Measurements of the Self-diffusion of Water in Pure Water, H₂O-D₂O Mixtures and Solutions of Electrolytes

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Dedicated to Professor Ole Lamm on his 60th birthday

The self-diffusion of water was measured at 25.0°C in pure water, H₂O-D₂O mixtures and solutions of NaCl, LiBr and MgSO₄. The diffusion cells used were of the shearing boundary type and are described. Deuterium and tritium were used as tracers. Analysis of deuterium was performed by means of a mass spectrometer. Tritium has been detected by means of liquid scintillation technique, or by an improved version of the bremsstrahlung method. Comparative measurements in pure water at 25.0°C with deuterium and tritium as tracers gave identical results $(2.25 \pm 0.02) \times 10^{-5}$ cm²/sec, in good agreement with Longworth's extrapolated value (2.27) obtained from measurements on H₂O-D₂O mixtures using a precision optical method. The result thus indicates that the isotope effect is within experimental error. The self-diffusion of water in H₂O-D₂O mixtures, having tritium as tracer, seems to decrease linearly with the increase in deuterium content. The self-diffusion coefficient in dilute salt solutions was very moderately affected. In concentrated solutions decreasing effects were most pronounced in solutions of MgSO₄. A comparison of the inverse viscosity *versus* solute concentration with the self-diffusion shows a similar course for the two functions. The results in the case of salt solutions is discussed briefly in terms of the theory of Wang. Data of others are included for comparison.

The purpose of the present investigation was to study the self-diffusion of water and especially the influence of electrolytes. Previous measurements with different tracers and methods have resulted in different diffusion coefficients for the self-diffusion of pure water. Contradictory data obtained from measurements with ¹⁸O and D have been interpreted even as an indication of different mechanisms for the transfer of oxygen and hydrogen¹. In the present work with HDO and HTO as tracers similar experimental techniques have been used for the two isotopes in order to reduce systematic errors.

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By measuring the self-diffusion with D and T as tracers it was intended to make a rough extrapolation to the true self-diffusion coefficient of water. The present result, however, indicate that the isotope effect from measurements with D and T is within experimental error. Measurements using spin echo techniques have been rather inaccurate so far and cannot yet serve as a measure of the isotope effect.

EXPERIMENTAL

In the diffusion experiments the principle of restricted diffusion was used. The diffusion cells were of sheared boundary type.

Apparatus. The two cells, which were of the type developed by Undeman, consisted of cylinders made of stainless steel and divided into four segments. In each segment circular holes (three in one cell, six in the other) were drilled, which could be separated or made to overlap by turning a screw. Thus one experiment could give three or six values of the diffusion coefficient. In Fig. 1 one of the cells is sketched. The centre parts were of equal height (3.998 ± 0.001 cm). The normal procedure for a diffusion experiment was as follows. The cell was placed upside down and the bottom part filled with the thermostated (± 0.2) sample, by means of a syringe, the cell was then turned over and the upper part filled. The cell was placed vertically in a thermostat bath and when temperature equilibrium was reached the experiment was started (by means of turning the two centre segments). The correct position was indicated by a conical bolt which locked the segments in place. The diffusion experiment was stopped when the average concentration difference was about half of the original value. It takes from one to three days for these conditions to be reached. Disturbances from vibrations were eliminated by means of a firm cell holder, which was fixed on a steady pillar in the building. The stirrer in the bath was not allowed to have any mechanical contact with the cell. Variations from the vertical position were investigated in some experiments and values of about 0.5° were found. This gives an estimated error in the diffusion coefficient of less than 0.3 %. Convection during the shearing procedure was determined in some experiments, with very short diffusion times, and was found to contribute 0–2 % to the randomised errors in the diffusion coefficient.

Fig. 1. Diffusion cell (for explanation see text).

On completing the diffusion process the liquid in the two parts of the chamber were well mixed and samples withdrawn by means of a syringe. The samples were then analysed for deuterium and tritium content.

