THE HYDROGEN BOND AND COÖRDINATION

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The concept of the hydrogen bond was developed by W. M. Latimer and the author in 1920 (7) to account for the behavior of associated solvents. The article which was published at that time grew out of a discussion concerning some work that had been done upon the dielectric constant of liquid ammonia at the University of Kansas under the direction of H. P. Cady some years earlier.[1] At that time there was a great deal of confusion in regard to the use of the term "polar." While the measurement of dipole moments was not then the common practice that it became a few years later, it was, of course, recognized that the molecules of both water and hydrogen chloride had moments in the gaseous state. These two substances behave very differently in the liquid state. The peculiar properties of water as a solvent were ascribed to association through the formation of hydrogen bonds. Not only was the hydrogen bond assumed to account for the action of the solvent on the ionization of acids and bases, but it was assumed that the high dielectric constant, and hence the solvent power of these peculiar solvents for electrolytes in general, was due to hydrogen-bond formation.[2]

It was not until nearly fifteen years later that the experimental proof

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[1] The author undertook the measurement of the dielectric constant of liquid ammonia in 1913. This work was subsequently finished by W. M. Latimer. The results were never published, but the data obtained were in substantial agreement with results which are now in the literature.

[2] It has often been assumed that another type of association would account for the low dielectric constant of hydrogen chloride in the condensed state, but it seems more probable that there is no association at all in this case. Hildebrand (5) has directed attention to the small energy involved in dipole interaction. Pauling (10) predicted that hydrogen chloride molecules would rotate in the crystal near the melting point and show a high dielectric constant. While Pauling's prediction is undoubtedly correct, the dielectric constant is not very great. In the gaseous state only those molecules which are in the zero rotational state contribute to the dielectric constant. While one would not be justified in considering the liquid simply as a condensed gas, one may suspect that the relatively low dielectric constant is accounted for in part, at least, by the presence of freely rotating unassociated molecules.

of the existence of this bond was obtained. The x-ray studies of Zachariasen (14) and of Pauling upon crystals, and the electron diffraction studies of Pauling (11) upon organic molecules have shown that it is a common occurrence for oxygen, nitrogen, or fluorine atoms to be linked together by a hydrogen atom. More recently Wulf (4) and his collaborators have discovered that the bond in the neighborhood of 1.5 μ is not shown in absorption when the hydrogen is doubly linked. This bond is the first harmonic of the vibration of a hydrogen atom linked to oxygen or nitrogen. We thus have not only a test, but a quantitative measure of the amount of hydrogen bonding present in a substance.

Formally the hydrogen bond may be regarded as a case of coördination of the simplest cation, the proton. The coördination number of a cation decreases with the ratio of the cation–anion radii; the limiting value of the coördination number for zero radius is two. The hydrogen ion from a strong acid in solution may, therefore, coördinate two molecules of the solvent just as the cupric ion may coördinate four molecules of ammonia. For example, the hydrate $HCl(H_2O)_2$ is well known. Of course, one of the coördinated molecules may be the anion of the acid itself, as in $(C_2H_5)_2OHCl$ and other oxonium compounds. If the acid is weak the anion of the acid is always coördinated, and if the acid is very weak, then there is no ionization, and no hydrogen bond is formed, as, for example, when hydrogen is linked to aliphatic carbon. The limitation to a certain range of acid strengths limits the hydrogen bond to the atoms of nitrogen, oxygen, and fluorine, although there is some evidence of weak bonding with other halogens. The energy of dissociation of a hydrogen bond probably never exceeds 6 to 7 large calories. It is, therefore, rather less than the bond energy of a typical coördination bond, as, for example, the $Ag^+—NH_3$ linkage, and for this reason molecular complexes involving hydrogen bonds have not received the attention in the past that has been given to the well-known class of complexes which were studied so extensively by Werner.[3]

As examples of hydrogen bonding, we may mention such widely different complexes as pyridine dihydrochloride and the amine oxide dihydrates. The amine oxides are an interesting group of compounds which are very soluble in water and form very stable hydrates. It was at first predicted that the amine oxides would be strong bases as are the quaternary am-

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[3] Efforts to formulate a quantum mechanical description of the hydrogen bond have not been particularly successful, for the obvious reason that the bonding energy is small and a very exact calculation would be required to ascertain even the sign of the energy. Sherman, Huggins, and Bernal have discussed this problem. The latter has introduced the concept of a "hydroxyl" bond, but it is not clear that he is talking about anything different from the hydrogen bond.

monium compounds, but when the possible electronic structures were considered it was seen that they could not be bases at all, except through hydrogen-bond formation.

$$R_3NO—H—OH$$

As a matter of fact, they are weak bases, as would be predicted.

