

lated from the concentrations by means of the equation

$$K_c = \frac{C_H(C_1 - C_2 + C_H)}{C_2 - C_H} \quad (2)$$

Here C_1 is the total buffer concentration and C_2 is the total acid concentration. In the case of the phosphate mixtures, K_c was taken as $C_H(C_1 - C_2)/C_2$. The buffer ratio, $(C_1 - C_2)/C_2$, was varied from 9:1 to 1:9 in the 25° series and from 4:1 to 1:4 in the 38° series. Inspection of the last column in Tables II and III shows no regular trend of K_c with changing buffer ratio, except possibly for the phosphates at 38°. The greatest average deviation from the mean of $\log K_c$ is ± 0.004 ; this is within the estimated error in E .

Discussion

The validity of our values for C_H and K_c depends on the assumption that the mean activity coefficient of hydrochloric acid is the same in the standard and unknown solutions. Such an assumption was not made by Harned and Hickey¹¹ in their study of the ionization of unbuffered acetic acid in salt solutions. Their k_A is equivalent to our K_c at infinite dilution of the buffer in a neutral salt solution. From their data, as tabulated by Harned and Owen,¹² we find by interpolation that the negative logarithm of k_A for acetic acid at infinite dilution in 0.16 M sodium chloride solution at 25° is 4.524. The small difference between this value and 4.515, our figure for $-\log K_c$ in the saline acetate buffers, makes it probable that our figures for C_H and K_c are not in error by more than 2%.

Brønsted^{6,13} showed that ionic equilibria can be accurately described by simple mass law equations in terms of concentrations, provided that

- (11) Harned and Hickey, *THIS JOURNAL*, **59**, 1284 (1937).
- (12) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, 1943, p. 523.
- (13) Brønsted, *Trans. Faraday Soc.*, **23**, 416 (1927).

the reaction in question is allowed to take place in solutions containing a constant and sufficiently great excess of other ions. This principle was applied to acid-base equilibria by Güntelberg and Schiödt,¹⁴ Kilpatrick,¹⁵ and others, but it has not been generally utilized for the preparation of buffer solutions. In a recent contribution, Brodersen¹⁶ emphasized the value of the Brønsted principle in the selection of buffers. He found, by measurements with a ferro-ferricyanide electrode, that phosphate buffers of constant concentration gave a salt effect which varied in one direction with changes in the buffer ratio, while buffers of constant ionic strength (0.1) produced a similar trend in the opposite direction. These variations were abolished by a 1 to 10 dilution of the latter buffers with 0.1 M sodium chloride solution. Our results lend support to his recommendation that a diluted buffer in a relatively concentrated salt solution should be used for experiments in which the main variable is to be the hydrogen ion concentration.

Summary

Buffer solutions of 0.025 M sodium acetate or phosphate, with the acidity varied by the addition of 0.1 to 0.9 as much hydrochloric acid, were given a constant ionic strength of 0.16 by the addition of sodium chloride. Hydrogen ion concentrations at 25 and 38° were determined by means of a glass electrode in a cell without liquid junction. Dissociation constants, from which these concentrations can be exactly calculated without the use of activity coefficients, were obtained. The two sets of buffers covered the range of hydrogen ion concentrations between 2.5×10^{-4} and 2.5×10^{-8} .

NEW HAVEN, CONN.

RECEIVED¹⁷ JUNE 11, 1946

- (14) Güntelberg and Schiödt, *Z. physik. Chem.*, **135**, 393 (1928).
- (15) Kilpatrick, *Chem. Rev.*, **16**, 57 (1935).
- (16) Brodersen, *Acta Physiol. Scand.*, **7**, 162 (1944).
- (17) Original manuscript received April 21, 1942.

[CONTRIBUTION NO. 487 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Heats of Dilution of Aqueous Solutions of α - and β -Alanine at 25°^{1,2}

BY H. A. BENESI,³ L. S. MASON AND A. L. ROBINSON

The properties of amino acids in solutions are in the process of extensive study. The monograph by Cohn and Edsall⁴ contains a review of a

considerable part of these investigations. Scatchard,⁵ Kirkwood⁶ and Fuoss⁷ have examined the properties of dipolar molecules in solution theoretically.

