

nitrate with nitron.<sup>4</sup> Fluorine was determined by precipitation as lead chlorofluoride. In order that the percentage of both nitrogen and fluorine could be calculated, the vapor density of the gas was taken as 82.0. The results are shown in Table II. The letter A represents the number of gram atoms of nitrogen in 22.4 liters of the gas at standard conditions, and B is the corresponding quantity of fluorine.

TABLE II  
ANALYSIS OF THE GAS

N, %	F, %	A	B
16.8	23.15	0.984	0.999
17.0	23.13	.996	.998

In addition to one atom of nitrogen and one of fluorine, found by the analyses, each molecule of the gas must have contained three oxygen atoms. This conclusion may be reached by considering the properties of the possible compounds of the elements which could have been present: nitrogen, fluorine, oxygen, hydrogen. A reaction such as that observed in the case of sodium hydroxide could have resulted only from the action of  $\text{NO}_3\text{F}$  or one of its hydrates. However, the vapor density of the gas, about 82.0, permits one to decide that the substance was not hydrated and that its formula was  $\text{NO}_3\text{F}$ , a compound of which the molecular weight is 81.0.

(4) Busch, *Ber.*, **38**, 861 (1905).

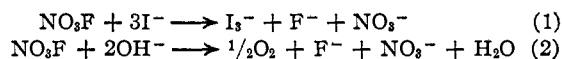
The selection of a good name for this compound is not an easy task. Most of the chemists who have been consulted agree that a correct but not very descriptive name would be nitrogen trioxyfluoride.

Two substances which are related to  $\text{NO}_3\text{F}$ ; namely, nitrosyl fluoride<sup>5</sup> and nitryl fluoride,<sup>6</sup> have been known for some time.

The author wishes to thank Professor W. C. Schumb and Dr. N. A. Milas for their interest and helpful advice.

### Summary and Conclusions

The reaction of fluorine with moderately dilute nitric acid produces a gaseous compound which has the formula  $\text{NO}_3\text{F}$ . When heated, the gas explodes, but it may be handled without difficulty at room temperatures. The substance has an irritating odor, is colorless and boils at about  $-42^\circ$ . It is moderately soluble in water, with which it reacts slowly, liberating oxygen. With solutions of potassium iodide and of potassium hydroxide, it reacts according to the equations



(5) G. Gore, *J. Chem. Soc.*, **22**, 391 (1889).

(6) H. Moissan and P. Lebeau, *Compt. rend.*, **140**, 1576 and 1621 (1905).

CAMBRIDGE, MASS.

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[CONTRIBUTION 292 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

## Integral Heats of Dilution, Relative Partial Molal Heat Contents and Heat Capacities of Dilute Aqueous Sodium Chloride Solutions<sup>1</sup>

BY E. A. GULBRANSEN AND A. L. ROBINSON

### I. Introduction

The thermochemical properties of aqueous sodium chloride solutions have been studied extensively recently<sup>2</sup> over rather wide temperature and concentration ranges but except at  $25^\circ$  there are no reliable measurements of heat contents or heat capacities at concentrations below  $0.05 m$ . It is in this dilute region that measurements are particularly important for extrapolation to infinite dilution and for comparison with the predictions of current theories of strong electrolytes. In this paper are reported meas-

(1) From the thesis of E. A. Gulbransen presented to the Graduate School of the University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1934.

(2) Randall and Bisson, *THIS JOURNAL*, **42**, 347 (1920); Richards and Gucker, *ibid.*, **51**, 712 (1929); and other references.

(3) Robinson, *ibid.*, **54**, 1311 (1932).

urements of intermediate heats of dilution of aqueous sodium chloride solutions at 25, 20, 15 and  $10^\circ$  from  $0.8 m$  ( $0.4 m$  at 15 and  $10^\circ$ ) to  $0.00016 m$  ( $0.00032 m$  at  $10^\circ$ ). From these results integral heats of dilution ( $\Delta H_\infty$ ),<sup>4</sup> relative partial molal heat contents ( $\bar{L}_1$  and  $\bar{L}_2$ )<sup>5</sup> and relative partial molal heat capacities ( $\bar{c}_{p_2} - \bar{c}_{p_1}^0$ ) have been calculated for the temperature and concentration ranges of the measurements.

### II. Apparatus and Experimental Procedure

A differential adiabatic calorimeter similar to the one

(4) The integral heat of dilution is the heat absorbed when a solution containing one mole of solute is diluted to  $m = 0$ .  $\Delta H_\infty = -m\bar{L}_1 - \bar{L}_2$  ( $m$  is the number of moles of water associated with one mole of solute).

