mately for the heat capacities of these mixtures.

Acknowledgment

We express our sincere gratitude to Professor J. Mochinaga for his suggestion in measuring the density.

Glossary

a, b	constants of the density equation
a_n, b_n	nth constants of eq 2
C_p	heat capacity at ambient pressure, J mol^{-1} K^{-1}
T	temperature, K
V_m	molar volume, cm^3 mol^{-1}
X	mole fraction of $NaNO_2$

Greek Letters

α	thermal expansivity, K^{-1}
ρ	density, kg m^{-3}
σ	standard deviation of the density equation, kg m^{-3}

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Supplementary Material Available: All of the original data on the density of molten $NaNO_2$–KNO_3 mixtures are listed (9 pages). In this data file, the densities of the mixtures are expressed as linear functions of temperature by a least-squares method. Four significant figures are given for density and temperature in each case (for example, 1.795 g cm^{-3} and 620.5 K). Ordering information is given on any current masthead page.

Low-Temperature Heat Capacity and Entropy of Oxalic Acid and of Biuret

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The low-temperature heat capacities of oxalic acid, $(COOH)_2$, and biuret, $NH_2CONHCONH_2$, were measured over the range 10–320 K by adiabatic calorimetry. The heat capacities (C_p), entropy ($S°$), and Gibbs function ($(G° - H_0°)/T$) at 298.15 K were calculated to be 25.31, 27.62, and −13.32 cal mol^{-1} deg^{-1}, respectively, for oxalic acid and 31.39, 34.91, and −17.53 cal mol^{-1} deg^{-1}, respectively, for biuret.

In a continuing program of the measurement of thermochemical properties of materials of interest in fertilizer technology, the heat capacities of oxalic acid, $(COOH)_2$, and biuret, $NH_2CONHCONH_2$, were measured by adiabatic calorimetry over the temperature range 10–320 K. Related thermodynamic properties were derived.

Materials and Handling

Oxalic acid dihydrate was prepared by recrystallizing reagent oxalic acid from distilled water and filtering on fritted glass. The damp crystals were transferred to a large crystallizing dish and allowed to dry in the laboratory atmosphere for several days with occasional stirring. Two samples of the air-dried material titrated with standard $KMnO_4$ solution showed the material to contain 100.0% and 100.3%, respectively, of the dihydrate.

The calorimeter was filled with the oxalic acid dihydrate and dried by vacuum desiccation over $MgClO_4$ until the weight loss of the compound was 28.72% (stoichiometric for water of crystallization is 28.58%). The more than theoretical weight loss for the formation of anhydrous oxalic acid was attributed to some sublimation. Samples desiccated in a similar manner to 28.68% weight loss and titrated with standard $KMnO_4$ solution contained 100.2% and 100.2%, respectively, anhydrous oxalic acid. The dry weight was corrected for buoyancy in air on the basis of a density of 1.89 g cm^{-3} (*1*) to give 50.5119 g or 0.561 02 mol in the calorimeter. The gram formula weight was taken as 90.035 84. The air in the calorimeter was replaced with helium by evacuating to a pressure of 100 mm and then relieving to atmospheric pressure with helium. This cycle was repeated twice, and then the pressure was adjusted to give the same mass of helium as was used in measurements on the empty calorimeter.

After the measurements were completed, the calorimeter was opened in the laboratory atmosphere. The material in the calorimeter was caked, and only a small portion could be removed in a dry condition in about 0.5 h. Two samples of this material titrated with standard $KMnO_4$ solution showed the material to contain 99.9% and 99.7%, respectively, anhydrous oxalic acid. The slightly less than theoretical anhydrous oxalic

