solubility.

Similarly with regard to pentane, or rather to the pentanes, alike represented by the formula C_5H_{12}. One pentane boils at 38°, another, known as isopentane, at 30°, and the third, which may be called neopentane, as low as 9·5°. The one yields an oily acid boiling at 185°, the other a like acid boiling at 175°, and the third a like acid boiling at 161°, all three acids of composition expressible by the same formula $C_5H_{10}O_2$.

Two or more bodies, having in this way the same composition and unit weight, are said to be isomeric; and this property of isomerism, manifested to such a degree by bodies of such a simple constitution as the paraffins, is certainly one of the most noteworthy phenomena as it is indeed one of the most suggestive problems of modern organic chemistry. And, passing from the paraffins to hydrocarbons in general, the number of bodies of this class with which the chemist has to deal is increased probably fourfold by the number of instances of isomerism met with among them.

IV. PARAFFINS AND ALCOHOLS.

Before considering further the nature of the paraffins, and of the isomerism manifested by the greater number of them, it is advisable to examine the relationship subsisting between the paraffins and a better known and far more active class of bodies, namely, the alcohols; and this relationship may well be considered first in the case of common or ethylic alcohol and its associated paraffin, ethane, —the paraffin producible by the hydrogenation of olefiant gas, and one of the few paraffins of which no isomers are known.

It has been said that the paraffins are not readily acted on by chemical agents; still they are attackable by chlorine, and with a proportionately less degree of difficulty in the case of the simpler members of the series. Accordingly when ethane C_2H_6, and chlorine Cl_2, are mixed together, although the paraffin does not combine directly with the chlorine, it nevertheless reacts with it, and so as to produce two new bodies, one of which is hydrochloric acid ClH, and the other chlorethane C_2H_5Cl,—a kind of ethane in which one proportion of hydrogen is replaced by one proportion of chlorine. Or the chlorine manifests its great tendency to unite with hydrogen, by taking some hydrogen away from the paraffin, subject to the condition of an equivalent quantity of chlorine filling the place of the hydrogen so taken away.

But while chlorine has the property, as illustrated above in the case of a paraffin, of replacing hydrogen directly, proportion for proportion, it can only replace oxygen by an exchange of two proportions of chlorine for one proportion of oxygen, this exchange being usually brought about by means of the very active chemical agent known as perchloride of phosphorus,—an agent which, by acting on a large number of oxidized organic compounds, takes away their oxygen, giving up to them an equivalent quantity of its own chlorine in exchange. Common camphor, for instance, $C_{10}H_{16}O''$, when acted on by perchloride of phosphorus, exchanges its one proportion of oxygen for two proportions of chlorine to form the compound $C_{10}H_{16}Cl_2$.

In the case of alcohol, however, C_2H_6O'', the action is somewhat different. Its one proportion of oxygen is indeed replaced by two proportions of chlorine, but with formation not of one di-chlorinated product, but instead, of two mono-chlorinated products, namely, chlorethane or chloride of ethyl C_2H_5Cl, and hydrochloric acid ClH, the identical products producible from ethane by the action of chlorine.

Now the substance known as chloride of ethyl or chlorethane, whether got from ethane or got from alcohol, is one and the same body, and convertible alike into either of the above two bodies from which it is obtainable. For its reconversion into the paraffin, it suffices to treat it with nascent hydrogen; for its reconversion into the alcohol, to heat it under pressure with dilute alkali. The paraffin and alcohol then, are mutually transformable through the intervention of the chloride producible from either of them.

The relationships of composition and mutual metamorphosis subsisting between the paraffin, chloro-paraffin, and alcohol, are precisely the relationships subsisting between hydrogen, hydrochloric acid, and water,—the action of chlorine on a unit of hydrogen H_2, leading to the production of two units of hydrogen chloride $HCl \ldots ClH$, and its action on a unit of ethane C_2H_6, leading to the production of two units of ethyl chloride and hydrogen chloride $C_2H_5Cl \ldots ClH$, jointly. Again, the exchange of chlorine for oxygen in a unit of water, H_2O or HOH, leading to the production of two units of hydrogen chloride, $HCl \ldots ClH$, its exchange for oxygen in a unit of alcohol, C_2H_6O or C_2H_5OH leads to the production of two units of ethyl-chloride and hydrogen chloride, $C_2H_5Cl \ldots ClH$, jointly.

