silver chloride electrode. Final values of the dissociation constant of acetic acid from 0 to 60° at 5° intervals have been tabulated. Our value of 1.754×10^{-5} agrees excellently with the value, 1.753×10^{-5}, determined from the conductance measurements by MacInnes and Shedlovsky.

3. The dissociation constant is given by the equation

$$\log K = -\frac{1500.65}{T} - 6.50923 \log T - 0.0076792T^2 + 18.67257$$

4. The heat of dissociation is given by the equation

$$\Delta H = 6871.0 - 12.9436T - 0.035161T^2$$

NEW HAVEN, CONNECTICUT

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Types of Chemical Reactions

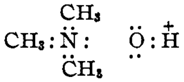
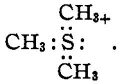
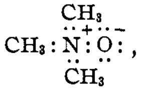
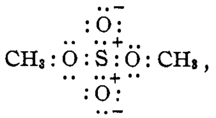
BY WILLIAM ALBERT NOYES

A study of the interaction of nitrogen trichloride with nitric oxide and with nitrogen tetroxide has given results from which, in conjunction with other experimental evidence and with current electronic theories, it is possible to define accurately, with a high degree of probability, the electronic course of several types of reactions.

The discussion which follows applies, primarily, to elements with atomic weights of 40 or below. For elements of higher atomic weights the outer shell of valence electrons seems to be less sharply defined.

Three principles are used. (1) On account of their "spin" and for other reasons, the electrons of the valence shell of an atom are usually, not always, associated in pairs, octets or sextets. (2) Every atom must have the positive charge of its nucleus balanced by the electrons immediately associated with it, or it must be an ion or form part of a complex ion, which is held to or in the neighborhood of another ion of the opposite sign, by static attraction. (3) In balancing the positive charge of the nucleus of an atom the pair of electrons of a covalence is equivalent to a single unshared electron.

1. Formation of Ions

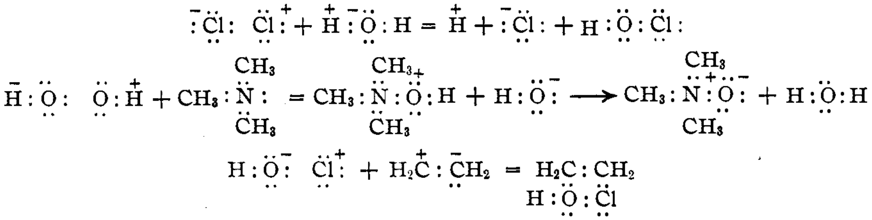
A. Permanent ions, formed with an outer shell of electrons (usually an octet) for some atom, in such a manner that the positive charge of the kernel or nucleus is overbalanced or underbalanced by the electrons surrounding it: (a) by the gain or loss of one or more electrons, as for sodium, calcium, chlorine or sulfur; (b) by the addition of a positive hydrogen or methyl ion to ammonia or to a tertiary amine, a positive hydroxyl group to a tertiary amine,  $CH_3:\overset{CH_3}{\underset{CH_3}{\ddot{N}}}:\ \underset{\cdot\cdot}{\ddot{O}}:\overset{+}{H}$ or a positive methyl to dimethyl sulfide,  $\mathrm{CH_3:\overset{CH_3+}{\underset{CH_3}{\ddot{S}}}:}$. In these cases the positive charge of the kernel of the nitrogen or sulfur atom is underbalanced because the sum of the covalences and unshared electrons is less than the number of their valence electrons. (c) By the removal of a positive ion from a covalence, as when the removal of a hydrogen ion from water gives an hydroxide ion, $\mathrm{H:\ddot{\underset{\cdot\cdot}{O}}\overset{-}{:}}$, in which the oxygen atom causes the ion to be negative because it has one covalence and six unshared electrons. The nitrogen and oxygen atoms of trimethylamine oxide,  $\mathrm{CH_3:\overset{CH_3}{\underset{CH_3}{N}}\overset{+}{:}\ddot{O}\overset{-}{:}}$, and the two oxygen and the sulfur atom of dimethyl sulfate,  $\mathrm{CH_3:\ddot{O}:\overset{:\ddot{O}:^{-}}{\underset{:\ddot{O}:^{-}}{S}}\overset{+}{:}\ddot{O}:CH_3}$, are held by one covalence and one ionic valence because the positive charges of the kernels of the nitrogen and sulfur atoms are underbalanced as they are in the ammonium and sulfonium ions, and because the positive charges of the kernels of the oxygen atoms are overbalanced as they are in the hydroxide ion.

