[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

Calcium Nitrate. IV. Heats of Dilution of Solutions of Calcium Nitrate in Water

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If n_2 moles of solute are dissolved in n_1 moles of water giving a solution of concentration m, the increase in heat content, ΔH, is a measure of the heat absorbed by the reaction. This is called the total or integral heat of solution. If n_2 moles of solute are dissolved in such a large volume of solution of concentration m that there is no change in concentration, the increase in heat content, $n_2\Delta\text{H}_2$ is called the partial, or differential, heat of solution of the solute. Similarly, if n_1 moles of water are dissolved in such a large volume of solution that there is no change in concentration, $n_1\Delta\text{H}_1$ is termed the partial, or differential, heat of solution of water in the solution. These quantities are related by the equation

$$\Delta H = n_2\Delta\text{H}_2 + n_1\Delta\text{H}_1 \tag{1}$$

where ΔH_2 and ΔH_1 are the partial molal heats of solution of solute and solvent, respectively. If ΔH is known at several concentrations, ΔH_2 can be evaluated by determining the slope of the curve obtained by plotting ΔH against m. ΔH_1 can then be evaluated by means of equation (1). ΔH_1 can also be calculated from vapor pressure data if the vapor pressures of the solutions are known at two temperatures. In this article, the determinations of the partial heat of solution of water in calcium nitrate solutions from calorimetric data and from vapor pressure data are presented.

Previous studies on heats of dilution in concentrated solutions have been made by a few workers, notably by Randall and Bisson[1] on sodium chloride solutions; and by Harrison and Perman[2] on calcium chloride and potassium chloride solutions; but the solubility of the substances studied had only a limited range, the highest concentration of sodium chloride, for example, being only 6.12 molal. The concentration of a saturated solution of calcium nitrate anhydride in water at 25° is 77.3%, or 20.75 moles in 1000 g. of water. At this concentration, the solution is supersaturated with respect to the dihydrate, the trihydrate and the tetrahydrate. The solution is stable enough that it can be kept for long periods of time, however; and it withstands considerable experimental manipulation without crystallizing. Solutions of calcium nitrate, therefore, serve as systems on which heat of dilution studies can be carried out over a very large range of concentrations.

Randall and Bisson[1] and MacInnes and Braham[3] have measured ΔH_1 directly by dissolving small quantities of water in large volumes of solution.

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(1) Randall and Bisson, THIS JOURNAL, **42**, 347 (1920).

(2) Harrison and Perman, *Trans. Faraday Soc.*, **23**, 1 (1927).

(3) MacInnes and Braham, THIS JOURNAL, **39**, 2110 (1917).

This procedure was not feasible with calcium nitrate solutions because the concentrated solutions were both viscous and in a metastable condition. When small quantities of water were added to the viscous solution, it was difficult to obtain uniform distribution. There was also danger that the manipulation in the calorimeter would disturb the metastable equilibrium whereupon the whole solution would crystallize. The procedure followed was to dissolve small quantities of solution in 1000 g. of water. These heats of dilution could be calculated to infinite dilution since Lange and Streeck[4] have measured heats of dilution of calcium nitrate solutions from one-tenth molal to infinite dilution. From these heats of dilution and the heat of solution of calcium nitrate anhydride, the quantities involved in equation (1) can be calculated.

Experimental

The apparatus used has been described in a previous article.[5] The only alteration was the replacement of the mercury-in-glass thermometer by a platinum resistance thermometer. This thermometer was of the knife blade type, made by Leeds and Northrup, and calibrated at the Bureau of Standards. The resistance of this thermometer was measured by means of a Mueller type temperature bridge, made by the Eppley Laboratory, Inc. The resistances of this bridge were immersed in oil, of which the temperature was maintained constant by a thermostatic control. Resistances could be measured to 0.0001 ohm, and estimated to 0.00003 ohm. This gave temperature differences accurate to 0.0005°.

