[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

VALENCE AND TAUTOMERISM.

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I have had the pleasure of reading in manuscript the preceding paper by Professor Bray and Mr. Branch, and I am glad to have the opportunity of opening the discussion which their interesting article is sure to excite. There is always the danger in scientific work that some word or phrase will be used by different authors to express so many ideas and surmises that, unless redefined, it loses all real significance. Thus the term valence has been used in discussing a large number of ideas which perhaps have nothing more in common than the acceptance of Dalton's law of multiple proportion. Even the conception of valence as an integral number has been abandoned by those who speak of "partial valence."

Out of the haze of valence theory two separate ideas stand forth prominently. Bray and Branch have performed an important service to theoretical chemistry in differentiating these two ideas and in suggesting a terminology which adequately expresses the distinction. I adopt their terms valence number[1] and polar number, the former a pure integer, the latter a positive or negative integer, and shall attempt to show that it is possible to distinguish between the two even more completely than they have done. In terms of theory the valence number is the number of positions, or regions, or points (bond-termini) on the atom at which attachment to corresponding points on other atoms occurs; the polar number is the number of negative electrons which an atom has lost (in an algebraic sense). Now these two conceptions are radically distinct, and even if our theories should be expressed in some other form, the difference in character of these two numbers could not disappear.

Polar and Non-polar Combination.—The independence of these two conceptions, valence number and polar number, is, I believe, even more complete than Bray and Branch have considered it to be. Apparently we must recognize the existence of two types of chemical combination which differ, not merely in degree, but in kind. To illustrate the two types we may choose a salt such as potassium chloride, and a paraffin hydrocarbon such as methane. The first type may be called polar, the second non-polar.

The first important difference between the two types would be expressed if we should designate them as *mobil* and *immobil*, instead of polar and non-polar. To the non-polar, immobil class belong the characteristic organic compounds that are unreactive, inert, and slow to change

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[1] Bray and Branch sometimes use "total valence number" instead of "valence number." I have avoided the former, not merely for the sake of brevity, but because the word "total" may lead to certain false implications.

into more stable forms, as evidenced by the large number of separable isomers. Inorganic compounds, on the other hand, approach more frequently the ideal polar or mobil type, characterized by extreme reactivity.[1]

To both types of compounds we should ascribe a sort of molecular structure, but this term doubtless has a very different significance in the two cases. To the immobil compounds we may ascribe a sort of *frame* structure, a fixed arrangement of the atoms within the molecule, which permits us to describe accurately the physical and chemical properties of a substance by a single structural formula. The change from the non-polar to the polar type may be regarded, in a sense, as the collapse of this framework. The non-polar molecule, subjected to changing conditions, maintains essentially a constant arrangement of the atoms; but in the polar molecule the atoms must be regarded as moving freely from one position to another, falling now into one place, now into another, like the bits of glass in a kaleidoscope.

In the strictly non-polar type of compounds the phenomenon of tautomerism between two forms, without the intervention of a polar form, is probably unknown. Only when the compound assumes at least in part the polar form does tautomerism occur. It is, of course, to be understood that a given molecule may be polar in one part, non-polar in another. Thus in the majority of tautomeric organic molecules the polar condition presumably prevails only in certain regions, for example in the neighborhood of a nitrogen or an oxygen atom. In the well-known cases of organic tautomerism the compound behaves as though it were a mixture of two different substances in mobil equilibrium. This, however, is the same phenomenon as appears in more exaggerated form in almost all inorganic compounds, where the molecule varies, not between two, but perhaps between dozens of possible forms. Thus we may account for the signal failure of structural formulae in inorganic chemistry.

An evidence of, perhaps indeed a cause of, the mobility of polar compounds, is the freedom of one especially important atom, the atom of electricity or the electron, to move from one position to another. This mobility of the electron is responsible for the striking electrical properties of polar substances. The typical polar compounds are the typical electrophiles.[2] The assumption that in a polar compound free charges exist

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[1] It must not be assumed that any one compound corresponds wholly and at all times to either one type.

[2] An electrophile is defined by Lewis and Wheeler (*Proc. Amer. Acad.*, 41, 419 (1906)) as a substance which in the pure state is an electrolytic conductor, which ionizes when dissolved in other solvents, and which permits the ionization of other substances dissolved in it. Sodium chloride is a strong electrophile; water, acetic acid and ammonia are weaker electrophiles; ether and benzene are very poor electrophiles.

There is evidence that the neighborhood of other polar combinations increases the at certain points in the molecule explains not only the tendency of these substances to form ions, but also their high dielectric constant.[1]

A neutral body which is oppositly charged at opposit ends will attract a similar body. We should therefore expect polarized molecules to unite more or less firmly with one another to form molecular complexes. The formation of the so-called molecular compounds is unknown among strictly non-polar substances. Among polar substances, not only are many complex molecules known, composed of different polar units, but polar molecules of the same kind combine to cause the phenomenon known as association. Thus, for example, the order in the series methane, ether, alcohol, acetic acid, water, represents the order not only of increasing association, but also of increasing tendency to assume the polar form.