(5) Where possible the nomenclature of Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York City, 1923, is used.

developed by Lange and his co-workers<sup>6</sup> was employed. The following details indicate the principal changes (mostly minor) incorporated into the present apparatus.

The thermopile, built according to the design of Lange and Streeck,<sup>6c</sup> consists of 1330 iron-constantan thermocouples and has a total resistance of 70 ohms. It is connected directly to a Leeds and Northrup narrow coil type HS galvanometer which has a sensitivity of 0.089 microvolt per mm. deflection at a scale distance of one meter. With a scale distance of 6 meters the maximum sensitivity used in this work was equivalent to 0.0003 calorie per mm. deflection corresponding to a temperature change of about  $2.5 \times 10^{-7}^\circ$ . For most of the measurements a sensitivity of about one-fourth of this value was sufficient and was obtained by use of a shunt of proper resistance.

To obtain a continuous reading of the galvanometer before, during and after a dilution a semi-automatic recording device<sup>6b</sup> driven by an electric clock motor was used.

The calorimeter is an unsilvered Dewar flask of about 2.5 liters capacity. Each half of the calorimeter contained 1000 cc. of water or solution, depending on whether a first or second dilution was being carried out. The pipets, holding the solution to be diluted, have volumes of  $25.67 \pm 0.02$  cc.

The heating elements, used for compensating the heat effect of a dilution and for electrical calibration of the calorimeter, are of cupron wire enclosed in glass capillaries a few hundredths of a millimeter larger in internal diameter than the wire. The resistances of the two heaters are matched and have remained constant to within 0.02% over a period of months. To switch the heating

calorimeter, are driven by a governed motor of the universal type through a chain drive.

The heat conductivity constant of the calorimeter is 0.006 minute<sup>-1</sup>. The temperature difference between the calorimeter contents and the outside bath is measured by a 24-junction copper-advance thermopile. The adiabatic control is constant to  $\pm 0.0001^\circ$ . Since the two halves of the calorimeter are very nearly symmetrical (to within 1 or 2%) disturbances due to a difference in temperature between the calorimeter and the outside bath are negligible. For most of the dilutions the temperature changes produced in the calorimeter were less than  $10^{-4}^\circ$ ; the method of measurement is practically "isothermal-adiabatic" calorimetry.

The toluene-mercury regulator for the outer bath is constructed of soft copper tubing coiled into a form convenient for the dimensions of the bath.<sup>7</sup> The tubing has a volume of 1470 cc. and a surface area of 5720 sq. cm. To hold the temperature of the bath constant (for runs near room temperature) the heat generated by stirring is balanced by a fine stream of cold water controlled by electromagnets activated by the regulator or (for runs above or below room temperature) by fine streams of cold or hot water. The regulator responds to a temperature change of  $5 \times 10^{-4}^\circ$  within three seconds.

The experimental procedure and method of determining the value of the heat effect are the same as previously described.<sup>6a,b</sup>

Mallinckrodt c. p. sodium chloride was recrystallized three times and dried for twenty-four hours at  $220^\circ$ .

### III. Results

TABLE I  
HEATS OF DILUTION OF AQUEOUS SODIUM CHLORIDE SOLUTIONS

$m_1$	$m_2$	Runs	Cal./mole NaCl						
			25°	20°	15°	10°			
0.816	0.02025	3	+39.6±0.7	2	+73.7±0.6				
.816	.0425	3	+54.0±0.5	2	+86.8±0.4				
.404	.01025	4	-30.6±0.8	2	-6.45±0.1	2	-25.5±0.0	2	+60.8±0.3
.404	.02025	4	-18.1±0.4	2	+6.2±0.1	2	-34.4±0.2	2	+68.3±0.2
.2	.00512	5	-57.1±0.5	2	-41.8±0.1	2	-20.7±0.4	2	-1.9±0.1
.2	.0101	5	-48.8±0.6	2	-32.7±0.1	2	-14.2±0.2	2	+4.9±0.1
.1	.00257	7	-65.1±0.3	4	-50.3±0.1	2	-40.3±0.3	3	-26.3±0.4
.1	.00507	7	-55.9±0.4	4	-43.5±0.7	2	-32.7±0.1	2	-22.1±0.3
.05	.001285	10	-56.2±0.8	2	-49.2±0.1	3	-39.1±0.5	3	-28.9±0.6
.05	.002535	9	-51.1±0.6	2	-43.9±0.9	3	-34.7±0.9	2	-24.6±0.7
.025	.000642	13	-46.4±1.4	2	-45.9±0.5	2	-38.0±0.2	2	-30.6±0.0
.025	.00128	10	-41.1±1.5	2	-39.9±0.9	2	-33.1±0.1	2	-28.1±0.3
.0125	.000322	5	-34.6±1.0	2	-32.2±0.1	4	-32.5±0.4	2	-24.7±0.1
.0125	.000634	5	-30.8±0.7	2	-30.4±0.6	4	-29.0±0.4	2	-23.3±0.1
.00625	.000161	6	-27.6±1.6	4	-25.3±0.6	3	-23.7±0.8		
.00625	.000318	6	-24.6±1.6	4	-20.2±0.3	2	-20.2±0.2		

