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THE VALENCE OF NITROGEN AND HYDROGEN

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Valence has always been recognized as being a definite whole number which gives the combining capacity of an atom or radical. In the simple binary compounds the significance of this number is perfectly obvious but in molecular compounds ($NH_4Cl = NH_3.HCl$) there has been and still is a great diversity of opinion as to, first, what the number is, and second, what it signifies. The perplexity arises from the fact that even yet there is no universally accepted definition of valence. For example the valence of nitrogen in ammonium, alkyl ammonium, etc., compounds is correctly given as 3, 4 or 5, according to the point of view that is taken.

G. N. Lewis[1] may be said to be the first who proposed a system of electronic arrangement which made possible a rationalization of the conflicting views of valence. Langmuir[2] extended the scope of the electronic interpretation of valence. Bury[3] offered an important modification of the Langmuir theory, giving the maximum number of electrons which can occupy the succeeding levels as 2, 8, 18, 32, respectively; and Bohr comes to a similar conclusion, namely, that the maximum number in an atom that can possess the succeeding total quantum numbers 1, 2, 3, 4. . .is 2, 8, 18, 32. . ., respectively.

The valence electrons of nitrogen are in the second Bury layer and have the total quantum number two. Their number, therefore, should not exceed 8. If through the presence of hydrogen or alkyl groups surrounding the nitrogen, the eight electrons of the valence shell are more than balanced by the combined positive charges, the nitrogen kernel may be considered to exert some attraction for additional electrons outside the second level. But the latter are not valence electrons of the nitrogen, for they are not held exclusively by the charge of the nitrogen but rather by the combined attraction of the positive charges of the kernels of all the atoms in the group. Furthermore, they are not held in a definite position with respect to the nitrogen, but the atom to which they are attached is mobile (in the ionic condition).

A lone nitrogen atom would have nuclear charge and layers N_7 2–5. The tendency to complete the sheath of eight results in the formation of the nitrogen molecule in which three pairs are shared; a very stable structure would result if the four pairs of each atom were at the corners of a tetrahedron and the three shared pairs were at the corners of the tri-

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[1] Lewis, THIS JOURNAL, **38**, 762 (1916).

[2] Langmuir, *ibid.*, **41**, 868 (1919).

[3] Bury, *ibid.*, **43**, 1602 (1921).

angular face common to both.[4] A convenient way of representing the location of the pairs by a plane diagram is shown in Fig. 1, in which the corners and the dot are projections of electron pairs and the numbers are the kernel charges. (The N kernel consists of the nucleus of charge +7 and the first layer of two electrons.)

Fig. 1.

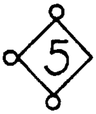

Fig. 2.

Fig. 3.

A nitrogen atom may fill its octet by sharing with three hydrogen atoms (Fig. 2); the small circles represent the hydrogen atoms with kernel charge of one and the intersections with the corners of the square the projections of the pairs held in common. The non-polar valence of nitrogen is obviously three (three pairs held in common = three chemical bonds) in ammonia.

The one lone pair of the nitrogen octet is unsymmetrically placed and has enough stray electrostatic field to attract and hold a hydrogen ion, thus forming the ammonium ion (Fig. 3). The non-polar valence, if by this term we mean the number of bonds or pairs held in common, is now obviously four, but the group has a polar valence of +1. This consists of a surplus of one plus charge, the field of which is symmetrically distributed over the whole group. This is quite different from a chemical bond; if there were room for more electrons in the valence shell two electrons of a chloride or of an hydroxyl ion might be drawn into this shell and an un-ionized compound result, or at least a compound like phosphorus pentachloride or sulfur hexafluoride which can exist as vapor without dissociation. The low ionization of ammonium hydroxide must be explained on the basis either of hydrogen bonds,[5] or of a dissociation into ammonia and water, because the tetra-alkyl ammonium hydroxide is as highly ionized as its salts. The polar valence of nitrogen itself in the ammonium ion depends very much on how we define valence. We may define it as the charge of the nitrogen kernel (N_7 2) which is +5. This charge will balance the four negative hydrogen ions (H_1 2), which are held fixed because their electron pairs fit into the nitrogen valence shell, and one free negative ion which is quite outside the region of the chemical bonds. Since, however, in electrochemical or in oxidation and reduction reactions the valence of nitrogen in ammonia and ammonium compounds is taken as —3, we may perhaps better define the polar valence as the net charge

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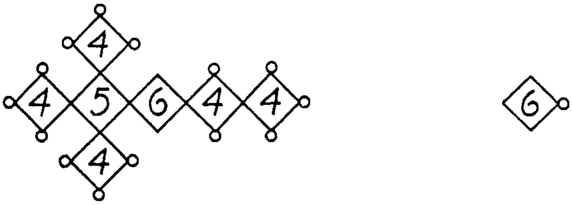
[4] Lewis, "Valence and the Structure of Atoms and Molecules," American Chemical Society Monograph Series, Chemical Catalog Co., **1923**, p. 93.

