303. *The Rate of Diffusion of Deuterium Hydroxide in Water.*

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Isotopic indicators have been employed in a number of cases to determine rates of self-diffusion, and the discovery of deuterium has made it possible to apply similar methods to hydrogen compounds. This paper records an investigation of the diffusion of deuterium hydroxide in comparatively dilute solutions in ordinary water. On account of the significant difference between the masses of the molecules H_2O and DOH it cannot be asserted that the diffusion rate is identical with the diffusion of water molecules themselves, but if the rates of diffusion of the two molecules are inversely proportional to the square roots of their masses the difference to be expected is only about 2%, which is less than the possible error of the experimental figures. Thus for practical purposes the results may be regarded as coefficients of self-diffusion of water.

In the first place one of Graham's methods was tried, *viz.*, cylinders containing 2—4% deuterium hydroxide solution were immersed in a large bath, through which ordinary water was circulated at a very slow rate, and the loss of deuterium hydroxide from the cylinder in a given time was determined. This method gave erratic results varying between 8 and 30 $\times 10^{-5}$ cm.^{2}/sec. at 15°. The failure was apparently due to the slight difference of density of the liquid in the diffusing column and that in the bath outside ($<$ 0·2%), which is insufficient to prevent turbulent mixing.

Northrup and Anson's method (*J. Gen. Physiol.*, 1929, **12**, 543) of determining the diffusion through sintered glass membranes, previously calibrated with a substance for which the diffusion coefficient is known, gave satisfactory results. The vessels were similar to those of McBain and Liu (*J. Amer. Chem. Soc.*, 1931, **53**, 59). Two filters were employed (I, II) similar to that illustrated by McBain and Dawson (*Proc. Roy. Soc.*, 1935, *A*, **148**, 32, Fig. 2A), the volumes of the deuterium hydroxide solution above the membrane being (I) 24·0 c.c., (II) 23·4 c.c. These vessels were tightly fitted by means of rubber bands into beakers containing an equal volume of ordinary distilled water below the membrane. The liquids used were thoroughly degassed and the general technique of McBain and Liu was followed. The "cell constants" were determined at 20° with potassium chloride, for which $D = 1{\cdot}448$ cm.^{2}/day.

During the diffusions the apparatus was placed in tall narrow glass vessels immersed in thermostats at the required temperatures, except in the experiments near 14°, which were carried out in a constant-temperature room.

The deuterium concentrations of the liquids above and below the glass membrane were determined at the end of the diffusion by means of density measurements at 25° ± 0·002°, a Sprengel pyknometer having a capacity of 13·6964 g. of ordinary distilled water being used. Before the density was determined, the liquids were thoroughly degassed by distillation in a vacuum, and this was repeated if necessary until a constant weight was obtained (± 0·0001 g.). To avoid changes of the DOH : H_2O ratio by fractionation, the distillations were always carried to completion.

The diffusion coefficient is given by

$$D = (1/kt) \log (c + c')/(c - c')$$

where k is the cell constant, t the time in secs. of the diffusion, and c and c' the final volume concentrations of deuterium hydroxide in the cell and beaker. The value of the cell constant was 0·0541 for cell I, and 0·0903 for cell II.

The abundance of deuterium in ordinary water being assumed to be 1 part in 6000 (Edwards, Bell, and Wolfenden, *Nature*, 1935, **135**, 793) and the density difference of pure H_2O and D_2O being taken as 0·10782, the weight of pure H_2O filling the pyknometer is 13·6962 g. On the assumption that there is a linear relationship between the mol. fraction of deuterium [$x = D/(D + H)$] and the density (Lewis and Luten, *J. Amer. Chem. Soc.*, 1933, **55**, 5061), the value of x is given by $x = (M - 13{\cdot}6962) \times 0{\cdot}99704/0{\cdot}10782 \times 13{\cdot}6962$, where M is the weight of the sample filling the pyknometer.

Since the molecular volumes of H_2O and D_2O differ by only 0·4%, the volume concentration of deuterium hydroxide may be taken as proportional to its mol. fraction. However, since only a ratio of two concentrations appears in the equation by which D is calculated, it is unnecessary to determine the actual concentrations, which may be represented for practical purposes by $\Delta = M - 13{\cdot}6962$. The only assumption made is that over the limited concentration range employed the concentration of deuterium hydroxide is proportional to the difference in density of the sample and pure H_2O.

In the measurements of the diffusion rate in N-sulphuric acid and N-sodium sulphate, the liquids on the two sides of the membrane were initially (1) a solution of the electrolyte in approx. 3% deuterium hydroxide, (2) a solution adjusted as near as possible to the same volume concentration of the electrolyte in ordinary water. The sodium sulphate was removed from the solutions before analysis, by distillation, and the sulphuric acid was neutralised with calcium oxide, followed by distillation.

The results are in Table I.

TABLE I.

Diffusion coefficients of deuterium hydroxide (2—3%).

