

THE PECULIAR PROPERTIES OF WATER IN LIGHT OF ITS MOLECULAR STRUCTURE.

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Water is such a common substance that we usually take it for granted and it is seldom that we stop to consider the reason for its peculiarity. Occasionally when we examine some of its physical and chemical properties we are struck by their difference from similar properties of numerous organic liquids. The old saying that "oil and water will not mix" is based on actual fact and the reason lies in their molecular structures.

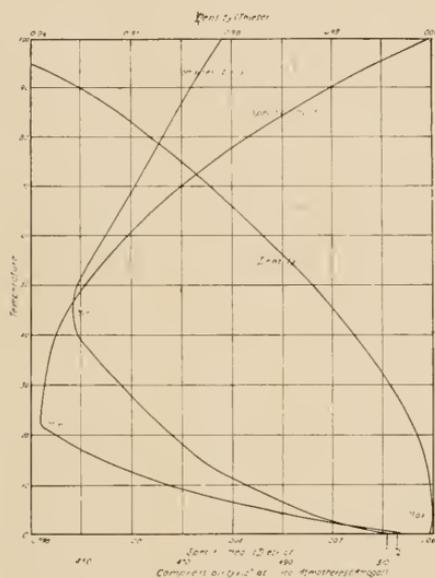


Fig. 1. The specific heat, compressibility and density of liquid water are plotted against the temperature. The data are taken from the 4th ed. of Landolt and Boernstein.

Water has the formula H_2O and hence a molecular weight of 18 and yet it is a liquid at ordinary temperatures with a remarkably high boiling point, and exceptionally high latent heat of vaporization. Its large dielectric constant is coincident with its great solvent and ionizing power for electrolytic compounds. It is, comparatively, a rather dense liquid but its density reaches a maximum at $4^\circ C$. On cooling below this temperature expansion takes place and finally, on freezing, a further notable increase in volume occurs. Water is one of the very few substances known, which expands on solidifying. A plausible explanation will be given for this expansion.

The specific heat of water is the largest of any known substance; it varies with the temperature but not regularly. A minimum is reached between 20 and 25° (figure 1). The curve to the left of this point

corresponds to the increase in volume on cooling the liquid below 4° . These breaks in the curves indicate points where marked changes occur in the character of the liquid. The compressibility curve shows a similar change.

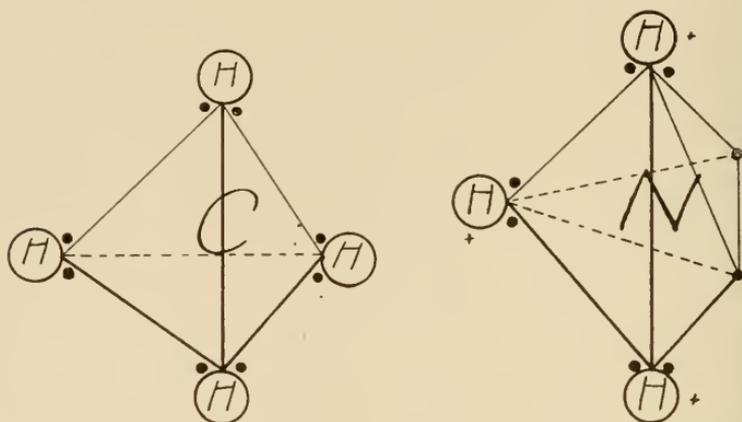


Fig. 2. The methane molecule consists of a tetrahedral carbon atom in combination with four hydrogen atoms. The dots represent the valence electrons which take part in the combination. This is probably the most non-polar molecule known.

Fig. 3. Ammonia, NH_3 , is distinguished by a pair of electrons on the surface of the nitrogen which gives to that part of the molecule a negative character. The hydrogens are slightly positive.

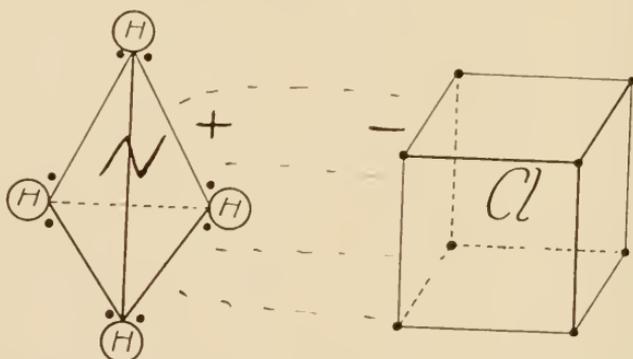


Fig. 4. Ammonium chloride is formed by the action of hydrogen chloride on ammonia gas. The positively charged H from HCl adds onto the extra pair of electrons shown in figure 3 to form the ammonium which is held to the chloride ion by electrostatic forces.

