(2) Bennett, J.E., Benson, G.C., *Can. J. Chem.* **43**, 1912 (1965).
(3) Larkin, J.A., McGlashan, M.L., *J. Chem. Soc.* **1961**, p. 3425.
(4) Lundberg, G.W., J. CHEM. ENG. DATA **9**, 193 (1964).
(5) Manufacturing Chemists Association Research Project, "Selected Values of Properties of Chemical Compounds," College Station, Tex.
(6) Savini, C.G., Winterhalter, D.R., Kovach, L.H., Van Ness, H.C., J. CHEM. ENG. DATA 11, 40 (1966).
(7) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, N. Y., 1950.
(8) Winterhalter, D.R., Ph.D. thesis, Rensselaer Polytechnic Institute, Troy, N. Y., 1965. On file with University Microfilms, Ann Arbor, Mich.

RECEIVED for review September 8, 1965. Accepted December 16, 1965.

Heat of Solution, Heat Capacity, and Density of Aqueous Urea Solutions at 25° C.

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Measurements were made of the heat of solution at 25° C. of urea in water over the concentration range 0 to 54.79% urea and of the densities and specific heats of the solutions. The partial molal heat contents were calculated from the results.

UREA, $(CONH_2)_2$, is used both as a solid and in solution in nitrogen fertilizers. As part of a continuing program of determination of thermochemical data on fertilizer compounds, measurements were made of the heat of solution of urea in water at 25° C. The measurement technique permitted the simultaneous determinations of the specific heats and densities of the solutions. The partial molal heat contents were calculated from the results.

MATERIALS AND APPARATUS

Reagent-grade urea was dissolved in water at 70° C. and the solution was filtered through fritted glass and allowed to cool slowly to room temperature. The crystals were filtered by suction on fritted glass, dried at 55° C. for 16 hours, and cooled and ground lightly to pass a 20-mesh screen. The product was stored in capped bottles until transferred to the thin-walled glass sample bulbs for use in the calorimeter. The filled bulbs were dried to constant weight at 55° C. before use.

The solution calorimeter has been described (*1*). Corrections for vaporization of water into the 160-cc. vapor space of the calorimeter were calculated to be less than 0.1% of the measured heats and were ignored. Temperature differences were determined to 0.0001° C. The unit of thermal energy was 1 defined calorie = 4.1840 absolute joules.

OBSERVATIONS

The concentration range 0 to 52.37% urea was covered in 40 measurements. A saturated solution at 25° C. was calculated to be 54.792% (20.181*m*) urea (*6*).

The observed integral heats of solution, all endothermic, are shown in Table I. The values of ΔH from Table I were fitted by a polynomial in molality. The equation giving the best fit was

$$\Delta H, \text{ cal. per mole} = 3656.308 - 83.9082m + 5.54228m^2 - 0.24071m^3 + 0.00449022m^4 \quad (1)$$

where m = concentration (molality) of urea. The mean probable error of Equation 1 was 0.624 cal. per mole urea, or ±0.02%. Integral heats of solution at even molalities to saturation are listed in Table II, together with partial molal quantities calculated by conventional methods (*2*).

Gucker and Pickard (*4*) measured heats of dilution directly in a differential calorimeter at low concentrations and at a few concentrations up to 12*m* urea. Their equation for the relative apparent molal heat content, ϕ_{L_2}, agrees with the present measurements with an average deviation of 6 cal. per mole urea, but they measured very small heat effects and their precision was of the order of 1%.

SPECIFIC HEATS

Electrical calibrations of the calorimeter system were made immediately before and after the dissolution of each portion of urea. The second electrical calibration for one dissolution and the first electrical calibration for the next dissolution referred to the same concentration of urea, and both values were used in the calculation of the specific heat of this solution. The weights of fixed volumes of solution, the observed temperature rise, and the electrical energy input permitted the calculation of the specific heat of each solution. The base for the specific heat calculations was the average of three determinations of the water equivalent of the calorimeter. The known specific heat of crystalline urea (*5*) at 25° C. permitted correction for variations in the weight and the sensible heat of the urea in the sample bulbs in the calorimeter before the bulbs were broken. The thin-walled glass bulbs were of uniform size and the variations in the amounts of glass were not significant.