The above kind of relationship subsisting between ethane and common alcohol is found to prevail generally,—every paraffin being similarly associated with its corresponding alcohol. Thus with propane C_3H_8, is associated propylic alcohol C_3H_8O, boiling at 97°; with butane C_4H_{10}, butylic alcohol $C_4H_{10}O$, boiling at 116°; and with isobutane $C_4H^{\sigma}_{10}$, isobutylic alcohol $C_4H_{10}O^{\sigma}$, boiling at 109°. With pentane C_5H_{12}, is associated pentyl alcohol $C_5H_{12}O$, boiling at 137°, and with isopentane $C_5H^{\sigma}_{12}$, isopentyl or amyl alcohol $C_5H_{12}O^{\sigma}$, boiling at 129°. The alcohol corresponding to neopentane $C_5H^{\nu}_{12}$ has not been examined.

V. ALCOHOLS IN GENERAL.

As regards the sources of the different alcohols, although the chief product of the alcoholic fermentation is common alcohol, there is always formed in addition a considerable proportion of isopentyl or amyl alcohol $C_5H_{12}O^{\sigma}$, which constitutes the chief constituent of what in English distilleries is called "faints," and in foreign distilleries "fousel oil." The propylic, isobutylic, and even isohexylic alcohols, C_3H_8O, $C_4H_{10}O^{\sigma}$, and $C_6H_{14}O^{\sigma}$ respectively, are also met with, as minor products of fermentation, and are capable of extraction from crude spirit of different kinds. But the greater number of the alcohols are derived by various processes from other and various sources, and are procured especially by the metamorphosis of their corresponding paraffins.

From the relationship subsisting between the alcohols and paraffins, it follows that the alcohols are as varied in their obvious properties as are the paraffins themselves. The simpler alcohols, typified by common alcohol and wood-spirit, are volatile or spirituous liquids, freely miscible with water and burning with a non-luminous flame; the higher alcohols are oily in appearance, immiscible with water, have high boiling points, and burn with a luminous and even smoky flame; while the yet higher alcohols, as those procurable from spermaceti, Chinese wax, and beeswax, are fusible, crystallizable, combustible solids.

Unlike the paraffins, however, the alcohols, whether spirituous, oily, or solid, are readily oxidizable; and in the case of certain alcohols, which constitute the class of alcohols proper or primary alcohols, the oxidation takes place in this fashion. The first stage of the oxidation results in the formation of an aldehyd—a body of very characteristic properties, differing in composition from the alcohol yielding it by a loss of two proportions of hydrogen. The next stage of the oxidation consists in the conversion of the aldehyd into a volatile acid, by the gain of one proportion of oxygen; while any further oxidation results in the breaking up of the substance into two or more carbon compounds.

Now it is the relationship of the paraffins to this particular variety of alcohols which has been already illustrated. And so far at least as the study of this relationship has gone, there would appear to be as many isomeric primary alcohols as there are isomeric paraffins; and the nature of the difference between the several isomeric members of the one class, whatever that may be, would appear to be also the nature of the difference between the several isomeric members of the other class,—the mutual convertibility of the paraffin and its alcohol not throwing any light upon the question.

VI. SECONDARY AND TERTIARY ALCOHOLS.

But the majority of the paraffins are found to be associated each one of them not only with an alcohol of the above-described character, that is to say a primary alcohol, but also, and by a very similar mode of metamorphosis, with an isomeric alcohol of a different character, either of the class known as secondary or of the class known as tertiary alcohols; while in many instances, the paraffins are associated similarly not only with either a secondary or a tertiary alcohol, but with both a secondary and a tertiary alcohol, in addition to a primary alcohol. In other words, some paraffins are associated each with a primary alcohol only, others with a primary and secondary, others with a primary and tertiary, others with a primary, secondary, and tertiary alcohol.