Hydrogen ions are unique because they have no electrons. In general, hydrogen ions held by covalences ionize slightly, and since it is probable that hydrogen ions may be held by static attraction to atoms or molecules having complete octets it is often difficult to determine whether the atom is held in this manner or by a covalence. Physical methods are most suitable for an answer to this question.

For these reasons reactions in which hydrogen ions are involved have an intermediate position between the ordinary ionic reactions and covalence reactions. The hydrogen ionization of water, of ammonia, of ethyl alcohol, of hypochlorous acid and of hydrogen atoms held by a covalence to carbon, is trifling, but it has been demonstrated by conductivity measurements in the first four cases. The ionization of hydrogen attached to carbon is important for an understanding of nitration and sulfonation reactions, the tautomerism of actoacetic ester and similar compounds, the Perkin, Kolbe and other condensation reactions involving the ionization of hydrogen atoms which are alpha to a carbon atom combined with oxygen, and many molecular rearrangements.

Some chemists have assumed negative hydrogen ions. It is doubtful if these ever occur in organic reactions.

B. Six-electron-ephemeral ions are formed by the separation of two atoms held by a covalence in such a manner as to form a negative ion with a complete octet of electrons and a positive ion with only six electrons in the outer shell of the other atom. This is illustrated by the following equations

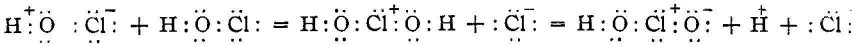


$$\overset{-}{:}\ddot{\mathrm{Cl}}:\ \ \ddot{\mathrm{Cl}}\overset{+}{:} + \overset{+}{\mathrm{H}}\overset{-}{:}\ddot{\mathrm{O}}:\mathrm{H} = \overset{+}{\mathrm{H}} + \overset{-}{:}\ddot{\mathrm{Cl}}: + \mathrm{H}:\ddot{\mathrm{O}}:\ddot{\mathrm{Cl}}:$$

$$\overset{-}{\mathrm{H}}:\ddot{\mathrm{O}}:\ \ \ddot{\mathrm{O}}:\overset{+}{\mathrm{H}} + \mathrm{CH_3}:\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\ddot{\mathrm{N}}}}: = \mathrm{CH_3}:\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_{3+}}}{\ddot{\mathrm{N}}}}:\ddot{\mathrm{O}}:\mathrm{H} + \mathrm{H}:\ddot{\mathrm{O}}\overset{-}{:} \longrightarrow \mathrm{CH_3}:\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\overset{+}{\mathrm{N}}}}:\ddot{\mathrm{O}}\overset{-}{:} + \mathrm{H}:\ddot{\mathrm{O}}:\mathrm{H}$$

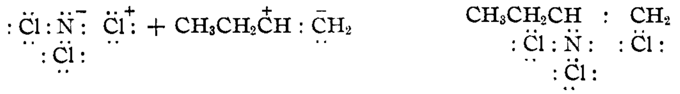
$$\mathrm{H}:\ddot{\mathrm{O}}\overset{-}{:}\ \ \ddot{\mathrm{Cl}}\overset{+}{:} + \mathrm{H_2}\overset{+}{\mathrm{C}}:\overset{-}{\mathrm{C}}\mathrm{H_2} = \begin{matrix}\mathrm{H_2C}:\mathrm{CH_2}\\ \mathrm{H}:\ddot{\mathrm{O}}:\ddot{\mathrm{Cl}}\end{matrix}$$

