the literature, and predicting the entropy of two compounds we have calculated the free energies of seven amino acids.

PASADENA, CALIF. RECEIVED AUGUST 13, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Specific Heats of Aqueous Solutions of Urea from 2 to 40° and the Apparent Molal Heat Capacity of Urea[1]

BY FRANK T. GUCKER, JR., AND FRED D. AYRES

Introduction

A study of the properties of non-electrolytic solutions may help the interpretation of electrolytic solutions, by indicating a *normal* solute behavior, deviations from which may be ascribed to the charges of the ions. We have undertaken a study of the heat capacities of solutions of non-electrolytes and already have determined[2] the specific heats of aqueous sucrose solutions. In the same place we discussed the apparent molal heat capacity of sucrose and of other non-electrolytes for which suitable results were found in the literature. The present work deals with solutions of urea, studied over a wide range of temperature and concentration, to find the effect of each upon the apparent molal heat capacity.

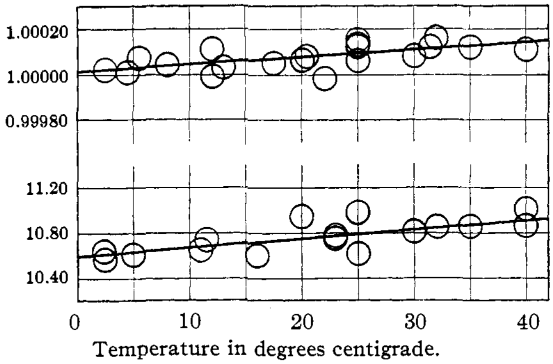

Fig. 1.—Temperature variation of the balancing ratio (x_0) and the heat capacity of the working calorimeter (c_1).

Preparation of the Urea Solutions.—The urea used in these experiments was prepared from the commercial C. P. product by two crystallizations from water with centrifugal drainage. The temperature of the solutions during the crystallizations was not allowed to exceed 65°, to prevent the conversion of urea to ammonium cyanate. After a preliminary drying in air, the product was ground to a fine powder in an agate mortar and then dried *in vacuo* (about 0.01 mm.) at 50–60° for five hours. The melting point of the product was 132.6–132.8° as determined with a standard thermometer totally immersed in a well-stirred bath. The rate of temperature rise near the melting point was about 0.2° per minute. This agrees very well with the values of 132.6 and 132.7° given by Shnidman and Sunier[3] for specially purified urea from different sources. All solutions were made up determinate from urea and freshly deaerated distilled water, except for three which were prepared by quantitative dilution of more concentrated solutions. All weighings were made with standardized weights, and reduced to the vacuum basis.

Experimental Methods and Results.—The differential twin-calorimeter apparatus which has been described previously[4] was used for determining the specific heats of the urea solutions. Since these measurements were to be made over a range of temperature extending from 2 to 40°, the apparatus was standardized over this same temperature range. The procedure was identical with that described in the previous paper, to which the reader is referred for details. The same symbols are used in this paper. The balancing ratio for equal weights of water in both calorimeters (x_0) was found to increase by about 0.01% as the temperature rose from 2 to 40°. Figure 1 shows a plot of the results of all these determinations, which were made at more or less evenly spaced intervals throughout the course of the measurements. The radius of each circle represents 0.005% in the ordinate. Of the twenty points only one falls more than 0.006% from the straight line. The heat capacity of the hollow copper displacer, used in determining that of the working calorimeter, was also measured at intervals over the entire temperature range. The effective heat capacity of the working calorimeter (c_1) was then calculated at frequent intervals. It increases linearly from 10.60 cal.$_{2°}$ at 2° to 10.91 cal.$_{40°}$ at 40°, as Fig. 1 shows. The method of calculation makes the percentage uncertainty in c_1 much larger than in x_0, but the effect of this upon the final specific heat is reduced in the same ratio to a negligible quantity. These calibrations made possible the direct calculation of all heat capacities, including those of the urea solutions, in calorie units at the various experimental temperatures and all the results are so expressed.

The usual experimental procedure was to make up by weight 269 ml. of the solution in a special volumetric flask, weigh this fixed volume into the working calorimeter and the same volume of distilled water, freshly deaereated by means of a water aspirator, into the tare and assemble the

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[1] Part of this paper was presented before the Division of Physical Chemistry at the Chapel Hill meeting of the American Chemical Society, April 14, 1937.

[2] Gucker and Ayres, THIS JOURNAL, **59**, 477 (1937).

[3] Shnidman and Sunier, *J. Phys. Chem.*, **36**, 1232 (1932).