The following results are presented in continuation⁸ of a projected study of the heats of dilution of some of the simpler amino acids.

(1) From a thesis submitted by Hans A. Benesi in partial fulfillment of the requirements for the degree of Master of Science at the University of Pittsburgh, 1943.

(2) The financial assistance of the Buhl Foundation in support of this investigation is gratefully acknowledged.

(3) Present address: Department of Chemistry, Princeton University, Princeton, New Jersey.

(4) E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides as Ions and Dipolar Ions," Reinhold Publishing Corp., New York, N. Y., 1943.

(5) G. Scatchard and J. G. Kirkwood, *Physik. Z.*, **33**, 297 (1932).

(6) J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

(7) R. M. Fuoss, *THIS JOURNAL*, **68**, 982 (1936).

(8) W. E. Wallace, W. L. Offutt and A. L. Robinson, *ibid.*, **65**, 347 (1943).

TABLE I
 INTERMEDIATE HEATS OF DILUTION OF α -ALANINE

Moles/1000 g. of water $10^4 m_1$ $10^4 m_2$ $10^4 m_3$			Calories							Cal./mole of acid $-\Delta H_{1 \rightarrow 2}$ $\Delta H_{2 \rightarrow 3}$	
			Expt. $-10^3 \times$ $q_{1 \rightarrow 2}$	Eq. 5 $-10^3 \times$ $q_{1 \rightarrow 2}$	$10^3 \times$ $\Delta q_{1 \rightarrow 2}$	Expt. $-10^3 \times$ $q_{1 \rightarrow 3}$	Expt. $10^3 \times$ $q_{2 \rightarrow 3}$	Eq. 3 $10^3 \times$ $q_{2 \rightarrow 3}$	$10^3 \times$ $\Delta q_{2 \rightarrow 3}$		
12851	124.4	247.7	769.6	782.4	+12.8	769.5	-0.1	-17.1	+17.0	64.5 \pm 1.2	-0.2 \pm 0.0
			815.5		-33.1	807.7	-7.8		+ 9.3		
8391	83.26	165.8	355.0	347.7	- 7.3	353.8	-1.2	+ 3.3	- 4.5	42.0 \pm 0.7	+0.2 \pm 0.0
			336.7		+11.0	344.8	+8.1		+ 4.8		
6213	62.44	124.3	196.9	194.8	- 2.1	200.9	+4.0	+ 7.0	- 3.0	32.3 \pm 0.3	+0.3 \pm 0.1
			202.0		- 7.2	205.7	+3.7		- 3.3		
4112	41.82	83.24	82.6	87.3	+ 4.7	89.6	+7.0	+ 6.2	+ 0.8	20.7 \pm 0.6	+0.8 \pm 0.1
			89.6		- 2.3	95.0	+5.4		- 0.8		
3065	31.37	62.44	44.7	49.1	+ 4.4	51.1	+6.4	+ 4.5	+ 1.9	14.3 \pm 0.1	+0.9 \pm 0.1
			44.0		+ 5.1	49.2	+5.2		+ 0.7		
2041	21.01	41.82	21.8	22.0	+ 0.2	25.3	+3.5	+ 2.6	+ 0.9	10.7 \pm 0.1	+0.9 \pm 0.2
			22.7		- 0.7	26.9	+4.2		+ 1.6		
1526	15.77	31.38	13.3	12.4	- 0.9	14.2	+0.9	+ 2.0	- 1.1	9.4 \pm 0.6	+0.8 \pm 0.2
			16.0		- 3.6	20.0	+4.0		+ 2.0		
1019	10.55	20.99	6.3		- 0.9						
			4.9	5.4	+ 0.5					4.9 \pm 0.3	
			4.8		+ 0.6						
			4.4		+ 1.0						

Method and Materials

Heats of dilution were determined with a Lange-type calorimeter.⁹

α -Alanine secured from the Amino Acid Manufacturers, Los Angeles, California, was negative to tests for chlorine, ammonia, phosphorus pentoxide, iron, and heavy metals; an average purity of 100.4% was indicated by formol titration, and the ash content was less than 0.02% after ignition. It decomposed at 273–275°. An additional supply of α -alanine obtained from Merck and Company was purified by recrystallization until its properties were essentially the same as the material described above. Parallel experiments with the two samples gave the same results within the error of experiment.

