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XXVII. *On the Tetravalency of Oxygen; with Remarks on the Varying Valency of the Elements and the Present Chemical Aspect of the Valency Problem.* By J. F. HEYES, M.A., F.C.S., F.R.G.S., of Magdalen College, Oxford*.

THE actual state, or rather phase, of philosophic Chemistry presents us with a remarkable paradox. Simultaneous with the discovery and chemical analysis of countless new compounds and many new elementary or non-resolved substances during the present century, there have emerged a series of views on the constitution of matter and the correlation of material forces which will for many centuries to come mark the greatest epoch in scientific philosophy. Although this molecular theory of matter has been chiefly developed on the physical and dynamical side, the contributions from the chemical side of the hedge of this great field of research have been very striking—such, in fact, as to stimulate the work of our greatest physicists. Scientific chemists, it may be said, have established the law of the conservation of mass; physicists, that of energy: now both are united in searching out the nature and influences of the masses and forces which are at work in the material world of chemical substances. But while the smaller limit, so to speak, of physical analysis is the molecule, it forms the upper limit of chemical analysis and synthesis. The main studies of the physicists are inter-molecular, those of the chemists intra-molecular phenomena. From this point of view, strict Chemistry begins where Physics ends; but, viewed historically, a growing interaction must be confessed, and, indeed, a friendly struggle has begun for the wells of the border-land which the one side calls molecular physics and the other physical chemistry. Both are peculiarly interested and puzzled just now in what are somewhat curiously termed “molecular compounds” or aggregations. Undoubtedly the trouble is chiefly and naturally on the chemical side; and, in the conventional system of shorthand or formulæ which the chemist uses to express (1) his *facts* about their composition and (2) his *views* about their constitution, it may be said to take the form of a discussion as to the meaning of certain dots and dashes with which our new text-books are plentifully (and to many students, I fear, misleadingly) sprinkled.

If, therefore, in calling attention to the question of the

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valency of an element, and the so-called atomicity of atoms, the ordinary language of chemical theory is used, it is not because I have any belief in an ultimate solution of the problems on the chemical side, but because, as the problems now stand, the conditions of the great mystery of chemical affinity can best be attacked, and perhaps by chemists can only be attacked, by facing the problems of what has been termed atomicity, valency, and quantivalence.

There is so much confusion of language on this subject that I must beg leave to make a very elementary start with our three historic typical compounds— HCl , H_2O , H_3N .

Let us most carefully recognize the facts conveyed in these formulæ first; for these facts, if fully ascertained, must remain good when our transitional conceptions of them "have faded into the infinite azure of the past."

(1) There are the facts of definite composition by weight and volume. The three gas formulæ weights occupy the same volume.

(2) Experience, aided by comparison of composition, has led us to the laws and facts of definite and multiple proportion.

(3) The latter can only, as far as we can see, be *explained* in terms of the old atomic theory.

(4) Referring to this theory, Dalton showed us it was possible to obtain the *ratio-weights of the atoms*.

The symbol O in our formulæ has therefore more than one interpretation. It stands for (1) oxygen stuff, (2) an atom of oxygen, and (3) for a number. Here is the material for a confusion of thought which is observable in the history of our science. This has been increased by the natural coincidence of our selection of the lightest stuff known (hydrogen) as the unit to which we refer (1) densities (that is, the ratio-masses of equal volumes), which are absolute facts, (2) atomic weights (that is, the most probable ratio-masses of atoms whose volumes are unknown), which are relative facts. Thus

$$\frac{\Delta_o}{\Delta_h} = \frac{16}{1} \text{ expresses pure fact;}$$

but

$$\frac{O}{H} = \frac{16}{1} \text{ expresses well-grounded belief,}$$

based upon the cumulative probability resulting from the consideration of many physical and chemical data. It is to be noted, moreover, that the question of the most probable value $O=15.96$, accepted by many chemists, *versus* the exact integer 16, does not, so far as I can see at present, affect con-

siderations of valency or atomicity. But it may subsequently affect the questions as to the actual number of hydrogen and chlorine atoms in a molecule of hydrogen chloride, and the discussion of what Professor Armstrong calls "residual affinity." The atomic weight—that is, ratio-atomic weight—of oxygen is in this sense 16. But it is well to bear in mind that the number *can*, if necessary, be taken in the more natural sense of a "combining proportion" or combining weight, and that this number 16 is not indissolubly bound up with the statement that the oxygen atom is diatomic or divalent, as is sometimes supposed. Indeed, Professor Odling, in his historic paper* on the weight of the oxygen atom, demonstrated that $O=16$, and not 8 as then usually taken *if* $N=14$, as was universally accepted *whether in a strictly atomic sense or not*.

