ACKNOWLEDGMENT

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Low Temperature Heat Capacity and Entropy of Oxamide, 10° to 310° K.

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The heat capacity of triclinic oxamide, $(CONH_2)_2$, was measured over the temperature range 10° to 310° K. The calculated entropy at 298.15° K. is 28.23 e.u. and the enthalpy 4407 cal. per mole. A small anomalous peak was observed between 262° and 277° K. with a maximum at 273° K. A table of thermodynamic functions for the ideal gas state is included.

OXAMIDE, $(CONH_2)_2$, mol. wt. 88.0664, is of interest as a fertilizer material—it has a relatively high nitrogen content (31.81%N), it is slightly soluble in water, and its rate of release of nitrogen varies inversely with its particle size (*3*). In a continuing program of collection of thermodynamic data on fertilizer materials, the low temperature heat capacity of triclinic oxamide was measured over the temperature range 10° to 310° K., and the entropy and enthalpy were calculated from the results.

Oxamide exists in at least two crystalline forms, triclinic and orthorhombic, but the orthorhombic form reverts spontaneously to the triclinic form on standing at room temperature (*6*). These measurements were made on the apparently stable triclinic form.

MATERIALS AND APPARATUS

Triclinic oxamide was recrystallized, at least twice, from a distilled water solution that was saturated at 95° C. and cooled slowly to room temperature in an insulated beaker. It contained 31.7%N (stoichiometric, 31.81%) and was in the form of a single phase of severely intergrown crystals with only a small fraction of single crystals.

A second sample of oxamide was prepared by subliming the recrystallized material at 180° C. in a stream of dry nitrogen at atmospheric pressure and retaining the portion of crystals that condensed from the vapor phase near 165° C. The sublimed crystals were expected to be anhydrous, but they apparently contained traces of water; analysis showed 31.80, 31.70, and 31.74%N. On petrographic examination, the sublimed crystals appeared the same as those crystallized from solution. Infrared and x-ray examination did not distinguish between the preparations, but differential thermal analysis showed a distinct difference in behavior between 200° and 300° C.

The low temperature calorimeter has been described (*4, 5*). Temperatures were measured to 0.0001° for use in calculation of temperature differences; they were rounded to two decimal places in the preparation of tables. The defined calorie is taken as 4.1840 absolute joules—the ice point as 273.15° K. The density of oxamide to be used in vacuum corrections is 1.667 grams per cc. (*1*). The heat capacities were corrected for curvature where it was significant. The calculations were made on a digital computer (*4*).

OBSERVATIONS

The observed heat capacities of oxamide that had been crystallized from solution (not reported) showed a complex peak that extended from 235° to 305° K. with a sharp maximum at 273° K. The peak was reproducible if the sample was held at 195° K. overnight or longer; otherwise, the observed values depended on the thermal history of the sample. Variation in the conditions of crystallization from solution had little effect on the shape or magnitude of the peak.

The observed heat capacities of sublimed oxamide showed a peak of about the same shape that started at 262° K. and extended to 277° K. with a maximum at 273° K., but the peak was about a tenth the size of that of the oxamide crystallized from water.

The excess heat capacity in the region of the peak for both water-crystallized and sublimed oxamide is shown in Figure 1. The "normal" heat capacities under the peak were calculated from a least-squares fourth-degree polynomial that fitted six observed points between 226° and 261° K. and 11 observed points between 277° and 305° K. with an average deviation of 0.01%.

Table I. Observed Molal Heat Capacity of Oxamide (Triclinic)