current into the heaters, and to control accurately the time of heating by means of an electric clock, a special electrical circuit<sup>6a</sup> is used by means of which the time of heating can be determined to 0.01 second.

The mirror image stirrers, one in each half of the

(6) (a) Lange and Monheim, *Z. physik. Chem.*, **149A**, 51 (1930); (b) Lange and Robinson, *Chem. Rev.*, **9**, 89 (1931); (c) Lange and Streeck, *Z. physik. Chem.*, **157A**, 1 (1931).

The first two columns of Table I give the initial and final concentrations of a dilution, respectively. The remainder of the table indicates the number of duplicate runs, the average value of the intermediate heat of dilution and the probable

(7) The Ruud Manufacturing Company very kindly aided in the forming of this coil.

error at each temperature. It is estimated that systematic errors (errors in the measurement of concentration, time, potential, resistance, etc.) are less than one %.

**Treatment of Results.**—The data of Table I are plotted against the square root of the molality in Fig. 1. Below  $m^{1/2} = 0.1$  the experimental points lie on a straight line within the limit of experimental error and the curves have been extrapolated linearly to infinite dilution to obtain integral heats of dilution by applying the method of least squares to all measurements below  $m^{1/2} = 0.1$ . An additional uncertainty of about one calorie is introduced into the values of the integral heat of dilution by this extrapolation. There is some evidence of continuously changing slope to  $m = 0$  but the heat effects below  $m^{1/2} = 0.1$  are too small to decide this question definitely.

The relative partial molal heat content of sodium chloride ( $\bar{L}_2$ ) was evaluated from  $\bar{L}_2 = -\Delta H_\infty - (m^{1/2}/2)d/dm^{1/2} (\Delta H_\infty)$ .<sup>8</sup> The slopes of the smoothed curves of Fig. 1 were determined from a large scale plot by use of the differentiated form of the Lagrange interpolation formula.  $\bar{L}_1$  values were obtained from the relation  $\bar{L}_1 = (-\Delta H_\infty - \bar{L}_2)/n_1$  where  $n_1$  is the number of moles of water associated with one mole of sodium chloride. In Table II are listed values of  $\Delta H_\infty$ ,  $\bar{L}_1$  and  $\bar{L}_2$  for various concentrations in the range of these measurements.

mittedly the temperature range of these measurements is too small to allow a definite decision. The slopes of the straight lines so obtained ( $d\bar{L}_2/dT = \bar{c}_{p_2} - \bar{c}_{p_2}^0$ ) have been plotted against  $m^{1/2}$  in Fig. 2, where for comparison also are shown the results of Randall and Rossini<sup>9</sup> and Harned and Nims<sup>10</sup> and the limiting law slope according to

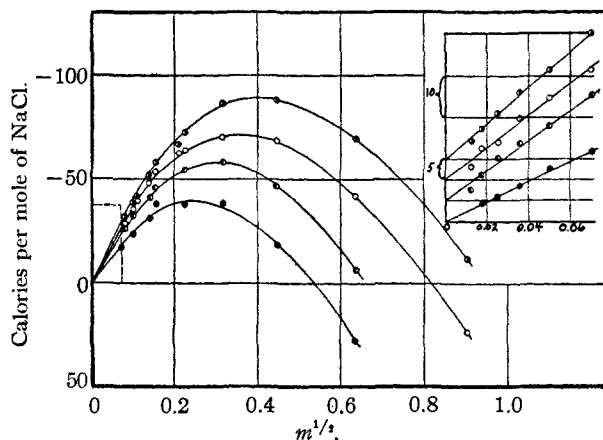


Fig. 1.—Heats of dilution of aqueous sodium chloride solutions:  $\bullet$ , 25°,  $\circ$ , 10°,  $\ominus$ , 15°,  $\bullet$ , 10°. Measurements below  $m^{1/2} = 0.07$  are shown in the larger scale plot where each curve is offset 5 calories from the preceding curve for convenience in plotting.

the theory of Debye and Hückel. A straight line with a slope of 15.8 expresses the results  $\bar{c}_{p_2} - \bar{c}_{p_2}^0 = 15.8 m^{1/2}$  cal. mol.<sup>-1</sup> deg.<sup>-1</sup>.

