THE RELATION OF SHARED ELECTRONS TO POTENTIAL AND ABSOLUTE POLAR VALENCES

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Dalton proposed his atomic theory of the constitution of matter and of the combinations between elements about 125 years ago. Since then the advances in chemistry and physics have been, almost continuously, in agreement with the hypothesis that matter is discontinuous in what may be called its fine structure. For some time, now, there has been a growing belief that energy is also discontinuous and that matter and energy are interconvertible. When we find a theory of this sort, which has been continuously and increasingly useful for more than a century, it is wise for us to consider whether new hypotheses which may seem, at first, incompatible with the older ideas, may not be reconciled with them.

With this principle in mind, the endeavor will be made to show that the electron theory of valence proposed by G. N. Lewis (1) may be reconciled with the original theory of valence proposed 75 years ago, and with the positive-negative theory proposed by Arrhenius 40 years ago (2) and applied to compounds not usually thought of as forming ions, a few years later (3). This will be done with the use of three rather simple principles:

1. In the majority of chemical reactions, a pair of electrons forming a covalence remains with one of the two atoms which separate (4).

2. In every ion, whether simple or complex, there is some atom for which the sum of the covalences plus the number of unshared electrons is greater or less than the number of valence electrons for that atom (5).

3. In every compound having only covalences, the number

of covalences plus the number of unshared electrons is equal to the number of valence electrons for each atom (5).

The second and third principles are partly implied in many things which have been said by G. N. Lewis and Langmuir but they have not stated it clearly in the above form and they and others have not always recognized that valence is a property which changes by *whole* numbers. These numbers are not dependent on the stability of the compounds or on electrical moments of compounds which may render some covalences potentially polar (see below). They have not made the sharp distinction between polar and non-polar valences on the basis that at a given instant any valence must be either an ionic valence or a covalence. They have used the term "semipolar valence" not as something which is half ionic and half covalence but as a single covalence in which there is an unusual electrical moment. The practical difference, here, is not very great and is partly a question of nomenclature rather than a difference of opinion about what may be actually present in the molecule.

These principles, if accepted, not only furnish a reconciliation between the older and newer theories of valence but they also account for the variable valences which gave chemists so much trouble 50 or 60 years ago.

The original idea of valence, as developed by Frankland, Couper and Kekulé, is that each atom has one or more unit powers of attraction for other atoms. This idea is still true, as will be seen in what follows. I think of it as one phase of the discontinuity which lies at the foundation of all natural phenomena. It is expressed by the following well known formulas:
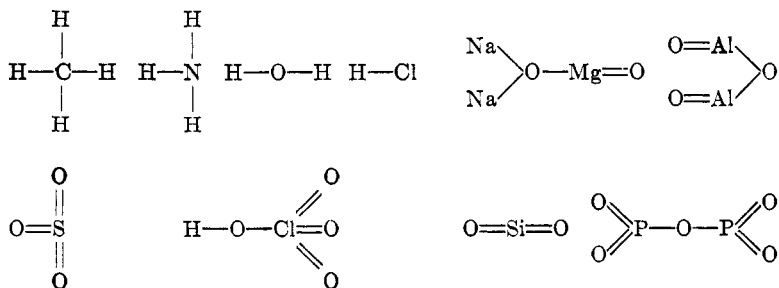
Pasteur, LeBel and van't Hoff added the idea that each atom is held to a central atom having four valences, in such a manner that right handed and left handed arrangements are possible, with sufficient stability to prevent the easy interchange of the positions of the groups:
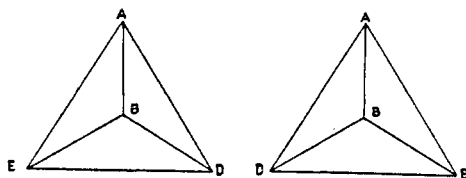
Van't Hoff furnished the further idea that doubly bound carbon atoms do not rotate freely about the axis of the double union, while singly bound atoms may do this:
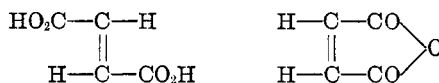
Baeyer suggested that rings contining 5 or 6 atoms are more stable than those having only 3 or 4 atoms:
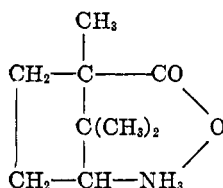

