

the solutions were determined and are listed in Table I. The densities were determined at room temperature, $25.0 \pm 0.5^\circ\text{C}$. 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

$$\rho = 0.9974 + 0.002625W + 0.06401W^2 \quad (3)$$

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.

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

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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

$$\Delta H, \text{ cal./mole} = 443.896 - 22.6614m + 0.891566m^2 - 0.0200228m^3 + 0.000188406m^4 \quad (1)$$

$m = 0 \text{ to } 25$

$$\Delta H, \text{ cal./mole} = 439.114 - 371.120w - 649.972w^2 + 1280.681w^3 - 699.154w^4 \quad (2)$$

$w = 0.53 \text{ to } 1.00$

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

$$w = \frac{45.04116m}{1000 + 45.04116m} \quad (3)$$

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

$$\frac{d\phi_L}{dm} = \frac{d\phi_L}{dw} \cdot \frac{dw}{dm} \quad (5)$$

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

Formamide Concentration		Density, G./ML.	Heat of Solution		Specific Heat, s, Cal./° C./G.
Wt. %	Molality, m		-Q, cal./run	Integral, ΔH, cal./mole	
Series 1					
0	0	0.9971	0.9991
3.24	0.743	1.0020	269.0738	427.4141	0.9801
6.94	1.655	1.0076	295.5332	408.7017	...
9.68	2.381	1.0110	210.2869	394.8892	0.9453
12.46	3.161	1.0148	204.7039	380.9014	...
15.09	3.944	1.0186	183.4821	366.8538	0.9165
17.66	4.763	1.0219	175.8156	354.0461	0.9020
20.49	5.723	1.0263	186.6778	340.2549	0.8915
22.80	6.556	1.0292	142.4409	328.3601	0.8780
25.27	7.509	1.0328	148.8240	316.0345	0.8676
27.93	8.605	1.0361	152.7737	302.8622	0.8552
30.24	9.626	1.0392	130.1045	292.0221	...
32.62	10.750	1.0422	129.1030	280.9991	...
35.21	12.066	1.0452	135.3336	269.1301	0.8255
37.10	13.094	1.0487	95.3421	260.6626	0.8163
39.04	14.221	1.0501	97.0974	252.1805	0.8081
41.16	15.534	1.0537	102.6367	243.0242	0.7994
43.14	16.847	1.0561	92.8666	234.5434	...
44.88	18.074	1.0581	80.7283	227.3748	0.7840
46.58	19.356	1.0610	79.0002	220.5437	0.7779
48.22	20.677	1.0622	75.1347	213.9992	0.7698
49.95	22.160	1.0656	76.8101	207.0939	0.7627
51.61	23.681	1.0664	71.5820	200.4697	0.7557
53.31	25.354	1.0688	74.7591	193.9625	0.7493
54.98	27.112	1.0708	72.1574	187.6670	...
Series 2 ^a					
53.90	25.960	1.0705	67.4213	191.7180	...
55.47	27.652	1.0722	72.5187	185.7070	0.7395
57.12	29.569	1.0744	75.9232	179.4412	0.7334
58.78	31.655	1.0767	90.1053	173.0814	0.7257
60.71	34.312	1.0789	90.9559	165.7874	0.7195
62.67	37.267	1.0810	92.6566	158.6676	0.7121
64.62	40.547	1.0840	99.1284	151.6536	...
66.61	44.291	1.0867	102.5328	144.3933	0.6976
68.62	48.548	1.0887	99.1688	137.1148	0.6886
70.54	53.168	1.0911	106.5746	130.2821	0.6812
72.53	58.609	1.0936	134.7124	123.1578	...
74.91	66.294	1.0963	124.1230	114.4592	0.6649
77.03	74.451	1.0994	154.6317	106.6856	0.6565
79.52	86.232	1.1022	151.6799	97.3288	0.6476
81.84	100.041	1.1047	153.3397	88.4303	0.6388
84.01	116.665	1.1076	136.1873	79.6907	0.6311
85.84	134.571	1.1098	150.5316	72.1073	0.6220
87.77	159.367	1.1122	210.6079	63.9285	0.6159
90.21	204.652	1.1150	188.4156	52.8205	0.6080
92.19	262.112	1.1179	233.5582	43.1239	0.6009
94.42	375.341	1.1212	286.4919	31.4168	0.5929
96.87	686.183	1.1241	428.9137	17.4541	0.5831
100.00	∞	1.1280	...	0	0.5718

^a Listed in reverse order to that in which runs were made.

