nitrogen 63.14 to 78.01°K., $\log_{10} P$ (cm.) $= -(339.8/T) + 6.71057 - 0.0056286\ T$.

The free energies and equilibrium constants for the reactions $^1/_2\ N_2 + {}^1/_2\ O_2 = NO$ and $N_2 = 2N$ have been calculated to 5000°K. with the assistance of spectroscopic data. The free energy of formation of nitric oxide was found to be $\Delta F^\circ_{298.1} = 20{,}650$ calories per mole.

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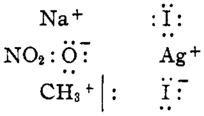
The Electronic Structure of Inorganic Complexes

BY WILLIAM ALBERT NOYES

Soon after Arrhenius proposed his theory of ionization a distinction was made between "heteropolar" and "homopolar" compounds. This corresponds closely to our distinction between ionic and covalent compounds. Chemists have very generally supposed that ionic compounds react very rapidly and that covalent compounds react slowly or not at all. Professor Kahlenberg, many years ago, showed the illusory nature of such a method of distinguishing the two classes of compounds but, because his views of ionization were considered heterodox, the facts which he stated have been too generally disregarded.

The fact that covalent methyl iodide reacts with silver nitrate in an alcoholic solution almost or quite as rapidly as ionic sodium iodide demonstrates that the two classes of compounds cannot be distinguished by the speed of their reactions.



$$\begin{array}{ll} \mathrm{Na}^+ & :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{I}}}: \\ \mathrm{NO_2}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:^- & \mathrm{Ag}^+ \\ \mathrm{CH_3}^+ \,\big|\, : & \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{I}}}:^- \end{array}$$

Both reactions are ionic but the positive methyl has only an ephemeral existence.

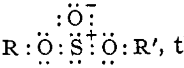
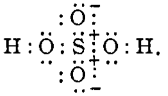
Instead of speed of reactions we must rely on other properties to distinguish between covalences and ionic valences. The most important of these are conductivity in solutions, molecular weights in solutions, Sugden's parachor, optical activity and, especially, electronic structure. The last can frequently be inferred with a high degree of probability.

That there is an absolute balance between the positive charge of the nucleus of an atom and the negative charges of the electrons surrounding the nucleus is universally accepted by chemists and physicists. That every ion consisting of a single atom has a stable group of electrons the sum of whose negative charges overbalances or underbalances the positive charge of its nucleus and that in every complete molecule the sum of the charges of the electrons balances the sum of the charges of the nuclei, are universally accepted.

It has not been so generally accepted that in every complex ion its positive or negative charge is due to some atom or atoms the charge of whose nucleus (or kernel) is not balanced by the electrons immediately surrounding it, counting the pair of electrons of a covalence as equivalent to a single unshared electron; conversely, that any atom the charge of whose nucleus is not so balanced is an ion or part of a complex ion. In the light of what follows, it seems reasonable to consider these statements as forming a hypothesis which deserves serious consideration until someone can furnish a well-established exception.

One reason why this relation has not been generally recognized is because chemists have failed to see clearly the sharp distinction between "potentially polar"[1] covalences and fully polar (or ionic) valences. This distinction was first vaguely recognized in 1901 when Noyes and Lyon[2] supposed that chlorine molecules reacting with ammonia separate into chloride ions and positive chlorine atoms; by Stieglitz,[3] who pointed out that hypochlorous acid is formed by replacing the hydrogen of water by positive chlorine; and by Lapworth,[4] who showed a similar conduct for bromine.

Potential polarity was shown more clearly[5] by the quantitive decomposition of nitrogen trichloride by hydrochloric acid and by explaining the positive potential polarity of the chlorine of nitrogen trichloride as due to the fact that the nitrogen kernel has only two electrons and the negative potential polarity of the chlorine of phosphorus trichloride as due to the fact that the kernel of the phosphorus atom has ten electrons.[6]

Potentially polar atoms united by a covalence often give an electrical moment to the molecule containing them and such molecules are called "polar" by many chemists and physicists. Since this usage is quite general, the suggestion that the term polar should be used only for ions[7] seems to have little chance of success and may as well be abandoned. In that case, however, the term "semi-ionic" should be used instead of "semi-polar" for the oxygen of the optically active sulfinates,  $\mathrm{R:\ddot{O}:\overset{:\ddot{O}:^{-}}{\ddot{S}}{}^{+}:\ddot{O}:R'}$, the amine oxides, $\mathrm{R_3N^{+}:\ddot{O}:^{-}}$ and sulfuric acid,  $\mathrm{H:\ddot{O}:\underset{:\ddot{O}:^{-}}{\overset{:\ddot{O}:^{-}}{\ddot{S}}}{}^{++}:\ddot{O}:H}$.