In this case both the hypochlorous acid and the ethylene form six-electron ions.



$$\mathrm{H}\overset{+}{:}\ddot{\mathrm{O}}\ \ :\ddot{\mathrm{Cl}}\overset{-}{:} + \mathrm{H}:\ddot{\mathrm{O}}:\ddot{\mathrm{Cl}}: = \mathrm{H}:\ddot{\mathrm{O}}:\ddot{\mathrm{Cl}}\overset{+}{:}\ddot{\mathrm{O}}:\mathrm{H} + :\ddot{\mathrm{Cl}}\overset{-}{:} = \mathrm{H}:\ddot{\mathrm{O}}:\ddot{\mathrm{Cl}}\overset{+}{:}\ddot{\mathrm{O}}\overset{-}{:} + \overset{+}{\mathrm{H}} + :\ddot{\mathrm{Cl}}:$$

This is the first step in the formation of chloric acid from hypochlorous acid.



$$\begin{matrix}:\ddot{\mathrm{Cl}}:\ddot{\mathrm{N}}\overset{-}{:}\ \ \ddot{\mathrm{Cl}}\overset{+}{:}\\ :\ddot{\mathrm{Cl}}:\end{matrix} + \mathrm{CH_3CH_2}\overset{+}{\mathrm{C}}\mathrm{H}:\overset{-}{\mathrm{C}}\mathrm{H_2}\qquad \begin{matrix}\mathrm{CH_3CH_2CH} & : & \mathrm{CH_2}\\ :\ddot{\mathrm{Cl}}:\ddot{\mathrm{N}}: & & :\ddot{\mathrm{Cl}}:\\ :\ddot{\mathrm{Cl}}: & & \end{matrix}$$

Because of the ephemeral character of positive, six-electron ions the evidence for their existence is indirect and similar to the evidence for organic radicals long used so successfully by organic chemists. In addition to the list given, they furnish a very simple explanation of nitration and sulfonation (the first step may be an addition), of the transfer and interchange of positive chlorine and hydrogen between nitrogen and carbon, of the interchange of methyl or phenyl groups and hydroxyl in other rearrangements, and of many intramolecular shifts of atomic attachments.

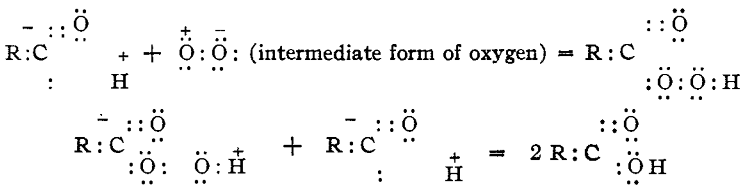
Because the evidence is indirect, we cannot expect complete agreement in the explanations given by different chemists. The situation is quite like that of tautomerism thirty to fifty years ago. We should be very careful to avoid dogmatism and should look diligently for experimental evidence for one view or another.

2. Ionic Reactions

A. Permanent Ions with Full Octets.—These are reversible and so rapid that the speed can rarely be measured. Three causes may make them nearly complete and may often reverse their direction: (a) formation of an insoluble or difficultly soluble product; (b) formation of a volatile product or of a compound which dissociates, giving a volatile product; (c) formation of a product which ionizes slightly, such as water, or which rearranges to a compound which ionizes slightly. Organic indicators belong to this class.

B. Covalence Reactions; Six-Electron Ions.—Such reactions are, superficially considered, very similar to the reactions of permanent ions, but there are important differences. One at least of the compounds reacting must be held together by a covalence; the number of six-electron ions is always very small and the speed of the reaction is frequently of such a rate that it can be measured; the covalence compounds formed may separate less readily than the original compounds and the reaction may be practically irreversible; covalence compounds may separate at different points and in different ways, causing different reactions to proceed at the same time—this is particularly true of organic compounds. Covalence compounds may also dissociate to electrically neutral parts with odd electrons and these free radicals (see below) may react in a different manner. Very often one of the reacting compounds and one of the products consist of permanent ions, as when methyl iodide reacts with silver nitrate. The same factors which cause reactions of permanent ions to become nearly complete are often important in covalent reactions.

