K^+, Cs^+, Mg^{++}, Ca^{++}, Sr^{++}, and Ba^{++} salts as well as the free acid of the clay mineral montmorillonite. Variations in X-ray diffraction patterns and behaviors upon differential thermal analyses were determined for the materials at the various relative humidities.

Results obtained indicate that the exchangeable cations are located between the silicate layers of which the mineral is formed. In the magnesium and alkaline earth salts, the first step of water sorption is the hydration of the cation with six molecules of water which is followed by completion of a water layer having a hexagonal type structure. A second water layer of similar structure is taken up at high relative humidities. Similar results were obtained for the lithium salt except that only three molecules of water were required for the hydration of the lithium ion. In sodium, potassium, and cesium salts the cation apparently was not hydrated. This was also true for the hydrogen ion in the clay acid.

The methods used in the work although inexact give a clear picture of the sorption process for water, which is entirely different from van der Waals adsorption of gases such as nitrogen.

WASHINGTON, D. C. RECEIVED FEBRUARY 10, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Heats of Dilution, Heat Capacities, and Activities of Urea in Aqueous Solutions from the Freezing Points to 40°[1,2]

BY FRANK T. GUCKER, JR., AND HUGH B. PICKARD

Introduction

In the study of solutions of non-electrolytes, a number of thermodynamic properties of aqueous solutions of urea have been determined in this Laboratory. We have found that, up to a concentration of 3 M, the apparent molal volume[3] of urea at 25 and 30° and the apparent molal expansibility[4] at 27.5° are linear functions of the first power of the concentration. Such a relationship is to be expected for many properties of non-electrolytes. Redlich and Klinger[5] found that it was the limiting law for the apparent molal volume of sucrose, and work in this Laboratory showed that it also was the limiting law for the apparent molal heat capacity[6] and heat content[7] of sucrose. An exhaustive study of the specific heats of aqueous solutions of urea[8] failed to determine unequivocally what limiting law was obeyed by the apparent molal heat capacity of urea. Heats of dilution can be measured in very dilute solutions, the specific heats of which differ from unity by an amount too small to measure directly. Hence the limiting value of the apparent molal heat content can be determined more accurately than that of the heat capacity. We therefore undertook a study of the heats of dilution of solutions of urea in order to find the limiting law for this property.

Our results also provide the final thermal data necessary for an accurate calculation of the change of the osmotic and activity coefficients of urea over a temperature range from 2 to 40°. Thus we can compare the results of vapor pressure measurements at different temperatures, and of freezing point depressions, with recent precise measurements of the vapor pressures of aqueous solutions of urea at 25°.

Heats of Dilution at 25°

Materials and Solutions.—The urea used in experiments 1–6 had been purified and used in the density determinations carried out in this Laboratory. It had been reclaimed several times by precipitation from 50% alcohol, as described in this work.[3] The urea used in experiments 7–23 was prepared from Mallinckrodt analytical reagent. It was recrystallized once from water, washed once with 95% alcohol, filtered on a sintered glass filter and dried overnight in a vacuum desiccator connected to a water aspirator. After being ground in an agate mortar, it was dried for seven or eight hours *in vacuo* at 50–60°. This purified material showed a conductance corresponding to only 0.004% electrolyte calculated as sodium chloride.

The distilled water used in making up the solutions had a specific conductance of 3 × 10^{-6} reciprocal ohm or less.

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[1] Most of the material in this paper was presented before the Division of Physical and Inorganic Chemistry at the Boston Meeting of the American Chemical Society, September 14, 1939.

[2] This work was supported by grants from the Penrose Fund of the American Philosophical Society and from the Committee on Research of the Graduate School of Northwestern University.

[3] Gucker, Gage and Moser, THIS JOURNAL, **60**, 2582 (1938).

[4] Gucker and Moser, *ibid.*, **61**, 1558 (1939).

[5] Redlich and Klinger, *Sitzber. Akad. Wiss. Wien.*, Abt. IIb, **143**, 489 (1934); *Monatsh.*, **65**, 137 (1934).

[6] Gucker and Ayres, THIS JOURNAL, **59**, 447 (1937).

[7] Gucker, Pickard and Planck, *ibid.*, **61**, 459 (1939).

[8] Gucker and Ayres, *ibid.*, **59**, 2152 (1937).

The solutions used in experiments 1, 5, 7–10, 13, 14, 16 and 19–23 were made up determinate. Those used in the other experiments were the products of previous dilutions.

Experimental Methods.—The twin-calorimeter apparatus, sensitive to 1 microdegree, which was used to measure the heats of dilution of urea, has been described in a previous paper.[7] The experimental procedure was the same except for a few slight modifications. In order to increase the rate of heating, the 50-ohm calorimeter heaters were replaced by 25-ohm heaters in experiments 19–23.

In our apparatus, electrical heating cannot always be supplied rapidly enough to balance the heat of dilution at each instant. Since the thermal conductance constant is very low, no appreciable error is caused by heat leakage unless a heat change of more than a quarter of a calorie is involved. In these experiments, the pipet is opened not at the *beginning* but in the *middle* of the heating period.

Two types of experiment were carried out. In the first, a small amount of water (2.8–58 ml.) in the pipet was added to a large volume of solution (900 ml. to 1 liter) in the calorimeter. This caused a small change in molality, Δm, and gave a short chord on the heat content–molality curve. In the second type of experiment, a small quantity of solution was diluted with a large amount of water, giving a long chord on the heat content–molality curve.

