through the flask before it was connected to the apparatus. Not more than 2 g. of phosphonium iodide crystallized out during the preparation of 650 g. of anhydrous hydrogen iodide. Its solubility in the calcium iodide solution is practically nil since the amount at the end of successive runs increased in proportion to the total hydrogen iodide produced. During each run there was formed in the generating flask a small amount of reddish powder, an intermediate reduction product of the phosphorus pentoxide, which was not investigated.

A saturated aqueous solution of hydrogen iodide prepared by this method gave a negative test for phosphate with ammonium molybdate.

The authors wish to express their appreciation to Professor Howard J. Lucas for his helpful suggestions in the work.

Summary

The description of a method and apparatus is given for the rapid formation of pure anhydrous hydrogen iodide. This is generated by dropping concentrated hydriodic acid upon phosphorus pentoxide and purified by bubbling through saturated calcium iodide, drying with phosphorus pentoxide and cooling to −30°.

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THE ELECTRONIC INTERPRETATION OF OXIDATION AND REDUCTION

BY WILLIAM ALBERT NOYES

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In several papers the attempt has been made to reconcile the positive–negative theory of valence, formerly advocated by myself, Stieglitz, Falk and Nelson, Fry, L. W. Jones and others,[1] with the theories of G. N. Lewis, Kossel and Langmuir, on the basis of the following principles.

1. Nearly all reactions occurring at ordinary temperatures are ionic in character.[2] For electrolytes this is identical with the positive–negative theory and is universally accepted. For other compounds this principle implies that the pair of electrons forming a covalence remains with one or the other of two atoms which separate as they prepare to enter into new combinations.[3]

2. There is a sharp difference between completely polar valences, in which one atom gains and the other loses an electron, and covalences, in which a pair of electrons is shared by two atoms. At the symposium of the Faraday Society in Cambridge, in 1923, I said "The difference

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[1] For references to the literature see THIS JOURNAL, **50**, 2902 (1928).

[2] Noyes, *Chem. News*, **90**, 228 (1904); THIS JOURNAL, **45**, 2959 (1923).

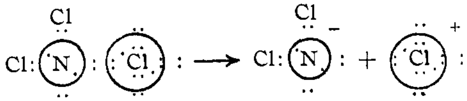
[3] For the hypothesis that a covalence consists of a pair of electrons rotating in opposite directions and including two nuclei within their orbits, see Robert Müller, "Der Aufbau der chemischen Verbindungen (Molekülbau)," Sammlung chem., chem.-tech. Vorträge, Bd. **30** (1928) and Noyes, *Proc. Nat. Acad. Sci.*, **13**, 377 (1927).

between polar and non-polar valences is one of degree and not one of kind."[4] In making the statement I had in mind the ionization of weak acids and of tautomeric compounds and of carbon compounds which take part in condensations. It now seems to me better to make the distinction used here and to call covalences which more or less easily separate into positive and negative parts "potentially polar."[5] The distinction is chiefly one of nomenclature.

3. Covalences may be "potentially polar" for three reasons: (a) because one of the atoms has a larger kernel charge than the other and, therefore, a stronger attraction for the pair of electrons. The halogens, with a kernel charge of 7, nearly always retain the pair of electrons when they separate from a carbon atom, which has a kernel charge of 4. Hydrogen, with a nuclear charge of 1, leaves the pair with almost any atom from which it separates. There is no good evidence that it retains the pair and becomes a negative ion, except in separating from a metallic hydride.

(b) Because neighboring atoms in the molecule have a large kernel charge. The bromine of bromo-acetoacetic ester, $CH_3COCHBrCO_2C_2H_5$, is affected in such a manner that it leaves the pair of electrons with the carbon atom and separates in the positive form, $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Br}}}$, titrating with sodium thiosulfate as equivalent to two atoms of free bromine.[6] Hydrogen atoms attached to a carbon atom adjacent to a carboxyl or aldehyde group or to a carbon atom bearing an hydroxyl group, readily become hydrogen ions. This accounts for many condensation reactions and for the reactivity of alcohols in comparison with hydrocarbons.

(c) Because one of the atoms has a larger number of electrons in the kernel than the other and, for this reason, has less attraction for its valence electrons. The chlorine atoms of nitrogen trichloride give up their pairs of electrons to the nitrogen when the compound is decomposed by hydrochloric acid,[7] in spite of the kernel charge of 5 on the nitrogen atom and of 7 on the chlorine atom, because there are only 2 electrons in the kernel of the nitrogen atom and 10 in the kernel of the chlorine



Phosphorus trichloride, on the other hand, hydrolyzes to phosphorous acid and hydrochloric acid because there are 10 electrons in the kernels

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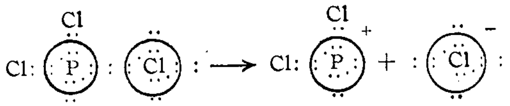
[4] Noyes, *Trans. Faraday Soc.*, **19**, 476, 478 (1923).

[5] Noyes, *Z. physik. Chem.*, **130**, 325, 329 (1927).

