ON THE

THEORY OF CHEMICAL COMBINATION:

A THESIS

PRESENTED TO THE FACULTY OF MEDICINE OF THE UNIVERSITY OF EDINBURGH.

BY

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1861.

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This paper was presented in 1861 to the Faculty of Medicine, when I was a candidate for the degree of M.D.

In consequence of a somewhat adverse opinion expressed as to the speculations contained in it, I exercised the discretion allowed (I think unwisely) by the University to graduates, and did not print it.

Some of my friends have urged me to do so now, and although I am quite aware that it contains much that is crude and some things that are erroneous, and that all that was then new or important in it has since been much better expressed by others, I still think that it is not altogether unworthy of preservation as a contribution to the history of the subject.

It is printed *verbatim*, and I would ask such of my friends as may read it to recollect that it was written eighteen years ago by a medical student.

A. C. B.

UNIVERSITY OF EDINBURGH,
March 1879.

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ON THE

THEORY OF CHEMICAL COMBINATION.

THE fundamental questions in chemistry,—those questions the answers to which would convert chemistry into a branch of exact science, and enable us to predict with absolute certainty the result of every reaction—are (1) What is the nature of the forces which retain the several molecules or atoms of a compound together? and (2) How may their direction and amount be determined? We may safely say that, in the present state of the science, these questions cannot be answered; and it is extremely doubtful whether any future advances will render their solution possible.

It is not, however, the less important to collect and arrange the data which we possess; as this will, at least, give us a more comprehensive view of these data themselves, if it does not indicate the direction in which the answers to the questions enunciated above are to be found. The data for the solution of the problem are the general laws of *chemical reaction*. These fall under two great heads—the law of Equivalence or Substitution, and what may be called the law of Polarity. We purpose to sketch the history of the development of these laws; to discuss the bearing of recent discoveries on them; and to endeavour to determine what is the form in which they may be best expressed, so as to include all the facts, and be, as nearly as possible, a strict generalisation from them.

The first observation on record, leading to the establishment of a law of equivalence, was that of Bergman[*], that a mixture of neutral salts continues neutral although double decomposition take place. This fact contains in it the germ of a theory of chemical equivalents, but it does not appear that its discoverer carried his speculations so far. About the end of the last and the commencement of the present century, Wenzel, Richter, and Fischer[†] determined the combining or equivalent weights of a large number of acids and bases; and about the same time, Proust, by analysis of the metallic oxides and sulphurets, proved, in opposition to Berthollet, that the law of *definite combination* applied to these bodies also.

It was not, however, till Dalton,[‡] generalising from these cases and from his own analyses, enunciated the law of multiple proportion, and based upon it his Atomic Theory, that a clear view was obtained of the mutual equivalence of certain fixed definite weights of chemical substances.

It is unnecessary here to go into the details of Dalton's theory. It is sufficient to state that, although the improvement of analysis has rendered changes necessary in many of Dalton's numbers, and the advance of theory has induced us frequently to adopt a multiple or sub-multiple of Dalton's atomic weights, still the formulae now in use are essentially Dalton's formulae.

The next great discovery bearing upon the question was that of the law of atomic volume by Gay Lussac,[§] which was destined to exert so powerful an influence on chemical speculation. It is curious to note that Dalton did not see the bearing of this most important

[*] Bergman, De attractionibus electivis. Opuscula iii. 291: referred to in Gmelin's "Handbook."

[†] Berzelius, vol. v. p. 16 (Ed. 1835). Kopp, "Geschichte der Chemie," vol. ii. pp. 357–366. Referred to in Henry's "Life of Dalton," pp. 72, 73. Wenzel, "Lehre von der Verwandtschaft" (1777). Richter, "Aufangsgründe der Stöchiometrie" (1792–4), referred to in Gmelin's "Handbook."

[‡] "Memoir on Absorption, and Table" (1803); "New System of Chemical Philosophy" (1808).

[§] "Nouveau Bulletin des Sciences," par la Soc. Philom. 1809, I. 298 (Gmelin).

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discovery on the Atomic Theory, and even refused to credit the accuracy of the observations on which it was established. In 1815 Berzelius,[*] taking up the train of experiment and reasoning started by Gay Lussac, proceeded, with characteristic patience and judgment, to form a table of the atomic weights of chemical elements and compounds. He took oxygen as his standard, and, assuming that the atom of each gaseous element occupied the same space, he assigned atomic weights to the simple gases, thus :—

$$O = 100, H = 6.25, N = 87.5.$$

Assuming, again, that the relation between the number of atoms of the one and that of the other element in binary compounds is the simplest possible, he wrote anhydrous potash KO, protoxide of iron FeO_2, and peroxide of the same metal FeO_3.

In 1819 Dulong and Petit[†] threw a further light on this subject by the discovery of the relation which exists between the atomic weight of an element and its *specific heat*. They found that, taking Berzelius's numbers, the product of the atomic weight into the specific heat was between 41 and 36, or double or half of these numbers. This close approach to constancy in the atomic heat of elements (and, when we consider the great difficulty attending any process for estimating the specific heat of bodies, the approximation is close) is certainly very remarkable; and it is impossible not to believe that the arithmetical relation is founded on some real relation in the ultimate constitution of matter.

The following is a table by Regnault[‡] of the atomic heat of elements, using the equivalents in common use :—

Al 36.6	Sb. 76.2 = 2 × 38.1	As 76.3 = 2 × 38.15	
Rb 40.6	Br (solid) 84.3 = 2 × 42.15	Fe 39.8	
Au 79.4= 2 × 39.7		I 85.6 = 2 × 42.8	Ir 44.7
Cd 39.7	K 82.6 = 2 × 41.3	Co 40.1	
C (charcoal) 18.1= ½ × 36.2		Mn 40.7	Na 84.2= 2 × 42.1
Ni 40.2	Os 38.2	Pd 39.3	P 77.5= 2 × 38.75
Pt 40.4	(Hg.= 1250) 41.6	Rh 35.2	S 40.5
Se 37.5	Ag 76.9= 2 × 38.45	Te 37.9	Bi 40
W 41.9	Zn 39.8	Sn 40.7	

We have said above, and it may be seen from a glance at the table, that occasionally the atomic heat of an element calculated from the numbers of Berzelius is double, and occasionally half, the number which represents the atomic heat of the majority of the elements. From this it is obvious that if we assume that the atomic heat is the same in all elements, we must halve the atomic weight of the one class of bodies and double that of the other. To do so, however, would, in many cases, be in direct opposition to the indications of the vapour density; and as the atomic weight derived from the latter so generally agrees with the chemical reactions, we must at present look on the results of the examination of the atomic heat as curious, interesting, and certainly not fortuitous coincidences; but we cannot hope to employ them in determining or confirming the atomic weight of a body.

This will be manifest when we look at the difference which the specific heat of a substance presents according to its physical state. Thus the specific heat of charcoal is .244,[§] diamond .1469, vitreous selenium .103, crystallised selenium .076 at temperatures above the freezing point of water, below which the specific heat of both varieties of selenium is .075.

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[*] Various papers in Gilbert's and Poggendorff's "Annalen," and in "Annales de Ch. et de Ph."

[†] "An. de Ch. et de Ph." x. 395

[‡] "An. de Ch. et de Ph." [III.] xlvi. 257, as quoted in Liebig, Poggendorff, and Wöhler's "Handwarterbuch."