[4] Gucker, Ayres and Rubin, THIS JOURNAL, **58**, 2118 (1936).

apparatus. It was left overnight with ice and water packed in the water-bath, and by morning the calorimeter temperature had fallen slightly below 1.5°. The excess ice was now removed and the temperatures equalized for the first experiment at the lowest temperature (1.5–2.5°). The apparatus was cooled again and a second experiment made at the same temperature. The experiments at the successively higher temperatures were then carried out as rapidly as possible, but the whole series occupied four or five days. At the end of the series, the calorimeters were removed and weighed again. The loss in weight due to evaporation was not greater than 0.01 g. from each calorimeter, and the differential effect was completely negligible. The number of experiments at 40° was cut down, because of the tendency of the bakelite insulating sections in the stirrer shafts to warp at this temperature.

In carrying out experiments above room temperature, the loss of heat from the adiabatic water-bath was prevented by supplementary heating coils, covering the entire surface of the bath and its lid. Under these conditions the control of adiabatic conditions was as good as at room temperature (±0.005°). For experiments below room temperature, the adiabatic bath was cooled by means of an adjustable drip of ice water, falling nearly on top of one of the stirrers. The maintenance of adiabatic conditions was somewhat more difficult than at room temperature. At 2°, the temperature difference between calorimeters and bath was about ±0.03°, while at 5° the control was somewhat better. These fluctuations may increase somewhat the experimental uncertainty at the lower temperatures, but they should not cause any systematic errors in the results.

The experimental results are collected in Table I. The experiments are numbered chronologically. Solutions 3a and 3b were prepared by quantitative dilution of two portions of 3, while 10a was made in the same way from 10. The other solutions were made directly from urea and water. The values of the molality m (moles of solute per 1000 g. of water) were calculated from the weights of solvent and solute, using the value M_2 = 60.057 for the molecular weight of the latter, based on the 1937 Atomic Weight Report. The values of the molarity, c (moles of solute per liter of solution at 25°), were calculated from the weight of urea used and the volume of the solution in the volumetric flask in which it was made up. The most concentrated solutions were only studied at the higher temperatures, since they would have been supersaturated at the lower.

TABLE I. THE SPECIFIC HEATS (s) AND APPARENT MOLAL HEAT CAPACITIES (Φ) OF UREA SOLUTIONS[a]

Expt.	m	c(25°)	$m^{1/2}$	$c^{1/2}$	2° s	2° Φ	5° s	5° Φ	10° s	10° Φ	20° s	20° Φ	30° s	30° Φ	40° s	40° Φ
	0.00000	0.0000	0.0000	0.000	1.00000		1.00000		1.00000		1.00000		1.00000		1.00000	
8	.09353	.0928	.3059	.305	0.99543	10.92	0.99569	13.72	0.99590	15.98	0.99630	20.28	0.99654	22.86	0.99676	25.22
6	.16398	.1623	.4049	.403	.99195	10.49	.99236	13.01	.99281	15.78	.99353	20.22				
5	.30232	.2974	.5498	.545	.98551	11.26	.98619	13.55	.98706	16.48	.98815	20.15	.98887	22.58	.98943	24.46
7	.50556	.4917	.7110	.701	.97645	12.06	.97747	14.14	.97871	16.67	.98046	20.24	.98162	22.60	.98247	24.33
9	.76971	.742	.8773	.861	.96532	12.92	.96653	14.57	.96848	17.21	.97097	20.60	.97254	22.73	.97368	24.28
4	1.0428	.994	1.0212	.997	.95444	13.631	.95613	15.353	.95849	17.758	.96160	20.927	.96362	22.985		
3b	1.9689	1.805	1.4032	1.344	.92214	15.836	.92460	17.233	.92803	19.181	.93285	21.919	.93616	23.799		
1	2.2842	2.068	1.5114	1.438	.91262	16.555	.91528	17.879	.91894	19.701	.92414	22.290	.92774	24.082	.93048	25.447
12	3.4826	3.007	1.8661	1.734	.88016	18.449	.88334	19.553	.88766	21.053	.89404	23.268	.89849	24.813		
2	4.7930	3.938	2.1893	1.984	.85108	20.043	.85451	20.964	.85917	22.217	.86622	24.111	.87135	25.489	.87536	26.567
3a	6.4168	4.971	2.5331	2.230	.82147	21.513	.82498	22.271	.82994	23.341	.83742	24.956	.84292	26.144		
11	8.0736	5.906	2.8414	2.430	.79682	22.689	.80037	23.341	.80537	24.261	.81311	25.685	.81895	26.759		
3	10.5323	7.130	3.2453	2.670			.77062	24.502	.77562	25.277	.78348	26.496	.78960	27.444	.79467	28.230
10a	13.5186	8.374	3.6767	2.894							.75531	27.261	.76149	28.090		
10	17.5767	9.761	4.1925	3.124									.73255	28.778	.73817[b]	29.436

[a] s and Φ are given in calories per degree at the temperature of the experiment, which is the mean of a 1° temperature rise.

