that the adsorptive power of the German charcoal with the most fixed oxygen was the lowest and the English charcoal with the least fixed oxygen the highest, the presence of undecomposed hydrocarbons was also greatest in the German and least in the English charcoal. So, since in the preliminary treatment of the charcoals (Part I), most of the fixed oxygen was removed while the hydrocarbon content was not much altered, the differences observed are more likely due to this latter cause.

Conclusions.

1. The anomalous behavior of the adsorption of oxygen by charcoal extending over long periods of time, overlooked by recent investigators, has been confirmed. This is shown to be due to the presence of 2 phenomena, adsorption and surface combination.

2. A method has been developed for heating charcoal in a vacuum out of contact of oxygen-containing materials, as quartz, to high temperatures by use of the Northrup induction furnace. The gases evolved were collected and analyzed.

3. The formation of a carbon-oxygen complex, essentially a stable solid oxide of carbon, has been shown to occur on the surface of charcoal at ordinary temperatures. This complex decomposes on heating to carbon dioxide and carbon monoxide and can thus be considered to be an intermediate step in the combustion of charcoal, which supports the view suggested by Armstrong and supported with experimental evidence by Rhead and Wheeler and by Langmuir.

4. The amounts of oxygen thus combined to the charcoal has been found to vary with 2 samples of charcoal from 1.71% to 3.75% of the *weight* of the charcoal.

PRINCETON, N. J.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

POLARITY AND IONIZATION FROM THE STANDPOINT OF THE LEWIS THEORY OF VALENCE.

BY WENDELL M. LATIMER AND WORTH H. RODEBUSH.

Received April 26, 1920.

Some years ago Abegg and Bodlander[1] discussed the general facts concerning strong and weak electrolytes, the solubility of salts and the formation of complex ions in solution. They showed that these facts may be coördinated and explained to a surprising extent by attributing to each element or radical, in greater or less degree, a property which they called electro-affinity. This property has been more commonly designated as electropositive or electronegative character, and its relation to position in the periodic table is clearly recognized. It now seems possible to go

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[1] Bodlander, *Z. anorg. Chem.*, **20**, 453 (1899).

further and show this property to be a consequence of the structure of the atom.

In accordance with the Rydberg relationship, the elements from lithium to argon may be arranged in order of their atomic numbers, so that they fall in 2 short series of 8 each. Starting with potassium, there follow 2 series of 18 elements each, and with cesium, 2 series of 32 elements each, the last series, however, being incomplete. The elements in the middle of these long series are peculiar in their behavior, although it is difficult to say with what particular element the abnormality begins or leaves off. However, the elements at the beginning and end of the long series show the same gradation of properties as the elements in the first 2 series of 8. If we somewhat arbitrarily omit the elements of peculiar behavior in the middle of the long series, we can construct a simplified periodic table in series of 8 throughout, each column then consisting of a group of elements of the same valence. Thus, for example, the first group will contain the alkali metals from lithium to cesium, the fifth group the elements from nitrogen to bismuth, and the seventh group, the halogens.

The theory proposed and outlined by G. N. Lewis[1] gives us a definite picture of the structure of the atom for the elements in this simplified periodic table. From the standpoint of the Lewis theory, if the net positive charge upon the kernel be assumed to behave as if centered in the nucleus, the amount of the attraction of this charge for the valence electrons determines the degree of electronegativity of the element. The element becomes more electronegative as we go across the table from left to right because of the increasing net positive charge upon the kernel. As we go down any valence group the attraction of a positive nucleus for the valence electron is decreased because of the increased distance of the valence electron due to the interposition of additional shells of electrons between it and the nucleus. Thus sulfur with a net positive charge on the kernel of 6 is more electronegative than phosphorus with a net positive charge of 5. On the other hand, phosphorus is less electronegative than nitrogen because the valence electrons are separated from the nucleus by an additional shell of electrons.

The term polar[2] has been used in connection with many different properties, but we shall consider it here in its simplest sense. A compound will be said to be polar in which a valence electron has passed from one atom to another, leaving a positive charge upon the one atom and giving a negative charge to the other, thus forming, if the compound contain but the two atoms, an electric dipole. In the extreme case it seems probable that the electron passes completely from the one atom

[1] Lewis, THIS JOURNAL, 38, 762 (1916); Langmuir, *ibid.*, 41, 868, 1543 (1919).

[2] Bray and Branch, THIS JOURNAL, 35, 1440 (1913); Lewis, *ibid.*, 35, 1448 (1913).

to the other and that the two atoms behave as though the respective charges of positive and negative electricity were located at the centers of the atoms themselves. All the intermediate stages between polar and non-polar compounds doubtless occur, depending upon the extent to which the neutrality of the molecule is disturbed as the electron is more or less completely displaced from one atom to the other.