In each run four small sealed bulbs containing a calcium nitrate solution of known concentration were placed in the calorimeter containing 1000 g. of water. The solution

TABLE I

HEATS OF DILUTION AND OF SOLUTION

	Orig. concn.		Total heat of dilution ΔH in joules per mole $Ca(NO_3)_2$				Total heat of solution	
1	Moles per 1000 g. H_2O, m 2	n_2/n_1 3	Run 1 4	Run 2 5	Run 3 6	Av. 7	1 mole $Ca(NO_3)_2$ in req. amt. H_2O 8	m moles $Ca(NO_3)_2$ in 1000 g. H_2O 9
$Ca(NO_3)_2$	0.01	0.0002				− 640[a]	−18,610	− 186
	.1	.0018				− 900[a]	−18,350	− 1,835
	1.393	.0244	+2488	+2507	+2442	+2479	−21,729	− 30,269
	2.552	.0460	+4111	+4124	+4152	+4129	−23,379	− 59,663
	3.96	.0714	+5036	+5000		+5018	−24,268	− 96,101
	4.03	.0726	+5027	+5055	+5066	+5049	−24,299	− 97,925
	6.73	.1213	+4487	+4492	+4492	+4490	−23,740	−159,750
	8.08	.1456	+3666	+3676	+3676	+3673	−22,923	−185,218
	10.65	.1919	+1964	+1952	+1938	+1951	−21,201	−225,790
	13.85	.2495	− 284	− 190	− 327	− 267	−18,983	−262,915
	19.55	.3595	−3423	−3427	−3447	−3432	−15,818	−309,241
$Sr(NO_3)_2$	1.147	.0207	+4371	+4550	+4490	+4470	+13,070	+ 14,991
	1.985	.0358	+7257	+7193	+7233	+7228	+10,312	+ 20,469
	3.123	.0563	+9571	+9599	+9543	+9571	+ 7,969	+ 24,887

[a] Values of Lange and Streeck, Ref. 4.

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[4] Lange and Streeck, *Z. physik. Chem.*, **157A**, 15 (1931).

[5] Ewing, Rogers, Miller and McGovern, THIS JOURNAL, **54**, 1335 (1932).

was introduced into the water by breaking the bulbs and the temperature change accurately measured. From this temperature change and the heat capacity of the calorimeter, the changes in heat content were calculated. The data are given in Table I. Also data for strontium nitrate solution are included in this table. These results for strontium nitrate will be discussed when vapor pressure measurements, which are now being made, are completed. Column 7 contains the change in heat content when one mole of calcium nitrate contained in a solution of the concentration designated in Column 2 is diluted in enough water to give infinite dilution. These heats were plotted against concentration in Curve I, Fig. 1.

Accuracy of Results.—Applying the equations of the theory of errors to our results, we find that the root mean square deviation is 43.5 joules. The probable error of any observation is 0.6745 × 34.5 = 29.3 joules. It is immediately obvious, however, that this is not a true measure of the accuracy, for the "spread" or maximum deviation of the results for any particular solution varies from 5 to 179 joules. The deviations can be accounted for as follows.

The heat capacity of the calorimeter and its contents was determined for each individual heat determination by passing a known current I through a resistance R inside the calorimeter for a time t. The heat evolved, RI^2t, caused a rise in temperature ΔT, the heat capacity being obtained from the relation

$$C = Q/(\Delta T) = RI^2t/(\Delta T)$$

Now the error in Q is

$$\Delta Q = RI^2\Delta t + 2RIt\Delta I + I^2t\Delta R$$

Since I and R can be measured with great precision, the second and third terms are negligible. This leaves us

$$\Delta Q = RI^2\Delta t = 17.07 \times (0.444)^2 \times 0.4 = 1.346 \text{ joules}$$

