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A Theory of Water and Ionic Solution, with Particular Reference to Hydrogen and Hydroxyl Ions

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SHORT SUMMARY

ON the basis of the model of the water molecule derived from spectral and x-ray data and a proposed internal structure for water, the following properties of water and ionic solutions have been deduced quantitatively in good agreement with experiment.

- (1) The crystal structure of ice.
- (2) The x-ray diffraction curve for water.
- (3) The total energy of water and ice.
- (4) The degree of hydration of positive and negative ions in water.
- (5) The heats of solutions of ions.
- (6) The mobility of hydrogen and hydroxyl ions in water.

And the following inferred in a qualitative way.

- (7) The density and density changes of water.
- (8) The explanation of the unique position of water among molecular liquids.
- (9) The dielectric properties of water and ice.
- (10) The viscosities of dilute ionic solutions.
- (11) The viscosities of concentrated acids.

ice, and of the density of water, leads to the proposing of an irregular four-coordinated structure for water. This structure is tested and found to account for the positions of the maxima of x-ray diffraction by water, and for the change in these positions with temperature, which are quite different from those of a simple liquid such as mercury. Three different intermolecular arrangements are postulated for water at different temperatures.

(1) Ice-tridymite-like (four-coordinated) at low temperatures below 4°C.

(2) Quartz-like (four-coordinated) between 4–200°C, roughly.

(3) Ammonia-like, close-packed, 200–340°C.

These forms are not distinct and pass continuously into each other. This hypothesis accounts for the abnormal changes of density of water. It is further tested by the behaviour of water under pressure, and by the Raman spectra of water at different temperatures.

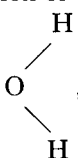
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The large dielectric constant of water and ice, and its variation with temperature and frequency is discussed, and it is concluded that it can be explained by existing theories based on molecular rotation, but only if by far the greater part of the water molecules are not free to respond by orientation to the external electric field. In the course of this discussion a new structure for ice

FULL SUMMARY. PART I

1

A consideration of the spectroscopic molecular

model of H₂O, , of the crystal structure of

is proposed, based on electrostatic grounds and accounting for the position of the H atoms.

3

The physical properties of water are compared with those of its neighbours in the periodic table, particularly with NH_3 , HF, H_2S , and CH_3OH . This discussion brings out the fact that the unique position of water is due not only to its dipole character but even more to the geometrical structure of its molecule, which is the simplest one that can form extended four-coordinated networks.

It has been found possible to calculate on the basis of this model the total energy of ice and water, due mainly to the electrostatic potential of neighbouring molecules, and the agreement with experiment furnishes another proof of the correctness of the hypothesis.

4

Turning now to ionic solutions, we discuss the nature of ionic hydration. A method of estimating the degree of hydration from the specific gravity of the solutions is developed, and the results compared with those calculated theoretically on the basis of the molecular model. It is concluded that all the strongly polarizing ions H^+ , Li^+ , Na^+ , and all divalent and trivalent positive ions as well as $(\text{OH})^-$ and F^- are hydrated, while $(\text{NH}_4)^+$, Rb^+ , Cs^+ , and most negative ions are not. The degree of hydration depends mainly on the ionic radius and is the same in solutions as in crystals: e.g., $\text{Be} \cdot 4\text{H}_2\text{O}$, $\text{Mg} \cdot 6\text{H}_2\text{O}$.

Further it has been shown possible to calculate the total heat of solution of any atomic ion. This is to a first approximation of the form $a + bP$ where P is the mutual potential of the ion and a water molecule depending on the radius and charge of the ion while a and b depend only on the ionic charge. This formula gives excellent agreement with experiment.

The effects of the ions on the water in which they are dissolved is discussed, and from a study of various properties, particularly viscosity, it is concluded that their effect is that of increasing or decreasing the intermolecular coherence and regularity. The concept of a structural temperature is introduced, which is increased by large and decreased by small ions. With respect

to these properties, H^+ and $(\text{OH})^-$ ions appear quite anomalous, and on this account, as well as for their mobility, require a new theory.

PART II

5

The H^+ ion must exist in solution as $(\text{OH}_3)^+$. But this makes the anomalous mobility of H^+ still more difficult to account for. A break with current theory is proposed. The hydrogen positive ion, effectively $(\text{OH}_3)^+$ moves through water under a potential gradient of 1 volt/cm at a rate 32.5×10^{-4} cm/sec. at room temperature. The corresponding rate for $(\text{OH})^-$ is 17.8×10^{-4} , and for all other ions much less (e.g., K^+ , $(\text{NH}_4)^+$, Cl^- , 6.7×10^{-4}). This discrepancy is analysed and it is claimed that the excess velocities of these ions over 6.7×10^{-4} cm/sec. must be due to a mechanism entirely different from bodily transport through the solution. It is suggested that this different mechanism is the transfer by a jump of one proton from one water molecule to another when favourable configurations are presented. Such an idea has also been proposed by Hückel but quite differently developed by him. This transfer is analysed quantum-mechanically with simple models, and it is shown that the result of the imposed e.m.f. will be to cause a bias in the transfers in favour of transfer down the field, and that the order of magnitude of this bias on the most reasonable assumptions as to distances and heights of potential barriers is just such as to account for the extra (abnormal) velocity of these ions in water. The hydrogen isotope H^2 will possess practically no extra (abnormal) velocity, and therefore have a mobility about $1/5$ that of H^1 . The explanation given automatically leaves unaffected the ordinary theory of the mobilities of *foreign* ions in water. The theory requires the degree of organization in the structure of water to be considerable, in complete agreement with the discussions of Part I.

INTRODUCTION

§1. The abnormal mobilities of H^+ and $(\text{OH})^-$ in water

The present theories of ionic mobility are based on a picture of water as a homogeneous

fluid, of definite viscosity and dielectric constant varying with the temperature, and on a picture of ions as spherical charged particles subject to resisting forces proportional to their velocity. This accounts satisfactorily for the mobilities of large ions, K^+ , Cl^- , etc., and also for the slower mobility of small ions on the hypothesis of a rather indefinite amount of hydration. More exact fit can be obtained for concentrated solutions by taking into account the mutual electrostatic interactions of the ions as in the Debye-Hückel-Onsager theory.

However, all such theories fail to account for the mobilities of the ions H^+ and $(OH)^-$ in water. The equivalent Stokes law radii for H^+ and $(OH)^-$ calculated from their mobilities* are 2.6×10^{-9} cm and 4.8×10^{-9} cm, quite impossibly small on physical grounds (and neither hydration nor ionic interaction can do anything but reduce mobility). These abnormal mobilities of the H^+ and $(OH)^-$ ions are confined to water and closely related solvents, e.g., methyl alcohol, and it is clear that to explain them it is necessary to examine more closely the molecular structure of water in order to show where the hypothesis of the simple viscous dielectric fluid fails to give an adequate account of experimental facts. A study of the anomalous mobility of the H^+ ion which was our original theme has thus turned itself into a general attack on the nature of water, expounded in Part I. We return to the original theme in Part II.

PART I. THE STRUCTURE OF WATER AND IONIC AQUEOUS SOLUTIONS

§2. Nature of the water molecule

Pure water, apart from a slight natural ionisation, consists of molecules of H_2O . There is no reason to assume that these molecules, except for small mutual deformations, differ from the H_2O molecules in steam. This is supported by the evidence of Raman and infrared absorption spectra of water. The H_2O molecule in steam consists according to the last results of Mecke¹ from band spectra, of a V-shaped arrangement of the nuclei, the OH distances

* By direct calculation from $6\pi a\zeta v = F$ (a radius, ζ viscosity), where $v = 32.5, 17.8, \times 10^{-4}$ cm/sec. for a field F of 1 volt/cm.

¹ Mecke and Baumann, *Phys. Zeits.* 33, 833 (1932).

being 0.96 Å and the $\hat{H}OH$ angle 103° – 106° , very nearly the tetrahedral angle 109° .†

It is more difficult to picture the electronic distribution. If it were simply spherical and centred on the O nucleus the molecular dipole moment would be 5.6×10^{-18} e.s.u. instead of 1.87×10^{-18} as observed. There must, therefore, be a considerable screening effect by a concentration of negative charge around the protons. (See below, p. 529.) The wave mechanical theory of the water molecule gives some qualitative information on this point. According to Mulliken² the 10 electronic wave functions of the water molecule can be designated as

$$(1s)^2[2s_1]^2[2p_x]^2[2p_y]^2[2p_z]^2$$

where x , y , and z are orientated as in Fig. 1; of these $[2s_1]^2[2p_x]^2[2p_y]^2$ are responsible for the binding of the protons and combined give an electron density surrounding the protonic positions, while $[2p_z]^2$ is not a binding wave function and gives a concentration of negative electricity

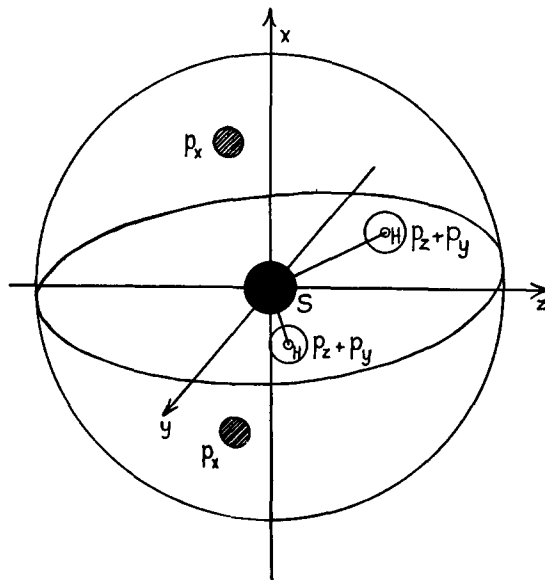
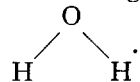


FIG. 1. The electron distribution in the water molecule.

† These results cannot be taken as exact since no fine structure analysis of the rotation spectra of an asymmetrical top has yet been completed. But most spectroscopists would agree that the molecule forms an isosceles triangle, that the vertex angle is between 90° and 120° , and that the OH distance lies between 0.9 and 1.1 Å.

² Mulliken, *Phys. Rev.* 41, 756 (1932).

in two regions at right angles to the plane of . The net electronic density distribution will therefore resemble a tetrahedron with two corners of positive and two of negative charge.

The "radius" of the water molecule is more easily fixed. The nearest approach of water molecules in ice³ is 2.76Å, and very similar figures follow from the most reliable measurements of water of crystallisation.⁴ This would make the radius of the water molecule 1.38Å, slightly larger than that of the isoelectronic O²⁻ (1.35) and F⁻ (1.33), (OH)⁻ (1.33) ions, but considerably smaller than that of A (1.9), CH₄ (2.08) or NH₃ (1.80) also measured in the solid state.

§3. The arrangement of water molecules in water

If we attempt to account for the structure of water on the basis of such a molecule and a knowledge of the structure of simple monatomic liquids such as mercury, we are faced at the outset by the difficulty of accounting for the density. A simple disordered close packed assembly of water molecules of radius 1.4Å would have a density of 1.84; or conversely, for a density of 1.00 the equivalent radius would be 1.72Å. We have therefore the choice of assuming either that water is a simple close packed liquid in which the effective molecular radius has changed from 1.4Å in the solid to 1.72Å in the liquid, or that the radius is still approximately 1.4Å but that the mutual arrangements of the molecules are far from that of a simple liquid. Both all the well-known abnormal properties of water and the extremely asymmetrical and electropolar properties of the H₂O molecule would lead us to the latter alternative, but here luckily there exists independent evidence from x-ray diffraction as to the internal structure of water.

The best results on the x-ray diffraction of water corrected for absorption, Compton effect, incoherent scattering, etc., are furnished by the independent researches of Meyer,⁵ Steward⁶ and

Amaldi,⁷ all of whom are in almost perfect agreement. The observed diffraction curve of water is shown in Fig. 2, experimental curve (2). This curve shows immediately by contrast with that of mercury, which is similar to curve (1) Fig. 2 the theoretical curve for random close packing, that the association of molecules in water is different from that of a simple liquid, for instead of the sequence of maxima in the theoretical sequence at equivalent spacings of 2.6, 1.65, 1.1Å we have a very strong maximum at 3.27Å followed by very much weaker ones at 2.3Å and 1.4Å. It is more difficult to find what is the variation from the simple liquid arrangement. The best method is to build up models of the distribution functions of the molecules (i.e., the function $g(r)$ giving the probability of finding the centre of any molecule between distances r and $r+dr$ from the centre of a given molecule) on different hypotheses, to construct from these, according to the formula⁸

$$I_{\theta} = \int_0^{\infty} 4\pi r^2 \{g(r) - \rho\} \frac{\sin sr}{sr} dr, \quad (1)$$

where

$$s = (4\pi \sin \frac{1}{2}\theta)/\lambda, \quad (2)$$

the theoretical x-ray diffraction, and to compare it with experiment. Various functions $g(r)$ are shown in Fig. 3, and the deduced x-ray scattering curves in Fig. 2 and Fig. 5.

Curve *a* of Fig. 3 represents $g(r)$ for a simple close packed liquid arrangement, curve *b* for an ice-like arrangement, and *c* for one somewhat similar to quartz. It can be seen that only *b* and *c* give diffraction curves at all resembling the observed curve, with greater resemblance in the case of *c*.

The distribution *a* is constructed for molecules of radius 1.4Å. The distributions *b* and *c* are constructed on the basis of an H₂O molecule of 1.4Å radius, each of which is surrounded by four others in a more or less regular tetrahedron (Fig. 4). This is the arrangement found in ice and necessarily follows from the quasi-tetrahedral angle of the H₂O molecule. The proton near the surface of one molecule lies opposite the empty

³ Barnes, Proc. Roy. Soc. A125, 670 (1929).

⁴ Cf. C. Beevers and H. Lipson, Zeits. f. Kryst. 82, 297 (1932); 83, 123 (1932).

⁵ A. W. Meyer, Ann. d. Physik 5, 701 (1930).

⁶ Steward, Phys. Rev. 35, 1426 (1930); 37, 9 (1931).

⁷ Amaldi, Phys. Zeits. 32, 914 (1931).

⁸ Debye and Menke, Phys. Zeits. 31, 799 (1930); Prins, Zeits. f. Physik 56, 617 (1929).

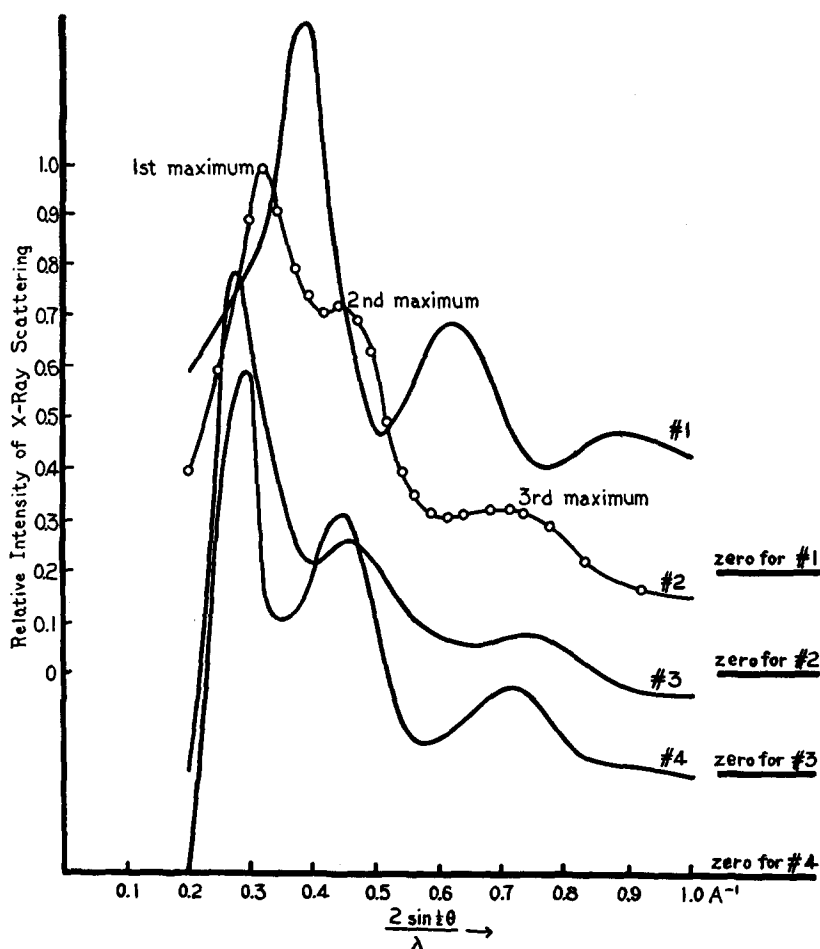


Fig. 2. X-ray scattering curves for water. Curve 1, theoretical curve for irregular close packing; curve 2, experimental curve; curve 3, theoretical curve for a quartz-like distribution; curve 4, theoretical curve for an ice-tridymite-like distribution.

place in a neighbouring molecule, that is a place where a proton would be in such a molecule as CH_4 . These are just the positions of the concentration of negative elasticity due to the wave function $[2p_x]^2$, Fig. 1.