The average temperature of the calibration period in each measurement was 25.1° to 25.7° C., but the values are listed in Table I as at 25° C. Since the specific heats at the observed concentrations fell on a smooth curve, errors introduced by the small variations in temperature from 25.0° C. were within the error of the observations. The observed values of specific heat from Table I were fitted to

Table I. Observed Properties of Aqueous Urea Solutions at 25° C.

Urea Concentration			Heat of Solution		
Wt. %	Molality, m	Density, G./Ml.	$-Q$, cal./run	Integral ΔH, cal./mole	Specific Heat, s, Cal./ ° C./G.
0	0	0.9971	...	...	0.9980
1.88	0.319	1.0022	982.81	3633.82	0.9890
3.72	0.643	1.0071	967.88	3604.48	0.9749
5.57	0.982	1.0123	986.35	3577.56	0.9634
7.39	1.329	1.0172	981.10	3552.56	0.9518
9.31	1.709	1.0224	1046.57	3526.44	0.9391
11.25	2.110	1.0277	1070.63	3500.73	0.9300
12.72	2.426	1.0317	820.53	3481.23	0.9223
14.36	2.791	1.0358	927.75	3459.59	0.9118
16.01	3.175	1.0400	950.18	3438.17	0.9045
17.64	3.567	1.0449	948.23	3418.34	0.8954
19.31	3.985	1.0493	982.18	3396.62	0.8848
20.77	4.366	1.0534	869.14	3377.30	0.8753
22.24	4.761	1.0579	887.49	3359.21	0.8673
23.67	5.163	1.0618	881.82	3341.92	0.8620
25.08	5.575	1.0656	877.43	3324.01	0.8509
26.49	6.001	1.0698	893.77	3307.04	0.8469
27.88	6.438	1.0737	892.36	3289.84	0.8371
29.20	6.867	1.0773	857.01	3274.04	0.8324
30.50	7.307	1.0814	857.63	3258.23	0.8260
31.92	7.806	1.0853	953.56	3241.15	0.8171
33.24	8.290	1.0890	904.49	3225.45	0.8114
34.48	8.763	1.0924	861.59	3210.71	0.8052
35.56	9.190	...	759.34	3198.20	0.8025
36.72	9.660	1.0991	821.59	3184.72	0.7947
37.75	10.097	1.1020	750.87	3172.57	0.7893
38.85	10.576	1.1054	809.94	3160.25	0.7841
40.01	11.106	1.1088	872.24	3146.09	0.7782
41.01	11.573	1.1119	754.70	3134.54	0.7747
42.01	12.061	1.1147	773.97	3122.85	0.7710
43.02	12.573	1.1177	796.28	3110.96	0.7658
44.02	13.093	1.1207	787.45	3098.47	0.7604
44.96	13.600	1.1234	762.11	3088.02	0.7583
46.06	14.218	1.1268	909.88	3075.70	0.7514
46.99	14.760	1.1296	780.63	3065.08	0.7481
47.89	15.302	1.1320	760.88	3054.29	0.7440
48.86	15.907	1.1354	841.39	3043.52	0.7387
49.79	16.512	1.1379	818.54	3032.52	0.7343
50.71	17.132	...	822.04	3022.36	0.7328
51.47	17.659	1.1432	687.17	3013.90	0.7264
52.37	18.309	1.1458	837.79	3004.02	0.7222

Table II. Integral Heats of Solution and Relative Partial Molal Heat Contents of Aqueous Urea Solutions at 25° C.