The disadvantage of the word "polar" as applied to covalent compounds is that we have all degrees of polarity from that of the hydrogen of

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(1) W. A. Noyes, *Z. physik. Chem.*, **130**, 329 (1927).

(2) Noyes and Lyon, THIS JOURNAL, **23**, 463 (1901).

(3) Stieglitz, *ibid.*, **23**, 797 (1901).

(4) Lapworth, *J. Chem. Soc.*, **79**, 267 (1901).

(5) W. A. Noyes, THIS JOURNAL, **42**, 2167, 2173 (1920).

(6) Noyes and Noyes, "Modern Alchemy," p. 107.

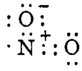
(7) W. A. Noyes, *Z. physik. Chem.*, **130**, 327 (1927).

hydrocarbons to that of the iodine of methyl iodide. The only sharp line that can be drawn is the point where the pair of electrons ceases to be *shared*—in other words, when the two atoms joined by a covalence become ions.

Sidgwick in his classical book on "The Electronic Theory of Valency" points out that covalences may be formed in two ways. In the first, each atom furnishes one of the pair of electrons. Each nitrogen atom furnishes its three valence electrons and each hydrogen atom furnishes one electron in the synthesis of ammonia. In the second, one atom or molecule, which he calls the "donor," furnishes the two electrons for the covalence and the other, which he calls the "acceptor," furnishes none.

In the first case the product is electrically neutral because each atom exchanges a single unshared electron for the covalence. The resulting molecule may be "potentially polar" and have an electrical moment but it will never be an ion unless one of the constituents was an ion. In the second case the donor, which exchanges a pair of unshared electrons for a covalence, increases its positive ionic valence by one. The acceptor increases its negative ionic valence by one.

Sidgwick has recognized that the donor increases its positive character and that the acceptor increases its negative character but he has hesitated to accept this as a unit change in the ionic valence of each atom because the electrons of a covalence are usually not shared equally by the two atoms. He has noticed that the group containing the donor acquires a positive charge of one unit but has not seemed to see that, in effect, the donor increases its valence by two; one covalence and one ionic valence. The acceptor, on the other hand, increases its negative ionic valence by one, becoming electrically neutral if it was a positive ion, or acquiring a negative ionic valence of one if it was electrically neutral. It also acquires a covalence.

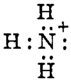
On p. 114 he makes the confusing, if not positively erroneous, statement that, "In order to become quadrivalent nitrogen must, as we know, lose an electron." The nitrogen of methylammonium chloride, which he is considering, is quinquivalent, not quadrivalent, since it has four covalences and one positive ionic valence. The methyl which unites with the nitrogen must do so as a positive methyl ion, with a carbon atom having only six electrons. In uniting with the unshared electrons of the nitrogen this positive methyl becomes electrically neutral, increasing its negative ionic valence by one. The only well-known compound in which nitrogen is really quadrivalent is nitrogen dioxide,  $\begin{array}{l} \;\;:\ddot{\mathrm{O}}\overset{-}{:} \\ \cdot\ddot{\mathrm{N}}\overset{+}{\vdots}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}} \end{array}$, in which the nitrogen has three covalences and one positive ionic valence.

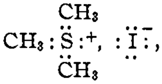
Sidgwick has performed a very great service by explaining the "coordination" of inorganic complexes as due to covalences. This unifies the electronic theory by applying it to all elements and to all classes of compounds. His definition of a "coördinate link" as one in which one of the atoms furnishes the pair of electrons for a covalence is not satisfactory, however. The covalence which holds the fourth hydrogen atom of the ammonium ion is identical with the other three covalences of the group. The "covalent link" when it has been formed does not differ from other covalences except that the number of coördinated covalences may exceed the number of normal covalences for the atom which accepts them. This is an important principle of Werner's system.

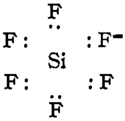
Sidgwick has given rules for determining the ionic valence of an inorganic complex. A simpler system can be based on the relationship between the changes in the ionic valences of donors and acceptors stated above, the coördination number of Werner, which is also the number of covalences around the central atom, six for cobaltic cobalt, four for platinous platinum, six for platinic platinum, etc., and the ionic valence of the central atom, three for cobaltic cobalt, two for platinous platinum, four for platinic platinum, etc.

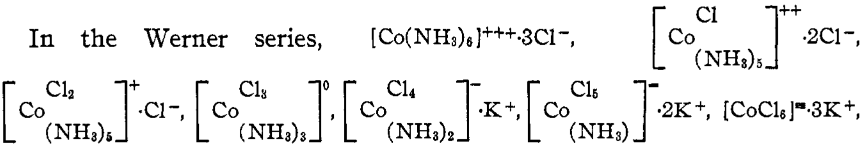
The application of these principles will be easily understood from the following illustrations. For a part of these Sidgwick has not recognized the principle of "donor" and "acceptor."