β -Alanine was prepared by the Hofmann degradation of succinimide.¹⁰ The initial yield of 200 g. supplied 80 g. of purified material after five recrystallizations. It decomposed at 203–204° and had an ash content of less than 0.02%. A quantity of Merck and Company β -alanine was recrystallized twice. It had the same decomposition point and ash content as the synthesized material. The two samples gave consistent heats of dilution.

All of the samples were thoroughly dried before use.

Distilled water was prepared as previously.⁸ The same precautions to exclude carbon dioxide were observed. All solutions were prepared immediately before use by weighing the acids directly and diluting to a definite volume. Molarities were converted to molalities by means of the density data of Gucker and Allen.¹¹

(9) A. L. Robinson and W. E. Wallace, *Chem. Rev.*, **30**, 195 (1942).

(10) "Organic Syntheses," ed. by J. R. Johnson, Vol. XVI, John Wiley and Sons, New York, N. Y., 1936, pp. 1–3.

(11) F. T. Gucker, Jr., and T. W. Allen, *THIS JOURNAL*, **64**, 191 (1942).

Experimental Results and Treatment of Data

Relative Apparent Molal Heat Contents.—In Tables I and II are shown the heat effects (column 4) and the molal heats of dilution (column 11) for the long chord dilutions (m_1 to m_2), and the corresponding quantities (columns 8 and 12) for the short chord dilutions (m_2 to m_3) for solutions of α - and β -alanine. The short chords are calculated from two long-chord experiments (m_1 to m_2) and (m_1 to m_3) as explained previously.¹² The q values tabulated correspond to the heat effects resulting from the dilution of solutions from pipets having volumes of 10.39 and 10.35 ml. into 997 and 998 ml. of water, respectively. The short chord dilutions for the lowest concentration were omitted because the magnitude of the heat effects was less than the precision of the present measurements. The short chords for the two acids are plotted in Figs. 1 and 2. The curves represent equations for the slopes, $S = \partial(\Phi L_2)/\partial m$, for α -alanine

$$S = -468.1 + 56,724m - 1,601,600m^2 \quad (1)$$

and for β -alanine

$$S = 89.10 - 4222m - 42,302m^2 \quad (2)$$

derived by established methods.^{12,13}

Integration of the above equations gives, for α -alanine

$$\Phi L_2 = -468.1m + 28,362m^2 - 533,900m^3 \quad (3)$$

and for β -alanine

$$\Phi L_2 = 89.10m - 2111m^2 - 14,101m^3 \quad (4)$$

Equations (3) and (4) are valid in the range $m = 0$ to $m = 0.025$.

ΦL_2 values calculated from equations (3) and (4)

(12) A. L. Robinson and W. E. Wallace, *Chem. Rev.*, **30**, 195 (1942).

(13) T. F. Young, *et al.*, *THIS JOURNAL*, **54**, 3030 (1932); **58**, 187 (1936); **60**, 2379 (1938).

