lation. Thus, it is felt that the *m*-xylene-1,1,2,2-tetrachloroethane azeotrope is real.

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Zirconium Carbide: Heat Capacity and Thermodynamic Properties from 5 to 350° K.

EDGAR F. WESTRUM, Jr.
Department of Chemistry, University of Michigan, Ann Arbor, Mich.

GEORGE FEICK
Arthur D. Little, Inc., Cambridge, Mass.

The heat capacity of a characterized, zone-melted sample of ZrC was measured by adiabatic calorimetry from 5° to 350° K. and found to be of normal sigmoid shape without transitions or thermal anomalies. At 298.15° K. the measured heat capacity at constant pressure (C_p), the practical entropy ($S°$), the enthalpy function ($[H° - H^\circ_0]/T$), and the Gibbs function ($-[G° - H^\circ_0]/T$) are 9.06, 7.96, 4.70, and 3.26 cal. (g.f.m. ° K.)$^{-1}$. Values of the heat capacity and entropy, adjusted to pure ZrC on the basis of the impurity content obtained by chemical analysis, are 9.13 and 7.90 cal. (g.f.m. ° K.)$^{-1}$.

PREVIOUS studies (*3, 6-9, 11, 12*) have provided values for thermodynamic properties of zirconium carbide (ZrC). The enthalpy of combustion of zirconium carbide was measured by Mah and Boyle (*9*) who derived the value −44.0 ± 1.5 kcal. for the enthalpy of formation at 298.15° K. Krikorian reviewed the available data for the carbides and estimated heat capacity and entropy by assuming that the difference between the heat capacities of zirconium carbide and zirconium nitride was equal to that between titanium carbide and titanium nitride. Using the entropies of these compounds recommended by Kelley and King (*5*) the entropy of zirconium carbide was estimated at 7.8 ± 0.5 cal. (g.f.m. ° K.)$^{-1}$. The heat capacity estimate was made by using the data of Coughlin and King (*1*) on zirconium nitride and the data of Naylor (*10*) on titanium carbide and titanium nitride. Kelley and King (*5*) recently estimated the entropy at 298.15° K. as 9.3 ± 0.3 cal. (g.f.m. ° K.)$^{-1}$. Experimental enthalpy increments over the range of 470° to 1174° K. referred to 298° K. have been obtained by Margrave [reported by McClaine (*8*)] and accord well with the present measurements. The other investigations cited involve studies on the vaporization and equilibrium properties of systems involving zirconium carbide at high temperatures. The present investigations were made to provide a definitive value for the entropy and low temperature chemical thermodynamic properties.

EXPERIMENTAL

Cryostat and Calorimeter. Measurements were made in the Mark II adiabatic vacuum cryostat, which provided an instrument of greater efficiency, mechanical rigidity, and operating convenience than a prototype previously described (*13*). A heat exchanger in the metal cryostat utilizes the enthalpy of the effluent helium gas to furnish a thermal dam for the conduction of heat by the bundle of electrical leads and thus minimize vaporization of the liquid helium from the lowest temperature reservoir. The calorimeter itself is surrounded by a cylindrical adiabatic shield; three portions of the shield are individually controlled by separate channels of automatic regulation which provide a.c. power to the several separate heaters. Copper-Constantan thermocouples monitor the temperature difference between calorimeter and shield and between shield and the ring used to temper the gradient in the bundle of leads. Three separate channels of recording electronic circuitry having proportional, rate, and reset control actions regulate temperature differences to within a millidegree over the range 50° to 350° K. Energy exchange between the calorimeter and the surroundings is so reduced that it is negligible compared with other sources of error. The adiabatic method of operation has been described (*13*).