It follows from the Lewis theory of valence that the degree of polarity of a compound of 2 atoms would depend upon the difference in electronegative character of the 2 atoms, and this conclusion is readily verified by consideration of the facts. Thus in lithium chloride the lithium atom has a net positive charge on the kernel of one, the chlorine atom has a net charge of 7, and we should expect the valence electron to be completely taken away from the lithium and drawn into the outer shell of the chlorine, forming an extremely polar compound. This we find to be the case. Beryllium chloride is not as polar as lithium chloride, since beryllium has a net positive charge on the kernel of 2, and consequently the attraction of the kernel for the valence electrons is twice as great. Boron trichloride shows very little polarity, owing to the fact that the net positive charge of 3 on the boron kernel exerts a powerful attraction for the valence electrons. Carbon tetrachloride is non-polar. Here the net positive charge of 4 on the carbon kernel exerts so strong a pull on the valence electrons that the carbon and the chlorine atoms are simply drawn closer together and the valence electrons may be said to exist in the shells of both atoms. If the compounds of the elements are considered at random we find that whenever there is sufficient difference between the attraction of the positive kernels of 2 atoms for the electrons forming the bond between them, the compound is polar, and the degree of polarity can always be predicted from the structure of the atoms.

Ionization of Polar Compounds.

The criteria by which we shall judge whether a compound is ionized or not will depend on our definition of ionization. The X-ray spectrum of a crystal of sodium chloride shows that each atom of sodium is surrounded by 6 atoms of chlorine, and each atom of chlorine by 6 atoms of sodium. Presumably the valence electron of the sodium has been entirely removed from the sodium atom and forms a part of the shell of the chlorine atom. We cannot say to which particular chlorine atom the electron of the sodium has gone. Sodium chloride does not conduct a current because the atoms are not free to move. However, if we bring the sodium chloride into the liquid state, by fusion for example, it becomes a very good conductor indeed. In the fused state the arrangement of the atoms of sodium chloride is probably not greatly different from that in the crystal, except as it is disturbed by the mobility of the liquid. Since a sodium atom is surrounded on all sides by chlorine atoms it is free to move in any direction upon the application of an electric field, and conduction in the fused salt consists presumably of the movement of atoms of one kind of electric charge through the nearly uniform field produced by a mesh of atoms having the opposite electric charge.

It seems logical to say that a polar molecule is ionized when the ions are able to move independently of each other under the influence of an applied electric field. By this definition fused sodium chloride appears to be completely ionized, but solid sodium chloride, while completely polar, would not of course be considered ionized.

When we form a dilute solution of sodium chloride in an ionizing solvent of negligible conductivity, we meet with a new phenomenon. The most conspicuous characteristic of an ionizing solvent is an abnormally high dielectric constant. The connection between the high dielectric constant and the ionizing power of the solvent has often been explained as follows. In order that sodium chloride in solution may ionize, the powerful electrostatic forces between the ions must be overcome. It is necessary that the solvent act as a depolarizing medium and partially neutralize these forces. The power of the solvent to do this is presumably measured by the dielectric constant. From these considerations the Nernst-Thomson rule was formulated, which states that the ionizing power of a solvent should vary more or less directly with the dielectric constant.

The Nernst-Thomson rule presumes that if a sodium and a chloride ion are separated in solution by a greater distance than they are in the crystal there are strong electrostatic attractions between them. This may not be the case. The molecular volume of sodium chloride is only about half the sum of the atomic volumes of metallic sodium and solid chlorine. Atomic volume of course has no significance as far as actual size of the atoms is concerned, but it does indicate the strength of the forces between the atoms of the crystal. When an atom of chlorine approaches within a certain distance of an atom of sodium there must be some sort of a repulsive force which opposes a closer approach of the 2 atoms. The distance between an atom of sodium and at atom of chlorine in the crystal then represents the distance at which the repulsive forces just balance the attractions between the atoms. If the attractive force between the atoms is less than in sodium chloride, as it is in metallic sodium, the equilibrium positions are farther apart. Now when we dissolve sodium chloride in water which has a dielectric constant of 80, the attractive force between the atoms is reduced to a little more than 1% of its original value. If the repulsive forces between the atoms, of the nature of which we are entirely ignorant, be not reduced to a proportional amount, the interatomic distance for equilibrium between the 2 forces may be considerably increased. In a concentrated solution of sodium chloride the average distance between the sodium and the chloride ions is only about twice that of the crystal, and from the foregoing considerations it is by no means certain that the ions would tend to approach each other any closer than this average distance, especially since an ion is not in the field of a single ion of opposite charge but is acted upon by a number of ions in different directions, the forces of which more or less neutralize each other. In other words, a concentrated solution of sodium chloride may be analogous to fused sodium chloride, except for somewhat greater interatomic distances.

