the dissociation theory, especially if, in addition, the explanation, which has just been mentioned, is accepted.

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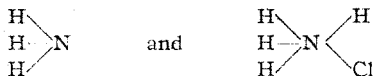
VALENCE AND TAUTOMERISM.

BY WILLIAM C. BRAY AND GERALD E. K. BRANCH.

CONTENTS.—1. Two Valence Numbers, Polar and Total. 2. A Method of Classifying Tautomeric Changes.

So much has been written on valence and tautomerism that we are making, with some hesitation, an attempt to state certain ideas in simple language, and in a way which we hope will be acceptable to organic, inorganic and theoretical chemists. In the present brief paper we shall not attempt to trace the historical development and we cannot hope properly to assign credit for the various ideas. We wish, however, to mention that these subjects have often been discussed in the colloquiums at the Massachusetts Institute of Technology and at the University of California, and that we are indebted in particular to Professor G. N. Lewis for his suggestions and criticisms.

Polar Number and Total Valence Number.—In the first place, it is necessary to differentiate the two ideas embodied in the term valence number, each of which is frequently emphasized to the exclusion of the other. We suggest that these be distinguished by the names *polar* number and *total* valence number. The latter, alone, is met with in elementary organic chemistry; and the former is becoming more and more popular in elementary inorganic chemistry.

The difference between the two ideas may be illustrated by means of ammonia and ammonium chloride. Many organic chemists insist that the valence numbers of the nitrogen in these compounds are 3 and 5 respectively, and thus emphasize the total number of valence bonds of the nitrogen, as illustrated by the following structural formulas:

$$
\begin{array}{ccc}
\begin{array}{l} H \diagdown \\ H - N \\ H \diagup \end{array}
&
\text{and}
&
\begin{array}{l} H \diagdown \quad \diagup H \\ H - N \diagup \diagdown \\ H \diagup \quad \diagdown Cl \end{array}
\end{array}
$$

On the other hand, many inorganic chemists consider that it is more important to emphasize the relationship between ammonia and ammonium chloride, and insist that the valence number of the nitrogen is —3 in both cases. From this point of view the valence number of hydrogen in its compounds is in general +1, that of chloride chlorine is —1, and that of nitrogen is —3 in ammonia, ammonium ion, or any ammonium salt.

Many of the misunderstandings which have arisen in this matter seem to us to be due to the failure to recognize that two separate ideas are in-

volved, namely, that of polarity and that of the total number of bonds. The latter idea has probably the better right to the name valence; but the polarity idea is of so great value in elementary inorganic chemistry that it is doubtful if the term valence could be ousted from the text-books. It therefore seems advisable to retain the term valence[1] for the two ideas, and to use the distinguishing terms *polar* number and *total* valence number whenever necessary. The valence of nitrogen in ammonium chloride can then be completely described as $(-3, 5)$, where, for convenience, the *polar number* is placed first.

The number of teachers[2] who use what we have called polar number in elementary inorganic chemistry is rapidly increasing, and as far as we can ascertain, all who have tried it are enthusiastically in favor of its adoption. The polar number of any element in a compound can be determined whenever the polar numbers of all the other elements are known simply by considering the sum of all the polar valences—as illustrated by the following examples:

$$\begin{cases} NH_4Cl \\ x + 4 - 1 = 0 \end{cases} \quad x = -3 \text{ for nitrogen,}$$

$$\begin{cases} KMnO_4 \\ 1 + x - 8 = 0 \end{cases} \quad x = +7 \text{ for manganese,}$$

$$\begin{cases} MnO_4^- \\ x - 8 = -1 \end{cases} \quad x = +7 \text{ for manganese.}$$

The great value of this idea lies in the simplification of the teaching of oxidation—reduction reactions. Thus in the reduction of permanganate ion, MnO_4^-, in acid solution, to manganous ion, Mn^{++}, there is a decrease in the polar number of 5 for each atom of manganese; and the equivalent amount of ferrous ion which can be oxidized is evidently $5Fe^{++}$, since there is an increase of 1 in the polar number in the oxidation of Fe^{++} to Fe^{+++}. The equation, balanced with respect to oxidation and reduction changes, thus becomes

$$MnO_4^- + 5Fe^{++} + mH^+ = Mn^{++} + 5Fe^{+++} + nH_2O$$
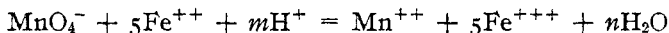
and the methods of determining m and n are obvious.