Here, we are assuming a probable error of 0.4 second in the heating interval due to closing and opening of the heater switch. Now

$$\Delta C = \frac{\Delta Q}{(\Delta T)} - \frac{Q}{(\Delta T)^2}\Delta(\Delta T)$$

or for the *probable* error in C

$$\text{probable } \Delta C = \sqrt{\left(\frac{\Delta Q}{\Delta T}\right)^2 + \left[\frac{Q}{(\Delta T)^2}\Delta(\Delta T)\right]^2} =$$

$$\sqrt{\left(\frac{1.346}{0.59}\right)^2 + \left[\frac{2600}{(0.59)^2}(0.00045)\right]^2} = \pm 4.1 \text{ joules per } 1°$$

As stated before, the temperature could not be estimated more closely than 0.0003°. A temperature change, therefore, may be in error by as much as 0.0006°. A probable error of 0.00045° was considered a fair estimate of the precision of the temperature measurement This is the value used in obtaining ΔC above.

The error in heat capacity together with the temperature error when combined by a process similar to the above, produces an error in heat of dilution. In order to convert the latter into joules per mole of dry salt, we must multiply by a factor depending on the original concentration of the solution, the weight of the solution diluted, and the molecular weight of the salt in question. The resulting probable error ranges from 86.2 joules per mole $Sr(NO_3)_2$ for the 19.5% $Sr(NO_3)_2$ solution down to 15.8 joules per mole $Ca(NO_3)_2$ for the 69.5% $Ca(NO_3)_2$ solution. In general, our calculations show that the lower the original concentration, the higher the probable error. This conclusion is corroborated by our observations.

Discussion

These heat data can be compared with vapor pressure data by thermodynamic methods. In order to do so, it is necessary to calculate them on a different basis. The values required are the partial molal heats of solution of water, $\Delta \bar{H}_1$, in the solutions of various concentrations. These can be calculated from the above data and the total heat of solution of calcium nitrate anhydride. The latter value has been given in a previous article,[5] as $\Delta H = -19{,}250$ joules. The following calculation illustrates the method.

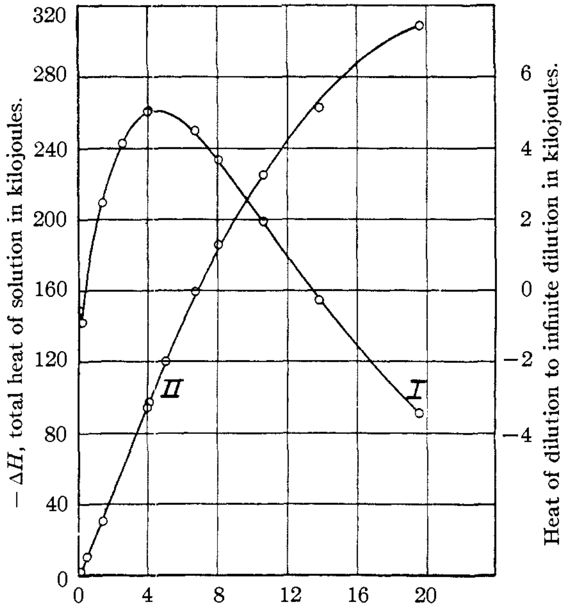

Fig. 1.—Curve I, heat of dilution to infinite dilution. Curve II, total heat of solution.

Let xH_2O designate the amount of water required to form a 1.393 molal solution of $Ca(NO_3)_2$ containing one mole of $Ca(NO_3)_2$.

$$Ca(NO_3)_2(s) + yH_2O \longrightarrow Ca(NO_3)_2(aq.);\ \Delta H = -19{,}250\text{ j.}$$
$$Ca(NO_3)_2(1.393\ m) + (y - x)\ H_2O \longrightarrow Ca(NO_3)_2(aq.);\ \Delta H = +2479\text{ j.}$$
$$\text{Subtracting } Ca(NO_3)_2(s) + xH_2O \longrightarrow Ca(NO_3)_2(1.393\ m);\ \Delta H = -21{,}729\text{ j.}$$

This gives the change in heat content when a mole of solid calcium nitrate anhydride is dissolved in enough water to give the designated concentration. These heats of solution are tabulated in Column 8, Table I. These heats multiplied by the values of the concentrations, *m*, in column 2, give the heats of solution of *m* moles of calcium nitrate anhydride in 1000 g. of water, as tabulated in Column 9. The total heats of solution in Column 9 were plotted against the concentrations in Column 2, giving Curve II in Fig. 1. The slope of this curve, $d(\Delta H)/dm$, gives the partial molal heat of solution of calcium nitrate, ΔH_2, at the designated concentrations. This slope was obtained by setting up equations for the curve and differentiating with respect to *m*. The circles represent the values given in Column 9. The solid line represents the graph of the equations.