Such fourfold coordination of molecules is not, however, sufficient to fix the whole distribution. In the case of silica, SiO_2 , where a similar fourfold coordination holds, there are three main crystalline forms, cristobalite, tridymite and quartz, besides the amorphous silica glass. Of these the tridymite structure corresponds to that of ordinary ice, and it would seem natural to imagine water as simply an irregular version of this (distribution *b*). It is difficult, however, in this case to account for the great diminution of volume on passing from ice to water. A regular

crystalline arrangement might be expected to increase in volume on becoming irregular. This suggests the possibility that water does not correspond in the main to the ice-tridymite pattern, but to the quartz pattern. In such a pattern, while the intermolecular distance between nearest neighbours is the same at 2.8\AA , that between next nearest decreases to 4.2\AA from the 4.5\AA in the ice-tridymite pattern, leading to a 17 percent decrease of volume. Remembering that the density of ice is 0.91 which is therefore the density of the ice-tridymite structure, the density of the corresponding quartz pattern would be 1.08. Water might reasonably be expected to have a lower density due to irregularities. A closer examination of the theoretical curves enables these considerations to be pushed much

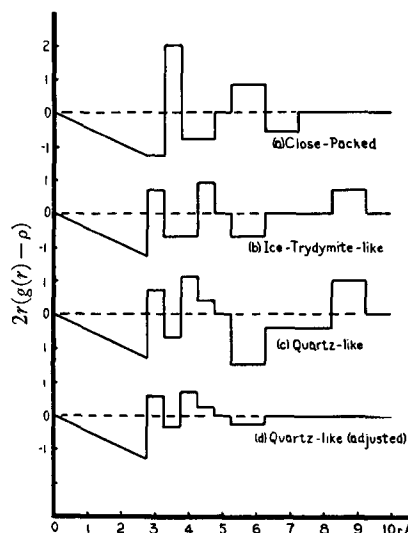


FIG. 3. The distribution function $g(r)$ for the neighbours around a water molecule (closest distance of approach 2.76 Å) for various types of arrangement.

further. The chief difference between curve 3 of Fig. 2 for the quartz-like distribution and the observed curve is that the main maxima of the former are at spacings 3.5 and 2.2 instead of 3.3 and 2.3, and that the intervening minimum at 2.5 is relatively much deeper—42 percent of the chief maximum instead of 72 percent. It is at once apparent that this may be due to a tendency towards a close packed water arrangement (curve 1) which has a maximum precisely in this region. It can be seen from the distribution curves for $g(r)$ that beyond $r = 2.7$ Å the density

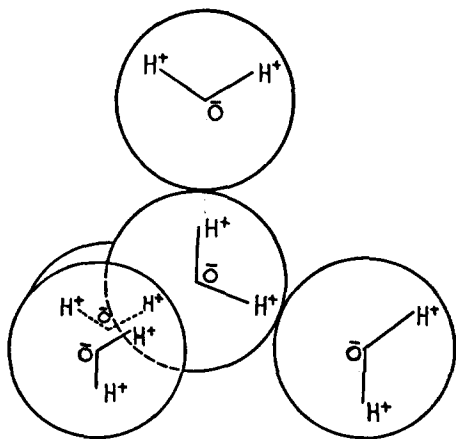


FIG. 4. Tetrahedral coordination of water molecules. The four molecules surrounding one water molecule are shown. Of these, two are in the plane of the paper, one above and one below it.

of the quartz and close packed structures are out of step for the same radii and consequently the effect of adding distribution a to b is to smooth out differences from that of a uniform fluid or, physically speaking, to diminish the regularity of the packing particularly at greater distances than 4 Å from any molecule. A scattering curve constructed from such an altered distribution function (d of Fig. 3) is shown in curve 5 of Fig. 5. It shows an almost perfect fit with the experimental curve as far as the position of the maxima and minima, but it still differs in intensity, the second maximum being undoubtedly low compared with the first. The physical basis of the difference between the ideal quartz-like structure and the actual water structure is the temperature movement of the molecules. At higher temperatures this causes a breakdown of the quartz structure, leading more and more toward the close packed structure, and shows itself in the x-ray pattern as a shift of the first and second maxima in opposite directions towards the mean position of 2.7 Å, and of the wiping out of the minimum between them. Thus between 2° and 98° the main maximum moves from 3.27 to 3.1, while the second moves from 2.2 to 2.4 at 40° and afterwards disappears.

The inward movement of the main maximum gives rise to the appearance of a contraction on heating water which can now be seen to be

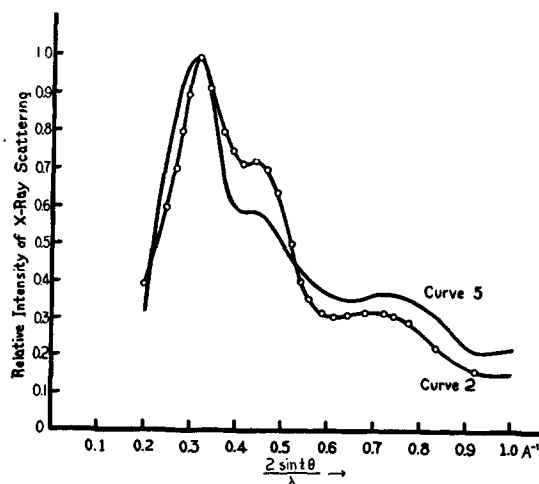


FIG. 5. X-ray scattering curves for water. Curve 2, experimental; curve 5, theoretical curve for quartz-like water modified by some close packing.

	max.	min.	max.	min.	max.	min.
Observed	3.27	2.37	2.27	1.60	1.45	1.1
Calculated	3.33	2.4	2.2 (inflection)	1.55	1.40	1.1

spurious. At the lowest temperatures, 2°C, the deepening of the first minimum suggests a distribution in which the tridymite-ice-like arrangement is beginning to occur. This arrangement might be expected to be common in supercooled water, and its disappearance the reason for the anomalous contraction of water on heating above 0°C. But as these anomalous changes of volume are small compared with the ice-water change, we must not say more than that cold water is on the whole quartz-like with appreciable tridymite-ice-like tendencies.

We may therefore consider that there are three chief forms of arrangement of the molecules of H₂O in water:—*water I*, tridymite-ice-like, rather rare, present to a certain degree at low temperatures below 4°C: *water II*, quartz-like, predominating at ordinary temperatures: *water III*, close packed, ideal liquid, ammonia-like, predominating at high temperatures for some distance below the critical point at 374°C. These forms pass continuously into each other with change of temperature. Throughout, as G. W. Stewart has insisted, there is no question of a mixture of volumes with different structures; at all temperatures the liquid is homogeneous but the average mutual arrangements of the molecules resemble water I, II and III in more or less degree. The sequence of water I—II—III is one of increasing rotatory and translatory molecular movement and of the consequent diminution of the dipole forces of cohesion of the liquid and relative increase of the van der Waals component. It is a sequence of increasing fluidity but not one of increasing volume. The immediate effect of breaking down the relatively empty ice-like structure of water I is a decrease of volume to water II, followed by an increase of a more normal kind to water III, where the increase of the mean distance of the neighbouring molecules due to thermal agitation more than compensates for the geometrical contraction of the transition from the quartz-like to the close packed structures. The theory of polymorphic forms of water is familiar to chemists, particularly from the work of H. E. Armstrong. If the view put forward above is accepted it will be seen that these theories have a close relationship to the facts, but have been conceived too much in the manner of molecular chemistry. Trihydrol (H₂O)₃, di-

hydrol (H₂O)₂, and hydrol (H₂O) have no direct structural analogy with water I, II, and III, but the latter explain, by means of the geometrical internal structure of the liquid, physical properties which the former attempted to explain in terms of hypothetical molecules.

§4. Effects of high pressures

These considerations may be supported by an examination of the behaviour of water under pressure. The equilibrium diagram of water, has been given by Bridgman.⁹ At different pressures four kinds of ice, I, III, V, and VI are found in equilibrium with water. Their relative volumes (normal cold water 1.000) and that of the water in equilibrium with them, are shown in Table I. Ices III, V, and VI are all denser than water, showing that the latter has not a close packed structure.

In considering these equivalent volumes the effect of the compressibility of the water molecules themselves has to be taken into account. A rough way of doing this is provided by assuming that the volume change of any one ice at different pressures inside its range of stability is due to the compression of the atoms themselves (this is only strictly true for crystal structures without variable parameters). We thus interpret the volume ratio of any one ice over its extreme pressure range in Table I as the volume ratio of the water molecules over the same pressure range. In this way it is possible to determine what part of the actual loss of volume of water at high pressures is due to the compression of the molecules, (column 6, relative volume of water molecule), and what part to the crushing of the organized structure of the liquid, (column 7, geometrical equivalent volume of water). It will be seen that at the highest pressures, 10,000 atmospheres, this geometrical crushing amounts to 11 percent, though the volume is still 44 percent from that of the close packed structure of water molecules of radius 1.4A. The geometrical compression factor is far greater for ices III, V and VI than for water. The full meaning of this would only appear if the crystal structures of these forms could be determined by x-rays. The isomorphism between tridymite and ice I suggests forcibly that of the structures of ices

⁹ Bridgman, Proc. Nat. Acad. Sci. **47**, 441 (1912).

TABLE I. *Equivalent volumes of water and various types of ice (Bridgman).*

1	2	3	4	5	6	7
Pressure atmospheres	Ice form	Ice volume (observed)	Equivalent water volume (observed)	Geometrical equivalent volume of ice	Relative volume of water molecule	Geometrical equivalent volume of water
1	I	1.0900	1.0000	1.090	1.000	1.000
2000	I	1.0571	0.9253		0.970	0.955
2000	III	0.8774				
3500	III	0.8636	0.8815	0.905	0.956	0.922
3500	V	0.8085				
6000	V	0.7929	0.8472	0.847	0.937	0.904
6000	VI	0.7636				
10000	VI	0.7385	0.8055	0.816	0.906 From the change in volume of the preceding ice	0.890
				Observed vol. corrected for size of water molecule Col. 3/Col. 6		
				Col. 4/Col. 6		

III, V and VI, at least one must be that of quartz. However, this may be, the considerable diminutions of volume, 5 percent, 9 percent, and 11 percent on passing from water to ices III, V and VI respectively confirms the x-ray evidence that the structure of water is far from being a close packed one.

§5. Evidence from Raman spectra

The nature of this difference is further brought out by studying the interaction with water of the longer electromagnetic waves. The Raman spectrum of water has been much studied. It consists of three bands at $\Delta\nu = 3216, 3435$ and 3582 ; these plainly correspond to the fundamental frequency $\nu = 3700$ of the H_2O molecule found from the infrared absorption of water vapour. The water bands differ from those of other liquids by being so broad as to overlap almost completely. This indicates the effect of local dipoles in disturbing the term levels and itself is evidence for internal structure of a different kind from that of normal liquids. The lines corresponding to the water bands are shown in the Raman spectrum of ice at $\Delta\nu = 3193, 3391$ and 3549 . This shows that to a first approximation the effect of neighbouring molecules on any molecule is the same in both phases, and that probably the structure of water is, like that of

ice, a 4-coordinated tetrahedral one. That this coordination is not exact and tends to break down at higher temperatures is shown by the relative intensities of the lines. In ice the 3200 line is the predominant one, in cold water that at 3400 and in hot the 3600 line. The weakening of the 3200 line in the Raman spectrum is therefore a parallel indication with that of the 2.2A maximum in the x-ray diffraction, and marks the beginning of the transition to the close packed structure. It is tempting to identify the 3200, 3400, 3600 bands as corresponding respectively to the previously defined water structures I, II and III, but such a correspondence cannot be maintained until the nature of the transitions corresponding to these bands has been worked out.

There is also a shift towards the higher frequencies indicating weakening of the mutual polarization forces of the molecules in water relative to ice.

§6a. The structure of ice

Before discussing the dielectric constants of water and ice it is necessary to examine closely the structure of ice. In the normal ice structure the positions of the H nuclei and consequently the orientations of the molecules are fixed. This follows from the x-ray determination of the

positions of the O atoms combined with the knowledge of the molecular structure derived from band spectra. Every molecule is surrounded by four others in a tetrahedron and this arrangement will have least energy if the H nuclei, which subtend an angle of about 109° at the centre of the molecule,* lie opposite two of the neighbours, while one of the H-nuclei of each of the remaining neighbours lies opposite a negative corner of the original molecule. (See Fig. 4.) Such an arrangement has, of course, no trigonal symmetry and is impossible at first sight to fit with the x-ray structure of ice.³ But in the derivation of the latter, only the effects of the O atoms can be taken into account and so no structure leaving the positions of these unchanged can be rejected on x-ray grounds. The simplest of physically possible structures is shown in Fig. 6. It requires a cell three times as large as that proposed by Barnes, but is still of trigonal symmetry. It belongs, however, to a polar class, whereas Barnes' structure belongs to the holohedral class. The crystallographic evidence is conflicting, but the careful work of Adams¹⁰ suggests that the polar class is the correct one, though often masked by twinning on the basal plane. The attempt by Dr. W. A. Wooster to prove the polar character of ice from its pyro-electricity by Martin's method¹¹ gave, however, negative results; this may have been due to twinning.

It is of course possible to construct regular ice structures without polar properties. For geometrical reasons, however, this implies a very large cell and extreme complexity: the simplest of these with the symmetry $C_3^2-C_3$, still geometrically but not physically polar, contains 96 molecules in the unit cell. The formation of such a complex arrangement under ordinary circumstances is most improbable. The structure of Fig. 6 is the simplest *regular* structure for ice. Therefore it is quite conceivable and even likely that at temperatures just below the

melting point the molecular arrangement is still partially or even largely irregular, though preserving at every point tetrahedral coordination and balanced dipoles. In that case ice would be crystalline only in the position of its molecules but glass-like in their orientation. Such a hypothesis may be still necessary to explain the dielectric constant and the absence of pyro-electricity.

§6b. A theoretical discussion of the dielectric constants of water and ice

One of the most characteristic properties of water is its high dielectric constant, 88 at 0°C for frequencies up to 10^8 cycles/sec. The dielectric constant of ice is sometimes thought of as being low. The difference between them is, however, largely a matter of the frequencies at which the dielectric constant is measured. The frequency variation of the dielectric constant for water and ice at different temperatures is shown in Fig. 7.

The nature of the dielectric constant as a function of frequency is much the same at all temperatures and apparently both for water and ice; the only important change is in the frequency scale for the different curves. For sufficiently low frequencies the dielectric constant of even quite cold ice can reach large values, possibly even values larger than the ordinary values for water. For sufficiently high frequencies the dielectric constant of water falls below its constant low-frequency value, but only at higher frequencies for higher temperatures. The value of the low frequency dielectric constant falls for water with rising temperature and probably for ice with falling temperature. The greatest values are reached for cold water (or perhaps warm ice). The most modern values are shown in Fig. 7a and some old low temperature values.

The dielectric properties of water and ice have been carefully analysed by Debye.¹² He uses a model consisting of spherical dipole carriers for the H_2O molecules, free to rotate under the combined influence of the effective electrical field acting on them and the inner viscosity of the water or ice. This viscosity must be interpreted for the ice in a generalised sense. He shows that the form of the curves as functions

* The angle $103-106$ given above on p. 517 refers to the angle between the H and O nuclei. Here the centre of the molecule is not its centre of mass near the O nucleus but its electronic centre, which is shifted toward the pair of H nuclei, see below p. 529.

¹⁰ Adams, Proc. Roy. Soc. **A128**, 588 (1930).

¹¹ Martin, Mineral. Mag. **21**, 519 (1931).

¹² Debye, *Polare Molekeln*, Chapter V, (1929).

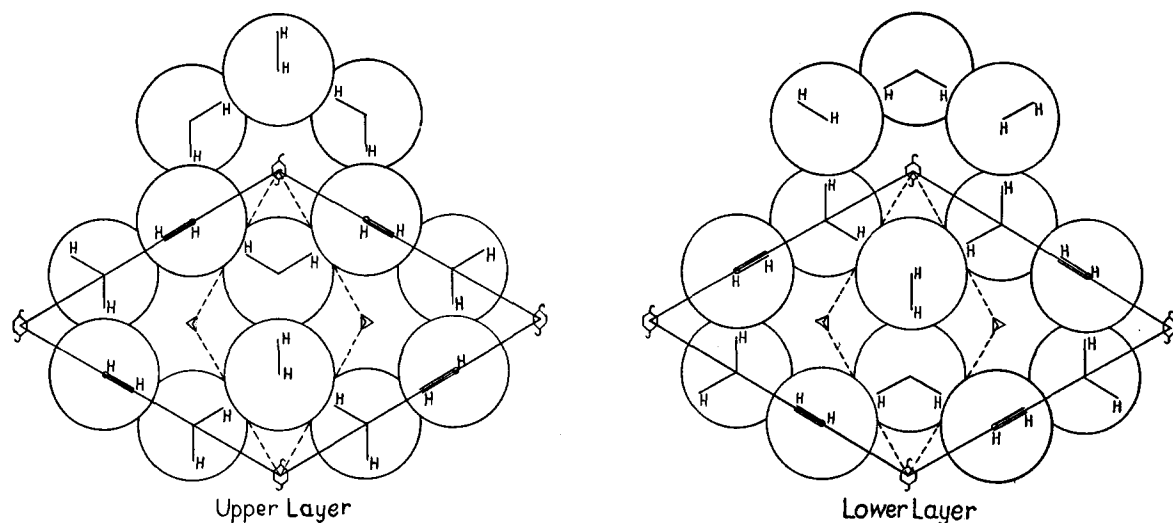
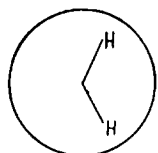
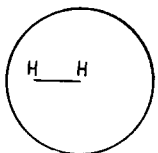


FIG. 6. Ice structure viewed along hexagonal axis.

Explanation: The structure* is shown in two layers; — marks the edges of the true cell, $a = 7.81\text{\AA}$; - - - marks the edges of Barnes' cell, $a = 4.51\text{\AA}$.



Indicates in upper layer molecules, $(5/8)c = 4.61\text{\AA}$ above base of cell;
Indicates in lower layer molecules $-(1/8)c = -0.92\text{\AA}$ above base of cell;
The two H lie above the O, and the OH directions are inclined at $10^\circ 16'$ to the c axis.