All mention of total valence can, if desired, be omitted in elementary inorganic chemistry, and this involves also the omission of structural formu-

[1] Strictly speaking the term valence should be used only as a number, but it is also frequently employed to express the idea of the nature of the union between atoms. To avoid ambiguity we have used in general the redundant term valence number; but ordinarily the word number can be omitted.

[2] Polar number is snyonomous with "Wertigkeit" as used by Boettger in the third edition of his "Qualitative Analyse," pp. 97–100 (1913). The idea of positive and negative valence numbers has been used for several years by the authors and by many chemists of their acquaintance. One of the earliest and clearest statements of this idea and of its application in balancing oxidation—reduction equations was made by Prescott and Johnson in the fifth edition of their "Qualitative Analysis," pp. 238–242 (1903).

las. But in more advanced courses it is necessary to use the two valence ideas and it seems desirable to represent both of them in structural formula. Two methods of formulation which have been suggested are illustrated by the following formulas for ammonium chloride:
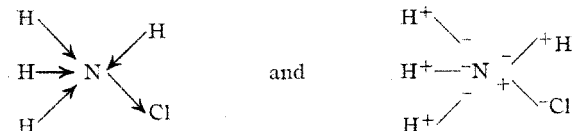
The first method is that used by Falk and Nelson[1] and Falk,[2] and the second by Fry,[3] in recent papers on the "electron conception of valence." Either method is satisfactory, but Falk's arrow method seems to be more convenient. We consider that these structural formulas will prove of great value in many cases. They might even be used as a means of representing empirically the polar number of each of the atoms in the compound, without introducing the idea that an electron has moved in the direction of the arrow from one atom to another.

Such an attempt to treat the matter empirically however, is very similar to the refusal to admit the reality of atoms and molecules, and is hardly necessary at the present time. The evidence in favor of the existence of the electron and of atoms and molecules is now almost as conclusive as we can desire. Also it is no longer necessary to apologize when stating that the chief reaction in the union of sodium and chlorine is the passing of an electron from the sodium atom to the chlorine atom, and that consequently the forces that hold together the atoms of sodium chloride are largely electrical in nature. We believe, therefore, that chemists in general are ready to adopt the electron conception of atomic union in the case of most inorganic compounds; and in these cases the polar number and the total valence number of the different atoms may be determined and represented as we have indicated.

It is, however, doubtful whether the advocates of the electron conception of valence are justified in applying it in all cases. Thus, in a saturated hydrocarbon, the problem of assigning the proper polar valences to the individual carbon atoms is unsolved at present. This fact alone seems to nullify the significance of any attempt to apply the electron conception of valence in such cases. It seems, in fact, more reasonable to admit the possibility also of non-polar bonds, such as are ordinarily used by organic chemists.

Striking difficulties are also encountered when such formulas as the following are assigned to methane and carbon tetrachloride:

[1] Falk and Nelson, THIS JOURNAL, **32**, 1637 (1910).
[2] Falk, *Ibid.*, **33**, 1140 (1911).
[3] Fry, THIS JOURNAL. **34**, 664 (1912); *Z. physik. Chem.*, **76**, 385 (1911).