Point[a]	T, ° K.	C_p, Cal./° K.	Point[a]	T, ° K.	C_p, Cal./° K.
133	9.14	0.0460	74	190.66	18.98
134	11.84	0.1280	99	194.32	19.30
146	11.97	0.1335	42	198.13	19.58
147	13.58	0.2051	100	201.74	19.87
135	13.68	0.2131	43	206.16	20.21
148	15.62	0.3162	101	209.87	20.51
136	15.84	0.3281	44	214.21	20.85
149	18.36	0.5166	102	218.62	21.20
137	18.76	0.5465	45	222.40	21.49
150	21.33	0.7962	103	226.93	21.85
138	21.98	0.8566	46	230.62	22.13
151	24.62	1.187	172	238.44	22.70
139	26.09	1.376	47	238.49	22.72
152	28.37	1.714	173	244.93	23.21
140	31.00	2.131	48	246.16	23.32
153	33.43	2.548	174	251.32	23.70
141	36.47	3.083	49	254.41	23.95
154	38.89	3.520	50	261.24	24.45
142	41.84	4.033	51[b]	265.33	24.77
155	43.94	4.417	52[b]	267.23	24.91
143	46.38	4.841	53[b]	269.04	25.05
156	48.97	5.300	54[b]	270.41	25.18
144	51.41	5.695	55[b]	271.13	25.23
80	53.29	5.994	56[b]	271.63	25.30
75	54.23	6.143	57[b]	271.98	25.39
81	57.14	6.586	58[b]	272.16	25.47
76	59.64	6.968	33[b]	272.29	25.46
82	62.21	7.346	59[b]	272.35	25.44
77	65.16	7.763	34[b]	272.47	25.44
83	67.79	8.102	35[b]	272.65	25.47
78	71.10	8.500	36[b]	272.84	25.54
84	74.39	8.893	37[b]	273.02	25.56
79	77.99	9.320	38[b]	273.21	25.46
60	81.52	9.734	39[b]	273.39	25.50
85	85.11	10.13	109[b]	273.56	25.50
61	88.86	10.51	40[b]	273.58	25.47
86	92.94	10.88	41[b]	273.77	25.54
62	96.03	11.16	110[b]	273.87	25.51
87	99.63	11.48	111[b]	274.16	25.51
63	103.45	11.82	112[b]	274.44	25.57
88	106.27	12.06	113[b]	274.82	25.55
64	111.09	12.47	114[b]	275.32	25.58
89	114.11	12.73	115[b]	276.11	25.60
65	118.96	13.15	128[b]	277.57	25.67
90	122.44	13.44	123	279.93	25.86
66	127.04	13.82	119	280.64	25.93
91	130.96	14.14	163	282.37	26.03
67	135.06	14.48	129	284.44	26.19
92	139.14	14.81	124	286.97	26.39
68	143.05	15.13	169	287.68	26.43
93	147.03	15.46	164	288.93	26.52
69	151.03	15.79	130	291.22	26.70
94	154.91	16.10	170	293.38	26.86
70	158.99	16.42	125	294.11	26.93
95	162.79	16.73	160	294.58	26.95
71	166.95	17.07	165	295.40	27.01
96	170.91	17.39	131	297.70	27.18
72	174.88	17.71	171	299.02	27.30
97	179.18	18.06	126	300.76	27.42
73	182.87	18.35	132	304.10	27.67
98	186.84	18.67	127	307.50	27.94

[a] Points numbered in chronological order. [b] Values between 261.24° and 277.57° K. are on the peak.

The calculated entropy, $S°$, of triclinic oxamide is 28.23 e.u. of which 0.0027 e.u. represents the excess entropy under the peak between 262° and 277° K. The enthalpy, $(H° - H_0°)$ at 298.15 K., on the assumption that the crystalline solid represents the ideal state, is 4407 cal. per mole. The heat capacities at 1° intervals below 10° K. were read from a large-scale plot of the observed values of C_p *vs.* T between 10° and 30° K. that was extrapolated smoothly to 0° K.

The observed molal heat capacities are listed in Table I, and molal heat capacities at even increments of temperature are listed in Table II. The estimated uncertainty is 0.1 cal./mole/° K.

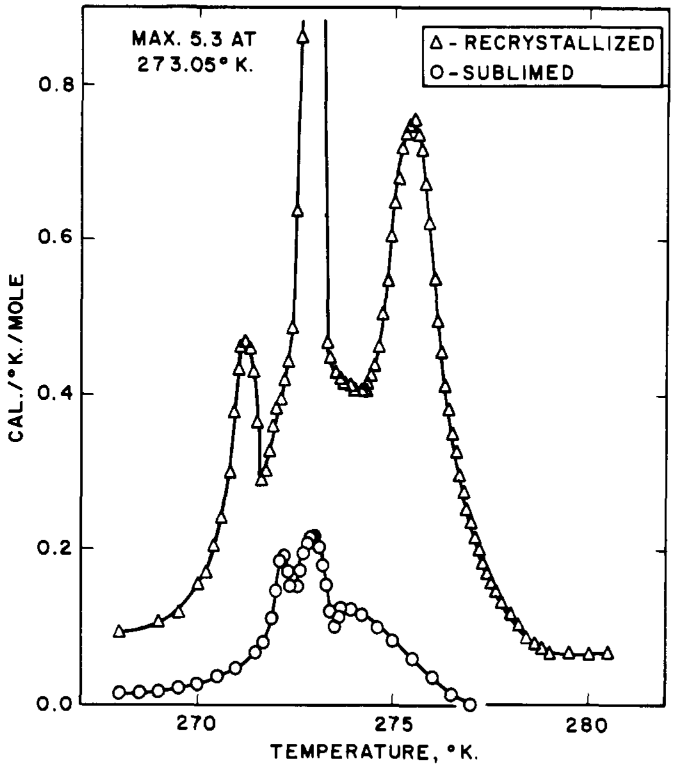

Figure 1. Excess molal heat capacity of oxamide

Table II. Molal Thermodynamic Properties of Oxamide (Triclinic)

