[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

The Densities of D_2O-H_2O Mixtures at 5 and 25°

BY ELIJAH SWIFT, JR.[1]

Longsworth[2] has shown that at 25° mixtures of H_2O and D_2O are apparently ideal from the standpoint of volume changes on mixing. Whether the slight deviations from ideality he observed are real or due to experimental errors can be determined by a repetition of his experiments carried out in such a manner as either to increase the sensitivity of the measurements or to increase the deviations from ideality. Since it is impractical to increase the sensitivity of the measurements due to the difficulties inherent in making the dilutions with sufficient accuracy, it was decided to carry out the measurements at a lower temperature. According to Hildebrand[3] deviations from ideality usually increase with decreasing temperature, and so the deviations observed at 5°, for example, should be somewhat greater than those observed at 25°.

Since the publication of Longsworth's paper, a new value of the density of pure D_2O has appeared in the literature.[4] The value calculated for d^{25}_{25} by Tronstad and Brun from their measured value of d^{20}_{20} is 1.10750, as compared with the value of 1.10790 obtained by Selwood, Taylor, Hipple and Bleakney.[5] A more recent direct measurement at 25° in Tronstad's laboratory[6] gives for d^{25}_{25} 1.10764. This new value necessitates a recalculation of the data in Longsworth's paper and a re-evaluation of the constants of his equation.

Experimental

Twenty-five grams of heavy water from the Ohio Chemical Co. of density 1.1074 was used as the starting material. Since the water had been equilibrated with carbon dioxide at every stage in the electrolysis it was assumed that the oxygen isotope ratio was normal within experimental error and no correction was applied for it.

The ampule containing the water was placed in a larger evacuated capsule connected to the evacuated system, and opened by freezing the contents with a dry ice–ether mixture. The water was then distilled onto alkaline permanganate and allowed to stand for several days with occasional shaking. It was distilled onto a small drop of sulfuric acid and finally twice distilled in vacuum through traps to avoid spattering.

The different concentrations of D_2O used were prepared by successive dilutions of the original sample in a small Erlenmeyer flask equipped with carefully ground glass cap fitting over the neck. After weighing the heavy water in the flask, it was opened and the necessary tap water to dilute it added without spattering. The flask was then quickly closed and the weight of the added tap water found. The flask was weighed with a counterpoise and weighings were recorded to 0.1 mg. Vacuum corrections were applied to all weighings in the usual manner.

The density determinations were made in a Pyrex pycnometer similar to those used by Washburn and Smith[7] and by Smith and Wojciechowski.[8] This had a capacity of approximately 20 cc. and a capillary neck of 1 mm. internal diameter. The capillary was calibrated by weighing known lengths of mercury and was found to be free from appreciable taper. A small bulb of approximately 0.05 cc. capacity was blown in the capillary near the top to take care of the expansion of the liquid between 5° and the temperature of the balance case. A single scratch made with a diamond served as reference mark. The pycnometer was annealed carefully at 525° to avoid internal strains in the glass. After several days at room temperature the volume was found to be constant within the limits of accuracy of the measurements. Thereafter it was never heated above room temperature and was dried by sucking a current of air through it.

In order to fill the pycnometer, a piece of No. 22 stainless steel hypodermic tubing was used. One end of this was waxed into a ground cap, fitting over the neck of the Erlenmeyer flask used to contain the solutions, and extended to the bottom of the flask. The other end was inserted into the neck of the pycnometer. By applying a slight air pressure to the surface of the liquid by means of a small atomizer bulb in series with a drying tube, the liquid could be forced over into the pycnometer. By applying suction, the liquid could be drawn back into the flask. This method avoided contamination from the moisture in the air, and was free from losses, except for surface films left on the walls.

After filling, the pycnometer was placed in the thermostat in a vertical position and the height of the meniscus roughly adjusted by sucking out the excess liquid with a hypodermic needle. Any liquid on the walls above the meniscus was also removed by this process, air being sucked through the needle for several minutes to make sure the walls of the capillary were dry. After standing for about half an hour in the thermostat, the distance between the mark and the meniscus was read with a traveling telescope reading to 0.01 mm. A 10-watt bulb behind a flashed opal

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[2] L. G. Longsworth, THIS JOURNAL, **59**, 1483 (1937).

