(3) Franck, E.U., Meyer, F., Z. Elektrochem. **63**, 571 (1959).
(4) Franck, E.U., Spalthoff, W., Ibid., **61**, 348 (1957).
(5) Fredenhagen, K., Z. Anorg. allgem. Chem. **218**, 161 (1934).
(6) Hougen, O.A., Watson, K.M., Ragatz, R.A., "Chemical Process Principles," Part II, 2nd ed., John Wiley and Son Co., New York, 1959.
(7) Hu, J., White, D., Johnston, H.L., J. Am. Chem. Soc. **75**, 1232 (1953).
(8) Jarry, R.L., Davis, W. Jr., J. Phys. Chem. **57**, 600 (1953).
(9) Lewis, G.N., Randall, M., "Thermodynamics," 2nd ed., McGraw-Hill, New York, 1961.
(10) Seufzer, P.R., Katz, J.J., Division of Industrial and Engineering Chemistry, 126th Meeting, ACS, New York, September 1954.

(11) Simons, J.H., J. Am. Chem. Soc. **46**, 2179 (1924).
(12) Strohmeier, W., Briegleb, G., Z. Elektrochem. **57**, 662 (1953).

Thermodynamic Properties of Inorganic Substances VII.

The High Temperature Heat Content of Zirconium Diboride

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The high temperature heat content of a high-purity sample of ZrB_2 has been measured in a copper-block drop calorimeter over the range 410° to 1125°K., and the results correlated with low temperature heat capacity data on a similar sample. Derived thermodynamic properties over the range 0° to 2000°K. are presented based on experimental data up to 1200°K. and on extrapolations of computer-selected fits of the experimental points.

FIVE SETS OF HIGH TEMPERATURE thermodynamic data (1, 2, 7, 8, 10) and a single low temperature study (11) have previously been available for ZrB_2 samples of 95-99% purity but large positive and negative discrepancies (10-20% or more) have been observed even though all the calorimeters have been calibrated in standard ways. In a cross-check of data, Pears and coworkers (9) made runs on the same ZrB_2 used by Barnes and coworkers (1) and reproduced the results of Barnes within a few per cent, which indicates that the reported large differences between samples are real and not measurement errors. The AVCO results are pulse-type heat capacity measurements (2) over the temperature range 2000° to 2500°K. and seem to differ drastically from conventional extrapolations of the lower temperature results, as do the results of Prophet (10).

This report presents high temperature measurements on a sample of ZrB_2 prepared by Feick (3) which is from the same batch as the sample used by Westrum and Feick (11) for their low-temperature studies.

According to Feick (3), the samples used (Bar No. 80) had been zone-refined and had the stoichiometry $ZrB_{1.97}$. Representative impurities in such bars are: 0, 52 p.p.m.; C, 215 p.p.m.; N, 134 p.p.m.; Si, 100-1000 p.p.m.; Hf and Fe, 10-1000 p.p.m.; Mg, 10-100 p.p.m.; and Ag, Ca, Cu, Ti, V, Cr, and Mn, 10 p.p.m. There is also some possibility of ZrB being present originally (11), although it probably annealed out during the heating cycles.

RESULTS

Two sets of data were obtained. The first set, covering the range 410-773°K., was terminated when the capsule sprang a leak and allowed oxidation of the ZrB_2 as detected by a large, sudden weight gain in the next run attempted after 773°K. The second series covered the range 450–1126°K. and no weight changes were observed. The results were processed on a CDC-1604 high-speed computer to yield the data in Table I. These data were then used for

EXPERIMENTAL

The calorimeter used in this work has been described previously (4) and the samples were contained in platinum or platinum-rhodium capsules under an argon atmosphere. Temperature measurements were made with a Pt vs. Pt-10% Rh thermocouple calibrated against a reference which had been recently calibrated at the National Bureau of Standards. The reliability of the calorimeter was checked by rerunning a standard sample of synthetic sapphire. The heat content for the empty Pt capsules was measured at several temperatures and found to check well with the equation of Kelley (6) while the heat content of the Pt-10% Rh capsule was calculated from Kelley's data on the elements.

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Table I. Experimental Heat Contents of ZrB_2

T, °K.	$T_{cal.}$, °K.	$H_T - H_{T_{cal.}}$ Cal. Mole⁻¹
410.46	298.60	1510
463.46	298.69	2204
553.76	298.93	3564
598.66	298.81	4288
711.06	298.89	5926
773.06	298.97	7114
450.02	297.88	1998
514.25	298.92	3017
724.16	299.44	6031
888.46	299.26	8782
986.46	299.02	10626
1123.46	299.17	12781
1125.62	299.17	13000

obtaining a least squares fit and a Kelley equation (6) for $(H_T - H_{298})$ over the range 260–1126° K. by considering the higher temperature results of Westrum and Feick (11). The equations derived are:

$$(H_T - H_{298}) = (14.23T + 1.554 \times 10^{-3}T^2 + \frac{2.725 \times 10^5}{T}$$

$$- 5296) \pm 64 \text{ calories mole}^{-1}$$

and

$$C_p = 14.23 + 3.108 \times 10^{-3}T - \frac{2.725 \times 10^5}{T^2} \text{ cal. deg.}^{-1}\text{mole}^{-1}$$

where 260° K. $< T <$ 1126° K., but extrapolations above or below these limits must be made cautiously because of the empirical nature of the equation.