[§] Regnault, *op. cit.*

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In 1820 Mitscherlich[*] pointed out that when bodies of the same atomic constitution assume the crystalline form, they are usually isomorphous, and that such isomorphous compounds crystallise when mixed, as if they formed only one compound. He hoped that this fact might be useful in determining the constitution of compounds by comparing their crystalline form with that of others of known constitution. Thus, various metals may be substituted in varying proportions for one another without altering the crystalline form, as in the alums, and selenium and tellurium for sulphur, &c.

There can be no doubt that this method is of great value, either where no other can be applied, or as a means of confirming results obtained by other methods; but it is not universally applicable, as it sometimes leads to results that clearly show that crystalline form depends on some other cause as well as on the atomic constitution of the compound.

In order to trace the progress of chemical speculation chronologically, we must now turn to the other great law, which we have called that of Polarity. All chemical elements may be arranged in a series, the substances at the one extreme of which unite readily with those at the other, and form with them compounds of great stability, while those near one another unite with difficulty and form compounds easily decomposed. (If one element forms more than one set of compounds, it must occur more than once in the series.)

To account for this, and, at the same time, for chemical affinity generally, Berzelius[†] framed his *electro-chemical theory*. In this he was influenced not only by the facts mentioned above, but by the effect of a current of galvanism transmitted through a salt either fused or dissolved. He supposed that the metals, which occupy one end of the series spoken of, and which in electrolysis are deposited on the *negative* electrode, possess an excess of *positive* electricity, and that the salt-radicals, with the bodies allied to them, which occupy the other end of the series and appear at the *positive* electrode, possess an excess of *negative* electricity; and that it is the attraction of the one electricity for the other, and not the affinity of the one element for the other that brings them into a state of union. He further supposed that various circumstances, such as changes in temperature, light, &c., alter the absolute amount of electricity in an atom, but not the difference between the amount of the two electricities; and that, when two elements combine, the excess of positive in the one neutralises the excess of negative electricity in the other, and produces heat or light, as the union of the two does in the ordinary electric discharge.

This theory, here very briefly sketched, although open to numerous objections, requiring many assumptions, and raising more, and more difficult, questions than those which it was framed to explain, as the work of a master mind, and as the most plausible attempt to unite the facts, exercised a very great influence on rational chemistry. It became intimately incorporated with the Radical Theory, which, owing its origin to Lavoisier,[‡] was first applied to the details of organic chemistry by Berzelius, was employed, with some alterations, by Liebig, to explain his brilliant discoveries, and even now, modified in a variety of ways, is accepted by most chemists. The Radical Theory of organic chemistry may be shortly stated thus:—Organic compounds are similar in constitution to inorganic bodies, with this exception, that in the former certain groups of atoms play the same part which simple substances do in the latter. To these groups was given the name of Radicals. Some of them act as positive, some as negative substances. Of the former ethyl, of the latter cyanogen, may be taken as specimens. Some unite with oxygen to form acids; thus acetic acid is the teroxide of acetyl, &c.

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[*] "An. de Ch. et de Ph." xiv. 172, xix. 350, xxiv. 264, 355. Pogg. An. xlix. 401, "Journ. prakt. Ch." xix. 457 (Gmelin).

[†] Various memoirs in journals already cited, and "Lehrbach der Chemie."

[‡] "Traité Élémentaire de Chimie" (1793), pp. 251, 209, as quoted by Kekulé, "Lehrbuch der Organischen Chemie," p. 60.

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The main difference between the theory of Berzelius and that of Liebig is, that the former denies while the latter admits that electro negative elements, as chlorine and oxygen, can exist *in* a radical.

The theory was afterwards extended so as to include inorganic bodies which appear to act as simple substances, as peroxide of nitrogen, amidogen, uranyle. Among the negative radicals must also be placed the hypothetical salt-radicals of Davy, which consist of salt minus metal, as SO_4, NO_6, &c.; and among the positive, ammonium and its analogues.

Against this theory, as well as against the dualistic, with which it was always intimately connected, Laurent published an acute and energetic protest in his work entitled "Chemical Method." As far as it can be shortly stated, his view on this question is this :—that (1) the formulae deduced from vapour density are those which in all other respects satisfy the requirements of chemists, and generally agree best with the results obtained from comparison of boiling points, specific heat, crystalline form, and chemical reactions; (2) that in these formula there is always a whole number of atoms, and an even number of atoms of those substances (hydrogen, chlorine, nitrogen, metals, &c.), to which Laurent gave the name of "dyads." To these there are a few exceptions-some probably only apparent, but others which there is great difficulty in bringing under the law. Among these exceptions may be mentioned the ammoniacal salts, nitric oxide, and the peroxide of nitrogen, NH_4R, N_2O_2, and N_2O_4, each representing H_4 in volume, but H_2 in function.

The difficulty may be got over in the case of the ammoniacal salts by the very probable supposition that in volatilising they are decomposed into ammonia and acid, so that the vapour of *sal-ammoniac* is not NH_4Cl, but a mixture of NH_3, and HCl. This explanation is rendered the more probable by the discovery by Hofmann, of the fact that the hydrated diamines do actually undergo this decomposition when volatilised.

Laurent further regarded the so-called radicals as merely compounds from which a certain part had been removed,—*e.g.*, ethyl is alcohol minus HO,—ready again to combine with what has been removed from it, or with an equivalent, such as Cl, NO_2, &c. He held that radicals were mere creatures of the imagination, and that when a radical is said to exist free, it is formed by two atoms of the hypothetical radical which is supposed to exist in combination. Thus free ethyl and free cyanogen are not C_2H_5 and CN, but C_4H_{10} and C_2N_2; in the same way free hydrogen and free chlorine are not H and Cl, but H_2, and Cl_2. This not only accords with vapour density but also with chemical relations; for the smallest quantity of hydrogen or chlorine which can take part in or result from a chemical reaction is that which is represented by H_2 and Cl_2.

The great argument of Laurent against the dualistic theory was that chlorine, a highly "electro-negative" body, may be substituted for hydrogen, a highly "electro-positive" body, without materially altering the chemical or physical properties of the compound in which such replacement occurs. This was long denied by Berzelius and the German chemists, but is now admitted by every one—even by those who most strongly oppose the theoretical views of Laurent.

Gerhardt, the *collaborateur* and friend of Laurent, was the first clearly to enunciate, in his papers in the "Annales de Chimie et de Physique," and in his "Traité de Chimie Organique," the principle that a rational formula represents nothing but a set of equations; that it is, in fact, a sort of short-hand way of writing an equation. He says :—

> "Les formules chimiques, comme nous 1'avons dit, ne sont pas destinées à representer l'arrangement des atomes; mais elles ont pour but de rendre évidentes, de la manibre la plus simple et la plus exacte, les relations qui rattachent les corps entre eux sous le rapport des transformation.