Taking, then, equal volumes of these three gases, it is a fact that we have one, two, and three unit weights and volumes combined with the chemical unit weights of Cl, O, and N. Apart even from Avogadro's law, the chemist would, adopting the atomic theory, say that "atoms" of chlorine, oxygen, and nitrogen respectively combined with one, two, and three atoms of hydrogen *in these compounds*; and hence that these atoms were mono-, di-, and tri-atomic respectively. In the developments of the substitution- and type-theories, and above all in the development of the hydrocarbon theory, based upon the very strikingly constant "tetratomicity of carbon," this theory has been so useful that there has been a strong school of chemists to maintain this atomicity as a constant property—"a property inherent in the nature of atoms."†

The word "atomicity" is thus naturally associated with some inherent and occult property of the atom or some force centering from it. Since it has become more generally recognized that the atomicity of many elements seems to vary when either (1) the chemical conditions of A and B are altered, or (2) other elements are chemically associated with A or B, the word "atomicity" has wisely gone out of fashion. More strictly speaking, it is the phrase "the *atom* of oxygen is diatomic" which is disappearing, because physicists (*e. g.* Prof. J. J. Thomson) write about "diatomic molecules," meaning molecules which contain two chemical atoms. Thus it is now said that "the *molecule* of oxygen is diatomic," and that "the atom of oxygen is divalent," or, most briefly, that "oxygen is a dyad." The shorthand form remains distinct; it is O_2 for the diatomic molecule, but O'' or O^u for the divalent atom.

* Journ. Chem. Soc. London, vol. xi.

† Wurtz, 'Atomic Theory,' p. 224.

Now the development of the chemistry of the carbon compounds has shown us that not merely is there chemical contiguity of some sort between the atoms in a molecule (*e. g.* $\text{H}_2\text{O}=\text{HHO}$ or HOH), but that there are special and preferable contiguities between certain atoms or (for brevity's sake, and sometimes provisionally for want of knowledge) groups of atoms. These special associations, often termed "atomic linkings," are seen to keep together through many formative and transformative reactions; and they are indicated in our so-called constitutional formulæ, where these special associations are indicated by so-called "links" or "bonds." The extraordinary progress in complex organic synthesis, the thousands of syntheses which have resulted in so few years of labour in the great and, on the whole, wonderfully systematic and connected text-books of organic chemistry, compel us, I think, to retain the notion of "links" or "bonds," or, as I prefer to call them, "valencies," in writing these constitutional formulæ. Not merely, then, do we write divalent oxygen as $-\text{O}-$ but also as $\text{O}=\text{}$ in our constitutional formulæ, according as we interpret, and fairly consistently interpret, our reactions. Thus, in the case of water, alcohol and ether, with their analogues, do we find $-\text{O}-$, but in ketones and aldehyds $=\text{O}$, and in the organic acids both aspects of divalent oxygen. Similarly the nitrogen atom may be directly specially associated with three other atoms (as in ammonia, N), or it may not; but this does not necessarily interfere with its usually trivalent, and perhaps occasionally pentavalent, character.

It is in some such sense as this that I believe that oxygen is occasionally, and probably in more cases than is usually supposed, tetravalent. Pattison Muir* gives what is probably the most generally accepted definition:—"The atom of oxygen can directly act on and be acted on by two other atoms in a molecule;" but adds, "in some molecules there are only two atoms, one of which is oxygen." This of course refers to the well-known gaseous puzzles, NO , CO , compared with the standard molecule HCl . Perhaps it would be more cautious to say, instead of "act on," "are directly chemically associated with," since it is this *statical* aspect which our formulæ indicate. It is not therefore the case that a tetravalent element is necessarily associated with four monovalent elements. Where this is the case, as in the hydrides, halides, and methides, I should propose that the old word "tetratomic" be used. It is here, in fact, that the idea of the inherent

* Muir, 'Thermal Chemistry,' p. 67.