Material. The deuterium oxide (about 99.8 %) was obtained from Norsk Hydro, Rjukan, Norway, and the tritiated water (about 5 C/ml) from the Radiochemical Centre, Amersham. In preparing the salt solutions ordinary distilled or redistilled water was used and the salts were of analytical grade. In order to assure that no convection should arise in the cell in the case of diminutive density gradient in the cell, the same sort of water was used from a stock. This procedure also made it possible to eliminate the need for accurate knowledge of the deuterium content in the water.

Thermostating. In order to reduce the heat convection in the diffusion cell a thermostat bath has been developed, which maintained the temperature constant to within $\pm 0.0002^\circ\text{C}$. For the purpose, an isolated bath (45 l) was used and placed in a thermostated room ($25 \pm 0.2^\circ\text{C}$). To achieve such a constant temperature in the bath, the main principle was to supply and carry off as small amounts of heat as possible. By this means excellent stability was reached and the control instruments closely followed the slowly changes in temperature. In practice it was arranged so that the cooler and heater were adjusted on low and approximately equal values, thus given a cooling and heating effect to the bath of normally $0.002^\circ\text{C}/\text{min}$ in the steady state. The heater was a commercial water bath heater (60 W) connected to a power supply transformer. The cooling effect was obtained by the evaporation of the bath water, this was compensated for with a continual and automatic supply of water. A mercury contact thermo-regulator was used as the adjusting instrument. The mercury stem expansion was about $2 \text{ cm}/^\circ\text{C}$. With the control instrument, a Beckmann-thermometer, temperature differences of 0.0002°C could be detected with the aid of a cathetometer. Temperature gradients in the bath were eliminated by means of a propeller (70 rpm). Tests at several points in the bath showed no temperature variation ($\Delta T < 0.0002^\circ\text{C}$). The absolute temperature was measured with a calibrated (0.01°C) mercury thermometer.

Method of calculating the diffusion coefficient. Under favourable conditions, with practically no concentration gradients and no volume changes, Fick's second law is fulfilled. With the initial condition ($t = 0$)

$$\begin{aligned} c &= 0 & \text{for } 0 < x < h \\ c &= c_0 & \text{for } -h < x < 0 \end{aligned}$$

and the condition

$$\frac{\partial c}{\partial h} = 0 \quad \text{for } \begin{cases} x = h \\ x = -h \end{cases}$$

where x = distance from the shearing boundary
 h = half the height of the diffusion cell

the solution of the differential diffusion equation can be written:

$$\frac{c_{\text{av}}}{c_0} = \frac{1}{2} - \frac{4}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \exp \left\{ -\frac{(2n-1)^2 \pi^2}{4h^2} Dt \right\} \quad (1)$$

or

$$\frac{c_{\text{av}}}{c_0} = \frac{\sqrt{Dt}}{h} \left\{ \frac{1}{\sqrt{\pi}} + \sum_{n=1}^{\infty} (-1)^{n+1} \text{ierfc} \frac{nh}{\sqrt{Dt}} \right\} \quad (2)$$

where c_{av} = average concentration in the upper part of the cell. The function

ierfc $x \equiv \int_x^\infty (1 - \operatorname{erf} \eta) d\eta \equiv \frac{1}{\sqrt{\pi}} \exp(-x^2) - x \operatorname{erfc} x$ has been calculated

by means of tables of the error function². If the concentration of the tracer in the upper part differs from zero at $t = 0$ and has the value c_B the definition of c_{av} and c_0 is changed to:

$$c_{av} = c'_B - c_B \quad (3)$$

$$c_0 = c'_A - c_B \quad (4)$$

where c'_B and c'_A are the absolute concentrations of the tracer in the upper and lower parts of the cell. Eqns. (3) and (4) have been used in the analytical procedure concerning deuterium with the advantage that it was necessary to determine only the ratio of two concentrations above the natural deuterium content of water. In order to correlate the signal from the mass spectrometer with this ratio, standard solutions were made up with the known ratio c_{av}/c_0 from D_2O and the stock water. The same procedure is possible when ^{18}O is used as tracer thus eliminating most of the systematic errors in the analytical procedure. A valuable control of the analyses is the relationship

$$\frac{c_{av}}{c_0} + \frac{c'_{av}}{c_0} = 1 \quad (5)$$

where c'_{av} = the average conc. in the lower part of the cell.

