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III. *A Note on Valency, especially as defined by Helmholtz.*

By HENRY E. ARMSTRONG, *F.R.S.**

VERY little has been either said or written of late on the subject of Valency—not because the topic is admitted to be exhausted, nor because our views can be regarded as reposing on a fixed basis of fact, but more I believe on account of the feeling being almost universally entertained that little is to be gained by continuing the discussion from our present standpoint.

My purpose in this note is to call attention to the extreme importance of reopening the discussion on account of the intimate bearing that it has on the work in which the Electrolysis Committee, jointly appointed by this Section and by Section A, are now engaged; and to urge that it is time that the gage thrown down by Helmholtz in the Faraday lecture (*Chem. Soc. Trans.* 1881, p. 277) was uplifted by chemists.

We are told by Helmholtz that it is a necessary deduction from the fundamental law of electrolysis established by Faraday, that definite, as it were atomic, charges of electricity are associated with the atoms of matter; that, in fact, a monad bears a single charge, a dyad two, a triad three; and that when combination occurs, the charges are still retained by the atoms, but neutralize each other—"the atoms cling to their charges, and opposite electric charges cling to each other." I cannot help thinking, however, that Helmholtz deprives his statement of much of its force and simplicity by adding: "But I do not suppose that other molecular forces are excluded, working directly from atom to atom;" he is led to do this apparently by being aware of the distinction which it is usual to draw between atomic and molecular compounds. The attempt should at all events be made—and in my paper on "Residual Affinity" I have already ventured the first step—to include both classes of compounds, molecular as well as atomic, in the discussion; indeed it is somewhat difficult to reconcile the passage above quoted with the following statement which occurs previously in the lecture:—"The law of the conservation of energy requires that the electromotive force of every cell must correspond exactly with the total amount of chemical forces brought into play, not only the mutual affinities of the ions, *but also those minor*

* Communicated by the Author, being a communication to Section F of the British Association at Manchester.

molecular attractions produced by the water and other constituents of the fluid." The italics are mine. But if the "minor molecular attractions" contribute to the electromotive force of the cell, then conversely these also will have to be overcome in effecting electrolysis, and are as much to be reckoned as are the "mutual affinities of the ions"!

It is obvious that if it should prove possible to decide what number of charges are necessarily associated with any particular atom, the conception of valency will have acquired a definiteness which cannot possibly be attached to it as long as the views that have hitherto guided us are adhered to. A decision must involve the discussion of the question of the existence of molecular as distinct from atomic compounds.

To cast the apple of discord without further preface, I would direct attention to the insufficiency of the evidence on which it is usual to rely as proof that nitrogen, for example, is a pentad; nay more, I would assert that this very evidence should be interpreted as proof that nitrogen is not a pentad. It is commonly held that the behaviour of the alkyl tetra-substituted derivatives of ammonium is such as to negative the idea that these are "molecular compounds" of triad nitrogen, and that it must be assumed that the elements of the binary compound which are added on to the ammonia derivative are *distributed* in the ammonium derivative; for example, that in the formation of tetramethylammonium iodide from trimethylamine and methyl iodide, the methyl and iodine of the iodide part company, and separately attach themselves to the nitrogen, thus:—

But I contend that the properties of tetramethylammonium iodide and hydroxide prove that such is not the case: the iodide, it is well known, can be boiled for hours with the strongest caustic potash solution without undergoing change; there is not a single case on record, however, of any haloid compound other than an alkylic compound behaving in this manner, the chlorides, bromides, and iodides of every element except carbon are almost at once converted into hydroxides by such treatment, and a nitrogen iodide would surely be acted on. The behaviour of the iodine is much more nearly that of iodine in methyl iodide, and, it may be said, exactly that of the iodine in iodobenzene; indeed it would seem that in the alkyl-ammonium haloid compounds the halogen is

always less easily displaced by the action of alkalies than it is in the parent haloid alkylic compound.