[6] Kurt Meyer, *Ann.*, **380**, 217 (1911); Noyes, "Organic Chemistry," Henry Holt and Co., **1926**, p. 420.

[7] Noyes, THIS JOURNAL, **42**, 2173 (1920).

of both phosphorus and chlorine, while the kernel charge of phosphorus is 5 and that of chlorine is 7:



4. In compounds containing only covalences, the number of covalences plus the number of unshared electrons is equal to the number of valence electrons for each atom.

5. In ions, whether simple or complex, there is always some atom which has completed its octet by uniting with a larger or smaller number of electrons than is called for by 4.

6. Atoms may be doubly united either by a doubled covalence or by one covalence and one polar union.

Adherents of the positive–negative theory in its earlier form defined oxidation as the loss and reduction as the gain of electrons. A consideration of the electronic mechanisms in the light of the principles given, leads us to distinguish three types of oxidation.

1. **Transfer of an Electron.**—When sodium is oxidized by chlorine, the electrons of two sodium atoms are transferred to a molecule of chlorine, giving two chloride ions. When sodium reacts with water, each sodium atom gives its electron to a hydrogen ion, which is the real oxidizing agent. The hydrogen ions are reduced to free hydrogen.

When aluminum dissolves in a solution of sodium hydroxide, there is a similar exchange of electrons between the aluminum and the hydrogen ions of the solution, though the latter are present in small numbers. The fact that the hydroxyl ions unite with the aluminum with a covalence, giving an amphoteric hydroxide and reducing the hydroxyl-ion concentration, is probably an important factor in the phenomenon.

The oxidation of *o*- or *p*-cresol, with evolution of hydrogen,[8] when they are fused with potassium hydroxide, is best explained in a similar manner. The semipolar oxygen atom of the cresylate ion, $CH_3C_6H_4:\overset{..}{\underset{..}{O}}:^-$, enhances the tendency of the hydrogen atoms of the methyl group in the ortho or para position to assume the ionic form, as the hydrogen atoms in the ortho and para positions do in the Kolbe and Reimer–Tiemann syntheses. The hydrogen ions, in this case, do not escape as positive ions, however, but take the electrons from the carbon atom of the methyl group and unite with hydrogen ions of the water, forming free hydrogen. This is essentially the explanation given by Professor Fry, for a similar reaction, at the Columbus symposium.

2. **Oxidation by Positive Hydroxyl.**—This explanation has been given[9]

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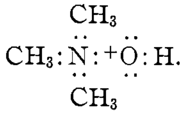
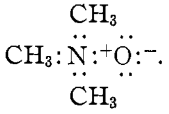
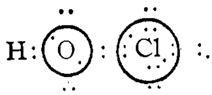
[8] Barth, *Ann.*, **154**, 359 (1870).

[9] Noyes, *Bull. soc. chim.*, **35**, 437 (1924).

for the oxidation of trimethylamine to trimethylamine oxide by hydrogen peroxide. Hydrogen peroxide separates into a positive hydroxyl, $H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}{}^{+}$, and a negative hydroxyl, $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:^{-}H$, in the same way that a molecule of chlorine separates into positive chlorine, $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}{}^{+}$, and negative chlorine, $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:^{-}$, in reacting with water. This positive hydroxyl can add itself to the two free electrons of the trimethylamine, oxidizing the electrically neutral nitrogen atom to the ionic form,  $CH_3:\underset{CH_3}{\overset{CH_3}{N}}:{}^{+}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H$. If hydroxyl ions, which have a strong affinity for hydrogen ions, are present, the hydrogen will unite with these, leaving a semipolar union between the oxygen and the nitrogen,  $CH_3:\underset{CH_3}{\overset{CH_3}{N}}:{}^{+}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:^{-}$. If a chloride or bromide ion is present, this does not happen.[10]

The intermolecular oxidation of three moles of hypochlorous acid to chloric acid and hydrochloric acid is most easily explained by a consideration of the close balance in the attraction of the oxygen and chlorine atoms for the pair of electrons forming the covalence between them: . The chlorine atom with a kernel charge of 7, and 10 electrons in its kernel, has almost the same attraction for the pair of covalence electrons as the oxygen atom has, with a kernel charge of 6 and only two electrons in its kernel.

It has been shown[11] that hypochlorous acid gives the four ions H^+, ClO^-, HO^- and Cl^+. Because of the balance between the oxygen and chlorine, two other ions are probable; a positive hydroxyl ion, $H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}{}^{+}$, and the negative chloride ion, $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:^{-}$. By the union of the positive hydroxyl with a mole of hypochlorous acid, the compound $H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}{}^{+}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H$ is formed. The chlorine atom of this compound is positive because the sum of the covalences and unshared electrons is only 6. The loss of a hydrogen atom as an ion leaves a semipolar union between the chlorine and oxygen, $H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}{}^{+}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:^{-}$. The hydrogen ion, on the other hand, balances the chloride ion left when the hypochlorous acid separates into positive hydroxyl and negative chlorine. A repetition of this process gives chloric acid.

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[10] Noyes, THIS JOURNAL, **47**, 3025 (1925).