Table I. Observed Heat Capacity of $(COOH)_2$, cal deg^{-1} mol^{-1}

T, K	C_p	T, K	C_p	T, K	C_p	T, K	C_p
9.96	0.0878	51.40	5.706	139.02	14.66	238.34	21.64
10.19	0.0868	53.31	6.008	142.34	14.92	241.46	21.88
11.53	0.1150	56.21	6.449	145.29	15.15	244.67	22.05
11.76	0.1120	57.79	6.781	148.73	15.43	247.74	22.27
12.99	0.1686	57.88	6.696	151.61	15.64	251.07	22.44
13.19	0.1637	60.24	7.140	154.96	15.89	254.11	22.66
14.30	0.2255	62.57	7.478	157.97	16.11	257.40	22.82
14.59	0.2413	65.19	7.832	161.25	16.36	260.40	23.05
15.62	0.3040	67.87	8.170	164.38	16.58	263.66	23.21
16.04	0.3303	70.62	8.479	167.60	16.83	266.67	23.41
16.99	0.3937	73.57	8.819	170.84	17.06	269.89	23.58
17.52	0.4353	76.28	9.136	174.00	17.30	272.82	23.80
18.49	0.5104	78.98	9.428	177.36	17.54	275.04	23.86
19.16	0.5697	80.26	9.582	180.46	17.76	276.02	23.95
20.24	0.6692	83.16	9.893	183.76	17.99	276.40	23.99
21.00	0.7427	85.86	10.18	186.80	18.21	279.67	24.15
22.32	0.8878	89.16	10.50	190.05	18.42	282.74	24.38
23.30	1.015	91.97	10.75	193.05	18.64	285.99	24.53
24.88	1.210	95.37	11.04	196.24	18.86	289.02	24.76
26.16	1.396	98.30	11.31	197.82	18.99	292.24	24.91
27.92	1.653	101.54	11.60	201.00	19.19	295.24	25.15
29.39	1.892	104.58	11.85	204.06	19.40	298.43	25.32
31.24	2.198	107.68	12.12	207.36	19.61	300.90	25.45
32.87	2.469	110.85	12.39	210.37	19.83	301.38	25.55
34.79	2.811	114.06	12.66	213.62	20.02	303.95	25.61
36.53	3.123	117.11	12.91	216.60	20.23	307.00	25.83
38.52	3.477	120.43	13.18	219.80	20.44	310.17	26.00
40.35	3.796	123.38	13.41	222.74	20.64	313.18	26.20
42.48	4.168	126.60	13.68	225.90	20.82	316.45	26.37
44.48	4.521	129.66	13.93	228.95	21.04	319.42	26.58
46.80	4.932	132.79	14.18	232.08	21.23		
48.97	5.300	135.98	14.42	235.25	21.47		

Table II. Observed Heat Capacity of $NH_2CONHCONH_2$, cal deg^{-1} mol^{-1}

T, K	C_p	T, K	C_p	T, K	C_p	T, K	C_p
8.16	0.1229	51.19	7.759	142.56	17.56	245.95	26.85
8.18	0.1858	55.42	8.446	145.69	17.84	249.00	27.10
8.96	0.2349	55.87	8.484	148.86	18.15	252.00	27.34
9.06	0.2599	56.04	8.543	151.92	18.39	255.14	27.65
9.92	0.3172	57.23	8.718	155.02	18.68	258.11	27.90
10.04	0.3362	59.34	9.041	158.18	18.96	261.22	28.21
11.06	0.4226	61.72	9.414	161.21	19.24	264.28	28.45
11.17	0.4270	64.01	9.744	164.48	19.52	267.34	28.71
12.38	0.5433	66.87	10.15	167.45	19.79	269.08	28.88
12.44	0.5619	69.28	10.44	170.64	20.08	270.36	28.97
13.67	0.7213	72.27	10.79	173.72	20.35	273.38	29.26
14.14	0.7837	75.09	11.13	176.85	20.65	274.78	29.31
15.11	0.9201	77.88	11.47	180.05	20.92	275.10	29.40
16.05	1.062	79.18	11.63	183.11	21.21	276.20	29.47
16.81	1.169	80.66	11.82	186.25	21.48	277.96	29.64
18.35	1.424	83.79	12.17	189.41	21.77	279.30	29.73
18.69	1.479	86.81	12.48	192.49	22.04	282.12	29.99
20.94	1.866	90.03	12.83	195.76	22.35	284.02	30.19
21.21	1.910	93.12	13.09	196.90	22.45	285.19	30.25
23.72	2.388	96.19	13.39	200.00	22.69	288.10	30.50
24.18	2.476	99.37	13.69	203.11	23.02	290.13	30.72
26.86	3.004	102.55	13.98	206.16	23.24	291.13	30.76
27.22	3.076	105.58	14.26	209.23	23.57	294.26	31.06
30.27	3.691	108.88	14.56	212.23	23.78	296.17	31.24
30.36	3.711	111.80	14.83	215.39	24.13	297.26	31.30
33.55	4.376	114.97	15.11	218.34	24.34	299.14	31.48
33.89	4.441	118.00	15.39	221.25	24.63	300.47	31.60
37.01	5.090	121.08	15.66	224.52	24.92	302.20	31.74
37.77	5.247	124.20	15.94	227.38	25.16	305.31	32.00
41.07	5.887	127.19	16.20	230.59	25.45	308.34	32.26
41.99	6.062	130.23	16.47	233.57	25.73	311.41	32.54
45.70	6.771	133.33	16.75	236.72	26.01	314.41	32.77
46.49	6.916	136.28	17.01	239.81	26.29	317.55	33.06
50.50	7.635	139.50	17.30	242.91	26.57	320.52	33.27

acid was attributed to its partial hydration during handling. Another sample was weighed periodically while standing in the laboratory, and this sample showed a weight gain of 1.5% in 1 h. Petrographic examination of the material showed the material to be essentially homogeneous α-form anhydrous oxalic acid. Both well-developed crystals and a minor component as pseudomorphs after oxalic acid dihydrate were present, with a very minor to trace component of oxalic acid dihydrate as a coating on some anhydrous oxalic acid crystals.