T, ° K.	C_p, Cal./° K.	$S°$, Cal./° K.	$H° - H_0°$, Cal.
5	0.0078	0.0032	0.0118
10	0.0651	0.0204	0.1503
15	0.2815	0.0828	0.9553
20	0.6616	0.2113	3.235
25	1.238	0.4173	7.904
30	1.972	0.7058	15.87
35	2.816	1.072	27.81
40	3.713	1.507	44.12
45	4.600	1.995	64.91
50	5.459	2.525	90.08
60	7.022	3.661	152.7
70	8.372	4.848	229.8
80	9.560	6.045	319.6
90	10.61	7.233	420.5
100	11.51	8.398	531.2
110	12.38	9.536	650.7
120	13.24	10.65	778.8
130	14.06	11.74	915.3
140	14.89	12.81	1060
150	15.69	13.87	1213
160	16.51	14.91	1374
170	17.31	15.93	1543
180	18.12	16.95	1720
190	18.93	17.95	1905
200	19.73	18.94	2099
210	20.52	19.92	2300
220	21.31	20.89	2509
230	22.08	21.86	2726
240	22.84	22.81	2951
250	23.60	23.76	3183
260	24.35	24.70	3423
270	25.11	25.63	3670
280	25.86	26.56	3925
290	26.61	27.48	4187
300	27.36	28.40	4457
273.15	25.35	25.93	3750
298.15	27.22	28.23	4407

The occurrence of the peak maximum at 273° K. strongly suggests that the peak is a fusion-solution process resulting from the presence of a film of aqueous phase trapped between crystals, even though the sublimed oxamide should have been free of water. The entropy reported above for the sublimed oxamide is about 0.2 e.u. lower than the calculated entropy (not reported) for the water-crystallized oxamide.

A statistical calculation for oxamide as an ideal gas was made by an HORR approximation for a polyatomic molecule. The moments of inertia, calculated from x-ray structure data (*1*), were $I_A = 1.38$, $I_B = 2.18$, $I_C = 3.56$, each $\times 10^{-38}$, gram cm.^{2} The crystal symmetry was taken as C_{2h} and the symmetry number as 2. Twenty-two of the 24 fundamental frequencies (12 infrared, 12 Raman) were taken from Scott and Wagner (*7*). The two missing infrared frequencies were estimated by analogy from similar compounds. Three of the Raman frequencies (240, 360, 620 cm.$^{-1}$) were from very weak bands and may not represent fundamentals. The fundamental frequencies used in the HORR calculation are listed in Table III. The reduced equation for the entropy of the ideal gas was

$$S^\circ = 18.8338 + 7.94516 \ln T + S_{\text{vib}}$$

The thermodynamic properties were calculated by conventional methods and are listed in Table IV. Oxamide decomposes above about 600° K., and the values in Table IV were extended only to 800° K.

The sublimation pressure of oxamide was measured between 80° and 96° C. (*2*). The heat of sublimation calculated from the straight-line vapor pressure equation was 26,965 cal. per mole. With the heat of sublimation taken as constant, the following value is obtained for the entropy of oxamide gas at 298.15° K.

S° (crystals)	28.23 cal./deg./mole
ΔS (sublimation)	90.44 cal./mole
ΔS (compression) = $R \ln (p_{\text{cm.}}/76)$	−46.11 cal./mole
S° (gas)	72.56 cal./deg./mole
S° (ideal gas)	72.51 cal./deg./mole

Table III. Fundamental Frequencies of Oxamide, Cm.$^{-1}$

(C_{2h} symmetry)

Infrared		Raman	
3363	792	3384	1100
3185	678	3141	805
1656	629	1699	620
1608	464	1593	448
1348	400[a]	1490	360
1103	350[a]	1205	240

[a] Estimated.

Table IV. Thermodynamic Functions of Oxamide (Ideal Gas)

T, ° K.	C_p, Cal./Mole/° K.	S°, Cal./Mole/° K.	$-\frac{F^\circ - H^\circ_0}{T}$, Cal./Mole/° K.	$H^\circ - H_{298.15}$, Cal./Mole
298.15	22.31	72.51	58.87	0
400	27.29	79.78	63.28	2534
500	31.32	86.32	67.24	5471
600	34.61	92.33	70.93	8773
700	37.31	97.87	74.39	12370
800	39.55	103.0	77.65	16220

No gas-imperfection correction has been added. The correction usually amounts to 0.1 cal./deg./mole or less and is smaller than some of the other uncertainties in the calculation.

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Zirconium Tetrafluoride—Heat Capacity and Thermodynamic Properties from 5° to 307° K.

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IN THE experimental approach to the formulation of a phenomenological corresponding states theory for thermal properties of nearly isostructural crystalline solids, a convenient series of isomorphous crystals extending well through the periodic system was an obvious desideratum. After careful consideration, the Group IV-B tetrafluorides were selected for study because, with the possible exception of the first member, TiF_4 (*8*), the series members are isostructural and free of magnetic contributions. Moreover, the isomorphism extends through the magnetically interesting, actinide tetrafluorides. Investigations of diamagnetic ThF_4 (*11*) and paramagnetic UF_4 (*2, 4, 15*) have already been reported. However, an improved resolution of magnetic and lattice contributions to the thermal properties