TABLE II
 INTERMEDIATE HEATS OF DILUTION OF β -ALANINE

Moles/1000 g. of water			Calories								Cal./mole of acid	
$10^4 m_1$	$10^4 m_2$	$10^4 m_3$	Expt. $-10^3 \times$ $q_1 \rightarrow 2$	Eq. 6 $-10^3 \times$ $q_1 \rightarrow 2$	$10^3 \times$ $\Delta q_1 \rightarrow 2$	Expt. $-10^3 \times$ $q_1 \rightarrow 2$	Expt. $-10^3 \times$ $q_2 \rightarrow 2$	Eq. 4 $10^3 \times$ $q_2 \rightarrow 2$	$10^3 \times$ $\Delta q_2 \rightarrow 2$		$-\Delta H_1 \rightarrow 2$	$-\Delta H_2 \rightarrow 2$
12822	124.3	247.4	586.4		13.2	594.5	-8.1		8.0			
			611.4	599.6	-11.8	613.2	-1.8	-0.1	1.7	48.8 \pm 0.4	-0.3 \pm 0.2	
			588.7		10.9	611.9	-23.2		23.1			
			611.7		-2.1	607.8	3.9		-4.0			
8379	83.24	165.7	268.7		-6.3	267.9	0.8		4.2			
			250.4		12.0	252.0	-1.6		6.6			
			271.6 ^a	262.4	-9.2	263.3	8.3	5.0	-3.3	32.1 \pm 0.3	0.3 \pm 0.0	
			262.0 ^a		0.2	251.8	10.2		-5.2			
			270.9 ^a		-8.5	270.6	0.3		4.7			
			261.3 ^a		1.1	254.1	7.2		-2.2			
6207	62.43	124.3	143.1	145.2	2.1	140.7	2.4	2.9	0.5	23.5 \pm 0.2	-0.0 \pm 0.2	
			147.3		-2.1	150.2	-2.9		5.8			
4109	41.82	83.23	72.5 ^a		-1.0	68.9	3.6		-1.5			
			70.1 ^a	71.5	1.4	68.6	1.5	2.1	0.6	17.3 \pm 0.1	0.3 \pm 0.0	
			72.5		-1.0	70.0	2.5		-0.4			
			71.0		-0.5	69.4	1.6		0.5			
3063	31.36	62.41	40.4	38.9	-1.5	39.9	0.5	1.3	0.8	12.5 \pm 0.3	-0.0 \pm 0.1	
			37.4		1.5	38.3	-0.9		2.2			
2040	21.01	41.81	19.3 ^a	18.9	-0.4	18.1	1.2		-0.5			
			18.5 ^a		0.4	18.0	0.5	0.7	0.2	9.1 \pm 0.1	0.2 \pm 0.0	
			18.7		0.2	18.7	0.0		0.7			
			18.6		0.3	17.6	1.0		-0.3			
1526	15.76	31.37	10.6		0.0	9.7	0.9		-0.5			
			11.8	10.6	-1.2	12.8	-1.0	0.4	1.4	6.8 \pm 0.2	0.3 \pm 0.2	
			10.6		0.0	9.7	0.9		-0.5			
			9.5		1.1	6.6	2.9		-2.5			
1019	10.56	21.01	5.6 ^a		0.5	5.4	0.2	0.2	0.0			
			5.6 ^a		0.5	5.5	0.1		0.1			
			7.0									
			9.1									
			5.3	6.1						5.8 \pm 0.4	0.1 \pm 0.0	
			7.8									
			4.6									
			4.8									
			7.2									
			4.2									

^a These measurements were made several months later than the others and with a different thermopile.

for the final concentrations of the long chords (m_2) were combined with the experimental ΔH 's

for the initial concentrations of the long chords (m_1) to give values of ΦL_2 for the latter concentrations.

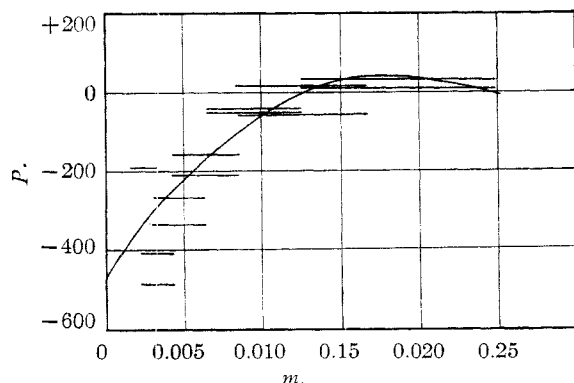


Fig. 1.—Plot of short chords, $\bar{P} = \Delta H / \Delta m$ vs. m for α -alanine and equation 1.