The oxidation of aldehydes and ketones, recently discussed by Haber and Willstätter[1] and previously by Wieland, is probably of the covalence type

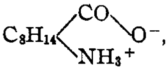


$$\mathrm{R{:}C}\begin{array}{l}-\,::\ddot{O}\\ :\quad \overset{+}{H}\end{array} + \overset{+}{\ddot{O}}{:}\overset{-}{\ddot{O}}{:}\ \text{(intermediate form of oxygen)} = \mathrm{R{:}C}\begin{array}{l}::\ddot{O}\\ :\ddot{O}{:}\ddot{O}{:}H\end{array}$$

$$\mathrm{R{:}C}\begin{array}{l}\bar{}\,::\ddot{O}\\ :\ddot{O}:\end{array}\ \overset{+}{\ddot{O}{:}H} + \mathrm{R{:}C}\begin{array}{l}-\,::\ddot{O}\\ :\end{array}\ \overset{+}{H} = 2\,\mathrm{R{:}C}\begin{array}{l}::\ddot{O}\\ :\ddot{O}H\end{array}$$

In the last reaction positive hydroxyl and positive hydrogen exchange places. Wieland has shown that acid peroxides are formed in some of these reactions.

3. Dissociation and Reactions of Free Radicals

The term "electrolytic dissociation" was originally used for ionization. It helps to clearer thinking if we use the word dissociation to designate separations which give electrically neutral atoms or molecules, and ionization to designate all cases where the positive charge of the kernel or nucleus of some atom is not balanced by the electrons immediately associated with it. Such ions, or the groups which contain them, may separate from the ions of opposite sign in solutions, or may be held to them by static attraction while retaining their ionic character as sodium and chlorine are held together in crystals and probably in the gaseous state, as the ammonium and carboxyl ions are held together in aminolauronic acid,  $C_8H_{14}\begin{array}{l}\diagup CO\diagdown\\ \diagdown NH_3^+\end{array}O^-$, and as atoms are held together in the semipolar unions of sulfuric acid and other compounds.

Dissociation is usually caused by heat, photochemical action or electrolysis. Typical examples are the dissociation of chlorine molecules to two chlorine atoms with seven electrons each; and the removal of an elec-

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[1] Haber and Willstätter, *Ber.*, **64**, 2849 (1931).

tron from the acetate ion in the electrolysis of sodium acetate. This is followed by the formation of a covalence between the oxygen atom which has lost the electron and the carbon of the carboxyl group, the other electron being taken from the covalence with the methyl. Carbon dioxide then separates in an electrically neutral state and the methyl, which is also electrically neutral, with its odd electron, immediately unites with another methyl radical to form ethane. Paneth and Rice have shown that similar free radicals may be formed by thermal dissociation and that such radicals are extremely reactive. Triphenylmethyl and similar compounds and the free radicals of nitrogen discovered by Wieland are more stable. Nitric oxide, an electrically neutral molecule with an odd electron takes an electrically neutral chlorine atom from nitrogen trichloride. The nitrogen dichloride unites with another mole of nitric oxide to form dichlorodinitrogen oxide. At −150° a third mole of nitric oxide takes an electrically neutral atom of chlorine from this compound.