The copper calorimeter of laboratory designation W-31, a gold-plated vessel with a capacity of 50 cc., has an offset thermometer well which projects through the bottom of the calorimeter for approximately a centimeter, but no thermal conduction vanes. The heat capacity of the empty calorimeter was determined in a separate series of measurements in which identical amounts of indium-tin solder for sealing the calorimeter and Apiezon-T grease for thermal contact with the heater-thermometer-calorimeter assembly were used. At the lowest temperatures the heat capacity of the sample represented 30% of the total. This increased to 50% at 55° K., to 70% at 170° K., and to 76% by 350° K. and hence was a favorable fraction of the total over most of the range. The mass of the calorimetric sample was 125.948 grams (in vacuo). Buoyancy corrections were made by using a density of 6.73 grams cc.$^{-1}$ for zirconium carbide. A pressure of 13.6 cm. of helium at 300° K. was used to facilitate thermal conduction in the sample space.

Temperatures were determined with a capsule-type, strain-free, platinum-resistance thermometer (laboratory designation A-5) contained within an entrant well in the calorimeter. Temperatures are considered to accord with the thermodynamic temperature scale to within 0.03° from 10° to 90° K. and within 0.04° from 90° to 350° K. The temperature increments may be determined with more precision and are probably correct to a few tenths of a millidegree after correction for quasi-adiabatic drift. All measurements of mass, resistance, potential, temperature, and time are referred to calibrations made by the National Bureau of Standards.

Preparation and Characterization of the Sample. The hafnium-free zirconium carbide (Carborundum Co.) obtained in powder form had the following analysis: 88.16% Zr; 11.45% C; 0.05% 0; 0.15% N; 0.12% Fe. To reduce the surface area and impurity level of this material it was sintered into bars about 1 cm. in diameter by 18 cm. in length. The bars were melted in an argon atmosphere containing 5% of hydrogen using the vertical floating-zone method with induction heating. Details of the apparatus and method have been presented (*2*).

About 1% of free carbon in the form of high-purity graphite was added to the powder before sintering in order to correct the carbon deficiency and to make up for expected losses in melting.

The zone-refined product was obtained in the form of dense, macrocrystalline rods about 6 to 8 mm. in diameter. A slight surface film was removed by etching with hot, conc. aq. HF. The average carbon content of four separate rods was 11.22 ± 0.07% by weight corresponding to a deficiency of 3.5% from the stoichiometric value of 11.63%. This deficiency could probably have been prevented by the addition of more carbon to the sintered rods before melting. Analysis of a single sample for zirconium gave 89.27% (theoretical, 88.37%) which, together with its carbon content of 11.20%, yielded a total of 100.47%. The carbon analysis is considered to be more reliable than that for zirconium. The oxygen content of the zone-refined product was 0.005% and the nitrogen content was 0.067%. Quantitative spectrographic analysis gave: 0.12% Ti; 0.07% each B and Fe; 0.01% each Al and Sn; 0.001 to 0.01% Mg; and 0.001% each Ca, Mn, Cu, Mo, Ag, Si, Hf, and Pb, all by weight. Metallographic examination showed the presence of a very small amount of a second phase, possibly ZrB_2, in some samples but not in others.

The proximate composition of the sample by weight is: 96.5% ZrC; 2.4% excess Zr; 0.5% ZrN; 0.4% ZrB_2, and 0.15% TiC. In interpreting these figures, however, it should be borne in mind that the ZrN, TiC, and excess Zr are probably all in solid solution in the ZrC. The actual structure is probably best represented as a ZrC lattice with 3.5% of the carbon sites vacant and with nitrogen and titanium substituted in some of the C and Zr sites, respectively.

RESULTS

The experimental heat capacities are presented in chronological order at the mean temperatures of the determinations in Table I. These data are based upon a defined thermochemical calorie equal to 4.1840 abs. joules, an ice point of 273.15° K., and a gram formula mass (g.f.m.) of 103.231 for zirconium carbide. These data have been corrected for curvature, i.e., for the difference between the $\Delta H/\Delta T$ and the corresponding derivative. The approximate values of ΔT used in the heat capacity determinations can usually be inferred from the increments between adjacent mean temperatures shown in Table I. Precision reflected by probable errors decreasing from about 5% at 5° K. to 1% at 10° K., and to less than 0.1% above 50° K. is considered to characterize these data.