property of the atom is most striking. We might usually confine this notion of the *thing* or *force* to "atomicity," and reserve the idea involved in the *number* or *ratio* to "valency." I propose that we should always look upon valency as a *number* and atomicity as a *property*, but both still to be investigated. That the valency of all known atoms is a small integer, and most probably 1, 2, 3, 4, 5, or 6, is surely one of the best assured facts in the present state of chemical knowledge. It is a separate question whether in particular compounds the valency of a selected atom may vary within the limits of these numbers. It is also a separate question what this number really means. But I would particularly point out that this valency is apparently independent of the discussions on and decimal revisions of our atomic weights. For valency as a number must be a ratio and referred to monovalent H'; and practically we have referred the valency of all atoms to either monovalent H', or to that unit weight of chlorine which combines with the unit weight of hydrogen in the H'Cl'. Unfortunately the word equivalent has had and has several meanings attached to it. But it is most convenient to take it as a weight, *viz.* that weight of the non-metal which combines with unit weight of the gaseous metal hydrogen, or that weight of a metal which combines with the chemical unit weight of the gaseous non-metal chlorine.

Our first most obvious and useful definition of valency is, first, that it is the numerical ratio,

$$\frac{\text{atomic weight}}{\text{equivalent weight}};$$

e. g. (1) valency of antimony (in antimony trichloride) is

$$\frac{120}{40} = 3, \text{ i. e. Sb}^{\text{III}},$$

(2) valency of oxygen (in steam) is

$$\frac{16}{8} \text{ or } \frac{15.96}{7.98} = 2, \text{ or O}^{\text{II}}.$$

As some elements have more than one equivalent weight, but can only have one atomic weight*, it is not surprising that the valency of an element may be a varying number. But although this is really a practical rule in the case of almost all the metals, we meet with difficulties in the non-metals. Thus, on the hydrogen standard, this kind of valency of oxygen is II. and I. (*cf.* mercury and chlorine, giving II. and I. also†),

* Dr. W. Crookes has recently speculated that the atomic weights of individual atoms may slightly vary, assuming that they contain the hypothetical *protyle*.

† Usually formulated Hg^{II} and (Hg₂)^{II}.

but the oxygen chlorides give $2, \frac{2}{3},$ and $\frac{1}{3},$ which ratios are those of 12, 4, and 3. It would be illogical to infer the multivalency of oxygen from these figures, but they seem to support clearly the *integral* character of valency. On this account I would venture to deprecate the use, except with extreme caution, of such phrases as "residual affinities" or "residual valencies," at any rate so long as we fully and strictly accept the fundamental laws of definite, constant, and multiple proportions. Whatever may emerge as the precise meaning of that well-known little . in those formulæ where the joint influence of reactions and of notions will neither consent to the distant chemical acquaintance of +, nor the intimate familiarity of the valence-link — (so prematurely thrust upon us in inorganic text-books), it would nevertheless seem clear that we are observing the action of *integral units of some sort*, and not residual or small decimal quantities of chemism, affinity, or attraction—whichever our mysterious force be called.

It is in such apparently simple cases as the oxides of chlorine and nitrogen that the combined doctrines of valency and linking seem to break down, or are at least not obvious. Here is the great paradox in our constitutional formulæ, even from the low standpoint of reactions' shorthand. The doctrines have been applied with marvellous success to analysis, synthesis, and prevision of thousands of organic compounds, including dozens of liquids which, although they give the same analytical and vapour-density results, are absolutely distinct in their properties and reactions. And, basing their work on the idea of the geometrical stability of a molecular system containing strictly tetravalent atoms, Van 't Hoff and others have gone still further. Yet in the apparently simple molecules of inorganic chemistry, we are still in a state of comparative chaos. At least we may say that, whereas in organic chemistry the young student finds the constitutional formulæ the most helpful shorthand-memoranda possible of reactions and relationships, the beginner in inorganic chemistry is usually disastrously affected, if not hopelessly muddled, by the presumed necessity of writing these so-called graphic(?) formulæ, in the case, for instance, of the oxides of nitrogen, chlorine, and manganese, or even for what are commonly called ammonia, hydrochloric acid and nitric acid.

