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) = $R \ln (p_{cm.}/76)$	−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.	$-\frac{F^\circ - H_0^\circ}{T}$, 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

The heat capacity of ZrF_4 has been determined from 5° to 307° K. by adiabatic calorimetry. No thermal anomaly was detected and a normal sigmoid curve represents the data. The heat capacity (C_p), entropy (S^0), enthalpy function $[(H^0 - H_0^0)/T]$, and free energy function $[-(F^0 - H_0^0)/T]$ are, respectively, 24.79, 25.00, 14.03, and 10.97 cal./(g.f.m. ° K.) at 298.15° K.

might ultimately be effected by such a theory. Although the monoclinic structure with 12 molecules per unit cell (*3, 5*) is not ideal for simple theoretical interpretation, the series was selected because of the interesting variation in parameters—e.g., atomic mass, interatomic distance, etc. ZrF_4 was the first member of the series of ZrF_4, CeF_4, and HfF_4 to be studied. Because of the current interest in zirconium chemistry and delays in the completion of measurements on the other tetrafluorides, heat capacity data on ZrF_4 are presented here.

EXPERIMENTAL

Cryogenic Apparatus. The Mark I cryostat and ancillary circuitry closely resembles the apparatus already described (*17*) as modified for larger calorimeters (*14*). The gold-plated, copper calorimeter (laboratory designation W-5) has also been described (*16*). The capsule-type platinum resistance thermometer (laboratory designation A-3) was calibrated by the National Bureau of Standards over the International Temperature Scale and from 10° to 90° K. by comparison with the Bureau's temperature scale (*10*). Below 10° K., a provisional scale was employed. The quasi-adiabatic technique of measurement was employed. The mass of the calorimetric sample was 218.750 grams (in vacuo). One atmosphere pressure of helium gas at 300° K. was employed to improve thermal contact with the sample, and a weighed amount of Lubriseal stopcock grease was used to establish thermal contact between thermometer, heater, and calorimeter. The heat capacity of the thermometer-heater-calorimeter assembly was determined separately with appropriate small corrections for the slight differences in the amounts of helium and solder used on the loaded and on the empty calorimeter. The heat capacity of the calorimeter represented from 50 to 90% of the total with sample below 10° K., 33% at 20° K., and gradually decreased to 20% at 300° K.

Preparation and Purity of ZrF_4 (*6*). The ZrF_4 sample used in this investigation was prepared by hydrofluorination of pure, dense ZrO_2 in a platinum vessel within a metal reactor at 700° C. The reaction was continued until constant weight was achieved. The fluoride was purified further and converted to macroscopic crystals by sublimation in vacuum (*1*). Spectrochemical analysis indicated (in parts per million): less than 2 of Ag, Ba, Co, Li, Be, Mg, V, Mn, Ca, Cu, Ti, B, Cd, and Na; 7 of Cr; 25 of Ni, Al, and Sn; 35 of Pb; 70 of Hf; less than 100 of P and Zn; 175 of Fe; and 600 of Si. Gravimetric determination for Zr indicated $54.9 \pm 1.0\%$ (theoretical: 54.55%) and for fluoride (as PbClF), $45.2 \pm 1.0\%$ (theoretical: 45.45%). The precision indices are standard deviations. X-ray diffraction and petrographic investigations of this material have failed to indicate the presence of oxide or oxyfluoride. Chemical tests for ZrO_2 in the presence of ZrF_4, based on the insolubility of the oxide in oxalic acid, substantiate this. Chemical analysis indicated less than 0.03% chloride and a total carbon content of 0.12%. The sample (in the form of transparent crystals several millimeters in average dimensions and faintly violet in color) is, therefore, probably 99.7% or purer ZrF_4.

RESULTS

The experimental values of the molal heat capacity of ZrF_4 are given in Table I in chronological sequence so that the temperature increments employed in the measurements may usually be inferred from the differences in the adjacent mean temperatures. These results are expressed in terms of a gram formula mass (g.f.m.) of 167.22 grams, the defined thermochemical calorie of 4.1840 j., and an ice point of 273.15° K. These data have been adjusted for "curvature" occasioned by the finite temperature increments employed in the measurements. The molal heat capacities from the smoothed curve are presented at selected temperatures in Table II. The latter values were obtained from large scale plots of the data and independently checked by the smoothing and curve-fitting digital computer program used for the evaluation of the thermodynamic functions. The heat capacity values have a probable error of about 0.1% above 35° K. and increase to 2% near 10° K. and to 6% below this temperature, because of the decreased sensitivity of the resistance thermometer, the provisional nature of the temperature scale, and the relatively small heat capacity of the sample in this region. Molal entropies and enthalpies were obtained by numerical integration of large scale plots of heat capacity data *vs.* the logarithm of the absolute temperature. Extrapolation below 6° K. was made on the basis of the Debye T^3 relation. Independent evaluation was later obtained from a digital computer program. The essentially identical values of these thermodynamic properties and of the free energy function are also presented in Table II. These functions are considered to have a probable error of less than 0.1% above 100° K.