Now the secondary and tertiary alcohols are distinguished from the primary alcohols, or alcohols proper, with which they are respectively isomeric, by a difference in boiling point, and more especially by a difference in the manner of their oxidation. The first stage of the oxidation of secondary alcohols, also called pseudo-alcohols or pseudols, as of the primary alcohols, consists in their deprivation of two proportions of hydrogen; but the products have no longer the characters of bodies belonging to the class of aldehyds, but of bodies belonging to a differently characterized class, that of the ketones. These ketones differ especially from the aldehyds in that they do not undergo any stage of oxidation corresponding to that by which the aldehyds are converted into acids, but undergo a further disruptive oxidation only. The tertiary alcohols, or carbinols proper, do not undergo even the stage of oxidation corresponding to that by which the primary and secondary alcohols are converted into aldehyds and ketones respectively, but suffer a disruptive oxidation only.

Now when ethane is acted upon by chlorine it yields only one monochlor-ethane of boiling point 12·5°, and corresponding to primary ethylic alcohol of boiling point 78·4°, which is indeed the only 2-carbon alcohol known. But propane, under different modes of treatment, is capable of yielding two distinct monochlorides C_3H_7Cl, the one boiling at 46·5°, and corresponding to primary propylic alcohol boiling at 98°, and the other boiling at 37°, and corresponding to pseudo-propylic alcohol boiling at 83°. Similarly butane and pentane each yield two monochlorides,—each a monochloride corresponding to primary butyl and primary pentyl alcohol, boiling at 116° and 137° respectively, and each a monochloride corresponding to pseudo-butyl alcohol and pseudo-pentyl alcohol, boiling at 99° and 119° respectively.

Corresponding, moreover, to isobutane, there is a primary alcohol —isobutyl alcohol, boiling at 109°, and yielding by oxidation isobutyraldehyd and isobutyric acid successively. There is not known, however, any isobutyl pseudo-alcohol yielding by oxidation a ketone, but instead a tertiary alcohol boiling at 82°, and susceptible of a disruptive oxidation only. While corresponding to isopentane is a primary alcohol, isopentyl or amyl alcohol, boiling at 129°, and yielding by oxidation valeraldehyd and valeric acid successively; also isopentyl pseudo-alcohol boiling at 107°, and yielding by oxidation isopentyl ketone; and lastly, isopentyl tertiary alcohol, boiling at 98°, and inoxidizable save into simpler carbon products. This series of relationships is illustrated in the following table.

TABLE I.

H_2	Hydrogen.	Water.		H_2O.
CH_4	Methane	66°	Methylic	CH_4O
C_2H_6	Ethane	78°	Ethylic	C_2H_6O
C_3H_8	Propane	97°	Propylic	C_3H_8O
		83°	Pseudo-propylic	”
C_4H_{10}	Butane	116°	Butylic	$C_4H_{10}O$
		99°	Pseudo-butylic	”
	Isobutane	109°	Isobutylic	”
		82°	Katabutylic	”
C_5H_{12}	Pentane	137°	Pentylic	$C_5H_{12}O$
		119°	Pseudo-pentylic	”
	Isopentane	129°	Amylic	”
		107°	Pseud-amylic	”
		98°	Kat-amylic	”
	Neopentane		?	
C_6H_{14}	Hexanes		Hexylic	$C_6H_{14}O$
C_7H_{16}	Heptanes		Heptylic	$C_7H_{16}O$
C_8H_{18}	Octanes		Octylic	$C_8H_{18}O$
$C_{16}H_{34}$	Cetane		Cetylic	$C_{16}H_{34}O$
$C_{27}H_{56}$	Cerane		Cerylic	$C_{27}H_{56}O$
$C_{30}H_{62}$	Melane		Melylic	$C_{30}H_{62}O$
C_nH_{2n+2}	Paraffin		Alcohol	$C_nH_{2n+2}O$

Of associated 2-carbon compounds then, there is only one paraffin and one alcohol known. Of the 3-carbon compounds, there is only one paraffin, but there are two alcohols; while of 4-carbon compounds there are two paraffins and four alcohols. Of 5-carbon compounds there are three paraffins known, corresponding alike to the formula C_5H_{12}; and there exist probably eight alcohols, four primary, three secondary, and one tertiary, corresponding alike to the formula $C_5H_{12}O$; but of these last, two primary, two secondary, and one tertiary alcohol are alone satisfactorily made out. While of 6-carbon compounds, there are probably five paraffins corresponding to the formula C_6H_{14}, and no fewer than sixteen alcohols corresponding alike to the formula $C_6H_{14}O$.