If the foregoing picture is correct, a concentrated solution of sodium chloride is completely ionized.[1] At infinite dilution where the ions are so far separated as to be out of each other's fields we must also have complete ionization. At intermediate concentrations, where the average distance between ions is greater than the equilibrium distance and yet not so great that the ions are out of each other's fields, there may be a tendency for the ions to form in pairs separated from each other by the equilibrium distance. Now since the independent movement of an ion depends upon its being acted upon by several other ions at such distances and directions as to neutralize each other, such a pair can hardly be said to be ionized. There seems to be some evidence that this effect is most pronounced at about molal concentration for sodium chloride.[2]

From the foregoing considerations, in a solution of a polar salt like sodium chloride the ions must always be separated by greater distances than in the solid. In order that a liquid may act as a solvent for a polar substance it must be a depolarizing agent of sufficient strength to permit the separation of ions which takes place when the salt dissolves. This seems to be the chief significance of dielectric constant. Obviously the minimum value of dielectric constant which a liquid must have in order to function as a solvent for polar substances will depend upon the forces between the ions in the solid. Sulfur dioxide, with a dielectric constant of about 14, is able to dissolve many salts. When we consider liquids of dielectric constant below 8 we find that salts do not dissolve in them appreciably as a rule. Solubility is of course affected by many factors, but it seems quite probable that the reason for the slight solubility of salts in these liquids is the inability of the solvent to neutralize the electrostatic forces between ions.

In the few cases[3] in which there is electrolytic conduction in solution

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[1] Cf. Noyes and MacInnes, THIS JOURNAL, **42**, 239 (1920).

[2] Allmand and Polack, *J. Chem. Soc.*, **115**, 1036 (1919).

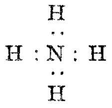
[3] Examples are: Methyl Alcohol in Liquid Hydrogen Chloride (Archibald, THIS JOURNAL, 34, 584 (1912)); Potassium Iodide in Liquid Iodine (Lewis and Wheeler, *Z. physik. Chem.*, **56**, 179 (1906)); Ether and Bromine (Plotnikow, *J. Russ. Phys. Chem. Soc.*, **38**, 1096 (1906)); Magnesium Iodide in Ether (unpublished investigation by Mr. R. F. Newton of this laboratory). See also Kraus and Bray, THIS JOURNAL, **35**, 1393 (1913).

in a solvent of low dielectric constant, we find the conductivity very small in dilute solutions, but increasing very rapidly with increasing concentration until it reaches a maximum at some concentration at which the ratio of mols of solvent to mols of solute is a small number, usually not greatly different from unity.

In all these cases the solubility appears to be due to the formation of more or less stable compounds between the solute and the solvent. The behavior of the conductivity is precisely what we should expect. The depolarizing action of the solvent is so small that positively and negatively charged ions are unable to separate and move freely with respect to each other. Hence conductivity in the dilute solution is negligible, the ions being in a condition precisely analogous to sodium chloride vapor, grouped in pairs or molecules. What little conductivity there is, is due to an accidental separation of ions not different from that which takes place in salt vapors. As the concentration approaches the composition of the molecular compound we approach the condition of a fused salt, where an ion is surrounded by ions of opposite sign and can move freely in any direction. The increased conductivity in concentrated solutions is then precisely analogous to fused salt conductivity.

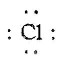
Ionization of Compounds Not Highly Polar.

So far we have discussed polarity the mechanism of which consisted of the transfer of electrons from one atom to another in the molecule. We shall now consider polarity due to the transfer of a hydrogen nucleus from one molecule to another. For example the formation of the ammonium ion



$$\begin{array}{c} \mathrm{H} \\ \mathrm{H} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}} : \mathrm{H} \\ \mathrm{H} \end{array}$$