Values for the partial molal heats of solution of calcium nitrate, $d(\Delta H)/dm = \Delta H_2$, are tabulated in Column 3, Table II. Column 1 contains the molal concentration and Column 2 the mole ratio in the various solutions. These partial molal heats of solution are plotted against concentration in Curve I, Fig. 2. The *y* intercept, −20,599 joules, was calculated at zero concentration from the equation for the total heat of solution.

TABLE II

PARTIAL MOLAL HEATS OF SOLUTION OF $Ca(NO_3)_2$ AND OF H_2O

Concentration			ΔH_1		
m 1	n_2/n_1 2	ΔH_2, j. 3	From heat measurements, j. 4	From v. p. measurements, j. 5	Deviation (5) − (4), j. 6
1.542	0.0278	−24,100	+ 50	+ 150	+100
2.687	.0484	−25,100	+ 60	+ 320	+260
6.021	.1085	−22,250	− 150	− 30	+120
8.805	.1586	−17,600	− 750	− 880	−130
12.150	.2189	−13,150	−1590	−2070	−480
15.826	.2852	− 8,500	−2780	−2750	+ 30
17.53	.3157	− 6,350	−3420	−3430	− 10
19.62	.3534	− 3,700	−4300	−4790	−490
20.29	.3655	− 2,750	−4650	−4960	−310
20.87	.3760	− 2,000	−4920	−5300	−380

Partial molal heats of solution of water, ΔH_1, were calculated from the total heats of solution and the partial heats of solution of calcium nitrate by means of equation (1). Curve II, Fig. 2, is the partial molal heat of solution of water determined in this manner; the values are tabulated in Table II, Column 4.

Partial heats of solution of water from vapor pressure data can be calculated by means of thermodynamic equations. The process of dissolving one mole of water in a large body of solution without change in concentration can be considered to take place in three isothermal steps. One mole of water vapor is evaporated at its own vapor pressure. This vapor is then expanded from the vapor pressure of water to the vapor pressure of the solution. It is then condensed into an infinite quantity of solution. The heat involved in this process, ΔH_1, is the sum of the individual heat changes in the three steps. If water vapor is assumed to be a perfect gas at these low pressures, the heat involved in step 2 becomes negligible. Applying the Clapeyron–Clausius equation, with the usual assumptions, to the first and third steps gives the equation

$$\Delta \text{H}_1 = (RT_2T_1/(T_2 - T_1)) \ln (p_2p_1'/p_1p_2') \qquad (2)$$

where p_1 and p_2 are the vapor pressures of water at temperatures T_1 and T_2 and p_1' and p'_2 are the corresponding properties for the solution. Equation (2) is essentially the Kirchhoff[6] equation. Porter[7] derived and discussed Kirchhoff's equation from a standpoint of change in internal energy and pointed out that the steps indicated above are applicable to changes in heat content.