[b] Due to stirrer friction, the second experiment at this temperature was not completed. The resistance ratio corresponding to zero galvanometer deflection was calculated from the observed galvanometer deflection (Δg) during the first experiment and the usual change of balancing ratio with galvanometer deflection. The correction amounted to only 0.027% in s, but this value is somewhat less certain than the others.

The apparent molal heat capacity was calculated from the usual equation

$$\Phi(C_{p_2}) = \left[\frac{1000}{m} + M_2\right] s - \frac{1000}{m} \qquad (1)$$

Since s is given in calorie units at the experimental temperature, Φ is expressed in the same units. The apparent molal heat capacities are plotted against the square root of the molality in Fig. 2. They described a series of elongated S-shaped curves, which are represented fairly well by equations of the type

$$\Phi = \Phi^\circ + am^{1/2} + bm - cm^{3/2} \qquad (2)$$

The lines in Fig. 2 are the graphs of this series of equations. The coefficients of the equations and the differences between the calculated and observed values of the specific heats are summarized in Table II. The average deviation is ±0.0085% for all the results, and ±0.0075% for all the series except that at 5°. This series was not represented nearly so well and the average deviation was nearly twice as large as in the others. In all cases the experimental results showed positive deviations in the dilute region, but these were not great enough to be unequivocal. The arrows in Fig. 2 represent an uncertainty of ±0.008% in the specific heats, and the deviations are not much more than this. Nevertheless, the results seem to indicate a decreased slope at low concentrations and an upturn at higher temperatures.

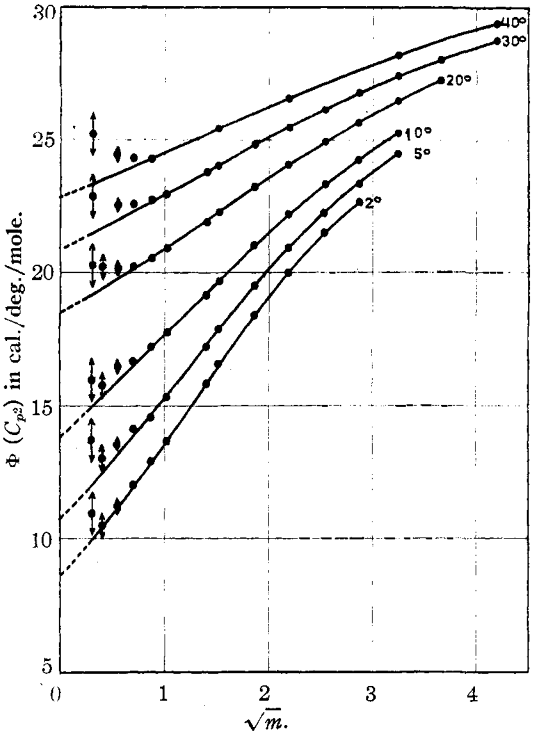

Fig. 2.—Apparent molal heat capacities of urea.

Equations (2) are useful in calculating the apparent molal heat capacity, and hence also the specific heat by means of equation (1). Their coefficients can also be used to calculate the partial molal heat capacities of solute and solvent, by means of the equations

$$\bar{C}_{p2} = \Phi(C_{p2})^\circ + 3/2\, am^{1/2} + 2\, bm + 5/2\, cm^{3/2} \qquad (3)$$

$$\bar{C}_{p1} = \bar{C}_{p1}^\circ - 10^{-3} M_1 (1/2\, am^{3/2} + bm^2 + 3/2\, cm^{5/2}) \qquad (4)$$

Since the molecular weight of water, M_1 = 18.0156, equation (4) becomes

$$\bar{C}_{p1} = 18.0156\, [1 - 10^{-3} (1/2\, am^{3/2} + bm^2 + 3/2\, cm^{5/2})] \qquad (4')$$

if we express the result in calories per degree at the temperature of the experiment.

Comparison with Previous Work.—The most reliable previous work on urea solutions is

TABLE II

COEFFICIENTS OF EQUATION (2) AND DIFFERENCES BETWEEN CALCULATED AND OBSERVED SPECIFIC HEATS

Temp.	2°	5°	10°	20°	30°	40°
Φ°	8.644	10.710	13.868	18.506	20.859	22.850
a	4.116	4.077	3.433	2.112	2.020	1.589
b	1.192	0.7262	0.4758	0.3883	0.1215	0.1085
c	− 0.3179	− .2080	− .1392	− .08595	− .03658	− .02691
Expt.	Calculated minus observed values of s (in 0.001%)					
8	− 9	−16	− 9	−11	−13	−17
6	0	− 9	− 7	−13	..	..
5	0	−12	−18	−11	−17	−21
7	0	−11	− 8	− 3	−12	−15
9	3	10	− 4	0	− 2	1
4	12	5	− 4	5	2	..
3b	9	9	10	14	6	..
1	−13	−13	− 8	0	− 4	− 8
12	−11	−17	− 7	− 8	0	..
2	− 4	−11	− 5	− 8	− 4	0
3a	18	21	6	− 2	8	..
11	−10	24	5	− 8	−10	..
3	..	−14	− 9	10	0	0
10a	..	..	..	−10	15	..
10	..	..	..	..	− 9	0
Av. diff.	± 7.3	±13.2	± 7.7	± 7.4	± 7.3	± 7.8