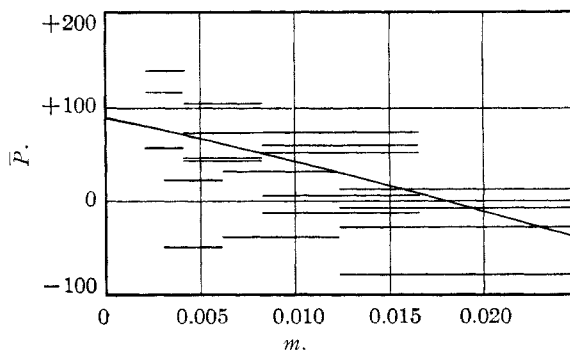


Fig. 2.—Plot of short chords $\bar{P} = \Delta H / \Delta m$ vs. m for β -alanine and equation 2.

The long chord and short chord ΦL_2 's were then treated by the least squares method to obtain equations for the concentration range studied. For α -alanine

$$\Phi L_2 = 47.62m - 515.7m e^{-58.79m} \quad (5)$$

For β -alanine

$$\Phi L_2 = 49.07m - 21.56m^2 + 10.49m^3 \quad (6)$$

A two-constant equation for β -alanine gave much larger deviations of calculated from observed results than equation (6). Equations (5) and (6) are shown in Fig. 3.

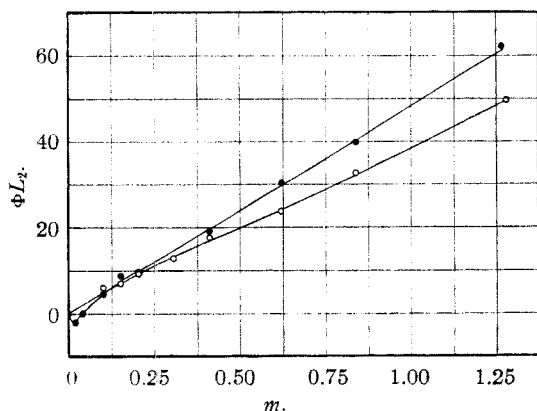


Fig. 3.— ΦL_2 vs. m for α - and β -alanine, equations 5 and 6: ●, α -alanine; ○, β -alanine.

q -Values for the long chords calculated from equations (5) and (6) are listed for both acids in column 5 of Tables I and II. The differences between calculated and observed values are in column 6. The corresponding quantities for the short chords calculated from equations (3) and (4) are shown in columns 8 and 9.

Relative Partial Molal Heat Contents.—The following equations for \bar{L}_1 and \bar{L}_2 were obtained from equations (5) and (6) by means of the well-known Rossini expressions.¹⁴ They are, for α -alanine

$$\bar{L}_1 = 9.291m^2 e^{-58.79m} - 546.2m^3 e^{-58.79m} - 0.8579m^2 \quad (7)$$

$$\bar{L}_2 = 95.24m - 1032m e^{-58.79m} + 30,320m^2 e^{-58.79m} \quad (8)$$

and for β -alanine

$$\bar{L}_1 = -0.8840m^2 + 0.7768m^3 - 0.5669m^4 \quad (9)$$

$$\bar{L}_2 = 98.14m - 64.68m^2 + 41.96m^3 \quad (10)$$

Values for \bar{L}_1 and \bar{L}_2 at several molalities are shown in Table III.

Discussion of Results

The inversion in the ΦL_2 vs. m curve for α -alanine (equation 5) below $0.01m$ is similar to the effect observed by Wallace, Offutt and Robinson⁸ in the case of glycine. The ΦL_2 's are of opposite sign and the curves are roughly mirror images except that the magnitudes of the heat effects above $0.1m$ for α -alanine are about two-thirds of

(14) F. D. Rossini, *J. Research Natl. Bur. Standards*, **4**, 313 (1930).