Tetrahedron, 109° 28′
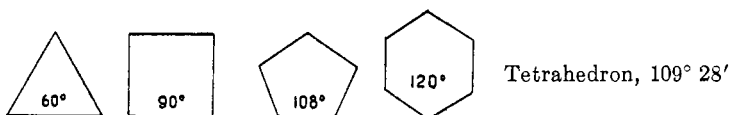
Arrhenius gave us the modern idea of polar valences when he assumed that the ions of an electrolyte are more or less completely separated in solutions and exist as independent molecules, having positive and negative charges. Some of the followers of G. N. Lewis have carried this thought so far as to deny that there is a genuine valence between such ions. They seem to have overlooked three important facts:

1. Every negative ion must have a positive ion in the immediate neighborhood. The attractions between the ions hold them together in this way.

2. If hydrochloric acid or sodium chloride is vaporized, the atoms are held together in pairs in the gaseous state. Whether

the atoms are held together by a polar valence or a covalence is not certainly known.

3. Aminolauronic acid is held in a stable configuration,

$$
\begin{array}{c}
CH_3 \\
| \\
CH_2\!-\!C\!-\!\!-\!\!CO \\
|\quad\quad | \quad\quad\quad\searrow \\
|\quad\; C(CH_3)_2 \quad\;\; O \\
|\quad\quad |\quad\quad\quad\nearrow \\
CH_2\!-\!CH\!-\!NH_3
\end{array}
$$

in solution, by the polar valence between the oxygen atom and the ammonium group (6).
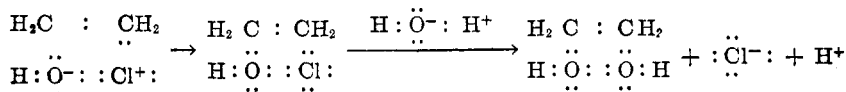
About 25 years ago, J. J. Thomson proposed the first definite electronic hypothesis (7) to account for chemical combination. He assumed that after the transfer of an electron from one atom to another the atoms were held together by the static attractions between them. This idea has been made the basis for a discussion of chemical reactions by Falk and Nelson and a number of others, including myself. I was finally convinced that the pair of electrons forming a covalence are held by the two atoms in common, as supposed by G. N. Lewis, by the following considerations:

1. The theory that an electron is transferred from one atom to the other implies the possibility of the electromers:

$$
\begin{array}{cc}
-+Cl & +-Cl \\
N-+Cl & N+-Cl \\
-+Cl & +-Cl
\end{array}
$$
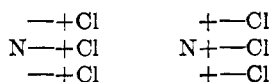
A fruitless search, continued for nearly ten years, with the aid of several able assistants, failed to disclose the existence of such electromers.

2. Hypochlorous acid adds to ethylene forming ethylene chlorohydrin and the latter hydrolyses to glycol and hydrochloric acid. It is evident that in the first reaction the chlorine atom adds to the carbon in the positive form with only six electrons (8) and leaves it in the negative form with eight:

$$
\begin{array}{c}
H_2C \;:\; CH_2 \\
H\!:\!\ddot{O}\!-\!:\;:\!\ddot{C}l^+\!:
\end{array}
\;\rightarrow\;
\begin{array}{c}
H_2\,C \;:\; CH_2 \\
H\!:\!\ddot{O}\!:\;:\!\ddot{C}l\!:
\end{array}
\;\xrightarrow{\;H\!:\!\ddot{O}^-\!:\,H^+\;}\;
\begin{array}{c}
H_2\,C \;:\; CH_2 \\
H\!:\!\ddot{O}\!:\;:\!\ddot{O}\!:\!H
\end{array}
\;+\;:\!\ddot{C}l^-\!:\;+\;H^+
$$

This is easily understood if the pair of electrons is shared by the chlorine and carbon in the chlorohydrin but it is not readily explained if the electron is transferred completely from one atom to the other.