[11] Noyes and Wilson, *ibid.*, **44**, 1630 (1922).

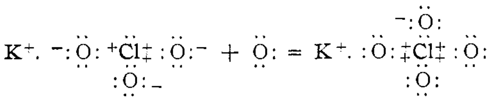
Because of the accumulation of semipolar oxygen atoms, chloric acid has a high ionization constant while that of hypochlorous acid is very small.

F. Foerster[12] nearly thirty years ago gave the following ionic interpretation for the formation of chloric acid

$$\mathrm{ClO^{-} + 2HOCl = ClO_3^{-} + 2H^{+} + 2Cl^{-}}$$

It will be seen that this is equivalent to the electronic interpretation here given, but less detailed.

3. Oxidation by Semipolar Oxygen Atoms.—When potassium chlorate is kept at its melting point, in the absence of a catalyst, it may be largely converted to potassium perchlorate. This may be explained by supposing the transfer of an electrically neutral oxygen atom from one mole of the potassium chlorate to another



$$\begin{array}{ccccccccccc}
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\end{array}$$

The oxidation of alcohols by nitric acid, potassium permanganate and other agents which contain semipolar oxygen atoms is probably of this type.

The presence of oxygen in a carbon compound enhances the tendency of the hydrogen atoms attached to the same or to an adjacent carbon atom to separate as positive hydrogen ions. It is well known, of course, that the hydrogen of a primary or secondary alcohol or of an aldehyde group is easily replaced by hydroxyl. In the simplest case, methyl alcohol separates into $\mathrm{H}{:}\underset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{C}}}}{:}^{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}{:}\mathrm{H}$ and H^{+}. An electrically neutral oxygen atom would engage the pair of electrons of the carbon atom, but the added oxygen atom would now be negative, $\mathrm{H}{:}\underset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{{:}\overset{\cdot\cdot}{\mathrm{O}}{:}^{-}}{\overset{\cdot\cdot}{\mathrm{C}}}}}{:}\mathrm{O}{:}\mathrm{H}$ and would take up the hydrogen ion. In the compound which results, $\mathrm{H}{:}\underset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{{:}\overset{\cdot\cdot}{\mathrm{O}}{:}\mathrm{H}}{\overset{\cdot\cdot}{\mathrm{C}}}}}{:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}{:}\mathrm{H}$, the balance of the affinity of the carbon for the hydroxyl and of the oxygen for the hydrogen, which causes these to separate as water, leaving a double union between the carbon and the oxygen, is well known. That the carbon is doubly united with the oxygen in aldehydes, ketones and acids has been shown by Sugden.[13]

Theoretically any semipolar oxygen atom may separate with its six

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[12] F. Foerster, *J. prakt. Chem.*, [2] **63**, 147 (1901).

[13] Sugden, *J. Chem. Soc.*, **125**, 1183 (1924); **127**, 1525, 1530 (1925).

valence electrons without disturbing the electronic balance of the atom from which it separates.

Summary

There seem to be at least three types of oxidation reactions.

1. Oxidation by the transfer of an electron from one atom to another.
2. Addition of a positive hydroxyl group, $\mathrm{H}:\ddot{\underset{\cdot\cdot}{\mathrm{O}}}^{+}$, to an unshared pair of electrons, either of a negative ion or of an electrically neutral molecule. In the latter case a hydrogen ion separates and a semipolar union is formed.
3. Separation of a semipolar oxygen atom in an electrically neutral condition followed by its union with an unshared pair of electrons. The oxygen atom may either remain in the semipolar condition in the new compound or may take up a hydrogen ion and form an hydroxyl group.

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TERNARY SYSTEMS. VIII. POTASSIUM CARBONATE, POTASSIUM SULFATE AND WATER AT 25°

BY ARTHUR E. HILL AND SAMUEL MOSKOWITZ

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The solubilities of potassium carbonate and potassium sulfate in water have been studied by Blasdale[1] and more recently by de Ropp,[2] in both cases as part of a study of a four-component system. The two papers give data for the solubilities, however, at the isothermally invariant points only; the solubilities at intermediate concentrations having been determined in this Laboratory, the results are communicated to complete the picture.

Anhydrous potassium carbonate (Kahlbaum's "zur Analyse") and potassium sulfate (purified by recrystallization) were taken in weighed amounts and agitated with measured amounts of water at 25 ± 0.05° until equilibrium was attained, three days being found to be a sufficient time. The saturated solution was analyzed for carbonate by titration against acid, using methyl orange as indicator, with correction for the effect of the sulfate on the end-point. Water was determined as loss by evaporation from platinum dishes. Sulfate was determined only when the amounts had become small, in Line 6 by precipitation as barium sulfate from an acid solution, and in Lines 7, 8 and 9 turbidimetrically. Direct weighing of small pipetted samples gave values for the density of the solution.

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[1] Blasdale, THIS JOURNAL, **45**, 2935 (1923).

[2] Teeple, "Industrial Development of Searles Lake Brines," Chemical Catalog Company, New York, **1929**, p. 72.