Isotope analyses. At first deuterium was determined by a modified version of the gradient tube method^{3,4}, but this was considered to be too time consuming to give the necessary accuracy. Most of the deuterium analyses were performed instead by the mass

Table 1. The effect on the stability of the output signal (n) from the liquid scintillation unit, caused by small changes of certain variables, compared with error due to the vial position and the statistical disintegration rate (Typical values).

Amount of water (x_1 ml)		Amount of ethanol (x_2 ml)		Amount of scintillator (x_3 ml)		Temperature changes ($t^\circ C$)		Number of measurements *		Statistical dis. rate	
x_1	$\left \frac{\partial n}{\partial x_1} \right $	x_2	$\left \frac{\partial n}{\partial x_2} \right $	x_3	$\left \frac{\partial n}{\partial x_3} \right $	t	$\left \frac{\partial n}{\partial t} \right $	a	$\frac{\Delta n^{**}}{n}$	*** $\mu C/ml$	$\frac{\Delta n}{n}$
0.4	<0.1	6	0.3	9.5	< 3	-17	0.3	1	0.01 — 0.04	0.12	0.004
0.5	<0.1	8	0.3	10	< 3	-20	0.06	2	0.007 — 0.03	0.6	0.002
0.7	0.6	10	0.3	10.5	< 3	-22	0.02	4	0.005 — 0.02		

* in different vial positions.

** n = standard deviation of the average.

*** quoted figures indicate the conc. interval normally used.

spectrometer technique. In the region of low deuterium content ($< 1\%$ D) the spectrometer measurements were reproducible to within 0.5 %.

Tritium analyses were performed with the aid of the bremsstrahlung method⁵ or by the liquid scintillation technique. The latter method required removal of the water from the salt solutions by distillation before measurements were made. The distillations were carried out to completion to avoid isotope effects. In the bremsstrahlung method the high tritium content required (> 1 mC/ml), caused heat to be generated in the cell, and thus, at least from a theoretical point of view, convection could occur. It was therefore worthwhile to compare the results from the two independent analytical methods. By a systematic search for different sources of inaccuracies in the liquid scintillation method the standard deviation of single analyses could be reduced to about 0.6 %. No standard solution was needed either in the liquid scintillation method or in the bremsstrahlung method, as the net pulses were shown by experimental tests to be proportional to the tritium content.

An Ekco liquid scintillation unit (model N-612) with single photomultiplier working at -22°C was used normally. Another instrument, the Packard Tri-Carb spectrometer (model 314-X), was tested in order to obtain increased reproducibility, but no improvement was attained. The liquid scintillation system was a conventional one: 0.2–0.5 g water, 10 ml scintillator (6 g PPO/l toluene) and 8 ml ethanol. Some of the effects influencing the stability of the output signal such as amount of sample, quenching effects of the components, temperature, stability of the instrument, vial placing, randomized disintegration rate, are quoted in Table 1. Every sample was counted 4–5 times with different vial positions in order to reduce the random variation due to vial location and each sample was counted 3–5 times in 100 sec in a single vial position. The whole instrument was kept in a dark room which had only a red light, and the vials were kept in the refrigerator for at least 20 min before counting.

The bremsstrahlung method⁵ has been improved now by including two GM-tubes with mica windows (Philips PW 1962) and a more suitable cell (Fig. 2). The bremsstrahlung method was developed originally to give a good reproducibility. The reproducibility was of the same order as the deviations due to the randomized disintegration rate. The amount of sample necessary for counting was about 1.2 ml with a tritium content of normally 10–50 mc/ml given 1000–5000 cpm. The background was 100 cpm and the counting time 20–60 min. The background was measured before and after each c_{av} and c_0 , to ensure that instability or increased background would not influence the net counting rate. In order to avoid contamination and health hazards, precautions must be taken when working with tritiated water having a high T-content. Special care should be taken to avoid skin permeation and lung absorption. Some urine analyses, however, indicated no body burden of tritium.