and the chloride ion



$$: \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}} :$$

by the transfer of a hydrogen nucleus from a molecule of hydrogen chloride to a molecule of ammonia. In discussing compounds of hydrogen it must be borne in mind that the hydrogen kernel is also the hydrogen nucleus and as such is very different from the kernel of any of the other elements. Here in all probability we are dealing with the elementary unit of positive electricity, seemingly a particle of minute size even in comparison with the electron. It has already been pointed out that the relative electronegativity of the elements depends upon the net nuclear charge and the distance of the valence electrons from the nucleus as determined by the number of electron shells. Now the hydrogen nucleus, though its nuclear charge is but one, has no surrounding shell of electrons, and may for that reason approach many times closer to the electrons of a valence bond than any other element. What knowledge we have concerning the structure of the nuclei of the elements of higher atomic weight indicates that hydrogen nuclei and electrons may be packed together very closely indeed. In one sense, then, hydrogen is the most electronegative of all the elements,[1] and it is doubtful if the hydrogen nucleus ever gets very far away from one or more electrons. It is this unique character of the hydrogen nucleus which differentiates the polarity of hydrogen compounds. In the pure state, although differing a good deal in degree, they are all extremely non-polar. Thus even as strong an acid as hydrochloric acid is in the pure liquid state a nonconductor of the same order as water. Nor is its conductivity appreciably increased when dissolved in acetone or nitrobenzene,[2] substances with fairly high dielectric constants. Even in liquid hydrogen cyanide, which has a very high dielectric constant, hydrogen chloride does not show a conductivity comparable with that of some salts in the same solvent.[3] Walden[4] has shown that ionization of acids in solvents is independent of the Nernst-Thomson rule of dielectric constant and is greater the more basic the solvent. In the light of the experimental facts, then, the ionization of acids, or indeed extreme polarity of any compounds involving hydrogen, must be interpreted as due to the transfer of a hydrogen nucleus from one molecule to another, thus forming a complex ion. Indeed, from the nature of the hydrogen nucleus, it seems as unlikely that in a solution hydrogen ions should exist as such, as that the electrons should be present moving about freely. It is true that hydrogen shows great mobility in water solutions, but it will appear later that this does not of necessity argue the existence of free hydrogen ions.

Obviously any discussion of the degree of ionization from the standpoint of atomic structure[5] must deal not only with the tendency of the acid to give up hydrogen, but also with the tendency of the solvent to take it up. Let us first consider the hydrogen compounds

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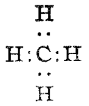
[1] This conclusion is borne out by the fact that atomic hydrogen has such a powerful tendency to form H_2. Extremely electronegative elements such as nitrogen, oxygen and the halogens all show this tendency to form a "saturated" diatomic molecule, that is one of very low or at least uniform external field. Since the external fields of these molecules are nearly neutral, these strongly electronegative substances are extremely volatile in the molecular state. The ease of replacement of acid hydrogen by metals and the volatility of the diatomic gas are both due to the powerful tendency for the formation of molecular hydrogen.

[2] Sackur, *Ber.*, **35**, 1248 (1902).

[3] Kahlenberg and Schlundt, *J. Phys. Chem.*, **6**, 447 (1902).

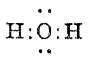
[4] Walden, *Trans. Faraday Soc.*, **6**, 71 (1910).

[5] Some of the conclusions reached in the following paragraphs have been indicated by Langmuir in a paper, THIS JOURNAL, **42**, 274 (1920), which appeared while the present paper was yet in the manuscript.

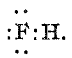


$H:\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{C}}:H$

$H:\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{N}}:$



$H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H$



$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:H.$

The increasing charge on the kernels of the elements from carbon to fluorine must tend to pull in closer the electrons of the groups of 8, or, as Langmuir has called them, the octets formed about the kernels; and at the same time the hydrogen is held off by the increasing repulsion between the positive nuclei. Consequently, the total force holding the hydrogen becomes less, that is, the compound becomes more acid when dissolved in a solvent, the molecules of which have a field sufficiently negative to pull the hydrogen away. Now let us consider the tendency of these same hydrides to take up hydrogen kernels, in other words their ability as solvents to ionize other acids. One of the fundamental postulates of the Lewis theory is that a valence bond in those elements which form octets consists of a pair of electrons held in common by 2 atoms. An octet about an atom is then capable of uniting with 4 other atoms, providing of course that the total number of electrons in the atom is such as to complete all the shells. This tendency to complete the group of 4 atoms about an octet of electrons is in many ways as striking as the tendency to complete the octet of electrons about a positive kernel. Now methane has completed its group of 4 atoms and has no free pairs of electrons left; while ammonia has one free pair of electrons, water 2, and hydrogen fluoride 3. Moreover the force with which a pair of electrons of an octet is holding a hydrogen nucleus gives us a good indication of the tendency of a free pair of electrons of the same octet to add another hydrogen nucleus. From these considerations, we should expect ammonia to form readily the ion NH_4^+ and water and hydrogen fluoride to show strong but decreasing tendencies to form at least the ions, H_3O^+ and H_2F^+. It follows that for an acid dissolved in liquid ammonia a relatively larger number of the molecules will react with the solvent to form a polar compound than for the same acid dissolved in water. And in general it may be said that the degree of ionization of weak acids as determined by conductivity measurements will be greater the more basic the solvent. However, the situation is somewhat different when we compare solutions of a strong acid, for example, hydrochloric acid, in water and liquid ammonia, since in both solvents the hydrogen chloride has probably completely reacted with the solvent to form polar molecules. In fact Kraus and Bray,[1] from comparative measurements, have calculated the degree of ionization of hydrochloric acid to be greater in dilute solution in water than for solutions of corresponding concentration in ammonia.

