of solution data of Lipsett, Maass and Johnson[25] at 25 and 20° to infinite dilution with the aid of the data presented here the integral heat of solution is found to be 916 and 1087 calories per mole at the temperatures 25 and 20°, respectively. The heat of solution data of Cohen and Kooy[26] treated in the same manner give 916 and 1083 calories.[27] The temperature coefficient of the integral heat of solution is $(\bar{c}_{p_s} - \bar{c}^0_{p_2})$. Assuming a linear variation of the integral heat of solution over this small temperature range and substituting the value of $\bar{c}_{p_s}$ given in the "International Critical Tables"[18] the value of -21.9 calories per mole is obtained for $\bar{c}^0_{p_2}$. Randall and Ramage[28] found -21 and Randall and Rossini[9] give -23.3 calories per mole from the extrapolation of direct calorimetric measurements. $\bar{c}_{p_2}$ may be calculated from $\bar{c}_{p_2} = -21.9 + 15.8\ m^{1/2}$.

We are greatly indebted to the National Research Council for two Grants in Aid which made possible the construction of the calorimeter used in this investigation.

Summary

Heats of dilution of aqueous sodium chloride solutions have been measured at low concentrations at intervals of 5° from 25 to 10° and have been extrapolated to infinite dilution to obtain integral heats of dilution. The values of relative partial molal heat contents and partial molal heat capacities have been calculated for the concentration and temperature ranges of the measurements.

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[25] Lipsett, Johnson and Maass, THIS JOURNAL, **49**, 925 (1927); **49**, 1940 (1927).

[26] Cohen and Kooy, *Z. physik. Chem.*, **139**, 273 (1928).

[27] The heat of solution data of Wüst and Lange[12] when combined with our dilution measurements at 25° give 926 calories per mole sodium chloride for the integral heat of solution. We have used the data of Lipsett, Maass and Johnson and Cohen and Kooy because they are available at two temperatures.

[28] Randall and Ramage, THIS JOURNAL, **49**, 93 (1927).

PITTSBURGH, PA. RECEIVED OCTOBER 13, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Freezing Point of Mixtures of H_2O and D_2O. The Latent Heat of Fusion of D_2O

BY VICTOR K. LA MER AND WELDON N. BAKER

In a preliminary communication,[1] we pointed out that the solid phase which separates on freezing a mixture of the isotopic waters, H_2O and D_2O, is a solid solution and that we had been unable to effect a perceptible separation by slow crystallization of a mixture containing 40% D_2O. Since the two components, A = H_2O and B = D_2O, differ only in the isotopic masses of the hydrogen atoms, H and D, it is reasonable to expect that the solid phase will behave as an ideal solid solution. The system should therefore furnish an unusually appropriate example for testing the equations of the perfect solid solution recently developed by Seltz.[2]

In Table I we summarize our cryoscopic measurements obtained with a 15-cc. sample using the ordinary Beckmann technique. The experimental data of the two series of experiments, as shown in Fig. 1, fall upon a smooth curve which may be represented satisfactorily by the formula $\Delta t = 39.42\Delta S - 38.8(\Delta S)^2$. By correcting the formula of Lewis and Luten[3] (relating ΔS, the increase in specific gravity, to N_B the mole fraction of D_2O) from $\Delta S = 0.1056$ for 100% D_2O, to $\Delta S = 0.1079$ at 25°,[4] we obtain the relation $\Delta t = 4.213\ N_B - 0.411\ N_B^2$.

TABLE I

OBSERVED FREEZING POINTS OF D_2O–H_2O MIXTURES

S Sp. gr. 25/25	N_B $N_B = 9.377\Delta S - 1.01(\Delta S)^2$	Δt Obs. increase in f. p., °C.	Δt $\Delta t = 39.42\Delta S - 38.8(\Delta S)^2$	Δt $\Delta t = 4.213\ N_B^2 - 0.411\ N^2_B$
1.001376	0.0129	0.053[5]	0.054	0.054
1.01644	.1539	.632[1]	.638	.639
1.02135	.1997	.824[1]	.824	.825
1.04411	.4117	1.670[1]	1.663	1.665
1.04456	.4158	1.679[1]	1.680	1.681
1.06351	.5915	2.351	2.347	2.348
1.08918	.8282	3.207	3.207	3.207
1.10068	.9338	3.578	3.576	3.576
1.1079	1.000		3.802	3.802

The extrapolated value for the freezing point of pure D_2O is 3.802° ($T_B = 276.98$) in good agreement with the preliminary measurements of Lewis and Macdonald (3.8°),[6] and the later measurements of Taylor and Selwood (3.82°).[4]

For the equilibrium state between a perfect

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[1] La Mer, Eichelberger and Urey, THIS JOURNAL, **56**, 248 (1934).

[2] Seltz, *ibid.*, **56**, 307 (1934).

[3] Lewis and Luten, *ibid.*, **55**, 5061 (1933).