Fig. 2. Scheme of T-measurement on active liquids by bremsstrahlung.

RESULTS

Natural water. The self-diffusion of water was determined at $25.0 \pm 0.05^\circ\text{C}$ with deuterium at the average concentrations (N) 0.025, 0.135 and 2.0 molar percent. The results, averages of n single determinations, are given in Table 2. The initial concentration difference in the diffusion cell is quoted (ΔN). Analyses at the two lower concentrations were performed with a mass spectrometer, while the 2 % solution was analysed by means of the gradient tube method. Because of the larger standard deviation of the latter method these results are not included in the total average. The measure of accuracy is given both as the standard deviation of the mean (σ) and the deviation of the mean at the 90 % confidence limit (σ_{90}).

Table 2. The self-diffusion coefficient of water at 25.0°C . Deuterium as tracer.
 N = av. deuterium conc. (molar fraction), ΔN = initial conc. difference
 n = number of measurements
 σ = standard deviation in the mean
 σ_{90} = deviation at 90 % confidence limit

$N \times 10^2$	$\Delta N \times 10^2$	n	$D \times 10^5$ cm ² /sec	σ	σ_{90}	Method of analysis *
0.025	0.065	4	2.24	0.02	0.05	M
0.135	0.29	5	2.27	0.02	0.04	M
2.0	4.0	(7)	(2.37)	(0.09)	(0.18)	G
average		9	2.25	0.01	0.02	

* M = mass spectrometer, B = bremsstrahlung method, L = liquid scintillation technique
 G = gradient tube method.

Table 3. The self-diffusion coefficient of water at 25.0°C . Tritium as tracer.

$N \times 10^2$	$\Delta N \times 10^2$	n	$D \times 10^5$ cm ² /sec	σ	σ_{90}	Method of analysis
0	0	5	2.29	0.03	0.06	B
0.5-2	1-4	6	2.23	0.01	0.02	B
0.5-2	1-4	6*	2.22	0.02	0.03	B
0.5	1	(9)	(2.26)	(0.06)	(0.11)	L
average		17	2.25	0.01	0.02	

* these measurements at pH = 4.9.

Table 4. The self-diffusion of water at 25.0°C. Comparison of literature data. ΔD = reported accuracy.

Tracer or method	D	ΔD	Authors	Ref.	Remarks
NMR	2.13	7 % (a), 3 % (b)	Simpson and Carr (1958)	16	25.5°C; from diagram
	~2.33	—	Douglass and McCall (1959)	17	
^{18}O	2.66	± 0.12 (c)	Wang <i>et al.</i> (1953)	11	from diagram
	2.57	± 0.02 (c)	Wang (1954)	14	
D	~2.57	± 2 % (e)	Adamson and Irani (1957)	1	extrapol. value
	2.34	± 0.08 (c)	Wang <i>et al.</i> (1953)	11	
	2.26	± 0.001 (c)	Longworth (1954)	13	extrapol. value
	2.25	± 0.01 (d)	Undeman (1955)	15	
	2.38	± 4 % (e)	Adamson and Irani (1957)	1	extrapol. value
	2.27	± 0.001 (c,g)	Longworth (1960)	18	
	2.25	± 0.02 (f)	This work	Table 2	extrapol. value
T	2.44	± 0.06 (c)	Wang <i>et al.</i> (1953)	11	
	2.64	5 % (e)	Cuddeback <i>et al.</i> (1953)	12	
	2.25	± 0.02 (f)	This work	Table 3	

(a) estimation of the max. deviation

(b) » of max. systematic error

(c) standard deviation

(d) » » in the mean

(e) reproducibility

(f) deviation in the mean at 90 % confidence limit

(g) this value replaces 2.26 in Ref.¹³

Table 5. The self-diffusion of water in $\text{H}_2\text{O}-\text{D}_2\text{O}$ mixtures at 25.0°C. Tritium as tracer.