TABLE III
RELATIVE PARTIAL MOLAL HEAT CONTENTS

m	α -Alanine		β -Alanine	
	\bar{L}_1 Cal./mole H ₂ O	\bar{L}_2 Cal./mole acid	\bar{L}_1 Cal./mole H ₂ O	\bar{L}_2 Cal./mole acid
0.001	$+7.4 \times 10^{-6}$	—	-8.8×10^{-7}	0.10
.005	$+1.0 \times 10^{-4}$	—	-2.2×10^{-5}	0.49
.010	$+1.3 \times 10^{-4}$	—	-8.8×10^{-5}	0.97
.050	-4.6×10^{-3}	+ 6.10	-2.1×10^{-3}	4.75
.075	-7.1×10^{-3}	+ 8.35	-4.7×10^{-3}	7.02
.150	-2.0×10^{-2}	+ 14.37	-1.8×10^{-2}	13.37
.300	-7.7×10^{-2}	+ 28.57	-6.0×10^{-2}	24.75
.600	-3.1×10^{-1}	+ 57.14	-2.0×10^{-1}	44.84
1.200	-1.2	+114.3	-9.2×10^{-1}	97.26

the values for glycine at corresponding concentrations. However, the apparent molal heat capacities at 25° of glycine, α - and β -alanine for concentrations up to $2m$ are of the same sign and give approximately parallel curves when plotted against m .¹⁵

If the values of ΦL_2 for α -alanine below $0.01m$ are omitted, the remaining values of ΦL_2 are essentially linear with respect to m , in qualitative agreement with theory. The limiting slope would be positive (about 50) instead of negative (-468) and of a magnitude similar to the limiting slope for β -alanine. However, the omission of values below $0.01m$ can hardly be justified in terms of the precision of these measurements. The ΦL_2 values at low concentrations are quite small and it is evident that any unknown small extraneous effects in this region could have a marked influence on the limiting slope.

Zittle and Schmidt¹⁶ obtained a limiting slope of 56.5 for α -alanine by measuring heats of dilution in the range 0.1 to $3.3m$. The following linear equation expresses their data

$$\Phi L_2 = 56.5m \quad (11)$$

The ΦL_2 's calculated from the above equation are compared to ΦL_2 's calculated from equation (5) at two concentrations.

	0.1 m	1.0 m
Zittle and Schmidt	5.65	56.5
This work	4.62	47.62

Results for β -alanine are best represented by a three-constant equation, equation (6), although the resultant curve does not deviate greatly from a straight line. The limiting slope is 49 ± 29 .

There seems to be no obvious correlation between the limiting slopes for glycine, α - and β -alanine and the magnitudes of the dipole moments of "zwitterions."

Amino acid	Limiting slope	Dipole moment* Debye units
Glycine ⁸	167 ± 233	15
α -Alanine	-468 ± 40	15
β -Alanine	49 ± 29	19

(15) F. T. Gucker, I. M. Klotz and T. W. Allen, *Chem. Rev.*, **30**, 181 (1942).

(16) C. A. Zittle and C. L. A. Schmidt, *J. Biol. Chem.*, **108**, 161 (1935).

Heat of dilution measurements for four amino-butyric acids will be reported soon.

Summary

Intermediate heats of dilution of aqueous solutions of α - and β -alanine have been measured over the concentration range from 1.3 to 0.001*m* at

25°. By extrapolation to zero concentration, relative apparent molal heat contents have been evaluated and relative partial molal heat contents have been calculated.

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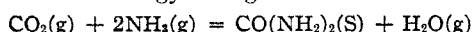
RECEIVED DECEMBER 21, 1945

[CONTRIBUTION FROM THE WILLIAM G. KERCKHOFF LABORATORIES OF THE BIOLOGICAL SCIENCES, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Thermal Data. XIX. The Heat Capacity, Entropy and Free Energy of Urea

BY ROBERT A. RUEHRWEIN AND HUGH M. HUFFMAN¹

Urea is of considerable interest as an organic compound and also because of the important role it plays in physiological processes. Lewis and Burrows² studied the equilibrium between urea, carbon dioxide, ammonia and water and calculated the free energy change in the reaction



A comparison of third law and equilibrium free energy data is of value in helping to settle the question of randomness in the crystal lattice of urea due to hydrogen bonding. Urea has also been reported³ to undergo higher order transitions in the temperature ranges -6 to 5° and 25 to 37° .