Atomic ions of the first two periods of the periodic system have the same electronic shell as that of the nearest noble gas. They differ from the noble gas in the positive charges of their nuclei. The positive charge of the nucleus of the sodium ion is one unit greater than that of the nucleus of neon. The positive charge of the nucleus of the chloride ion is one unit less than that of the nucleus of argon:

$$: \overset{\cdot \cdot \; +11}{\underset{\cdot \cdot}{Na}} : \qquad : \overset{\cdot \cdot \; +10}{\underset{\cdot \cdot}{Ne}} \cdot \qquad : : \overset{\cdot \cdot \; +17}{\underset{\cdot \cdot}{Cl}} : : \qquad : : \overset{\cdot \cdot \; +18}{\underset{\cdot \cdot}{A}} : :$$
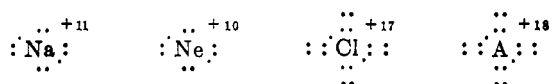
In complex ions there is some atom which has more or fewer electrons than those required for atoms having only covalences. Nitrogen has 5 valence electrons; ammonium has only four pairs of shared electrons and is a positive ion. Oxygen has 6 valence electrons; the hydroxide ion has 6 unshared electrons and one pair of shared electrons. It is a negative ion.

$$\begin{array}{c} H \\ \cdot \cdot \quad + \\ H : N : H \\ \cdot \cdot \\ H \end{array} \qquad \overset{\cdot \cdot}{\underset{\cdot \cdot}{: O :}} \overset{-}{H}$$
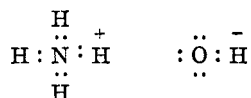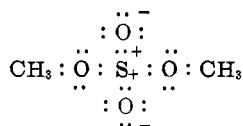
The noble gas structure of ions seems to be closely related to their semi-independent existence in solutions (9).

There seem to be two different kinds of double unions; double covalences, as in aldehydes, ketones, ethylene, etc.,

$$CH_3CH : : \overset{\cdot \cdot}{\underset{\cdot \cdot}{O}}, \qquad CH_3 : C : CH_3, \qquad H_2C : : CH_2$$
$$\overset{\cdot \cdot}{\underset{}{: O :}}$$
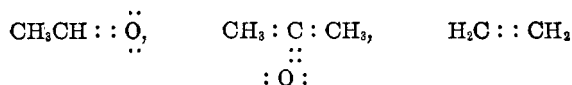
and a combination of a covalence and a polar union, as in dimethyl sulfate,

$$\begin{array}{c} \overset{\cdot \cdot}{\underset{\cdot \cdot}{: O :}}^{-} \\ CH_3 : \overset{\cdot \cdot}{\underset{\cdot \cdot}{O}} : \overset{\cdot \cdot +}{\underset{}{S_+}} : \overset{\cdot \cdot}{\underset{\cdot \cdot}{O}} : CH_3 \\ : O : \\ \overset{}{\underset{\cdot \cdot \; -}{}} \end{array}$$

Here the sulfur atom, which has six valence electrons, has only four covalences and two positive polar valences. The oxygen atoms, above and below, have one negative polar valence and six unshared electrons. The oxygen atoms connected with the methyl groups have two covalences and four unshared electrons, in accordance with the rule. It is to be noted that the semi-polar oxygen atoms show no more tendency to form covalences by sharing their electrons than chloride ions do. They seem to be genuine half ions, and resemble the noble gases in the same manner as other ions.

The point of view here presented furnishes a satisfactory reconciliation between the formula proposed by G. N. Lewis for the sulfate ion and the older view that oxygen is bivalent in nearly all of its compounds and that sulfur has a valence of six in sulfur trioxide and sulfuric acid. It receives strong support from the "parachor" relations established by Sugden (10) and from the optical activity of sulfinic compounds (11).

T. W. Richards suggested that some of the phenomena of chemical combination may be accounted for by the hypothesis of compressible atoms. The diminution in volume occasioned by the transfer of the valence electron of a metal to a halogen or other atom, completing its octet and the more compact volumes of molecules having octets completed by sharing electrons or drawn together by semipolar unions furnish a picture somewhat resembling that of Richards but much more definite than this.
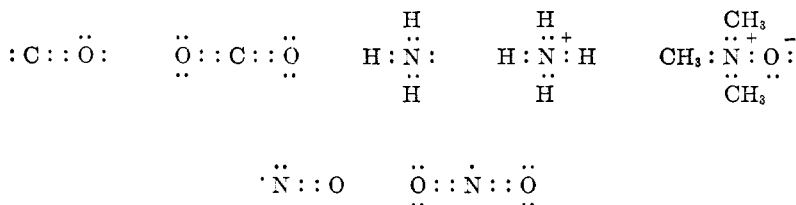
The distinction between the polar valences of ions and the covalences of other unions is so sharp that the author has proposed (12) to restrict the term "polar valence" to the designation of substances which are ions or semi-ions. In advocating such a nomenclature it is clearly recognized that some molecules have an electrical moment at the covalence and may separate, momentarily, into ions when reacting with other molecules. It will contribute greatly to clarity and definiteness in our discussions if such covalences are called *potentially* polar instead of merely polar.

