TABLE II

VALUES OF HEAT CONTENTS OF THE IONIZATION REACTIONS

		10°	25°	40°
Formic acid	Calcd. Eq. 6	550	− 12	− 690
	Reported	573	− 13	− 657
Acetic acid	Calcd. Eq. 6	470	− 100	− 730
	Reported	389	− 112	− 628
Propionic acid	Calcd. Eq. 6	410	− 170	− 860
	Reported	384	− 168	− 746
Chloroacetic acid	Calcd. Eq. 6	− 560	−1240	−2030
	Reported	− 593	−1170	−1639
$H_2PO_4^-$	Calcd. Eq. 6	1230	740	140
	Reported	..	..	..
HSO_4^-	Calcd. Eq. 6	−1400	−2150	−3040
	Reported	− 934	−2229	−3665
Glycine (K_A)	Calcd. Eq. 6	1670	1180	630
	Reported	1567	1165	655
Glycine (K_B)	Calcd. Eq. 6	3090	2780	2370
	Reported	3044	2765	2377
Alanine (K_A)	Calcd. Eq. 6	920	750	155
	Reported	..	720	210

employing the less arbitrary function represented by equation (6).

There does not appear to be any general quantitative relation between Θ and $\ln K_m$. It appears that the weaker the electrolyte the greater the value of Θ but this is a very rough statement of the facts and a number of exceptions occur.

As a result of this study one important observation concerning any discussion of ionization constants in relation to the constitution of the ionizing electrolytes should be made. For such a comparison to have real value, it will be essential to select the values of the ionization constants at their maxima or at their corresponding temperatures, Θ.

Summary

1. Recent accurate determinations of ionization constants of weak acids, bases and ampholytes reveal that at one atmosphere pressure and in aqueous solution

$$\log K - \log K_m = f(t - \Theta)$$

where $f(t - \Theta)$ is a general function and K_m and Θ are constants characteristic of each ionization reaction. K_m is the maximum value of the ionization constant which occurs at the temperature Θ.

2. The approximation equation

$$\log K = \log K_m - 5.0 \times 10^{-5}(t - \Theta)^2$$

is valid within experimental error in the region near the maximum values of K. As a matter of fact, it can be employed with confidence over a range of $t - \Theta = \pm 75$.

3. The change in heat content of ionization is given by

$$\Delta H = 2.3\ RT^2\ (\partial f(t - \Theta)/\partial T)$$

and its value given by the use of only one characteristic constant Θ.

4. Some values of ΔH given by the approximate equation

$$\Delta H = 2.3 \times 10^{-4}\ RT^2\ (t - \Theta)$$

have been calculated and compared with values computed by other methods.

NEW HAVEN, CONN. RECEIVED JANUARY 22, 1934

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

Studies on the Vapor Pressure–Temperature Relations and on the Heats of Hydration, Solution and Dilution of the Binary System Magnesium Nitrate–Water

BY WARREN W. EWING, ERNST KLINGER AND JOHN D. BRANDNER

This article, presenting heat and vapor pressure data obtained on the binary system magnesium nitrate–water, is a continuation of the studies which are being carried out in this Laboratory on the nitrates of certain bivalent metals. These nitrates are peculiarly rich in hydrates and are quite soluble in water, hence they serve as fertile fields for the investigation of hydration phenomena and of the properties of concentrated solutions. Results for calcium nitrate have been presented already. The strontium nitrate system and the zinc nitrate system are being investigated at the present time.

It has been shown[1] that magnesium nitrate exists as the anhydride and in the following hydrated forms: the dihydrate melting at 130.9°, the hexahydrate melting at 89.9°, and the enneahydrate having a transition temperature of −14.7°. In this investigation vapor pressures of unsaturated solutions, of saturated solutions, and of mixed hydrates have been measured. Likewise, heats of dilution and of solution have been determined. From both vapor pressure and calorimetric measurements, partial molal heats of

[1] Ewing, Brandner, Slichter and Griesinger, THIS JOURNAL, **55**, 4822 (1933); Ewing and Klinger, *ibid.*, **55**, 4825 (1933).

solution of water and the heats of hydration of the hexahydrate have been calculated and compared.