$N \times 10^2$	$\Delta N \times 10^2$	n	$D \times 10^5$ cm ² /sec	σ	σ_{90}	Method of analysis
0—2	0—4	Table 3	2.25	0.01	0.02	B
50	4	6	2.11	0.01	0.02	B
98	1.5	6	1.90	0.02	0.04	B

Results with tritium as tracer are given in Table 3. The total average value for tritium does not include the results from the liquid scintillation method due to the increased standard deviation. To obtain a positive density gradient in the diffusion cell, 1 % D_2O was usually added to the solution in the lower part of the diffusion cell. This amount of deuterium causes only a very slight change in the diffusion coefficient as can be seen from Fig. 3. A moderate decrease of pH to 4.9 had no influence on the diffusion coefficient (Table 3).

Comparison between the results in Tables 2 and 3 shows that the isotope effect seems to be within the experimental error. Data on the self-diffusion

Fig. 3. Comparison of literature data concerning the self-diffusion coefficient of water at 25.0°C in H_2O — D_2O mixtures. Figures within brackets indicate reference numbers. Viscosity data are normalized to 2.0 for pure H_2O .

coefficient of water obtained from measurements with different tracers and methods may be inaccurate and could contain systematic errors, thus making it impossible to estimate the isotope effect from literature data. Results of known data measured at 25°C and obtained with different techniques ^{1,11-18} are given in Table 4. Measurements of Orr and Thomson⁶, Temkin⁷, Orr and Butler⁸, Lamm⁹ and Rögner¹⁰ are not included. It is intended to do further investigations using ¹⁸O and the present method in order to verify if the isotope effect is insignificant in that case too.

Table 6. The self-diffusion of water in electrolytic solutions at 25.0°C. Tritium as tracer. c = solute conc. (molarity).

	c	n	$D \times 10^5$ cm^2/sec	σ	σ_{90}
NaCl	0.17	3	2.30	0.02	0.06
	0.99	6	2.15	0.01	0.02
	1.96	9	1.99	0.05	0.09
LiBr	4.05	8	1.64	0.03	0.06
	0.012	2	2.30	0.01	0.06
	0.12	8	2.26	0.02	0.04
	0.52	3	2.26	0.04	0.12
MgSO_4	3.27	5	1.70	0.02	0.04
	0.078	3	2.29	0.01	0.03
	0.36	6	1.96	0.03	0.06
	0.72	5	1.68	0.01	0.02

H₂O—D₂O mixtures. To justify the addition of 1 % D₂O to the solutions in the lower part of the cell the diffusion coefficient of HTO in 50 % and 100 % D₂O was differentially measured at 25°C. The results are given in Table 5. These measurements together with those of other workers are plotted in Fig. 3. As can be seen from Fig. 3 the self-diffusion coefficient and the inverse viscosity follow the same course when increasing the deuterium content, and the product ηD_0 is almost constant within the whole concentration interval.

Salt solutions. The results from measurements in dilute and moderately concentrated solutions of NaCl, LiBr and MgSO₄ at 25.0°C are given in Table 6 and normalized in Fig. 4. This figure also includes measurements of Wang¹⁴ and unpublished data of Undeman¹⁵. The inverse viscosity obtained from literature data is given as a comparison. The absolute values of Wang's data obtained with ¹⁸O as tracer differ from the present data, but on normalizing at $c = 0$ the agreement is excellent as can be seen from the NaCl data.

Estimation of errors. With the present technique efforts were made to minimize the systematic errors. The only data necessary to calculate D , apart from c_{av}/c_0 , are the diffusion time and the length of the cell. The values of the analyses of the D and T content in both compartments of the cell were tested by inserting them in eqn. (5) thus reducing the possibility of inaccuracy.

Fig. 4. Normalized self-diffusion coefficient of water at 25.0°C in salt solutions. Comparison of data of Wang, Undeman and the present work.