In most of the experiments, the pipets were only partially filled with liquid. For example, in experiments 13 and 14 at 3 m, the pipets contained only about 3 ml. of water and 57 ml. of air. This introduced unexpected complications. The air is saturated with water vapor, at the vapor pressure of pure water, p_0. After the pipet is opened, this same air is in contact with the *solution*, having a vapor pressure $(p_0 - \Delta p)$. A small quantity of water therefore will condense and the heat of condensation will be added to the observed heat of dilution. This is practically the same as the heat of condensation of the same amount of water vapor on pure water, since the values of $\bar{L}_1$ which we calculate later are quite small. Taking the recent value of Osborne, Stimson and Ginnings[9] for the latent heat of vaporization of water at 25°, the heat evolved for V ml. of air in the pipet is

$$-\delta q = \frac{273}{298} \times \frac{\Delta p}{760} \times \frac{V}{22{,}400} \times 10{,}510$$
$$= 0.000566\, V \Delta p \text{ cal.}_{15}$$

Values of the vapor pressure of urea solutions, which are very nearly those calculated from Raoult's law, were taken from the paper of Scatchard, Hamer and Wood.[10] This correction then was applied to the experimentally measured values of q to give the actual heat effect caused by the dilution.

In experiments 13, 14, and 19–23, a small amount of solution was added to a large amount of water. In this case δq was positive (heat was absorbed) since the vapor pressure of the final 0.01 m solution was greater than that of the 3 m solution over which the air originally stood. In experiments 3–7 the volume of air in the pipet was 10 ml. or less and Δp was small so that δq was negligible and no correction was applied.

Experimental Results.—The experimental results are summarized in Table I, which includes all but eight dilutions. Seven of these could not be completed, because of mechanical failures. One dilution of experiment 13 was rejected. This result was very low, probably because the valves of the pipet leaked.

The temperature at which the dilution took place was read from a standardized Beckmann thermometer. This temperature seldom varied from 25° by more than 0.03° and never by more than 0.05°. No correction was necessary for this difference, since the slope of the apparent molal heat capacity curve for urea at 25° is small.

We analyzed the results by the same methods we had used for sucrose.[7] The values of $\Delta H/\Delta m$ obtained from the short chord experiments, when plotted against m, were found to lie along a smooth curve, which could be represented by the equation

$$\Delta H/\Delta m = -85.87 + 12.88\, m - 0.795\, m^2 \qquad (1)$$

The coefficients of this equation were determined by the method of least squares, weighting each experiment in proportion to the heat change which was measured. The experimental results, together with the graph of this equation, are plotted in Fig. 1. The chords are short, corresponding to a change of only 0.01 in m, so that they are plotted simply as points. The satisfactory agreement is apparent from the graph.

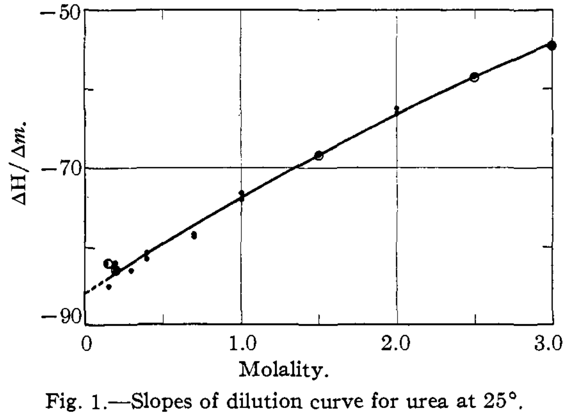

Fig. 1.—Slopes of dilution curve for urea at 25°.

Integration of equation (1) gave for the apparent relative heat content the equation

$$\Phi L_2 = \Phi H_2 - \Phi H_2^0 = -85.87\, m + 6.44\, m^2 - 0.265\, m^3 \qquad (2)$$

From this equation we calculated the values of q which are given in column 5 of Table I. The values for the two dilutions of an experiment usu-

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(9) Osborne, Stimson and Ginnings, *Bur. Standards J. Research*, **23**, 197 (1939), Table 13.

(10) Scatchard, Hamer and Wood, THIS JOURNAL, **60**, 3061 (1938).