Preparation of Materials

A C. P. grade of magnesium nitrate was purified by recrystallizing three times, the first time as the dihydrate, the second and third times as the hexahydrate. The molten C. P. hexahydrate crystals were evaporated at 120° until crystals of dihydrate began to form. The temperature was then lowered to 110° and the crystals which formed were filtered hot on a Buchner funnel. These dihydrate crystals were dissolved in just sufficient hot water that the hexahydrate separated out on cooling. A third crystallization, again as the hexahydrate, was then made. These *hexahydrate* crystals were dried over 60% sulfuric acid under a vacuum to constant weight. *Dihydrate* crystals were prepared by dehydrating the hexahydrate crystals over phosphorus pentoxide in a vacuum to constant weight. *Anhydride* crystals were prepared only with considerable difficulty. When an attempt was made to drive off the excess water by boiling the hydrates, decomposition occurred. The method which proved most successful was to dry the dihydrate in a desiccator with constant evacuation at a temperature slightly below the melting point of the di-anhydride eutectic, 130.5°, to a constant weight. The loss in weight corresponded to the loss of two molecules of water. The dihydrate samples were placed in the bulbs which were to be used in the calorimetric measurements, and when the desired loss of weight was attained and the weights remained constant the bulbs were quickly sealed. This drying process took several weeks.

Vapor Pressure Part

The vapor pressure measurements were carried out in the apparatus which was used in the calcium nitrate work.[2] The only important modification was the substitution of dibutyl phthalate for cotton seed oil as the confining liquid in the tensimeter. When a vapor pressure measurement was made on a solution at 20°, using cotton seed oil as the confining liquid, the temperature subsequently raised to 70°, and again restored to 20°, the original vapor pressure reading could not be duplicated without further evacuation. It seemed probable that at the low temperature air dissolved in the oil. This air then escaped into the sample bulb at the higher temperatures. This necessitated making corrections to the readings at the higher temperatures. The use of dibutyl phthalate minimized this effect. In other respects, it seemed to be fully as satisfactory as cotton seed oil.

Vapor pressure studies were made on the following systems: (1) a mixture of the hexahydrate and the dihydrate crystals from below the melting point of the eutectic, 53.8°, down to 25° (Table I); (2) saturated solutions of the various hydrates ranging from a saturated solution of the hexahydrate at 20°, 41% concentration, to a saturated solution of the dihydrate at 85°, 71% concentration (Table II); (3) solutions ranging in concentration from 11 to 38% over the temperature range 20 to 60°, and ranging in concentration from 42 to 47% over the temperature range from their respective freezing points to 70° (Table III).

TABLE I

VAPOR PRESSURE-TEMPERATURE RELATIONS OF THE SYSTEM $Mg(NO_3)_2 \cdot 6H_2O-Mg(NO_3)_2 \cdot 2H_2O$-WATER VAPOR

Temp., °C.	50.00	45.00	40.00	35.00	30.00	25.00
Vapor p., mm.	3.10	2.16	1.46	1.00	0.72	0.49

TABLE II

VAPOR PRESSURE-TEMPERATURE RELATIONS OF THE SYSTEMS: CRYSTALS-SATURATED SOLUTION-WATER VAPOR

Temp., °C.	V. p., mm.	Temp., °C.	V. p., mm.	Temp., °C.	V. p., mm.
I. Crystal Phase		75.05	97.0	70.04	15.5
$Mg(NO_3)_2 \cdot 6H_2O$		80.04	109.4	65.03	10.4
20.00	9.46	85.05	117.9	60.03	6.89
25.00	12.44	86.51	118.6	55.03	4.45
30.00	16.27	88.43	116.9	II. Crystal Phase,	
35.00	21.03	88.47	117.0	$Mg(NO_3)_2 \cdot 2H_2O$	
40.00	26.52	89.23	113.8	55.00	4.28
45.00	33.19	89.76	108.4	60.00	5.56
50.00	41.16	89.67	86.9	65.03	7.1
55.05	50.37	88.55	74.8	70.05	8.7
60.00	60.2	85.00	53.2	75.03	10.9
64.98	71.6	80.00	34.3	80.00	12.7
70.01	83.6	75.02	23.1	85.05	16.0
		70.02	15.4		

These data are all given graphically in Fig. 1. Curve ABC represents the vapor pressure-temperature relations of saturated solutions in which the hexahydrate is the solid phase. Curve