To illustrate the foregoing remarks let us compare the two molecules Cl_2 and I_2.[2] We should expect iodine, as the more positive element, to lose an electron more readily, and this is evidently the case. Indeed liquid iodine is not only an ionizing solvent, but is itself in the pure state a conductor of electricity,[3] showing in all probability the presence in appreciable amount of the ions I^+ and I^-. Iodine, moreover, is decidedly a more mobil compound than chlorine, taking part more rapidly in a large number of reactions, in most of which, however, the actual driving force of the reaction, as measured by the free energy change, is greater in the case of chlorine. Finally iodine shows a far greater ability to form molecular compounds, such, for example, as the polyiodides.

Polar.	Non-polar.
Mobil	Immobil
Inert	Reactive
Condensed structure	Frame structure
Tautomerism	Isomerism
Electrophiles	Non-electrophiles
Ionized	Not ionized
Ionizing solvents	Not ionizing solvents
High dielectric constant	Low dielectric constant
Molecular complexes	No molecular complexes
Association	No association
Abnormal liquids	Normal liquids[4]

tendency toward polarity. Thus we may account for the high ionizing power of polar solvents, and also for the fact pointed out by Abegg and Bodländer that a complex ion has invariably a higher "electro-affinity" than the simple ion from which it is made.

[1] The dielectric constant of a medium depends on the number of free charges and the distance that each charge can move when an electric field is applied. In a polarized molecule the motion of the charges in an electric field is doubtless to be ascribed primarily to the rotation of the molecules as they acquire a more stable orientation.

[2] The assumption of a polar form for elementary chlorine was, I believe, first made by W. A. Noyes and A. C. Lyons (THIS JOURNAL, 23, 463 (1901)).

[3] Lewis and Wheeler, *loc. cit.*

[4] A normal liquid is one that obeys the laws of corresponding states, etc.

The properties of the polar and non-polar types of combination which have been pointed out in the paper of Bray and Branch and in this paper may be summed up in the preceding table.

Valence Formulas.—The application of the idea of valence number to typical non-polar compounds presents no inherent difficulties. It is in fact the idea upon which the whole of structural organic chemistry is based. We need only assume that upon each atom there are definit regions, or points, at which direct connection to similar points on other atoms may be made, and that the number of occupied regions on a given atom is the valence number of that atom. We thus visualize a structure in which each atom is tied directly to one or more other atoms at one or more points. One such point or region can be attached to one and only one point of another atom or atoms. According to this view such terms as partial or distributed valences have no significance. In some compounds it may be difficult to determin beyond reasonable doubt the actual valence number of the atoms, for the valence number of an atom in a given compound need not be the maximum valence number exhibited by the atom in other compounds. Thus we may, as is commonly done, assign to carbon the valence number two in carbon monoxide, and three in triphenylmethyl. In the case of benzene we may attribute to each carbon atom the valence number three or four, according as the properties of benzene seem to point to the single bonding of the atoms in the ring or to the double bonding of alternate pairs.

Turning now to the condensed structure, if structure it be called, of the polar compounds, it is evident that the prime consideration is the distribution of electrons in the molecule, or in other words the polar number of each atom. Thus in sulfuric acid we assign to each hydrogen atom the polar number $+1$, to each oxygen atom, -2, and to the sulfur, $+6$. Since we are dealing with a neutral molecule all the polar numbers add to zero. Oxidation of any element means an increase of its polar number, reduction means a decrease, and this simple system furnishes an adequate method of dealing with all cases of oxidation and reduction. It must be remarked, however, that on account of its very generality this system would apply equally well even if purely fanciful values of the polar number were chosen, provided that the rules required by the fundamental law of the conservation of electricity be observed. Moreover, non-polar compounds may be treated provisionally as polar, and fictitious polar numbers may be assigned without leading to any false conclusions.

The mere statement of the polar numbers tells nothing about the structure of the molecule. The difficulty has already been mentioned of representing by a single graphical formula a polar substance of which the molecules are probably alternating between numerous tautomeric forms. But the question remains as to whether it is possible, by means of any of the various structural formulas which have been suggested, to represent even a single one of these momentary polar states through which the molecule passes. In answering this question I must take issue with Bray and Branch who make use of various "bond" formulas as well as the valence number in discussing polar compounds. This procedure seems to me undesirable for the following reasons.