Two atoms of sodium give their odd electrons to electrically neutral chlorine atoms, forming sodium chloride

$$2\text{Na}. + :\underset{\cdot\cdot}{\ddot{\text{Cl}}}:\underset{\cdot\cdot}{\ddot{\text{Cl}}}: = 2\overset{+}{\text{Na}} + 2:\underset{\cdot\cdot}{\ddot{\text{Cl}}}\overset{-}{:}$$

In a similar manner two atoms of sodium give their electrons to a molecule of oxygen, forming sodium peroxide

$$\text{Na}.\,\cdot\underset{\cdot\cdot}{\ddot{\text{O}}}:\underset{\cdot\cdot}{\ddot{\text{O}}}\cdot\,.\,\text{Na} \longrightarrow \text{Na}:\underset{\cdot\cdot}{\ddot{\text{O}}}:\underset{\cdot\cdot}{\ddot{\text{O}}}:\text{Na}$$

The reaction of sulfite ions with cupric ions giving cuprous ions and dithionate ions, recently discussed by Haber and Willstätter,[2] is probably of this type

$$2(\text{Cu}^{\underset{\cdot}{+}+}\cdot\text{SO}_3^{=}) = 2\text{Cu}^{+} + (\text{O}_3\text{S:SO}_3)^{=}$$

An electron is transferred from each sulfur atom to a cupric ion, reducing it to a cuprous ion. Then the sulfur atoms with odd electrons unite.

The decomposition of nitrogen trichloride and of acetylene and the chain reactions between hydrogen and chlorine and between hydrogen and oxygen, are almost certainly of this class. When such reactions are strongly exothermic they will be explosive.

The catalytic hydrogenation reactions are very probably due to hydrogen atoms with odd electrons.

I wish to express my thanks to a number of my friends, who have kindly read this paper and whose criticisms have been very helpful.

Summary

Reactions are classified, in accordance with their electronic character, under three heads: (1) formation of ions; A, with complete octets; B, from covalences, one with eight electrons, one with six; (2) ionic reactions;

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(2) Haber and Willstätter, *Ber.*, **64**, 2844 (1931).

A, ions with complete octets; B, ions formed from covalences; (3) dissociation and reactions of electrically neutral atoms and molecules.

The following principles, which the space allowed does not permit me to discuss, give a satisfactory explanation of the inorganic complexes: 4. Atoms may form covalence groups with a larger number of covalences than the number of valence electrons of the central atom. 5. A valence electron may be transferred, either to form a negative ion which enters the complex or one that is exterior to the complex. 6. If the "donor" (Sidgwick) is an electrically neutral molecule (ammonia or water), it becomes a positive ion in the complex; if it is a negative ion (Cl^-, NO_2^-), it becomes electrically neutral in the complex. 7. The "acceptor," in every case, develops a negative charge for each covalence, which may be balanced by the positive charge of the "kernel" (Lewis), by the positive ions of the complex or by positive ions exterior to the complex.

URBANA, ILLINOIS

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The Linear Thermal Expansion of a Single Crystal of Sodium Nitrate

BY J. B. AUSTIN AND R. H. H. PIERCE, JR.

The results of a recent series of studies of the physical properties of sodium nitrate conducted by Kracek[1] and his colleagues[2] have firmly established the existence of a gradual transition in the crystalline salt between 150 and 280°. The transition appears to be practically completed at 275° but abnormal changes in the heat capacity and volume are distributed over an extended temperature interval below this critical point.

The basis for a satisfactory explanation of the phenomenon seems to have been found in the theoretical treatment by Pauling[3] of the problem of the diatomic homopolar molecule free to rotate in an axially symmetrical field of force. His analysis together with the available x-ray evidence[2] makes it seem almost certain that during the transition interval the rotational degree of freedom of the nitrate ion about an axis normal to the plane of the group becomes excited. At the critical temperature this degree of freedom is fully excited and the nitrate ion begins to rotate about the trigonal axis of the crystal unit. The transition corresponds, therefore, to a change from oscillational to rotational motion for the nitrate ion.

One of the properties studied in detail by Kracek was the volume ex-

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[1] Kracek, THIS JOURNAL, **53**, 2609 (1931).

[2] Kracek, Posnjak and Hendricks, *ibid.*, **53**, 3339 (1931).

[3] Pauling, *Phys. Rev.*, **36**, 430 (1930).