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> "Toute transformation, toute réaction chimique peut se rendre par une *équation* entre les matières réagissantes et les produits de la réaction. Représenter un corps par une *formule rationnelle* c'est résumer par des signes de convention un certain nombre d'équations dane lesquelles figure ce corps, un autre corps étant pris pour unité de comparaison. Les formules rationnelles sont done en quelque sort des équations contractées." [*]

Laurent had previously arranged organic substances with reference to the manner in which they are, or may be, produced, grouping each series round the "nucleus," which in general was the most stable hydrocarbon of the series—olefiant gas, *e.g.*, in the alcohol series, naphthaline in the naphthalic series, &c. Gerhardt, while grounding his classification on the same principle, with greater consistency made use of the *radicals* as the starting-point in each series, using the word "radical" according to the following definition :—

> "J'appelle *radicaux*, ou *résidues*, les éléments de tout corps qui peuvent être ainsi transportés dans un autre corps par l'effet d'une double décomposition, ou qui y ont été introduits par une semblable réaction. . . . On voit, d'après cela, que, contrairement à la plupart de chimistes, *je prends l'expression de radical dans le sens de rapport, et non dans celui de corps isolable ou isolé*. Je distingue donc le radical hydrogène du gaz hydrogène, le radical chlore du chlore libre; bien mieux, si l'on vent représenter par des formules rationnelles l'hydrogène ou le chlore libres, l'étude des réactions conduit à écrire le gaz hydrogène par les deux radicaux HH, et le gas chlore par les deux radicaux ClCl." [†]

In arranging the various series he took advantage of the principle of homology, which Schiel[‡] was the first (in 1842) to point out. Gerhardt called those bodies homologous which, while presenting analogies in their chemical relations, differ from one another in composition by a multiple of CH_2. Thus, formic and acetic acids, vinic and amylic alcohols, are homologous. To the series which contain the same radical he gave the name "heterologous." He used the word "isologous" to distinguish those bodies which are analogous in their chemical relations but do not present that relation which he denominated homology; thus, acetic and benzoic acids, aniline and methylamine, are "isologous."[§] He happily compared this classification to the following arrangement of a pack of cards:—If a pack of cards be arranged on a table, each suit forming a vertical line in which the cards are placed according to their value, each card will lie in two lines—the one vertical, containing cards of the same suit but different values; the other horizontal, containing cards of the same value but different suits. Of these two lines the former represents a heterologous, the latter a homologous (or isologous) series. If a card be wanting from the pack its place will still be marked in this arrangement, and we may form an exact idea of it without having seen it. Similarly, though every term of each series may not be discovered, we can predict what the properties of the unknown terms will be.

Besides these two kinds of series, Gerhardt uses, for the purpose of classification, the method of "types,"[**] (by which he brings together all bodies possessing a similarity of constitution, whether they belong to the same series or not. He assumes four primary types:

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[*] "Traité de Chimie Organique," §2451, t. iv. p. 566 (Paris, 1853–1856).
[†] *Ib*., p. 568
[‡] "An. der Ch. und Pharm.," July 1842; May 1859; "Répertoire de Chimie pure," i. 573.
[§] Op. cit., t. i. pp. 121–142.
[**] § 2455, t. vi. pp. 585–593.

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(1) that of water, $n\mathrm{O}\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}$; (2) hydrochloric acid, *n*ClH; (3) ammonia, $n\mathrm{N}\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}$; and (4) hydrogen, $n\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}$. All substances which can be formed from water by a double decomposition, or by a series of double decompositions, or which in the same way give rise to water, are classed under the first type, and so of the rest. As hydrochloric acid is formed from hydrogen by double decomposition, thus, $\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}+\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}=2\begin{matrix}\mathrm{H}\\\mathrm{Cl}\end{matrix}$, the second type might have been dispensed with, and all the substances belonging to it placed under the fourth. Indeed, all the types may be brought under that of hydrogen, $n\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}$, for water is $\mathrm{O}^{\mathrm{ii}}\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}$, corresponding to $2\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}$, or $\begin{matrix}\mathrm{HO}\\\mathrm{H}\end{matrix}$ to $\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}$; and ammonia is $\mathrm{N}^{\mathrm{iii}}\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}$, corresponding to $3\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}$, or $\begin{matrix}\mathrm{NH}^{\mathrm{ii}}\\\mathrm{H}_2\end{matrix}$ to $2\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}$, or $\begin{matrix}\mathrm{NH}_2\\\mathrm{H}\end{matrix}$ to $\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}$. But we shall discuss this subject more fully after considering the "atomicity" of radicals.

Gerhardt's definition of a radical—a definition founded solely on fact—led to the observation of what have been called "polyatomic radicals." It was found that some radicals always combine with two, some always with three, some always with four atoms of a monatomic radical. Thus the radical oxygen O is "diatomic," as H_2O water, C_2H_5HO alcohol, $(C_2H_3O)_2O$ anhydrous acetic acid. Again, glycery1, C_3H_5, always combines with three monatomic atoms, as $C_3H_5(HO)_3$ glycerine, $C_3H_5Cl_3$ trichlorhydrine, &c. Glyceryl is therefore "triatomic." Carbon, C, is an example of a "tetratomic" radical, as shown by the compound CH_4, marsh gas, $CHC1_3$, chloroform, &c. Some substances form more than one series of compounds, possessing in each a different "atomicity;" but, as a compound of one series is always transformed by double decomposition into a compound of the same series, we must regard each as containing a different radical. Nitrogen is an example of this, being sometimes triatomic and sometimes pentatomic. It is triatomic in ammonia $N^{iii}H_3$, hydrocyanicacid $C^{iv}HN^{iii}$, &c., pentatomic in the ammoniacal salts $N^{v}H_4Cl$, &c., and in urea it seems probable that half of the nitrogen is the triatomic radical N^{iii} and half the pentatomic radical N^{v}. C_3H_5 and its analogues form other examples of the same kind. In the glyceryl series they are triatomic, and in the allyl series monatomic. It is probable that in these latter cases there is some change of relative position of the atoms composing the radical—indeed it is difficult otherwise to conceive how the change of atomicity could take place; but the two radicals $(C_nH_{2n-1})^{i}$ and $(C_nH_{2n-1})^{iii}$ are closely connected, as shown by the process for preparing the allylic compounds from glycerine. This alternative atomicity of compound radicals seems to me very interesting when viewed in connection with the same peculiarity—as seen in the supposed simple radicals, nitrogen, phosphorus, &c. It is one of the indications of the compound nature of these bodies.

For the development of the theory of polyatomic radicals we are principally indebted to Williamson, Odling, Wurtz, and Kekulé.* Gerhardt had a clear view of this theory as applied to the explanation of the polybasic acids (originally, I believe, proposed by Williamson), but his formula for glycerine $\left.\begin{matrix}\mathrm{C}_6\mathrm{H}_5\mathrm{O}_2\\\mathrm{H}_3\end{matrix}\right\}\mathrm{O}_4$ shows that he had not carried it out generally. This formula may indeed be pronounced not only an improbable, but even an impossible one.

* Williamson, "Lond. R. S. Proceedings," vii. 11, 135; "Chem. Soc. Q. J." vii, 180. Odling, "Chem. Soc. Q. J." vii. 1. Wurtz, various papers in "An. de Ch. et de Phys." [III.], on glycerine, glycol, lactic acid, &c. Kekulé, papers in Journals and "Lehrbuch der Organischen Chemie," pp. 93, 94.

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One diatomic radical, viz., imidogen, was, it is true, recognised as such before the publication of Williamson's views; but so averse were chemists to admit any but monatomic radicals that it was generally formulated $N^{\frac{1}{2}}H^{\frac{1}{2}}$, so that it might be represented as replacing *one* atom of hydrogen.