Indicates in upper layer molecules $(7/8)c = 6.45\text{\AA}$ above base of cell;
Indicates in lower layer molecules $(1/8)c = 0.92\text{\AA}$ above base of cell.
One H lies above O on the c axis, the other below O at $70^\circ 16'$ to the c axis. In both cases the dipole axis points with its positive direction upwards, inclined at 54° to c axis.

$6O_I$ at	$\begin{cases} \frac{1}{3} \\ \frac{2}{3} \end{cases}$	$\begin{cases} 0 \\ 0 \end{cases}$	$\begin{cases} \frac{1}{16} \\ \frac{9}{16} \end{cases}$	$\begin{cases} \frac{2}{3} \\ \frac{1}{3} \end{cases}$	$\begin{cases} \frac{2}{3} \\ \frac{1}{3} \end{cases}$	$\begin{cases} \frac{1}{16} \\ \frac{9}{16} \end{cases}$	$\begin{cases} 0 \\ 0 \end{cases}$	$\begin{cases} \frac{1}{3} \\ \frac{2}{3} \end{cases}$	$\begin{cases} \frac{1}{16} \\ \frac{9}{16} \end{cases}$
	$\begin{cases} \frac{2}{3} \\ \frac{1}{3} \end{cases}$	$\begin{cases} 0 \\ 0 \end{cases}$	$\begin{cases} \frac{15}{16} \\ \frac{7}{16} \end{cases}$	$\begin{cases} \frac{2}{3} \\ \frac{1}{3} \end{cases}$	$\begin{cases} \frac{2}{3} \\ \frac{1}{3} \end{cases}$	$\begin{cases} \frac{15}{16} \\ \frac{7}{16} \end{cases}$	$\begin{cases} 0 \\ 0 \end{cases}$	$\begin{cases} \frac{2}{3} \\ \frac{1}{3} \end{cases}$	$\begin{cases} \frac{15}{16} \\ \frac{7}{16} \end{cases}$
$6H_I$ at	$\begin{cases} \frac{1}{3} \\ \frac{2}{3} \end{cases}$	$\begin{cases} 0 \\ 0 \end{cases}$	$\begin{cases} \frac{1}{16} + 3z \\ \frac{9}{16} + 3z \end{cases}$	$\begin{cases} \frac{2}{3} \\ \frac{1}{3} \end{cases}$	$\begin{cases} \frac{2}{3} \\ \frac{1}{3} \end{cases}$	$\begin{cases} \frac{1}{16} + 3z \\ \frac{9}{16} + 3z \end{cases}$	$\begin{cases} 0 \\ 0 \end{cases}$	$\begin{cases} \frac{1}{3} \\ \frac{2}{3} \end{cases}$	$\begin{cases} \frac{1}{16} + 3z \\ \frac{9}{16} + 3z \end{cases}$
	$\begin{cases} \frac{1}{3} + y \\ \frac{2}{3} - y \end{cases}$	$\begin{cases} 0 \\ 0 \end{cases}$	$\begin{cases} \frac{1}{16} - z \\ \frac{9}{16} - z \end{cases}$	$\begin{cases} \frac{2}{3} - y \\ \frac{1}{3} + y \end{cases}$	$\begin{cases} \frac{2}{3} - y \\ \frac{1}{3} + y \end{cases}$	$\begin{cases} \frac{1}{16} - z \\ \frac{9}{16} - z \end{cases}$	$\begin{cases} 0 \\ 0 \end{cases}$	$\begin{cases} \frac{1}{3} + y \\ \frac{2}{3} - y \end{cases}$	$\begin{cases} \frac{1}{16} - z \\ \frac{9}{16} - z \end{cases}$
$12H_{II}$ at	$\begin{cases} \frac{2}{3} + y \\ \frac{2}{3} \\ \frac{1}{3} \\ \frac{1}{3} - y \end{cases}$	$\begin{cases} y \\ -y \\ y \\ -y \end{cases}$	$\begin{cases} \frac{15}{16} + z \\ \frac{15}{16} + z \\ \frac{7}{16} + z \\ \frac{7}{16} + z \end{cases}$	$\begin{cases} \frac{1}{3} \\ \frac{1}{3} - y \\ \frac{2}{3} \\ \frac{2}{3} + y \end{cases}$	$\begin{cases} \frac{1}{3} - y \\ \frac{1}{3} \\ \frac{2}{3} \\ \frac{2}{3} \end{cases}$	$\begin{cases} \frac{15}{16} + z \\ \frac{15}{16} + z \\ \frac{7}{16} + z \\ \frac{7}{16} + z \end{cases}$	$\begin{cases} y \\ -y \\ y \\ -y \end{cases}$	$\begin{cases} \frac{2}{3} + y \\ \frac{2}{3} \\ \frac{1}{3} \\ \frac{1}{3} - y \end{cases}$	$\begin{cases} \frac{15}{16} + z \\ \frac{15}{16} + z \\ \frac{7}{16} + z \\ \frac{7}{16} + z \end{cases}$
	$\begin{cases} \frac{2}{3} \\ \frac{1}{3} \\ \frac{1}{3} - y \\ \frac{2}{3} + y \end{cases}$	$\begin{cases} -y \\ y \\ -y \\ y \end{cases}$	$\begin{cases} \frac{15}{16} + z \\ \frac{15}{16} + z \\ \frac{7}{16} + z \\ \frac{7}{16} + z \end{cases}$	$\begin{cases} \frac{1}{3} \\ \frac{1}{3} - y \\ \frac{2}{3} \\ \frac{2}{3} + y \end{cases}$	$\begin{cases} \frac{1}{3} - y \\ \frac{1}{3} \\ \frac{2}{3} \\ \frac{2}{3} \end{cases}$	$\begin{cases} \frac{15}{16} + z \\ \frac{15}{16} + z \\ \frac{7}{16} + z \\ \frac{7}{16} + z \end{cases}$	$\begin{cases} y \\ -y \\ y \\ -y \end{cases}$	$\begin{cases} \frac{2}{3} + y \\ \frac{2}{3} \\ \frac{1}{3} \\ \frac{1}{3} - y \end{cases}$	$\begin{cases} \frac{15}{16} + z \\ \frac{15}{16} + z \\ \frac{7}{16} + z \\ \frac{7}{16} + z \end{cases}$
	$\begin{cases} \frac{2}{3} + y \\ \frac{2}{3} \\ \frac{1}{3} \\ \frac{1}{3} - y \end{cases}$	$\begin{cases} y \\ -y \\ y \\ -y \end{cases}$	$\begin{cases} \frac{15}{16} + z \\ \frac{15}{16} + z \\ \frac{7}{16} + z \\ \frac{7}{16} + z \end{cases}$	$\begin{cases} \frac{1}{3} \\ \frac{1}{3} - y \\ \frac{2}{3} \\ \frac{2}{3} + y \end{cases}$	$\begin{cases} \frac{1}{3} - y \\ \frac{1}{3} \\ \frac{2}{3} \\ \frac{2}{3} \end{cases}$	$\begin{cases} \frac{15}{16} + z \\ \frac{15}{16} + z \\ \frac{7}{16} + z \\ \frac{7}{16} + z \end{cases}$	$\begin{cases} y \\ -y \\ y \\ -y \end{cases}$	$\begin{cases} \frac{2}{3} + y \\ \frac{2}{3} \\ \frac{1}{3} \\ \frac{1}{3} - y \end{cases}$	$\begin{cases} \frac{15}{16} + z \\ \frac{15}{16} + z \\ \frac{7}{16} + z \\ \frac{7}{16} + z \end{cases}$
	$\begin{cases} \frac{2}{3} \\ \frac{1}{3} \\ \frac{1}{3} - y \\ \frac{2}{3} + y \end{cases}$	$\begin{cases} -y \\ y \\ -y \\ y \end{cases}$	$\begin{cases} \frac{15}{16} + z \\ \frac{15}{16} + z \\ \frac{7}{16} + z \\ \frac{7}{16} + z \end{cases}$	$\begin{cases} \frac{1}{3} \\ \frac{1}{3} - y \\ \frac{2}{3} \\ \frac{2}{3} + y \end{cases}$	$\begin{cases} \frac{1}{3} - y \\ \frac{1}{3} \\ \frac{2}{3} \\ \frac{2}{3} \end{cases}$	$\begin{cases} \frac{15}{16} + z \\ \frac{15}{16} + z \\ \frac{7}{16} + z \\ \frac{7}{16} + z \end{cases}$	$\begin{cases} y \\ -y \\ y \\ -y \end{cases}$	$\begin{cases} \frac{2}{3} + y \\ \frac{2}{3} \\ \frac{1}{3} \\ \frac{1}{3} - y \end{cases}$	$\begin{cases} \frac{15}{16} + z \\ \frac{15}{16} + z \\ \frac{7}{16} + z \\ \frac{7}{16} + z \end{cases}$

$$y = 0.105 \quad z = 0.037$$

* The full description of the structure is as follows: hexagonal $a = 7.82$, $c = 7.36$, 12 molecules H_2O per cell; space group $C_{6v}^3 - C6mc$; atomic positions (somewhat idealised).

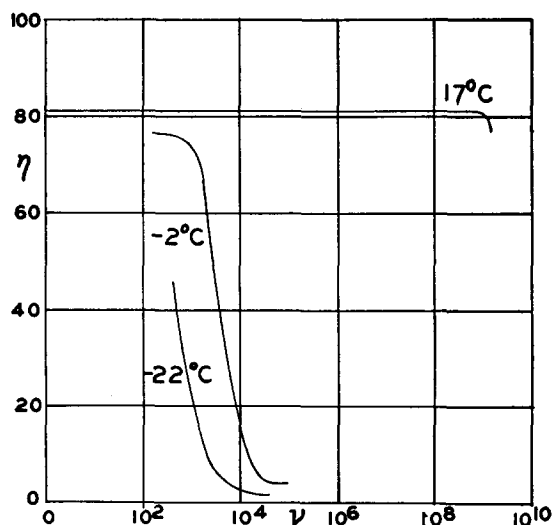


FIG. 7. Variation of the dielectric constant of water and ice with frequency (*International Critical Tables*).

of frequency are in surprisingly complete accord with this very crude theory. The inner viscosity, the relaxation time, and therefore the wavelength of the oscillations at which the great change of dielectric constant occurs, appear to increase discontinuously by a factor of 10^5 on freezing, (this is perfectly natural), but otherwise the water-ice properties pass smoothly and continuously over into each other.

To this part of the discussion we cannot and need not attempt to add anything, but Debye does not analyse the absolute values of the low frequency dielectric constant as a function of

the temperature and we think that further insight can be obtained from such an analysis, by the same model.¹³ It is essential to remember that this analysis uses Mosotti's hypothesis that the effective inner field strength at any point acting on one of our dipole carriers, is $E + (4/3)\pi P$, where E is the electrical force (or intensity) and P is the polarization of the medium. The applicability of Mosotti's hypothesis is open to question as is carefully pointed out by Debye. Its applicability is strictly only guaranteed by Lorentz's¹⁴ lemma for completely random distributions of dipoles around any selected dipole or for distributions with cubic symmetry. These latter include distributions in which all the neighbours can be grouped into sets of four at the corners of regular tetrahedra whose centres lie at the selected molecule. For this model of rotating dipoles the Weiss-Langevin ferromagnetic theory applies in its simplest form so that—

$$P = N\mu L\left(\frac{\mu\{E + (4/3)\pi P\}}{kT}\right), \quad (3)$$

where N is the number of orientating dipoles, of moment μ , per unit volume and $L(x)$ is Langevin's function,

$$L(x) = \coth x - 1/x. \quad (4)$$

From (3) and (4) it follows that for small fields

$$P\{1 - 4\pi N\mu^2/9kT\} = (N\mu^2/3kT)E,$$

or

$$P = [N\mu^2/3k(T - T_c)]E \quad (T_c = 4\pi N\mu^2/9k). \quad (5)$$

The dielectric constant η is given by $\eta - 1 = 4\pi P/E$, so that

$$\eta = 1 + 4\pi N\mu^2/3k(T - T_c) = 1 + 3T_c/(T - T_c). \quad (6)$$

If all the water dipoles are freely orientable, then $N = 6.06 \times 10^{23}/18$, $\mu = 1.87 \times 10^{-18}$, $T_c = 1200$. This is naturally impossible—it would correspond to a state of permanent polarization of ferromagnetic type. If we are to account for the observed values of $\eta(T)$ by an orientating dipole theory we must determine T_c from (6) and the observed $\eta(T)$, and then N from (5). We must, that is, use a variable number of effective freely rotating dipoles; this is *a priori* a perfectly acceptable conclusion. The actual

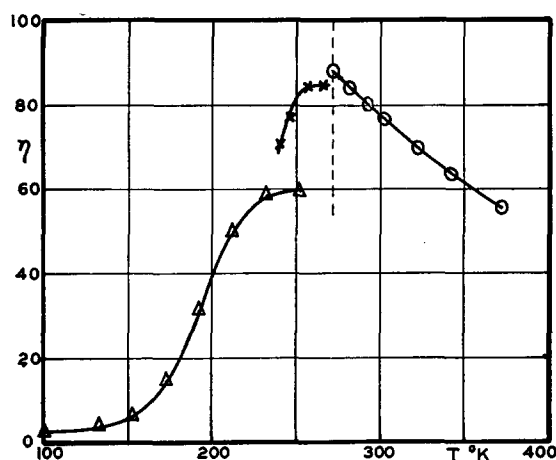


FIG. 7a. The dielectric constant of water and ice at low frequencies. Circle, Lattey, 1931; triangle, Fleming and Dewar, 1897; cross, Wintsch, 1932 (*Helv. Phys. Acta* V, 126 (1932)).

¹³ See also Zwicky, *Phys. Zeits.* 27, 271 (1926).

¹⁴ Lorentz, *Theory of Electrons*, notes 54, 55.

effective numbers of freely rotating dipoles, expressed as a fraction of N , required to give the values of Fig. 7a are given in Table II. In these rough calculations the part of the dielectric constant to be referred to the orientations is taken as $\eta(T) - 2$.

TABLE II. Fraction f of orientable molecules required to account for $\eta(T)$.

Water		Ice	
$T^\circ\text{K}$	f	$T^\circ\text{K}$	f
273	0.220	270	0.216
293	0.235	250	0.200
325	0.26	225	0.178
350	0.28	200	0.154
—	—	175	0.118

These variations are in themselves entirely reasonable even if we can provide no special theory of them. They require us to assert that, from a 1/5 to a 1/4 of the water molecules or from a 1/10 to a 1/5 of the ice molecules must be regarded as free rotators in the sense of the theory. At the same time, the great bulk of the water or ice molecules must be definitely regarded as *not free to rotate*. This is in accord with the theory of water which we are developing here, but the proportion of *non-rotatable* molecules is perhaps rather far from unity, especially for crystalline ice. It is commonly held on the basis of a calculation by Debye¹⁵ that so few ice molecules have to turn round in fields of any ordinary intensity (1 in 5,000,000 in a field strength of 1 volt/cm) that the ice lattice could not be upset. But this is not the same thing—what we have calculated is not how many turn but how many are really free to turn and perhaps this latter number is of more importance than Debye's number for the lattice stability.

We may summarize the discussion up to this point by admitting (1) that it is possible to accept a rotating dipole theory of the dielectric constant of water and ice without contradiction with the theory of the structure which we are discussing here, but (2) that there are inherent difficulties in a rotating dipole theory which requires us to accept it with caution if at all. These difficulties will become more prominent when we show below (p. 530) that the total

energy of ice or water probably derives mainly from the interactions of dipoles not free to rotate (except for the irrelevant form of rotation about a dipole axis). But if the free dipole theory has to be abandoned or modified, it is probable that the dielectric constant can be derived from the re-orientation of blocks of polar crystal by the applied field. In water, the blocks would be very indefinite liquid crystals, very easily interconvertible; in ice the time of conversion would necessarily be longer and increase as the temperature falls. It is not yet necessary to attempt to construct such a theory in detail, but in some such way one might remove what seems to us to be the chief objection to the free dipole theory—namely that very small changes in f correspond to enormous changes in dielectric constant, so that the factors determining f ought somehow to be explicitly present in the theory.

§7. A comparison of water with other liquids

The physical properties of water and ice seem all the more abnormal when compared with other compounds of similar electronic structure. The H_2O molecule is of the neon type with ten electrons, as are also CH_4 , NH_3 and HF . The significant properties of these substances are shown in Table III. For comparison the same properties are also shown for the hydrides of the second row elements PH_3 , SH_2 and HCl , as well as for some hydrides of diatomic complexes such as CC , CN , CO , CF , NN , NO , OO . It can be seen at once that these substances fall into three classes. The majority are typically molecular with low critical and boiling points and short liquid ranges. Others like hyponitrous acid HNO , formaldehyde H_2CO and acetylene HCCH , tend to polymerise. The remainder, H_2O , HF , H_3COH , H_2NNH_2 , H_2NOH , H_2O_2 and HCN form the group of typical associated liquids with relatively high boiling and critical points and long liquid ranges. All these molecules except H_2NNH_2 possess single highly polar $\text{OH}(\text{FH}, \text{C}-\text{H})$ groups, and it is plainly the attraction between the positive end of these dipoles and the negatively charged remainder of the molecule that determines the extra cohesive forces in these cases. In HF the cohesion is better regarded as due not to dipoles but to "the H-

¹⁵ Debye, reference 12, p. 122.

TABLE III. Properties of simple molecular substances.