A computer program has been developed for selecting combinations of Debye and/or Einstein functions to fit the experimental points and, in this way, to make possible extrapolations to high temperatures with somewhat more confidence than with the empirical Kelley equation. One of the basic problems is a choice of the proper functional representation and runs were made in which either heat contents (or heat capacities) were fitted to three equations:

$$C_p = D(\theta_1/T) + 2D(\theta_2/T) + aT \qquad (1)$$

$$C_p = D(\theta_1/T) + 2E(\theta_2/T) + aT \qquad (2)$$

$$C_p = [D(\theta_1/T) + 2D(\theta_2/T)][1 + aT] + bT \qquad (3)$$

These first two equations neglect differences between C_p and C_v to a first approximation while the third represents an effort to do this by introducing the additional constant.

Kaufman (5) has suggested the value $a \approx 10^{-4}$ for borides and carbides, in lieu of the necessary experimental data, by comparison with data for metals.

The low-temperature C_p data of Westrum and Feick (11) have been fitted over the range 0–350° K. with these three equations with absolute r.m.s. deviations $\approx$ 0.03–0.06 cal. deg.$^{-1}$ mole^{-1}. Results based on fits of the low temperature data only are presented in Table II. The combination of high and low temperature data lead to the three following "best fits:"

Equation 1: $C_p = D(1550/T) + 2D(670/T) + 7.58 \times 10^{-6}T$ cal. deg.$^{-1}$ mole^{-1} which reproduces $(H_T - H_{298})$ with a r.m.s. deviation of $\pm$49 cal. mole^{-1} over the range 0–1125° K. and predicts S°_{298} = 8.52 cal. deg.$^{-1}$ mole^{-1}.

Equation 2: $C_p = D(1570/T) + 2E(500/T) + 1.47 \times 10^{-5}T$ cal. deg.$^{-1}$ mole^{-1} which reproduces $(H_T - H_{298})$ with a r.m.s. deviation of $\pm$51 cal. mole^{-1} over the range 0–1125° K., and predicts S°_{298} = 7.94 cal. deg.$^{-1}$ mole^{-1}.

Equation 3: $C_p = [D(360/T) + 2D(1530/T)][1 + 10^{-4}T]$ $+ 4.85 \times 10^{-5}T$ cal. deg.$^{-1}$ mole^{-1} which reproduces $(H_T - H_{298})$ with a r.m.s. deviation of $\pm$121 cal. mole^{-1} over the range 0–1125° K. and predicts S°_{298} = 8.89 cal. deg.$^{-1}$ mole^{-1}.

Of these three equations the first two give the best fits while the last has a form more consistent with theory and Debye θ's closer to those predicted from considerations of the elements. Also, the trend in C_p at high temperatures (1500–2000° K.) is in the direction indicated by the work of Prophet (10) over the range 1300–2150° K. although his experimental data are uncertain by $\pm$10%. Table III

Table II. Properties of ZrB₂ Derived from Low Temperature Data

Equation	$C_p(298)$ Cal. Deg.$^{-1}$ Mole^{-1}		$H_{298} - H_0$ Cal. Mole^{-1}		S°_{298} Cal. Deg.$^{-1}$ Mole^{-1}		$C_p(2000°$ K.) Cal. Deg.$^{-1}$ Mole^{-1}	$H_{2000} - H_{298}$ Cal. Mole^{-1}
	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Calcd.	Calcd.
$C_p = D(500/T) + 2D(1190/T)$ $+ 9.93 \times 10^{-4}T$	11.53	11.51 ±0.04	1590	1594	8.59	8.68 ±0.1	19.64	30,180
$C_p = D(440/T) + 2E(860/T)$ $+ 2.43 \times 10^{-5}T$	11.53	11.59 ±0.06	1590	1591	8.59	8.67 ±0.1	17.74	28,510
$C_p = [D(490/T) + 2D(1200/T)]$ $[1 + 10^{-4}T] + 4.86 \times 10^{-5}T$	11.53	11.53 ±0.03	1590	1593	8.59	8.46 ±0.1	21.28	31,660

Table III. Smoothed Thermodynamic Functions for ZrB₂[a]