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

Formamide Concentration		Cal. Per Mole Formamide				Formamide Concentration		Cal. Per Mole Formamide			
Wt. %	Molality, m	ΔH	-Φ ₁	-L ₂	L ₁	Wt. %	Molality, m	ΔH	-Φ ₁	-L ₂	L ₁
4.31	1	422.11	21.79	42.73	0.38	49.77	22	207.79	236.10	334.69	39.07
8.26	2	401.98	41.91	80.57	1.39	51.95	24	199.28	244.62	341.76	42.00
11.90	3	383.41	60.48	113.98	2.89	52.96	25	195.33	248.57	344.83	43.36
15.27	4	366.28	77.61	143.38	4.74	55	27.14	187.48	256.42	352.73	47.09
18.38	5	350.49	93.40	169.17	6.82	60	33.30	168.47	275.43	364.71	53.57
21.28	6	335.94	107.95	191.73	9.06	65	41.23	150.18	293.72	375.81	60.98
23.97	7	322.54	121.36	211.41	11.36	70	51.80	132.25	311.64	386.77	70.11
26.49	8	310.18	133.71	228.55	13.67	75	66.61	114.24	329.66	398.05	82.07
28.84	9	298.80	145.10	243.46	15.95	80	88.81	95.57	348.32	409.77	98.31
31.05	10	288.30	155.60	256.43	18.17	85	125.81	75.59	368.30	421.55	120.70
35.09	12	269.65	174.24	277.58	22.34	90	199.81	53.53	390.36	432.46	151.55
38.67	14	253.68	190.22	293.86	26.14	95	421.84	28.51	415.39	440.86	193.62
41.88	16	239.89	204.01	306.76	29.62	99	2198	5.71	438.19	444.19	237.58
44.77	18	227.86	216.03	317.41	32.88	99.9	22180	...	443.72	444.34	248.95
47.39	20	217.26	226.64	326.58	36.01	99.99	222000	...	444.28	444.35	249.89

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

Formamide Concn., Wt. %	Density, G./Ml.	s , Cal./°C./G. Solution
5	1.0046	0.9700
10	1.0115	0.9428
15	1.0183	0.9170
20	1.0252	0.8925
25	1.0319	0.8691
30	1.0386	0.8466
35	1.0453	0.8248
40	1.0519	0.8036
45	1.0584	0.7828
50	1.0649	0.7625
55	1.0714	0.7424
60	1.0778	0.7226
65	1.0842	0.7030
70	1.0905	0.6835
75	1.0967	0.6643
80	1.1029	0.6453
85	1.1091	0.6265
90	1.1152	0.6081
95	1.1213	0.5900
100	1.1273	0.5725

The partial molal quantities are listed in Table II.

SPECIFIC HEAT

Electrical calibrations of the calorimeter system were made immediately before and after the dissolution of each portion of formamide. The second electrical calibration for one dissolution and the first electrical calibration for the next dissolution referred to the same concentration of formamide, and both values were used in the calculation of the specific heat of this solution. The weights of fixed volumes of the solution, the observed temperature rise, and the electrical energy input permitted 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. Three measurements of the specific heat of pure formamide at 25° C. permitted correction for variations in the weight and sensible heat of the formamide in the sample bulbs in the

calorimeter before the bulbs were broken. The thin-walled sample bulbs were of uniform size, and the variations in the amounts of glass were not significant.

The two observed specific heats for each concentration of formamide were made at temperatures that differed from 25.0° C. by several tenths of a degree. The observations were corrected to 25° C. by linear interpolation between the observed temperatures.

The observed specific heats, listed in Table I, were fitted by the equation

$$s = 0.9990 - 0.005979w + 0.03957w^2 - 0.063589w^3 + 0.051347w^4 \quad (6)$$

where s = specific heat, cal. per °C. per gram solution; and w = weight % formamide. The mean probable error for Equation 6 was 0.0006 cal. per °C. per gram solution. Specific heats calculated at even values of w are listed in Table III.

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. These densities were represented by the equation

$$\rho = 0.9977 + 0.001396w - 0.00992w^2 \quad (7)$$

where ρ = density, gram per ml., and w = weight % formamide. The mean probable error in Equation 7 was 0.0003 gram per ml. Equation 7 was solved at even values of w and the results are listed in Table III.

The densities were determined at room temperature, 25.0 ± 0.5° C. The good agreement of the observed densities with Equation 6 shows that the temperature coefficient of density for aqueous formamide solutions is small and that precise temperature control was not required.

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