The remarkable resemblance of the tetra-substituted ammonium hydroxides to potassium hydroxide has led to their being regarded as in every respect analogous to this latter, and would appear to preclude the idea that they are molecular compounds of an alcohol with an ammonium derivative. But attentive consideration of their properties will suffice, I think, to show that the apparent discrepancies are not only explicable, but that they actually support the molecular compound hypothesis. Thus it might be said to be improbable that tetramethylammonium hydroxide should behave as a powerful base, and have the same heat of neutralization as potassium hydroxide, if methyl-alcohol were one of its proximate constituents; but it is to be remembered that the salt which results from the action of an acid on methyl-alcohol is liable to suffer reconversion into the alcohol by the action of the water produced in the interchange; also that in many cases the methyl salt is insoluble in water, or nearly so. The heat developed on neutralizing methyl-alcohol therefore falls far short in amount of that which would be evolved if the interchange were complete, and if the product were capable of interacting with water, and perhaps also with itself in the way that apparently is possible in the case of metallic salts. In the case of the tetramethylammonium hydroxide, the action of acids is total as the change is irreversible, or almost so, under the conditions which obtain during the formation of the salt, just as in the case of the conversion of potassium hydroxide into a salt; moreover, the product is easily soluble, even when acids like muriatic are used. Why the methyl-alcohol, or other methyl derivative, retained in the ammonium compound behaves so differently as compared with the unassociated methyl derivative, is a question which, for the present, we must be content to put aside unanswered. I am also of opinion that in discussing their constitution, no particular weight can be attached to the mode in which the tetralkylic ammonium hydroxides undergo decomposition when heated, as the products in some cases are an amine and an alcohol, but in others an olefine and water, instead of an alcohol; in the case of the phosphonium salts the diversity is still greater (Chem. Soc. Proceedings, 1886, p. 164). That amines may act as "dehydrating" agents in the manner required, if the molecular compound hypothesis be adopted, appears by no means improbable.

What is here stated of the tetramethyl compounds is true of tetralkylic ammonium haloid compounds generally, in the

sense that they are all less readily acted on by alkalies than are the parent alkylic haloid compounds ; but just as these latter are more readily attacked by alkalies and other agents the more complex the alkyl, so are the tetralkyl ammonium compounds ; in no case, however, do they manifest a reactivity at all comparable with that of simple metallic or non-metallic haloid compounds—always excepting those of carbon.

The argument used above would apply equally to the phosphonium and sulphine compounds ; indeed with greater force.

In many other respects, the behaviour of nitrogen in aminic compounds is altogether peculiar and irreconcilable with the assumption of pentadecity. Thus it is commonly pointed out that the basic properties of aniline, for example, become lessened and ultimately almost annulled by the introduction of chlorine or bromine into the phenyl radical ; and that acetamide, $C_2H_5O \cdot NH_2$, and other similar compounds formed by the introduction of acid radicals into ammonia are all but destitute of basic properties ; the power to form ammonium compounds, therefore, is not a simple function of the nitrogen atom, but is largely dependent on the nature of the radicals associated with the nitrogen atom. Other illustrations are afforded by the hydrazines. Thus phenyl-hydrazine, $C_6H_5 \cdot NH \cdot NH_2$, although it contains two atoms of (triad) nitrogen, forms with hydrogen chloride the compound $C_6H_5 \cdot N_2H_3 \cdot HCl$, which crystallizes unchanged from fuming muriatic acid, in which, moreover, it is almost insoluble. Ethyl-hydrazine, however, forms a dichlorhydride, $C_2H_5 \cdot N_2H_3 \cdot 2HCl$; but on evaporating the aqueous solution of this salt a monochlorhydride is obtained ; and unsymmetric diethyl-hydrazine, $(C_2H_5)_2N \cdot NH_2$, is a monobase like phenyl-hydrazine.

Hence it may well be argued that we have no reason to assume that nitrogen is pentad in the ammonium compounds, or phosphorus pentad in the phosphonium compounds, or sulphur tetrad in the sulphine compounds ; but that these are all to be reckoned as molecular compounds.

What then is the valency of the elements in question ? and what is a molecular compound ?

In answer to the first of these questions, the proposition may be advanced that gaseifiable hydrogen compounds are the only compounds available for the direct determination of valency, and that the valency of an element—the number of unit charges necessarily associated with its atom—is given by the number of hydrogen atoms combined with the single atom

of the element in its gasifiable hydride*. In cases where such hydrides are unknown, the determination of valency is very difficult ; it can be but provisionally effected, and only by most carefully weighing all the evidence relating to the constitution of the compounds available for discussion.

But if it be granted, for example, that nitrogen is a triad, and that iodine is a monad, How are we to explain the fact that the methyl compounds of these two elements unite to form so well characterized a molecular compound as tetramethyl-ammonium iodide? How are such molecular compounds constituted? My own view has long been that the nitrogen and iodine in such a case are both possessed of a certain amount of *residual affinity*; and I would define a molecular compound as one formed by the coalescence of two or more molecules, unattended by redistribution of the constituent radicals, and in which the integrant molecules are united by residual affinities. In other words, the unit charge must be capable in certain cases of directly promoting the association, not merely of two, but of at least three, atoms. To put this hypothesis into terms which cannot be misunderstood, let unit valency or charge be represented by a unit line, and further be it supposed that the charge *penetrates the atom*, then the atom with its unit charge may be represented thus:—

i. e., the unit charge may be held to consist of three portions, the buried portion *a*, and the free portion *f*+*f'*. The facts, as they present themselves to me, also appear to necessitate the assumption that, in the case of different elements, the charge penetrates the atom ; and in the case of some polyad atoms, different directions in the atom with varying degrees of freedom†. The union of two atoms may then be pictured as an overlapping of the unit lines. If the atoms are freely penetrated by their charges, each atom may tend to move out to the end of the line, leaving either no portion, or but a very small portion, free ; a conception of this order would

* If this be granted, it follows that the maximum number of charges which an atom can carry is four ; in other words, that the possible maximum valency is attained in the case of carbon.