In the case of hydrogen dioxide, H_2O_2 , the only reasons assigned, so far as I know, for the usual formula $(\text{OH})_2$ or

$$\begin{array}{c} \text{O} - \text{H} \\ | \\ \text{O} - \text{H} \end{array} \text{ or } \text{H} - \text{O} - \text{O} - \text{H},$$

are (1) that it is "free hydroxyl,"

(2) that it is obtained from $\text{Ba} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ | \end{array}$, and (3), in the words of Wurtz (*l. c.*):—"If $\text{O}=\text{O}$ represents a saturated couple, the symbol $-\text{O}-\text{O}-$ will represent a couple which is unsaturated and capable of attaching, for example, two atoms of hydrogen. *This conception explains the constitution of hydrogen peroxide, $\text{H}-\text{O}-\text{O}-\text{H}$.*"

Now this is one of the most numerous class of bodies whose true molecular weight we have at present no means of ascertaining, or at least of comparing with gaseous molecules. It is, like BaO_2 , PbO_2 , MnO_2 , SnO_2 , SiO_2 , *versus* CO_2 , simply a chemical unit formula. As such formulæ are not strictly comparable like our two-volume formulæ, the chief, if not the only, use of constitutional formulæ in such cases should surely be to explain or indicate reactions, and thus to contribute something from the purely chemical standpoint to the solution of the problems of valency. It can scarcely be said

that $\begin{array}{c} \text{OH} \\ | \\ \text{OH} \end{array}$ or $\text{Ba} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ | \end{array}$ are, on these grounds, useful formulæ.

There is no chemical equality, so to speak, in the oxygen atoms, and no suggested explanation of why some peroxides have what is technically termed "available oxygen" and others have not.

One chief stumbling-block in our theories of quantivalence seems to be due to an apparently unanimous faith in the constant divalency of oxygen, as well as the constant monovalency of the halogens. This has been curiously illustrated in the adoption by many chemists of extreme views in two directions. Either the valency has been very largely varied between 1 and 7 in the case of the halogens, or the valency-power or atomicity of the multivalent metals has been largely increased. The late Professor Wurtz advocated the first view, and Professor Williamson's address at York furnishes an instance of the second standpoint. Certainly, rather than recognize so many valency powers* for the non-metals, it

* Thus Wurtz gave to chlorine the valencies 1, 3, 4, 5, and 7, and to nitrogen 1, 2, 3, 5. Heptavalent chlorine is also suggested by several philosophers, especially in connexion with the periodic arrangements of the elements. In such cases, at least equal weight must be given to aluminium and gallium as trivalent in the periodic series, whereas the tetravalency is constantly asserted, based on the two-volume molecular

formula, $\text{M}_2^{\text{IV}}\text{Cl}_6$. I have suggested the alternative, $\text{Al} \begin{array}{c} \text{Cl}=\text{Cl} \\ \diagup \quad \diagdown \\ \text{Cl}-\text{Cl}=\text{Cl} \\ \diagdown \quad \diagup \\ \text{Cl}=\text{Cl} \end{array} \text{Al}$, in

these and similar cases as more probable than the usually assumed metallic nucleus, $\begin{array}{c} \text{M} \equiv \\ | \\ \text{M} \equiv \end{array}$ or $\begin{array}{c} \text{M} \equiv \\ ||| \\ \text{M} \equiv \end{array}$.

would be preferable to accept the high valencies of metals suggested. But this is not necessary; and still less necessary is it to return in despair to unitary formulæ. Both extremes seem to involve the idea that the atom of highest valency is a sort of nucleus in the molecule, and enforces an immediate proximity or association of all the other atoms of inferior valency*. Organic chemistry has clearly shown that this is not true. It is thus most improbable that avoiding the controversial dot (.) in such ways as

and similarly,

should involve changes in the already high valency of tin or zirconium. Similarly, in H_2PtCl_6 it is not very probable that Pt is octovalent; nor in K_2BeF_4 that beryllium is hexavalent. The alternative is that the halogens are in some compounds more than monovalent. This view I have taken during the last five years. But we need not, as Wurtz appears to have done, take the higher valency as more than trivalent; for it is not likely that the halogen atom, any more than the metallic atom, is directly associated with all the others. This hypothesis of the occasional trivalency of the halogens (especially iodine, whose evidence is the strongest†), together with the not infrequent tetravalency of oxygen will, I think, be found to simplify our ground very much and practically reduce alternative valencies to two—an alternative which, in the case of such elements as phosphorus and tin, has been recognized for many years.