In order to understand the peculiar properties of water it is necessary to understand its molecular structure and for that we must know the structure of the atoms of which water is built up. Although there are a great many details about atomic structure which are in an unsatisfactory state, the theory has developed enough to show the great value, not only in giving us understanding of the properties of most compounds, but also in predicting the new properties which a substance

will acquire under a given set of conditions. The following ideas have been worked out during the past three years at Purdue University in a seminar course for graduate students.

The ideas contained herein are an extension of the Lewis-Langmuir theory of atomic structure which has already proved so fruitful.¹ For the topic under consideration, we need to consider only some of the elements in the first two periods.

Let us consider the simplest hydrocarbon and the hydrogen compounds of nitrogen and oxygen. Methane, CH_4 , with a molecular weight of 16 and a very small external field of force is characterized, in addition to its chemical inertia, by a low boiling point, 160°C . Ammonia is NH_3 (figure 3). The nitrogen atom has completed its octet by joining on three hydrogens, each with a single electron. These are probably placed at three of the corners of a tetrahedron. But there is a pair of electrons left over which gives that part of the molecule a negative character. Corresponding to this, one or more of the hydrogens will have a slight positive character; that is, the electrons will be shifted a bit from one or more hydrogens toward the central nitrogen. This results in giving a certain "polarity" to the molecule. Such a polar molecule ought to have much more attraction for other NH_3 molecules than corresponds to its molecular weight, 17. As a matter of fact it boils at -33.5° which is an increase of nearly 130° over methane, although there is an increase in molecular weight of but one. Liquid ammonia is known to be associated. This association gives it a high specific heat and high latent heat of vaporization because considerable energy is used up in separating the complexes that result from these polar attractions.

Chemically, ammonia is very interesting. Bring it into contact with a very polar substance like hydrogen chloride gas. The hydrogen in that compound, as we have seen, is charged positively. When this molecule comes in contact with ammonia the positively charged hydrogen is attracted by the pair of electrons which make that part of ammonia negative (figure 4). This gives a methane-like structure to the ammonium ion which, of course, now bears as a whole the positive charge it picked up with the hydrogen. Then the chloride ion is held by electrostatic forces just as in sodium chloride. Nitrogen forms a great variety of organic compounds and this property of polarity and of adding on a positively charged hydrogen is found there also. This accounts for the formation of such compounds as aniline hydrochloride and the alkaloid complexes with different acids. Incidentally, such addition of polar acid will increase the polarity of the organic compound with important results which will be referred to when we study solutions. Certain metallic ions like silver, copper, cobalt, platinum, etc., due to their structure, have the ability, like a hydrogen ion, of sharing that extra pair of electrons in the ammonia molecule. The result is the possibility of the preparation of an almost bewildering series of ammonia compounds such as the cobaltamines. These are the "higher order compounds" of Werner.

¹ Lewis. *J. Am. Chem. Soc.*, *38*, 762 (1916). Langmuir. *ibid.*, *41*, 1543 (1919). *Science*, *54*, 59 (1921).

According to these conceptions of the nature of nitrogen, it can take on three or four hydrogens or organic groups. Langmuir² calls the number of groups that can be added to an atom its covalence. Carbon, nitrogen and oxygen have the same maximum covalence. The atoms are very nearly the same size as we should expect from their position in the periodic table and, in combination with four groups, they are all probably tetrahedral in shape. This is a modification of

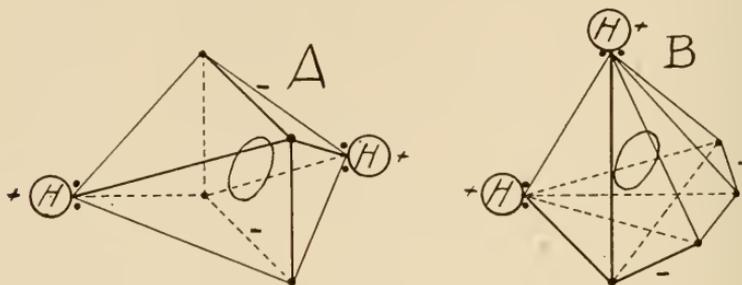


Fig. 5. Two possible forms of the steam molecule or monohydrol are given. In one the hydrogens are adjacent; in the other they are opposite.