Substance	Crystal structure	Mol. vol. in liquid cuA	Melting point $T^{\circ}\text{abs.}$	Boiling point $T^{\circ}\text{abs.}$	Crit. temp. $T^{\circ}\text{abs.}$	van der Waals constants a	b	Latent heats kcal./g mol. Fusion	Evap.	Viscosity at temp. $T^{\circ}\text{C}$	Dielectric const.	Dipole moment
CH ₄	CP	63	89	109	191	0.0036	0.00162	0.023		0.0025, - 34		0
NH ₃	CP'	45	196	234	405	.0080	.00161	1.84	5.6	0.0179, 0	25.4	1.5
OH ₂	T	30	273	373	647	.0118	.00150	1.41	9.72	Mobile	80	1.87
FH	Pol	33	190	293				1.09	6.02		83.5	
PH ₃	CP'	76	140	188	327	.0094	.00233					0.55
SH ₂	CP'	63	187	211	373	.0089	.00193		4.23	0.00435, - 63	5.93	1.10
ClH	CP	65	160	190	325			0.050	3.54	0.00455, - 45	8.85	1.03
H ₃ CCH ₃	HCP	110	102	184	305	.0119	.00312					0
H ₃ CNH ₂		80		267	430	.0144	.00272			0.00236, 0	10.5	1.31
H ₃ COH		65	175	338	513	.0199	.00318	0.052	11.0	0.0055, 25	34	1.73
H ₃ CF				195	316	.0092	.00235					
H ₂ NNH ₂		52	274	386	653					Viscous		
H ₂ NOH		44.5	306	340 †								
HOOH		38.5	271	357				0.25	12.3	Viscous	92.8	
H ₂ CCH ₂		76	103	170	282	.0089	.00255					0
H ₂ CO	Pol	61	181	252								
HNO	Pol		Solid at 290	Unstable								
HCCH	Pol	69		191	308	.0087	.00239					
HCN		64	259	300	457				5.6	0.0026, - 7		

CP=cubic close packing.

CP'=polar modified cubic close packing.

HCP=hexagonal close packing.

T=tridymite structure.

Pol=Polymerises.

† At 60 mm Hg. Unstable at higher temperatures.

|| At 68 mm Hg. Unstable at higher temperatures.

bond." But even in this group water is unique. It has the highest van der Waals constant a corresponding to the greatest intermolecular attraction, and the lowest b corresponding to the smallest distance between molecular centres. This emphasises what we have tried to show above, that the peculiar cohesion of water is due not only to the presence of dipoles, but to the geometrical possibility of the fitting together of the molecules. It is only in water that the tetrahedral arrangement of molecules is possible. The presence of two and only two H atoms per molecule gives the possibility of attaching two molecules by this means, and two others by means of their own H atoms, thus mimicking the ionic structure of quartz with one H between every two oxygens instead of one oxygen between every two silicons (see Fig. 8).

Such a three dimensional self-perpetuating structure is impossible for ammonia with 3 H atoms and place for only one more, or for hydrofluoric acid with only one H atom. It is natural

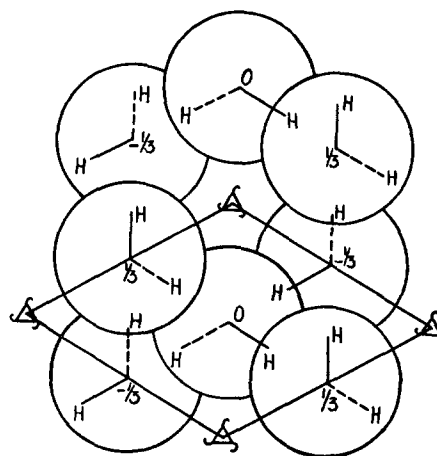
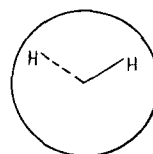
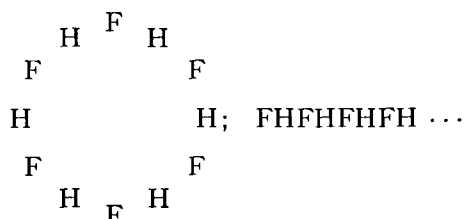


FIG. 8. "Quartz" water structure.



The molecules are in three layers, $-(1/3)c, 0, (1/3)c$ from the base of the cell. The OH directions pointing upwards are shown —H. The OH directions pointing downward are shown - - -H. The central atom shows the distorted tetrahedral coordination.

to suppose that in HF we have merely a linear dipole, that the tetrahedral skeleton is not developed and that the only point of attachment of another H is more or less opposite the first H. In that case we can only have a linear coordination and HF must form either rings or chains:—



In NH_3 , or in HF if we should rather assume that the latent tetrahedron is still present, we can still only obtain single rings or chains. For example, in NH_3 , we can have such a structure as in Fig. 9 in which the + signs denote H-nuclei and the O signs vacancies. If we wish to add

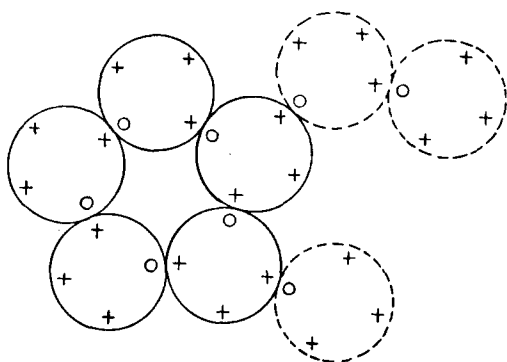


FIG. 9. Rings or chains in NH_3 .

further molecules we can do so in the manner shown by the dotted circles, but these rays can never connect up again and must tend to loosen each other's attachments. The same diagram illustrates HF if + and O signs are interchanged. H_2S with an internal structure similar to H_2O has its H atoms too deeply buried to be effective as dipoles against the thermal rotation. Of all liquids, methyl alcohol most closely resembles water, but the apolar methyl group gives it a distinctly more molecular character. The coherent nature of liquid hydrazine (H_2NNH_2) cannot, however, be accounted for in any of the above ways. Its properties would repay more careful investigation. Two possibilities may be

suggested: either H bonds can be formed between neighbouring molecules—though these have not so far been observed in N—H compounds, or the molecules in the liquid become zwitter ions $(\text{H}_3\text{N})^+(\text{NH})^-$ holding together by their electrostatic attraction.

We conclude, therefore, that the unique properties of water are due to a structure of the molecule which permits it to form in solid and liquid phases an extended electropolar complex characterised by tetrahedral (four) coordination.

§8. The total internal energy of water

It is possible to give a rough quantitative check to this conception of the water structure. The total energy of water on this model is due mainly to the mutual potential between neighbouring molecules arising from their electropolar character. If the charge distribution in the H_2O molecule were known, this could be calculated rigorously, but failing this, approximate values can be found by combining the information from spectra as to the mutual positions of the mass centres in the molecule, the value of the molecular dipole moment and the intermolecular distance calculated from the x-ray data.

If we take the spectroscopic model (Fig. 10) and place a charge ϵ at the H positions and -2ϵ on the O nucleus we arrive at a molecule of dipole moment 5.6×10^{-18} instead of the observed

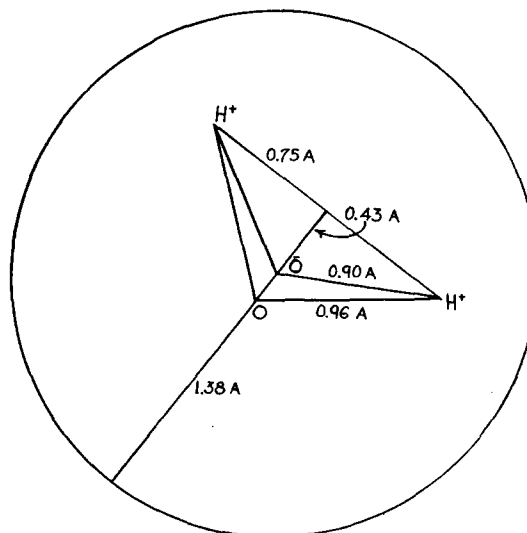


FIG. 10. The water molecule model. H^+H^+ are the hydrogen nuclei; O, the oxygen nucleus; $\bar{\text{O}}$ is the centre of negative charge and of the molecule.

1.87×10^{-18} . It is clear that this discrepancy is due to having made no allowance for the effect of the two H^+ on the O^- ion. This will be two-fold. The centre of negative electronic charge will be moved from the O nucleus to some position intermediate between it and the H nuclei, and a certain concentration of negative charge will screen the H charges. The simplest assumption is to assume effective charges of ϵ' (less than ϵ) at the H positions, and a charge $-2\epsilon'$ situated x Å from the O nucleus on the bisector of the $H\hat{O}H$ angle. With an electric moment of 2×10^{-18} these are connected by the relation

$$(0.58 - x)\epsilon' = 0.21\epsilon.$$

This leaves only the choice of x arbitrary between 0 and 0.37Å. It is plainly nearer the former value because for six of the ten electrons of the system the negative centre must be very near the O nucleus. A value 0.15 for x , giving $\epsilon' = 0.49\epsilon = 2.33 \times 10^{-10}$ would not be unreasonable, and has the advantage for calculation of giving a tetrahedral arrangement of $+$ and $-$ charges.* Luckily we can find an entirely independent check on this value from the measurement of the dipole moment of hydroquinone. In this dihydroxy compound HOC_6H_4OH the hydroxy groups rotate quite independently, and as they are symmetrically placed only the transverse electric moments μ_t are effective. (See Fig. 11.) By the theory of Fuchs¹⁶ the observed moment μ represents the

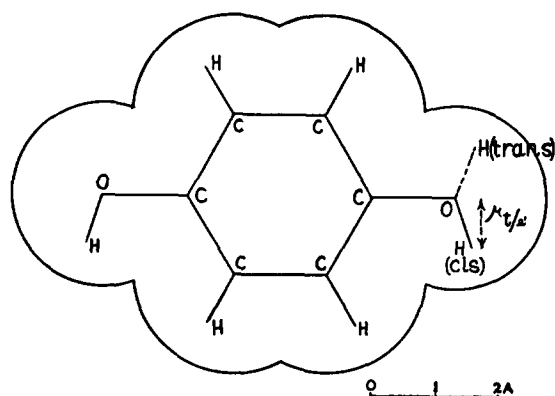


FIG. 11. Hydroquinone.

* In several of the subsequent calculations the value is taken as 0.5 for simplicity.

¹⁶ Fuchs, Zeits. f. physik. Chemie B14, 339 (1931).

time average of the moments of end groups which neutralise each other in the trans and are additive in the cis position, and $\mu = 2^{\frac{1}{2}}\mu_t$.

Now $\mu = 2.34 \times 10^{-18}$ and therefore $\mu_t = 1.66 \times 10^{-18}$. In our water model $\mu_t = 0.75\epsilon' = 1.75 \times 10^{-18}$. Thus the transverse moment derived from the model is 5 percent larger than that derived from the hydroquinone molecule. This difference of 5 percent is to be expected, as we have already assumed an increase of 5 percent, from 1.9 to 2.0×10^{-18} , in the direct moment, to allow for the effect of the polarising power of neighbouring water molecules.

We may therefore assume that the model of the water molecule is to a first approximation the correct one. It could be in fact derived purely from dipole moment measurements independently of spectroscopic data.

The mutual potential energy of two such molecules placed in such relations to each other as are found in ice (see Fig. 6) that is, with their centres 2.72×10^{-8} † apart and their effective OH directions making tetrahedral angles with each other, can be calculated by simple electrostatics. (In most cases these calculations were made graphically.) For the model chosen above this amounts to 0.533×10^{-12} ergs in the mean. Actually there are three possible positions in ice satisfying these requirements: they may be called cis, trans, and skew arrangements, differing only in the azimuthal angular position of the two water tetrahedra in respect to the line joining them. The respective mutual potential energies can be found to be $0.504, 0.527, 0.551 \times 10^{-12}$ ergs per molecule pair. In any ice structure these types must occur in the ratio 1 : 1 : 2 and the mean weighted in this way is 0.533×10^{-12} ergs per molecule pair. Every molecule has four neighbours, thus the potential energy per molecule is 1.066×10^{-12} ergs, each molecule counting only once. This is equivalent to -15.3 kcal./g molecule.

In this calculation three factors have been omitted.

(1) *The mutual potential energy of molecules not in contact.* This is not very considerable. The mutual potential energy of two dipoles falls off as the cube of the distance, and owing to the

† The value of 2.76Å at 0°C reduces by thermal contraction to 2.72Å at 0°Abs.

mutual orientation contains approximately equal numbers of + and - terms. We need only consider next neighbours. A rough calculation gives for the potential energy due to the 13 next neighbours of an ice molecule 0.154×10^{-12} ergs corresponding to +1.1 kcal./g.

(2) *The van der Waals attraction.* By London's theory¹⁷ the van der Waals attraction between two like molecules at distance r apart is given by the expression $(3/4)I\alpha^2r^{-6}$, where I is the ionisation potential and α the polarisability. Born¹⁸ considers this too small, and would multiply it by a factor 3/2. Accepting this correction, and inserting the experimental values of 13 volts for I , and 1.575×10^{-24} for α , we find for the van der Waals energy of a pair of water molecules -0.143×10^{-12} ergs or -4.1 kcal./g molecule of ice. This value is almost certainly too small, for it is very artificial to apply London's treatment to a molecule as unsymmetrical as water, but it must be of the right order.

(3) *The repulsive forces* are more difficult to calculate, but since they must contribute considerably to the total energy, a rough attempt will be made to arrive at an approximate value. It will be sufficiently accurate for the purpose to consider only neighbouring molecules. If the total potential is given as

$$V = -F(r) - C/r^6 + B/r^n,$$

we can arrive at B if n is known from the equilibrium condition

$$-F'(r_0) + \frac{6C}{r_0^7} = \frac{nB}{r_0^{n+1}}.$$

$F'(r)$ the electrostatic force between the molecules can be obtained graphically from the model. It is found to be 0.731×10^{-4} dynes per molecule pair. 0.316×10^{-4} dynes is the contribution of the van der Waals force, so that

$$\frac{nB}{r_0^{n+1}} = 1.047 \times 10^{-4} \text{ dynes.}$$

Now n cannot be very different from its value

¹⁷ London, Zeits. f. physik. Chemie B11, 222 (1930).

¹⁸ Born, Zeits. f. Physik 75, 1 (1932).

for the rare gases¹⁹ ≈ 12 we have therefore

$$B/r_0^n = 1.047 \times 2.72 \times 10^{-12} / 12 = 0.238 \times 10^{-12}$$

ergs per molecule pair. The contribution of the repulsive forces is therefore 0.475×10^{-12} ergs per molecule, or +6.8 kcal./g molecule.

Introducing these corrections we have the *a priori* theoretical value for the energy of sublimation of ice at 0°K of $15.3 - 1.1 + 4.1 - 6.8 = 11.5$ kcal./g molecule. To compare with this we have the experimental value 10.70 kcal./g molecule for the heat of evaporation of water at 273°K. To this must be added (1) Latent heat of ice, 1.44 kcal./g mol. (2) $\int_0^{273} C_p(\text{ice}) dT = 1.28$ kcal./g mol. (3) $-\int_0^{273} C_v(\text{water vapour}) dT = -1.61$ kcal./g mol. No account is taken of zero point energy or rotation in the solid. This gives an experimental value for the heat of sublimation of ice at 0°K of 11.81 compared with the theoretical 11.5 kcal./g mol. The closeness of the agreement is fortuitous as a change in the position of the effective molecular centre by as little as 0.05Å would change the theoretical energy by 2.5 kcal./g mol.; a small change in the repulsive index* would produce an even greater effect. Nevertheless, the agreement is sufficiently real to show without doubt that by far the greater part of the cohesion of ice and also, therefore, of water at low temperatures is due to the electrostatic interaction of tripolar molecules in relatively fixed tetrahedral configuration.

This calculation is made for a regular structure without heat motion and therefore refers strictly only to ice at absolute zero. The energy of water is naturally greater, partly due to molecular movement, and partly to the breakdown of the regular four coordinated structure which proceeds more and more rapidly at higher temperatures until the critical point is approached

¹⁹ Lennard Jones, Proc. Roy. Soc. A112, 214 (1926).

* If instead of the older form of the theory the repulsive term takes the form $ae^{-r/\rho}$ with $\rho = 0.34\text{Å}$ found from the alkali halides (Born and Meyer, Zeits. f. Physik 75, 1 (1932)) the repulsive term becomes about 10 kcal./g. This would lower the theoretical energy to 8 kcal. instead of 11.5. This value is certainly too low, but it is not certain that the same value ρ can be used for water as for the ionic salts with their much greater attractive terms. If, however, this should prove the correct value it would become necessary to find the correct van der Waals term which might easily redress the balance.

at which the condition of water cannot be essentially different from that of NH_3 or CH_4 at corresponding temperatures. The high values of the latent heat of fusion of ice and the specific heat of water can be accounted for by the gradual breakdown of the four coordinated structure. The breaking of one $\text{H}_2\text{O}-\text{H}_2\text{O}$ bond in eight would account for the latent heat of ice; to account for the specific heat of water, at 100°C one bond in four would be broken, at 250°C half the bonds. The sharpness of the ice-water transformation still remains to be explained. It is quite clear, however, that the melting of ice is not as that of the solid rare gases, the paraffins, or the close packed metals, a mere change from a regular to an irregular ordering of atoms or molecules without change of coordination. Such melting, with its small latent heat and positive volume change, might be called isomorphous melting. With ice, on the other hand, as with bismuth and many organic solids (salol, azoxyanisole) melting is equivalent to molecular disorder plus change of coordination—i.e., corresponding to a change of crystalline state, and might be called morphotropic. This type of melting involves a large latent heat, large volume change, usually negative; and the possibility of extensive overcooling, as the liquid does not correspond in inner structure to the solid that crystallises from it. The solid form of water II is probably ice II melting at -20° . But this can never be formed at ordinary pressures as here water II spontaneously transforms to the ice-like water I, even when, owing to absence of nuclei, ice does not crystallise out. It is possible on the assumptions used in this section to calculate the energy of the presumed solid water II. It is found to be 11.0 kcal./g mol. The difference between it and the theoretical value 11.5 kcal./g mol for ice I is chiefly due to the additional repulsion terms introduced by bringing next neighbours closer together. The instability of water II in the solid form is compensated in the liquid by the greater possibility of molecular rotation and interchange of neighbours at higher temperatures. It must be emphasized, however, that the calculations for the internal energy of water are altogether less reliable than those for ice and the agreement of the figures must be considered fortuitous. In particular the large latent

heat of fusion of ice cannot as yet be quantitatively accounted for.