VII. PARAFFIN OXIDATION.

What then is the nature of the difference between primary, secondary, and tertiary paraffin alcohols? How comes it that, being three, there should be no more than three classes of these alcohols? How comes it that while every paraffin yields a primary alcohol, and some paraffins more than one, certain paraffins should yield a primary alcohol only, other paraffins should yield each a secondary alcohol in addition, yet others a tertiary alcohol, and yet others both secondary and tertiary alcohols? And what bearing, if any, has this property of yielding alcohols of different kinds upon the nature and origin of the isomerism manifested by the paraffins furnishing them respectively?

Some light may be thrown on these associated questions, by considering the course of oxidation in the case of the simplest paraffin, namely, marsh-gas. Methane, or marsh-gas, CH_4, like the other paraffins, is not readily susceptible of direct oxidation; but by acting on it with chlorine under suitable conditions, there is produced the chloro-derivative CH_3Cl, which, decomposed by caustic alkali KHO, yields wood-spirit or methyl alcohol CH_4O, together with potassium chloride KCl. The first stage of the oxidation being thus effected, the remaining stages are easy. By exposure of the alcohol to a current of heated air it is converted into formic aldehyd CH_2O; this aldehyd, by further absorption of oxygen, yields formic acid CH_2O_2; and this last is converted by even the feeblest oxygenants into carbon dioxide CO_2.

In the successive formation then of these several products, the first stage consists in an addition of oxygen O, the second in an abstraction of hydrogen H_2, the third in a further addition of oxygen O, and the fourth in a further abstraction of hydrogen H_2. There is not a continuously successive addition of oxygen, or removal of hydrogen, but a succession of one and the other action alternately. Now among paraffins in general the stages of oxidation, so far as they extend, are the same as in marsh-gas. Thus in the case of primary compounds there occur the three stages of plus oxygen, minus hydrogen, and then plus oxygen again; in the case of secondary compounds there occur the two stages of plus oxygen and then minus hydrogen; while in the case of tertiary compounds there is the one stage of plus oxygen only, as set forth in the upper part of the following table.

TABLE II.

		Methyl.	Ethyl.	Propyl.$^{\pi}$	Butyl.$^{\kappa}$
Chloride		CH_3Cl	C_2H_5Cl	C_3H_7Cl	C_4H_9Cl
Paraffin		CH_4	C_2H_6	C_3H_8	C_4H_{10}
Alcohol	$+ O$	CH_4O	C_2H_6O	C_3H_8O	$C_4H_{10}O$ Carbinol.
Aldehyd	$- H_2$	CH_2O	C_2H_4O	C_3H_6O Ketone.	
Acid	$+ O$	CH_2O_2	$C_2H_4O_2$ Acid.		
Carboxide	$- H_2$	CO_2			
Paraffin		CH_4	XCH_3	YCH_2	ZCH
Alcohol	$+ O$	$CH_3(HO)'$	$XCH_2(HO)'$	$YCH(HO)'$	$ZC(HO)'$
Aldehyd	$- H_2$	CH_2O''	$XCHO''$	YCO''	
Acid	$+ O$	$CH(HO)'O''$	$XC(HO)'O''$		
Carboxide	$- H_2$	CO_2''			

It is observable that in the case of marsh-gas, there are four proportions of hydrogen and four stages of oxidation to be dealt with; and this association of four stages of oxidation with four proportions of hydrogen becomes more suggestive when it is found, on further study, that the four stages of oxidation, though on the face of them alternate, are in reality successive, and consist, not indeed in four successive additions of oxygen, but in four successive substitutions of oxygen for the four proportions of hydrogen in marsh-gas,—in a replacement, that is to say, of the first proportion of hydrogen by a proportion of oxygen half saturated with hydrogen $(HO)'$, then in a replacement of two proportions of hydrogen by one proportion of unsaturated or diad oxygen O'', then in a replacement of three proportions of hydrogen by one proportion of half-saturated oxygen $(HO)'$ and one proportion of diad oxygen O'', jointly—and lastly in a replacement of four proportions of hydrogen by two proportions of diad oxygen $O'' + O''$, jointly.