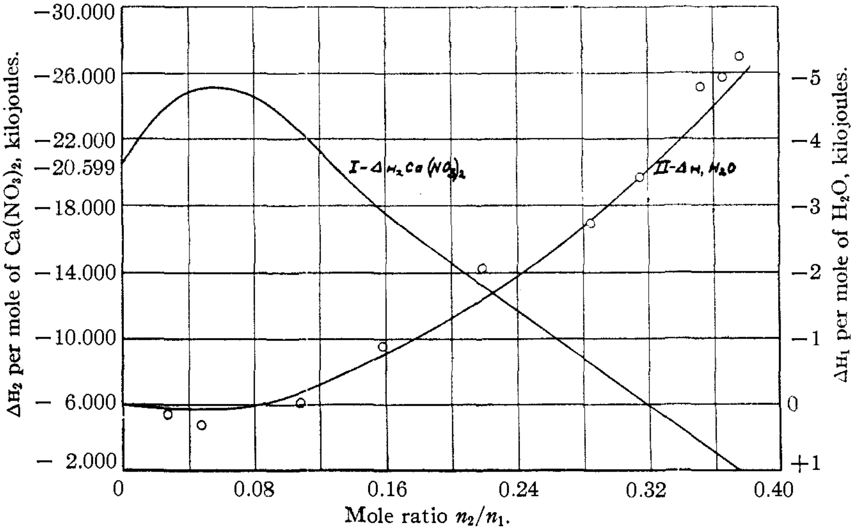

Fig. 2.—Partial molal heats of solution of $Ca(NO_3)_2$ and of H_2O.

Values of ΔH_1 calculated from equation (2) using the vapor pressures of calcium nitrate solutions measured by Ewing[8] are tabulated in Table II, Column 5. Values of ln p were plotted against $1/T$ and pressures were picked from the resulting straight lines at 20 and 30°. These calculated values of ΔH_1 are indicated as circles on Curve II, Fig. 2. The deviations of the values of ΔH_1 calculated from heat measurements and from vapor pressure measurements are tabulated in Column 6, Table II. The average deviation of 230 joules represents a deviation of 0.1 mm. in the vapor pressure of the 1.4 *m* solution and 0.003 mm. for the 19 *m* solution. The author estimated a maximum error of 0.1 mm. in the vapor pressure measurements.

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(6) Kirchhoff, *Ann. Physik Chem.*, [2] **103**, 200 (1858).

(7) Porter, *Trans. Faraday Soc.*, **11**, 19 (1915).

(8) Ewing, THIS JOURNAL, **49**, 1963 (1927).

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Summary

1. Heats of dilution of calcium nitrate solutions to infinite dilution have been measured. The concentrations of the solutions studied range from 1.39 *m* to 19.55 *m*.

2. The total heat of solution of calcium nitrate and the partial heats of solution of calcium nitrate and of water have been evaluated by means of the heat of dilution measurements.

3. Values of the partial heat of solution of water calculated from calorimetric measurements have been compared with those calculated by means of Kirchhoff's equation from vapor pressure measurements.

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Properties of Electrolytic Solutions. VIII. Conductance of Some Ternary Salts in Liquid Ammonia

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I. Introduction

In the three preceding papers of this series,[2] results have been presented for the conductance of various types of binary salts in liquid ammonia with a view to determining the influence of ion constitution on the properties of electrolytes, particularly the dissociation constant. It seemed of interest to extend the investigation to ternary salts. Little is known regarding the behavior of ternary salts in non-aqueous solvents, particularly of ternary salts of divalent negative ions. Usually, ternary salts are very difficultly soluble in liquid ammonia although there are a few salts, most of them of somewhat complex structure, which are readily soluble.

When benzophenone is treated with two atomic equivalents of sodium, the well-known disodium ketyl salt is formed. With one equivalent of sodium,[3] a monosodium salt is formed which may be looked upon either as a binary salt derived from the anion $(C_6H_5)_2CO^-$ or as a disodium salt of the divalent benzpinacol ion. It was hoped that conductance measurements might throw some light on this question. The dialkyl and diaryl tin derivatives, when treated with two atomic equivalents of sodium, yield

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(1) Metcalf Fellow in Chemistry at Brown University.

(2) Kraus and Hawes, THIS JOURNAL, **55**, 2776 (1933); Kraus and Kahler, *ibid.*, **55**, 3537 (1933); Kraus and Johnson, *ibid.*, **55**, 3542 (1933).

(3) Wooster, *ibid.*, **50**, 1388 (1928).