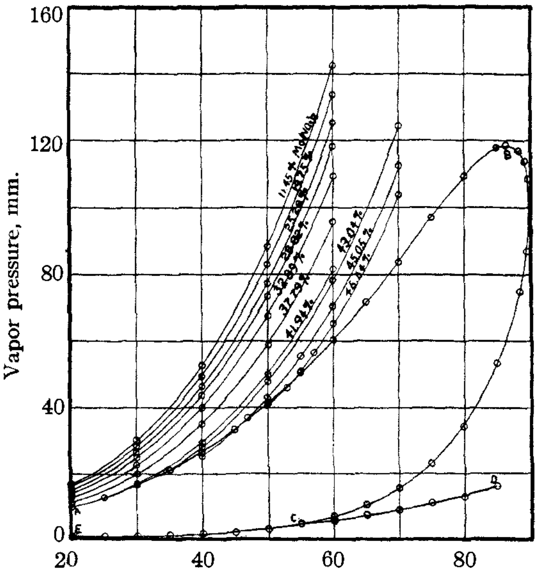

Fig. 1.

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(2) Ewing, THIS JOURNAL, 49, 1963 (1927).

CD represents saturated solutions in which the dihydrate is the solid phase. CE is the vapor pressure curve for a mixture of hexahydrate and dihydrate crystals. The remaining curves represent the vapor pressure–temperature relations of solutions of the concentrations designated. The temperatures at which these curves cross ABC are the freezing points of the various solutions. It will be noted that supersaturation is obtained in a few cases. In general it is difficult to attain a large degree of supersaturation in this system. The calcium nitrate system on the other hand can be easily supersaturated. Consequently metastable regions, similar to those found for calcium nitrate, have not been found for magnesium nitrate. Furthermore, for the same reason vapor pressure studies could not be made over as large a concentration range as with calcium nitrate.

Using the method of least squares on an equation of the form $\ln p = A/T + BT + C$, (1) and solving for the constants A, B and C, vapor pressures of the various solutions were calculated for the temperatures at which the vapor pressures were measured. The variation of the calculated pressures from the experimental data are shown in Table III.

TABLE III

TEMPERATURE-VAPOR PRESSURE RELATIONS OF SOLUTIONS OF MAGNESIUM NITRATE IN WATER

Equation used in calculations: $\ln p = A/T + BT + C$

$Mg(NO_3)_2$, %	Vapor pressure in millimeters with deviations of calcd. 20.00°		30.00°		40.00°		50.00°		60.00°	
0.00	17.535[a]	+0.004	31.824[a]	−0.007	55.324[a]	−0.011	92.51[a]	+0.003	149.38[a]	+0.02
11.45	16.46	− .006	30.08	+ .037	52.69	− .033	88.40	− .087	142.5	+ .11
19.75	15.40	+ .010	28.29	− .045	49.35	+ .070	82.97	− .067	133.8	+ .04
25.28	14.46	+ .019	26.50	− .052	46.26	− .070	77.16	+ .283	125.3	− .19
28.82	13.66	+ .015	24.90	+ .080	43.70	− .076	73.25	− .107	118.3	− .13
32.89	12.50	− .004	22.79	+ .028	39.98	− .037	67.32	− .033	109.4	+ .06
37.79	10.87	+ .004	19.94	− .006	35.00	− .034	58.86	+ .070	95.8	− .03

[a] Data taken from "International Critical Tables."

$Mg(NO_3)_2$, % / Temp., °C.	25.00	30.00	35.00	40.00	45.00	47.00	50.00	53.00	55.00	57.00	60.00	70.00
41.94	12.45	16.71	...	29.48	...	...	49.95	...	...	...	81.60	...
43.04	...	...	21.38	28.18	...	...	47.76	...	...	...	78.22	124.3
45.05	...	...	...	25.45	33.22	36.85	42.88	...	55.28	...	70.35	112.4
46.64	...	...	...	...	...	...	40.96	45.95	50.89	56.28	65.05	103.7