In 1854 Berthelot investigated anew the reaction of glycerine upon the acids[*]; these he found to have the general formula:— $C_3H_8 + nA - nH_2O$, when A is a monobasic acid and *n* 1, 2, or 3. These facts led M. Wurtz[†] to suggest the formula $\left.\begin{matrix}(C_3H_5)^{iii}\\ H_3\end{matrix}\right\}O_3$ for glycerine, corresponding to three molecules of water $\left.\begin{matrix}H_3\\ H_3\end{matrix}\right\}O_3$, and containing the triatomic radical C_3H_5. He then attempted to obtain the triacetine of the glycerine $\left.\begin{matrix}(CH)^{iii}\\ H_3\end{matrix}\right\}O_3$ by acting on iodoform with acetate of silver; in this he failed.[‡] Williamson had already (1854) obtained a compound related to this glycerine; by acting on chloroform by means of sodium alcohol (ethylate of soda) he replaced the three atoms of chlorine by three atoms of the group C_2H_5O, thus $\begin{matrix}(CH)^{iii}\\ Cl_3\end{matrix} + 3\left.\begin{matrix}C_2H_5\\ Na\end{matrix}\right\}O = 3\left.\begin{matrix}(CH)^{iii}\\ (C_2H_5)_3\end{matrix}\right\}O_3 + 3NaCl$. This compound $\left.\begin{matrix}(CH)^{iii}\\ (C_2H_5)_3\end{matrix}\right\}O_3$, which was called tribasic formic ether, is a glycerine in which 3H are replaced by 3 atoms of ethyl.[§]

Wurtz next directed his attention to the iodide of ethylene $C_2H_4I_2$. He thought that that compound might be regarded as containing a diatomic radical united to two atoms of iodine, and that other compounds of the same radical might be obtained by acting on it with a salt of silver. This turned out to be the case, a reaction taking place which may be thus represented:—[**]

$$C_2H_4I_2 + \begin{matrix}\left.\begin{matrix}C_2H_3O\\ Ag\end{matrix}\right\}O\\ \left.\begin{matrix}C_2H_3O\\ Ag\end{matrix}\right\}O\end{matrix} = 2AgI + \begin{matrix}\left.\begin{matrix}C_2H_3O\\ C_2H_4\end{matrix}\right\}O\\ \left.\begin{matrix}C_2H_4\\ C_2H_3O\end{matrix}\right\}O\end{matrix}$$

This new substance is the acetate of the oxide of ethylene or "Glycol diacetique." It stands in the same relation to glycol that acetic ether does to alcohol, and from it glycol $\left.\begin{matrix}C_2H_4\\ H_2\end{matrix}\right\}O_2$, and a great variety of compounds of the same heterologous series may be obtained. Many of these are formed by the replacement of one or both of the atoms of typical hydrogen by radicals, such as "glycol diacetique," "glycol dibenzoique." There are, however, some very remarkable bodies, formed on the type of three or more molecules of water, such as M. Lourenço's "éther intermediaire du glycol,"[††] and Wurtz's polyethylenic alcohols.[‡‡] The following are the formulae of these compounds according to Lourengo and Wurtz:—

$\left.\begin{matrix}C_2H_4\\ C_2H_4\\ H_2\end{matrix}\right\}O_3$ "éther intermediaire," or diethylenic alcohol.

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[*] "Compt. rendus," xxxviii. 668.
[†] "An. de Ch. et de Ph." xliii. 492.
[‡] "Compt. rendus," xliii. 478.
[§] Williamson and Kay, "Chem. Soc. Q. J." vii. 224.
[**] "An. de Ch. et de Ph.," [III.] lv. 400.
[††] "Compt. rendus," xlix. 781.
[‡‡] "Compt. rendus," xlix. 813, l. 1195. Lourenço, "Compt. rendus," li. 365; "Répertoire de Ch. pure," ii. pp. 36, 66, 467. Lourenço has very lately obtained several polyglyceric compounds, corresponding to the polyethylenic alcohols mentioned in the text.

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$$\left.\begin{matrix}3(C_2H_4)\\H_2\end{matrix}\right\}O_4$$ triethylenic alcohol.

$$\left.\begin{matrix}4(C_2H_4)\\H_2\end{matrix}\right\}O_5$$ tetraethylenic alcohol.

$$\left.\begin{matrix}5(C_2H_4)\\H_2\end{matrix}\right\}O_6$$ pentethylenic alcohol.

$$\left.\begin{matrix}6(C_2H_4)\\H_2\end{matrix}\right\}O_7$$ hexethylenic alcohol.

By the oxidation of glycol and these polyethylenic alcohols Wurtz obtained various acids, glycolic, diglycolic, diglycolethylenic, &c.,* which show a great similarity in empirical formula and in physical characters to the natural vegetable acids. That this indicates a real similarity in constitution has been pretty clearly made out by the decompositions of lactic, tartaric, malie, and succinic acids; and very recently by the formation by Mr Maxwell Simpson of succinic acid by the action of alkalis on cyanide of ethylene.† We quote from Kekulé's “Lehrbuch der Organischen Chemie,”‡ the table of acids connected with ethylic, and series homologous with it, formulated according to the type theory of Gerhardt and Williamson.

	Alkohole.	*Säuren.*		
		Einbasich.	Zweibasich.	Dreibasich.
Einatomig	GRUPPE I. $\left.\begin{matrix}(C_nH_{2n+1})^{i}\\H\end{matrix}\right\}O$ $\left.\begin{matrix}(C_2H_5)^{i}\\H\end{matrix}\right\}O$ Aethylalkohol. $\left.\begin{matrix}(C_3H_7)^{i}\\H\end{matrix}\right\}O$ Propylalkohol.	GRUPPE II. $\left.\begin{matrix}(C_nH_{2n-1}O)^{i}\\H\end{matrix}\right\}O$ $\left.\begin{matrix}(C_2H_3O)^{i}\\H\end{matrix}\right\}O$ Essigsäure. $\left.\begin{matrix}(C_3H_5O)^{i}\\H\end{matrix}\right\}O$ Propionsäure.		
Zweiatomig	GRUPPE III. $\left.\begin{matrix}(C_nH_{2n})^{ii}\\H_2\end{matrix}\right\}O_2$ $\left.\begin{matrix}(C_2H_4)^{ii}\\H_2\end{matrix}\right\}O_2$ Glycol. $\left.\begin{matrix}(C_3H_6)^{ii}\\H_2\end{matrix}\right\}O_2$ Propylglycol.	GRUPPE IV. $\left.\begin{matrix}(C_nH_{2n-2}O)^{ii}\\H_2\end{matrix}\right\}O_2$ $\left.\begin{matrix}(C_2H_6O)^{ii}\\H_2\end{matrix}\right\}O_2$ Glycolsäure. $\left.\begin{matrix}(C_3H_4O)^{ii}\\H_2\end{matrix}\right\}O_2$ Milchsäure.	GRUPPE V. $\left.\begin{matrix}(C_nH_{2n-4}O)^{ii}\\H_2\end{matrix}\right\}O_2$ $\left.\begin{matrix}(C_2O_2)^{ii}\\H_2\end{matrix}\right\}O_2$ Oxalsäure. $\left.\begin{matrix}(C_4H_4O_2)^{ii}\\H_2\end{matrix}\right\}O_2$ Bernsteinsäure.	

* “Compt. rendus,” li. 162, July 1860; “Bulletin de la Société Chimique de Paris," séance du 8 Juillet 1860; “Répertoire de Chimie pure," ii. 342.
† “Royal Soc. Proceedings,” August 1860; “Répertoire de Ch. pure,” iii. 100.
‡ Pp. 362, 363.