The elements may, indeed, be arranged in two divisions, viz. those whose valency is a single number unchallenged (*e.g.* K, Na, Ba, Sr, Ca, Mg, Zn, Cd), and those whose valencies are more than one number but probably only

* To take a metaphor, we are apt to look at the maypole, and the children dancing round it, and to neglect the possible interactions of the children themselves, even granted there is juvenile (chemical) equality among them.

† *E.g.* ICl_3 , $\overline{\text{I}\text{Ac}_3}$,

two, which valence-powers probably all conform to the remarkable law of odd and even numbers, or, as Prof. Odling termed atoms with such valencies, perissads and artiads. If, therefore, I ask that oxygen, chlorine, iodine, and fluorine should be placed in this second class, it is not to complicate but to simplify the great valency problem. Monovalent atoms in such gaseous molecules as WCl_6^* and PF_5 seem highly probable, but they may be questioned in the oxides of chlorine and in the allied oxy-acids. Thus, in the simplest

oxide we really have the choice of $\begin{array}{c} \text{Cl} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$, $\begin{array}{c} \text{Cl} \\ || \\ \text{O} \end{array}$, and $\begin{array}{c} \text{Cl} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$.

Many chemists have accepted $\begin{array}{c} \text{Cl} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$ and $\begin{array}{c} \text{K} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$ and $\begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$

somewhat hastily, because of their historic place in the water-type theory, rather than from positive evidence†.

If the KO Cl formula be adopted there is the alternative between K—O—Cl and $\text{K—O}\equiv\text{Cl}$. But the chemical evidence seems rather in favour of $(\text{K} \cdot \text{Cl} \cdot \text{O})_x$, in which case chlorine is trivalent or tervalid as K—Cl=O ; or in $\text{K}_2\text{Cl}_2\text{O}_2$

as $\begin{array}{c} || \\ \text{K—Cl=O} \end{array}$. The remarkable increasing chemical stability

of the series KClO , KClO_2 , KClO_3 , KClO_4 remains to be explained; but I believe that the hypothesis of the valency variation of one or both the negative elements must be adopted, so long as valency language is useful in focusing mysteries enshrined within a chemical molecule. Possibly the oxygen atoms are in some sort of "closed ring." Certainly the old tandem arrangement K—O—O—O—O—Cl must be abandoned. In KClO_3 and KClO_4 , the K and Cl may each be separately associated with an oxygen atom; or, seeing that KCl is such a constant product whether by wet or dry reactions, there is something to be said for Cl''' in some such

* Just above the boiling-point.

† Undoubtedly the formula $\text{Cl}(\text{OH})$, that is, $\text{Cl}'\text{—O}''\text{—H}$, and notably the $\text{CN}(\text{OH})$ formula for cyanic acid, established themselves under shelter of a somewhat dangerous, or at least premature, extension of the hydrate theory, or (OH) , so well established in the case of organic acids. The tendency to introduce unwarrantable OH -groupings is especially shown in such cases as $\text{Ag}(\text{OH})$ and even $\text{NH}_4(\text{OH})$. The distinctions between hydrates and hydroxides should also be more carefully observed; the former are really quite in a minority. The reaction against the indiscriminate use of OH -groupings in inorganic chemistry in many "not proven" cases is now beginning to show itself clearly.

formulae as $\text{K}-\text{Cl}=(\text{O}_3)''$ and $\text{K}-\text{Cl}=(\text{O}_4)''$, where the (O_3) and (O_4) are at present indeterminate bivalent radicals.

There is of course no evidence at present available for the quadrivalency of oxygen to be clearly derived from the oxides of nitrogen. The means of determining whether N_2O is

but when any are given in our text-books the alternatives should surely be given and the whole marked with a conspicuous ?

It was in fact in the compounds already referred to, H_2O_2 and BaO_2 , that I at first concluded the tetravalency of oxygen to be the lesser of two puzzles. I look upon them as

allowing of course that neither are formulae of strictly comparable molecules.

(i.) The peculiar reactions of BaO_2 , MnO_2 , PbO_2 , and their inability to form what are curiously called "corresponding salts," as contrasted with SnO_2 , SiO_2 , are suggested to me by the formulae $\text{X}''=\text{O}=\text{O}$ as opposed to $\text{X}^{\text{IV}}\text{O}_2$, *i. e.* $\text{O}=\text{X}=\text{O}$, the molecules being $(\text{XO}_2)_x$ where x is unknown.