A 2% solution of biuret was prepared by dissolving reagent-grade biuret in distilled water. The solution was concentrated to 4% biuret by boiling and then allowed to cool gradually to room temperature. The crystals that developed on cooling were filtered on fritted glass and allowed to come to constant weight in the laboratory atmosphere. Large agglomerates of the crystals were crushed lightly during the drying process. The air-dried material was ground lightly to pass a 20-mesh screen. This material was kept at 110 °C for 2 days with occasional stirring and then allowed to cool to room temperature in a desiccator over magnesium perchlorate. The container holding the material then was capped and installed in a glovebag along with the empty calorimeter, two weighing bottles, and a rubber stopper, all of which had been weighed previously. The glovebag was continuously flushed with nitrogen that had passed through an 8-in. column of Drierite and an 8-in. column of P_2O_5. The calorimeter was filled with the material and stoppered, and portions of the materials were transferred to the weighing bottles. Approximately 1 h was required for the filling operation. The calorimeter and the weighing bottles then were removed from the glovebag and immediately weighed. The rubber stopper was removed from the calorimeter and the evacuator tube was joined to the calorimeter as quickly as possible. The opening was sealed with a tared stopper for the final weighings and Wood's metal adjustment. Chemical analysis of the material in the sample bottles showed the material to contain 40.76 ± 0.04% N (stoichiometric = 40.76% N).

The calorimeter was charged with 56.8409 g (in vacuo) or 0.551 419 mol of biuret. The gram formula weight was taken as 103.081 05. The density of the air-dried material was measured by a sink-float procedure in a mixture of acetone and bromoform and found to be 1.506 g cm^{-3}. Chemical analysis showed this material to contain 35.98% N. Straight-line extrapolation of the density of water and that of the air-dried material to 40.76% N gives 1.573 g cm^{-3} for the density of anhydrous biuret. The air in the calorimeter was replaced with helium in the manner described previously.

Chemical analysis of the material removed from the calorimeter after completion of the measurements showed the material to contain 40.69 ± 0.03% N, but drying of 0.94 g of the material for 1.5 h at 110 °C showed less than 0.01% weight loss.

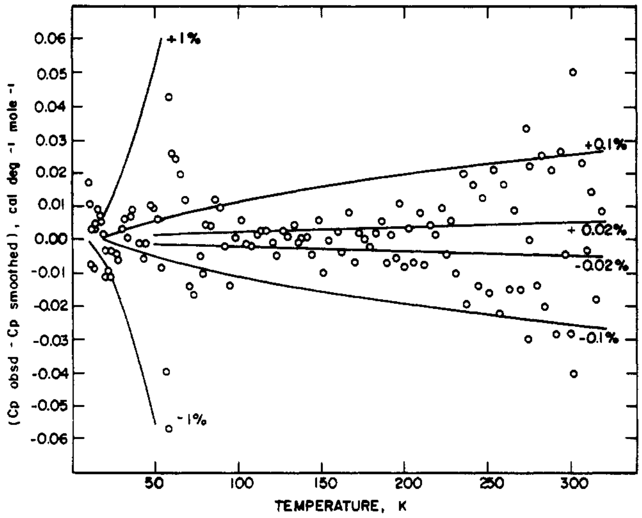

Figure 1. Deviations of observed heat capacities from smoothed values of $(COOH)_2$.

Table III. Molal Thermodynamic Properties of $(COOH)_2$

T, K	C_p, cal K^{-1}	$S°$, cal K^{-1}	$H° - H_0°$, cal	$-(G° - H_0°)/T$, cal K^{-1}
5	0.0084	0.0026	0.0102	0.0006
10	0.0720	0.0230	0.1749	0.0055
15	0.2593	0.0821	0.9358	0.0197
20	0.6490	0.2049	3.116	0.0491
25	1.239	0.4098	7.761	0.0994
30	1.988	0.6998	15.77	0.1741
35	2.842	1.069	27.81	0.2747
40	3.735	1.507	44.25	0.4008
45	4.613	1.998	65.14	0.5505
50	5.465	2.528	90.34	0.7215
60	7.078	3.670	153.2	1.117
70	8.420	4.866	230.9	1.566
80	9.550	6.065	320.9	2.054
90	10.57	7.250	421.6	2.566
100	11.46	8.411	531.8	3.092
110	12.32	9.543	650.7	3.628
120	13.14	10.65	778.0	4.167
130	13.95	11.73	913.5	4.707
140	14.74	12.80	1057	5.247
150	15.52	13.84	1208	5.786
160	16.26	14.87	1367	6.321
170	17.00	15.87	1534	6.854
180	17.73	16.87	1707	7.382
190	18.43	17.84	1888	7.907
200	19.13	18.81	2076	8.428
210	19.79	19.76	2270	8.945
220	20.45	20.69	2472	9.458
230	21.10	21.62	2679	9.966
240	21.77	22.53	2894	10.47
250	22.39	23.43	3114	10.97
260	23.01	24.32	3341	11.47
270	23.60	25.20	3575	11.96
280	24.19	26.07	3813	12.45
290	24.80	26.93	4058	12.93
300	25.42	27.78	4309	13.41
310	25.95	28.62	4566	13.89
320	26.61	29.46	4829	14.36
273.15	23.78	25.47	3649	12.11
298.15	25.31	27.62	4263	13.32