□ = KCl(D/D_0) D^{15} ; △ = MgCl₂(D/D_0) D^{15} ; × = NaCl(D/D_0) T , (Table 6);
○ = LiBr(D/D_0) T , (Table 6).

Fig. 5. Frequency distribution of the data on the self-diffusion coefficient in pure water. Tritium used as tracer. Analyses performed with the bremsstrahlung method.

Systematic errors may result *a priori* from convection in the diffusion cell; this has been observed in about 10 % of the experiments. Convection results in a cast Gaussian distribution of the self-diffusion coefficient. This distribution becomes extended at higher values of the coefficient as no compensating lowering effect exists. In Fig. 5 the distribution of the data from measurements on pure water demonstrates this phenomenon. Diffusion data appreciably higher than the average have therefore been excluded. This procedure is justified mathematically if one can make the assumption that the probability of a certain convection effect decreases when the effect increases. Though convection did occur it was possible to make accurate measurements at initial density differences as low as 10^{-5} g/cm³.

DISCUSSION

According to Lamm's^{19,20} theory concerning the relationship between mutual diffusion and self-diffusion, the latter can be written in the case of a two component system as:

$$D_0 = \frac{RT}{\Phi_{12} + \Phi_{0(3)}} \quad (6)$$

where the components 0 and 3 may be water and a salt respectively. Component 0 is composed of the two isotopic components 1 and 2 (*e.g.* H₂O and HTO). This formula thus takes into account the existence of different friction properties between the two components ($\Phi_{0(3)}$) compared with the friction between molecules of the same species (Φ_{12}). Even if there is no exact relationship between the mutual diffusion coefficient (D_{03}) and the self-diffusion coefficient (D_0) Lamm²⁰ has proposed the approximate relation

$$D_0 \approx \frac{D_0^0 D_{03}}{D_{03} n_0 v_0^0 + B_{03} N_3 D_0^0} \quad (7)$$

where n_0 = concentration of comp. 0
 v_0^0 = molar volume of pure 0
 N_3 = molar fraction of comp. 3
 D_0^0 = self-diffusion coefficient of pure 0
 B_{03} = thermodynamic factor

Johnson and Babb²¹ found that for the ideal organic system benzene-carbon tetrachloride the eqn. (7) holds to within 10 % and even in the non-ideal systems benzene-methanol and benzene-ethanol to within 15 %. As pointed out by Lamm²⁰ the approximate relationship expressed by eqn. (7) is not valid however if component 3 changes the specific friction properties of component 0. In the case of dilute and moderately concentrated salt solutions, where the solute does affect the water structure, the use of eqn. (7) would result in too small an effect on the self-diffusion coefficient.

The experimental results on the self-diffusion of water in salt solutions may hypothetically be interpreted in a qualitative manner according to Wang^{14,22}. There are two lowering factors, the obstruction and the direct hydration effects. The obstruction effects is due to the diffusion species having to diffuse by a longer path round the ions or hydrated ions, which are more immobile than the water molecules. The obstruction effect for a practically immobile solute can be written²²:

$$D_0 = D_0^0 (1 - \alpha x) \quad (8)$$

where α = factor depending on the shape of the obstructing molecules ($\alpha = 1.5$ for spherical molecules).

x = volume fraction of the hydrated obstructing molecules.

In the case of hydrated ions of strong electrolytes, where the mobility is not appreciably lower than that of water, it is expected that the obstruction effect is weak.