We have seen that for a horizontal row in the periodic system the

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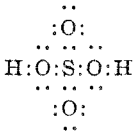
[1] Kraus and Bray, THIS JOURNAL, 35, 1337 (1913).

acidity of the hydride is greater the more electronegative the element. Consideration of the hydrides of any valence group leads to the conclusion that in this case the hydride is more acid the less electronegative the element. For example, hydrogen chloride is more acid than hydrogen fluoride, hydrogen sulfide more acid than water, phosphine more acid than ammonia. The elements sodium to chlorine differ from the corresponding elements lithium to fluorine in that the valence electrons are forming a new group of 8 around the first group of 8. Then in hydrogen chloride the valence electrons are (1) farther from the center of the kernel, and (2) farther from each other than in hydrogen fluoride. As a consequence of (1), an electron is held by less force, and, as one continues down the valence group, it becomes increasingly less difficult for the hydrogen to take the electron completely away from the halogen, and we find hydrogen iodide gas dissociating largely into molecular hydrogen and iodine. From (2) it seems reasonable to expect hydrogen chloride to be more acid than hydrogen fluoride in that the hydrogen, in the case of chlorine, is held by a pair of electrons which are farther apart than in fluorine. Indeed in the latter the octet may be sufficiently small so as to enable electrons other than the pair to exert considerable attraction upon the hydrogen nucleus.

The strength of an oxy-acid may be considered in terms of the forces tending to distort the oxygen octet. Lewis,[1] in his paper on "The Atom and the Molecule," has discussed the effect of substituting a chlorine in acetic acid. The ideas which he expressed may be extended considerably in connection with the inorganic oxygen acids. Thus in sulfuric acid



$$\begin{array}{c} \cdot\cdot \\ :\mathrm{O}: \\ \cdot\cdot\ \cdot\cdot\ \cdot\cdot \\ \mathrm{H}:\mathrm{O}:\mathrm{S}:\mathrm{O}:\mathrm{H} \\ \cdot\cdot\ \cdot\cdot\ \cdot\cdot \\ :\mathrm{O}: \\ \cdot\cdot \end{array}$$

the attraction of the sulfur kernel for electrons held in common with the oxygen, and the repulsion between the sulfur and the oxygen kernels tend to distort the oxygen octet from the cubical arrangement. Obviously this pulling of electrons in toward the sulfur and pushing of the oxygen kernel out will weaken the force with which the hydrogen is holding a pair of electrons in common with the oxygen. The higher the positive charge on the central kernel, the greater will be this distortion. Then for any horizontal row of the periodic system, the oxygen acids of highest valence, for example silicic acid (H_4SiO_4), orthophosphoric, sulfuric and perchloric acids, will become stronger as the atomic number increases. The close agreement of the densities of the last 3 acids above indicates that their structures are very similar and emphasizes the fact that rela-

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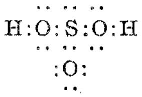
[1] Lewis, *loc. cit.*, p. 782.

tively small distortions of the oxygen octet may produce large differences in the degree of ionization when water is the solvent.

We have seen in any vertical or valence periodic group that as the atomic weight increases, that is, as each new shell is formed about the preceding one, both the attraction for the valence electron and the repulsion of a neighboring kernel decrease. Then in the case of an oxy-acid the distortion of the oxygen octet due to the central atom must become less as one goes down the group; their form doubtless approaches more and more that of the oxygen in the water molecule and the hydrogen consequently is held with corresponding firmness. In fact the attraction of the central kernel for the electrons may become so weak that the oxygen octet is no longer held in position but ionizes to form hydroxyl. Thus we have the amphoteric compounds. For illustration we need only mention HNO_3, H_3PO_4, H_3AsO_4, H_3SbO_4, $Bi(OH)_3$. Putting the two cases together we have the well known generalization that the more negative the element the stronger the oxygen acids. The condition for maximum distortion of the oxygen octet would be found in perfluoric acid. Doubtless this is the very reason that no oxygen compounds of fluorine are known.