† This is practically but a modification of Helmholtz's statement that "the phenomena are the same as if equivalents of positive and negative electricity were attracted by different atoms, and perhaps also by the different values of affinity belonging to the same atom, with different force."

appear to apply in the case of hydrogen, and may be represented thus :—

But if the atom be not easily penetrated by its charge, it will not move out to the end of its line, and the resulting compound molecule will possess more or less "residual affinity"; this conception would appear to apply to the non-metals generally, and to some of the metals; it may be illustrated thus :—

I have thought it permissible to state my views in this form merely in order to advance the study of molecular compounds by the introduction of a working hypothesis, an absolutely artificial mode of expression such as is here adopted being perhaps pardonable in the absence of any explanation which may serve to guide us in extending our enquiries as regards the structure of such compounds, a knowledge of which is all important to a rational conception of the nature of chemical change generally. Moreover, I do not hesitate to affirm that, from the chemical point of view, it is impossible to adopt the Helmholtz explanation of valency, unless physicists are prepared to grant the possibility of the "division" of the unit charge somewhat in the manner here suggested; and it is in order to impress this that I have ventured to give utterance to these speculations.

To return to the consideration of the compounds previously referred to, it may be supposed that the nitrogen of trimethylamine and the iodine of methyl iodide are possessed of residual affinity, and hence the two molecules unite to form the molecular compound tetramethylammonium iodide, which may be represented thus :—

The phosphonium and sulphine iodides may be regarded as similarly constituted. It is well known that the ammonium

haloid compounds and their analogues are also capable of forming still more complex molecular aggregates with the halogens, &c. : they are therefore to be regarded as possessed of residual affinity ; and that polyad elements, *e. g.* nitrogen, phosphorus and sulphur, should still exhibit residual affinity in such compounds is not surprising in the light of the hypothesis advocated in this note ; but it is scarcely compatible with the assumption that the halogen in the ammonium haloid compounds serves as the bond of union. On the other hand, if it be assumed, as I think it should be, that the formation of double metallic chlorides, &c., is the outcome of the possession of residual affinity by the halogen, the complete analogy which appears to exist between the ammonium haloid compounds and those of the alkali metals would seem logically to involve the inference that the halogen of the ammonium compound does serve as the bond of union. I see but one mode of escape from this conflict of evidence, and that is to call in question the time-honoured assumption that the radical ammonium is the true analogue of potassium and sodium, which, be it remarked, is of necessity subject to doubt if the hypothesis that the ammonium salts are molecular compounds be entertained ; and evidence which supports the conclusion that the per-haloid compound is formed by the addition of the halogen to the nitrogen (phosphorus or sulphur) is afforded by the observation that not only *haloid* ammonium and sulphine compounds, but also the *sulphates* combine with halogens (Dobbin and Masson, *Chem. Soc. Trans.* 1885, p. 56 ; 1886, p. 846).

It is now proved by abundant experimental evidence that, whatever the order in which the radicals A, B, C, D, are introduced in forming a tetralkylic ammonium compound N(ABCD)X, one and the same end product always results. This is commonly regarded as proof, not only that nitrogen is pentad, but also that the five affinities of the nitrogen atom are of equal value, and it would appear to favour the conclusion that the ammonium salts are in truth "atomic" compounds ; but I see no reason why isomeric change should not occur at the moment of formation of a molecular compound : why the integrant molecules, in fact, should not interchange radicals. If the statement be confirmed that the compound formed from dimethyl sulphide and ethyl iodide is different from that obtained on combining methylethyl sulphide and methyl iodide (Krüger, *Journ. pr. Chem.* 1876, xiv. p. 193), it will follow, not that sulphur is a tetrad, and that the four affinities are of unequal value, but that there is little or no tendency for isomeric change to occur in the formation of

sulphines. The possible occurrence of isomeric change in the formation of molecular compounds, however, is a subject which certainly deserves careful study at the present time.

In the case of phosphorus, the existence of the highly stable gaseous pentafluoride PF_5 , discovered by Thorpe, is undoubtedly regarded by many as final proof of the pentadecity of this element; but the existence of compounds such as H_2F_2 , $HFFR$, &c., which clearly belong to the class of molecular compounds, is an indication of so marked a tendency on the part of fluorine to combine with itself, that for this reason alone (as Naumann and others have asserted) the pentafluoride is by no means necessarily regarded as an atomic compound. And I would here add that stability affords no criterion as between atomic and molecular compounds, every degree of stability being met with even among those of the former class.