TABLE I

HEATS OF DILUTION OF UREA SOLUTIONS AT 25°

Expt.	Initial concn., m_1	Final concn., m_2	q (cal.$_{15}$) (obsd.)	Equation 2		Equation 3		ΔH, cal.$_{15}$/mole	$-\Delta H/\Delta m$
				q (cal.$_{15}$) (calcd.)	$10^3\Delta q$ (obsd. − calcd.)	q (cal.$_{15}$) (calcd.)	$10^3\Delta q$ (obsd. − calcd.)		
6	0.1420	0.1340	0.091	0.093	− 2	0.093	− 2	0.66	82
5	.1500	.1420	.096	.098	− 2	.098	− 2	.66	82
	.1500	.1420	.100	.099	+ 1	.099	+ 1	.68	85
4	.2000	.1900	.163	.163	0	.163	0	.83	83
3	.2100	.2000	.174	.175	− 1	.174	0	.83	83
	.2100	.2000	.171	.175	− 4	.174	− 3	.82	82
2	.3100	.3000	.247	.245	+ 2	.244	+ 3	.829	82.9
	.3100	.3000	.247	.244	+ 3	.243	+ 4	.830	83.0
1	.4100	.4000	.330	.331	− 1	.330	0	.807	80.7
	.4100	.4000	.332	.330	+ 2	.329	+ 3	.814	81.4
15	.7000	.6900	.506	.497	+ 9	.496	+10	.786	78.6
	.7001	.6901	.505	.499	+ 6	.497	+ 8	.783	78.3
11	1.0100	1.0000	.680	.685	− 5	.682	− 2	.732	73.2
	1.0154	1.0053	.703	.702	+ 1	.699	+ 4	.746	73.9
10	1.4997	1.4900	.867	.867	0	.867	0	.663	68.4
	1.4997	1.4900	.854	.855	− 1	.855	− 1	.662	68.2
18	2.0100	2.0000	1.111	1.126	− 15	1.131	−20	.625	62.5
	2.0100	2.0000	1.118	1.122	− 4	1.127	− 9	.631	63.1
17	2.5100	2.5000	1.291	1.295	− 4	1.314	−25	.584	58.4
	2.5100	2.5000	1.278	1.278	0	1.296	−18	.586	58.6
16	3.0100	3.0000	1.314	1.312	+ 2	1.343	−29	.545	54.5
	3.0100	3.0000	1.385	1.382	+ 3	1.415	−30	.545	54.5
9	0.2000	0.0050	0.078	0.080	− 2	0.081	− 3	15.8	
	.2000	.0050	.083	.080	+ 3	.081	+ 2	16.8	
8	.2000	.0050	.078	.080	− 2	.081	− 3	15.8	
	.2000	.0050	.085	.080	+ 5	.081	+ 4	17.2	
7	.2000	.0100	.157	.160	− 3	.159	− 2	15.8	
	.2000	.0100	.157	.160	− 3	.159	− 2	15.8	
14	3.007	.0100	1.970	1.963	+ 7	1.968	+ 2	207.1	
13	3.007	.0100	2.108	2.105	+ 5	2.110	− 2	206.7	
19	6.002	.0100	3.435	3.338	+ 97	3.425	+10	349.7	
	6.002	.0100	3.442	3.371	+ 71	3.459	−17	347.0	
20	8.010	.0100	4.174	4.033	+141	4.171	+ 3	424.3	
	8.010	.0100	4.184	4.038	+146	4.176	− 8	424.8	
21	10.003	.0100	4.619	4.585	+ 34	4.636	−15	484.4	
	10.003	.0100	4.825	4.808	+ 17	4.861	−36	482.5	
23	11.992	.0100	5.168	5.436	−258	5.171	− 3	532.2	
	11.992	.0100	5.204	5.469	−265	5.202	+ 2	532.7	

ally were slightly different, because different quantities were used in the two calorimeters, although the change in concentration was the same. As the figures in column 6 show, equation (2) reproduces the experimental results up to 3 m very satisfactorily, with an average deviation of ±3.3 microdegrees. The equation shows increasing deviations, however, when applied to our later results at higher concentrations. When all of our results were employed to calculate the coefficients by the method of least squares, the resulting cubic equation gave better agreement at high concentrations but yielded a limiting slope inconsistent with our experiments at low concentration.

Finally we obtained a fourth degree equation, retaining the limiting slope of equation (2) and calculating the other coefficients from the results of experiments 13 and 14, 20 and 23 at 3, 8 and 12 m. This equation was

$$\Phi L_2 = -85.87\,m + 6.815\,m^2 - 0.4569\,m^3 + 0.01471\,m^4 \quad (3)$$

Values of q for each dilution, calculated from this equation, are included in column 7 of Table I. As the figures in column 8 show, this gives reasonably satisfactory agreement with all our experimental results. Up to 1.5 m concentration, the difference averages ±2.7 microdegrees, and over the whole range it averages ±7.6 microdegrees.

From equation (3), the partial relative molal heat contents of urea and water were calculated by the methods used in our previous work.[7] The results are plotted in Fig. 2.

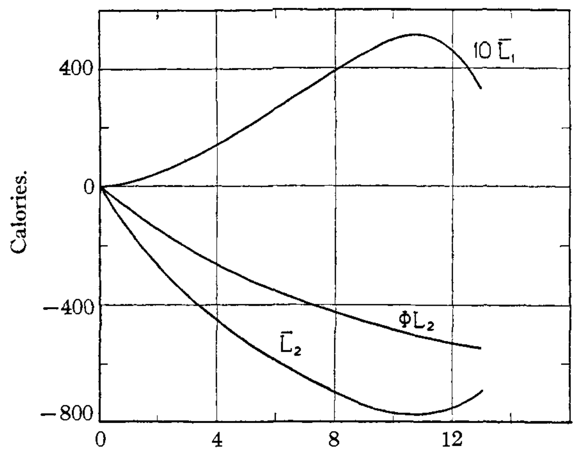

Fig. 2.—Apparent and partial relative molal heat contents for urea and water at 25°.

Discussion of the Heats of Dilution.—In magnitude, the heat of dilution of urea is even smaller than that of sucrose, showing that urea is more nearly an ideal solute. Our results are in general agreement with those of Naudé[11] at 18°, as we shall show in more detail after a discussion of the heat capacities.

In dilute solutions, the apparent molal heat content of urea is a linear function of the first power of the molality. It therefore parallels the volume properties. This is to be expected on the basis of what little theory has been developed for such solutes. For instance, Fuoss[12] has calculated the free energy of a dipolar solute of small dipole moment. From his theory, we can show that the apparent molal heat content of such a solute should be a linear function of the first power of the concentration. The surprising thing about the results is the *sign* of the heat of dilution. The separation of electrical dipoles, like that of ions, should cause a *liberation* of heat in a solvent having a dielectric constant with a temperature coefficient like that of water. It is hard to see how any purely electrostatic forces could account for a negative limiting slope. However, we have found the same negative slope in the case of glycine, which we expect to publish shortly.