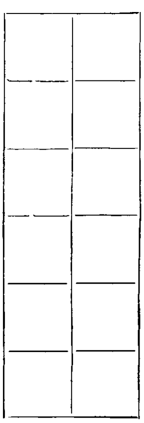
A. Diffusion in water.

Temperature.	Cell.	Time (mins.).	$\Delta \times 10^4$. Cell.	Beaker.	$D \times 10^5$, cm.^{2}/sec.	$D \times 10^5$, mean.
0·1° ± 0·1°	I	2517	226	30	1·42	1·46
	II	2537	207	48	1·49	
14·3 ± 0·005	I	1320	242	24	2·01	1·94
	II	1145	234	30	1·86	
25·0 ± 0·002	I	1429	236	33	2·63	2·64
	II	1207	225	44	2·65	
35·0 ± 0·01	I	1118	175	28	3·87	3·88
	II	1075	161	41	3·88	
45·0 ± 0·02	I	1060	154	29	4·81	4·75
	II	960	143	39	4·68	
		B. Diffusion in *N*-sulphuric acid.				
13·5 ± 0·05	I	1342	212	20	1·88	1·85
	II	1180	204	27	1·81	
		C. Diffusion in *N*-sodium sulphate.				
13·85 ± 0·05	I	1360	188	27	1·74	1·77
	II	1353	179	27	1·81	

DISCUSSION.

The observed rates of diffusion are of the magnitude to be expected for a molecule of the mass and size of the water molecule; *e.g.*, at 15° the observed coefficient is about 50% greater than that of methyl alcohol in water ($1{\cdot}28 \times 10^{-5}$) and nearly twice that of formic acid ($1{\cdot}04 \times 10^{-5}$). There is thus nothing abnormal about the diffusion of deuterium hydroxide in water, and presumably the self-diffusion of water has nearly the same magnitude.

FIG. 1.



A physical picture of the meaning of the diffusion coefficient can be obtained in the following way. Consider a plane of DOH molecules of unit area, placed in contact with a similar plane of HOH molecules, as shown in cross section in Fig. 1. Since the molecular volumes of HOH and DOH are nearly the same, the number of molecules in each unit plane will be nearly the same and, the molecular volume of water being taken as 18·1 c.c., equal to $1{\cdot}04 \times 10^{15}$. The concentration gradient between the two planes is obtained by dividing the difference of the numbers of molecules per c.c. of one kind on the two sides by the distance between the centres of the two planes, which is taken as (molecular volume)$^{\frac{1}{3}}$, *viz.*,

$$\frac{dc}{dx} = \left(\frac{6{\cdot}06 \times 10^{23}}{18{\cdot}1}\right) \Big/ \left(\frac{18{\cdot}1}{6{\cdot}06 \times 10^{23}}\right)^{\frac{1}{3}} = 1{\cdot}08 \times 10^{30} \text{ mols./cm.}^4$$

According to Fick's equation, $ds/dt = DA \,.\, dc/dx$, where ds/dt is the rate at which molecules pass a given plane of area A under a concentration gradient dc/dx. Taking D as 2×10^{-5} cm.^{2}/sec., we obtain for unit area

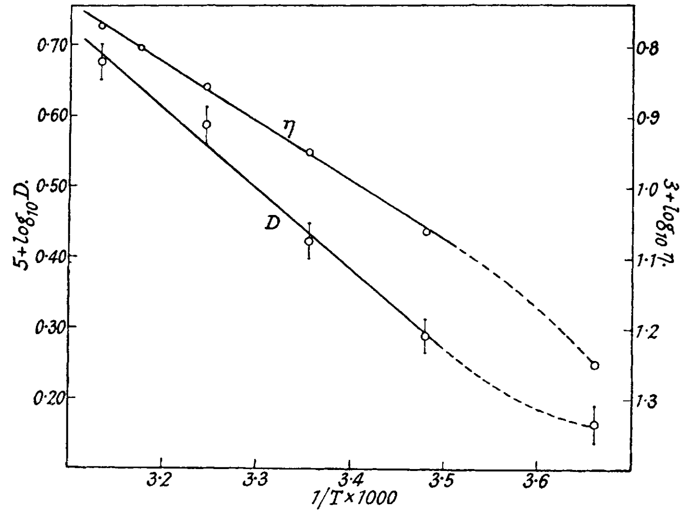
$$ds/dt = 2{\cdot}16 \times 10^{25} \text{ molecules/sec.}$$

The average life of a molecule in the original layers (with respect to diffusion across the central plane) is thus $1{\cdot}04 \times 10^{15}/2{\cdot}16 \times 10^{25} =$ *ca.* 5×10^{-11} sec. (at 15°).