In $\mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}\overset{+}{:}\overline{\mathrm{H}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}:$ the hydrogen atom with two covalences is acceptor from the first fluorine atom and negative. The first fluorine atom, as donor, is positive. The second fluorine atom is electrically neutral with six unshared electrons and one covalence. This formula helps us to understand the low ionization constant of hydrofluoric acid.

In the  $\begin{array}{ccc} & \mathrm{H} & \\ \mathrm{H}: & \ddot{\mathrm{N}} & \overset{+}{:}\mathrm{H} \\ & \ddot{\mathrm{H}} & \end{array}$ ion, the nitrogen as donor is positive and the hydrogen ion, increasing its negative charge by one, algebraically, is neutral.

In the formation of trimethylsulfonium iodide,  $\begin{array}{ccc} & \mathrm{CH_3} & \\ \mathrm{CH_3}: & \ddot{\mathrm{S}} & :^{+},\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{I}}}:^{-} \\ & \ddot{\mathrm{C}}\mathrm{H_3} & \end{array}$, from dimethyl sulfide and methyl iodide the iodide ion in separating from the methyl takes both the electrons of the covalence, leaving the methyl as a positive ion. The positive methyl, as acceptor from the sulfur atom of the dimethyl sulfide, becomes neutral and the sulfur, as donor, positive.

In the fluosilicate ion,  $\begin{array}{ccc} & \mathrm{F} & \\ & \cdot\cdot & \\ \mathrm{F}: & & :\mathrm{F}^{-} \\ & \mathrm{Si} & \\ \mathrm{F}: & & :\mathrm{F} \\ & \cdot\cdot & \\ & \mathrm{F} & \end{array}$, the kernel of the silicate atom, which has four positive charges, may be considered as the acceptor for six fluoride ions. The six negative charges convert it to a bivalent negative ion and each fluoride ion as a donor becomes neutral.



In the Werner series, $[Co(NH_3)_6]^{+++}\cdot 3Cl^-$, $\left[\overset{Cl}{\underset{(NH_3)_5}{Co}}\right]^{++}\cdot 2Cl^-$, $\left[\overset{Cl_2}{\underset{(NH_3)_4}{Co}}\right]^{+}\cdot Cl^-$, $\left[\overset{Cl_3}{\underset{(NH_3)_3}{Co}}\right]^{0}$, $\left[\overset{Cl_4}{\underset{(NH_3)_2}{Co}}\right]^{-}\cdot K^+$, $\left[\overset{Cl_5}{\underset{(NH_3)}{Co}}\right]^{=}\cdot 2K^+$, $[CoCl_6]^{\equiv}\cdot 3K^+$, the cobalt kernel, which has three positive ionic charges, is acceptor, in each compound, of six covalences from chloride ions or from molecules of ammonia, changing it to a trivalent negative ion. As donor each molecule of ammonia becomes a positive ammonium ion and each negative chloride ion becomes neutral. A little consideration will show that this gives the resultant complexes the charges shown in the formulas.

In other compounds, when molecules of water enter the complexes they become positive oxonium ions.

The negative nitrite and cyanide ions may enter the complexes in the same manner as the chloride ion does, becoming electrically neutral and assuming the forms, $R:\underset{\cdot\cdot}{\ddot{O}}:\ddot{N}::\underset{\cdot\cdot}{\ddot{O}}$ and $R:C:::N:$. Since the trivalent nitrogen atom of each group has a pair of unshared electrons, these groups may rearrange giving nitro or isocyanide groups with the structures, $R:\overset{:\ddot{O}:^{-}}{\ddot{N}^{+}}:\ddot{O}$ and $R:\overset{+}{N}:::\overset{-}{C}:$ or $R:\ddot{N}::C:$. The carbon in the last formula is bivalent, which might explain the preparation of carbon monoxide from potassium ferrocyanide and concentrated sulfuric acid.

In potassium chloroplatinate, $[PtCl_6]^{=}\cdot 2K^+$, the quadrivalent platinic ion becomes a bivalent negative ion. Platinum furnishes a series of complexes similar to those of coblat, with the differences caused by the quadrivalent platinum.

Summary

On the basis of Sidgwick's assumption that the "coördinated" ions and molecules of the Werner complexes are "donors" and the central metallic ions are "acceptors," combined with the principle that a donor increases its positive ionic valence by one and that an acceptor increases its negative ionic valence by one, a simple explanation of the ionic charges of the complexes is given.

The importance of the distinction between the "potentially polar" covalences and ionic valences is discussed.

The possibility of the rearrangement of the negative nitrite and cyanide ions to positive nitro and isocyanide groups is explained.

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