Assuming that the main forces holding together a polar compound are the forces of electrical attraction between free positive charges in one atom and free negative charges in another, Bray and Branch, following Falk and Nelson,[1] would write the formula of potassium chloride $K \longrightarrow Cl$, where the arrow or "polar bond" indicates that one electron has passed from K to Cl. They would assign to each atom in this compound the valence number one. Now such a system, which might be satisfactory enough if we had no more complicated cases than this to deal with, fails entirely in the case of a compound involving several atoms and electrons. The arrow purports to show between which atoms an electron has passed, but since all electrons are alike, and presumably leave no trail behind them, we cannot say that atom A loses an electron to atom B and atom C to atom D, but only that atoms A and C have each lost an electron and atoms B and D have each gained one. Thus, for example, the formula which Bray and Branch suggest as one possible form of hydrogen peroxide,

$$H \longrightarrow O \rightleftarrows O \longleftarrow H,$$

seems to have no meaning. It indicates that one atom of oxygen has given an electron to another, but has received one in return. Even supposing that the electron which returns goes to another part of the oxygen atom than that from which it departed, the formula would still mean nothing more than the formula

$$H \longrightarrow O\downarrow \quad \uparrow O \longleftarrow H$$

where the vertical arrows would indicate that an electron in each oxygen atom has moved from one position to another, so that each acquires thereby a positive charge at one point and a negative charge at another; but when written in this way the molecule is not bonded together!

If, on the other hand, the arrow merely indicates which atoms are bound together by the electric forces, this representation is equally misleading; for a positive charge does not attract one negative charge only, but all the negative charges in its neighborhood. Consider the compound H_2F_2; it seems extremely likely that it must assume, occasionally at least, the symmetrical form

$$\begin{array}{ccc} & F^- & \\ H^+ & & H^+ \\ & F^- & \end{array}$$

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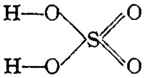
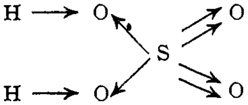
[1] Falk and Nelson, THIS JOURNAL, 32, 1637 (1910).

and yet such a form can in no way be expressed in terms of "polar bonds."

Compared with hydrofluoric acid sulfuric acid has a decidedly greater tendency to assume a non-polar form, and such a formula as



may retain much significance even when the molecule becomes partly polar (that is, polar in certain regions). But the formula



seems to be fundamentally erroneous, partly for the reasons already given and partly because such a formula leads to artificial distinctions in groups of entirely analogous compounds. Thus just as the oxide of hydrogen combines with other oxides to form acids, so the hydrogen halides combine with other halides to form similar acids. For example, completely analogous to boric and silicic acids are hydrofluoboric and hydrofluosilicic acids, $HFBF_3$ and $(HF)_2SiF_4$, but the latter compounds can in no way be represented by valence formulas.[1] It is best to use a less pretentious formula such as H_2SO_4, or the old Berzelius form, H_2OSO_3, rather than one that leads to such unjustified distinctions.

Even considering hydrates only, we find that for some a valence formula can be written but not for others. Thus for the bases BaO and $BaOH_2O$ such formulas may be written, but not for the very firm compound $BaO(H_2O)_2$. If we examin the following series of hydrates of similar metallic oxides, stable at ordinary temperature, namely, $BaO(17H_2O$ or $9H_2O)$, $SrO(9H_2O)$, $CaO(2H_2O)$, $MgO(1H_2O)$, $CuO(1H_2O$ or zero $H_2O)$, $HgO($zero $H_2O)$, we observe that the order is precisely that of the decreasing polarity of the oxides, that is, of the decreasing electrode potentials of the metals. It is evident that the addition of water in no way depends upon the possibility of writing a valence formula.

Polar Structure.—We have already considered the polar compound as a loose, mobil aggregate, varying rapidly between a number of tautomeric forms.[2] Hence we can rarely regard a polar compound as a pure

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[1] For a masterly presentation of many of the arguments against the valence formulas of polar compounds see Werner (*Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*). Werner does not distinguish between polar and non-polar compounds and therefore argues against the valence formula in general, but it will be noted that his arguments are based upon examples chosen from among polar compounds only.

[2] It would be an interesting although doubtless an extremely difficult task to determin under given conditions the fraction of the molecules existing in each of the chief polar forms. A similar problem arises when the molecules are sometimes polar and sometimes non-polar. In this case it is not unlikely that we already possess a quanti-

compound in the same sense that we can a non-polar compound, all of the molecules of which are essentially alike in form. But there is one condition, the crystallin, in which the molecules of a polar compound undoubtedly approach very closely to complete uniformity of type, for owing to the mutual insolubility of crystallin solids of different form, a substance in this state is one of the pure tautomers. An interesting illustration is offered by the substance known as thallic iodide, but which in the solid state is isomorphous with caesium and rubidium triiodides, and therefore must be regarded in the solid form as pure thallous triiodide. A study of the crystallin form of a polar compound may give some clue as to the ultimate form of the molecule. Further information may doubtless be obtained by a study of "Reststrahlen" and other phenomena depending upon the proper oscillation of the atoms within the molecule, for such investigation will tell us the distribution of the electrons among the atoms of the molecule.