Now what has been established with regard to the nature of the successive stages of marsh-gas oxidation has also been established with regard to the successive stages, so far as they proceed, of paraffin oxidation in general. In the indirect oxidation then of a paraffin into its alcohol, whether primary, secondary, or tertiary, there is an actual substitution effected for one proportion of hydrogen in the paraffin. In the further direct oxidation of the primary and secondary alcohol into aldehyd and ketone respectively, there is an actual substitution effected for two proportions of hydrogen in the paraffin;

and in the further direct oxidation of the aldehyd into its acid, there is an actual substitution effected for three proportions of hydrogen in the paraffin. But why, in the case of marsh-gas, there should be four successive substitutions of its four proportions of hydrogen, while in the case of other paraffins with six, eight, ten, twelve, and more proportions of hydrogen, the series of substitutions should be limited to three, two, and even one proportion of hydrogen, still remains to be accounted for.

Let it be imagined, however, that in some particular paraffin there exists the grouping CH as a distinct constituent of the paraffin, and further that, by the action of chlorine, it is the hydrogen of this particular grouping that is replaced so as to form the derived grouping CCl. Let it be imagined that, in another case, there exists the grouping CH_2, and that, by the action of chlorine, it is the hydrogen of this grouping that is replaced, so as to form the derived grouping CHCl; and lastly, let it be imagined that, in another case, there exists the grouping CH_3, and that, in the action of chlorine, it is the hydrogen of this grouping that is replaced, so as to form the derived grouping CH_2Cl,—on the substitution, in these several derived groupings, of their chlorine by half-saturated oxygen, there will result the oxidized groupings C(HO), CH(HO), and $CH_2(HO)$; and since, in the paraffins, direct oxidation does not occur save where indirect oxidation has initiated, it is intelligible that in the case of the grouping CH, the oxidation or substitution should cease at the indirect or alcoholic stage C(HO); while in the case of the group CH_2, there should be first the indirect or alcoholic stage CH(HO), and then the direct or ketonic stage CO''; while in the case of the group CH_3, there should be first the indirect or alcoholic stage $CH_2(HO)'$, and then the direct aldehydic and acid stages, CHO'' and $C(HO)'O''$, in succession—as set forth in the lower part of the preceding table.

VIII. SYNTHESIS OF PARAFFINS.

It remains to be considered whether or not the several differently oxidizable paraffins are actually constituted of the groupings CH_1, CH_2, and CH_3. This is a question to be decided more particularly by a study of their modes of formation—not indeed as conducted on a large scale in the process of destructive distillation, but as effected by definite synthetic reactions taken part in, as will appear, by certain halogen derivatives of the paraffins. Now it is well known that hydrogen, though in most of its chemical relations a somewhat inactive element, is not inactive in respect to chlorine and the halogens. Accordingly, when a paraffin such as ethane C_2H_6, is acted upon by chlorine, the chlorine takes away hydrogen from the paraffin to produce hydrochloric acid; and conversely, when nascent hydrogen acts on a chloro-paraffin such as chlorethane C_2H_5Cl, the hydrogen takes away chlorine from the chloro-paraffin to form hydrochloric acid — the two abstractions of hydrogen and chlorine respectively being alike attended by a substitution of the other element for the one taken away, as already illustrated.