[4] Taylor and Selwood, *ibid.*, **56**, 998 (1934).

[5] Washburn, Smith and Frandsen, *Bur. Stds. J. Res.*, **11**, 453 (1933).

[6] Lewis and Macdonald, THIS JOURNAL, **55**, 3058 (1933).

liquid and a perfect solid solution, Seltz[2] derives the thermodynamic equations

$$N_B = \frac{1 - \exp.\left[\frac{\Delta H_A}{R}\left(\frac{1}{T} - \frac{1}{T_A}\right)\right]}{\exp.\left[\frac{\Delta H_B}{R}\left(\frac{1}{T} - \frac{1}{T_B}\right)\right] - \exp.\left[\frac{\Delta H_A}{R}\left(\frac{1}{T} - \frac{1}{T_A}\right)\right]}$$

$$N_B' = N_B \exp.\left[\frac{\Delta H_B}{R}\left(\frac{1}{T} - \frac{1}{T_B}\right)\right]$$

Here N_B corresponds to the liquidus mole fraction of D_2O and N_B' to the solidus mole fraction. ΔH_B the heat of fusion of pure D_2O is the only unknown. By assigning various values to ΔH_B, we obtain the best agreement with experiment on the assumption that the latent heat of fusion of pure D_2O is 1600 calories per mole compared with 1436 calories for pure H_2O.

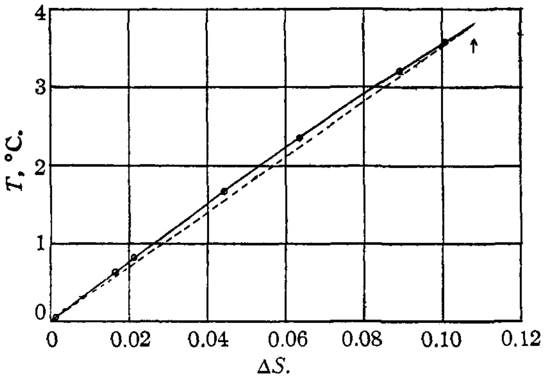

Fig. 1.

The maximum difference in liquidus and solidus points as given in Table II is less than one mole per cent. Since these calculations are based upon the assumption of reversible crystallization, a condition which is difficult to secure in practice, the separation of the isotopes by fractional crystallization offers little promise of success. In his latest communication, Bruni[7] reports a fractional crystallization of 4000 liters of water to a residue of 280 cc. without achieving any definite separation, although preliminary experiments by Bruni and Strada[8] had indicated some separation.

TABLE II

COMPARISON OF THE MOLE FRACTIONS FOR THE LIQUID AND SOLID PHASE, ASSUMING ΔH_B = 1600 IN THE SELTZ FORMULA FOR A PERFECT SOLUTION

Δt, °C.	N_B (exp.)	N_B (calcd.)	N_B' (calcd.)
0.053	0.0129	0.0124	0.0129
.632	.1539	.1512	.1563
.824	.1997	.1981	.2045
1.679	.4158	.4140	.4234
2.351	.5915	.5916	.6007
3.207	.8282	.8285	.8337
3.578	.9338	.9351	.9373

Since executing the above work, heavy water of S_{25}^{25} = 1.10733, N_{D_2O} (calcd.) = 0.9948, Δt = 3.762°, instead of 3.784° as calculated by the equation given above, has become available through a grant from The Chemical Foundation, Inc. The sample was prepared by the Ohio Chemical Company working in coöperation with the Chemistry Department of Pennsylvania State College, whereas the samples referred to above were prepared using the electrolytic apparatus in this Laboratory.

We have determined the mole fraction freezing point depression constant ($\Delta t/n$) using potassium chloride as solute with this sample and with ordinary water. Corrections for supercooling were made using the formula, weight of water in the solution, $G_1 = G_0(1 - (Ct/Q))$ where G_0 = amount of water present before ice is formed, C = the specific heat of the water per gram, t the supercooling in degrees, and Q the latent heat of fusion per gram. The results are given in Table III.

TABLE III

	KCl added, g.	N_{KCl}	$-\Delta t$	$(-\Delta t/N_{KCl})$
	H_2O used = 15.517 g. = 0.8614 mole			
1A	0.30168	0.004676	0.874	186.9
2A	.62616	.009657	1.778	184.1
3A	.95295	.01462	2.683	183.5
	D_2O used = 16.875 g. = 0.8431 mole			
1B	0.30523	0.004832	0.878	181.7
2B	.61316	.009660	1.743	180.4
3B	.91694	.01438	2.587	179.9

Since $\Delta t/N = \phi\ (\Delta H/RT^2)$, we have

$$\Delta H_B = \Delta H_A \times \frac{T_B^2}{T_A^2}\frac{(\Delta t/N)_A}{(\Delta t/N)_B}$$

From these pairs of values, interpolated to the same mole fraction, we obtain ΔH_B = 1518, 1507 and 1506, or an average value of 1510 calories for the latent heat of fusion of 99.48% D_2O. The assumption that ϕ, the osmotic coefficient of potassium chloride in H_2O, is the same in D_2O seems justifiable in the light of the statement of Lewis, Olson and Maroney[9] that the dielectric constant of D_2O is only 1% lower than that of H_2O.