One of the most important rôles of the hydrogen bond is in the association of solvent molecules. Presumably all cases of typical "association" in solvents involve hydrogen-bond formation. Both water and ice are highly associated in this way. One of the most interesting results of such association is the tendency of the alcohols to form glasses on supercooling. This tendency has been shown by Zachariasen (15) to be due to hydrogen bonding in the case of methyl alcohol. A glass is likely to be formed when a molecule has the possibility of coördinating a small number, four or less, of its neighbors through definite linkages, whereas the geometry of the situation permits a larger number. Under these conditions, there is opportunity for the disorientation characteristic of a glass.

By far the most interesting of the associated solvents is hydrogen fluoride, and it is here that the strongest hydrogen bond is formed. The remarkable work of Fredenhagen (2) probably needs to be confirmed in some particulars by other investigators, but it furnishes us with conclusions. It will be more logical, however, to consider this substance in connection with anion solvation and to continue the discussion of its behavior under that topic in the latter part of this paper.

The hydration of the lyophilic substances found in living tissue, such as the carbohydrates and proteins, must be in a large part due to the hydrogen bond. There are no cations of the heavy metals present to account for hydration by the Werner type of coördination, and no ions at all in many cases. The problem of bound water, which has been regarded in the past as a colloidal phenomenon, seems likely to resolve itself into a chemical problem. The term "colloidal," like the term "catalytic," is often used to cover chemical ignorance.

As a matter of fact, there is evidence to confirm this idea. In 1911, Coblenz observed that the infra-red absorption band at 1.5 μ was missing in gelatin, which presumably contained a good deal of water, thus anticipating the discovery of Wulf by twenty-five years. Buswell (1), in 1929, noted the fact and suggested that the hydrogen bond might be involved in the binding of water by gelatin.

It has been assumed by some that any water in a salt hydrate which is not coördinated with the cation through the Werner type of bonding must be associated with the anion. The recent work of Hendricks (3) and collaborators on the ammonium oxalate crystal indicates that this is not necessarily so; the water in the crystal may simply be filling holes. However, no one would doubt the existence of anion solvation. It is usually due to the formation of the hydrogen bond, and because this bond is relatively weak, it is more difficult to determine the extent of solvation of the anion.

The anion has not only a negative electron atmosphere in its periphery, but a negative over-all charge, so that hydrogen bonding is favored, whereas in the cation the net positive charge must repel the hydrogen strongly.

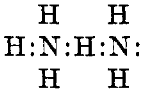
Just as the simplest proton is the cation, so the simplest anion is the electron, and we have a beautiful example of solvation of the electron in the extremely interesting solutions of the alkali metals in liquid ammonia. While the existence of these solutions has been known for a long time, it is due to the work of that great trio of investigators, Franklin, Cady, and Kraus, who began their researches in this field at the University of Kansas, that we understand their nature as well as we do. The brilliant and daring hypothesis that the electron in these solutions is solvated is due to Kraus (6). But many chemists have wondered how it is possible for an ammonia molecule which, in the light of our present knowledge of electronic structure can have no electron affinity, to attract and hold an electron.

Before we attempt to answer this question, we will do well to ask ourselves: Why does sodium dissolve in liquid ammonia in the first place? Every possible sort of guess has been made by speculators upon this subject, and some of them were undoubtedly upon the right track. It is only necessary for us to select the plausible hypotheses.

We may note that sodium alloys with mercury and other liquid metals, but that it does not dissolve in any non-metallic solvent except ammonia and the amines. It may be argued, of course, that sodium dissolves in the more polar solvents, but that it reacts with them so rapidly that the solution cannot be observed. This argument cannot be disproved, but we may suspect that sodium will form solutions only with metals, and that the clue to the solubility of sodium in liquid ammonia lies in the possibility of the formation of metallic ammonium. This is, of course, not a new idea.