There is evidently no such difference between these substances as between the corresponding nitrogen compounds, ammonia and nitrogen trichloride, and certainly no such difference as might be expected between compounds containing carbon with valences of (—4, 4) and (+4, 4). Furthermore, if the nature of the bond between carbon and chlorine in carbon tetrachloride is exactly the same as between sodium and chlorine in sodium chloride, we should expect to find a less striking difference in the properties, such as the power of ionization. The behavior of these compounds suggests, in fact, that the valence of carbon is (o, 4) in both cases, or, in other words, that the polar valence of carbon need not be considered.[1]

We are accordingly in favor of adopting the ordinary organic structural formulas, and of altering them only at the bonds where there is definit evidence as to the polar nature of the union. Polar and non-polar bonds[2] may thus appear in the same formula. Such cases will be met with in organic acids and bases and in organic derivatives of such elements as nitrogen and sulfur.

In the preceding paragraphs we have suggested that there are two distinct types of union between atoms: polar, in which an electron has passed from one atom to the other, and non-polar, in which there is no motion of an electron. It seems probable that these types are limiting cases, and that most examples are actually intermediate in character, i. e., intermediate in the sense that, for each pair of atoms in a compound, the electron has actually passed from one atom to the other in a definit fraction of the total number of molecules. This implies, of course, that the electrons are continually in motion within the molecules.

This view leads to the grouping of substances into two general classes, according as the valence bonds are chiefly polar or non-polar in nature. The first class is characterized by high dielectric constants, the power of forming ions, and high chemical reactivity; and the second class by the opposit properties. This classification corresponds roughly to the division into inorganic and organic compounds. Further characteristics of the non-polar type are the ability to form chain compounds, and the existence of separable isomers. The far-reaching character of this classification is a strong argument in favor of the existence of the non-polar, as well as the polar type of union between atoms.

[1] If in these compounds the polar number of carbon is taken as zero, then that of hydrogen and chlorine is evidently also zero.

[2] It is scarcely necessary to point out that the polar number of an atom in a compound does not signify the total number of its polar bonds, but is the algebraic sum of these.

In the present brief paper we shall not attempt to discuss Werner's extensive investigations. Such a discussion would involve a careful consideration of the evidence with respect to the nature of the polar and non-polar bonds in the compounds, and of the relation of the "polar number" and "total valence" of the central atom to its "coördination number." The idea contained in coördination number is a new one adopted to express a large number of additional experimental facts, and would not be essentially altered by restatement in the language used in this paper.

A Method of Classifying Tautomeric Changes.—Tautomerism furnishes some interesting illustrations of the usefulness of considering both valence numbers. The idea of tautomerism was introduced when it was found that the properties of certain substances could be expressed completely only by means of two (or more) formulas. Chemists are now united in considering that the different tautomeric forms of a substance actually exist in equilibrium with each other in the fluid state, and that the transformation of one form into another takes place rapidly. A consideration of the nature of the valence changes in these tautomeric reactions leads to a classification into two groups:

A. Those in which no change of polar numbers is involved.

B. Those in which the polar numbers of two elements are altered.

All the familiar cases of tautomerism in which a hydrogen atom shifts from one part of the molecule to another belong to type A, which does not involve any change of polar number. This group may be further divided into classes according as the total valence number of one of the elements does or does not change. This classification coincides in general with that based on the wandering of the hydrogen from an atom either to the adjoining one or to the atom just beyond the adjoining one, *i. e.*, to the familiar cases of $\alpha-\beta$ (or 1-2) and $\alpha-\gamma$ (or 1-3) tautomerism.

Acetamide is a simple example of $\alpha-\gamma$ tautomerism, and the equilibrium between the two forms may be written as follows:[1]
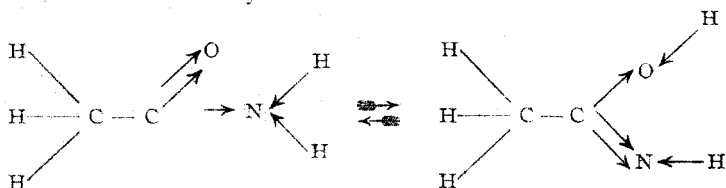

It is evident in this example that the total valence numbers of nitrogen, oxygen and carbon undergo no change. If an electronic or ionic explanation is adopted as the mechanism of these reactions it at once becomes evident that neither the polar number nor the total valence number

[1] When arrows are used in the structural formulas it is advisable to use some sign for equilibrium other than the double arrow ⇄.

of any element will alter in tautomeric changes of this class. For this reason there is no difficulty in showing that acetoacetic ester belongs to this sub-group, but we do not wish to discuss at present the polar nature of the double bond between carbon atoms.