Urea Concentration		Cal./Mole Urea			
Wt. %	Molality, m	ΔH	$-\phi_L$	$-\bar{L}_2$	$\bar{L}_1$
0	0	3656.31	...	...	...
5.67	1	3577.71	78.60	152.13	1.32
10.72	2	3508.81	147.50	276.47	4.65
15.27	3	3448.33	207.98	377.98	9.19
19.37	4	3395.10	261.21	461.11	14.40
23.09	5	3348.04	308.27	529.73	19.95
26.49	6	3306.21	350.10	587.21	25.63
29.60	7	3268.74	387.57	636.35	31.37
32.45	8	3234.90	421.41	679.43	37.19
35.09	9	3204.04	452.26	718.18	43.12
37.52	10	3175.65	480.66	753.81	49.21
39.78	11	3149.29	507.02	786.96	55.48
41.88	12	3124.66	531.65	817.77	61.86
43.84	13	3101.55	554.75	845.81	68.17
45.68	14	3079.87	576.44	870.12	74.07
47.39	15	3059.62	596.69	889.20	79.05
49.00	16	3040.92	615.38	901.02	82.34
50.52	17	3024.01	632.30	903.01	82.91
51.95	18	3009.21	647.10	892.05	79.43
53.29	19	2996.96	659.35	864.48	70.22
54.79	20.18	2986.54	669.77	804.80	49.09

Table III. Calculated Densities and Specific Heats of Aqueous Urea Solutions at 25° C.

Urea Concentration, Wt. %	Density, G./Ml.	s, Cal./° C./G. Solution
5	1.0105	0.9670
10	1.0240	0.9367
15	1.0376	0.9077
20	1.0514	0.8799
25	1.0654	0.8533
30	1.0797	0.8277
35	1.0941	0.8030
40	1.1087	0.7792
45	1.1235	0.7561
50	1.1386	0.7336
54.79	1.1533	0.7126

a polynomial in weight % urea. The equation giving the best fit was

$$s = 0.9988 - 0.006494W + 0.0_{4}3025W^{2} - 0.0_{6}1286W^{3} \qquad (2)$$

where s = cal. per deg. per gram solution and W = weight % urea. The mean probable error of Equation 2 was 0.0007 cal. per deg. per gram solution. Specific heats at even values of weight % are listed in Table III.

Gucker and Ayres (*3*) measured the specific heats of urea solutions at several temperatures, but not at 25° C. Their results, interpolated to 25° C., agree with the present results with an average deviation of 0.0004 cal. per deg. per gram solution.

DENSITY

The initial bulk charge of liquid for each heat of solution measurement was weighed in a modified volumetric flask that held 851.39 ml. From these weights the densities of the solutions were determined and are listed in Table I. The densities were determined at room temperature, 25.0 ± 0.5° C. The observed densities fell on a smooth curve, so that the small differences of temperature from 25.0° C. were not significant. The equation giving the best fit to the observed values in Table I was

$$\rho = 0.9974 + 0.002625W + 0.0_5401W^2 \tag{3}$$

where ρ = density in grams per ml. and W = weight % urea. The mean probable error of the equation was 0.0001 gram per ml. Smoothed densities are listed in Table III.

LITERATURE CITED

(1) Egan, E.P., Jr., Luff, B.B., *J. Phys. Chem.* **65**, 523 (1961).
(2) Glasstone, S., "Thermodynamics for Chemists," Chap. XVIII, Van Nostrand, New York, 1947.
(3) Gucker, F.T., Jr., Ayres, F.D., *J. Am. Chem. Soc.* **59**, 2152 (1937).
(4) Gucker, F.T., Jr., Pickard, H.B., *Ibid.*, **62**, 1464 (1940).
(5) Ruehrwein, R.A., Huffman, H.M., *Ibid.*, **68**, 1759 (1946).
(6) Seidell, A., "Solubilities of Organic Compounds," 3rd ed., Vol. **II**, p. 55, Van Nostrand, New York, 1941.

RECEIVED for review October 21, 1965. Accepted January 17, 1966.