[5] See Latimer and Rodebush, THIS JOURNAL, **42**, 1431 (1920). Langmuir, *Science, N. S.*, **54**, 67 (1921).

of the nitrogen atom and consider the pairs held in common as a part of this atom. The polar valence of the hydrogen would then be +1.

The phosphorus kernel (P_{15} 2–8) has, like the nitrogen kernel, a charge of +5, but the valence electrons fall in the third layer and they have the quantum number 3. There is room in this layer for 18, and hence in phosphorus pentachloride it is possible that five pairs of electrons may be held in the valence layer in common with five chlorine atoms and that the non-polar valence of phosphorus may be five. Likewise, in sulfur hexafluoride a non-polar valence of six is quite reasonable for sulfur.

The high degree of ionization of trimethylethoxy ammonium hydroxide recently found by W. A. Noyes,[6] confirming conclusions to the same effect by Stewart and Maeser,[7] is beautifully in accord with the interpretation of valence just outlined (Fig. 4).



Trimethylethoxyammonium hydroxide[8,9].

Fig. 4.—The valence shells in every atom of each group are filled to the maximum; there being no place where a pair of one group may fit into a vacancy in the other and establish a chemical bond, the two charged groups remain as ions held, it is true, by electrostatic attraction but are not deprived of freedom of motion within the sphere of this attraction.

The Hydrogen Bond

The low ionization of trialkylamine oxide hydrate is explained by Stewart and Maeser on the basis of the hydrogen bond shown according to the Lewis notation as follows: $(CH_3)_3N:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H$. This is a satisfying explanation and a reasonable one except for the one particular that it violates the principle that only two electrons of quantum number one can surround an atom. The notion that electrons can be shared only in pairs has gained such ascendency that Lewis[10] would leave the first energy level around the hydrogen unoccupied and remove the valence electrons to the

[6] Noyes, This Journal, **47**, 3025 (1925).

[7] Stewart and Maeser, *ibid.*, **46**, 2583 (1924).

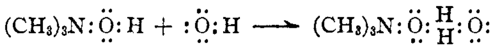
[8] This diagrammatic method of showing the positions of the valence electrons in compounds was developed by Crocker in a paper on the structure of aromatic ring compounds, This Journal, **44**, 1618 (1922).

[9] The justification for assigning localized positions in molecules to the electrons held in common is briefly discussed by Blanchard and Gilliland, This Journal, **48**, 872 (1926).

[10] Ref. 4, p. 110.

second level rather than allow the hydrogen atom to share one electron each with two oxygen atoms.

As a matter of fact, the valence in other compounds such as nitric oxide and chlorine dioxide which have caused so much perplexity, may be easily explained if an uneven number of electrons may be held in common. Small, highly charged kernels have a high repulsion for hydrogen nuclei. Thus, in the ion $(CH_3)_3N\!:\!\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}\!:\!H$ as written by Stewart and Maeser the repulsion of the oxygen kernel with six charges would tend to drive the hydrogen nucleus out from its position between the two electrons of the oxygen sheath to the new position shown as follows:



$$(CH_3)_3N\!:\!\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}\!:\!H + :\!\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}\!:\!H \longrightarrow (CH_3)_3N\!:\!\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}\!:\!\genfrac{}{}{0pt}{}{H}{H}\!:\!\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}\!:$$

The hydrogen bond according to this idea consists of the hydrogen nucleus and pair of electrons in the first level, each electron shared in a different atom.

Summary

Except in simple binary compounds, valence can be precisely defined only in terms of postulates regarding electron arrangements. For the sake of clearness in describing this important property, the use of such postulates is justified when the postulates are reasonable in the light of our present knowledge. Whatever the electrons may be doing in the atom it is already clearly indicated that they can occupy only certain definite and widely separated levels, and that the maximum numbers at the succeeding levels are 2, 8, 18, 32, ...

The average or static positions of electrons held in common is governed by Coulomb's law of electrostatic attraction and repulsion subject, of course, to the requirements of the energy levels.

Nitrogen can have but eight and hydrogen but two electrons in its valence shell although phosphorus may have more than eight. Defining the non-polar valence as the number of pairs held in common with other atoms, nitrogen can have a maximum non-polar valence of four. The polar valence may be regarded as plus five if we define it as the net charge of the nitrogen kernel, or as minus three if we define it as the charge of the nitrogen atom and consider the eight electrons of the sheath as a part of the atom.

The hydrogen bond is believed to consist of a hydrogen atom holding in its valence layer one electron of the valence layer of each of the two atoms thus bound together.

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