Other cases in which there is no change of valence are those of 1–5 and 1–7 tautomerism, and those of geometric tautomerism, as for example, the two benzaldoximes at high temperature; and these therefore belong to this sub-group.

The simplest cases of α–β tautomerism are furnished by certain inorganic acids, for example, nitrous and sulfurous acids, as shown by the following equilibria:
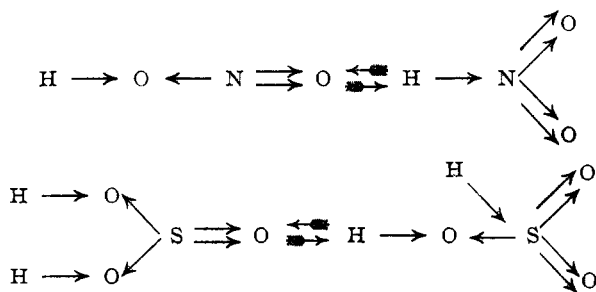
The valence changes are evidently

$$N(+3, 3) \text{ to } N(+3, 5), \text{ and}$$
$$S(+4, 4) \text{ to } S(+4, 6) \text{ respectively.}$$
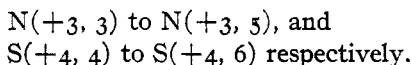
Hydrocyanic acid also belongs to this class, as far as the shift of the hydrogen is concerned; but the question as to the polar nature of the bonds between carbon and nitrogen in H $\longrightarrow$ CN $\rightleftarrows$ CN $\longleftarrow$ H is a complex one and will be discussed later.

In the second main division of tautomerism, type B, there are present in the molecule two adjoining atoms whose polar numbers are capable of change. It is interesting to note that, for each pair of tautomers in Class A, the corresponding isomeric derivatives can be obtained; this is in general not true for substances of type B. This evidently increases the difficulty of investigating the nature of tautomers of this group.

Phenylsulfuric acid, $C_6H_5SO_3H$, is one of the best examples. The evidence of tautomerism is based chiefly on the fact that this substance yields on hydrolysis in acid solution benzene and sulfuric acid, and in alkaline solution phenol and sulfurous acid. This suggests the equilibrium
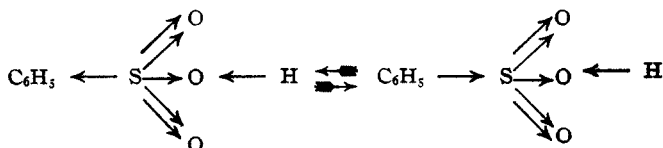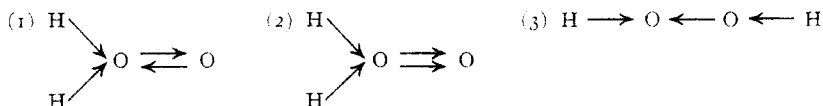
in which the valence of the sulfur changes from $(+6, 6)$ to $(+4, 6)$, and the polar number of the phenyl radical changes correspondingly from -1 to $+1$.

Compounds in which the sulfur of the sulfonic acid radical is attached to nitrogen[1] furnish very interesting examples of polar tautomerism, but these will be discussed in a later paper.