An argument in favour of the pentadecity of phosphorus, which apparently cannot be disposed of by any explanation based on conventional considerations, has, however, been advanced by La Coste and Michaelis (*Berichte*, 1885, p. 2118), who have shown that the compounds obtained from diphenylchlorophosphine, $PCl(C_6H_5)_2$ and phenol is not identical with the triphenyl-phosphine oxide, $OP(C_6H_5)_3$, obtained by oxidizing triphenyl-phosphine, as it should be if the latter were a compound of the formula $(C_6H_5)_2P \cdot OC_6H_5$; this last corresponding to the formula $Cl_2P \cdot OCl$ which has been suggested as that of phosphorus oxychloride, and which appears to derive considerable support from Thorpe's observations on the specific volume of the oxychloride (*Chem. Soc. Trans.* 1880, p. 388). It is, however, conceivable that the oxygen and phosphorus are united by residual affinities, thus:—

Michaelis and Polis (*Berichte*, 1887, p. 52) have argued in the case of bismuth, which also is a member of the nitrogen group, that the pentadecity of this element is proved by the existence of the triphenyl dibromide $(C_6H_5)_3BiBr_2$. But the mere production of such a compound proves nothing so long as its constitution is undetermined; it at most serves to strengthen the conviction gained from the general study of the element, that bismuth is a member of the nitrogen-phosphorus group.

In other cases also it is possible that undue importance

may have been attached to the existence of alkylic compounds of particular types: thus lead, judging from its general chemical behaviour, would appear to be a dyad; yet the existence of the tetrathide $\text{Pb}(\text{C}_2\text{H}_5)_4$ is commonly held to be a proof that it can function as a tetrad. But the properties of lead are such that I am tempted to suggest that it is one of the metals in which the "charges" have but a small degree of freedom; and it is conceivable that the tetrathide is actually a compound of dyad lead, each charge serving to bind two ethyl groups, thus:—

The same may be true of tin, although in this case the fact that we are dealing with an element of the carbon-silicon family tends to favour the conclusion that it may be a tetrad.

Also too much importance must not be attached to the existence of stable volatile chlorine compounds: thus tellurium tetrachloride may well be a compound of dyad tellurium, thus:—

Iron, and the other members of the family which boron heads, in like manner, I feel convinced, are triads even in their *ic* compounds: recent vapour-density determinations all support this conclusion.

It is even conceivable that chlorine may form *closed-chain* compounds, and that a tetrachloride may exist, such as is represented by the formula:—

I think it is especially noteworthy that so many well characterized and comparatively stable double chlorides exist formed by the union of chlorides, of which one at least is *per se* very unstable; the tin-sulphur chloride $\text{SnCl}_4 \cdot 2\text{SnCl}_4$, and the remarkable series of aurous compounds recently described by Lepetit (*Ann. Chim. Phys.* 1887, p. 11) may be cited as examples.

If my contention in this and previous papers be correct, that residual affinity thus plays a far more important part than has hitherto been supposed, and that it must be taken into account in all discussions on valency, it follows of necessity that our views regarding the constitution of the

majority of compounds at present rest upon a most uncertain basis : the constitution of the paraffins, of the benzenes, and of the haloid compounds and alcohols derived from the hydrocarbons of these series, may be regarded as determined with a degree of precision almost amounting to certainty ; but in the vast majority of other cases we have as yet no secure method of arriving at conclusions which in any sense approach finality. There can be little doubt that in framing our modern conceptions of valency, we have been too much influenced by the graphic symbols which have been so widely made use of. In the future it will be necessary to attach a more liberal interpretation to the facts, and it may be hoped that it will some day be possible also to take into account differences depending on the relation of the different forms of matter to the pervading medium.

IV. *On a Geometrical Determination of the Conditions of Maximum Efficiency in the case of the Transmission of Power by means of Alternating Electric Currents.* By THOMAS H. BLAKESLEY, M.A.*

1. **T**HIS paper treats the above problem as a particular application of the method of representing Combinations of Electromotive Forces possessing a simple Harmonic Law of Change, already given by the author more than three years ago, and detailed in a series of papers published during 1885 in the 'Electrician.'

It was then pointed out that, though with two constant electromotive forces acting in a simple circuit the transmission efficiency does not exceed the ratio of the smaller to the larger, yet with alternating electromotive forces [denominated by their maximum values] the efficiency may exceed this ratio, owing to the self-induction of the circuit, and to the possibility of varying the interval of time at which the phases of one electromotive force may follow the corresponding phases of the other.

It is here proposed to show how the particular interval of time which will give the maximum efficiency may be geometrically determined, and what the value of that maximum efficiency is for two given electromotive forces undergoing harmonic repetition in the same given period, in a simple circuit possessing a known resistance and a known coefficient of self-

* Communicated by the Physical Society: read November 12, 1887.