Calorimetric Part

The calorimetric determinations were carried out in the adiabatic calorimeter previously described.[3] The measurements were made by dissolving known weights of the anhydride, of the dihydrate, of the hexahydrate or of the various solutions in 1000 g. of water. Lange and Robinson[4] have measured the heats of dilution of dilute solutions of magnesium nitrate to infinite dilution. Their values, added to our heats of solution, give the integral heats of solution when one mole of each salt is dissolved in an infinite quantity of water. These heat data are listed in Table IV and lead to the following equations

$$Mg(NO_3)_2(s) + aq \longrightarrow Mg(NO_3)_2(aq);\ \Delta H = -90{,}100 \text{ j.}$$

$$Mg(NO_3)_2\cdot 2HO_2(s) + aq \longrightarrow Mg(NO_3)_2(aq) + 2H_2O(l);\quad \Delta H = -43{,}170 \text{ j.}$$

$$Mg(NO_3)_2\cdot 6H_2O(s) + aq \longrightarrow Mg(NO_3)_2(aq) + 6H_2O\ (l);\quad \Delta H = +18{,}150 \text{ j.}$$

The changes in heat content at 25° for the hydration processes were obtained by a summation of the above equations. The heat of hydration was calculated also from vapor pressure data on the hexahydrate–dihydrate mixture of crystals. The following comparison was obtained

	Experimental (Calorimetric)	Calculated (from v. p.)
$Mg(NO_3)_2(s) + 2H_2O(l) \longrightarrow Mg(NO_3)_2\cdot 2H_2O(s)$;	$\Delta H = -46{,}930$ j.	
$Mg(NO_3)_2\cdot 2H_2O(s) + 4H_2O(l) \longrightarrow Mg(NO_3)_2\cdot 6H_2O(s)$;	$\Delta H = -61{,}320$ j.;	$\Delta H = -61{,}720$ j.

The method of calculating the ΔH values from vapor pressure data is given by Ewing, Rogers, Miller and McGovern.[3] Vapor pressure data were not available for calculating the change in heat content for the hydration of the anhydride to form the dihydrate. The vapor pressures of this mixture were too small to be measured in the apparatus used in this investigation.

Data on the heats of dilution are given in Table V. Column 3 contains the heat absorbed

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

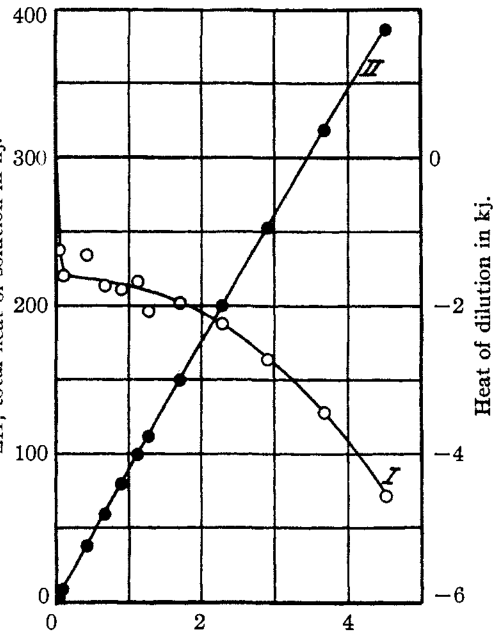
[4] Lange and Robinson, *Naturwissenschaften*, **19**, 359 (1931).

TABLE IV

HEATS OF SOLUTION OF $Mg(NO_3)_2$ TO INFINITE DILUTION

Salt		$Mg(NO_3)_2 \cdot 6H_2O$	$Mg(NO_3)_2 \cdot 2H_2O$	$Mg(NO_3)_2$
Heat of soln. per mole of $Mg(NO_3)_2$, joules	Individual measurements	+18,140 +18,160	−43,080 −43,050 −43,230 −43,320	−90,100 −89,970 −90,240 . . .
	Av.	+18,150	−43,170	−90,100
Prob. error. *r*		±10	±85	±90

when one mole of magnesium nitrate, dissolved in enough water to give the concentrations in columns 1 and 2, is diluted to infinite dilution.



Concentration of Mg $(NO_3)_2$ − m./1000 g. H_2O.

Fig. 2.—Curve I, heat of dilution; Curve II, total heat of solution.