The  $\bar{L}_2$  values at 25° given in Table II agree well with those previously reported by Robinson<sup>3</sup>

TABLE II  
INTEGRAL HEATS OF DILUTION AND RELATIVE PARTIAL MOLAL HEAT CONTENTS OF AQUEOUS SODIUM CHLORIDE SOLUTIONS

$m$	$\Delta H_\infty$ , cal./mole, NaCl				$\bar{L}_2$ , cal./mole, NaCl				$\bar{L}_1$ , cal./mole, H <sub>2</sub> O			
	25°	20°	15°	10°	25°	20°	15°	10°	25°	20°	15°	10°
0.0001	-4.2	-3.7	-3.4	-2.3	6.3	5.3	4.7	3.0	-0.000038	-0.000036	-0.000024	-0.000013
.0005	-9.4	-8.2	-7.7	-4.3	14.8	13.1	12.0	8.3	-.000049	-.000044	-.000039	-.000036
.001	-13.2	-11.6	-10.8	-7.5	20.1	17.9	16.5	11.5	-.00012	-.00011	-.00010	-.000072
.005	-29.6	-26.0	-24.3	-16.9	42.2	38.1	35.8	25.6	-.0011	-.0011	-.0010	-.00078
.01	-39.3	-36.2	-33.3	-23.9	55.8	51.0	46.0	34.8	-.0030	-.0027	-.0029	-.0020
.05	-71.3	-63.5	-54.2	-40.6	93.7	76.3	65.0	43.2	-.020	-.012	-.0098	-.0023
.1	-86.5	-70.0	-58.3	-38.6	99.6	76.6	57.7	30.2	-.024	.051	.00011	.015
.2	-87.6	-68.3	-46.3	-18.3	85.0	54.2	9.4	-20.0	.0094	.44	.13	.14
.404	-69.4	-42.3	-6.6	27.2	30.0	-19.4	-89.9	-130.0	.28	2.11	.70	.65
.816	-11.7	+23.5			-123.3	-169.7			1.19			

To obtain  $(\bar{c}_{p_2} - \bar{c}_{p_2}^0)$  the  $\bar{L}_2$  values of Table II have been plotted against the temperature for the concentrations listed in Table II. The data do not cover a sufficient temperature range to permit the drawing of anything but straight lines. A slight but definite S curvature is apparent at all concentrations and seems to be more than can be accounted for by experimental error but ad-

(8) Rossini, *Bur. Standards J. Research*, **6**, 799 (1931).

and are also in good agreement with the calorimetric results of Young and Vogel<sup>11</sup> for the concentration range in which the two series of measurements overlap (0.8 to 0.05  $m$ )<sup>12</sup> but differ by

(9) Randall and Rossini, *THIS JOURNAL*, **51**, 323 (1929).

(10) Harned and Nims, *ibid.*, **54**, 423 (1932).

(11) Young and Vogel, *ibid.*, **54**, 3030 (1932).

(12) The values for  $\Delta H_\infty$  and  $\bar{L}_2$  are also in agreement with the values at 18° calculated by Rossini [*Bur. Standards J. Research*, **6**, 791 (1931)] from the calorimetric data of Richards and Rowe [*THIS JOURNAL*, **43**, 770 (1921); Wüst and Lange, *Z. physik. Chem.*, **116**, 161 (1925); Pratt, *J. Franklin Inst.*, **185**, 663 (1918); *et al.*].

10 to 40% from the results of Harned and Nims<sup>10</sup> obtained from e. m. f. measurements. It is estimated that the  $\bar{L}_2$  values of Table II are accurate to within 5%. It is more difficult to estimate the probable error in  $(\bar{c}_{p_2} - \bar{c}_{p_2}^0)$ , but it is probably not more than 15%.