Heat of Solution, Heat Capacity, and Density of Aqueous Formamide Solutions at 25° C.

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Measurements were made of the heat of solution at 25° C. of formamide in water over the concentration range 0 to 100% formamide and of the densities and specific heats of the solutions. The partial molal heat contents were calculated from the results.

FORMAMIDE, $HCONH_2$, contains 31.10% nitrogen and is completely miscible with water. It is potentially useful as a component of fertilizer solutions in which its high nitrogen content is advantageous. Only meager thermodynamic data on formamide are available (*2*); as part of a continuing program of determination of thermochemical data on fertilizer compounds, measurements were made of the heat of solution of formamide in water at 25° C. The concentration range extended from water to formamide, and the measurement technique permitted the simultaneous determinations of the specific heats and densities of the solutions. The partial molal heat contents were calculated from the results.

MATERIALS AND APPARATUS

Reagent-grade formamide was sealed in a glass V-tube and frozen in one arm of the tube. The crystals were warmed slowly and the melt was decanted periodically into the other arm of the V-tube. After about one-fourth of the crystals had melted and the liquid phase had been decanted off, the remaining crystals were melted and refrozen, and the process was repeated. The remaining crystals then were melted and transferred to a dark-glass bottle in a glove bag filled with dry nitrogen. Thin-walled glass sample bulbs were each filled in the glove bag with about 30 grams of the purified formamide from the storage bottle.

The solution calorimeter has been described (*1*). Corrections for vaporization of water or formamide (*3*) into the 160-cc. vapor space in the calorimeter were calculated to be less than 0.1% of the measured heats and were ignored. Temperature differences were determined to 0.0001° C. The unit of thermal energy was 1 defined calorie = 4.1840 absolute joules.

OBSERVATIONS

The concentration range 0 to 100% formamide was covered in two series of measurements: in series 1, successive 30-gram portions of formamide were added to water to a final concentration of 55.0% formamide; in series 2, successive 30-gram portions of water were added to formamide to a final concentration of 53.9% formamide. The temperature change in series 1 fell from 0.3° C. for the first portion of formamide to 0.09° C. at 55.0% formamide. In series 2, the temperature change fell from 0.6° C. for the first portion of water to 0.09° C. at 53.9% formamide.

The sample weights and calories per run were combined (*1*) to give total grams dissolved and total calories developed at each final concentration to yield integral heats of solution at each final concentration.

The observed heats of solution, all endothermic, are listed in Table I, and the calculated integral heats of solution in calories per mole at the observed final concentrations are listed in Table II. The values of ΔH from Table II were fitted by polynomial equations in molality or weight fraction. The equations giving the best fit were

$$\Delta H,\ \text{cal./mole} = 443.896 - 22.6614m + 0.891566m^2 - 0.0200228m^3 + 0.000188406m^4 \qquad m = 0 \text{ to } 25 \tag{1}$$

$$\Delta H,\ \text{cal./mole} = 439.114 - 371.120w - 649.972w^2 + 1280.681w^3 - 699.154w^4 \qquad w = 0.53 \text{ to } 1.00 \tag{2}$$

where m = molality and w = weight fraction of formamide. The mean probable error for Equation 1 was 0.109 cal. per mole; that for Equation 2 was 0.143 cal. per mole. The intercept in Equation 1 was subtracted from the values of ΔH calculated from Equations 1 and 2 to obtain ϕ_L, the relative apparent molal heat content for formamide in water. The values of ϕ_L are included in Table II.

Calculation of relative partial molal heat contents at molalities up to 25 was straightforward. For solutions containing more than 50% formamide, the weight fraction was converted to molality by the equations

$$w = \frac{45.04116m}{1000 + 45.04116m} \tag{3}$$

$$\frac{dw}{dm} = \frac{45.04116}{(1000 + 45.04116m)^2} \tag{4}$$

$$\frac{d\phi_L}{dm} = \frac{d\phi_L}{dw} \cdot \frac{dw}{dm} \tag{5}$$