Unlike hydrogen, however, chlorine and the halogens are possessed of a very general activity; and accordingly, when substituted directly or indirectly for the hydrogen of a paraffin, are capable of being removed, not only by hydrogen but by many of the metals. But while under certain conditions, so far at least as the final result is concerned, the metal behaves like hydrogen, abstracting the halogen and taking its place, under other conditions it effects a mere removal of the halogen, this removal being attended however by a phenomenon of a very remarkable kind—namely, the formation of a new and more complex paraffin, by the combination of two hydrocarbon residues with each other. Thus when iodethane C_2H_5I is acted on by mercury under the influence of sunlight, there is produced not the residue or radical C_2H_5, but instead the paraffin, butane, C_4H_{10}. Similarly when iodomethane CH_3I is acted on by sodium, there is produced not the radical CH_3, but instead the paraffin, ethane, C_2H_6; while when a mixture of iodethane C_2H_5I, and iodomethane CH_3I, is acted upon by sodium, there is produced not a mixture of the two radicals C_2H_5 and CH_3, but instead the paraffin, propane, C_3H_8, and so in other cases.

Arguing then from its above mode of formation, ethane is $H_3C.CH_3$; iodethane is consequently $IH_2C.CH_3$, or $H_3C.CH_2I$; and propane, resulting as it does from the reaction between iodethane $IH_2C.CH_3$ and iodomethane CH_3I, is $H_2C.CH_3,CH_3$. Or, so far as regards their above mode of formation, both ethane and propane are really constituted in part by a grouping CH_3; and, through the intervention of a chloro-derivative of this grouping, CH_2Cl, should yield each of them the three successive oxidation products, namely, alcohol, aldehyd, and acid,—with the formation of which last product the stages of oxidation should (save by an initiatory substitution of some further hydrogen by halogen) come to an end, in each instance, as is actually the fact.

But while ethane is constituted solely of the group CH_3 or H_3C, twice repeated, propane is constituted in part of a grouping H_2C or CH_2; and through the intervention of a chloro-derivative of this grouping, $ClHC$, should yield the series of only two successive oxidation products, namely, pseudo-alcohol and ketone. What the fact is, has been already stated, namely, that while ethane furnishes only one monochloro-derivative—this monochloride, howsoever produced, corresponding to an alcohol, oxidizable into an aldehyd and acid successively—propane is capable of furnishing two distinct monochlorides, C_4H_7Cl and $C_4H_7{}^{\pi}Cl$, distinguishable from one another by the difference in their boiling points; and of these two chloropropanes, the one of highest boiling corresponds to an alcohol oxidizable into an aldehyd and acid successively, while the one of lowest boiling point corresponds to a pseudo-alcohol oxidizable into a ketone only.

But not from the above considerations only may the chloride of higher boiling point be inferred to contain the grouping CH_2Cl, and that of lower boiling point, the grouping $CHCl$ or $ClHC$; for the chloride of higher boiling point is actually producible by the introduction and subsequent metamorphosis of the group CN''', while the chloride of lower boiling point is similarly producible by the introduction and metamorphosis of the group CO'', the single proportion of nitrogen being representative of three, and the single proportion of oxygen being representative of two proportions of halogen or hydrogen, as is well known. These relationships are illustrated in the following formulæ :

$H_2C.CH_3,CH_3$	Propane.	$H_2C.CH_3,CH_3$	Propane.
$ClHC.CH_3,CH_3$	Chloropropane.	$H_2C.CH_2Cl,CH_3$	Chloropropane.
$(HO)HC.CH_3,CH_3$	Propyl-pseudol.	$H_2C.CH_2(OH)',CH_3$	Propyl-alcohol.
$O''C.CH_3,CH_3$	Acetone.	$H_2C.CN''',CH_3$	Propionitrile.

The reaction between iodomethane and iodethane, with abstraction of their iodine by metal, resulting in the formation of propane $H_2C.CH_3,CH_3$, the similar reaction between iodomethane CH_3I and each of the two iodopropanes, $H_2C.CH_2I,CH_3$ and $IHC.CH_3,CH_3$, should furnish the two butanes $H_2C.CH_2.CH_3,CH_3$ and $HC.CH_3,CH_3,CH_3$; each of them constituted in part by a grouping CH_3, and capable of furnishing a distinct primary alcohol further oxidizable into aldehyd and acid; the former of them also constituted in part of the grouping H_2C, and capable of furnishing also a pseudo-alcohol oxidizable into a ketone only; the latter of them not constituted at all of the grouping H_2C, or capable of furnishing a pseudo-alcohol oxidizable into a ketone, but constituted in part of the grouping HC, and capable of furnishing a tertiary alcohol oxidizable only into simpler carbon products,—results which have in each case been satisfactorily established by experiment.