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Dreiatomig	GRUPPE VI. $\left.\begin{matrix}(C_nH_{2n-1})^{iii}\\H_3\end{matrix}\right\}O_3$ $\left.\begin{matrix}(C_3H_5)^{iii}\\H_3\end{matrix}\right\}O_3$ Glycerin.	GRUPPE VII. $\left.\begin{matrix}(C_nH_{2n-3}O)^{iii}\\H_3\end{matrix}\right\}O_3$ $\left.\begin{matrix}(C_3H_3O)^{iii}\\H_3\end{matrix}\right\}O_3$ Glycerinsäure.	GRUPPE VIII. $\left.\begin{matrix}(C_nH_{2n-5}O_2)^{iii}\\H_3\end{matrix}\right\}O_3$ $\left.\begin{matrix}(C_4H_3O_2)^{iii}\\H_3\end{matrix}\right\}O_3$ Aepfelsäure.	
Vieratomig	$\left.\begin{matrix}(C_nH_{2n-2}O)^{iv}\\H\end{matrix}\right\}O_4$	$\left.\begin{matrix}(C_nH_{2n-4}O)^{iv}\\H_4\end{matrix}\right\}O_4$ $\left.\begin{matrix}(C_6H_8O)^{iv}\\H_4\end{matrix}\right\}O_4$ Mannitan.	GRUPPE IX. $\left.\begin{matrix}(C_nH_{2n-6}O_2)^{iv}\\H_4\end{matrix}\right\}O_4$ $\left.\begin{matrix}(C_4H_2O_2)^{iv}\\H_4\end{matrix}\right\}O_4$ Weinsäure.	GRUPPE X. $\left.\begin{matrix}(C_nH_{2n-8}O_3)^{iv}\\H_4\end{matrix}\right\}O_4$ $\left.\begin{matrix}(C_6H_4O_3)^{iv}\\H_4\end{matrix}\right\}O_4$ Citronensäure(?)*
Einatomig	GRUPPE XI. $\left.\begin{matrix}(C_nH_{2n-1})^{i}\\H\end{matrix}\right\}O$ $\left.\begin{matrix}(C_3H_5)^{i}\\H\end{matrix}\right\}O$ Allylalkohol.	$\left.\begin{matrix}(C_nH_{2n-3}O)^{i}\\H\end{matrix}\right\}O$ $\left.\begin{matrix}(C_3H_3O)^{i}\\H\end{matrix}\right\}O$ Acrylsäure.		

* Die Citronensäure und das Mannitan sind in der Tabelle aufgefuhrt obgleich ihre typischen Formeln noch nicht mit sicherheit fest gestellt sind.

In looking over this table, the formulae in which, with the exception of those marked (?), are derived from carefully studied reactions, we shall find that the *basicity* of an acid does not depend on the *atomicity* of the radical, nor on the amount of the unreplaced typical hydrogen:—for lactic acid is monobasic with a diatomic radical and two atoms of typical H; glyceric acid, monobasic with a triatomic radical and three of typical H; tartaric acid, dibasic with a tetratomic radical and four, &c. The basicity appears rather to depend on the number of atoms of O *in* the radical. This is clearly seen when we compare bodies of the same type and series in which the hydrogen of the radical is gradually replaced by oxygen as glycol, glycolic acid, and oxalic acid. The first is neutral, with no oxygen in the radical; the second monobasic, with one atom of O; and the third dibasic, with two atoms of O in the radical; while each contains a radical of the same atomicity, and has the same amount of typical H. We here obtain a glimpse of a law of Polarity which seems to prevail with remarkable uniformity in organic chemistry; but we cannot, from this indication alone, enunciate the law, for it fails when any element is present besides carbon, hydrogen, and oxygen. Thus we have phosphoric acid $\left.\begin{matrix}PO^{iii}\\H_3\end{matrix}\right\}O_3$, tribasic, with only one atom of O in the radical, and cyanic acid $\left.\begin{matrix}CN\\H\end{matrix}\right\}O_3$, monobasic, with none.

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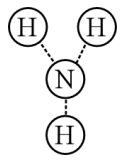
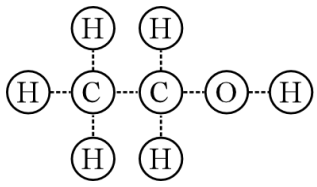
The theory of polyatomic radicals leads directly to that of multiple and mixed types.* The latter may thus be shortly stated. A polyatomic radical may replace two or more atoms of hydrogen in two or more molecules of water, hydrogen, or ammonia, and thus, as it were, *bind together* these molecules into one. Thus Williamson formulates sulphuric acid $\left.\begin{matrix}H\\(SO_2)^{ii}\\H\end{matrix}\right\}\begin{matrix}O\\O\end{matrix}$, two molecules of water bound together by having one atom of hydrogen in each replaced by the single, indivisible, diatomic radical SO_2. Similarly the amidic acids are $\left.\begin{matrix}H\\R^{ii}\\H\end{matrix}\right\}\begin{matrix}O\\O\end{matrix}$ and mono- and di- chlorhydrine are respectively $\left.\begin{matrix}Cl\\(C_3H_5)^{iii}\\H_2\end{matrix}\right\}O_2$ and $\left.\begin{matrix}Cl_2\\(C_3H_5)^{iii}\\H\end{matrix}\right\}O$, representing $\left\{\begin{matrix}\left.\begin{matrix}H\\H\end{matrix}\right\}O\\\left.\begin{matrix}H\\H\end{matrix}\right\}N\end{matrix}\right.$, and $\left.\begin{matrix}Cl\\H\\H_2\\H_2\end{matrix}\right\}O_2$, and $\left.\begin{matrix}Cl_2\\H_2\\H\\H\end{matrix}\right\}O$. Still more complex molecules are, of course, produced when substances containing polyatomic radicals react upon other substances of similar constitution; as instances of this, may be taken the bodies produced by M. Desplats by acting on glycerine by means of tartaric acid.†

It is plain that if we take into account the simple polyatomic radicals, as O^{ii}, S^{ii}, N^{iii}, C^{iv}, N^{v}, &c., all these bodies, and in fact all bodies, may be reduced to the simplest type—viz., the multiple type of hydrogen. For, if we consider the two monatomic atoms in the single hydrogen type to be connected together by one line of force, thus $\begin{matrix}H\\H\end{matrix}$, and the two monatomic and one diatomic atoms in the double hydrogen type $\begin{matrix}HH\\O^{ii}\end{matrix}$, to be connected by two, thus $H\cdots O\cdots H$, the atoms of the treble type $\begin{matrix}HHH\\N^{iii}\end{matrix}$ by three, thus



&c., we may represent any substance by the type $n\begin{matrix}H\\H\end{matrix}$ where n is the number of lines of force connecting the atoms, or half the sum of the atomicities of the atoms. Thus, in alcohol C_2H_6O, the sum of the atomicities is $(2 \times 4) + (6 \times 1) + (1 \times 2) = 16$; $\therefore n = 8$. Alcohol may therefore be represented on the type of $8\begin{matrix}H\\H\end{matrix}$, thus—



* Williamson, "R. S. L. Proc.," vii. 11; and various papers in "Chem. Soc. Q. J.," &c. Gerhardt, "Traité de Ch. Org." iv. *passim.* Wurtz, "Ann. de Ch. et de Ph." [III.] xliii. lv. 466; "Compt. rendus," Aug. 1868, &c. Kekulé, "Lehrbuch der Ch. Org." pp. 93, 120, 155, &c. Wislicenus, "Zeitschrift für die gesammten Naturwissenschaften," xiv. Sterry Hunt, "Compt. rendus," Feb. 1861.

† "Compt. rendus," xlix. 216, Aug. 1859.