Apparent Molal Heat Capacities

Since the apparent molal heat content is a linear function of the molality at low concentrations, its temperature coefficient, the apparent molal heat capacity, doubtless obeys the same limiting law and should be expressed by a power series in m.

$$\Phi C_{p_2} = \Phi C^0_{p_2} + am + bm^2 + cm^3 + \ldots \quad (4)$$

Accordingly we took the data of Ayres[6] and plotted the apparent molal heat capacity against the molality at each of the six temperatures he investigated. The results, as shown in Fig. 3, lie along smooth curves. The best coefficients for cubic equations in m were determined by the method of least squares. Each value of the apparent molal heat capacity was weighted in proportion to its accuracy, assuming the same precision for the specific heat s at all concentrations.

The resulting equations reproduced all 74 of the experimental points satisfactorily. Only one deviation was greater than 0.03% in s, seven were between 0.02 and 0.03%: and eighteen between 0.01 and 0.02%. The average deviation, ±0.007% in s, is slightly smaller than the average of ±0.0085% from the third degree equations in $m^{1/2}$ which were used in the original publication[6] of these data. This comparison emphasizes the difficulty in determining the limiting law from specific heat measurements. However, it shows that the limiting slope linear in m, indicated by the more sensitive measurements of heats of dilution, is consistent with the specific heats.

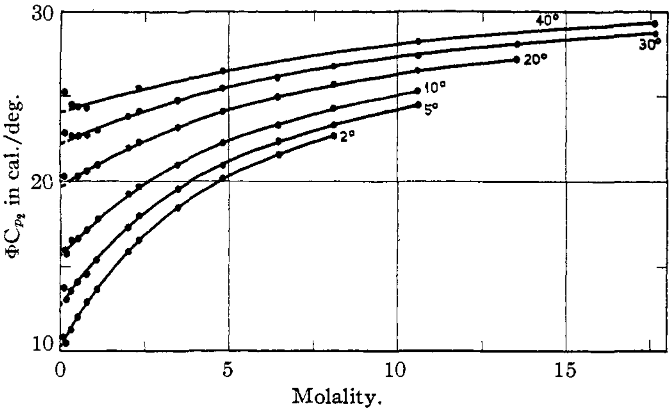

Fig. 3.—Heat capacities of urea.

The coefficients of equation (4) are measured in calories at the experimental temperature. In order to be combined with our heats of dilution they are first changed to 15°-calories, using the values of the heat capacity of water at different

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(11) S. M. Naudé, *Z. physik. Chem.*, **135A**, 209 (1928).

(12) Fuoss, This Journal, **58**, 982 (1936).

temperatures recently determined by Osborne, Stimson and Ginnings at the National Bureau of Standards.[13] The coefficients then were plotted against the centigrade temperature, t. As shown in Fig. 4, all four change in about the same way with temperature. The values of $\Phi C^0_{p_2}$ and b increase more rapidly at low temperatures, while those of a and c decrease correspondingly. Assuming the change of each coefficient is a quadratic function of $(t - 25)$, *e. g.*

$$\Phi C^0_{p_2} = \Phi^0_{25} + k_1(t - 25) + k_2(t - 25)^2 \qquad (5)$$

we evaluated the constants k_1 and k_2 by the method of least squares, weighting each according to the accuracy with which it was calculated from the original data. Thus the value of c, the coefficient of m^3 in equation (4), is fixed 20 times as accurately at 30°, by the series of fourteen experiments extending up to 17.6 m, as at 2°, where the twelve experiments extended only to 8.1 m. The differences in the accuracy of the coefficients of the lower powers of m were progressively less.

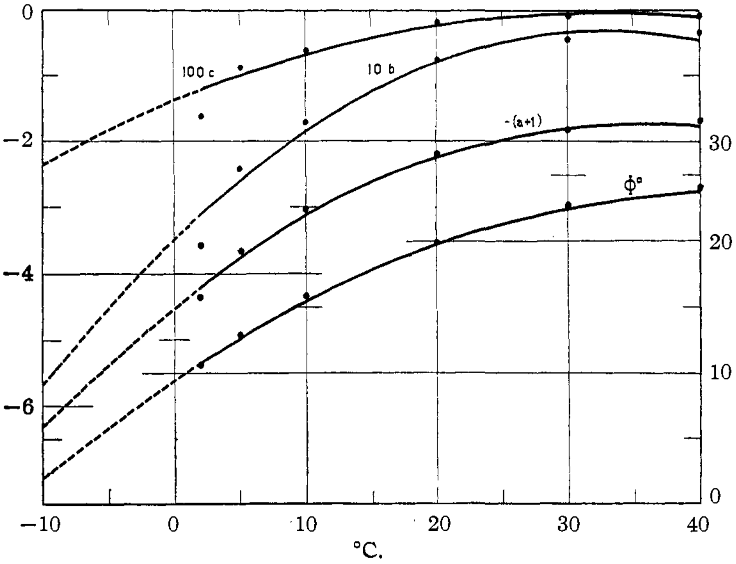

Fig. 4.—Constants for heat capacities of urea.