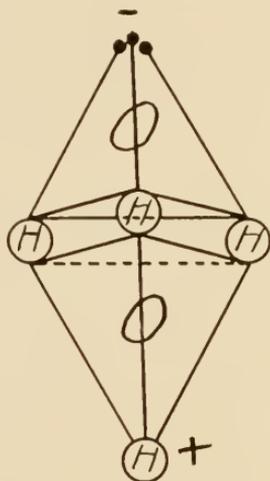


Fig. 6. Dihydrol or liquid water must have a condensed form to explain its great density. Three hydrogens are active in connecting two negative oxygens. Note that this aggregate is still polar, one end negative and the other positive.

the old idea of quinivalent nitrogen. The polarity of the nitrogen, of course, is diminished according to the length and nature of the organic groups combined with it.

Oxygen combines with two hydrogens to form a liquid at ordinary temperatures. The oxygen atom with its six electrons in the outer shell completes its octet with the electrons from the two hydrogens. But here there are two pairs of extra electrons corresponding to the single pair of the ammonia molecule. That means that half the molecule is more

² Langmuir. *J. Am. Chem. Soc.*, 41, 1543 (1919).

negative than in ammonia and that here the hydrogens are even more positive. The water molecule has, roughly, twice the polarity of ammonia. With a molecular weight of 18 it boils at 100° C. The boiling point of ammonia is about half way between those of methane and water. The other physical properties of ammonia also lie intermediate between those of water and methane.

Association of Water.—The considerable degree of polarity of water is very intimately connected with its peculiarities. When one water vapor molecule (figure 5) comes in contact with another the positive part of the one attracts the negative part of the other and they tend to stick together (figure 6) in a very compact structure. One of the two corners of the aggregate is positive and the other is negative so that this dihydrol, the name that has been suggested for liquid water, is still polar. Dihydrol³ is often spoken of as liquid water. But liquid water is not dihydrol. It is a solution, especially at higher temperatures, of varying amounts of monohydrol, as steam is often designated, in dihydrol. As the temperature falls, there is an ever increasing amount of ice or ice-like molecules dissolved. Trihydrol is the name that has been given to these aggregates. But as we shall see presently the name, trihydrol, should refer to an arrangement of bondings between molecules rather than to the total number of molecules in the aggregates. Analogous to the dynamic equilibrium of evaporating and condensing molecules above the surface of water so there is within the liquid a dynamic equilibrium between monohydrol, dihydrol and trihydrol; e. g.,



The reactions from left to right are exothermic and are favored by lowering of temperature. When the temperature rises the molecules become so active in their movement that the aggregates are broken up.

The Arrangement of the Atoms in Ice.—It has recently been shown by Bragg⁴ that in the ordinary ice crystal arrangement of atoms each oxygen is surrounded by four hydrogens at the corners of tetrahedra and that each hydrogen is situated between two oxygens, joining them together (figure 7). In this manner all the stray fields of force of water are satisfied and the change from dihydrol to ice should be exothermic; the latent heat of freezing of the water is 80 calories per gram. The ice lattice is not as compact as dihydrol so that there is an expansion when this re-arrangement occurs. Similarly the increase in volume below 4° is caused by an ever increasing shift of dihydrol into the larger ice molecules or state of aggregation.

The specific heat curve for water sheds some light on the equilibrium between dihydrol and trihydrol with respect to the temperature. The extra heat required to shift the equilibrium gives water a high specific heat at 0° and with ever decreasing ice dissolved in the water the specific heat decreases to a minimum at about 22°. Beyond this point the curve rises again as is the general rule for all substances. But here

³ Symposium on Water. Trans. Faraday Soc., 6, 71-123 (1910). The proposal is made there that the water molecules are coupled together directly through the oxygens.

⁴ Bragg. Proc. Phys. Soc. (London), 34, 98 (1922).

there is a steeper rise than is customary aided by the ever increasing amount of heat required to transform the dihydrol into monohydrol, or dissolved steam. Steam, also, has an abnormal specific heat curve. Over the range 250-300° it increases with the temperature as all gases do. Below this range the curve rapidly becomes nearly horizontal at a specific heat of about 0.5. The reason for this is because of the extra amount of heat energy required to overcome the intermolecular attraction, which is abnormally high in proportion to its molecular weight, because of the polar nature of the molecule.