Nevertheless the evidence from the thermal properties of water reinforces that derived by the study of the variation of the x-ray pattern of water with temperature, particularly the change from water II (quartz-like) to water III (ammonia-like).

§9. Properties of ionic solutions: Density of solution and ionic hydration

This investigation into the structure of water itself was undertaken in order to account for properties of ionic solutions, particularly those containing hydrogen and hydroxyl ions. We are now in a position to examine the molecular picture of ionic solution. As the internal field of water is controlled by the electrostatic field of the dipoles, the introduction of charged ions will obviously modify that field considerably. The effect will clearly be roughly proportional to the polarising power of the ion, i.e., its charge divided by its radius. Large monovalent ions will have the least effect, small highly charged ions the greatest. This corresponds to the long familiar hypothesis of the hydration of ions, introduced to account for the apparently anomalous fact that the mobilities of the large ions K^+ , Rb^+ , Cs^+ , Cl^- , Br^- and I^- are all approximately the same whereas small ions such as Li^+ or Mg^{++} move much more slowly. Several experimental methods have been used to find the degree of hydration of ions, but they give widely varying results, and are plainly theoretically unsatisfactory. Methods based on transport of water by ions in non-aqueous solvents are not really relevant, as then the water molecules are held not against the attraction of other water molecules but those of less polar molecules, and tend to give too high values. Those based on mobilities assume the validity of Stokes' law to extend much further than can be justified, and even then measure not so much the actual water molecules attached to a particular ion, as the mass of water carried hydrodynamically by the ion in its movements through the liquid, thus giving always much too high values.

The simplest and possibly the most accurate method of estimating the real degree of hydration

TABLE IV. *Additional volume of uni-univalent salts in dilute aqueous solution, cuA per ion pair.*

	OH ⁻	Difference F-OH	F ⁻	Difference Cl-F	Cl ⁻	Difference Br-Cl	Br ⁻	Difference I-Br	I ⁻
H ⁺					29.3	9.5	38.8	20.3?	59.1?
Difference Li-H					-0.8		-1.0		+2.7?
Li ⁺	-8.3				29.0	10.8	39.8	16.6	56.4
Difference Na-Li	-0.9				-0.9		-0.4		+0.2
Na ⁺	-9.2	+5.0	-4.2	32.3	28.1	10.3	38.4	18.2	56.6
Difference K-Na	+14.7		+17.6		+16.4		+17.1		+17.5
K ⁺	+5.5	+7.9	13.4	31.1	44.5	11.0	55.5	18.6	74.1
Difference Rb-K			+7.2		+8.0		+7.5		+7.7
Rb ⁺			20.6	31.9	52.5	10.5	63.0	18.8	81.8
Difference Cs-Rb					+11.9		+11.8		+11.2
Cs ⁺					64.4	10.4	74.8	18.2	93.0
NH ₄ ⁺			31.8	29.1	60.9	2.1	63	13.5	76.5

is the measurement of densities of ionic solutions. In sufficiently dilute solution the volume alteration per ion pair becomes constant. The value of this for certain salts is shown below (Table IV) calculated as additional volume in cubic A. It is at once apparent from the constancy of differences of rows and columns that the volume alteration is additive for ions. It is also apparent that the additional volume is roughly proportional to the ionic size. Assuming this and dividing the contribution of caesium chloride (for which the positive and negative ions have most nearly the same size) in proportion to their

ionic volumes in the solid, we derive the apparent ionic volumes in water as shown in Table V. With the values of 27.4 for Cs⁺ and 37 for Cl⁻, the apparent ionic volume of other ions can be found. If the distribution of volume between Cs⁺ and Cl⁻ has been incorrect, all the volumes for positive ions will be too large and for negative too small, or *vice versa*, but relative values for either will be correct. The table shows a normal relation between volume in solution and in the solid only for Rb⁺ and Cs⁺ among positive ions and for all negative ions except (OH)⁻ and F⁻. All other cases show apparent volumes either

TABLE V. *Apparent ionic volumes in dilute aqueous solution.*

Ion	Apparent vol. in solution obs.cuA per ion	Vol. in solution calculated from vol. in solid	Vol. of ion with nH ₂ O observed vol. (n)	Vol. of ion with nH ₂ O calculated from crystal data	Ion	Apparent vol. in solution	Ion	Apparent vol. in solution
H ⁺	- 8	0.0	+ 51 (2)	+ 39			(HS) ⁻	+ 40
Li ⁺	- 8	+ 3	+170 (6)	+150			(CN) ⁻	+ 41
Na ⁺	- 8.5	+ 6	+225 (8)	+180			(N ₃) ⁻	+ 52
K ⁺	+ 8	+15					(CNS) ⁻	+ 72
Rb ⁺	+15.5	+21					(NO ₃) ⁻	+ 38
Cs ⁺	+27	+28					(CO ₃) ⁻	+ 7†
NH ₄ ⁺	+12?	+18					(HCO ₃) ⁻	+ 45
Tl ⁺		+21					(ClO ₃) ⁻	+ 61
Be ⁺⁺	-42.4	+ 0.2	+ 77 (4)	+ 74	Mn ⁺⁺	-41	(BrO ₃) ⁻	+ 64
Mg ⁺⁺	-48	+ 3	+130 (6)	+150	Fe ⁺⁺	-39	(IO ₃) ⁻	+ 42
Ca ⁺⁺	-45	+ 7	+133 (6)	+180	Co ⁺⁺	-48	(SO ₃) ⁻	+ 28
Sr ⁺⁺	-44?	+13	+134 (6)	+230	Ni ⁺⁺	-66	(SO ₄) ⁻	+ 39
Ba ⁺⁺	-33	+18	+145 (6)	+270	Cu ⁺⁺	-50	(SeO ₄) ⁻	+ 46
Al ⁺⁺⁺	-87	+ 1.1	+ 91 (6)	+110	Zn ⁺⁺	-56	(H ₂ PO ₄) ⁻	+ 55
					Fe ⁺⁺⁺	-77	(MnO ₄) ⁻	+ 80
(OH) ⁻	- 2	+15	+ 28 (1)	+ 34	Cr ⁺⁺⁺	-93	(CrO ₄) ⁻	+ 45
F ⁻	+ 6	+15	+ 36 (1)	+ 34			(MoO ₄) ⁻	+ 59
Cl ⁻	+37	+37					(WO ₄) ⁻	+ 54
Br ⁻	+47.5	+47					(S ₂ O ₃) ⁻	+ 85
I ⁻	+66	+66					(Cr ₂ O ₇) ⁻	+139
							(SiO ₃) ⁻	+ 9†
							(VO ₃) ⁻	+ 53

Data from Landolt-Bornstein referred to 20°, most values rough.

† Low values due to (OH)⁻.

much smaller than in the solid or actually negative. The conclusion almost forces itself that in the first case the ions are not hydrated, and in the second they are to a greater or less degree. The open structure of water postulated above will obviously lead to a reduction in volume if it is disturbed by the permanent aggregation of several molecules around a single ion. If an ion is completely hydrated it will carry a number of water molecules around it, determined by Goldschmidt's coordination number. That is, the maximum hydration will be limited by the number of water molecules which can be packed in mutual contact around the ion. This depends only on the ionic radius. The theoretical coordination number of the different ions with water is shown in column 2 of the Table VI. This coordination number is, however, not only theoretical, but empirically observed as water of crystallisation in known crystal structures. These conclusions are reinforced by an examination of water of crystallisation. Water exists in crystals in three forms, (1) Structural water, water existing in holes, tubes or sheets in an otherwise rigid ionic structure, which can be driven off by heat without necessarily disrupting the structure, for example in the zeolites. (2) Ice, in polyhydrates such as $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ in which the ions are the dispersed phase. Such crystals are said to melt in their own water of crystallisation. (3) Coordinated water, in which the water molecules are grouped around particular ions. This is the only type that concerns us here. Taking only crystals of known structure into account we find the coordination numbers and only the coordination numbers shown in brackets in column 4, Table V. Assuming this coordination number we can calculate the apparent volume in solution occupied by the hydrated complex, by adding the values of column 1 to n times 29.7, the volume occupied by each natural water molecule. This is shown in column 4. We can compare this with the volume of the coordination spheres of the same ions as they occur in crystals. This volume is shown in column 5. The agreement is fairly good except for the large divalent ions Sr^{++} , Ba^{++} , when the approximation of a coordination sphere is only an extremely rough one which overestimates the volume actually

occupied. In general we may say that the examination of the specific gravity of solutions shows some ions to be completely hydrated and some unhydrated.

An attempt can be made to determine the degree of hydration theoretically starting from the model of water here developed. The hydration of an ion will occur when the potential energy of a water molecule forming part of the coordination shell round an ion is less than that of a molecule in free water. Now in free water, every molecule has four neighbours and a single molecule coordinated to an ion has three, the ion and two water molecules on the other side. This follows because the charge of the ion must be expected to attract the *two* H-nuclei or the *two* vacant places in the water molecule symmetrically and from the point of view of further coordination occupy them both. The condition for an ion having at least one coordinated water molecule is therefore that the potential energy for a water molecule due to the ion is less than that due to two other water molecules.*

The potential energy P of a water molecule due to an ion depends only on the ionic radius and the charge. The values calculated for univalent ions are shown in Fig. 12. Taking 15 kcal./g ion as the electrostatic potential energy due to two water molecules, we can show that for univalent ions of radius greater than 1.6Å no hydration is to be expected, while for all monatomic polyvalent ions, hydration will always occur. Where more than one water molecule is coordinated with an ion, a correction must be made for the mutual effect of these, which will always be in the direction of reducing the negative potential due to the ion and will be greater the larger the coordination number. The value of this correction can be calculated: it is given by $D_n[\mu^2/(r+r_w)^3]$ where D_n is a purely geometrical factor depending only on n the coordination number and tabulated below. μ is the dipole moment, r and r_w the radius of the ion and water molecule respectively.

* In the case of negative ions the considerations of §9a suggest that the coordinated water molecule may have three water neighbours; but for every negative ion except F^- and $(\text{OH})^-$ the potential energy of coordination is so small that there is no true hydration.

n	2	3	4	6	8	12
D_n	0.0625	0.334	0.573	1.188	1.99	3.89.

This term is only significant for monovalent ions. Introducing it we can calculate the extra energy

$$n\{P - D_n\mu^2/(r+r_w)^3 - 15\}$$

due to coordinating an ion with 2, 3, 4, 6, ... water molecules. It will be seen from Table VI that for Na^+ , K^+ , F^- this is a maxi-

TABLE VI. Extra energy, kcal./ion, derived from coordination of water molecules on ions allowing for the effect of mutual interactions of water molecules. These figures do not represent experimental hydration energies.

Ion	$n=1$	2	3	4	6
Li^+	15	28	39	46	49
Na^+	11	21	29	33	28
K^+	4.0	7.2	8.8	9.2	2.0
Rb^+	2.6	4.6	5.6	4.9	<0
F^-	4.1	7.4	9.0	9.7	3.0
$\text{Cs}^+\text{Cl}^-\text{Br}^-\text{I}^-$	<0	<0	<0	<0	<0

mum for $n=4$.* But 4 is the coordination number of water itself, therefore we may argue that the larger ions Rb^+ , Cs^+ , Cl^- , Br^- , I^- with small or negative coordinating energy are in fact also 4-coordinated, to judge from their negligible volume alterations on solution. Hence all monovalent ions are 4-coordinated in water solution. Further evidence for this is given below.

The difference between the permanently hydrated Li^+ , Na^+ (K^+ , F^-) ions and the others is not geometrical but physical, the smaller ions carry with them through the water their permanently attached hydration shell; the larger ions on moving exchange water neighbours.

For divalent, and *a fortiori* for polyvalent, simple ions the coordination number is always the highest sterically possible, which is 6 for all rare gas and most 18-shell ions, except for Sr^{++} , Ba^{++} which may be 8-coordinated. For these, however, owing to the greater effect of the water shell, there is very little gain of energy by changing from 6 to 8 coordination, and they seem generally to be found in the former state.

* Li^+ gives a maximum at $N=6$. But we have other reasons from crystallography and observed heats of solution to show that its coordination number is 4

9a. A calculation of the heat of hydration

When the potential energy of a molecule of water is lowered by being associated with an ion, this energy appears as an additional term in the heat of hydration of the ion.

If water were an ideal insulator of dielectric constant η and an ion a conductor of radius a and charge ze the energy of hydration would be given by

$$\frac{1}{2}[(\eta-1)/\eta](z^2e^2/a).$$

As Debye²⁰ has pointed out, this will only hold if the field near the ion is less than the saturation field of the dielectric and therefore not for any monatomic ion in water. The critical radius a inside which water no longer has true dielectric properties has been calculated by Debye to be 11A for monovalent, and 31, 57, and 88A for 2, 3, and 4 valent ions. The present theory of water suggests the definition of another critical radius a' as the radius where the polarisation reaches the maximum value possible while retaining a tetrahedral structure, that is $4\pi n\mu/(3)^{\frac{1}{2}}$ or 136×10^2 volts per cm. Inside this sphere the water molecules are orientated no longer by their mutual dipole attractions, but by the ion. It may in fact be called the coordination sphere of the ion. We would therefore expect the heat of hydration of an ion to be due to four terms.

(1) The energy of the coordination sphere proportional to the number of water molecules coordinated, and to the mutual energy of ion and molecule, with certain corrections to be mentioned below.

(2) The energy of the intermediate sphere.

(3) The energy of the main body of water outside the Debye sphere.

(4) The mutual energy of water molecules reoriented in the neighbourhood of the ion must plainly be subtracted from the expression for the hydration energy.

For ions of known charge and radius the energy of the first and third of these terms could be calculated. To calculate the second involves a knowledge of the polarisation of water in fields approaching saturation, which is not known experimentally and is difficult to calculate on the present theory. We can get round the difficulty, however, by virtually abolishing the

²⁰ Debye, reference 12, Chapter 6.

intermediate sphere and assuming a sphere of radius R_z of sharp discontinuity, inside which the energy is that of ionic coordination, while outside it is that of ordinary water. R_z must naturally lie between a and a' and be dependent only on the charge and not on the ionic size, but its actual value can only be derived empirically. Making these assumptions we may therefore write for the energy of hydration U_h of an ion the expression

$$U_h = \frac{\eta - 1}{2\eta} \frac{z^2 \epsilon^2}{R_z} + n P_{\text{eff}}(r) - u_w.$$

In this formula R_z is the radius of the virtual saturation sphere depending only on z , n the coordination number of the ion, $P_{\text{eff}}(r)$ the mutual potential energy of one ion and a water molecule in its sphere of hydration which depends on r and z , and u_w , the electrostatic energy of the water molecules disoriented, a small term which may be taken as before as 31 kcal./g ion, the electrostatic energy of 1 water molecule in water (see p. 530). To a first approximation the $P_{\text{eff}}(r)$ is proportional to the potential energy P of a water molecule due to a charge $z\epsilon$ at distance $r + r_w$ where r and r_w are the radii of the ion and water molecule respectively.

P can be calculated from the molecular model of water. Its value in terms of r is plotted in Fig. 12. The curves for $+$ and $-$ ions are prob-

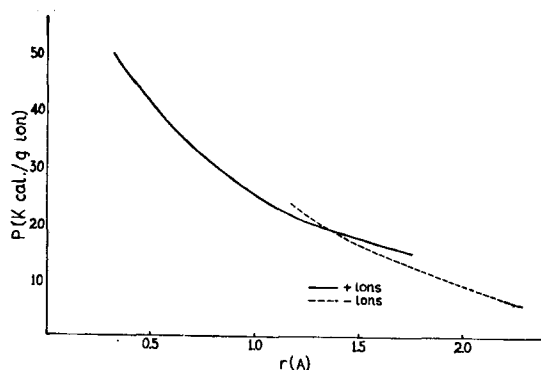


FIG. 12. Relation of ionic radius and mutual potential energy for water molecules and monovalent ions. For polyvalent ions, multiply P by z .

ably not the same, as the water molecules arrange themselves in these two cases as shown in Fig. 13, a, b. The reason is that the H^+ in the water molecule is a definite centre of positive charges,

while it is doubtful whether in the absence of another H^+ , the molecule should be regarded as having two definite centres of negative charges rather than a general negative charge on the side remote from the H^+ 's present. For most $+$ ions the value of P is sufficiently close to the simple dipole expression $\mu \epsilon z / (r + r_w)^2$.

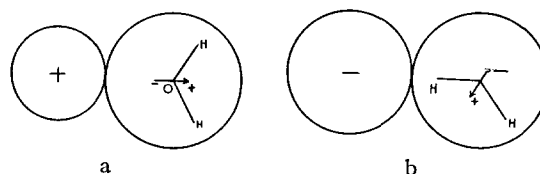


FIG. 13a, b. Orientation of water molecules with respect to positive and negative ions. \rightarrow , Water molecule dipole.