In the mobil structure of the polar compound it might be predicted that at times some one atom would acquire paramount importance and act as a center about which the other atoms would group themselves. That such is indeed the case has been shown almost beyond question by the researches of Werner, and we must consider Werner's theory of the coördination numbers as the most important principle at present available for the classification of polar compounds.

A Third Type of Chemical Compound.—To the polar and non-polar types of chemical compound we may add a third, the metallic. In the first type the electrons occupy fixed positions within the atom. In the second type the electrons move freely from atom to atom within the molecule. In the third or metallic type the electron is free to move even outside the molecule. For the classification of the metallic compounds or alloys no principle of far-reaching importance has as yet been discovered. It is interesting to observe that just as tautomerism occurs between polar and non-polar compounds so it occurs likewise between polar and metallic compounds. Perhaps the most interesting case of such tautomerism which has hitherto been observed is one discovered by Kraus,[1] who found that the metallic compound $NaPb_2$, when present in dilute solution in liquid ammonia, is a pure electrolyte of which the ions are Na^+ and Pb_2^-. When electrolyzed between lead electrodes this metal

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tative solution of the problem in an important class of compounds. It seems reasonable to suppose that the low degree of ionization of a weak acid, such as acetic acid, is due to the existence of a large percentage of non-polar molecules. If we assume that the polar molecules are ionized to the same extent as a strong electrolyte, such as potassium chloride, then the ratio of the degrees of dissociation of the weak and of the strong electrolytes (at the same ion concentration) is the fraction of the weak electrolyte existing in the polar state.

[1] Kraus, This Journal, 29, 1562 (1907).

dissolves at the cathode and is precipitated at the anode, two gram-atoms of lead being thus transferred for each Faraday equivalent. In more concentrated solutions the metallic character comes into evidence, and the conductivity is in part electrolytic and partly electronic.

All known chemical compounds may be grouped in the three classes: non-polar, polar and metallic; except in so far as the same compound may in part or at times fall under two of these groups.

POTASSIUM AMMONOMAGNESATE, $Mg(NHK)_2.2NH_3$.

BY EDWARD CURTIS FRANKLIN.

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Introduction.

It will be recalled that the writer and his collaborators have shown that just as zinc hydroxide and lead-hydroxide dissolve in aqueous solutions of the aquo base, potassium hydroxide, to form potassium zincate and potassium plumbite, respectively, so similarly zinc amide and lead imide are acted upon by liquid ammonia solutions of the ammono base, potassium amide, to form potassium ammonozincate,[1] $Zn(NHK)_2.2NH_3$, and potassium ammonoplumbite,[2] $PbNK.2^1/_2NH_3$; thus showing that the amphoteric properties of zinc and lead hydroxides are carried over into the corresponding derivatives of the ammonia system.[3]

It has been a matter of some surprise, however, to find that cadmium and copper, metals whose hydroxides are not known to exhibit amphoteric properties,[4] form respectively potassium ammonocadmiate,[5] $Cd(NHK)_2.2NH_3$, and potassium ammonocuprite,[6] $CuNK_2.4NH_3$, and that thallous nitride, the ammonia analog of the strong base forming thallous oxide, dissolves in liquid ammonia solutions of potassium amide to form potassium ammonothallite,[7] $TlNK_2.4NH_3$. All these compounds, excepting potassium ammonocadmiate, which is amorphous or at best microcrystallin, have been obtained beautifully crystallized and of sharply definit composition, while it will be recalled that, generally speaking, only indifferent success has attended the many efforts to obtain the corresponding aquo compounds from aqueous solution.[8]

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[1] THIS JOURNAL, **29**, 656, 274 (1907).

[2] *J. Physic. Chem.*, **15**, 509 (1911).

[3] For a systematic exposition of the writer's ammonia system of acids, bases and salts, cf. *Am. Chem. J.*, **47**, 285 (1912).

[4] The fact is noted, however, that the preparation of a sodium cuprate of the formula $Cu(ONa)_2$, is recorded in the literature, *Z. anal. Chem.*, **9**, 463 (1870). Furthermore, it is well known that without exception metallic oxides are soluble in fused potassium hydroxide.

[5] Prepared by G. S. Bohart in the laboratory of the Leland Stanford Junior University. Experimental results not yet published.

[6] THIS JOURNAL, **34**, 1501 (1912).

[7] *J. Physic. Chem.*, **16**, 682 (1912).

[8] Comey and Jackson, *Am. Chem. J.*, **11**, 145 (1894); Woods, *J. Chem. Soc.*, **97**, 878 (1910); Hantzsch, *Z. anorg. Chem.*, **30**, 289 (1902).