The generalization may be made in terms of the older idea of valence, that the oxygen acids of any element become stronger the higher the positive valence of the element. The reason for this becomes clear if considered in reference to the position of the electrons in the atoms. For example consider sulfurous acid



$$\begin{array}{c} \mathrm{H:\underset{..}{\overset{..}{O}}:\underset{..}{\overset{..}{S}}:\underset{..}{\overset{..}{O}}:H} \\ \mathrm{:\underset{..}{O}:} \end{array}$$

Six of the 8 electrons around the sulfur are held in common with the 3 oxygens. The remaining 2 electrons may then be drawn in by the sulfur to such an extent as practically to reduce the positive charge on the sulfur from 6 to 4. The distortion of the oxygen octet then corresponds more to carbonic acid than to sulfuric acid, although of course the neutralization is not complete, and sulfurous acid is somewhat stronger than carbonic acid. It may then be stated that weakness of the acids containing less oxygen is due to the presence of one or more pairs of electrons on the central kernel which are not shared with other atoms.

The acids of phosphorus offer an exception to the rule as ordinarily stated regarding the dependence of the strength of an acid upon the valence of the element. The following table is quoted from "Leitvermögen der Elektrolyte."[1]

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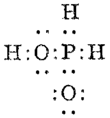
[1] Kohlrausch, "Leitvermögen der Elektrolyte," pp. 160, 167 (Teubner, Leipzig, 1898).

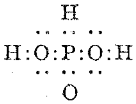
MOLECULAR CONDUCTIVITY AT 25°.

V in liters.	2.	8.	32.	128.	512.	1024.
H_3PO_4	64	96	156	246	317	341
H_3PO_3	129	187	257	318	351	358
H_3PO_2	140	207	281	335	361	367

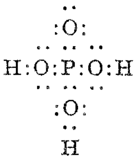
The acids of lower valence are apparently even more highly ionized than phosphoric acid. Considering the inability to replace but one of the hydrogens in H_3PO_2 and but two in H_3PO_3, whereas all three are replaceable in H_3PO_4, the following structural formulas are probably correct.



$$H:\ddot{O}:\overset{H}{\underset{:\underset{..}{O}:}{\ddot{P}}}:H$$



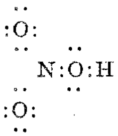
$$H:\ddot{O}:\overset{H}{\underset{O}{\ddot{P}}}:\ddot{O}:H$$



$$H:\ddot{O}:\overset{:\ddot{O}:}{\underset{\underset{H}{:\underset{..}{O}:}}{\ddot{P}}}:\ddot{O}:H$$

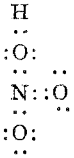
Here the tendency to pull in a pair of electrons which took place in sulfurous acid is prevented, in this case by hydrogen attached directly to the central atom. That the acids which have the hydrogen attached to the phosphorus are even stronger than phosphoric acid is in agreement with our postulate regarding the electronegative hydrogen and with other facts to be considered later.

The structure of nitric acid may be either



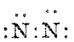
$$\begin{array}{l}:\ddot{O}:\\ \quad \ddot{N}:\ddot{O}:H\\ :\ddot{O}:\end{array}$$

or



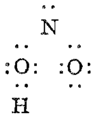
$$\begin{array}{l}\quad H\\ :\ddot{O}:\\ \ \ddot{N}::\ddot{O}\\ :\ddot{O}:\end{array}$$

Under the pull of a strong electronegative element such as oxygen, the nitrogen octet may not be stable and a sextet is formed instead. The structures of the nitrate group in sodium nitrate from X-ray analysis[1] seems to bear out this idea. The same is doubtless true of boric and carbonic acids. Indeed molecular nitrogen may be explained on the tendency of nitrogen to form sextets as



$$:\ddot{N}:\ddot{N}:$$

The structure of nitrous acid then may be written as



$$\begin{array}{c}\ddot{N}\\ :\ddot{\underset{..}{O}}:\ :\ddot{\underset{..}{O}}:\\ H\end{array}$$

Here we have another example of a free pair of electrons on the central atom. This accounts for nitrous acid being weaker than nitric acid.

The ionization of organic acids may be explained along similar lines.

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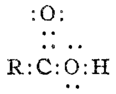
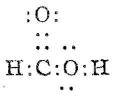
[1] Bragg and Bragg, "X-Rays and Crystal Structure."