[3] J. H. Hildebrand, "Solubility," second edition, Reinhold Publishing Co., New York, N. Y., 1936.

[4] L. Tronstad and J. Brun, *Trans. Faraday Soc.*, **34**, 766 (1938).

[5] Selwood, Taylor, Hipple and Bleakney, THIS JOURNAL, **57**, 642 (1935).

[6] Private communication from K. Stokland, Norges Tekniske Høiskole.

[7] E. W. Washburn and E. R. Smith, *Bur. Standards J. Research*, **12**, 305 (1934).

[8] E. R. Smith and M. Wojciechowski, *Roczniki Chem.*, **16**, 104 (1936).

glass behind the capillary provided a very satisfactory source of illumination.

The thermostats used were gallon (4-liter) Thermos jugs, equipped with stirrers and mercury–ether regulators. The temperature in the 25° thermostat was maintained by means of an intermittent heater controlled by a Thyratron relay. The temperature in the 5° bath was maintained by an intermittent stream of prechilled water controlled by a Thyratron relay operating a solenoid valve. Both thermostats were steady to ±0.01°. Temperatures were read with a telescope, using thermometers compared with Bureau of Standards calibrated thermometers.

Results and Discussion

In order to find the deviations of these solutions from ideality, the ideal equation of the form derived by Longsworth was applied to the data. The constants for the equation were found, and the deviations of the observed results from the ideal were calculated. The results are shown in Table I. The first column gives the values of the ideal mole fraction, calculated from the density by the ideal equation, and the fourth column gives the deviations, expressed as the percentage difference between the ideal mole fraction and the experimentally found mole fraction. The values obtained by Longsworth have also been recalculated and included. The values of ΔS in the third column are referred to pure protium oxide, where the difference in density between this and Cambridge tap water is taken to be 16 p. p. m. All calculations were made using the same constants as used by Longsworth, except for the specific gravity of pure deuterium oxide, which was taken as 1.10764 at 25°.

TABLE I

MEASUREMENTS AT 25°

N_{D_2O}	d^{25}_4	ΔS	$N_i - N_e$, %
0.9985	1.10422	0.10748	0
.9353	1.09746	.10070	0
.7780	1.08083	.08402	0
.6051	1.06208	.06521	−0.05
.3784	1.03777	.04084	− .05
.1866	1.01715	.02015	− .11
Longsworth's recalculated data			
0.9942	1.10376	0.10702	0
.8255	1.08570	.08891	0
.6116	1.06279	.06593	0
.4034	1.04044	.04351	0.01
.2024	1.01884	.02185	.05

It is apparent that these solutions can be considered as being ideal, at least from the standpoint of densities. While neither the results of this research nor those of Longsworth fall on the ideal curve, the deviations of the two sets of data from ideality are in opposite directions, and it would be inferred that the true value lies between them. Although the greatest deviations from the equation lie at the lowest concentrations of deuterium oxide, Voskuyl[9] has shown that the densities of these solutions are ideal in the tap-water range, where the concentration of deuterium oxide is extremely low. This being the case, it is evident that the observed deviations from the ideal equation are due to cumulative experimental errors, rather than an abnormal behavior at low concentrations. At the higher concentrations, there is no deviation of the experimentally observed mole fraction from that calculated by the ideal equation.

Thus, at 25°, the equation[2]

$$N_{D_2O} = \frac{9.257\,\Delta S}{1 - 0.033\,\Delta S}$$

can be used to calculate the mole fraction of deuterium oxide from the density of the mixture with entire confidence.

Table II gives the results of the measurements at 5°. In this case also ΔS is referred to pure protium oxide, which is taken as being 15 p. p. m. lighter than tap water.[9] An equation of the same form as the ideal equation was fitted to the data by the method of least squares since the value of the density of pure deuterium oxide at 5° is not known, but is necessary to calculate the value of the ideal constants. This equation was used to calculate the density of pure deuterium oxide at this temperature, the resulting value of d^5_4 being 1.10555. This value is probably correct to ±0.00002.

