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THE ELECTRON CONCEPTION OF VALENCE. V. POLAR AND NON-POLAR VALENCE.

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The dualistic view of the nature of valence was considered at some length in a paper by Bray and Branch entitled "Valence and Tautomerism" which appeared recently in THIS JOURNAL.[1] That is to say, the union between two atoms in a molecule was taken to be "either polar or non-polar in character, according as it is assumed that an electron passes completely or does not pass from one atom to the other," a view that is not entirely new.[2] The present writers have been interested for some years in questions of this nature and have published a series of papers[3] in which were presented the conclusions drawn when valence is considered to be polar in character only. The views of Bray and Branch with regard to the two kinds of valence are somewhat at variance with this point of view.

It is desirable, in the first place, to compare the nomenclature of Bray and Branch with that used in the IV Paper of this series in which a "Classification of Chemical Reactions" was developed. Their "polar number" corresponds to the algebraic sum of the charges carried by an atom as

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[1] 35, 1440 (1913).

[2] The nature of valence as dualistic in character was taken up by Nernst in the different editions of his "Theoretische Chemie," for instance, in the IV edition (1903), p. 400; VII edition (1913), p. 435.

[3] S. of M. Quarterly, 30, 179 (1909). THIS JOURNAL, 32, 1637 (1910); 33, 1140 (1911); 35, 1810 (1913). *Orig. Communications VIII Intern. Congr. Applied Chemistry*, 6, 212 (1912); *J. prakt. Chem.* (*N. F.*), 88, 97 (1913).

stated in the IV Paper, and their "total valence number" to the arithmetical sum of these charges.

In the second place the important fact must be mentioned that the non-polar valence view in itself is now generally recognized not to be a sufficiently broad basis upon which to classify valence phenomena. Either the dualistic view of polar and non-polar bonds, or the unitary view of polar bonds alone appears to be essential for a satisfactory classification.

Bray and Branch assume that polar and non-polar bonds differ fundamentally in kind. The consideration of oxidation and reduction leads to some anomalous relations when taken up from this point of view. The correct definition for these phenomena with inorganic compounds is unquestionably that involving a change in the electrical charges of the atoms taking part in the reaction,[1] gain of positive charges by the reacting atoms for oxidation, loss of positive charges for reduction. For compounds with non-polar valences it is difficult to formulate a definition. A description of the different oxidation or reduction reactions of organic compounds on the dualistic valence view leads to contradictions. The organic reactions in which a hydrogen atom attached to carbon is replaced by a halogen atom and the halogen atom by a hydroxyl group, may be taken up briefly. When chlorine, combined with carbon is replaced by a hydroxyl group, the experimental evidence, mainly that derived from hydrolysis experiments,[2] points to the same kind of valence for the chlorine and oxygen atoms when these are combined with carbon. If this is admitted, then the replacement of hydrogen by halogen will be an oxidation reaction, and in general, the definition of oxidation might then be stated as "an increase in the proportion of its oxygen or acid-forming element (or group)" and of reduction as "subtracting oxygen or an acid-forming element (or group)."[3] This is however a re-statement in a somewhat different form of the definition of oxidation and reduction in which electric charges are involved as was shown in the IV Paper. The dualistic view, on the other hand, assumes the hydrogen atoms and the chlorine atoms to be combined with the carbon atom by non-polar valences. If it is not admitted that the chlorine-carbon linking is polar, it would be necessary, since experimental evidence shows no change in charges when halogen is replaced by hydroxyl in these compounds, for the bond between carbon and oxygen (of hydroxyl) to be non-polar in character. If this is done, then the phenomenon of oxidation in organic compounds would possess

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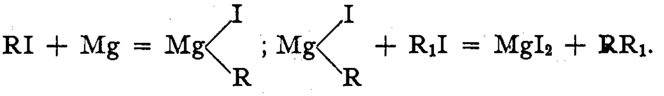
[1] Practically every modern text-book of inorganic or analytical chemistry, which takes up these relations uses the change in electrical charges as the principle underlying the phenomena of oxidation and reduction. The treatment given by Stieglitz in his "Qualitative Analysis," Vol. I, Chapter 14, is particularly clear and instructive.

[2] Cf. IV paper of this series, p. 1816, as well as the work of Stieglitz, Selivanow, W. A. Noyes, and others there referred to.

[3] Cf. Treadwell-Hall, "Qualitative Analysis" (1911), p. 3, and other text-books.

an entirely different significance from that which it does in inorganic reactions. On the non-polar view, chlorination consists of a simple replacement of hydrogen by chlorine, oxidation would then consist of a simple replacement of hydrogen by hydroxyl (or oxygen), and the series of transformations methane ⟶ methyl alcohol ⟶ formaldehyde ⟶ formic acid ⟶ carbon dioxide, for example, would represent replacements with no change in the charge of the carbon. Such a view is evidently untenable, if only because of the artificial differentiation between reactions, some of which, for convenience of treatment, are classed with organic compounds, others with inorganic compounds, which it introduces, and the absolutely separate characterization of reactions involving oxidation for organic and inorganic substances as distinct and unrelated phenomena.