For reasons stated above, it may be supposed that the interchange of molecules in pure water takes place at the same rate. It may be supposed that the molecules in a liquid occupy a certain territory and are vibrating about mean positions. Occasionally a molecule acquires sufficient energy to escape from its territory. If the vibrational frequency is known, the fraction of the total number of vibrations which give rise to an " escape " can be calculated. The vibrational frequencies of liquid water, as determined from infra-red and Raman spectra, are of the order of 3400 cm.$^{-1}$, *i.e.*, 1×10^{14} sec.$^{-1}$ (Rank, *J. Chem. Phys.*, 1934, **2**, 464). The escape frequency in one direction, which is the inverse of the average life of a molecule in a given plane, is 2×10^{10} sec.$^{-1}$. The total frequency of escape in all directions may be taken as about 6 times this value or about 10^{11} sec.$^{-1}$, so that it can be seen that one escape takes place in *ca.* 1000 vibrations. The molecules of water thus have a considerable mobility, which is not easily reconciled with a very definite structure.

The diffusion coefficient increases rapidly with the temperature. It can be seen from Fig. 2, in which log D is plotted against $1/T$, that within the experimental error a linear relation holds except at the lowest temperatures. From 10° to 45° the equation $D = 0{\cdot}197e^{-5300/RT}$ is reasonably accurate. The " activation energy " of the diffusion process, as determined in this way, is thus 5300 cals. (cf. Bradford, J., 1934, 1910).

FIG. 2.



According to Einstein's equation, which is probably only strictly applicable when the diffusing molecule is large compared with the solvent molecules, the diffusion coefficient is given by $D = RT/6\pi\eta rN$, where η is the viscosity of the medium and r the radius of the diffusing molecule. If r is regarded as constant, the quantity $D\eta/T$ should be independent of the temperature. The following table shows that this is only very approximately the case.

TABLE II.

T(K)	273·2°	287·4°	298·1°	308·1°	318·1°
$D \times 10^5$, cm.^{2}/sec.	1·46	1·94	2·64	3·88	4·75
$\eta \times 10^3$, c.g.s.	17·86	11·65	8·949	7·208	5·970
$D\eta/T$	0·095	0·079	0·079	0·091	0·089

In order to make Einstein's equation compatible with an exponential form of diffusion equation it is necessary to use equations such as $D = K\sqrt{T}e^{-A/RT}$ and $\eta = K'\sqrt{T}e^{A/RT}$. It is not possible to distinguish experimentally between an expression of this form and that given above. $-\log\eta$ is plotted against $1/T$ in Fig. 2, and though a linear relation is obtained the slope is less than that of the corresponding D curve. However, the viscosity of water is known to be anomolous in this region, for at higher temperatures the slope changes and a still flatter curve is obtained.

The diffusion rate in *N*-sulphuric acid was determined in order to find the influence of the ionic mobility of hydrogen ions on the diffusion. The diffusion coefficient of deuterium ions can be calculated from their mobility by Nernst's equation (*Z. physikal. Chem.*, 1888, **2**, 631), *viz.*, $D_{D^+} = 0{\cdot}026 \,.\, U_{D^+} \times 10^{-5}$ cm.^{2}/sec., where U_{D^+} is the mobility in electrical units. Taking the mobility of D^+ ions in 3% deuterium hydroxide solution at 14° as 290, we obtain $D_{D^+} = 7{\cdot}5 \times 10^{-5}$ cm.^{2}/sec.

However, since the *total* concentration of hydrogen ions ($H^+ + D^+$) is everywhere *N*, the concentration gradient of deuterium ions is 1/55·5 that of deuterium hydroxide. Thus the complete diffusion equation is

$$\begin{aligned} ds/dt &= D_{DOH}A \,.\, dc/dx + (D_{D^+}\,A \,.\, dc/dx)/55{\cdot}5 \\ &= (D_{DOH} + D_{D^+}/55{\cdot}5)A \,.\, dc/dx. \end{aligned}$$

Since the total concentration of deuterium is determined in the analysis, it follows that the observed value of D is

$$D = D_{DOH} + (1/55{\cdot}5)D_{D^+}.$$

Thus the effect of the mobility of the ions on the diffusion coefficient will be negligible in neutral solutions, but in *N*-sulphuric acid an increase of D of the order of $(1/55{\cdot}5)D_{D^+} = 0{\cdot}14 \times 10^{-5}$ cm.^{2}/sec., which should be just detectable, is to be expected. Actually the value observed at 13·5° (*viz.*, 1·70) is smaller than that of pure water at the same temperature (1·77), and is less than the expected value by more than the experimental error. It thus appeared that the value of D_{DOH} is decreased by the presence of sulphuric acid, possibly on account of the electrostriction of the water by the ions. To test this point, similar experiments were made with *N*-sodium sulphate, and a lowering of D by $0{\cdot}12 \times 10^{-5}$ cm.^{2}/sec. was observed. The electrostrictive effect of the ions on the diffusion coefficient may thus be greater than the addition term due to the mobility of hydrogen (or deuterium) ions in an acid solution.

SUMMARY.

Measurements have been made of the diffusion coefficient of deuterium hydroxide (*ca.* 3%) in water at temperatures between 0° and 45°, and from the results an estimate is made of the rate of self-diffusion in water. In neutral solutions the effect of the mobility of the hydrogen ions is probably negligible. It should be an observable quantity in a *N*-acid solution, but the effect is obscured by a decrease of the diffusion coefficient caused by the electrostriction of water by the ions.

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