The curves of Fig. 4 represent these equations. The deviations, which appear to be random, average ±0.236 in $\Phi C^0_{p_2}$, ± 0.0898 in a, ±0.0175 in b and ±0.00120 in c. Because of the decreased accuracy of the coefficients of higher powers of m at low temperatures, the scattering in Fig. 4 is more pronounced at low temperatures. Fortunately the importance of these coefficients also decreases at low temperature, because of the decreased solubility of urea. Using the equations thus derived, coefficients of equation (4) were calculated at all six temperatures. Values of specific heats, calculated from these smoothed equations, were compared with the original experiments. The average deviation was ±0.033%. The two largest deviations, −0.236 and −0.500%, were for the 17.6 m solution at 30 and 40°. The average deviation of all the other results, up to and including 13.5 m, was ±0.024%. Of the individual deviations, 22 are less than 0.01%, 26 lie between 0.01 and 0.02%, 4 between 0.02 and 0.03%, 7 between 0.03 and 0.04%, 5 between 0.04 and 0.05%, 4 between 0.05 and 0.06%, 2 between 0.06 and 0.07% and 1 (13.5 m at 20°) is 0.22%. At any one temperature, the deviations are of the same sign, but the average net deviation is only −0.01%.

These figures indicate that, up to 12 m, which is the limit of the heats of dilution, the results can be expressed fairly satisfactorily by means of quadratic equations in the temperature, over the range from 2 to 40°. The values plotted in Fig. 4 indicate, however, that the coefficients of equation (4) approach zero at higher temperatures, instead of going through a maximum value and then decreasing as demanded by a quadratic equation in the temperature. A different type of equation might be required to fit the results of a series of heat capacity measurements extended to higher temperatures. At the lower temperatures, our equations are consistent with the experimental results and seem reasonable bases for extrapolation. Also, the decreased solubility at low temperatures limits the range to which the equations can be applied, and this helps to compensate some of the uncertainty of extrapolation.

Apparent and Partial Relative Heat Contents at Different Temperatures.—From equation (4) we can obtain the apparent relative heat capacity of the solute, $\Phi C_{p_2} - \Phi C^0_{p_2}$. Since this is the temperature coefficient of the apparent relative heat content, and a, b and c are known functions of temperature, we can integrate to obtain the apparent relative heat content at any temperature between 2 and 40°. The equation is

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(13) Reference 9, Table 6.

$$\Phi L_2 = \Phi L_2'' + \Delta\Phi C_{p_2}(t - 25) + \Phi P_2(t - 25)^2 + \Phi Q_2(t - 25)^3 \quad (6)$$

where $\Phi L_2''$ at 25° is given by equation (3), and the other terms are

$$10^3 \Delta\Phi C_{p_2} = 940.0\, m - 49.4\, m^2 + 1.11\, m^3 \quad (7)$$

$$10^5 \Phi P_2 = -2306\, m + 236.9\, m^2 - 1.88\, m^3 \quad (8)$$

$$10^7 \Phi Q_2 = 7423\, m - 955\, m^2 + 1.71\, m^3 \quad (9)$$

In 1928, Naudé[11] studied the heats of dilution of urea from 1 to 0.001 M, at temperatures near 18°, using one of the first microcalorimeters. Previous work in this Laboratory[3] has shown that the apparent molal volume of urea changes very little with temperature, hence the difference between molarity (moles per liter) and molality, m, is practically the same at 18 as at 25°. On this basis we have converted Naudé's results to 25°. For dilutions from 0.333 M (0.340 m) to 0.0067 M (or m) at 18.51°, he found $\Delta H = 28.5$ cal./mole. From equation (6) the value should be 2.4 cal./mole less, or 26.1 cal./mole at 25°. Our equation (3) gives 27.8 cal./mole for this dilution. His value of 14.0 for the dilution from 0.1 to 0.003 M is decreased by 0.8 to 13.2 cal./mole, compared to 8.3 calculated from equation (3). These differences of −1.7 and +4.9 cal./mole correspond to −11 and +15 microdegrees. This agreement was typical of the five results up to 0.5 M. His 2 results at 1 M gave larger deviations of about 60 microdegrees.

From equation (3) for the apparent relative heat content of urea, the equations for $\bar{L}_2$ and $\bar{L}_1$, the partial relative heat contents of urea and water are calculated by the general thermodynamic relations. If G represents any extensive property of a solution of n_1 moles of water and n_2 of solute, and G_1 is the corresponding molal property of the water, the apparent molal property, ΦG_2 is defined by the equation

$$G = n_1 G_1 + n_2 \Phi G_2 \quad (10)$$

If ΦG_2 is represented by the equation

$$\Phi G_2 = \Phi G_2^0 + am + bm^2 + cm^3 + \ldots \quad (11)$$

the corresponding equations for $\bar{G}_2$ and $\bar{G}_1$, the partial molal properties of solute and water, respectively, are

$$\bar{G}_2 = \Phi G_2^0 + 2\,am + 3\,bm^2 + 4\,cm^4 + \ldots \quad (12)$$

$$\bar{G}_1 = G_1 - 0.018016\,[am^2 + 2\,bm^3 + 3\,cm^4 + \ldots] \quad (13)$$

These relationships hold for the arguments of equations (3), (7), (8) and (9).