The complete expression for $P_{\text{eff}}(r)$ on the present theory is

$$P_{\text{eff}}(r) = P \left\{ 1 - F(r + r_w) + \frac{C}{(r + r_w)^4} + \frac{K \epsilon z}{(r + r_w)^2} - \frac{D_n \mu}{(r + r_w) \epsilon z} \right\}.$$

The correcting terms in the bracket are:

$F(r + r_w)$ to allow for the repulsion between ion and water molecule.

$C/(r + r_w)^4$ to allow for van der Waals attraction.

$K \epsilon z / (r + r_w)^2$ to allow for the change of dipole moment in the field round the ion ($K = d\mu/dE$).

$D_n \mu / (r + r_w) \epsilon z$ to allow for the mutual potential energy of the water molecules in the coordination sphere of the ion. D_n is the geometrical factor tabulated on p. 533.

Of these terms $F(r + r_w)$ is difficult to estimate, and the value of K is not known, so that no attempt will be made to calculate $P_{\text{eff}}(r)$ exactly.

However, a qualitative consideration of the terms in the bracket shows that they tend to compensate each other for different values of r . The ratio $P_{\text{eff}}(r)/P = p_z$ will not be very different from 1, and will be approximately constant for the same value of z , increasing with higher z owing to the predominance of the polarisation term $K \epsilon z / (r + r_w)^2$. The actual value of the ratio can best be determined empirically. For this we use

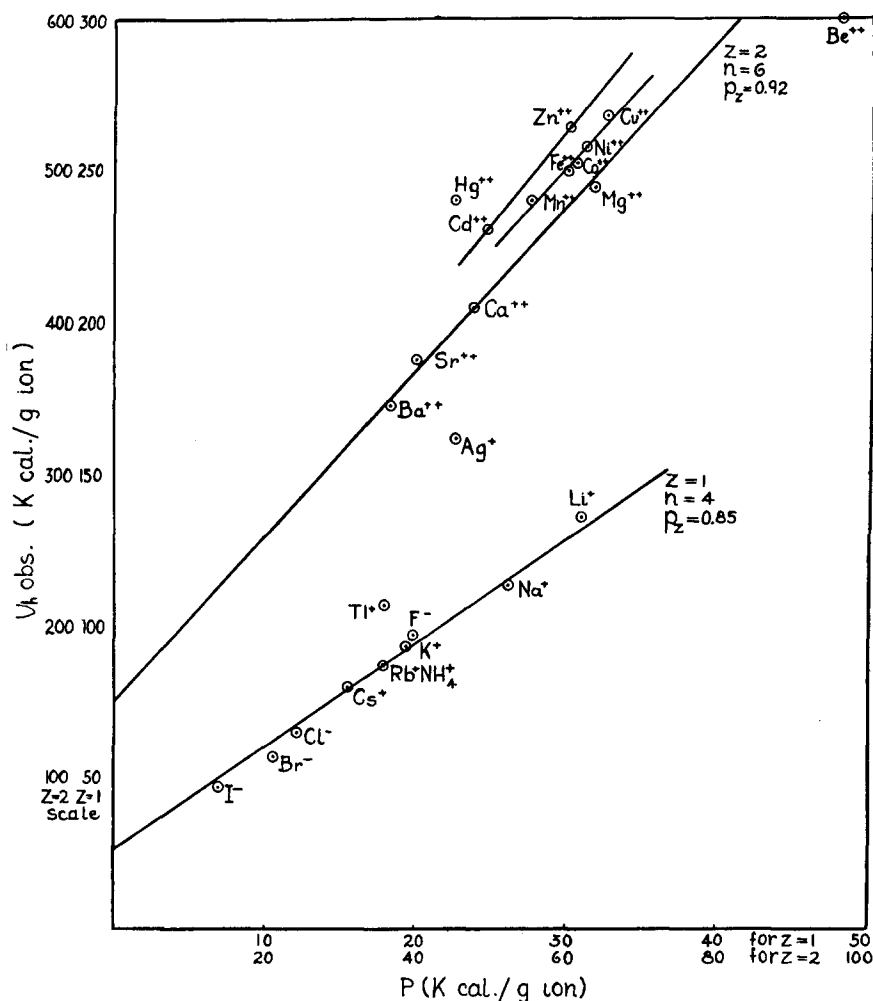


FIG. 14. Relation between heat of solution of ion U_h and mutual potential energy with water molecule P . Details for ions of charge 1 and 2. (Values for the latter are plotted $\frac{1}{2}$ scale.)

the simplified expression

$$U_h = \frac{\eta - 1}{2\eta} \frac{z^2 e^2}{R_z} + n p_z P(r) - u_w.$$

This on expressing V_h as a function of $P(r)$ is of the simple form

$$U_h = a + bP(r)$$

where a and b are functions of z only. If we attempt to check these theoretical considerations by comparison with experiment we are met at the outset by the difficulty that the absolute heats of the hydration of ions are not known, and cannot be directly measured. What can be observed is only the sum of heats of hydration of opposite signs, as when a salt is dissolved in

water. For example for a metallic halide M^+X^-

$$U_h(M) + U_h(X) = U_{MX \text{ cryst}} + U_s \\ = Q_{MX \text{ aq}} + D_X + S_M - E_X + I_M,$$

where V_{MX} is the lattice energy and V_s the heat of solution of the salt; $Q_{MX \text{ aq}}$ is the heat of formation of the aqueous salt at infinite dilution from $[M]$ cryst and X_2 gas; S_M the heat of sublimation and I_M the ionisation potential of the metal; D_X the heat of dissociation and E_X the electron affinity of the halogen. For monovalent salts the calculations of Meyer²¹ and Sherman²² have been extensively used. For others, calculations have been made from data in the Int. Crit. Tables. As in the problem of the

²¹ Meyer and Helmholtz, *Zeits. f. Physik* 75, 19 (1932).

²² J. Sherman, *Chem. Rev.* 11, 93 (1932).

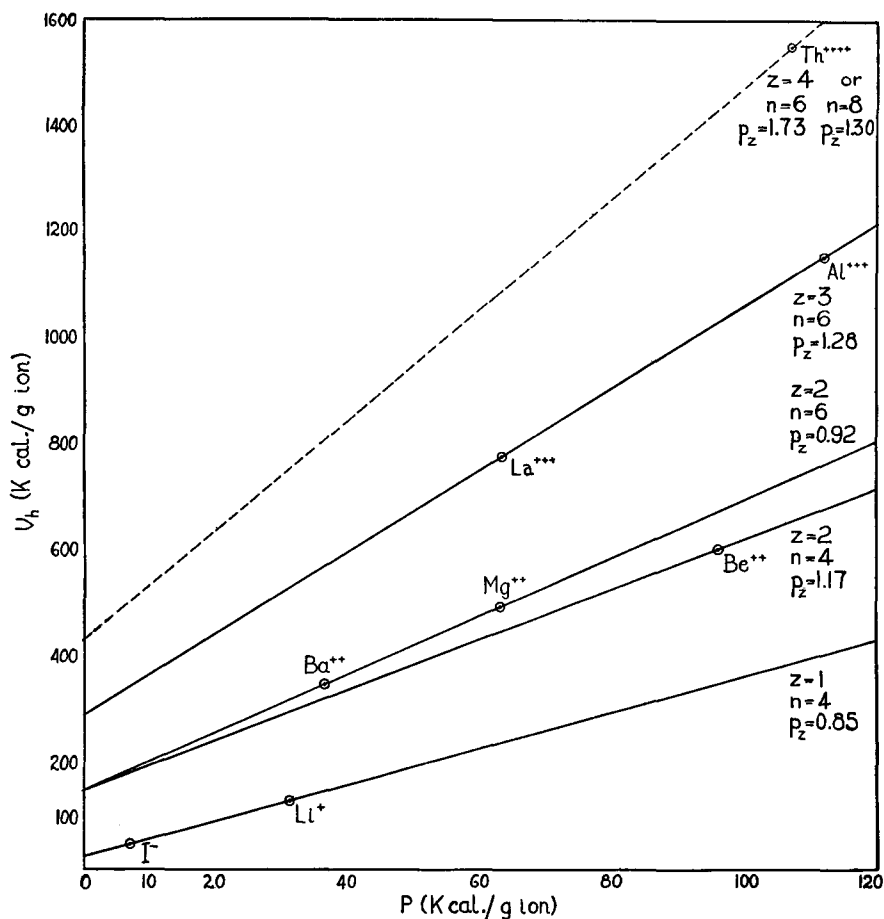


FIG. 14a. Relation between heat of solution of ion U_h and mutual potential energy with water molecule P . General scheme.

determination of ionic radii the knowledge of one absolute ionic heat of one ion will give that of all the others. Attempts to assign such values have been made by Fajans²³ and Webb.²⁴

Webb's treatment is much more thorough mathematically than that attempted here. However, being put forward before accurate values of atomic and molecular radii were known, it is essentially a theory treating water as a continuum of variable dielectric properties. It is interesting to note that by quite independent method he arrives at a value 82 for the heat of solution of K^+ instead of the 94 found here. If our arguments are granted this makes all his values for positive ions too low, and for negative ions too high.

Here we can proceed directly from our theory.

²³ Fajans, *Zeits. f. Elektrochemie* **34**, 502 (1928).
34, 546

²⁴ Webb, *J. Am. Chem. Soc.* **48**, 2589 (1926).

For ions of opposite sign but the same valency U_h can only depend on the radius r . Two ions of the same radius will have approximately the same heat of solution. Such a pair is furnished by K^+ and F^- with empirical radii 1.33Å for both. (Goldschmidt's empirical radii are used throughout as more directly applicable than those of Pauling or Zachariasen). The corresponding values of P are 17.5 and 18.0 kcal./g ion. The value $U_h(K^+) + U_h(F^-)$ is 191 kcal./g ion pair. We may therefore take $U_h(K^+)$ as 94 and $U_h(F^-)$ as 97. With these values U_h can be plotted against P . For any values of $U_h(K^+)$ or $U_h(F^-)$ the points for + and - ions lie on parallel straight lines. The above values were chosen to make all the points fall as near as possible to one line. Fig. 14. Any error must be small, and affect ions of the same charge by a constant term. The experimental results shown in Figs. 14 and 14a amply confirm the theory

sketched above. For all rare gas ions of the same charge, the points lie on one straight line whose slope gives $n\bar{p}_z$ and whose intersection with the axis of U_h gives

$$\frac{\eta - 1}{2\eta} \frac{\epsilon^2 z^2}{R_z} - u_w.$$

The values of n , R_z , and \bar{p}_z are given in Table VII, and using these values the observed and

TABLE VII. Constants in equation for heats of solution of ions. R_z and a are given in Angstroms.

z	1	2	3	4
n	4	4	6	6
\bar{p}_z	0.85	1.17	0.92	1.28
R_z	2.9	3.6	4.6	(5.7)
a	11	31	57	88

$u_w = 31$ kcal./g ion.

calculated values for U_h are given for all rare gas ions in Table VIII. The agreement is inside the experimental error in most cases. The greatest sources of error for the experimental values are in the heats of vaporisation of the metal, and in some cases in the ionisation potentials. For Be^{2+} , La^{3+} , Th^{4+} , the heat of vaporisation has been estimated from the melting point, while for Fe^{3+} and Th^{4+} the ionisation energy has been guessed at by analogy from similar atoms. No reliance must therefore be placed on the data for 3^+ and 4^+ ions which are only put in to show how they conform to the general scheme.

The only apparent exception to the linear law for ions of the same valency is for Be^{2+} . This may be due to incorrect heat of vaporisation, but more probably to the fact that Be^{2+} is 4-coordinated and is the only representative of such a divalent ion.

As might be expected the 18 electron shell and the paramagnetic ions do not conform to the simple laws for rare gas ions, but have consistently higher heats of hydration. This is in perfect accordance with Goldschmid's views that such ions exert an extra polarising effect due to electronic interaction for which opportunity is provided by low lying excited states.

It is extremely interesting to note that, as far as can be seen, the points for Mn^{++} , Fe^{++} ,

TABLE VIII. Heats of solution of ions in kcal./g ion.

Ion	Ionisation energy	U_h obs.	U_h calculated
H^+	313	276	
Li^+	124	136	131
Na^+	118	114	116
K^+	99.6	94	92
Rb^+	95.9	87	87
Cs^+	89.4	80	79
NH_4^+		87	87
OH_3^+			130
OH^-			105
F^-	98.5†	97	94
Cl^-	92.5†	65	67
Br^-	87.1†	57	63
I^-	79.2†	47	49
Be^{++}	633	608	≈ 600
Mg^{++}	521	490	495
Ca^{++}	413	410	410
Sr^{++}	384	376	370
Ba^{++}	349	346	350
Al^{+++}	1220	1149	1149*
Sc^{+++}	1020		980
V^{+++}	910		830
La^{+++}	833	768	768*
Th^{++++}	≈ 1600	≈ 1540	1540*
Ag^+	174	162	
Tl^+	140	107	
Mn^{++}	534	479	
Fe^{++}	561	500	
Co^{++}	580	504	
Ni^{++}	594	516	
Cu^{++}	645	536	
Zn^{++}	626	528	
Cd^{++}	596	462	
Hg^{++}	672	480	
Fe^{+++}	≈ 1346	1185	
In^{+++}	1210	980	

* Used to determine \bar{p}_z and R_z .

† Electron affinity.

|| Energy required to remove in succession the proper number of electrons.

Co^{++} , Ni^{++} , Cu^{++} and Zn^{++} , Cd^{++} (but not Hg^{++} which is probably not fully ionised) lie on two lines nearly parallel to the rare gas ion line, and can be made to fit the general formula by the addition of a constant term to P of $P_{\text{mag}} = 4$ kcal./g ion for the first group and $P_{18} = 8$ kcal./g ion for the second.

If more data were available on heats of formation and solution, a number of further regularities might appear, particularly for the ions of the rare earths.

A more general and fairly obvious implication emerges from a consideration of the heats of hydration of ions. The heat of hydration is never much less than the ionisation potential of the ion. Physically this means that the function of the ionising medium is simply to return to the ion its missing electrons. This is primarily

effected by the coordination shell, which for all polyvalent ions contributes the greatest part of the energy of hydration. We now can see the reason for the persistence of liquids and solids of such ion hydrates as $\text{Be}(\text{OH}_2)_4^{++}$, $\text{Al}(\text{OH}_2)_6^{+++}$ which have as much right to be considered as complex ions as PtCl_4^{--} or $\text{Fe}(\text{CN})_6^{4-}$.

§10. The effect of dissolved ions on the structure of water

The effect of the hydration of ions on the properties of the water in which they are dissolved is well shown by the work of Fajans' on the refractivity of ionic solutions. He finds that the effect on refractivity is an additive one for ions, but that while some ions give refractivities in solution similar to those expected for the free ion or in the solid crystal, others—precisely those which we have seen to be hydrated, such as Li^+ , Ca^{++} , Al^{+++} —show negative values only explicable by the lowering of the refractive index of the solvent water by the coordination of water molecules round these ions.

The simplest way of considering the effect of ions on solvent water is in relation to the degree of disorder of the molecules. This is brought out by the observations of x-ray diffraction⁵ and Raman spectra²⁵ of solutions. In both cases the addition of ions such as Li^+ or H^+ produces sharpening of lines and intensity shifts corresponding to more regular arrangement—i.e., one further back in the series:—Water I→II→III. The observations are not numerous or reliable enough for quantitative treatment, but the indications are overwhelming that small ions increase the regularity of the water arrangement.

This effect is shown in another way by the viscosity of ionic solutions. The viscosity of a solution is a complex effect but its nature is well brought out by the viscosity concentration curve of CsCl, Fig. 15. For dilute solutions at low temperatures there is first a decrease of viscosity with increasing concentration which afterwards changes to an increase. At higher temperatures no such decrease is observed and it is entirely lacking at all temperatures for salts of small ions such as LiCl or CaCl_2 . Three factors may

be thought of as contributing to the viscosity of ionic solution.

(a) The ions considered as independent massive particles carry momentum from one part of the liquid to another by their Brownian movement. This term will be proportional to the concentration, as the mean free path is independent of concentration, and probably to some small power of the temperature as in the case of gases.

(b) The ions, however, are not strictly independent and the lattice formed by them on the Debye-Hückel theory will present a certain

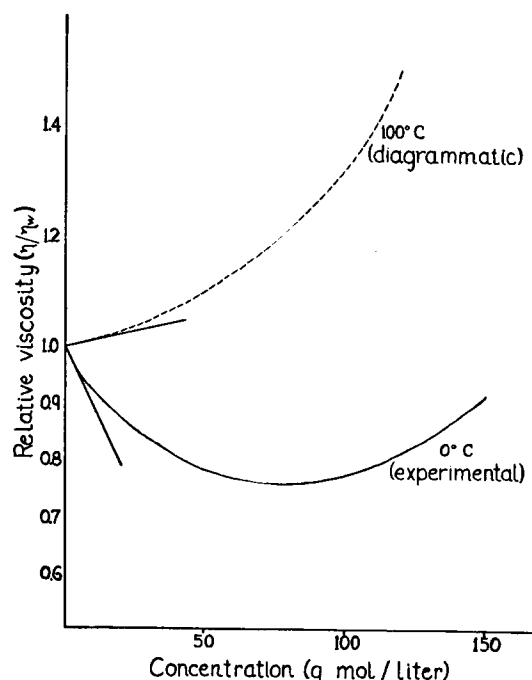


FIG. 15. Viscosity of CsCl solutions.

resistance to shear which will appear as viscosity. This effect might be expected to increase with some high power of the concentration but to decrease exponentially with the temperature.