The familiar quinone tautomerism also belongs to this class, since one tautomer contains ketone oxygen and the other peroxide oxygen. One of the methods of representing this equilibrium is shown in the following equation:

$$O \rightleftarrows C_6H_4 \rightleftarrows O \rightleftarrows \quad C_6H_4$$
$$O \longleftarrow O$$
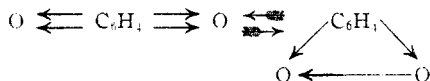
An understanding of the significance of this and other formulas for the peroxide tautomer requires the consideration of the various structural formulas for hydrogen peroxide. If it is assumed that all the valence bonds in hydrogen peroxide are polar in nature, then the following formulas must be considered:[2]

$$
\begin{array}{ccc}
(1) \; \overset{H}{\underset{H}{>}}O \rightleftarrows O & \quad (2) \; \overset{H}{\underset{H}{>}}O \rightleftarrows O & \quad (3) \; H \longrightarrow O \longleftarrow O \longleftarrow H
\end{array}
$$

The total valences of the oxygens are 2 or 4, the polar numbers are in each case -2 and 0,[3] and the average polar number of oxygen is evidently -1.[4] If we wish to write a formula in which the polar valence of each oxygen is -1, then we may adopt either the symmetrical formula mentioned in footnote 1, or the following:

$$(4) \qquad H \longrightarrow O{-}O \longleftarrow H,$$

in which the central bond is non-polar in character. Structural formulas for the peroxide tautomer of quinone may be written corresponding to

[1] See, for example, the experimental results discussed by Raschig, *Z. angew. Chem.*, **17**, 1399–1420 (1904), and Angeli, *Ahrens Sammlung*, **13**, 26 (1908).

[2] Certain other formulas may be written but probably do not deserve serious attention, for example, $\overset{H}{\underset{H}{>}}O \rightleftarrows O$ in which the polar number of one oxygen is
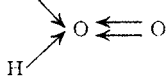
assumed to be -4, and $H \longrightarrow O \rightleftarrows O \longrightarrow H$, where the oxygens are assumed to have a total valence number of 3.

[3] It is interesting to note that there is an α-β shift of hydrogen between (1) and (3), and that this is an example of Type A tautomerism. Also (1) and (2) furnish an example of Type B tautomerism.

[4] The decrease of polar valence of oxygen when hydrogen peroxide is reduced to water is 2 for each molecule of H_2O_2, and the corresponding increase when it is oxidized to oxygen is also 2.

each of these formulas for hydrogen peroxide; but chemists have not considered (1) and (2), doubtless because these would involve a tautomeric shift of oxygen. It is evident for each formula, however, that there is a change in the polar valence of oxygen in the quinone tautomerism.

In the case of hydrocyanic acid the possibility of Type B tautomerism must be considered. Several different formulas may be written, depending on the number and arrangement of the bonds between the nitrogen and carbon atoms, but it seems scarcely worth while to consider the various possibilities. In fact, in such cases as this and hydrogen peroxide it seems more reasonable to consider that all the possible tautomeric forms are in rapid equilibrium with each other, and that there is but little justification for an attempt to exclude all but one or two of these.

In this connection we wish to refer to an idea mentioned several years ago by Professor Lewis, namely, the possible existence of several tautomeric forms in the case of many inorganic substances not usually considered tautomeric in character, e. g.

Chlorine. $\qquad$ Cl $\longrightarrow$ Cl and Cl — Cl;

Sulfuric acid.
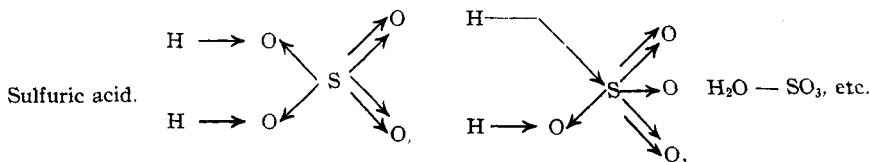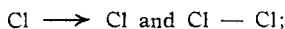
In fact, we regard this prevalence of tautomers as a characteristic of the reactive, polar class of substances referred to in the first part of this paper.

Summary.

1. It is suggested that the idea involved in the two common uses of the term valence number be distinguished by means of the names polar number and total valence number. The valence of nitrogen in ammonium chloride, for example, may be completely described as (—3, 5), which signifies that the polar number and total valence number are —3 and 5 respectively.

2. A comparison of the properties of inorganic and organic substances leads to the conclusion that the nature of the union between two atoms may 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.

3. Tautomeric equilibria are discussed, and classified on the basis of the valence changes involved.