The heat capacities and thermodynamic functions at selected temperatures, as presented in Table II, are obtained from the heat capacity data by a least squares-fitted curve through the experimental points (carefully compared with a large-scale plot of the data) or by the integration thereof. Both the fitting and quadrature are performed by high-speed digital computers using programs previously described (*4*). The thermodynamic functions are considered

Table I. Heat Capacity of Zirconium Carbide

ZrC: g.f.m. = 103.23 Units: cal. (g.f.m. ° K.)$^{-1}$

T, ° K.	C_p	T, ° K.	C_p	T, ° K.	C_p
Series 1		258.94	8.330	14.83	0.0118
		267.76	8.502	16.52	0.0159
71.02	1.659	276.48	8.678	18.44	0.0219
77.48	1.978	292.81	8.973	20.59	0.0311
84.53	2.333	301.41	9.105	22.95	0.0447
92.01	2.688	336.31	9.604	25.57	0.0654
99.71	3.039	345.16	9.721	28.44	0.0955
107.56	3.392			31.45	0.1383
115.66	3.748	Series II		34.62	0.1975
123.93	4.107			37.91	0.2747
132.58	4.475	313.69	9.297	41.60	0.3783
141.47	4.831	322.55	9.427	45.97	0.5227
150.35	5.182	331.36	9.556	50.94	0.7166
159.30	5.514			56.46	0.9557
168.31	5.839	Series III		62.43	1.2391
177.30	6.146			68.86	1.549
186.29	6.442	5.59	0.0011	75.78	1.890
195.30	6.721	6.75	0.0016	201.94	6.914
222.32	7.476	7.85	0.0024	205.90	7.033
231.69	7.712	9.11	0.0034	209.81	7.136
240.94	7.937	10.43	0.0048	213.67	7.240
250.03	8.138	11.81	0.0064	217.49	7.346
		13.30	0.0087		

Table II. Thermodynamic Properties of Zirconium Carbide

ZrC: g.f.m. = 103.23 Units: cal., g.f.m., ° K.

T, ° K.	C_p	$S°$	$H° - H_0°$	$\frac{-(G° - H_0°)}{T}$
5	0.0008	0.0003	0.001	0.0001
10	0.0043	0.0017	0.012	0.0005
15	0.0121	0.0047	0.041	0.0013
20	0.0282	0.0101	0.147	0.0028
25	0.0600	0.0194	0.359	0.0051
30	0.1167	0.0349	0.788	0.0087
35	0.2057	0.0592	1.579	0.0140
40	0.3307	0.0944	2.905	0.0218
45	0.4899	0.1422	4.944	0.0324
50	0.6777	0.2033	7.852	0.0463
60	1.1229	0.3652	16.80	0.0852
70	1.609	0.5746	30.44	0.1397
80	2.102	0.8217	49.00	0.2091
90	2.586	1.0974	72.46	0.2923
100	3.055	1.3943	100.68	0.3875
110	3.507	1.7067	133.50	0.4931
120	3.943	2.0307	170.8	0.6077
130	4.365	2.3631	212.3	0.7299
140	4.771	2.7015	258.0	0.8586
150	5.163	3.0441	307.7	0.9929
160	5.539	3.3894	361.2	1.1318
170	5.897	3.7361	418.4	1.2748
180	6.237	4.0828	479.1	1.4212
190	6.558	4.429	543.1	1.570
200	6.861	4.773	610.2	1.722
210	7.147	5.115	680.3	1.875
220	7.415	5.453	753.1	2.030
230	7.669	5.789	828.5	2.186
240	7.908	6.120	906.4	2.344
250	8.135	6.448	986.6	2.501
260	8.350	6.771	1069.7	2.659
270	8.552	7.090	1153.6	2.817
280	8.743	7.404	1240.1	2.976
290	8.922	7.714	1328.4	3.134
300	9.088	8.020	1418.5	3.291
310	9.244	8.320	1510.1	3.449
320	9.390	8.616	1603.3	3.606
330	9.528	8.907	1697.9	3.762
340	9.658	9.194	1793.8	3.918
350	9.778	9.475	1891.0	4.072
273.15	8.614	7.189	1181	2.867
298.15	9.058	7.964	1401	3.262