Table I. Heat Capacity of Zirconium Tetrafluoride[a]

T, ° K.	C_p	T, ° K.	C_p	T, ° K.	C_p
6.65	(0.005)	34.16	1.294	151.59	16.24
7.86	0.008	37.26	1.601	161.97	17.24
9.38	0.017	40.69	1.962	171.97	18.11
10.73	0.030	44.56	2.395	181.81	18.90
11.94	0.043	48.86	2.918	191.61	19.63
12.98	0.060	53.59	3.520	201.48	20.31
13.84	0.077	58.75	4.207	211.46	20.94
14.65	0.096	64.61	5.026	221.58	21.52
15.38	0.115	71.33	5.969	231.71	22.07
16.42	0.145	78.63	7.024	241.81	22.58
17.72	0.188	86.45	8.167	251.90	23.04
19.29	0.250	94.52	9.309	262.04	23.48
21.19	0.339	102.49	10.40	272.21	23.88
23.40	0.460	111.11	11.54	282.29	24.26
25.86	0.617	120.52	12.74	292.27	24.60
28.50	0.806	130.48	13.95	302.20	24.93
31.26	1.032	140.93	15.12		

[a] ZrF_4, g.f.m. = 167.22; in cal./(g.f.m. ° K.)

Table II. Thermodynamic Functions of Zirconium Tetrafluoride[a]

T, ° K.	C_p^{b}	S^{0b}	$H^0 - H_0^{0c}$	$(H^0 - H_0^0)/T^b$	$-(F^0 - H_0^0)/T^b$
10	0.022	0.007	0.06	0.006	0.002
15	0.105	0.029	0.34	0.022	0.007
20	0.282	0.081	1.26	0.063	0.018
25	0.561	0.172	3.33	0.133	0.039
30	0.927	0.305	7.01	0.234	0.071
35	1.376	0.480	12.73	0.374	0.116
40	1.888	0.696	20.87	0.522	0.175
45	2.448	0.950	31.68	0.704	0.246
50	3.060	1.239	45.44	0.909	0.330
60	4.379	1.911	82.55	1.376	0.536
70	5.782	2.691	133.35	1.905	0.786
80	7.225	3.556	198.33	2.479	1.076
90	8.675	4.490	277.89	3.088	1.402
100	10.06	5.475	371.64	3.716	1.759
110	11.40	6.496	478.94	4.354	2.142
120	12.68	7.542	599.36	4.995	2.547
130	13.89	8.604	732.25	5.633	2.971
140	15.03	9.674	876.86	6.263	3.411
150	16.08	10.745	1032.4	6.883	3.862
160	17.06	11.814	1198.2	7.489	4.325
170	17.95	12.874	1373.2	8.078	4.796
180	18.75	13.921	1556.8	8.649	5.272
190	19.51	14.954	1748.1	9.201	5.753
200	20.21	15.972	1946.8	9.734	6.238
210	20.85	16.973	2152.1	10.248	6.725
220	21.43	17.955	2363.6	10.743	7.212
230	21.98	18.919	2580.7	11.220	7.699
240	22.49	19.864	2803.0	11.679	8.185
250	22.96	20.791	3030.3	12.121	8.670
260	23.39	21.699	3262.0	12.546	9.153
270	23.80	22.588	3498.0	12.956	9.633
280	24.17	23.460	3737.8	13.349	10.111
290	24.52	24.313	3981.3	13.729	10.584
300	24.85	25.149	4228.2	14.094	11.055
273.15	23.92	22.89	3574	13.08	9.81
298.15	24.79	25.00	4182	14.03	10.97

[a] ZrF_4, g.f.m. = 167.22. [b] Units = cal./(g.f.m. ° K.). [c] Units = cal./g.f.m.

DISCUSSION

The heat capacity curve (*8*) has a typical sigmoid shape, with no thermal anomalies. Because the electronic structure of the Zr^{+4} ion is that of a rare gas ($^1S_0$ ground state) and because isostructural ThF_4 is also diamagnetic (*7*), the low-temperature, heat capacities of both these compounds are dependent only upon thermal oscillations of the atoms. Hence, except for small differences occasioned by the smaller cationic mass (Zr:Th = 0.393) and the smaller interatomic distance (for the monoclinic cell: $a_{o_{ZrF_4}}:a_{o_{ThF_4}}$ = 0.89) (*18*), the heat capacity behavior of ZrF_4 resembles closely that of ThF_4. The data of this research join smoothly with heat capacities derived from enthalpy determinations of McDonald and coworkers (*12*).

The entropy of ZrF_4, combined with the enthalpy of formation data of Greenberg and coworkers (*9*) (ΔHf_{298} = −456.8 ± 0.3 kcal./g.f.m.), and with entropy from Circular 500 (*13*), yields an entropy and free energy of formation of −81.4 cal./(g.f.m. ° K.) and −432.6 kcal./g.f.m. for the reaction:

$$Zr_{(c,\,\alpha)} + 2F_{2(g)} \rightarrow ZrF_{4(c,\,\beta)}$$

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