The hydration effect arises when solvent molecules are attached to the solute and the rate of exchange between free and bound water is slow compared with the diffusion displacement. With a modification of the formula of Douglas *et al.*²³ the direct hydration effect concerning an immobile solute can be written:

$$D_0 = D_0^0 \left[1 - f \left(1 - \frac{v_b}{v_0} \right) \right] \quad (9)$$

Where v_b and v_0 are the frequencies of the diffusion displacement of the hydrated water and free water, respectively. f is the fraction of water molecules attached to the solute. In the case of slow interaction between bound and free water eqn. (9) is simplified to

$$D_0 = D_0^0 (1 - f) \quad (10)$$

In salt solutions the distortion effect increases the self-diffusion and is due to the breaking down of the water structure outside the hydrated complex and thus decreases the local viscosity. Our results and those of Undeman agree with the concept of Wang. Mg^{2+} is more strongly hydrated than Na^+ , and MgCl_2 therefore has an enhanced obstruction and direct hydration effect compared with Na^+ . The distortion effect of Mg^{2+} is weaker than that of Na^+ and weaker still for K^+ . The net result expected is a decrease in the self-diffusion coefficient of water in Mg^{2+} -salts compared with the data valid for Na^+ . The hydration and obstruction effect of Li^+ is stronger and the distortion effect is weaker than that for Na^+ . On the other hand Br^- is thought to have more radical structure-breaking properties than Cl^- . Thus the self-diffusion of water in solutions of LiBr is expected to be approximately the

same as in NaCl solutions. This agrees with the experimental results. If the above theory of Wang is correct the results from measurements on MgSO_4 indicate that, in the case of SO_4^{2-} , the obstruction and hydration effect dominate over the distortion effect. The maxima found by Wang in measurements on KCl and KI solutions at about 2 and 3 mole/l respectively and the decrease in the self-diffusion at higher concentrations (see Fig. 4) may be due to the fact that in these concentrated solutions most of the water molecules are bound and thus any further solute molecules added have no water structure to distort.

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REFERENCES

1. Adamson, A. W. and Irani, R. R. *J. Am. Chem. Soc.* **79** (1957) 2967.
2. Natl. Bureau of Standard *Tables of the Error Function and its Derivatives*, Washington 1954.
3. Linderstrøm-Lang, K. and Lanz, Jr., H. *Compt. rend. trav. lab. Carlsberg, Ser. chim.* **21** (1938) 315.
4. Linderstrøm-Lang, K., Jacobsen, O. and Johansen, G. *Compt. rend. trav. lab. Carlsberg, Ser. chim.* **23** (1938) 17.
5. Westermarck, T., Devell, L. and Ghanem, N. *Nuclear Instr. and Methods* **9** (1960) 141.
6. Orr, W. J. C. and Thomson, D. W. *Nature* **134** (1934) 776.
7. Temkin, M. *Nature* **136** (1935) 552.
8. Orr, W. J. C. and Butler, J. A. V. *J. Chem. Soc.* **1935** 1273.
9. Lamm, O. *Nova Acta Regia Soc. Sci. Upsaliensis Ser IV* **10** (1937) No. 6.
10. Rögener, H. Z. *Elektrochem.* **47** (1941) 164.
11. Wang, J. H., Robinson, C. V. and Edelman, I. S. *J. Am. Chem. Soc.* **75** (1953) 466.
12. Cuddeback, R. B., Koeller, R. C. and Drickamer, H. G. *J. Chem. Phys.* **21** (1953) 589.
13. Longworth, L. G. *J. Phys. Chem.* **58** (1954) 770.
14. Wang, J. H. *J. Phys. Chem.* **58** (1954) 686.
15. Undeman, C. L. *Unpublished*.
16. Simpson, J. H. and Carr, H. Y. *Phys. Rev.* **111** (1958) 1201.
17. Douglass, D. C. and McCall, D. W. *J. Chem. Phys.* **31** (1959) 569.
18. Longworth, L. C. *J. Phys. Chem.* **64** (1960) 1914.
19. Lamm, O. *Acta Chem. Scand.* **6** (1952) 1331.
20. Lamm, O. *Acta Chem. Scand.* **8** (1954) 1120.
21. Johnsson, P. A. and Babb, A. L. *J. Phys. Chem.* **60** (1956) 14.
22. Wang, J. H. *J. Am. Chem. Soc.* **76** (1954) 4755.
23. Douglass, D. C., Frisch, H. L. and Anderson, E. W. *Biochim. et Biophys. Acta* **44** (1960) 401.

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