From the compressibility curve (figure 1) some information about the molecular aggregation of water may be obtained. Since the compressibility of any substance decreases with its compression or density that region of minimum compressibility of water corresponds to a preponderance of denser aggregates, which would be dihydrol in this

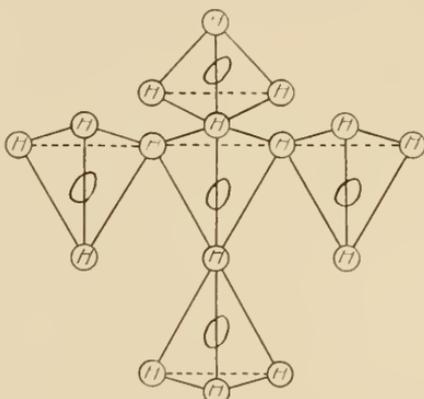


Fig. 7. The ice crystal consists of tetrahedral oxygen atoms surrounded each by four hydrogens. Each hydrogen is between two oxygens. There is no residual polarity. This arrangement is responsible for the hexagonal shape of snow crystals; cf. *National Geographic Magazine*, January, 1923.

case. The compressibility curve reaches a minimum at about 45°, and gives us, probably the best guide as to the relative proportions of these three kinds of aggregates in liquid water. The molecular weight of water dissolved in other solvents approximates 36 which gives us another reason for speaking of water as chiefly dihydrol.

The high latent heat of vaporization is required to complete the change of the compact complex molecule, dihydrol, into monohydrol as well as to separate the monohydrol molecules from each other and to do the work of expansion against the atmosphere. According to our method of reasoning ammonia should also have a high latent heat of vaporization, as it does. This property, together with its high specific heat has a great deal to do with the value of ammonia as a refrigerating agent. The magnitude of their values is caused, in large part, by the polarity of the ammonia molecule.

As a *solvent*, water is extremely important. Bring it into contact with a crystal of ordinary salt and, according to the orthodox method of expressing what happens, the salt dissolves and *then* breaks up into

ions. But the study of crystal structures by X-rays shows that the sodium and chlorine atoms in the crystal lattice are already polarized. The mechanism of solution involves the attraction of the polar water to the surface of the salt molecules. The positive part being attracted to the chloride ions and the negative part to the sodium ions. Other water molecules shove in between the ions and separate them. This separation, of course, requires energy which is made up in part from the heat of the hydration of the ions and in part from the surroundings as is evidenced by the cooling of the water as it dissolves the salt. With some substances, on dissolving, the heat of hydration exceeds that required to separate the ions. The strong acids and bases and several salts like anhydrous sodium and calcium sulfates all go into solution exothermically. Each ion is surrounded with an envelope of hydrated water which aids in holding them apart. This, it seems, is the real cause of the power of water as an ionizing substance rather than its high dielectric constant (specific inductive capacity).

The *dielectric constant* according to the conception of Faraday and Maxwell⁵ is due to the presence of dipoles in the medium which are orientated in an electric field. Other substances of high dielectric constant such as formic acid or hydrocyanic acid should, according to the older idea, cause marked ionization of dissolved water; but experiments of P. Walden⁶ proved that this is not the case. If the dielectric constant of a material depends upon Faraday's dipoles and if secondary valence combination depends upon polarity there should be a very close parallelism. It is one of the peculiarities of water that there exists a discrepancy in this respect. It seems to indicate that water possesses an exceptionally marked tendency to enter into those hydration reactions which are really physico-chemical; and this is just the point! This type of reactions is controlled, not merely by the attraction of unlike poles in different molecules, but also by the specific chemical character of the molecules themselves. Now the chemical character of the water molecule is such that it seems to bring about the greatest number of hydration reactions. This is to be connected with the small size of the water molecule in which the hydrogens occupy but a small fraction, as well as to the two pairs of extra electrons of the oxygen. This specificity of character is, I believe, confirmed by the remarkable effect on colloidal systems of the ions formed from water, namely, the hydrogen and hydroxyl ions. Jacques Loeb⁷ has emphasized the importance of their relative concentrations (pH) in all colloidal work.

According to the ideas here expressed solubility is sometimes a matter of secondary valence combination.⁸ It is for water, I feel sure, but there are many other solutions which do not exhibit any evidence of secondary valence combination. If two vessels containing different

⁵ Jeans, *Electricity and Magnetism*, 4th ed., pp. 126-135 (1920).