As with propane, so with butane, save that not merely two but even four isomeric iodobutanes are known, expressible by the following formulæ :

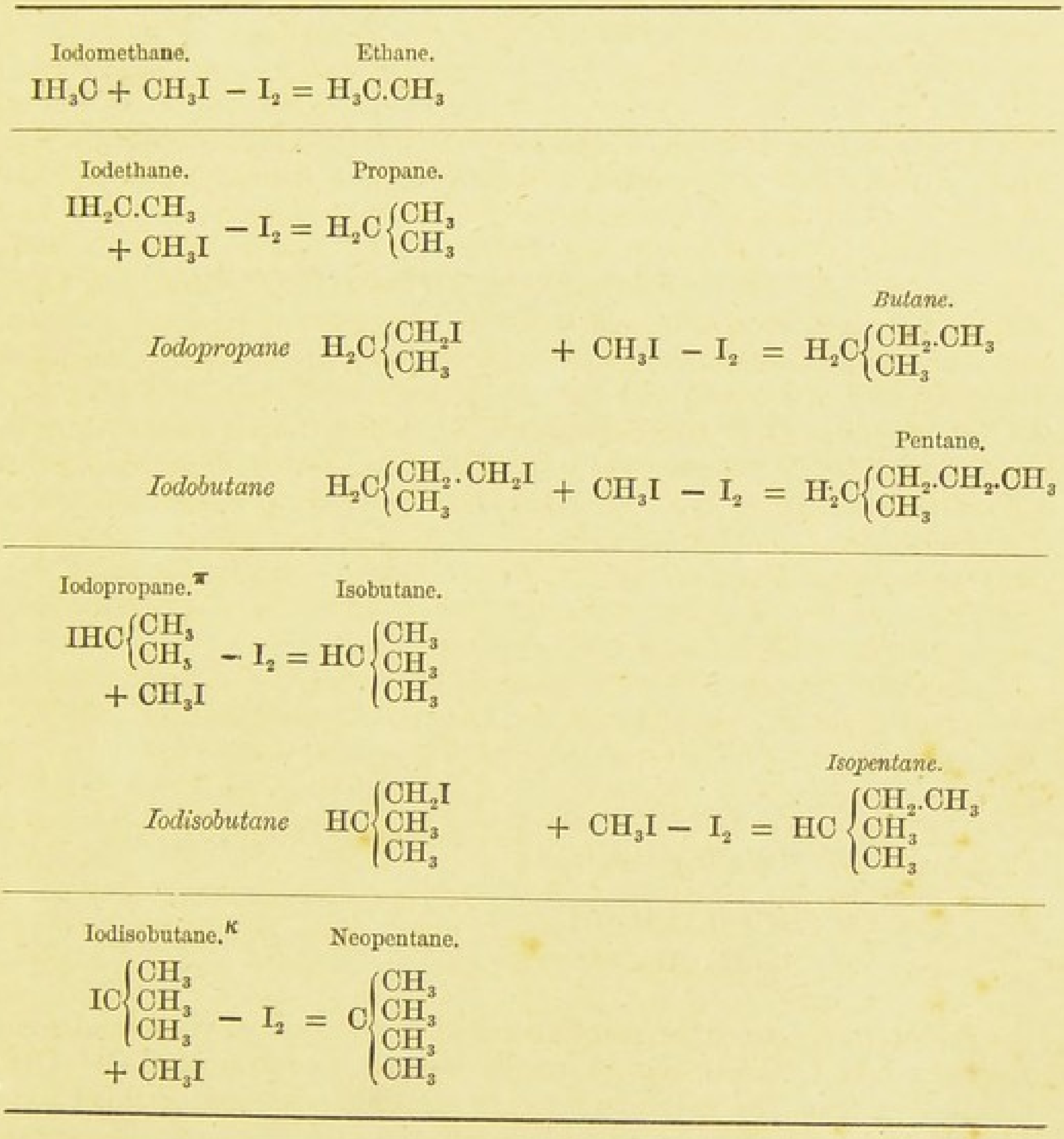
$$\left.\begin{array}{ll} 1^\circ & H_2C.CH_2.CH_2I,CH_3 \\ 2^\circ & IHC.CH_2.CH_3,CH_3 \end{array}\right\} \quad \text{from} \quad \overset{\text{Butane.}}{H_2C.CH_2.CH_3,CH_3}.$$