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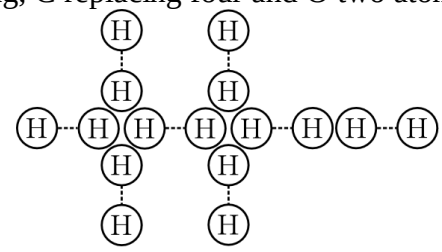
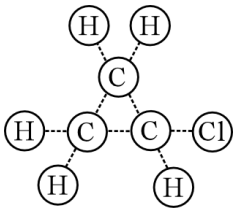
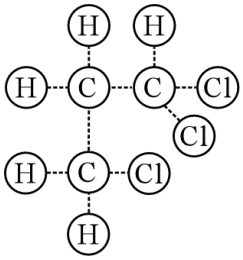
corresponding to the following, C replacing four and O two atoms of hydrogen—



In representing substances in this way, we see a possible explanation of the *alternative atomicity*, of which examples have been given; thus chloride of allyl may be represented in this way—



C_3H_5Cl; and trichlorhydrine in this:



$C_3H_5Cl_3$; in the former three, and in the latter two, of the lines of force being employed to connect together the carbon atoms. We can thus also see why, when a compound radical possesses two degrees of atomicity, these must always differ from one another by an even number; for when the atomicity of a radical is increased by setting free a line of force, as we have assumed to be the case in the change from allyl to glyceryl, it must be increased by two, *two* poles or active points being united by *one* line of force. The same law holds in the case of the (so-called) simple radicals; thus, we have N^{iii} and N^{v}, P^{iii} and P^{v}, As^{iii} and As^{v}, Sb^{iii} and Sb^{v}, Fe^{iv} and Fe^{vi} (Fe= 112). These would appear to indicate, as before mentioned, that these bodies are in reality compounds, and that one line of force less is employed to unite their component atoms together in N^{v}, &c., than in N^{iii}, &c.

From the consideration of this theory of combination we arrive at the following (hypothetical) conclusions :—

1. A compound atom, or molecule, resulting from the union of *any* number of "artiatomic"* atoms is artiatomic; for the atomicity of a compound is the sum of the atomicities of the component atoms, minus twice the number of lines of force uniting these atoms together. Let the sum of the atomicities = *n*, the number of lines of force taken up = *r*, and the atomicity of the compound = A; then

$$A = n - 2r .$$

In this case *n* is an even number, for it is the sum of a series of even numbers; ∴ A is even. Examples, $(CO)^{ii}$ $(SO_2)^{ii}$.

2. A compound atom or molecule resulting from the union of an *even* number of "Perissatomic"† atoms is artiatomic. Here *n* is even, because it is the sum of an even number of odd numbers; ∴ A is even. Example, $(N^{iii}H)^{ii}$.

---

* Artiatomic (??t??? = *even*), a body or radical in which the atomicity is represented by an even number.
† Perissatomic (pe??s s ?? = *odd*), a body or radical in which the atomicityis represented by an odd number.

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3. A compound atom or molecule resulting from the union of an odd number of perissatomic atoms is perissatomic. Here *n* is the sum of an odd number of odd numbers; *n* is ∴ odd; ∴ A is odd. Examples, $(N^{iii}H_2)^i$, $(N^vH_4)^i$.

4. Generally a compound atom or molecule is artiatomic or perissatomic, according as the number of perissatomic atoms which it contains is even or odd. Examples, $(C_2H_5)^i$, $(C_6H_5)^i$, $(C_2H_3O)^i$, $(NO_2)^i$, $(C_{10}H_7)^i$, $(C_3H_5)^{iii}$, $(C_6H_7O)^v$, perissatomic radicals having the sum of the perissatomic atoms, an odd number; $(CO)^{ii}$, $(C_2H_4)^0$, $(C_2H_4)^{ii}$, $(C_2H_2)^{iv}$, $(C_{10}H_8)^0$, $(C_{10}H_8)^{ii}$, $(C_4H_2O_2)^{iv}$, $(C_6H_8)^{vi}$ artiatomic radicals having an even number of perissatomic atoms.

This general law includes the "law of even numbers" of Laurent. His "monads" and "dyads" are what we have ventured to call artiatomic and perissatomic atoms. His law is,—that every substance capable of independent existence has an even number of dyads.* But a substance capable of independent existence is artiatomic, i.e., its atomicity is represented by an even number, viz., zero; therefore, by our law it must contain an even number of perissatomic atoms.

Before quitting this part of the subject, it may be well to give a list of those elements the atomicity of which has been clearly established. After each body is placed the formula of a few of its compounds according to their vapour density, with the name of the observer.†

I. Perissatomic bodies :-
   1. *Monatomic*—H^i, Cl^i, Br^i, I^i, F^i.
   2. *Triatomic*—N^{iii}, P^{iii}, As^{iii}, Sb^{iii}, B^{iii}, BBr_3, Wöhler and Deville; BCl_3, Dumas, Wöhler, and Deville; BF_3, J. Davy, Thomson, and Dumas; $B(CH_3O)_3$, Ebelmen; $B(C_2H_5O)_3$, Bowman and Ebelmen; $B(C_5H_{11}O)_3$, Ebelmen; V^{iii} (?) (V= 68.5) VCl_3, Šafarik; Bi^{iii}.
   3. *Pentatomic*—N^v, P^v, As^v, Sb^v.

II. Artiatomic bodies :—
   1. [Atomicity = 0. In this class Tschermak seems to include mercury, for he writes its *molecule* Hg = 200.]
   2. *Diatomic*—O^{ii}, S^{ii}, Se^{ii}, Te^{ii}, Zn^{ii}, (Zn = 65), $Zn(C_2H_5)_2$, Frankland, Wanklyn; Hg^{ii} (?) (Hg = 200), $HgCl_2$, $HgBr_2$, HgI_2, Mitscherlich; $Hg(CH_3)_2$, Buckton; $Hg(C_2H_5)_2$, Buckton; these correspond to H_2 volume. The following are exceptional, corresponding to H_4‡ :—Hg_2Br_2, Mitscherlich; Hg_2Cl_2, Mitscherlich, Deville, and Troost. Besides zinc and mercury, it is probable that many metals belong to this class.
   3. Tetratomic—C^{iv}, Si^{iv}, (Si = 28.5), SiF_4, J. Davy, Dumas; $SiCl_4$, Dumas; $Si(C_2H_5O)_4$, $Si(C_5H_{11}O)_4$, Ebelmen; Sn^{iv}, (Sn = 118), $SnCl_4$, Dumas; $Sn(CH_3)_3I$, $Sn(CH_3)_2Cl_2$, $Sn(C_2H_5)_3C1$, Cahours; $Sn(C_2H_5)_2(CH_3)_2$ Frankland; Ti^{iv} (Ti = 50), $TiC1_4$, Dumas; Zr^{iv} (Zr = 89), $ZrCl_4$, Deville and Troost; Fe^{iv}.
   4. *Hexatomic*—Fe^{vi} (Fe = 112), $FeCl_6$, Deville and Troost; Al^{vi} (Al = 55), $AlCl_6$, $AlBr_6$, AlI_6, Deville and Troost; Cr^{vi} (Cr = 53.5), $CrCl_2O_2$, Dumas, Walter.

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* "Chemical Method," Cav. Soc. Ed., p. 46.

† The details of these vapour densities will be found in a paper by Dr G. Tsehermak, entitled "Einige Sätze der Theoretischen Chemie" (xli. 67, des Jahrgangs 1860 der Sitzungsberichte der mathem. Naturw. Classe der k., Akademie der Wissenschaften, Wien, 1860).

‡ It will be observed that the protosalts of mercury present an exceptional case, similar to that of the ammoniacal salts, and the two oxides of nitrogen N_2O_2 and N_2O_4; and when we consider how readily the protosalts decompose into mercury and persalt, it seems probable that the explanation which has been suggested for the vapour density of the ammoniacal salts may be also applicable to this case.

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Having now examined most of the questions involving the atomicity of bodies, we may consider shortly what is known with regard to those phenomena which we have collectively designated polar.