In this paper we have reported the results of our investigation of the heat capacity of urea over the temperature range 19 to 320° K.

Experimental

Apparatus.—The measurements were made in an aneroid adiabatic calorimeter, the details of which have been published⁴ so that only a brief description need be given here. The calorimeter was made of copper. Temperature measurements were made with a platinum resistance thermometer of laboratory designation H-8. All electrical measurements were made with a "White" double potentiometer in conjunction with a sensitive galvanometer and calibrated resistors. Time was measured with an electric stop clock. The energy measurements were made in terms of the international joule and converted to conventional calories by dividing by 4.1833. The precision of the measurements was approximately $\pm 0.1\%$.

Material.—J. T. Baker C. P. urea was dissolved in redistilled water at 60° and then allowed to crystallize in a cold room at about 0° . The crystals were filtered from the mother liquor and dried to constant weight in phosphorus pentoxide vacuum.

The material was lightly compressed into the calorimeter in layers, about 2-mm. thick, separated by thin copper disks which were in thermal contact with the walls of the calorimeter and the reentrant thermometer well. The cover was then soldered in place, helium admitted to the gas space through a small tube in the cover, which was finally closed with a drop of soft solder.

Results

In Table I we have listed the experimentally determined specific heats over the temperature

TABLE I
MOLAL HEAT CAPACITY OF UREA
Mol. weight = 60.058; $0^\circ\text{C.} = 273.16^\circ\text{K.}$

T, °K.	ΔT	C_p , cal./degree	T, °K.	ΔT	C_p , cal./degree
19.45	0.994	1.139	152.43	11.180	13.031
20.53	1.166	1.286	163.35	10.676	13.715
22.09	1.947	1.529	173.81	10.254	14.372
25.25	4.384	2.026	183.87	9.868	15.007
29.56	4.232	2.719	193.57	9.536	15.615
33.36	3.371	3.324	202.95	9.238	16.204
36.82	3.551	3.858	210.50	5.753	16.698
40.68	4.160	4.414	217.75	8.743	17.130
44.57	3.626	4.950	226.38	8.527	17.648
48.52	4.281	5.477	234.81	8.324	18.165
52.59	3.857	5.956	243.04	8.134	18.682
55.97	2.705	6.348	248.97	2.074	19.082
56.72	4.390	6.429	251.04	2.062	19.209
59.42	4.205	6.722	251.09	7.954	19.197
63.48	3.904	7.141	266.44	7.615	20.197
67.27	3.677	7.492	268.66	3.904	20.357
72.21	6.196	7.905	272.54	3.858	20.640
78.18	5.757	8.386	274.00	7.460	20.712
83.77	5.415	8.829	276.39	3.822	20.854
87.92	6.226	9.105	281.42	7.329	21.161
89.06	5.157	9.192	282.06	7.528	21.220
93.02	4.991	9.471	288.72	7.202	21.619
99.34	7.637	9.825	289.52	7.382	21.706
106.79	7.259	10.273	296.83	7.247	22.172
113.89	6.945	10.698	304.02	7.115	22.648
121.31	7.904	11.148	311.07	6.985	23.089
130.10	9.940	11.669	318.01	6.877	23.544
140.95	11.765	12.342			

range 19 to 320° K. Values at integral temperatures, taken from a smooth curve through all of the data, are given in Table II. An excess absorption of energy, above the regular curve, was observed in the temperature range 255 to 265° K. Since this temperature was considerably below that reported by Sokolov³ for the second order transition, we suspected that it was probably due to some other cause. A calculation showed that the energy absorption was in the temperature range where a saturated aqueous solution of urea would be expected to melt. Hence the presence of

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(2) G. N. Lewis and G. H. Burrows, *THIS JOURNAL*, **34**, 1515 (1912).

(3) V. A. Sokolov, *C. A.*, **34**, 5733⁵ (1940).

(4) Ruehrwein and Huffman, *THIS JOURNAL*, **65**, 1620 (1943).