The depressions in experiments 1A, 2A, 3A and 1B were reproducible to 0.001° using different degrees of supercooling in several experiments, but in experiments 2B and 3B the individual values increased slightly with time, due, we be-

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[7] Bruni, THIS JOURNAL, **56**, 2013 (1934).

[8] Bruni and Strada, *Sci. Abst.*, **37**, 642 (1934).

[9] Lewis, Olson and Maroney, THIS JOURNAL, **55**, 4731 (1933).

lieve, to absorption of H_2O from the glass and from unavoidable contamination with the atmosphere. We estimate that these values of ΔH_B are at least ten calories too low, since the D_2O remained in the apparatus for forty-eight hours, although closed to the atmosphere, except during addition of potassium chloride and stirring. At the conclusion of the experiments S^{25}_{25} = 1.10641 or 98.6% D_2O; Δt = 3.760 (calcd.).

The discrepancy between our experimental value and that calculated by the Seltz equation may be due to the fact that the latter treatment neglects the role of the equilibrium, $H_2O + D_2O = 2HDO$.[10]

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[10] E. S. Gilfillan, Jr., THIS JOURNAL, **56**, 2201 (1934).

NEW YORK, N. Y. RECEIVED OCTOBER 15, 1934

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Transition Point of Sodium Sulfate Decadeuterate

BY HUGH S. TAYLOR

The transition point of sodium sulfate, a quadruple point involving sodium sulfate decahydrate, the anhydrous salt, saturated solution and vapor has been shown by Richards and Wells[1] to be 32.383 ± 0.001° on the International hydrogen scale of temperature. They concluded that this fixed point was equally as reliable as the ice point and more reliable than the boiling point of water unless the most careful precautions were exercised in the latter case. The extraordinary reproducibility of the transition point was attributed to the very small influence of the external pressure, the ready purification of the substance and "the certainty of obtaining a definite crystal form and homogeneity probably greater than with water, because, in the crystal growth, it is far easier to obtain independent and freely growing crystals."

The discovery of the isotopic forms both of hydrogen and of oxygen has revealed that a fourth parameter is involved in the reproducibility of such fixed points, namely, the constancy of isotopic concentration ratios of the several elements in the system under study. The isolation of deuterium oxide revealed that a disturbance of the hydrogen isotope ratio might produce deviations from the ice point amounting to 3.82°.[2] It was of interest, therefore, to ascertain the corresponding variation in the transition point of sodium sulfate when deuterium oxide was the solvent used. We have accordingly determined this transition point, producing the material from anhydrous sodium sulfate and deuterium oxide in the weight ratios given by Na_2SO_4 and $10D_2O$. The water used had a density d^{25}_{25} 1.10784, and was, therefore, better than 99.9% pure D_2O. It is probable that, in this water, prepared by the electrolytic process, the oxygen isotope ratio was normal since, in each stage of the electrolysis, this ratio should have been normalized to that of the carbon dioxide gas which was used to convert alkali hydroxide to carbonate. A thermometer reading in 0.1° was used and calibrated by means of the sodium sulfate decahydrate transition. Experiment showed that the deviation produced in the transition point was 2.10° and that the transition point with the deuterium oxide as solvent was 34.48 ± 0.02°. It is of interest to note that the magnitude of the deviation, approximately one-half that obtaining at the ice point, is sufficiently small that, assuming proportionality between deuterium concentration and deviation, the transition point of sodium sulfate in pure protium water solutions would be within the accuracy of the determination of Richards and Wells. With water from the equilibriated electrolyte in hydrogen–oxygen cells, containing one atom of deuterium to approximately 1600 of hydrogen, the deviation from 32.383° in the transition point would again be scarcely outside the limits of accuracy set by the original investigators. The data cited by Gilfillan[3] for the freezing point of $H^{1}_{2}O^{18}$, $-0.1 \pm 0.05°$, indicate quite definitely that disturbance of the oxygen isotope ratio will be equally ineffective in significantly altering the value of the transition point.

Summary

The transition point of sodium sulfate in pure deuterium water has been found to be 34.48°.

The influence of isotope ratio on the accepted value for the sodium sulfate decahydrate transition has been discussed.

PRINCETON, N. J. RECEIVED OCTOBER 20, 1934

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[1] Richards and Wells, *Z. physik. Chem.*, **43**, 465 (1903).

[2] Taylor and Selwood, THIS JOURNAL, **56**, 998 (1934).

[3] Gilfillan, THIS JOURNAL, **56**, 2201 (1934).