to have a precision corresponding to a probable error of less than 0.1% above 100° K. Additional digits beyond those significant are given in Table II for internal consistency and to permit interpolation and differentiation. The entropies and Gibbs energies have not been adjusted for nuclear spin and isotope mixing contributions and hence are practical values for use in chemical thermodynamic calculations.

DISCUSSION

Assuming the sample to have the proximate composition indicated with impurities of partial molal heat capacities equal to those for the bulk phases tabulated by Kelley and King (*5*), the heat capacity of pure zirconium carbide corrected for the impurities would have values of 0.62 cal. (g.f.m. °K.)$^{-1}$ at 50° K., 3.01 at 100° K., 5.15 at 150° K., 6.89 at 200° K., and 9.13 at 298.15° K. Corresponding adjustment of the thermodynamic functions at 298.15° K. yields estimates of 7.90 cal. (g.f.m. ° K.)$^{-1}$ for the entropy, −3.20 cal. (g.f.m. ° K.)$^{-1}$ for the Gibbs energy function, and 1400 cal. (g.f.m.)$^{-1}$ for the enthalpy increment of pure zirconium carbide.

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Dissociation Constant and Limiting Conductance of NaBr in Liquid SO_2 at 0.02°C.

NORMAN N. LICHTIN[1] and HARVEY KLIMAN
Chemistry Department, Boston University, Boston 15, Mass.

The dissociation constant, K_d, of NaBr and its limiting conductance, Λ_0, at 0.02° C. are respectively, $4.84 \pm 0.05 \times 10^{-5}$ mole per liter and 265 ± 2.8 mhos cm. sq. per mole. The Bjerrum distance of closest approach calculated from K_d is 2.87 ± 0.03A, in excellent agreement with the sum of ionic radii, 2.91 A. The value of Λ_0, although smaller than that calculated from Stokes' law and the ionic radii, indicates a smaller degree of solvation of free Na^+ in SO_2 than in several other solvents. The mobility behavior of Na^+ in SO_2 resembles that of K^+ more than Li^+.

WE HAVE previously reported (*10, 11, 12*) that ionic distances of closest approach calculated with Bjerrum's equation from values of the ion pair dissociation constant, K_d, of KCl, KBr, KI and LiBr in liquid SO_2 all fall within 0.2A of the appropriate crystallographic distances. The experimental limiting equivalent conductances of the potassium salts (*10, 11*) also fall within 5% of the value calculated from Stokes' equation using Pauling's values of ionic radii. The value of Λ_0, for LiBr (*12*), however, is less than half that calculated in this way. Thus Li^+ appears to be strongly solvated by SO_2 with respect to hydrodynamic transport but not with respect to association with bromide. Sodium bromide provides an additional case of close adherence to Bjerrum's equation in this medium, while Na^+ appears to be intermediate in its mobility behavior between Li^+ and K^+.

EXPERIMENTAL

The experimental procedures and bridge have been described previously (*9, 13*). An improved conductance cell, which is described in detail elsewhere (*14*) was employed. Baker's Analyzed Reagent NaBr was recrystallized three times from freshly boiled distilled water and dried at 135° for 10 days. The compound is considerably less soluble than is reported by Jander (*8*). Solubility measurements, as such, were not carried out, but observations made in the course of preparing solutions for measurement suggest a value in the vicinity of 0.0003 mole per liter. Because of the low solubility, samples of NaBr (about 1 mg.) were introduced into the conductance cell in the form of weighed aliquots in ethanol solution. The

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[1] Present address, Isotopes Dept., Weizmann Institute of Science, Rehovoth, Israel.