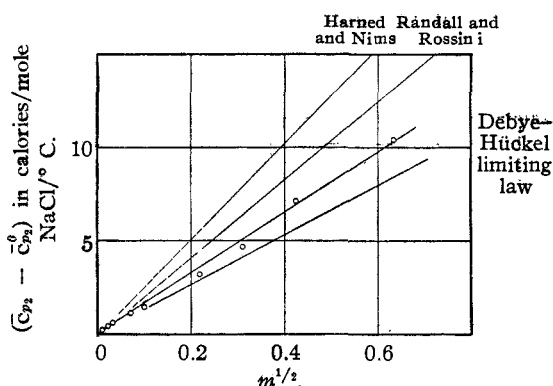


Fig. 2.—Relative partial molal specific heat of sodium chloride in dilute aqueous solutions.

#### IV. Discussion

The Debye-Hückel limiting law value for the integral heat of dilution of strong electrolytes as derived by Bjerrum<sup>13</sup> and modified by Scatchard<sup>14</sup> and Gatty<sup>15</sup> to take account of the fact that the dilution is carried out at constant pressure is

$$\Delta H_{\infty} = 2.889/10^8(e^3 N^{3/2}/D^{3/2})(\pi/10^8 kT)^{1/2}(\nu_1 z_1^2)^{1/2}(1 + T/D(dD/dT) + T/3V(dV/dT)) \text{ cal./mole}^{16}$$

The term in  $dV/dT$  reduces the value of the limiting slope by 7.2% at 25°. At lower temperatures the effect is much smaller since at 3.98°  $dV/dT = 0$ . To evaluate the theoretical limiting slope the dielectric constant measurements of Wyman<sup>17</sup> were used and the term in  $dV/dT$  was calculated from data given in the "International Critical Tables."<sup>18</sup> The theoretical slopes calculated in this manner are -480, -436, -412 and -360 at 25, 20, 15 and 10°; the corresponding values of the experimental slopes are -418, -370, -340 and -239. Some significance may be attached to the fact that when the theoretical slope changes rapidly the experimental slope also changes rapidly. An inflection point for both the theoretical and experimental slopes is indicated at 17-18°.

(13) Bjerrum, *Z. physik. Chem.*, **119**, 145 (1926).

(14) Scatchard, *THIS JOURNAL*, **53**, 2037 (1931).

(15) Gatty, *Phil. Mag.*, **11**, 1082 (1931).

(16)  $\nu_i$  is the number and  $z_i$  is the valence of ions of the  $i$ th kind; the other symbols have their usual significance.

(17) Wyman, *Phys. Rev.*, **35**, 623 (1930).

(18) "International Critical Tables," McGraw-Hill Book Co., New York City.

Randall and Rossini<sup>9</sup> have calculated limiting law values for the relative partial molal heat capacities of strong electrolytes by a double differentiation of the Debye-Hückel<sup>19</sup> free energy expression. For the dielectric constant of water they used the equation of Adams<sup>20</sup> which is based on the measurements of Kockel.<sup>21</sup> For uni-univalent electrolytes they obtained  $\bar{c}_{p_2} = 6 m^{1/2} + \bar{c}_{p_2}^0$ .<sup>22</sup> La Mer and Cowperthwaite<sup>23</sup> have recently derived a limiting law for heat capacities in the same manner but have taken account of the correction pointed out by Gatty<sup>15</sup> and Scatchard<sup>14</sup> and have used the dielectric constant data of Wyman.<sup>17</sup> For uni-univalent electrolytes they obtain  $\bar{c}_{p_2} = 13.25 m^{1/2} + \bar{c}_{p_2}^0$ . The agreement of the experimental value of the slope (15.8) with this theoretical value is largely fortuitous since a term in  $d^2D/dT^2$  in the expression of La Mer and Cowperthwaite has approximately this same magnitude (but opposite sign) and although  $dD/dT$  for water is probably known with an accuracy of 5%,<sup>24</sup>  $d^2D/dT^2$  is uncertain to within 50% or more. The temperature coefficient of  $(\bar{c}_{p_2} - \bar{c}_{p_2}^0)$  for uni-univalent electrolytes is 0.16 cal. mole<sup>-1</sup> °C.<sup>-2</sup> between 10 and 25° according to the equation of La Mer and Cowperthwaite but this value is even more uncertain than the theoretical value of the slope of  $(\bar{c}_{p_2} - \bar{c}_{p_2}^0)$  vs.  $m^{1/2}$  because of the large uncertainty in  $d^2D/dT^2$ . Drawing straight lines for the plots of  $\bar{L}_2$  vs.  $T$  is of course equivalent to a decision to interpret  $(\bar{c}_{p_2} - \bar{c}_{p_2}^0)$  as having constant values within the experimental error for the temperature range of these measurements. The experimental slope of 15.8 is lower than the value of 21 found by Randall and Rossini<sup>9</sup> from calorimetric measurements and the value of 24.8 obtained by Harned and Nims<sup>10</sup> from e. m. f. data. The measurements of these investigators extended to 0.05  $m$ . The zero temperature coefficient for  $(\bar{c}_{p_2} - \bar{c}_{p_2}^0)$  agrees with previous investigations.