The Change of Activity with Temperature

The difference between the activity a' of any component of a solution at a temperature T' and its activity a'' at a temperature T'' is given by the well-known thermodynamic equation[14]

$$\log a'' - \log a' = \frac{-0.43429}{R}\int_{T'}^{T''} \frac{\bar{L}}{T^2}\, dT \quad (14)$$

where R is the gas constant and $\bar{L}$ the partial relative heat content. If $\bar{L}$ is a cubic function of T, the integrated form of equation (14) is

$$\log a'' - \log a' = K_1\bar{L}'' + K_2\Delta\bar{C}_p'' + K_3\bar{P} + K_4\bar{Q} \quad (15)$$

where

$$K_1 = \frac{-0.43429}{R}\,\frac{\Delta T}{T'T''}, \text{ where } \Delta T = T'' - T' \quad (16)$$

$$K_2 = \frac{0.43429}{R}\left[\frac{\Delta T}{T'} - \ln\left(\frac{T''}{T'}\right)\right] \quad (17)$$

$$K_3 = \frac{-0.43429}{R}\left[\Delta T + T''\left\{\frac{\Delta T}{T'} - 2\ln\left(\frac{T''}{T'}\right)\right\}\right] \quad (18)$$

$$K_4 = \frac{0.43429}{R}\left[3T'\Delta T + 4.5(\Delta T)^2 + \frac{(\Delta T)^3}{T'} - 3T''^2\ln\left(\frac{T''}{T'}\right)\right] \quad (19)$$

The coefficients K_1, etc., are functions only of the temperatures involved. The first can be evaluated easily by direct substitution but the rest cannot, since the logarithmic term differs from the sum of the others by only 4, 0.1 and 0.005%, respectively. However, on expanding the logarithm in series, many of the largest terms cancel and we obtain the following expressions for the coefficients, chiefly in terms of the variable $v = \Delta T/T'$.

$$K_2 = \frac{0.43429}{R}\,v^2[1/2 - v/3 + v^2/4 + \ldots] \quad (20)$$

$$K_3 = -\frac{0.43429}{R}\,v^3[T' - 2T''/3 + 2\Delta T(1 + v)\,(1/4 - v/5 + v^2/6 + \ldots)] \quad (21)$$

$$K_4 = \frac{0.43429}{R}\,v^4\left[\frac{T'^2}{4} - \frac{T'\Delta T}{10} - \frac{9(\Delta T)^2}{20} - \frac{3(\Delta T)^2 v}{5} + 3(\Delta T)^2(1 + v)^2\,(1/6 - v/7 + v^2/8 + \ldots)\right] \quad (22)$$

In evaluating the coefficients, only four or five terms of each power series in v are necessary to give results to 0.01%. In Table II we have recorded values of these coefficients for changes from the given initial temperatures T' to the standard temperature $T'' = 298.16°$.

The values of K_1 are 0.03% higher than those tabulated by Lewis and Randall (p. 615), because of our use of $R = 1.9869$ cal.$_{15}$ deg.$^{-1}$ mol.$^{-1}$ for the gas constant and 273.16° A. as the freezing point of water.[15] Our values of K_2 agree with

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[14] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 289.

[15] These values were obtained from a critical compilation by Dr. F. D. Rossini, privately communicated to us through Professor Scatchard.

TABLE II[a]

COEFFICIENTS OF EQUATION (15) FOR THE CHANGE IN THE LOGARITHM OF THE ACTIVITY BETWEEN *t* AND 25°

t, °C.	K_1	K_2	K_3	K_4
−15	−0.00011359	0.0023807	−0.06500	1.9779
−14	− .00011032	.0022519	− .05991	1.7780
−13	− .00010708	.0021269	− .05510	1.5916
−12	− .00010387	.0020064	− .05058	1.4223
−11	− .00010067	.0018898	− .04632	1.2668
−10	− .00009750	.0017773	− .04233	1.1250
− 9	− .00009436	.0016688	− .03858	0.9958
− 8	− .00009123	.0015642	− .03508	.8784
− 7	− .00008814	.0014636	− .03181	.7721
− 6	− .00008507	.0013669	− .02876	.6761
− 5	− .00008201	.0012736	− .02592	.5894
− 4	− .00007898	.0011843	− .02328	.5116
− 3	− .00007598	.0010986	− .02084	.4420
− 2	− .00007300	.0010166	− .01859	.3800
− 1	− .00007003	.0009381	− .01651	.3248
0	− .00006709	.0008631	− .01460	.2761
10	− .00003884	.0002963	− .00299	.0338
20	− .00001250	.0000314	− .00011	.0004
30	.00001209	.0000301	.00010	.0004
40	.00003511	.0002590	.00257	.0288
50	.00005671	.0006899	.01134	.2127

[a] The energy unit of this table is the 15°-calorie, which is used throughout this paper: 1 cal._{15} = 4.1858 abs. j. (ref. 9, p. 238).

those of Lewis and Randall, but are carried two places farther. T. F. Young,[16] in his excellent treatment of the calculation of activities from freezing points, has taken account of the quadratic change of $\bar{L}$ with temperature. He has tabulated values of Ω, the coefficient defined in equation (10) of his paper, which is equal to $-{}^1/_2\, K_3$. This unpublished tabulation, extending from −25 to 0°, he kindly sent to us in a private communication.

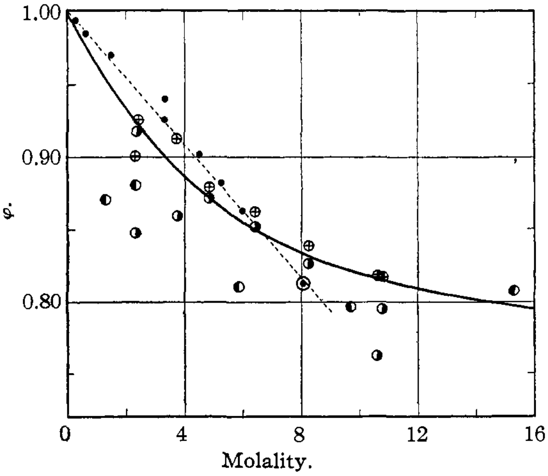

Fig. 5.—Osmotic coefficients of urea at 25° (curve from Scatchard, Hamer and Wood); ◑, Fricke at 0°; ⊕, Fricke at 10°; ◐, Perman and Lovett at 50°; ● and ○, Chadwell and Politi at f. p. (The first point represents 2 results.)