The theory of G. N. Lewis, combined with the rule for shared and unshared electrons, gives a very satisfactory explanation of the

variable valences which caused so much trouble to chemists 50 or 60 years ago. Thus, a chlorine atom is univalent toward hydrogen, with either a polar valence in the chloride ion or, possibly, a covalence in the molecule, $H:\overset{..}{\underset{..}{Cl}}:$. In sodium chloride the polar valence seems to be retained in the crystal. In perchloric acid the chlorine atom has a valence of seven, consisting of 4 covalences and 3 polar valences:

$$H:O:\overset{\overset{..}{O}:^-}{\underset{\underset{..}{O}:^-}{Cl^{+}:\overset{..}{O}:^-}}$$
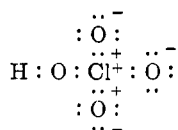
The valences of carbon in carbon monoxide and carbon dioxide and of nitrogen in ammonia, ammonium, the amine oxides and the various oxides of nitrogen are easily explained in the same manner:

$$:C::\overset{..}{O}: \qquad \overset{..}{\underset{..}{O}}::C::\overset{..}{\underset{..}{O}} \qquad H:\overset{\overset{H}{..}}{\underset{\underset{H}{}}{N}}: \qquad H:\overset{\overset{H}{..}}{\underset{\underset{H}{}}{N}}^{+}:H \qquad CH_3:\overset{\overset{CH_3}{..}}{\underset{\underset{CH_3}{}}{N}}^{+}:\overset{..}{O}:^{-}$$

$$\cdot\overset{..}{N}::O \qquad \overset{..}{\underset{..}{O}}::\overset{\cdot}{N}::\overset{..}{\underset{..}{O}}$$

These principles give a good explanation for the reaction between nitric oxide and nitrogen trichloride, which gives nitrosyl chloride, nitrous oxide and chlorine, with nitrogen dichloride as a probable intermediate compound. This reaction has been studied for two years past and is the subject of a separate communication (13).

It should be noted that the discussions and illustrations of this paper have been confined to hydrogen and the first two periods of the chemical elements. It seems probable that other considerations are involved as the shell of electrons increases in size. G. N. Lewis has considered some elements having higher atomic weights.

REFERENCES

(1) LEWIS: J. Am. Chem. Soc. **38**, 762 (1916).
(2) ARRHENIUS: Z. physik. Chem. **1**, 637 (1887).
(3) HOFF, VAN'T: Z. physik. Chem. **16**, 411 (1895).
NOYES AND LYON: J. Am. Chem. Soc. **23**, 463 (1901).
STIEGLITZ: Ibid. **23**, 796 (1901).
LAPWORTH: J. Chem. Soc. **79**, 267 (1901).
(4) NOYES: J. Am. Chem. Soc. **45**, 2959 (1923).
(5) NOYES: Z. physik. Chem. **130**, 323 (1927); Bicentenary No., Proc. Am. Phil. Soc. **66**, 302 (1927).
(6) NOYES AND POTTER: J. Am. Chem. Soc. **37**, 189 (1915).
(7) THOMSON: Phil. Mag. **7**, 237 (1904).
(8) NOYES AND WILSON: J. Am. Chem. Soc. **44**, 1630 (1922)
BALARD: Ann. chim. phys. (2) **57**, 272 (1834).
(9) NOYES: Proc. Nat. Acad. Sci. **13**, 379 (1927).
(10) SUGDEN: J. Chem. Soc. **125**, 1177 (1924); **127**, 1528 (1924); **131**, 1173 (1927).
(11) HARRISON, KENYON AND PHILLIPS: J. Chem. Soc. **129**, 2079 (1926).
(12) NOYES: Z. physik. Chem. **130**, 329 (1927).
(13) NOYES: J. Am. Chem. Soc., **50**, 2902 (1928).