We find, when we examine a series of bodies belonging to the same type, and consider the way in which they behave when treated with various reagents, we can construct a set of typical reactions and decompositions. But each body does not undergo all of these decompositions; each shows certain preferences, and decomposes more readily in one way, while another body, perfectly analogous in constitution, under the same circumstances decomposes in another way. The following are a few examples of this :—

Hydrated oxide of tetrethylium when heated decomposes into water, olefiant gas, and triethylamine.* Hydrated oxide of tetrethylphosphonium when heated gives rise to hydride of ethyl and oxide of triethylphosphine.

$$\left.\begin{matrix}(C_2H_5)^{i}_{4}\\ O^{ii}\end{matrix}\right\}\begin{matrix}N^{v}\\ H^{i}\end{matrix} = (C_2H_5)^{i}_{3}N^{iii} + \left.\begin{matrix}C_2H_5\\ H\end{matrix}\right\}O$$

$$\left.\begin{matrix}(C_2H_5)^{i}_{4}\\ O^{ii}\end{matrix}\right\}\begin{matrix}P^{v}\\ H^{i}\end{matrix} = \left.\begin{matrix}(C_2H_5)^{i}_{3}\\ O^{ii}\end{matrix}\right\}P^{v} + \begin{matrix}C_2H_5\\ H\end{matrix}.$$

Again, acetate of potash and trichloracetate of potash, when treated with caustic potash, break up, the one into marsh gas and carbonate of potash, the other into chloroform and carbonate of potash, perfectly analogous reactions; while monochloracetate of potash, when treated in the same way, gives glycolate of potash and chloride of potassium, thus :—

$$C_2H_3KO_2 + KHO = CH_4 + CK_2O_3$$
$$C_2H_2ClKO_2 + KHO = C_2H_3KO_3 + KCl$$
$$C_2Cl_3KO_2 + KHO = CHCl_3 + CK_2O_3.$$

Once more, aldehyde is converted, by the action of potash, into the resin of aldehyde, while oil of bitter almonds—a true “isologue” of aldehyde—is converted by treatment with the same reagent into benzoic acid and benzoic alcohol.

As the forces in these substances, at least in the first two examples, are equal in number, and their directions are the same, we are forced to refer these differences in reaction to differences in the *amount* of the forces, or some of them, in each case. Thus, it appears that phosphorus has a greater attraction for oxygen than nitrogen has, and that while the attraction which hydrogen and ethyl exert on oxygen is greater than that of nitrogen for the same element, it is less than that of phosphorus. And we see also that phosphorus has a greater tendency to maintain the pentatomic state than nitrogen has. This might be supposed to indicate that the affinity which holds together the component atoms is less powerful in the case of phosphorus than in that of nitrogen.

We have already alluded to the fact that the “basicity” of an acid is not measured by the number of typical hydrogen atoms which it contains. This is well illustrated by Wurtz in a Memoir in the “Annales de Chimie et de Physique,” [III] lv., and in a paper read before the Chemical Society of Paris (13th May 1859) on the constitution of lactic acid. He there points out that the second atom of typical hydrogen in lactic acid $\left.\begin{matrix}C_3H_4O\\ H_2\end{matrix}\right\}O_2$, can be replaced, but with difficulty, by metal; that the same is true of salicylic acid, $\left.\begin{matrix}C_7H_4O\\ H_2\end{matrix}\right\}O_2$, and glycolic acid, $\left.\begin{matrix}C_2H_2O\\ H_2\end{matrix}\right\}O_2$; that in all these acids the second atom is readily replaced by negative radicals, as in lactobutyric, benzolactic, benzoglycolic acids, &c.; and, in short, that these acids are

* See Kekulé’s “Lehrbuch,” 133.

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intermediate between diatomic alcohols and dibasic acids, in chemical relations as well as in composition. To quote his own words :—

> " * * * l'acide glycerique de M. Debus $\left.\begin{matrix}(C_3H_3O)^{iii}\\H_3\end{matrix}\right\}O_3$ est triatomique, parce qu'il dérive d'une combinaison triatomique et qu'il appartient au type trois fois condensé $\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3$; et, pourtant il ne peut échanger qu'un seul atome d'hydrogène contre 1 atome de métal; il n'est à proprement parler que monobasique, quoique triatomique. C'est que la capacité de saturation d'un acide vis-à-vis des oxydes basiques dépend non-seulement du nombre d'équivalents d'hydrogène typique qu'il renferme, mais aussi de la nature électronégative du radical oxygéné. À mesure que l'oxygène augmente dans ce radical, l'hydrogène typique devient de plus en plus hydrogène basique. L'example suivant va montrer qu'il en est ainsi :—

$\left.\begin{matrix}C_2H_4\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}C_2H_2O\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}C_2O_2\\H_2\end{matrix}\right\}O_2$
Glycol, neutre, 2 atomes d'hydrogène typique.	Acide gycolique, 2 atomes d'hyd typique, don fortement basique.	Acide oxalique, 2 atomes d'hyd typique, tous les 2 fortement basique."*

Besides the example of phosphoric acid already adduced to show that the basicity does not entirely depend on the number of atoms of O in the radical, the following may be mentioned :—

Cyanic acid $\left.\begin{matrix}CN\\H\end{matrix}\right\}O$, monobasic (if written, as perhaps it ought to be, rather as $\left.\begin{matrix}CO\\H\end{matrix}\right\}N$, the anomaly disappears). Cyanuric acid $\left.\begin{matrix}(CN)_3\\H_3\end{matrix}\right\}O_3$, dibasic (Wöhler). Rhodizonic acid $C_7H_6O_{10}$, hectabasic. Carbolic acid $\left.\begin{matrix}C_6H_5\\H\end{matrix}\right\}O$, in which the one atom of typical hydrogen is very nearly in the same case as that of the lactates, and the compound may be viewed either as an alcohol or as an acid.

Kekulé also notices the dependence of the basicity of an acid on the number of atoms of O in the radical, and thus attempts to explain it :—Glycolic and lactic acids are monobasic, although both contain *two* atoms of typical hydrogen, but that these two atoms do not occupy a similar position, that one lies near *two* atoms of O—viz., one in the radical and one typical, as the single atom of typical H does in acetic acid—while the other lies near only one atom of O like the typical H in alcohol; that this is the reason why one atom of H has the function of the H in acetic acid and is basic, positive, easily replaced by metals, while the other is negative and readily replaced by negative radicals.

In the same way he considers the three atoms of typical H in glyceric acid to occupy dissimilar positions in reference to the O, one lying near *two* atoms of O, and comporting itself like the H of acetic acid, and the other two occupying a position and exhibiting reactions similar to those of the H in alcohol; or generally thus :—

* Bulletin de la Société Chimique de Paris, I. p. 38.

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"Eine *unsymmetrische* constitution, d.h. eine unsymmetrische Stellung der Atome veranlaast also stets ein unsymmetriaches *Verhalten* der Verbindung, d.h. verachiedenes Verhalten einzelner an sich gleichartiger Atome.

Umgekehrt veranlasst symmetrische Stellung der Atome innerhalb des Molecüls stets gleichartiges verhalten." *

This explanation appears to me to be open to the following objections :—

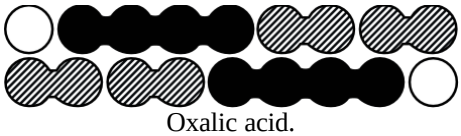
1st. We have no means of knowing that one of the typical H atoms is nearer the O of the radical than the other.

2d. We have no reason to suppose that such greater nearness would render that atom more basic than the other.