As mentioned before, Lewis has discussed chloro-acetic acid at some length. In general it may be said of acids of the type



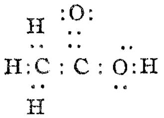
$$\mathrm{R:\overset{\overset{:O:}{\cdot\cdot}}{\overset{\cdot\cdot}{C}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H}$$

that whenever the nature of R is such as to exert a strong pull upon the electrons holding it to the carboxyl carbon, the acid will be correspondingly strengthened. Oxalic acid, in which the electrons in question are presumably half way between the two carboxyl carbons, is a strong acid. The strong neutralizing power of the hydrogen kernel considered in connection with the acids of phosphorus is observed again in formic acid



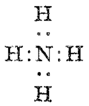
$$\mathrm{H:\overset{\overset{:O:}{\cdot\cdot}}{\overset{\cdot\cdot}{C}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H}$$

which is considerably stronger than acetic acid



$$\mathrm{H:\underset{\underset{H}{\cdot\cdot}}{\overset{\overset{H}{\cdot\cdot}}{C}}:\overset{\overset{:O:}{\cdot\cdot}}{\overset{\cdot\cdot}{C}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H}$$

Thus as far as concerns the carboxyl carbon the field due to the electrons of the bond is more nearly neutralized by the hydrogen than by the kernel of the methyl carbon. In view of their relative positive charges the opposite effect might have been expected. This emphasizes again the difference between the hydrogen kernel or nucleus and the kernel of any other element; the one a single positive unit and the other a complex structure of both positive and negative units. The amines are another excellent example of this characteristic of hydrogen. If one of the hydrogens in the ammonium group



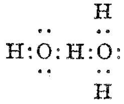
$$\mathrm{H:\underset{\underset{H}{\cdot\cdot}}{\overset{\overset{H}{\cdot\cdot}}{N}}:H}$$

be replaced by a carbon radical, the remaining hydrogens are held more firmly, that is the amine is more basic. This is the result to be expected if the field of the electron bond is less neutralized by the methyl group than by the hydrogen. The pair of electrons is shifted in toward the nitrogen; the positive charge on the nitrogen somewhat neutralized; and the remaining 6 electrons held less firmly by the nitrogen but more firmly by the remaining 3 hydrogens.

Associated Liquids.

The phenomenon of association in liquids has long been recognized as related to dielectric constant and ionizing power as a solvent. According to one view, a so-called polar solvent contains dipoles of considerable moment, that is, positive and negative charges separated by a considerable distance. The high dielectric constant of such a liquid is considered to be due to the orientation of these dipoles in an electric field. Likewise association is supposed to take place because of the attraction of two dipoles for each other. This explanation is open to serious objections. In the first place it is hard to see why the compounds of very high dielectric constant should be chiefly hydrogen compounds. Also hydrogen chloride should contain dipoles of greater moment than water or hydrogen fluoride, yet it has a much lower dielectric constant both in the vapor and liquid. Nor does hydrogen chloride appear to be associated. It seems then that the explanation is to be sought along other lines.

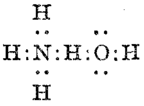
Let us compare again the compounds ammonia, water and hydrogen chloride. Ammonia adds a hydrogen readily but has little tendency to give one up. Hydrogen chloride, on the other hand, shows just the opposite tendencies. Water occupies an intermediate position and shows tendencies both to add and give up hydrogen, which are nearly balanced. Then, in terms of the Lewis theory, a free pair of electrons on one water molecule might be able to exert sufficient force on a hydrogen held by a pair of electrons on another water molecule to bind the two molecules together. Structurally this may be represented as



$$\mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H}:\overset{\mathrm{H}}{\overset{\cdot\cdot}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{O}}}}:$$

Such combination need not be limited to the formation of double or triple molecules. Indeed the liquid may be made up of large aggregates of molecules, continually breaking up and reforming under the influence of thermal agitation.