Table IV. Molal Thermodynamic Properties of $NH_2CONHCONH_2$

T, K	C_p, cal K^{-1}	$S°$, cal K^{-1}	$H° - H_0°$, cal	$-(G° - H_0°)/T$, cal K^{-1}
5	0.0445	0.0147	0.0555	0.0036
10	0.3166	0.1133	0.8435	0.0290
15	0.9030	0.3442	3.788	0.0917
20	1.699	0.7090	10.22	0.1978
25	2.632	1.186	21.01	0.3462
30	3.644	1.755	36.68	0.5324
35	4.672	2.394	57.47	0.7521
40	5.681	3.084	83.37	1.000
45	6.640	3.809	114.2	1.272
50	7.540	4.556	149.7	1.563
60	9.149	6.077	233.3	2.188
70	10.53	7.593	331.9	2.852
80	11.73	9.079	443.2	3.538
90	12.81	10.52	566.1	4.234
100	13.75	11.92	698.9	4.934
110	14.66	13.28	840.9	5.631
120	15.57	14.59	992.1	6.323
130	16.45	15.87	1152	7.008
140	17.34	17.12	1321	7.686
150	18.23	18.35	1499	8.356
160	19.12	19.55	1686	9.019
170	20.02	20.74	1881	9.673
180	20.92	21.91	2086	10.32
190	21.82	23.07	2300	10.96
200	22.71	24.21	2523	11.60
210	23.61	25.34	2754	12.22
220	24.52	26.46	2995	12.84
230	25.40	27.57	3244	13.46
240	26.31	28.67	3503	14.07
250	27.19	29.83	3770	14.74
260	28.08	30.84	4047	15.28
270	28.94	31.92	4332	15.87
280	29.81	32.99	4626	16.47
290	30.68	34.05	4928	17.05
300	31.55	35.10	5239	17.64
310	32.41	36.15	5559	18.22
320	33.24	37.19	5887	18.80
273.15	29.21	32.26	4424	16.06
298.15	31.39	34.91	5181	17.53

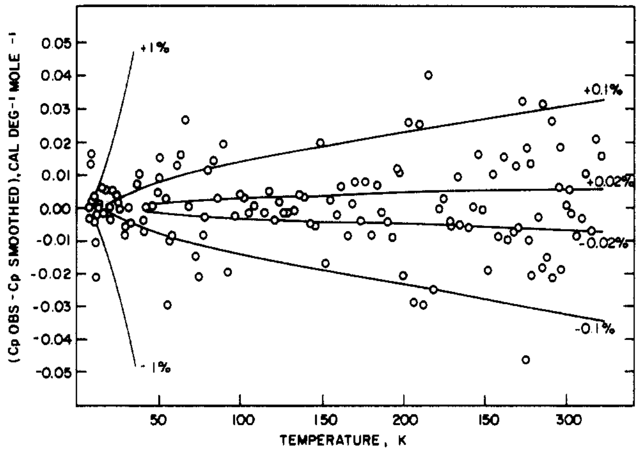

Figure 2. Deviations of observed heat capacities from smoothed values of $NH_2CONHCONH_2$.

Low-Temperature Heat Capacity. The adiabatic calorimeter and the method of operation have been described previously (*2*), and the overall accuracy of our technique has been reported (*3*). The defined calorie was taken as 4.1840 absolute J and the ice point as 273.15 K.

The measured heat capacities were corrected for curvature and for small differences in the amount of eutectic solder and copper relative to the empty calorimeter. The heat capacities below 10 K were read from a large-scale plot of C_p/T against T^2 that extrapolated smoothly to 0 K. Observed molal heat capacities of oxalic acid and biuret are shown in Tables I and II, respectively. Smoothed heat capacities and derived functions at round values of temperature are shown in Tables III and IV. The deviations of the observed heat capacity values from the smoothed curve are shown in Figures 1 and 2. The heat capacity curves had the normal sigmate shape and showed no thermal anomolies.

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