(c) The ions affect the water molecules in their neighbourhood, loosening or tightening the structure as already explained. A looser structure due to unhydrated ions will give rise to lower viscosity than pure water; a tighter structure, due to hydrated ions, a higher viscosity.

This term might be expected to depend linearly on the concentration, for low concentrations,

²⁵ Ganesan and Venkateswaran, *Ind. J. Phys.* **4**, 195 (1929).

and to be largely independent of the temperature.

The viscosity of an ionic solution of the salt AX might therefore be written (this η will not be confused with the former)

$$\eta(AX, C, T) = \eta(\text{aq}, T) - f_{(a)}(M_A, M_X)CT^3 - f_{(b)}(C, z)e^{-\alpha/T} - f_{(c)}(r_A, r_X, z)C.$$

Here

$\eta(AX, C, T)$ is the viscosity of a solution of AX of concentration C and temperature T ;

$\eta(\text{aq}, T)$ that of water at the same temperature;

$f_{(a)}(M_A, M_X)$ is the Brownian coefficient depending essentially on the masses of the ions and always positive;

$f_{(b)}(C, z)$ is the Debye-Hückel function depending on the charge of the ions and concentration, also always positive;

$f_{(c)}(r_A, r_X, z)$ is the "structural temperature" function depending on the ionic radii and the charge of the ions and able to have positive or negative values.

For low temperatures and low concentrations $f_{(c)}$ will be the principal term; for high concentrations, $f_{(b)}$; and for high temperatures, $f_{(a)}$. This qualitative hypothesis fully accounts for the shape of the CsCl curves. As far as $f_{(c)}$ is concerned the addition of a hydrated or non-hydrated ion is equivalent to that of a fall or rise of temperature. Following up this idea we arrive at the concept of the *structural temperature* of an ionic solution defined as that temperature at which pure water would have effectively the same inner structure, and therefore the same viscosity (x-ray diffraction, Raman spectrum, etc.). Naturally this can only apply to dilute solutions of strong electrolytes where the interaction of the ions and the momentum carried by their Brownian motion can be neglected. Both these factors tend to increase the viscosity at higher concentrations while the latter is the predominating effect at higher temperatures.

The change in the structural temperature of the solvent is seen most directly by the effects of ionic solutions on the temperature of the maximum density of water. The effect is always a lowering of the temperature of maximum density, that is, a raising of the structural

temperature, but it is much smaller for the chlorides with small ions H^+ , Li^+ , Mg^{++} , than for those with large ions, and it is clear that here the increase is due to the Cl^- ions, while the positive ions either do not contribute or actually lower the structural temperature. Of course the change in the temperature of maximum density cannot be quantitatively identified with the change in structural temperature, but it is satisfactory to observe that both vary in the same sense.

This conception of structural temperature may prove to be important in many physico-chemical fields, particularly where colloids are involved, as well as in many problems of bio-chemistry. It serves at once to show the reason for the antagonistic action of ions such as Ca^{++} and K^+ , the first lowering, the second raising the structural temperature. It is not, however, claimed to have a precise physical significance. It is only to a first rough approximation that the effect of adding an ion to a solution is that of a change in temperature. The real effect is not uniform, but gradually fades away at a distance from the ion, and it requires a much more rigorous theoretical treatment than that based on the crude model of the water molecule used above.

§11. Introducing ionic mobilities again

The theory of ionic solution sketched above, though rendering many of our concepts more precise, does not add anything substantially new to the solution of the problem of ionic mobility. It must be possible, starting from a calculated hydration energy, or better still, from the observed heats of solution, to build up a hydrodynamical theory of the motion of an ion at infinite dilution. Such a theory would make precise the obvious qualitative relation between large hydration energy and small ionic mobility, but no attempt is made to derive it in this paper, for it would not help to solve our original problem.

What has emerged from the study of the molecular structure of water and ionic solution is that it offers no hope of a trivial explanation of the large mobilities of the H^+ and $(\text{OH})^-$ ions. If we treat H^+ and $(\text{OH})^-$ empirically as the other ions, the densities of their solutions indicate that they are hydrated (see Tables

IV and V). On the basis of this hydration low mobilities approximating to that of the Li^+ ion would be attributed to them. But other properties, particularly viscosities, show that H^+ and $(\text{OH})^-$ do not behave normally. The effect of H^+ and $(\text{OH})^-$ ions on the structural temperature is very large and negative. This shows that another mechanism than simple hydration must be involved, a mechanism that allows H^+ and $(\text{OH})^-$ ions to move rapidly through the solution, and at the same time to impart to it a greater coherence. The second part of this paper is an attempt to describe such a mechanism, and so to explain the observed abnormal mobilities. We believe that the explanation presented is the only one possible, and further possible if, and only if the structure of water is substantially that described in Part I.

PART II. A QUANTUM MECHANICAL THEORY OF THE EXTRA MOBILITY OF H^+ AND $(\text{OH})^-$ IN WATER

§12. More exact statement of the problem

After the discussions of Part I it is impossible to accept the view that hydrogen positive ions are present in aqueous solution as naked protons. They must be firmly attached to at least one water molecule and the whole discussion may proceed on the assumption that the hydrogen positive ion is present in solution in the form $(\text{OH}_3)^+$, the oxonium ion, which like $(\text{OH})^-$ and all other small ions will be more or less hydrated. The extra proton in $(\text{OH}_3)^+$ is no doubt accommodated at or near one of the two vacant tetrahedral positions among the electron orbits, the whole structure being very similar to the ammonia molecule NH_3 .

Accepting this point of view which very simple considerations of energy are alone enough to demand, the exceptional mobility of this ion becomes all the more striking. If its mechanism of transport through the solution were the same as that of other ions, *which necessarily involve bodily transport of the identical ions to or towards the proper electrode*, it is impossible that its mobility should differ much from that of the ammonium ion $(\text{NH}_4)^+$ which it so closely resembles in electronic structure. But the observed mobility of $(\text{OH}_3)^+$ exceeds that of

$(\text{NH}_4)^+$ by a factor of five. We conclude as above that a special mechanism must be acting both for $(\text{OH}_3)^+$ and $(\text{OH})^-$, the ions of water in water, which is entirely distinct from bodily transport and this view which we shall develop leaves unaffected older views of the transport of any foreign ion through any solution. Whether an extra mobility is to be expected for the ions of any other solvent in that solvent is a matter for later examination. We shall see that special conditions must be satisfied, so that extra mobilities are likely to be uncommon, and in any case confined to ions in which the effective charge is derived from an extra or a missing proton.

An interesting confirmation of our view is provided by the mobility of $(\text{OH}_3)^+$ in hydrofluoric acid. Pure dry hydrofluoric acid does not conduct. Water present as an impurity acts as an electrolyte causing the formation of $(\text{OH}_3)^+$ and F^- ions, more or less solvated of course. But $(\text{OH}_3)^+$ in liquid HF has a perfectly normal mobility.

We try here to describe the actual mechanism and its relation to the structure of water and think we have succeeded in a qualitative way. The fundamental idea which must be introduced is quantum mechanical. Having recognised the presence of $(\text{OH}_3)^+$ structures in the solution, quantum mechanics at once tells us that an $(\text{OH}_3)^+$ ion in sufficiently close contact with a water molecule OH_2 need not retain its extra proton but can transfer it to the other molecule. The proton jumps to and fro from one to the other when the configuration of the two molecules is favourable, and we show that this leads to a large extra drift down the field.

In formulating this problem we do not claim to have done more than restate ideas which must nowadays be commonplaces to every student of chemical physics. Similarly, in proposing our solution of the problem in its quantum mechanical dress we do not claim to have done more than attempt to render more precise ideas freely current in a vague form. Indeed, these ideas are of venerable antiquity for we really do little more than resuscitate in modern dress the idea of Grottius' chains. More recently Hückel²⁶ in work of which we were igno-

²⁶ Hückel, *Zeits. f. Elektrochemie* **34**, 546 (1928).

rant when we began this investigation has put forward the same idea of proton jumps. He has, however, not attempted to calculate the frequency of these jumps and has developed the discussion in such a way that it overlaps very slightly with ours. On the quantitative side one cannot claim to get very far—a quantitative explanation perhaps is hardly yet possible if any account is to be taken of the probable structure of water itself. But our discussion, equally with Hückel's, allows the conclusion that orders of magnitude are correct and that proton jumping is the essence of the extra mobility. Such other exceptional mobilities as are known appear to admit the same general explanation.

§13. The mechanism of transport of $(\text{OH}_3)^+$ and $(\text{OH})^-$

We have already stated that according to quantum mechanics an $(\text{OH}_3)^+$ ion in sufficiently close contact with a water molecule suitably orientated need not retain its extra proton. The reason is of course that there is another possible configuration of equal energy in which the extra proton has changed molecules. Further we may suppose that the three protons in $(\text{OH}_3)^+$ are in equivalent states, or if not, that there is an exchange degeneracy between them so that any one of the three is capable, at least in turn, of functioning as the detachable proton. If the two systems are at all far apart, or in an unsuitable relative orientation, there will be a considerable hill for the proton to jump through by the tunnel effect, and such transitions will be very rare. The great mass of the proton makes it entirely unable to penetrate barriers freely penetrable by electrons. But when the two systems are in close contact as neighbours in the water, and if they are so orientated that one of the protons (or the detachable proton) of $(\text{OH}_3)^+$ is nearly opposite some position in OH_2 into which it must move when it changes partners, the distortion of the electron orbits may well be such that only a small barrier hill survives, or the barrier may have almost totally disappeared, so that in either case the proton moves fairly freely from one system to the other during the period of this intimate contact.

In the absence of any external field we may conclude from the symmetry that, when the

favourable conjunction is broken, the extra proton will be equally likely to be found on either of the original systems. Such exchange will lead to random migrations of the free protons and therefore of the apparent $(\text{OH}_3)^+$ systems through the solution, giving no net transport. On this view it is of course not the same proton, still less the same $(\text{OH}_3)^+$ system, that wanders about. But if there is an applied external field F , then the probability of the proton being found on separation attached to one or other of the two OH_2 systems will be slightly altered by an amount proportional to F (since the effect is a small one), that OH_2 system which lies in the region of lower potential energy for the proton being preferred. We will prove this rigorously for a simple model in §14. There will then be a steady drift of the apparent $(\text{OH}_3)^+$ ions down the potential gradient at a rate proportional to F , which exactly constitutes their observed extra mobility.

A very similar mechanism must hold for $(\text{OH})^-$. In a favourable conjunction of $(\text{OH})^-$ and another OH_2 , a proton can pass from OH_2 to the $(\text{OH})^-$ and the systems can separate again with the ion and neutral system interchanged. But it is clear that the two H's in OH_2 will lie slightly deeper in the electronic system than the three H's in $(\text{OH}_3)^+$ and have therefore somewhat less chance of making the exchange. Hence the smaller mobility.

It does not seem possible to prove *a priori* that these proton transitions *must* occur with the great rapidity demanded by the theory when the favourable configurations present themselves, but only that conditions may be such that they *can*. But we believe that we can argue backwards and assert first of all that the proposed mechanism of transfers certainly is *operative*—secondly that there is no other mechanism except bodily transport of the $(\text{OH}_3)^+$ complex through the medium which can convey appreciable mobility on the apparent oxonium ions and such bodily transport is known to be too slow. We may conclude therefore that the observed mobilities establish the sufficient rapidity of the transfers.

§14. Approximate calculations

The form of the necessary approximate calculations for proton transitions from an $(\text{OH}_3)^+$

to an OH₂ neighbour was given some years ago by McCrea²⁷ in a tentative theory of electronic conduction. His work can be taken over with very slight changes, and represents physically just the right type of calculation for the process under discussion.

Two water molecules in a suitable configuration present two possible adjacent homes for the proton. Let the wave equation for the proton in one of these locations when isolated be

$$\nabla^2 \chi + \kappa^2 \{E - U(r_1)\} \chi = 0 \quad (\kappa^2 = 8\pi^2 m_H / h^2) \quad (7)$$

with the normalized solution $\chi = f(r_1) = \psi$, $E = E_0$ for the state of lowest energy. We shall ignore the effect of excited states, a neglect which can be justified *a posteriori*. When two locations are available on neighbouring molecules we shall take the wave equation to be given to a sufficient approximation by

$$\nabla^2 \chi + \kappa^2 \{E - U(r_1) - U(r_2)\} \chi = 0. \quad (8)$$

with two solutions (to a zero order approximation)

$$\chi = f(r_1) = \psi; \quad \chi = f(r_2) = \varphi, \quad (E = E_0).$$

Solution ψ means that the proton is on molecule 1, solution φ on molecule 2. By familiar arguments the two lowest stationary states of this system are specified approximately by the wave functions

$$\chi_{\pm} = (\psi \pm \varphi) / q_{\pm}, \quad E = E_0 + \epsilon_{\pm} \quad (9)$$

where

$$q_{\pm} = \int \{2(1 \pm (\varphi\psi))\}^{\frac{1}{2}}, \quad (10)$$

$$\epsilon_{\pm} = (\bar{U} \pm U\ddagger) / (1 \pm (\varphi\psi)),$$

$$(\varphi\psi) = \int \varphi\psi d\tau, \quad \bar{U} = \int U(r_2)\psi^2 d\tau, \quad (11)$$

$$U\ddagger = \int U(r_2)\varphi\psi d\tau.$$

$\int \dots d\tau$ denotes integration over the whole configuration space of the proton. From the symmetry of these functions the proton in either stationary state is equally likely to be in either location.

²⁷ McCrea, Proc. Camb. Phil. Soc. **24**, 438 (1928).

Now let an electromotive force F act on the proton in the direction of x increasing, a direction which we shall for the present identify with the direction from the ψ -location to the φ -location. We take the origin of x midway between the two locations and can then represent the perturbing potential energy for the proton by $-\epsilon Fx$. This perturbation may be assumed to be small compared with the perturbation due to the interaction of the two locations, and so may be applied as a new perturbation to the two states detailed in (9)–(11); but the interaction perturbation is itself so small that in calculating the new perturbation only these two close states need be taken into consideration. The perturbed wave equation is then

$$\nabla^2 \chi + \kappa^2 \{E - U(r_1) - U(r_2) + \epsilon Fx\} \chi = 0, \quad (12)$$

and the perturbed solutions

$$\left. \begin{aligned} \chi_+^* &= \chi_+ - \zeta \chi_- & (E = E_0 + \epsilon_+) \\ \chi_-^* &= \chi_- + \zeta \chi_+ & (E = E_0 + \epsilon_-) \end{aligned} \right\}, \quad (13)$$

where

$$\zeta = \epsilon F \int x \chi_+ \chi_- d\tau / (\epsilon_- - \epsilon_+). \quad (14)$$

There is no first order change in the energies. We can go further in evaluating ζ , because

$$\int x \chi_+ \chi_- d\tau = \int x (\psi^2 - \varphi^2) d\tau / q_+ q_-.$$

From the assumed symmetry of the field $U(r)$ and therefore of the wave function ψ (or φ) of the fundamental mode it follows that

$$\int x \psi^2 d\tau = -\frac{1}{2}R, \quad \int x \varphi^2 d\tau = \frac{1}{2}R,$$

if R is the distance apart of the centres of the two locations. Thus

$$\zeta = \epsilon FR / q_+ q_- (\epsilon_- - \epsilon_+). \quad (15)$$

The general wave function for the perturbed system with time factors is therefore

$$\chi = \alpha (\chi_+ - \zeta \chi_-) e^{-2\pi i (E_0 + \epsilon_+) t / h} + \beta (\chi_- + \zeta \chi_+) e^{-2\pi i (E_0 + \epsilon_-) t / h}, \quad (16)$$

where α and β are constants. This represents the progress of the system in time. If we chose α and β so that $\chi = \psi$ for $t = 0$, representing the

proton initially in the ψ -location, then (16) shows how it leaks over into the φ -location, and how it is on the average distributed between the two. One can use either method. We shall calculate the average distribution starting with the proton on ψ (or φ) and deduce from this the average probability of a transition from $\psi \rightarrow \varphi$ (or $\varphi \rightarrow \psi$) being found on separation, which will be sufficiently accurate provided the state may be assumed to last long enough—that is for a time comparable to a half oscillation of (16).

For this purpose we express (16) in terms of ψ and φ and calculate $|\chi|^2$, the time average of $|\chi|^2$, which is given by

$$|\chi|^2 = \alpha^2 \left\{ \psi \left(\frac{1}{q_+} - \frac{\zeta}{q_-} \right) + \varphi \left(\frac{1}{q_+} + \frac{\zeta}{q_-} \right) \right\}^2 + \beta^2 \left\{ \psi \left(\frac{1}{q_-} + \frac{\zeta}{q_+} \right) + \varphi \left(\frac{1}{q_-} - \frac{\zeta}{q_+} \right) \right\}^2. \quad (17)$$

Only terms to the first order in ζ need be retained. In order that χ may reduce to ψ at $t=0$ we must have

$$\alpha = \frac{1}{2}(q_+ - \zeta q_-), \quad \beta = \frac{1}{2}(q_- + \zeta q_+).$$

With these values of α and β

$$|\chi|^2 = \frac{1}{2}\psi^2 + \frac{1}{2}\varphi^2(1 + 2\zeta(q_+^2 - q_-^2)/q_+q_-) - \varphi\psi\zeta(q_+^2 + q_-^2)/q_+q_-. \quad (18)$$

The $\varphi\psi$ term is symmetrical and represents an equal probability ϑ for the proton being in either location. Thus there is a probability $\frac{1}{2} - \vartheta$ that it will be found on ψ and $\frac{1}{2} - \vartheta + \zeta(q_+^2 - q_-^2)/q_+q_-$ that it will be found on φ . These probabilities add up to 1 so that

$$\vartheta = \frac{1}{2}\zeta(q_+^2 - q_-^2)/q_+q_-,$$

which can be checked by direct calculation. Thus there are probabilities for the proton being left behind of

$$\begin{aligned} \frac{1}{2}(1 - \zeta(q_+^2 - q_-^2)/q_+q_-) & \text{ on } \psi, \\ \frac{1}{2}(1 + \zeta(q_+^2 - q_-^2)/q_+q_-) & \text{ on } \varphi. \end{aligned}$$

There is therefore a probability

$$\frac{1}{2}(1 + \zeta(q_+^2 - q_-^2)/q_+q_-) \quad (19)$$

that the proton will be found, when the configuration is broken up, to have made a jump

down the applied field when it starts on the up field molecule. Similarly when it starts on the down field molecule there is a probability

$$\frac{1}{2}(1 - \zeta(q_+^2 - q_-^2)/q_+q_-) \quad (20)$$

that it will be found to have jumped up field.