To evaluate  $\bar{c}_{p_2}$  it is necessary to know  $\bar{c}_{p_2}^0$ . The integral heat of solution of sodium chloride is the heat absorbed when one mole of the salt is dissolved in an infinite amount of water and is equal to  $-(H_s - \bar{H}_2^0)$ . Extrapolating the heat

(19) Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

(20) Adams, *THIS JOURNAL*, **48**, 621 (1926).

(21) Kockel, *Ann. Physik*, **77**, 417 (1926).

(22) The use of Wyman's dielectric constant data in the equation of Randall and Rossini gives a value of 12.4 for the limiting slope.

(23) La Mer and Cowperthwaite, *THIS JOURNAL*, **55**, 1004 (1933).

(24) Lange and Robinson, *ibid.*, **52**, 2611 (1930).

of solution data of Lipsett, Maass and Johnson<sup>25</sup> 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<sup>26</sup> treated in the same manner give 916 and 1083 calories.<sup>27</sup> The temperature coefficient of the integral heat of solution is  $(\bar{c}_{p_s} - \bar{c}_{p_s}^0)$ . 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"<sup>18</sup> the value of -21.9 calories per mole is obtained for  $\bar{c}_{p_s}^0$ . Randall and

(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<sup>12</sup> 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.

Ramage<sup>28</sup> found -21 and Randall and Rossini<sup>9</sup> give -23.3 calories per mole from the extrapolation of direct calorimetric measurements.  $\bar{c}_{p_s}$  may be calculated from  $\bar{c}_{p_s} = -21.9 + 15.8 m^{1/2}$ .

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.

(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<sub>2</sub>O and D<sub>2</sub>O. The Latent Heat of Fusion of D<sub>2</sub>O

BY VICTOR K. LA MER AND WELDON N. BAKER

In a preliminary communication,<sup>1</sup> we pointed out that the solid phase which separates on freezing a mixture of the isotopic waters, H<sub>2</sub>O and D<sub>2</sub>O, is a solid solution and that we had been unable to effect a perceptible separation by slow crystallization of a mixture containing 40% D<sub>2</sub>O. Since the two components, A = H<sub>2</sub>O and B = D<sub>2</sub>O, 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.<sup>2</sup>

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<sup>3</sup> (relating  $\Delta S$ , the increase in specific gravity, to  $N_B$  the mole fraction of D<sub>2</sub>O)

from  $\Delta S = 0.1056$  for 100% D<sub>2</sub>O, to  $\Delta S = 0.1079$  at 25°,<sup>4</sup> we obtain the relation  $\Delta t = 4.213 N_B - 0.411 N_B^2$ .

TABLE I

OBSERVED FREEZING POINTS OF D<sub>2</sub>O-H<sub>2</sub>O MIXTURES

<i>S</i>	$\frac{N_B}{N_B} = \frac{9.377 \Delta S}{1.01 (\Delta S)^2}$	$\frac{\Delta t}{\text{Obs. increase in f. p., } ^\circ\text{C.}}$	$\frac{\Delta t}{39.42 \Delta S - 38.8 (\Delta S)^2}$	$\frac{\Delta t}{4.213 N_B - 0.411 N_B^2}$
Sp. gr. 25/25	1.01 ( $\Delta S$ ) <sup>2</sup>			
1.001376	0.0129	0.053 <sup>5</sup>	0.054	0.054
1.01644	.1539	.632 <sup>1</sup>	.638	.639
1.02135	.1997	.824 <sup>1</sup>	.824	.825
1.04411	.4117	1.670 <sup>1</sup>	1.663	1.665
1.04456	.4158	1.679 <sup>1</sup>	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<sub>2</sub>O is 3.802° ( $T_B = 276.98$ ) in good agreement with the preliminary measurements of Lewis and Macdonald (3.8°),<sup>6</sup> and the later measurements of Taylor and Selwood (3.82°).<sup>4</sup>

For the equilibrium state between a perfect

(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).

(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).