⁶ *Cit.* 3, p. 71-123.

⁷ Loeb, *Proteins and Theory of Colloidal Behavior* (1922). *Science*, 56, 731 (1922).

⁸ Secondary valence combination is due to the extra electrons in the oxygen, nitrogen or other atoms. Hydration is a typical example. When a molecule of dissolved substance is hydrated in water solution a rather indefinite envelope of water surrounds the molecule. In solid hydrated crystals a stoichiometrical amount of water is in secondary valence combination.

gases are connected there is a diffusion of the gases into each other which, unless the gases are appreciably polar like $\text{HCl} + \text{NH}_3$, is of the mixture type of solution. Here the laws of mixtures hold. In the same way, when a gas dissolves in a liquid, if the gas is not appreciably polar, Henry's law is obeyed. Non-polar organic liquids like the paraffins, or benzene and its homologs, have very little tendency toward secondary valence combination. The attraction of the molecules for each other is analogous to gravity and is proportional to their molecular weights. Indeed since the mutual attraction of two bodies is inversely proportional to the *square* of the distance between them gravity alone may well be sufficient, when they are touching, to hold the heavier molecules together. If these are the only forces acting, the laws of mixtures should hold. Thus we find that the vapor pressures of solutions of benzene and toluene may be exactly predicted from the concentration. Where there is a polarity effect superimposed, deviations from these simple laws are to be expected.

In the polar solvent, water, the lower alcohols, the lower organic acids, polyhydric alcohols and the sugars are found to be extremely soluble. These compounds have sufficient polarity to bring about the secondary valence type of solution. But when we come to the higher alcohols or acids, the ethers and similar compounds which do contain a polar oxygen, but which have so many nonpolar carbons that the polarity of the oxygen is greatly diminished, the solubility varies with the likeness in degree of polarity.⁹ This gives a valuable method for the prediction of solubilities.

The properties of many organic substances can be largely predicted from the principles laid down here. In general, nitrogen and oxygen in organic compounds are the seats of most reactions. The reason for this is chiefly because of their polarity, modified by the extent and arrangement of the carbons. The halogens, sulfur, phosphorus, etc., have similar properties to a lesser extent. Some work has been done on explaining organic reactions according to the octet theory by Langmuir, Stieglitz, Huggins and others,¹⁰ but only a start has been made. It is hoped to make a study of certain organic reactions along the line of the above reasoning.

SUMMARY.

A plausible explanation of the physical and chemical properties of water has been made by an extension of the Lewis-Langmuir theory of atomic structure.

⁹ The more nearly alike two substances are in their degree of polarity the greater the tendency to form miscible solutions. Substances widely separated in degree of polarity have very slight if any mutual solubility. The lower alcohols and organic acids are completely miscible in water; ether is somewhat soluble while benzene and the saturated hydrocarbons are so very non-polar that they are practically insoluble in water.

¹⁰ Langmuir. *J. Am. Chem. Soc.*, 42, 274 (1920). Stieglitz. *ibid.*, 44, 1293 (1922). Huggins. *ibid.*, 44, 1607 (1922). Crocker. *ibid.*, 44, 1618 (1922). Conant. *ibid.*, 43, 1705 (1921).

Water possesses properties which are different from other liquids. Some of these are:

- (1) The large density relative to its molecular weight and the way in which it changes with the temperature.
- (2) The change in compressibility with temperature.
- (3) The high specific heat and its change with temperature.
- (4) A very large latent heat of vaporization.
- (5) The magnitude of its dielectric constant.
- (6) Solvent power.
- (7) Remarkable tendency toward secondary valence combination or hydration.
- (8) Notable ionizing power.

Liquid water is largely composed of dihydrol in which may be dissolved some steam molecules or monohydrol and some ice molecules, sometimes called trihydrol. Equilibria between these three kinds of molecular arrangement occurs, so that the variation in the physical properties of water with the temperature is explained.

Oxygen imparts a polarity to the water molecule which causes it to unite into the remarkably compact dihydrol. The polarity is largely responsible for the secondary chemical reactions, the high dielectric constant as well as the solvent and ionizing powers.

In addition to the polarity there are certain specific characteristics of water of a chemical character that have a notable effect on its secondary valence or *physico-chemical* reactivity.

The structures of methane, ammonia and hydrofluoric acid are given according to the Lewis theory and the explanation of their chemical and physical properties is suggested.

The application of these ideas to organic chemistry is indicated.