Each of these values is the average of four independent determinations. These data are plotted in Fig. 2, Curve I. From any one of these data and from the heat of solution of one mole of magnesium nitrate anhydride in an infinite quantity of water, the integral heat of solution of one mole of magnesium nitrate in enough water to form a solution of concentration *m* can be calculated. Results are tabulated in column 5. Multiplying these data by *m* gave the integral heat of solution, ΔH, of *m* moles of magnesium nitrate in 1000 g. of water. These heats are tabulated in column 6 and plotted in Fig. 2, Curve II. The slopes of this curve gave the differential or partial heats of solution, $d(\Delta H)/dm = \Delta \mathrm{H}_2$. This is the change in heat content when one mole of salt is dissolved in an infinite quantity of solution without change in concentration. The slopes of the curve were obtained by setting up an equation for the curve and differentiating with respect to *m* at the various concentrations. $\Delta \mathrm{H}_2$ values are tabulated in Table VI, column 4, and plotted in Curve 1, Fig. 3.

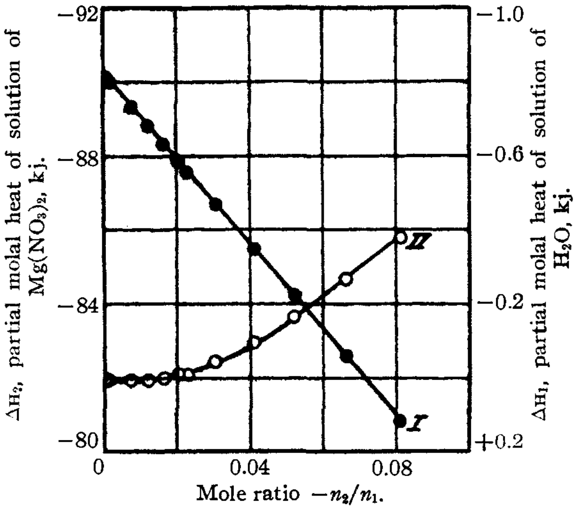
TABLE V

HEATS OF DILUTION AND INTEGRAL HEATS OF SOLUTION OF $Mg(NO_3)_2$ ANHYDRIDE

Concn. of $Mg(NO_3)_2$ m/1000 g. H_2O	n_2/n_1	Heat of diln. to infinite diln. in j.	Probable error, *r*	Integral heat of solution in j. Heat per mole of $Mg(NO_3)_2$ in req. H_2O	Integral heat of solution in j. ΔH in moles per 1000 g. H_2O
0.040[a]	0.0007	−1250		−88,850	− 3,550
.100[a]	.0018	−1600		−88,500	− 8,850
.427	.0077	−1310	±125	−88,790	− 37,910
.672	.0121	−1720	± 13	−88,380	− 59,390
.905	.0163	−1780	±157	−88,320	− 79,930
1.127	.0203	−1670	±108	−88,430	− 99,660
1.271	.0229	−2080	±315	−88,020	−111,870
1.702	.0307	−1960	±215	−88,140	−150,010
2.279	.0411	−2250	±112	−87,850	−200,210
2.896	.0522	−2730	± 24	−87,370	−253,020
3.675	.0662	−3440	± 8	−86,660	−318,480
4.513	.0813	−4560	± 86	−85,540	−386,040

[a] Determination of Lange and Robinson.

The general equation, $\Delta H = n_2 \Delta \mathrm{H}_2 + n_1 \Delta \mathrm{H}_1$, gives a method of calculating $\Delta \mathrm{H}_1$, the change in heat content when one mole of water is dissolved in an infinite quantity of solution. $\Delta \mathrm{H}_1$ data are tabulated in Table VI, column 5, and are plotted in Curve II, Fig. 3.



Mole ratio $-n_2/n_1$.

Fig. 3.—Partial molal heats of solution: Curve I, $Mg(NO_3)_2$; Curve II, H_2O.

TABLE VI

PARTIAL MOLAL HEATS OF SOLUTION

Concn. $m/1000$ g. H_2O	n_2/n_1	ΔH	ΔH_2	ΔH_1 Calorimetric
0.040[a]	0.0007	− 3,550	−90,120	+ 1
.100[a]	.0018	− 8,850	−90,000	+ 3
.427	.0077	− 37,910	−89,320	+ 4
.672	.0121	− 59,390	−88,820	+ 5
.905	.0163	− 79,930	−88,330	0
1.127	.0203	− 99,660	−87,870	− 11
1.271	.0229	−111,870	−87,580	− 10
1.702	.0307	−150,010	−86,690	− 45
2.279	.0411	−200,210	−85,490	− 97
2.896	.0522	−253,020	−84,220	−165
3.675	.0662	−318,480	−82,610	−268
4.513	.0813	−386,040	−80,870	−380

[a] Determination of Lange and Robinson.