TABLE II

MEASUREMENTS AT 5°

N_{D_2O}	d^5_4	ΔS	$V - V_a$, p. p. m.
0.9985	1.10539	0.10542	0
.9353	1.09876	.09878	0
.7780	1.08243	.08246	0
.6051	1.06402	.06404	−20
.3784	1.04009	.04011	−10
.1866	1.01978	.01981	0

As Luten[10] has pointed out, the density of an ideal solution is not necessarily a linear function of the mole fraction, but the molecular volume is so. These solutions were tested for ideality by comparing the sums of the volumes of the pure components in the solutions with the volume of the solution calculated from the density. The

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(9) R. J. Voskuyl, Thesis, Harvard University, 1938.

(10) D. B. Luten, Jr., *Phys. Rev.*, **45**, 161 (1934).

differences, although accurate to only 0.001%, are given in p. p. m. in the last column of Table II, where V represents the volume calculated from the density, and V_a the volume calculated additively. It is evident that, even at this temperature, the solutions are ideal. The average deviation from ideality is somewhat smaller than the experimental error, and the largest deviation is only twice the experimental error.

Lewis and Macdonald[11] have pointed out that if the molecular volumes of light and heavy water were the same, the density of deuterium oxide should be 1.1116 instead of 1.1076. Robinson and Bell[12] have shown that in dioxane solutions the partial molal volume of deuterium oxide is even smaller than that of protium oxide over a wide range of concentration, and so we might expect to find an even greater density for deuterium oxide than 1.1116. That this is not the case has been ascribed to a greater coördination of the molecules in deuterium oxide, producing a more open structure in the liquid. Cross, Burnham and Leighton[13] have shown that the coördination in liquid water can be shown to be due to bonds between neighboring oxygens through hydrogens. These bonds are much stronger in deuterium oxide than in protium oxide, and it would appear that the amount of bonding in mixtures of the two is intermediate and directly proportional to the mole fraction. That this is true, even at 5°, where the amount of four-coördination is quite large for both species, would be supported by the results of this research.

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Summary

1. The densities of a series of mixtures of protium and deuterium oxides have been measured at 5 and 25°.

2. From the standpoint of density, these mixtures form ideal solutions at both temperatures.

3. The equation derived for ideal solutions is recommended for calculating the composition of a mixture from the density.

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[11] G. N. Lewis and R. T. Macdonald, THIS JOURNAL, **55**, 3057 (1933).

[12] R. A. Robinson and R. P. Bell, *Trans. Faraday Soc.*, **33**, 650 (1937).

[13] P. C. Cross, J. Burnham and P. A. Leighton, THIS JOURNAL, **59**, 1134 (1937).

[CONTRIBUTIONS FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The Determination of Activity Coefficients from the Potentials of Concentration Cells with Transference. V. Lanthanum Chloride at 25°

BY THEODORE SHEDLOVSKY AND DUNCAN A. MACINNES

The previous papers in this series[1–3] described the underlying theory and the experimental procedure for obtaining activity coefficients from potential measurements on concentration cells with transference of the form

$$\mathrm{Ag;\ AgCl,\ MCl}(C_1)\mathrm{:\ MCl}(C_2)\mathrm{,\ AgCl;\ Ag}\quad\mathrm{(A)}$$

in which M represents the positive ion constituent. The results obtained for aqueous solutions of sodium chloride,[1] hydrochloric acid,[2] potassium chloride and calcium chloride[3] were shown to be in excellent accord with the Debye–Hückel theory at low concentrations. Lanthanum chloride has been chosen for this series as an example of a trivalent electrolyte. Unlike other trivalent chlorides it has the advantage of being practically free from hydrolysis.

The thermodynamic equation connecting the potential E of cell (A) for this salt, the transference number t of the positive ion, the concentration C in gram moles per liter of solution and the activity coefficient f is

$$-E = \frac{4RT}{3F}\int_{C_1}^{C_2} t\,\mathrm{d}\log{(Cf)} \qquad (1)$$

The factor $^4/_3$ arises from the fact that four gram moles of ions—one of lanthanum and three of chloride—are transported in the passages of 3 faradays of current through a corresponding concentration cell without transference. The apparatus, experimental procedure and method of compu-

[1] Brown and MacInnes, THIS JOURNAL, **57**, 1356 (1935).

[2] Shedlovsky and MacInnes, *ibid.*, **58**, 1970 (1936).

[3] Shedlovsky and MacInnes, *ibid.*, **59**, 503 (1937).