(ii.) The existence of a series of oxides in the case of some metals, and of only one oxide with others, is probably connected with this double valency—I use the phrase provisionally as the sequel will show—of oxygen. Some of the oxides are otherwise not accounted for, and in others there is an assumed linking or double linking of the metallic atoms of which we may well be sceptical. For it is, I believe, the peculiar characteristic of the non-metals or negative elements to preferably exhibit this single, double, or treble linking (if it exists, and whatever it may mean) and thus to accumulate. Thus the oxides of silver,

Similarly, Hg and Cu being clearly defined divalent metals,

I prefer to take their suboxides as

There is no clear evidence of the Hg—Hg association.

Similarly for Cu_2Cl_2 and Hg_2Cl_2 , usually assumed as $\begin{array}{c} \text{Cu}-\text{Cl} \\ | \\ \text{Cu}-\text{Cl} \end{array}$, I should prefer $\begin{array}{c} \text{Cl}=\text{Hg} \\ | \\ \text{Cl}=\text{Hg} \end{array}$ and $\begin{array}{c} \text{Cl}=\text{Cu} \\ | \\ \text{Cl}=\text{Cu} \end{array}$ as being more in accordance with the facts of the reactions of these bodies. The cases of the chlorides and double chlorides are very well known.

(iii.) There are certain suboxides which lurk in our textbooks and literature. In addition to $\text{Ag}_4\text{O}^{\text{IV}}$, perhaps the “blue crust” forming on recently cut potassium is $\text{K}_4\text{O}^{\text{IV}}$, and Pb_2O may be $\text{Pb}=\text{O}=\text{Pb}$ giving PbO , which can, like BaO , take up more oxygen from the air. Indeed the curious actions of heat on PbO and BaO as well as MnO_2 &c. seem to be due to this *conditional* tetravalency of oxygen, and not to change of valency of metallic atom or atoms usually assumed.

(iv.) The peroxides of potassium and sodium are puzzles. As Na_2O_2 is not decomposed on heating, it has a legitimate claim

$\begin{array}{c} \text{O}-\text{Na} \\ | \\ \text{O}-\text{Na} \end{array}$ which H_2O_2 has not. Moreover it forms a hydrate

$\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$. Whatever K_2O_4 may turn out to be, it is probable that all the O atoms are not divalent. The arrangement is undoubtedly a comparatively stable one, and when it is interpreted we shall probably see the constitution of, or at least the interrelations of, certain bodies not usually associated with it, *e. g.* K_2O_4 , KClO_4 , HClO_4 , Cl_2O_4 , all strikingly “stable.” Perhaps

may serve to suggest the problem before us.

(v.) But just as the remarkable way in which so many metallic chlorides combine with other chlorides, chlorhydric acid, and oxides, is a strong line of evidence for the trivalency of chlorine, so the peculiar actions of water as an active chemical reagent, even when it is not represented in our conventional equations, seem to be strong evidence of the ready way in which the oxygen atom in water can be stimulated, so to speak, to exhibit its tetravalent character.

We may recall the way in which “aldehyd hydrate

$C_2H_4O \cdot H_2O$," for instance, has fought its way out of the ambiguous company of dotted "molecular aggregations" to be viewed as aldehydrol

Similarly for acetal and other bodies. Even $C_2H_4O_2 \cdot H_2O$ has been suggested to be

though it is not easy to recognize the chemical equality of the first hydroxyl grouping with the others. There are facts which preferentially favour

and the recent researches by Ramsay and Young show the existence of the more complex gaseous molecules

(vi.) In the interesting so-called molecular compound discovered by Friedel, $(CH_3)_2O \cdot HCl$, a remarkably stable body, we have a most striking case for the tetravalency of oxygen, either as

or, as seems preferable,

(vii.) This stable compound brings us back to the three types HCl , H_2O , H_3N with which we started; but before resuming their consideration, allusion must be made to the polymerization of aldehyds, of cyanates, of the metaphosphates, and other bodies as closely connected with the tetravalency of oxygen*.