In describing the behavior of the solvent in an aqueous solution, Bjerrum's osmotic coefficient

$$\varphi = -\frac{55.506}{m}\ln a_1 \tag{23}$$

is a convenient function since it can be calculated directly from measurements of the vapor pressure or freezing point of the solution.

The activity coefficient is related to the osmotic coefficient by the isothermal equation

$$\ln\gamma = (\phi - 1) + \int_0^m (\phi - 1)\,\mathrm{d}\ln m \tag{24}$$

If values of ϕ or γ at any temperature are known at definite concentrations, and the thermal terms are also known, the values of ϕ or γ at any other temperature can be calculated. If either ϕ or γ at any temperature is known as a function of m, and the thermal terms are also known as functions of m, ϕ or γ at any other temperature in the experimental range can be determined as a function of m by algebraic addition of the necessary equations. These methods are applicable to the results of isothermal vapor pressure measurements.

When solvent activities are determined from freezing points, they corrrespond to the temperature of the freezing point, which decreases with concentration. Knowing ϕ' at a definite freezing point, we can interpolate values of the coefficients from Table II and calculate ϕ at 25° from our thermal data.

The Osmotic Coefficient of Urea at 25°

Scatchard, Hamer and Wood[10] have made a very careful study of isotonic solutions at 25°. By intercomparison with the best results for several standard substances, they have determined the vapor pressure and tabulated the osmotic coefficient of urea at this temperature. The smooth curve of Fig. 5 represents their results. Our thermal data allow a comparison between their results and other studies at different temperatures, excluding the early work, in which the experimental uncertainty is large.

Fricke[17] has measured the vapor pressure of urea solutions at 0 and 10°. From these data we have calculated ϕ, first at the experimental temperature and then, by means of equations (15) and (23), at 25°. The resulting values are plotted in Fig. 5. The deviations from the curve corresponded to

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[16] T. F. Young, *Chem. Rev.*, **13**, 103 (1933).

[17] Fricke, *Z. Elektrochem.*, **33**, 441 (1927); **35**, 631 (1929).

average differences of +0.010 mm. in the vapor pressure at 0° and −0.004 mm. at 10°, which appear to be within the experimental error. Perman and Lovett[18] measured vapor pressures at 50° and higher. We calculated values of ϕ from their results at 50°, which did not involve too great extrapolation of our thermal data. The points, plotted in Fig. 5, show an average deviation from the curve of +0.18 mm. in the vapor pressure, which also appears to be within the experimental error. The results of these three series of vapor pressure measurements therefore corroborate the curve of Scatchard, Hamer and Wood.

Recently, Chadwell and Politi[19] have determined the freezing points of aqueous solutions of urea from 0.3 to 8.08 *m*, the eutectic, and calculated ϕ', the osmotic coefficient at the freezing point. After interpolating the coefficients from Table II, we used equations (15) and (23) to calculate the corresponding values of ϕ, at 25°, which we plotted in Fig. 5. The deviations in ϕ are smaller than those among the vapor pressure measurements, but they are systematic. The points all lie along the dotted straight line which crosses the curve of Scatchard, Hamer and Wood at about 7 *m*. Below this concentration, the freezing point depressions observed by Chadwell and Politi are *higher* than those which would be expected from the vapor pressure and thermal data, while their two concordant results at 8.08 *m* are *lower*. The deviation is only +0.004° in the 0.3 *m* solution, but it increases to +0.25° at 3.4 *m* and −0.32° at 8.1 *m*.

We have estimated the part of this discrepancy which might be due to our thermal measurements, as follows. From the differences between the heats of dilution observed and those calculated from equation (3), the corresponding differences in $\bar{L}_1$ were determined at a series of even concentrations. The uncertainty in $\Delta\bar{C}_{p_1}''$ at the same concentrations was then estimated as the average difference between $\Delta\bar{C}_{p_1}$ at each temperature, calculated from the original equation (which best fitted the measured specific heats) and the final equation (which smoothed the results at all temperatures). The corresponding uncertainty in $\bar{P}_1$ and $\bar{Q}_1$ was estimated by assuming an error in $\Delta\bar{C}_{p_1}$ at 2 and 40° equal to that in $\Delta\bar{C}_{p_1}''$ at 25°, but opposite in sign. The resulting differences in these three terms, multiplied by the appropriate factors, gave the corresponding differences in ϕ. The sum of these differences, taken as a generous estimate of the error in the thermal terms, was 2, 3, 4, 5, 20 and 44 × 10^{-4} at 0.5, 1, 2, 4, 6 and 8 *m*. Up to 4 *m*, the three heat capacity terms made up 80–90% of the whole uncertainty, but at 6 and 8 *m* their contribution had fallen to about 50%. Up to 4 *m*, these figures would account for only 2% of the observed differences between ϕ calculated from freezing points and from vapor pressure measurements at 25°. At 6 and 8 *m* they would account for 38 and 20% of the difference. The remaining difference, at all but the lowest concentrations, is far larger than would be expected from the sensitivity of the measurements involved, and from the agreement between the results of freezing point and e. m. f. measurements in the case of hydrochloric acid, reported by Chadwell a few years ago.[20] We considered the possibility of solid solution of the urea in the ice, but this would lead to a negative error in ϕ at all concentrations.