C. M. White's recent publication.[5] Using a twin Dewar apparatus, he studied solutions at 25°, over a range of concentration from 0.01 to 1 *m*. He concluded that, over this range, the apparent molal heat capacity is a linear function of $m^{1/2}$. He also gave a summary of the earlier results, which will not be repeated here. Since we made no experiments at 25°, we could not compare our results directly with his. However, by plotting against temperature our values of the apparent molal heat capacities at each concentration, we have interpolated the values at 25° which are shown in Fig. 3. Our interpolated results, represented by the black circles, are joined by a nearly straight dashed line. White's results (open circles) and the line representing the graph of his equation are also plotted for comparison. On the average, his results differ from our interpolated curve by ±0.02% in the specific heats. As a whole they are 0.016% higher. This agreement is as satisfactory as could be expected from the uncertainty inherent in our interpolation. It is a welcome check on both series of measurements.

Discussion

In several respects the results for urea resemble those for sucrose.[2] The change of the apparent molal heat capacity with concentration is about the same and is much smaller than in the case of electrolytes. The slopes also decrease with rising temperature. The change from 0 to 1 *m* is 4 calories per degree per mole at 2° and only 1.6 at 40°. We found, however, that the apparent molal heat capacity of sucrose is more nearly a linear function of the first power of the molarity (c) than of its square root. In the case of urea, we investigated the square root and first power of the molality, molarity and mole fraction. The curves against $c^{1/2}$ were simplest, showing little if any downward concavity at the high concentrations. However, they were not strictly linear and, because of the additional mathematical operations involved in calculating the partial molal heat capacities and specific heats, these functions were not used.

Our results for urea show no clear-cut and simple relationship between the apparent molal heat capacity and any function of the concentration, like the linear relationship between $\Phi(C_{p_2})$ and $m^{1/2}$ discovered by Randall and Rossini[6] which is valid for most electrolytes.

In the case of most electrolytes studied so far, the apparent molal volumes, compressibilities and heat capacities have shown a striking parallelism.[7] This is true also of sucrose solutions,[2] but the behavior of urea is exceptional. Recent careful density measurements in this Laboratory have shown that the apparent molal volume of urea is a linear function of the first power of the molarity over a wide range of concentration.[8] Unfortunately the heat capacity obeys no such simple law.

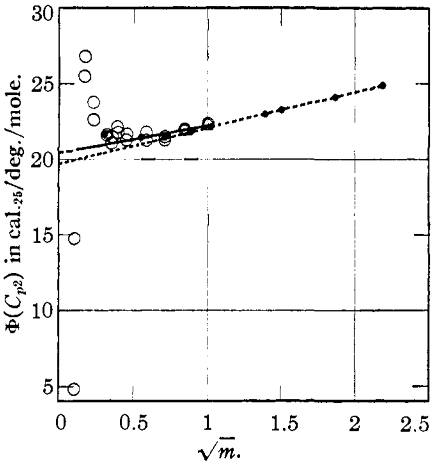

Fig. 3.—A comparison of the results of White (○) with our values interpolated to 25° (●).

Acknowledgment.—It is a pleasure to acknowledge our indebtedness to Mr. Paul Kleppisch who, working under an N. Y. A. grant, prepared the urea for these measurements.

Summary

Using a twin calorimeter method, we have measured the specific heats of solutions of urea from 0.1 *m* to a nearly saturated solution (8 to 17 *m*) at 2, 5, 10, 20, 30 and 40°. The results are presented in graphs and tables.

The apparent molal heat capacity changes less with concentration than does that of a 1–1 electrolyte. Its change is not linear with respect to c as is the apparent molal volume of urea, nor yet with respect to m, N_2 or the square root of any of these quantities.

Equations are given which reproduce the experimental results to ±0.008% and which may be used to calculate apparent and partial molal heat capacities and specific heats.

EVANSTON, ILLINOIS RECEIVED AUGUST 16, 1937

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(5) White, THIS JOURNAL, **58**, 1620 (1936).

(6) Randall and Rossini, *ibid.*, **51**, 326 (1929).

(7) Gucker, *Chem. Rev.*, **13**, 111 (1933).

(8) Gucker, Ayres and Gage, abstract of paper presented before the Chapel Hill meeting of the American Chemical Society. We hope to submit this work to THIS JOURNAL in the near future.