* The stimulus—if I may so term it—to polymerization in these cases seems to be due to the development, in ways that current research are seeking to explain, of the higher valency, or, as it may be preferably termed, the validity of oxygen, or the tervalidity, for instance, of chlorine in hydro-

(viii.) Again, the tetravalency of oxygen cannot well be dissociated from such compounds as

(ix.) The numerous hydroxides, as well as hydrates *, the so-called "basic salts" so numerous in the case of oxygen, be it noted, and probably also the complex poly-tungstates and silicates are also probably connected with this property of oxygen. Prof. Carnelley's vanadates of thallium form remarkable instances of the convenience of the mode of viewing a salt as a combination of two oxides.

(x.) The water of crystallization of salts may be due to this association of the water molecules

where the oxygen is tetravalent or quadrivalent. The tandem paper arrangement of course suggests nothing of the spatial arrangement, which in all crystals is probably symmetrical. The go-between influence of H_2O in Prof. Dixon's famous

chloric acid solution used as "a polymerizer" $\text{H}-\text{Cl} \equiv$. It is significant that there are few cases of polymerization where oxygen is not concerned. It does not seem probable, however, that oxygen is tetravalent or quadrivalent in cyanuric acid. The ordinary major valencies and the properties of the substance suggest

Probably more ring formulæ in inorganic bodies will come to light, and they will affect the maypole hypothesis—as it may be called—of the domination of the central polad atom.

* Even in the case of so-called "KHO" there is more to be said for $\text{K}_2\text{H}_2\text{O}_2$, at least, if not $(\text{KOH})_x$. $\text{Ag}_2\text{O}_2\text{H}_2$, though doubtful, is less misleading than AgOH .

experiments on the explosion of carbonous oxide* with oxygen is also probably due to this provisional tetravalency of oxygen.

Undoubtedly the chief difficulty which is present to the mind in using these links or conceding these valencies, in the case of proposed higher values, is the doubt whether the combination is of the same order or intensity so to speak, and can be strictly called chemical combination in all cases. On this account Professor Armstrong † wrote the compounds

But the valency as matter of discussion might perhaps be indicated as

There are many such compounds; *e. g.*

These formulæ clearly suggest the problem in quantivalence which lies before us. Certainly such phrases as "residual valency," "surplus affinity," "residual charge on the atoms" are open to the objections which have already been suggested. They may prematurely beg the problems of chemical affinity. Even in the case of PCl_5 there can scarcely be said to be observed a perfect chemical equality of the atoms such as we believe to be in CH_4 . The chlorine is apparently dealt with preferably in two fifths and three fifths in most chemical reactions. Such considerations have long induced Professor Kekulé and others to maintain that a phosphorus atom is constantly trivalent.

For the higher valency under discussion, in the case of oxygen and chlorine, if we are to use other words, it may be found convenient to use a kindred word *validity*, which has therefore been occasionally used in this paper. We

* Water-molecules necessarily present would be formulated $\text{H} \begin{array}{l} \text{H} \\ \text{O} = \end{array}$.
Cf. note on the last page.

† B. A. Report, Aberdeen, 1885.

could say, for instance, that chlorine is usually monovalent but occasionally tervalid. The latin prefixes, roman numbers, and broken lines in formulæ would help to keep up the distinction ; thus :—

—R'	monovalent,	---R ^I	univald.
=R''	divalent,	===R ^{II}	bivald.
≡R'''	trivalent,	≡≡R ^{III}	tervald.
≡≡R''''	tetravalent,	≡≡R ^{IV}	quadrivald, &c.

We might then say that carbon is tetravalent, except in the gaseous molecules CO and CNH, where it is bivald unless the tetravalency of oxygen and the pentavalency of nitrogen are admitted, when carbon is always tetravalent*.

Other open questions will suggest themselves to the mind†.

The general chemical observation that no atom is really known to be more than hexavalent to the standard monovalent atoms‡ finds remarkable independent support in Prof. J. J. Thomson's development of the vortex-atom theory. According to his view a triad atom consists of three vortex rings symmetrically linked together, and "no element could have an atom consisting of more than six vortex rings." He has also found that stable motion exists "when the distance between the rings was small compared with their apertures," and he adds: "We found that for each displacement there are two periods of vibration, a quick vibration and a slow one." Is it possible, it may be asked, that in these two periods of vibration there is a connexion with the two valencies or rather the valency and validity of so many of the negative or non-metallic elements which have been referred to in this paper?