Acknowledgments.—In addition to the grants-in-aid from the Penrose Fund of the American Philosophical Society and from the Graduate School of Northwestern University, it is a pleasure to acknowledge the courtesy of Professors George Scatchard and T. F. Young in reading the manuscript and making helpful suggestions in connection with it.

Summary

We have used a calorimeter sensitive to one millionth of a degree in measuring the heats of dilution of aqueous solutions of urea at 25°, from 12 *m* to 0.005 *m*. At low concentrations the heat of dilution is a linear function of *m*.

Combining these results with the heat capacities of urea from 2 to 40°, previously determined in this Laboratory, yields equations for the heat of dilution and the partial relative molal heat contents of urea and water as cubic functions of temperature.

These data are used to calculate ϕ, the osmotic coefficient at 25°, from measurements of freezing points and of vapor pressures at 0, 10 and 50°. The necessary equations are given and the numerical coefficients for the integration are tabulated.

The results of vapor pressure measurements

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[18] Perman and Lovett, *Trans. Faraday Soc.*, **22**, 1 (1926).

[19] Chadwell and Politi, THIS JOURNAL, **60**, 1291 (1938).

[20] Chadwell, *ibid.*, **49**, 2795 (1927).

agree within their own rather large experimental uncertainty with the recent precise isotonic measurements of Scatchard, Hamer and Wood. The results calculated from freezing points show smaller but systematic deviations, which apparently are considerably beyond the experimental error of the thermal measurements.

EVANSTON, ILLINOIS RECEIVED JANUARY 29, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

The System Magnesium Sulfate, Cadmium Sulfate and Water at 25 and 40°

BY W. C. VOSBURGH, VERNON H. DIBELER, HELEN C. PARKS AND WILLIAM J. MILLER

In the study of modified Weston cells[1] some difficulty was experienced in the preparation of a double salt of magnesium and cadmium sulfates. Schiff[2] prepared a double salt with the composition $MgSO_4 \cdot CdSO_4 \cdot 14H_2O$ in 1857, but no mention of later work on this compound has been found. Attempts to make the double salt by slow evaporation at room temperature of a solution containing the two component salts failed, and it was apparent that further study of the system magnesium sulfate, cadmium sulfate and water was desirable.

Mixtures were prepared of carefully weighed quantities of recrystallized magnesium and cadmium sulfates and water and brought to equilibrium in closed tubes which were rotated in an air-bath at 25 ± 0.1°. The time allowed for equilibrium varied considerably, but in only a few cases was it less than forty-eight hours. Often it was much longer than this, and the consistency of the data is an indication that equilibrium was attained in the time allowed.

After sufficient rotation, the saturated solution was drawn off through a glass-wool filter, this operation being carried out within the air-bath. The solution was weighed, diluted to a known volume and aliquot portions taken for analysis. Total solids were determined by evaporation to dryness and ignition in a muffle at 500°. Other samples were acidified with sulfuric acid, the cadmium was precipitated as sulfide, and the magnesium sulfate determined in the filtrate by evaporation, ignition at 500° and weighing. The cadmium sulfide was dissolved by hydrochloric acid, and the solution evaporated to dryness after addition of an excess of sulfuric acid. The cadmium sulfate was ignited at 500° and weighed.

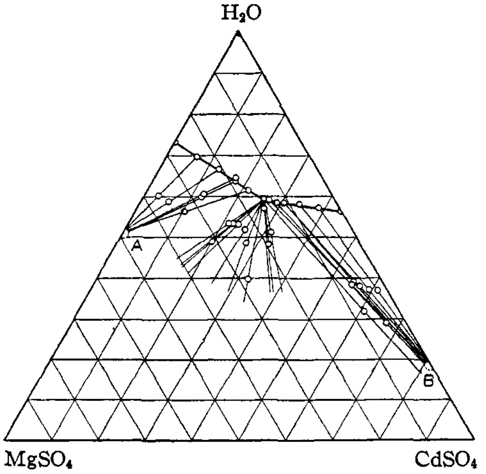

Fig. 1.—The system magnesium sulfate, cadmium sulfate and water at 25°. Points A and B represent the calculated compositions, in weight percentage, of hydrated magnesium and cadmium sulfates, respectively.

TABLE I

COMPOSITIONS OF SATURATED SOLUTIONS AND ORIGINAL MIXTURES AT 25°

Saturated solutions		Original mixtures	
$CdSO_4$, wt. %	$MgSO_4$, wt. %	$CdSO_4$, wt. %	$MgSO_4$, wt. %
6.5	23.8	3.1	36.8
12.5	20.9	5.9	35.4
17.2	18.3	12.2	26.9
17.4	18.9	12.3	27.8
21.7	17.0	10.3	33.2
25.5	15.2	27.1	16.3
25.7	14.9	20.0	31.1
25.8	15.4	32.4	19.4
26.0	15.0	21.2	25.5
26.1	15.0	31.3	17.6
26.2	15.3	22.2	24.4
26.2	15.1	25.5	22.6
26.4	15.0	32.3	28.1
26.4	15.2	23.4	23.4
26.4	15.2	27.6	21.9
26.9	14.9	60.9	7.2
27.0	13.9	55.0	6.6
29.1	12.5	54.9	5.9
30.5	11.2	56.8	5.1
30.5	11.0	67.0	3.9
34.0	8.0	59.3	3.6
38.6	4.3	61.3	1.9

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(1) Vosburgh, Derr, Cooper and Pettengill, THIS JOURNAL, **61**, 2687 (1939).

(2) Schiff, *Ann.*, **104**, 327 (1857); **107**, 73 (1858).