$$\left.\begin{array}{ll} 3^\circ & HC.CH_2I,CH_3,CH_3 \\ 4^\circ & IC.CH_3,CH_3,CH_3 \end{array}\right\} \quad \text{from} \quad \overset{\text{Isobutane.}}{HC.CH_3,CH_3,CH_3}.$$

Accordingly, from the reaction between the first of these and iodomethane CH_3I, there should result normal pentane $H_2C.CH_2.CH_2.CH_3,CH_3$; from the reaction between either the second or third iodobutane and iodomethane should result one and the same isopentane $HC.CH_2.CH_3,CH_3,CH_3$; while from the reaction between the fourth iodobutane and iodomethane should result neopentane $C.CH_3,CH_3$,

CH_3,CH_3; all these, or equivalent reactions having been actually realized with the above results. And isopentane being thus constituted in part of the group HC, in part of the group H_2C, and in part of the group H_3C or CH_3, is accordingly found to yield a tertiary alcohol inoxidizable save with disruption, a pseudo-alcohol oxidizable into a ketone, and a primary alcohol oxidizable into an aldehyd and acid successively. The scheme of the synthetic formation of ethane, propane, the two butanes, and three pentanes, is shown on the concluding table; wherein the combinations with one another of the different groupings taking part in the successive reactions are indicated by the lateral contiguity of their respective symbols.

TABLE III.



Iodomethane. Ethane.

$$IH_3C + CH_3I - I_2 = H_3C.CH_3$$

Iodethane. Propane.

$$\begin{matrix}IH_2C.CH_3\\ +\ CH_3I\end{matrix} - I_2 = H_2C\left\{\begin{matrix}CH_3\\ CH_3\end{matrix}\right.$$

Butane.

$$\textit{Iodopropane}\quad H_2C\left\{\begin{matrix}CH_2I\\ CH_3\end{matrix}\right. + CH_3I - I_2 = H_2C\left\{\begin{matrix}CH_2.CH_3\\ CH_3\end{matrix}\right.$$

Pentane.

$$\textit{Iodobutane}\quad H_2C\left\{\begin{matrix}CH_2.CH_2I\\ CH_3\end{matrix}\right. + CH_3I - I_2 = H_2C\left\{\begin{matrix}CH_2.CH_2.CH_3\\ CH_3\end{matrix}\right.$$

Iodopropane.[*] Isobutane.

$$\begin{matrix}IHC\left\{\begin{matrix}CH_3\\ CH_3\end{matrix}\right.\\ +\ CH_3I\end{matrix} - I_2 = HC\left\{\begin{matrix}CH_3\\ CH_3\\ CH_3\end{matrix}\right.$$

Isopentane.

$$\textit{Iodisobutane}\quad HC\left\{\begin{matrix}CH_2I\\ CH_3\\ CH_3\end{matrix}\right. + CH_3I - I_2 = HC\left\{\begin{matrix}CH_2.CH_3\\ CH_3\\ CH_3\end{matrix}\right.$$

Iodisobutane.[K] Neopentane.

$$\begin{matrix}IC\left\{\begin{matrix}CH_3\\ CH_3\\ CH_3\end{matrix}\right.\\ +\ CH_3I\end{matrix} - I_2 = C\left\{\begin{matrix}CH_3\\ CH_3\\ CH_3\\ CH_3\end{matrix}\right.$$

[W. O.]

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