Prof. J. J. Thomson at least clearly points out that, according to the vortex-atom theory of gases, "one atom of a

* In CO, according to Prof. J. J. Thomson's conception of links, "the atom of carbon has the same number of links as the atom of oxygen."

† CNH and NCH are metameric molecules. It is not easy to decide which is the formula of prussic "acid" gas. In the formula, I have assumed it to be the "imido" relative of CO, which is metameric with

formo-nitrile, $\begin{array}{c} \text{H} \\ | \\ \text{CH} \end{array}$. The two methyl and ethyl metamers seem distin-

guishable, but sometimes turn up together in "the same" reaction.

‡ The cases of M^{VII} and M^{VIII} are here considered as not proven. Prof. J. J. Thomson's views on this point will doubtless be dealt with in the course of further chemical research.

dyad might unite not only with two atoms of a monad, but also with four atoms of a monad, the four atoms of the monad splitting into two groups each." He says: "Regarding oxygen, then, as a dyad, the molecule of water consists of three primaries H_2-O-O ." I do not know the exact significance of his marks, but the analogous formula now proposed is $H_2=O=O$, or at least $H_2=\overset{\cdot}{O}=O$. It is at least

preferable to the symmetrical $\begin{array}{c} O-H \\ | \\ O-H \end{array}$ in better exhibiting its reactions, and as the modern representative of the late Sir B.

Brodie's $H_2\overset{+}{O}\overset{-}{O}$, which has the no small merit of distinguishing between the two atoms chemically dissimilar. The novelty (so far as I know) of formulating a divalent and a tetravalent atom of the same element in one chemical molecule will, I hope, provide fruitful discussion with those chemists who are not prepared to reject or scorn the childhood of constitutional formulæ.

However hypothetical our constitutional formulæ of most inorganic bodies may yet be, I venture to doubt the wisdom of abandoning the use of our valence-marks, linkings, so-called double bonds, &c. in favour even of the single mark proposed some years ago by Lössén. They may still be used with advantage to chemical science, but not usually to those who are beginning its study. The fact is that the one-sided study of inorganic chemistry, with its numerous elements, and therefore greater delicacy and intricacy of valency-variation, would make us pessimists, and the isolated study of organic chemistry, with its few elements, would keep us optimists. The reaction of the constitutional school of chemists upon the empirical formulæ of inorganic chemistry has been, in some respects; rather premature in its attempts to solve too much at the outset; but the real laws of valency must be substantially the same in both. Thus we have the radical or grouping—the organic atom so to speak—of ethyl (C_2H_5) always of one valency, but (C_3H_6) is both mono- and tri-valent. Nay, more. What would be called the allotropic modifications of this "atom"—were it an atom—are well known, and can be separably recognized. If (C_3H_6) were an elementary atom, it would be called usually trivalent but occasionally univalent; or, if no distinction is to be made, trivalent and monovalent after the fashion of gold or thallium. There are not less than five trivalent (C_3H_6)'; and their compounds with either chlorine, oxygen, or hydroxyl are all known.

If at present we cannot press the analogy too close in the alternating valency* of so-called elementary radicals or atoms, especially the non-metallic ones, we are surely not yet prepared to abandon formulæ which have been of such signal service in the development of organic chemistry, and to abolish the notation because we do not yet know the real meaning either of the marks or valency. But is it too bold a thing for us to look forward to the time when we can similarly deal with an elementary radical, the present provisional chemical atom? At present our notions of valency are chiefly conditioned by the experiments made, *and the chemical products constantly being beheld*, at about 16° C. and 76-centim. mercury pressure. It is, therefore, wonderful and encouraging that we should already have a theory which, on the whole, has such promise for the future. And it is not surprising that, as Clerk Maxwell wittily put it at Belfast,

Though they seem to cling together,
And form "associations" here,
Yet soon or late they burst their tether,
And through the depths of space career.

Oxford, 7th November, 1887.

* This theory of an *alternating* valency, as contrasted with both the "almost any" and the "constant one" theories, not only appears to have some support from the vortex-atom theory but from the periodic law, especially when this is exhibited on Prof. J. Emerson Reynold's plan, as exposed by Dr. Crookes. But I see no sufficient reasons for the septavalencies.