ΔH_1 values can be calculated also from vapor pressure data. d ln p/dT at 25° for each concentration in Table III was calculated by differentiating equation (1). This differential, substituted in the Clapeyron–Clausius equation for the vapor pressure of liquids, $\Delta H_{vap} = RT^2 \, d \ln p/dT$, makes possible the calculating of the change in heat content of vaporization of water, ΔH_w and ΔH_s, from pure water and from solutions, respectively. Since $\Delta H_1 = \Delta H_w - \Delta H_s$, ΔH_1 is at once obtained from vapor pressure data. The only assumption involved is that water vapor behaves as an ideal gas at these low pressures.

The ΔH_1 data, computed by the above two methods, compare as follows at the concentrations at which vapor pressure measurements were made

n_2/n_1	0.0157	0.0300	0.0411	0.0492	0.0595	0.0738	0.0877
(calorimetric), j.	5	−35	−95	−150	−315	−325	−430
(vapor press.), j.	−665	−761	−513	−511	−490	−771	−796

The discordance in ΔH_1 corresponds to a change in slope of the ln p *vs.* $1/T$ curve at 25° which would be caused by errors of 0.1 mm. in the vapor pressures of the most dilute solution at 20 and 30°. For the most concentrated solution, the corresponding error would be considerably less, even if the deviations were the same in the two cases.

Summary

Vapor pressure measurements have been made on solutions, on saturated solutions and on mixed hydrates of the system magnesium nitrate–water at various temperatures.

Heats of solution and of dilution have been determined for the same system.

Heats of hydration and partial molal heats of solution of the salt and of water have been calculated from the calorimetric data. The heat of hydration of the dihydrate to the hexahydrate and partial molal heats of solution of water have been calculated also from vapor pressure data.

BETHLEHEM, PA. RECEIVED JANUARY 23, 1934

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 394]

The Potentials of Cells in Liquid Ammonia Solutions. The Thermodynamic Constants of the Ammino Zinc Chlorides and of Zinc Chloride

BY NORMAN ELLIOTT AND DON M. YOST

Introduction

Liquid ammonia has long been known to be an ionizing solvent, and the nature of salt solutions in it has received the careful attention of Franklin, Kraus and other investigators.[1] The few electrode potentials in this solvent which have been investigated were complicated by liquid potentials or were not reversible.[2] A cell free from these objections and one which is also convenient as a reference electrode is highly desirable, especially if the electromotive series in liquid ammonia is to have more than a qualitative basis.[3]

Inasmuch as the thermodynamic constants of thallium amalgams and thallous chloride[4] are accurately known, and since the latter substance is not very soluble in liquid ammonia at 25°, the thallium amalgam–thallous chloride couple was chosen as one half-cell. Moreover, the solid phase consists of thallous chloride alone and not an ammoniated salt.[5] As the other half-cell the zinc amalgam–decammino zinc chloride couple was selected, since the activities of the amalgams[6]

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[1] *Cf.* Kraus, "The Properties of Electrically Conducting Systems," A. C. S. Monograph, The Chemical Catalog Co., New York, 1922. An excellent review of liquid ammonia systems is given by Fernelius and Johnston, *J. Chem. Ed.*, **7**, 2600 (1930), *et ante.*

[2] *Cf. e. g.*, Johnson and Wilsmore, *Trans. Faraday Soc.*, **3**, 77 (1907); Costeanu, *Compt. rend.*, **195**, 778 (1932).

[3] Bergstrom, THIS JOURNAL, **47**, 1503 (1925); Kraus, *Trans. Am. Electrochem. Soc.*, **45**, 175 (1924).

[4] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, pp. 93, 267, 607.

[5] Stollenwerk and Biltz, *Z. anorg. Chem.*, **119**, 97 (1921).

[6] Pearce and Eversole, *J. Phys. Chem.*, **32**, 209 (1928).