Let us recapitulate briefly the properties of dilute solutions of sodium in ammonia. The equivalent conductivity approaches a limiting value greater than 1000 reciprocal ohms. The sodium moves toward the cathode and the transference ratio as determined from E.M.F. measurements indicates that the sodium has the normal equivalent conductivity of the sodium ion (about 130 ohms^{-1}). If a little water be added to the solution, however, a violent reaction characteristic of sodium metal is obtained. The sodium plays a dual rôle as metal and as ion at one and the same time.

The whole behavior can be understood if we assume that the sodium atom is in resonance, so to speak, with an NH_4 radical, so that the electron passes readily back and forth between the two. There are no ammonium ions in solution, but ammonia molecules associated in groups of two or more through hydrogen bonds forming complexes such as



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

The tendency of the NH_4 ion to acquire an electron and behave as a metal is well known. It is stable until two such groups come together, when the reaction

$$2NH_4 = 2NH_3 + H_2$$

takes place. In the absence of ions, especially of the amide ion, there is no tendency for two NH_4 groups to come together and the hydrogen-forming reaction does not take place. There is also little or no tendency for the ammonium complex to dissociate according to the reaction

$$(NH_3)_2^- = NH_4 + NH_2^-$$

In dilute solution, the sodium exists in the form of ions and the electron is associated with the ammonium. When conducting, the electron jumps from one ammonium group to another. This is essentially metallic conduction.[4]

The more concentrated the solution, the greater the mobility of the electron. If the electron were firmly attached to any group, no such mobility would be possible, but the ionizing potential of the ammonium group must be small.[5] The high mobility of the electron is, therefore, analogous to the high mobility of the hydrogen ion in water solutions. The acquirement of the electron by the ammonium radical must be accompanied by a large increase in volume, which accounts for the surprising increase in volume of sodium in liquid ammonia. The sodium and ammonium are solvated in the solution, but the most important thing is the formation of complexes containing NH_4 groups through hydrogen-bond formation.

[4] The sodium ion probably forms a complex of the type $Na(NH_3)_n^+$, and it might be assumed that this is the group with which the electron is associated. In dilute solution, however, where the dissociation is complete, the electron must be associated with the ammonia. Triethylamine cannot form hydrogen bonds, and has a very low dielectric constant. It should not form metallic solutions of the alkali metals if the above considerations are correct.

[5] The work of Leighton (9) and colleagues seems to indicate that the photoelectric threshold for the ammonium ion itself is not much less than that of the alkali metals.

Let us return to hydrogen fluoride, already mentioned as a case of anion solvation. Apparently the strongest hydrogen bonds that occur are formed with fluorine, and Simons (13) has shown that the vapor of hydrogen fluoride tends to form benzene-like polymers $(HF)_6$, linked through hydrogen bonds. The single molecule HF is a weak acid, for reasons which have been pointed out elsewhere. On the other hand, H(FHF) must, for similar reasons, be a strong acid.

The F^- tends to associate HF to form the FHF^- ion just as it tends to hydrate, and the hydrogen bond formed here must be very strong. But there is very little tendency for two HF molecules to associate in water solution. With a high concentration of HF molecules, as in liquid hydrogen fluoride, there must be a great deal of this type of association, but now there can be no ionization, because acids only ionize in basic solvents.

On the other hand, if nitric acid is dissolved in the hydrogen fluoride, the molecule is solvated through hydrogen-bond formation (as it is in water), but this process is accompanied by ionization of the hydrogen fluoride, according to the reaction

$$HNO_3 + (HF)_2 = H_2NO_3^+ + FHF^-$$

Hence, as seems reasonable, hydrogen fluoride behaves as the strongest known acid when in high concentrations.

Anion solvation is an important factor in determining the solubility of salts. The actual solubility of a salt is a complex function of charge, radius, and coördination power (12). The coördination power may depend upon charge, the possibility of forming hydrogen bonds, and van der Waals' forces. The latter, for example, are very important in the case of silver iodide, where both ions contain a large number of electrons. It must not be forgotten that a cation may coördinate its own anion. The calculation of solubility is, therefore, very difficult, although Fajans has attempted to give some semiquantitative rules. There are cases, however, where the solvation of the anion plays a predominant rôle. The nitrate ion, for example, is a large ion of single charge with a strong tendency to hydration, and it is not surprising, therefore, that nitrates are soluble.

There is reason to think that deuterium forms stronger hydrogen bonds than does hydrogen (8). The investigation of deuterium compounds promises to be of great interest.

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