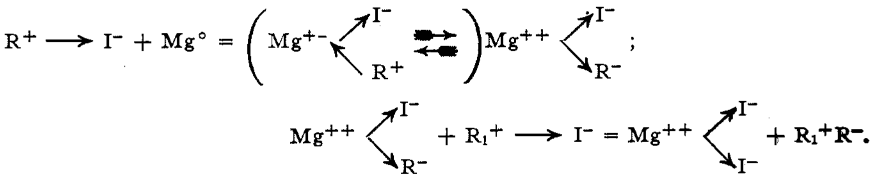
It is also of interest to study some specific substance or reaction in order to determine whether the dualistic polar and non-polar valence view, or the unitary polar valence view will supply the more satisfactory classification. In the simple hydrocarbons and their halogen derivatives, the dualistic view assumes non-polar valences.[1] The transformations which these substances undergo in the Grignard reaction, may therefore be chosen as a test. Here the reaction may be formulated in the most general form as follows:



$$\mathrm{RI} + \mathrm{Mg} = \mathrm{Mg}\Big\langle\begin{matrix}\mathrm{I}\\ \mathrm{R}\end{matrix}\ ;\ \mathrm{Mg}\Big\langle\begin{matrix}\mathrm{I}\\ \mathrm{R}\end{matrix} + \mathrm{R_1I} = \mathrm{MgI_2} + \mathrm{RR_1}.$$

In this reaction, omitting the action of the solvent or other catalytic agent, the change consists of RI and R_1I, both with non-polar valences on the dualistic view, reacting with the element magnesium to form non-polar, RR_1 and magnesium iodide. The latter substance must surely be assigned polar valences.[2] It is, therefore, necessary to assume a change at some stage in the character of some of the valences in the reactions, but no indication is apparent when this change is to be assumed. That the magnesium iodide may act as an electrolyte surely cannot be taken as an indication when this change takes place, since this is an effect and not the cause.

Take, on the other hand, the polar view of valence in this reaction; then the following formulation may be given:



$$\mathrm{R^+} \longrightarrow \mathrm{I^-} + \mathrm{Mg^\circ} = \left(\mathrm{Mg^{+-}}\Big\langle\begin{matrix}\nearrow \mathrm{I^-}\\ \nwarrow \mathrm{R^+}\end{matrix} \ \rightleftarrows\right)\mathrm{Mg^{++}}\Big\langle\begin{matrix}\nearrow \mathrm{I^-}\\ \searrow \mathrm{R^-}\end{matrix}\ ;$$

$$\mathrm{Mg^{++}}\Big\langle\begin{matrix}\nearrow \mathrm{I^-}\\ \searrow \mathrm{R^-}\end{matrix} + \mathrm{R_1^+} \longrightarrow \mathrm{I^-} = \mathrm{Mg^{++}}\Big\langle\begin{matrix}\nearrow \mathrm{I^-}\\ \searrow \mathrm{I^-}\end{matrix} + \mathrm{R_1^+R^-}.$$

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[1] Bray and Branch, *Loc. cit.*, p. 1443.

[2] *Ibid.*, p. 1442.

The first action consists of the combination of R^+I^- and atomic uncharged magnesium. The latter is indicated by the symbol Mg° in order to bring out more clearly the change which it undergoes in the course of the reaction. The possible intermediate product $Mg^{+-}\begin{matrix}\nearrow I^- \\ \nwarrow R^+\end{matrix}$, is given in the equation for the sake of completeness and to make the electrical character of the change involved clearer, but no stress is laid on the formulation of this hypothetical substance. The first definite product formed is represented by $Mg^{++}\begin{matrix}\nearrow I^- \\ \searrow R^-\end{matrix}$[1] The formation of this compound involves a change in the electrical character or valence of the magnesium and of one of the atoms of group R. As represented in the equation, the magnesium is oxidized, its valence changing from 0 to +2, and a carbon atom of the group R reduced two units of valence. The next reaction is a simple metathesis with the formation of magnesium iodide and $R_1^+R^-$. With the polar view of valence, no assumption as to a change in the nature of the valences is necessary, and it seems much simpler and more satisfactory to follow the transformations from this point of view than with the combination of the two kinds of valence, polar and non-polar.

Other examples of the Grignard reaction might be cited to illustrate the arbitrary nature of the changes which it would be necessary to assume in the character of the valences of the atoms undergoing change if the dualistic valence view be adopted. Other reactions also show this, the Würtz synthesis being a particularly instructive type of reaction. The reaction here may be written

$$2RI + 2Na = RR + 2NaI.$$

On the dualistic view, the sodium iodide contains polar valences, the

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[1] The reasons for giving the bonds the directions indicated, or for considering the electrical charges distributed as shown, have been given in some detail in the previous papers of this series. Briefly summarized, the principles employed are based upon the arrangement of the elements in the periodic system, in the horizontal groups the elements of smaller atomic weight tending to give up corpuscles in forming chemical bonds to the elements of higher atomic weight, while in the vertical groups, those of higher atomic weight give up corpuscles (are more positive) to those of lower atomic weight. These rules may only be looked upon as general guiding principles, in particular the main and sub-groups of the vertical series must be treated separately. The phenomenon of ionization in solution with those compounds for which it has been observed, furnishes an invaluable experimental method for determining the distribution of the electric charges. Caution must be exercised, especially with organic compounds where isomeric substances exist in which the isomerism may be taken to depend upon different directions of the valences. The general principles outlined apply to the more stable linkings between atoms, while the less stable linkings may be present in isomeric substances showing less stability. This question has been discussed more fully in the previous papers.