As to the first objection, it is true that Kekulé tells us in a note on the passage quoted, that if we employ his graphic method of representing compounds it will be seen that one atom of H lies nearer than the other to the O of the radical. This is the case, as may be seen by a glance at the accompanying diagrams of glycolic acid, glycol, and oxalic acid :—†

Glycolic acid.

Glycol.


Oxalic acid.

It must, however, be remembered that Kekulé's graphic method is a most artificial one, and, I think we may say, certainly does not represent the actual arrangement of the atoms.

It is easy to construct a diagram which, while still unsymmetrical, places both typical H atoms in the same relation to the O in the radical.‡

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* "Lehrbuch," p.175.

† Kekulé does not give diagrams of these bodies, but from the examples which he gives, viz., at page 162—

Marsh Gas.

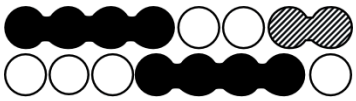
Chloride of Methyl.

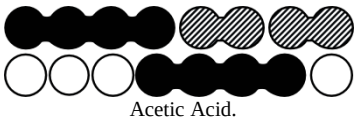
Phosgene.

Carbonic Acid.

Prussic Acid.

and page 164—


Alcohol.


Acetic Acid.

there can be no doubt that the diagrams in the text are what he would have given as the representation of glycol, glycolic acid, and oxalic acid.

‡ It would not, I think, be difficult to devise an experiment which would decide whether the two typical H atoms in lactic acid, &c., occupy similar positions or not. For instance, we might prepare the amine of, say, lactic acid, by treating it in the way in which alcohol is treated in the preparation of ethylamine; this might then be compared with lactamide, prepared as acetamide is from acetic acid. On Kekulé's hypothesis these should be two different bodies, while they should be the same if the two atoms of typical H occupy similar positions.

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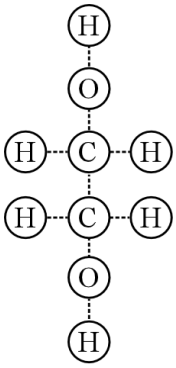
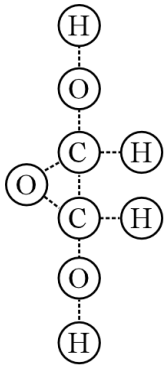
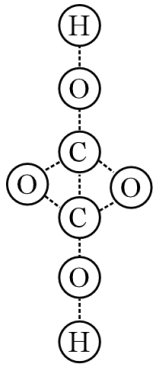


Glycol.



Glycolic acid.



Oxalic Acid.

Of course I do not intend it to be supposed that this represents correctly, or even more correctly than Kekulé's method does, the actual arrangement of the atoms, but it is at least as probable; and all that I wish to show is, that his is not the only possible arrangement.

As to the second objection, I cannot see how the *neighbourhood* of an atom of oxygen, fully saturated already, should influence the chemical relations of an atom of hydrogen not directly united to it.

In thinking over this subject, it occurred to me that most of the facts might be explained by such a hypothesis as the following, to a certain extent derived from the electro-chemical theory. I do not call it a theory, for it is not strictly a generalisation from facts, but merely a hypothesis which will, at least, show that it is not impossible for us to conceive a law under which the peculiar properties of one atom may influence the chemical relations of another atom in the same molecule, although the two are not *directly* combined.

Let us assume that there are in each atom various kinds of attractive force (for simplicity's sake say two, which we may call *positive* and *negative*[*]), that the points towards which these forces attract are the poles or *active points* (one or more according to atomicity) of the atom. When two atoms unite, an amount of the positive force of the one is employed equal to the amount of negative force employed in the other, and *vice versa*.

Now, when a diatomic atom combines with two monatomic atoms, the forces in the former will be divided between its two active points, in a certain proportion dependent on the proportion in which the two forces exist in each of the two monatomic atoms.

In water H_2O, for instance, the forces in the O will be equally divided between the two atoms of H; but if we now replace one atom of H by a body K, possessing more of one of the forces (viz., the positive) than H, the same equal division will not take place. More of the negative force in the O will accumulate at that pole which is next the K, and more of the positive force at that next the remaining H. This H will now not be so readily replaceable by positive atoms as it was previously, but will be easily removed in favour of a negative radical; its chemical relations have been altered by the properties of the atom K not in direct combination with it.

In a similar way, it may be explained why glycolic, lactic, salicylic acids, &c., are monobasic, or, at least, why basicity should depend on the oxygen of the radical; for (referring to the diagram above), if O^{ii}, a negative atom, replace H_2, two positive atoms, in glycol, the positive force in the C atoms will accumulate in greater amount than before on those active points turned towards the C thus introduced, and the negative force will

[*] It must be noted that in calling the two forces *positive* and *negative*, I do not mean it to be understood that they are supposed to be of an electric nature. There is this difference between electric forces and my hypothetical forces, that in the case of the latter I assume that two forces, one positive and the other negative, may act at the same time, and at the same point, while in the former one would wholly or partially neutralise the other.

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accumulate on the other active points of the C atoms, viz., on those uniting them to each other, to the typical O, and to the remaining H of the radical. The positive force in the typical O will therefore be in excess at those active points which are turned towards the C, and the negative on those turned towards the typical H. This typical H will therefore be more easily replaced by positive atoms than before, i.e., than in glycol.

If now one of the typical H atoms be replaced by a positive atom, say K, this will again alter the balance in the compound, and induce the accumulation of negative force at those active points throughout the molecule which are turned towards the K, and necessarily of positive force at those turned from the K, therefore at the active point of the O which is turned towards *the other typical H atom*. That atom will therefore be less easily replaced by metal than before—*i.e.*, the second atom of typical H is less basic than the first, or rather the remaining atom of typical H in the glycolates is less basic than *either* of those in glycolic acid.

In oxalic acid, where four atoms of H in the radical are replaced by O_2, the accumulation of negative force at the active points of the typical O next to the typical H will be still greater—so much greater that the replacement of one of these H atoms by metal does not reduce the positivity of the other so much as to destroy its basic character. This hypothesis might, I think, be applied to all chemical substances, to explain the alteration in chemical relation of some atoms, caused by the replacement of others, as in the chloranilines, &c.

Let us now collect what we know of Polar phenomena, and arrange them under a few general propositions.

1. Bodies (*i.e.*, radicals, simple and compound) may be arranged, with general accuracy, in a linear series, the members of which differ from each other in polarity (*i.e.*, as being positive or negative) according to their distance from each other in the series. The few exceptions to this seem to indicate that there is more than one cause producing the variations in polarity.

2. Bodies preserve their polar properties in combination, and in compound radicals, the substitution of one or more negative for one or more positive atoms renders the radical more negative, and *vice versa*.

3. As a particular and definite case of the last,—in acids consisting solely of carbon, hydrogen, and oxygen, the basicity depends on the number of O atoms in the radical, provided that number is not greater than the number of atoms of typical hydrogen.

Having now briefly considered the highest generalisations of chemical theory, we must come to the conclusion that the questions with which we set out are not yet capable of being answered, although a certain amount of progress has been made towards their solution. Chemistry, however, labours, and probably must always labour, under a great disadvantage as compared with most other branches of physics, in so far as the application of mathematical analysis is concerned. The very existence of the atoms, the consideration of which would form the starting-point for such analysis, is hypothetical. Still, it does not seem to me improbable that, by assuming that these atoms exist, and that certain forces act upon them under certain laws, we may be able to form a mathematical theory of chemistry, applicable to all cases of decomposition and "recomposition," the truth of whose results shall be independent of the truth of those assumptions by means of which the theory has been formed, just as the truth of the results of the undulatory theory of light is independent of the existence of a luminiferous aether.

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