Such an explanation amounts to saying that the hydrogen nucleus held between 2 octets constitutes a weak "bond."[1] Ammonium hydroxide



$$\mathrm{H}:\overset{\mathrm{H}}{\overset{\cdot\cdot}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{N}}}}:\mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H}$$

is an example in which the union is fairly strong. This is contrary to the view commonly held that the weak basicity of ammonium hydroxide is due to the fact that it consists largely of a solution of ammonia in water. The idea also departs somewhat from the view taken by Lewis in regard to the polarity of NH_4^+. However, there seems to be no reason for be-

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[1] Mr. Huggins of this laboratory in some work as yet unpublished, has used the idea of a hydrogen kernel held between two atoms as a theory in regard to certain organic compounds.

lieving that gradations may not exist all the way from the case of ammonium chloride, where the hydrogen is definitely transferred from the chlorine to the ammonia, to the case in the association of water where the hydrogen is still held quite firmly to the original water molecule. Ammonium chloride is probably nearly as completely polar with respect to the separation of charges as sodium chloride, and the crystal, at ordinary temperatures, is held together in a similar manner by forces only slightly less. As we raise the temperature, however, the hydrogen of the bond, being a heavy particle, acquires vibrational energy very rapidly. This breaks up the crystal structure and causes ammonium chloride to dissociate and volatilize without melting. Hydrogen chloride forms a compound of this type with water just as it does with ammonia, but it is even less stable than ammonium chloride for obvious reasons.

It is not assumed that all association is of this type. In acetic acid, for instance, the association doubtless takes place with the formation of definite polymers of 2 molecules. This kind of association however will produce properties radically different from those of a liquid like water.

If our picture of the association of water is correct, a hydrogen nucleus may be held between two oxygen octets by forces which, for quite a distance, obey Hooke's law. Such a hydrogen would be capable of considerable displacement by an electric field. This is just the mechanism postulated by the mathematical theory of dielectric polarization as giving rise to high dielectric constant. It is quite possible in the case of the hydrogen compounds of the most electronegative elements, hydrogen fluoride, for example, that the simultaneous attraction of a highly concentrated octet of electrons, and the repulsion of the powerful positive nucleus for the hydrogen, may result in the hydrogen in the single molecule being held elastically. The association of the molecules is, however, very probably the factor that produces the extremely high dielectric constant.

The high mobility of the hydrogen ion in water solution may be explained as due to a shifting of hydrogen nuclei from one water molecule to another, a sort of Grotthus chain effect, rather than to a rapid motion of any one H_3O^+ ion. Obviously such a mechanism is possible only when the molecule of the solvent adds and gives up hydrogen nuclei readily. This is not true of ammonia and the NH_4^+ ion does not show a high mobility in liquid NH_3. It seems worth while to emphasize that the so-called "Associated Liquids" or "ionizing solvents" are quite non-polar insofar as no considerable separation of positive and negative charges in the molecule takes place. One of the properties of a completely polar compound is that of crystallizing in a space lattice, of which the individual ions are the units. The ions are held together by powerful electrostatic forces, and the melting point of such a crystalline substance is high.

Non-polar compounds, on the other hand, crystallize presumably with the molecule as the unit. Since the intermolecular forces are of the nature of stray fields from the atoms, which are relatively weak, non-polar compounds do not have high melting points. The "ionizing solvents" are, however, quite different in properties from a non-polar liquid of the type of liquid nitrogen. The atoms of the nitrogen molecule are "saturated." This is another way of saying that the stray fields around the molecule are not strong enough nor diversified enough to produce much interaction between the molecules. On the other hand, the properties of the "ionizing solvent" depend upon the existence of moderately strong intermolecular fields.[1] Dielectric constant is a measure of this type of "polarity" but has no significance with regard to highly polar compounds.

The metals in the middle of the long groups of the periodic table, which we have previously avoided discussing, form compounds intermediate in character between the highly polar salts and the non-polar acids. They show to a high degree the property which Werner has designated as coördination number. Abegg and Bodlander[2] point out that the solubility and ionization of the salts of these metals is connected with this tendency to form ionic complexes. In other words the simple salts of these elements, which are in themselves not highly polar, become more polar through reaction with the solvent or other molecules. It is not surprising that a salt such as cadmium chloride should be slightly dissociated in water solution but rather that any salt of these metals should be a good electrolyte.

BERKELEY, CALIF.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE S. S. WHITE DENTAL MANUFACTURING COMPANY.]

THE SYSTEM ZINC OXIDE, PHOSPHORUS PENTOXIDE AND WATER AT 25° AND 37°.

BY N. E. EBERLY, C. V. GROSS AND W. S. CROWELL.

Received May 4, 1920.

Introduction.

The zinc salts of phosphoric acid are of interest in the study of dental cements. The following is a part of a more extended investigation of the reactions and equilibria involved in the manufacture and use of such plastic compounds.

The phosphates of zinc, particularly the acid salts, have been very little studied. Graham describes an acid salt, $ZnHPO_4.H_2O$. Heintz[3]

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[1] Cf. Harkins and King, THIS JOURNAL, 41, 971 (1919).

[2] Abegg and Bodlander, *loc. cit.*

[3] Heintz, *Ann.*, 143, 356 (1867).