RI and RR non-polar valences. Here also, as in the Grignard reaction, the question as to when the iodine changes its valence from the non-polar to the polar kind remains unanswered. On the polar view of valence, the reaction is formulated

$$2R^+ I^- + 2Na^\circ = R^+ R^- + 2Na^+I^-.$$

The change is seen to consist of the oxidation of the sodium, its valence changing from 0 to +1, and the reduction by two units of valence of one of the carbon atoms of one of the two molecules of reacting RI. The character of the iodine remains unchanged. The sodium in this reaction (as also the magnesium in the Grignard reaction) plays an analogous part to its behavior in purely inorganic reactions in which it is oxidized from the metallic state, at the same time causing a reduction of one or more atoms in some other substance. The only difference lies in the fact that these oxidation and reduction changes are not as apparent and as easily followed with carbon compounds as with some inorganic compounds. Fundamentally, however, there is no reason to assume a difference. Similar relations hold true for other organic reactions. In fact, in the experience of the writers, every organic reaction can be interpreted simply and satisfactorily and brought into relationship with the reactions of inorganic chemistry by using polar valences, while the use of the dualistic view involving polar and non-polar valences introduces arbitrary and unnecessary complications in following the chemical reactions. Other reactions will not be considered here, but will be presented in extended form in another connection.

A possible way out of the difficulties involved in the dualistic view is contained in the paper by Bray and Branch and also in a paper by Lewis.[1] They assume the same compound or grouping to contain at one time polar valences and at another time non-polar valences. No direct evidence can, of course, be presented against such a view, and it might serve a useful purpose if it were possible to determine the conditions of such hypothetical changes, but until this has been done, it appears to add only a further arbitrary complication to the consideration of valence structures. Ionization in solution is of the greatest value in determining the distribution of electric charges in substances which ionize, but, on the other hand, the absence of ionization must not be taken as evidence regarding the presence or absence of polar valences. The phenomenon of ionization depends to a great extent on the nature of the solvent[2] and there is no evidence which leads us to suppose that the presence or absence of the property of ionization of substances depends altogether on the presence of polar or non-polar valences in them or on the nature of the linking between the atoms as presumed in the dualistic view.

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[1] THIS JOURNAL, 35, 1449 (1913).

[2] Cf. Walden, THIS JOURNAL, 35, 1649 (1913).

It will be seen, therefore, that the dualistic view of valence introduces complications in the theoretical treatment of chemical reactions which may be avoided to a great extent if the unitary polar valence view be adopted throughout. The positive results which have been obtained with the unitary view must also be emphasized. The work of Stieglitz[1] must be mentioned especially in this connection. Not the least important feature of this view is the possibility of grouping together all chemical phenomena. The IV Paper of this series dealt especially with this point of view and the Classification of Chemical Reactions developed there shows how the principles may be applied to organic as well as to inorganic reactions.

Finally, therefore, the relations pointed out in this paper and a number of other facts, some of which have been mentioned in the previous papers, have convinced the writers that the polar view of valence (or the valence view which considers chemical bonds to be formed by the transfer of corpuscles between atoms) is sufficiently broad to enable a satisfactory classification of valence phenomena to be developed at present, and it is this fact which it is desired to emphasize in this paper in contradistinction to the classification of Bray and Branch which involves both polar and non-polar valences. Especially in oxidation and reduction reactions with organic as well as with inorganic compounds does the unitary view, in which the changes are assumed to depend upon the electrical charges of the atoms, show a simpler and more satisfactory classification than does the dualistic view which leads to contradictions or to an arbitrary separation of phenomena fundamentally similar.

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The Nature of the Forces Holding Atoms in Combination.—The magnitude of electrical forces in comparison with that of gravitation, which seems to be the other force most worthy of consideration, makes it seem quite improbable that the atoms of such compounds as hydrochloric acid, hydriodic acid and water are held together by electrical forces while those of methane and ethane are held by gravitation or some other non-electrical force. From the experiments of E. C. Franklin, especially, it seems quite clear that we have positive hydrogen and negative amide, NH_2, in ammonia, just as we have positive hydrogen and negative hydroxyl in water. There is considerable evidence that acetylene, $H—C{\equiv}C—H$, contains positive hydrogen but, if this is true, it is hard to believe that ethane, $H_3C—CH_3$, from which it can be obtained by simple reactions, does not also contain positive hydrogen.

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[1] Stieglitz and Curme, *Ber.*, 46, 911 (1913). Curme, THIS JOURNAL, 35, 1143 (1913). Cf. also W. A. Noyes, THIS JOURNAL, 35, 767 (1913) and the references to the work of others along similar lines given there.