Any such jump effectively moves the oxonium ion through a distance Δ , where Δ is the average distance apart of the H_2O neighbouring molecules in water.* In a large number N of such events, half will start with the proton up field and half with it down field. The oxonium ion will have effectively moved *down field* through the water after these N events a distance D given by

$$\begin{aligned} D &= \frac{1}{2}N\frac{1}{2}(1 + \zeta(q_+^2 - q_-^2)/q_+q_-)\Delta \\ &\quad - \frac{1}{2}N\frac{1}{2}(1 - \zeta(q_+^2 - q_-^2)/q_+q_-)\Delta, \\ &= \frac{1}{2}N\Delta\zeta(q_+^2 - q_-^2)/q_+q_-. \end{aligned} \quad (21)$$

Written out in full, neglecting $(\varphi\psi)^2$ compared with 1, this becomes

$$D = \frac{N\Delta}{4} \frac{\epsilon FR \int \varphi\psi d\tau}{-\int \varphi\psi U d\tau + (\int \varphi\psi d\tau) \int U(r_2)\psi^2 d\tau}. \quad (22)$$

This formula can be used to give us the rate of movement of the effective hydrogen ion through the water in cm/sec. under unit potential gradient, which is equivalent to its mobility.

§15. Numerical values

The value of the velocity of migration for the effective hydrogen ion under a potential gradient of F^* volts/cm is given as $32.5 \times 10^{-4} F^*$ cm/sec.²⁸ The value for the hydroxyl ion is $17.8 \times 10^{-4} F^*$. The value for the ammonium ion is the same as for the potassium ion, namely $6.7 \times 10^{-4} F^*$. Both the oxonium and hydroxyl ions must be expected to have an ordinary velocity of this order $6.7 \times 10^{-4} F^*$ due to bodily transport through the fluid in the usual manner. They have

* It is necessary to recognize that by this simple jump the effective *charge* has not moved a distance Δ but of course only R ; the movement Δ is as it were only consolidated if thermal agitation comes in and rearranges the dipole groupings sufficiently often. As has been pointed out to us by Frenkel in discussion, this thermal reorientation must be an integral part of the full description of the phenomenon which so far we have omitted for simplicity. We comment further on this aspect of a more exact theory at the end of §18.

²⁸ Lewis, *System of Physical Chemistry*, I, 212 (1918).

therefore an extra velocity due to the interaction mechanism of

$$(\text{OH}_3)^+; 25.8 \times 10^{-4} F^* \text{ cm/sec.}$$

$$(\text{OH})^-; 11.1 \times 10^{-4} F^* \text{ cm/sec.}$$

The exact numerical values are not of importance. They refer to 291°K. It remains to be examined whether (22) can give comparable values when adjusted to correspond to the conditions in the solution.

(i) *Value of Δ .* Δ represents the average distance apart of the H_2O molecules in water when they are capable of interacting in this manner, one of them carrying the extra proton. For this distance we should probably take the average distance apart of the coordinated neighbours of Part I, 2.8×10^{-8} cm.

(ii) *Value of F .* The effective value of F must presumably allow for the dielectric constant of water! In building up a theory of bodily transport for ordinary ions in water it is certainly only the electric force which is effective. The motion of the ion can be regarded as taking place in a needle shaped cavity cleared of polarizable material, and in such a cavity the effective force is the electric intensity corresponding to the volts/cm applied between the electrodes. But in discussing the transitions of §14 in which the ionic system as a whole does not move, it is clear that the effective force biasing the jumps, a bias which is of the nature of a polarisation effect, must by Lorentz's argument be taken to be the force at the centre of a spherical cavity round the system, for the symmetry of the distribution round the immobile system maintains the usual zero contribution from the matter inside the sphere. It follows easily from this that the effective value of F in (16) must be taken to be

$$\frac{1}{3}(\eta+2)F^*/300,$$

where F^* is given in volts/cm between the electrodes, η being the dielectric constant of water. The factor $1/300$ of course reduces volts to absolute electrostatic units.

(iii) *Values of the interaction integrals.* The value of this last factor in (16) is more difficult to estimate and can best be arrived at by first making calculations for a simple model. If we take a model in which each location is repre-

sented by a vertical sided hole of a constant depth ($U=0$ outside the hole, $U=-B$ within the hole), then without computing the wave functions we can see that roughly

$$\int \phi \psi d\tau = 2 \int_{\text{hole}} \phi \psi d\tau$$

(actually this value is a lower limit),

$$- \int U(r_2) \phi \psi d\tau = B \int_{\text{hole}} \phi \psi d\tau,$$

while $\int U(r_2) \psi^2 d\tau$ is considerably smaller. Thus for this model

$$\frac{\int \phi \psi d\tau}{-\int \phi \psi U d\tau + (\int \phi \psi d\tau) \int U(r_2) \psi^2 d\tau} = \frac{2}{B}; \quad (23)$$

for any reasonably similar model we shall obtain a result of the same form if a suitable mean depth of the hole is used for B . It is important to observe that the ratio (23) does not depend on R to any important extent. R controls affairs not by affecting the distribution of the proton over the pair of water molecules but by affecting violently the rate of adjustment of the distribution, as we shall shortly verify.

(iv) *Conversion of (16) to three dimensions.* Eq. (22) refers to a one-dimensional world in which every jump is either up or down the field. In order to convert it to a three-dimensional world it is only necessary to recognise that situations will be offered for jumps to occur in every direction distributed at random. For directions making an angle θ with the applied field Δ becomes $\Delta \cos \theta$ and F^* , $F^* \cos \theta$. If then N continues to denote the rate of presentation of occasions for jumps in any direction we must multiply (16) by $\overline{\cos^2 \theta}$ or $\frac{1}{3}$ to make it apply to three dimensions. Another effect of converting to three dimensions is that in three dimensions the effect of a particular oxonium ion on the polarity of the water molecules does not necessarily extend indefinitely along a coordinated chain, but is broken up by the formation of rings. This favours the simple version of the theory here presented.

(v) *Values of R and B .* A pair of close water molecules are 2.8×10^{-8} cm apart and in a free water molecule the protons are about 10^{-8} cm from the oxygen nucleus. The centres of the two

locations would therefore be about 0.8×10^{-8} cm apart if there were no modification of the neutral OH_2 . But there will be such modification, for the third proton will tend to increase the distances of all the protons from the centre and the polarisation of the molecules by the proton near their point of contact will tend still further to pull out the proton and to lower the barrier between the locations. The effective distance apart of the locations will therefore be smaller than 8×10^{-9} cm and we shall take 6×10^{-9} cm as a fair estimate.

It is not easy to estimate B satisfactorily. The third proton is of course not bound so firmly as the second proton to $(\text{OH})^-$ in forming neutral OH_2 . But from the general magnitude of the energies involved it is clear that B is of the order of 1 volt rather than $1/10$ or 10 volts, and we shall take $B=0.75$, admitting that this may be considerably in error. Some preliminary calculations on the basis of the present theory confirm this guess of the order of magnitude.

If we now insert these numerical values we find

$$D = 1.04 \times 10^{-15} NF^*. \quad (24)$$

We observe that this will reproduce the observed values for $(\text{OH}_3)^+$ if $N = 2.5 \times 10^{12}$. The discussion of the value of N presents difficulties.

(vi) *The value of N .* N is the number of favourable configurations which the oxonium ion may be expected to enter into per second, each one offering to a proton a chance of jumping in some direction to a neighbouring molecule within the limitations imposed by the theory.

We should start by recalling that the calculations made here proceed on the assumption that the time during which a favourable configuration lasts is at the worst comparable with the time of transition of the proton to and fro between the two locations available to it. It is necessary, therefore, to estimate this time. For the model already used in (iii) of this section we have sufficiently nearly

$$\epsilon_- - \epsilon_+ = 2B \int_{\text{hole}} \varphi \psi dt \tau.$$

For estimating numerical orders of magnitude this may be taken to be equal to

$$2Be^{-\kappa R'(-E_0)^{\frac{1}{2}}}, \quad (25)$$

E_0 (<0) being in this model the depth of the natural energy level below the energy zero outside the holes, and R' the width of the barrier. If we take holes of a radius 10^{-9} cm then $E_0 = \frac{1}{2}$ volt and $R' = 4 \times 10^{-9}$ cm, approximately. From the time factors in (16) we see that the transition time τ is $\frac{1}{2}h/(\epsilon_- - \epsilon_+)$. Therefore

$$\tau \simeq (h/4B)e^{\kappa R'(-E_0)^{\frac{1}{2}}} = 1.3 \times 10^{-15} e^{7 \times 10^6 (-E_0)^{\frac{1}{2}}}, \quad (26)$$

$$= 1.3 \times 10^{-15+3.05 \times 10^6 (-E_0)^{\frac{1}{2}}}. \quad (27)$$

Inserting the value of E_0 for our model we obtain

$$\tau \sim 6.5 \times 10^{-13}. \quad (28)$$

We observe at once that this is practically equal to $1/N$, N having the value required by (24). We conclude that τ and $1/N$ are of the same order of magnitude. This enables us to carry the argument forward more precisely than we could by any quantitative *a priori* estimation of the actual value of N . For in fact we now see that the speed of the migration is so high that it is controlled by τ and not by N . The actual excess mobility is just of the order that one would expect *if the opportunities for jumping from one molecule to the next are infinitely frequent, or more exactly, are presented to the $(\text{OH}_3)^+$ ion at least as frequently as it can make use of them, the time required for any single jump being of the order τ .* It only remains, therefore, to see whether this conclusion fits in with our conception of the structure of water.

§16. The value of N , and the structure of water

Let us consider first of all what value of N we should expect if water were a quasi-close packed structure of freely rotating molecules and ions. This is the most disordered arrangement that a liquid could possess and presumably it represents fairly closely the actual structure of say liquid argon and the actual structure that water would have, were it not that the molecules carry strong dipoles.

Such water molecules could be regarded with sufficient accuracy as classical isotropic rotators whose moment of inertia I is about 2×10^{-40} g cm². Their average component of angular velocity, ω_x say, is given by

$$\frac{1}{2} I \omega_x^2 = \frac{1}{2} kT,$$

where k is Boltzmann's constant. At ordinary temperatures, therefore, $\omega_x = 1.4 \times 10^{13}$ rad./sec., and the resultant ω is about 2.5×10^{-13} rad./sec., a speed comparable with $1/\tau$. Now each $(\text{OH}_3)^+$ ion carries three protons and each OH_2 molecule at least one free location and in close packing there would be twelve closest neighbours round each ion. The locations, however, are fairly small and must be hit fairly accurately to be effective. In spite, therefore, of the large number of possible chances per rotation it is clear that a successful orientation as frequent as one per rotation is most unlikely.*

This conclusion fits in therefore most satisfactorily with the views here developed concerning the coordinated structure of water. In general the protons are permanently situated so that jumps from one OH_2 carrier to the next can

* The number of favourable configurations per revolution can be roughly estimated by the following argument.

On one full rotation of the oxonium ion, any one of the protons it carries, P in number, describe small circles of radii $\frac{1}{2}\Delta \sin \theta$ where θ is the angle that the proton's radius vector makes with the axis of rotation. The length of the path swept out, averaged for all axes of rotation, is therefore $\frac{1}{2}\pi\Delta$, Δ being as before the diameter of the ion. Round any ion there are χ closest neighbours and each of the χ lines of centres to these neighbours is a spot at which jumps might occur if a proton on the ion and an empty location on the molecule come simultaneously together there. The probability that on one rotation one of the protons comes within a small distance δ of one line of centres is the ratio of the area of the track of width 2δ swept out by the proton to the area of the oxonium sphere, that is

$$(\frac{1}{2}\pi\Delta \cdot 2\delta)/\pi\Delta^2.$$

The average number of close approaches per revolution is therefore

$$\chi P \delta / \Delta.$$

Such a close approach can only be effective if an empty location is also present at the right moment. The chance that a location at a given moment will be within δ' of the line of centres is $\pi\delta'^2/\pi\Delta^2$. Combining the chance with the previous calculation, the average number of double close approaches per revolution is

$$\chi P \delta \delta'^2 / \Delta^3.$$

This is, of course, only a rough estimate—calculations should strictly be made of the nature of those for *triple* gas collisions. But the order of magnitude should be correct for the number of intimate encounters per revolution in which transitions might occur. If we take $P=3$, $\chi=12$, $\delta=\delta'=2.5 \times 10^{-9}$, $\Delta=2.8 \times 10^{-8}$ cm then the number per revolution is $1/40$.

occur at a rate of the order of $1/\tau$ times per second, just sufficient therefore to account for the abnormal mobility. The arguments given here for our isolated pair of molecules will apply at least roughly to any pair of molecules in a chain or other coordinated structure when an extra proton is present.

§17. The hydroxyl ion

The extra mobility of the $(\text{OH})^-$ is about one-half that of $(\text{OH}_3)^+$. It is obviously necessary and possible to accept the same general explanation for the extra mobility of both ions. It only remains to ask whether one can account theoretically for the fact that the extra mobility of $(\text{OH}_3)^+$ is greater than that of $(\text{OH})^-$. It is clear that this follows from the theory for the two processes are: (1) A transfer of H^+ from $(\text{OH}_3)^+$ to OH_2 . (2) A transfer of H^+ from OH_2 to $(\text{OH})^-$. Now the proton levels in $(\text{OH}_3)^+$ will be slightly nearer the periphery of the molecule and perhaps be slightly less tightly bound than the proton levels in OH_2 owing to the repulsive effects of the extra proton. On referring to the formulae (22) and (26) for D and τ we see that there are small changes probable in R and B which will hardly alter D apart from the effect on τ . But slight increases in R and $-E_0$ will both increase τ and therefore diminish N ; and this must be the dominant effect since it occurs in a moderately large exponent, and we must expect on the theory a lesser extra mobility for $(\text{OH})^-$ just as is observed.

§18. Temperature effects

We do not propose to attempt a discussion of the theoretical temperature coefficient of D at this stage. We shall content ourselves at present with pointing out the general way in which temperature can come in. In the first place the only directly temperature dependent factor in the theory as it stands is η , the dielectric constant. η falls as the temperature rises and so the extra mobility would *fall*. (We assume that the structure of the water continues to be sufficiently organized for plenty of opportunities for proton jumps.) The extra mobility is abnormal and does not increase so fast as the ordinary mobility which is controlled in effect by the viscosity of the water. But it apparently does increase and

not fall at ordinary temperatures as the temperature rises. This could only be explained on this simple version of the theory as due to a diminution of τ for a certain fraction of the protons. This might occur because some protons are thermally excited into upper states and so able to make more rapid transitions. Or again the thermal agitation might cause a fraction of the water molecule pairs to be unusually close together. We shall not discuss such points further here, for no such discussion would be of value when based on a more elaborate version taking account of the rate of thermal rearrangements of the coordinated chains referred to in §14. We have been concerned here rather to show that even for the largest likely values of τ the transitions can be rapid enough to produce the extra mobility in a suitable coordinated water. It may well be that the real τ is smaller and that the mobility is controlled partly by τ and partly by the thermal rearrangement rate so that the observed temperature effect may enter here.

§19. The mobility of the isotope H^2

It is not intended that the preceding theory or the details of the model are to be relied upon too closely. In fact the details of the model on which the discussion of the mobility is based have been chosen rather unfavourably for the theory, so as to show that the quantum mechanical jumps must *at the worst* be capable of giving the extra mobility required, provided that there is a substantial amount of permanent coordination in

the water structure. Provided, however, that the details are only approximately correct we can show that the effective mobility of the isotope (H^2) must be much less than that of the ordinary (H^1). The only important effect of the change of mass will occur in τ . In τ we have $\kappa' = 2^{\frac{1}{2}}\kappa$ and also a slight increase in $-E_0$. This will change the second part of the index in (27) to $4.31 \times 10^6(-E_0')^{\frac{1}{2}}$ so that $\tau' \simeq 10^{-11}$, about 20 times greater. The extra mobility of (H^2) will therefore be about 20 times less than that of (H^1), and may therefore be neglected compared with the mobility by bodily transport even if the factor 20 is somewhat overestimated.

We conclude that the effective mobility of (H^1) is about 5 times that of (H^2) in aqueous solution. This conclusion may be of importance in the theory of the separation of the isotopes of hydrogen by electrolysis. It must not, however, be assumed that it is necessarily a dominant factor. Electrode processes which will also discriminate in favour of the more rapid removal of H^1 from the solution may be more important.

In concluding this paper at this point we must make some apology. It is clear that the ideas here developed, if they are at all correct, will lend themselves to a number of further applications along the same lines, particularly in physical and chemical applications of the hydrogen bond. But the recent success of G. N. Lewis and others in concentrating H^2 in bulk gives such great possibilities of new experiments in this field that it is undesirable to publish at this stage further uncontrolled speculations.