T,° K.	$H_T^\circ - H^\circ_{298.15}$ Cal. Mole^{-1}	C_p° Cal. Deg.$^{-1}$ Mole^{-1}	$S_T - S_{298}$ Cal. Deg.$^{-1}$ Mole^{-1}	$[(G_T^\circ - H^\circ_{298.15})/T]$
0	−1590	0	− 8.59	∞
50	−1585	0.503	− 8.45	31.83
100	−1503	2.870	− 7.42	16.21
150	−1296	5.410	− 5.77	11.46
200	−964	7.840	− 3.57	9.53
250	−518	9.919	− 1.89	8.77
298.15	0	11.53	0	8.59
300	21	11.59	0.07	8.60
350	635	12.88	1.96	8.74
400	1330	13.77	3.82	9.09
500	2750	14.70	7.00	10.08
600	4260	15.34	9.74	11.23
700	5820	15.85	12.14	12.42
800	7430	16.29	14.29	13.60
900	9080	16.69	16.23	14.74
1000	10,760	17.07	18.01	15.84
1100	12,490	17.43	19.65	16.89
1200	14,250	17.77	21.18	17.90
1300	(16,140 ± 200)	(18.3 ± 0.6)	(21.9 ± 0.5)	(18.1 ± 0.5)
1400	(17,950 ± 300)	(18.5 ± 0.6)	(23.2 ± 0.5)	(19.0 ± 0.5)
1500	(19,770 ± 400)	(18.7 ± 0.8)	(24.4 ± 0.5)	(19.8 ± 0.6)
1600	(21,600 ± 500)	(18.9 ± 0.8)	(25.5 ± 0.5)	(20.6 ± 0.6)
1700	(23,710 ± 600)	(19.0 ± 1.0)	(26.6 ± 0.5)	(21.3 ± 0.8)
1800	(25,620 ± 700)	(19.2 ± 1.2)	(27.6 ± 0.5)	(22.0 ± 0.8)
1900	(27,540 ± 800)	(19.3 ± 1.5)	(28.5 ± 0.5)	(22.6 ± 1.0)
2000	(29,470 ± 1000)	(19.4 ± 1.5)	(29.4 ± 0.5)	(23.2 ± 1.0)

[a] Data from 0–350° K. based on reference 11; from 350–1200° K. based on this work; above 1200° K. the parentheses indicate functions based on an average of the computer-selected Debye-Einstein fits and estimated confidence limits.

T, °K.	Krestovnikov (7)	SRI (8)	Barnes (1)	C_p in cal. deg.$^{-1}$ mole^{-1} AVCO (2)	Prophet (10)	Westrum (11)	This Work
298.15	(14.41)[a]	...	(13.0)	...	(10.55)	11.53	(11.53)
500	15.77	11.52	16.50	...	(14.06)	...	14.70
1000	17.74	19.36	19.66	...	(20.22)	...	17.07
1500	17.70	21.50	...	...	21.37	...	(18.7 ± 0.8)
2000	(15.64)	23.50	...	38.37[b]	22.99	...	(19.4 ± 1.5)
2500	...	25.20	...	41.76[b]	...	...	...

[a] Parentheses indicate extrapolated values, often beyond reliable limits of equations used.
[b] These excessively high results probably arise because no correction for sublimation of the sample was made.

presents thermodynamic functions based on experimental data up to 1200° K. and on the average extrapolations of the computer-selected fits up to 2000° K.

For comparison, high temperature heat capacities based on all the available measurements on ZrB_2 samples are tabulated in Table IV. The discrepancies clearly show the need for further studies, especially at temperatures over 1200° K., on well-characterized samples of ZrB_2.

ACKNOWLEDGMENT

LITERATURE CITED

(1) Barnes, D.W., Mezaki, R., Tilleux, E.W., Margrave, J.L., Proc. Intern. Symp. Thermodyn. Nuclear Materials, p. 775, Paper SM-26/48, Vienna, Austria, May 21, 1962.
(2) Barriault, R., and coworkers, Thermodynamics of Refractory Compounds, AVCO Reports to Wright-Patterson Air Force Base under Contract No. AF33(616)-7327, ASO-TR-61-260, Vol. I, pp. 350, 378-80. (1961), and Vol. II (1962).
(3) Feick, G., Arthur D. Little, Inc., under USAF Contract No. AF33(616)-7472.
(4) Grimley, R.T., Margrave, J.L., J. Phys. Chem. 62, 1436 (1958); 63, 1505 (1959).
(5) Kaufman, L., "Investigation of Boride Compounds for Very High Temperature Applications," Progress Reports to Aeronautical Systems Division, Wright-Patterson Air Force Base, Contract No. AF33(657)-8635, October 1962, April and December 1963.
(6) Kelley, K.K., U. S. Bureau of Mines, Bulletin 584 (1960).
(7) Krestovnikov, A.N., Vendrikh, M.S., Izvest. Vysshikh Ucheb. Zavedenii, Tsvetnya Met., No. 1, 73 (1958); also, C. A. 53, 19552 (1959).
(8) Neel, D., Pears, C., Oglesby, S., Southern Research Institute Report No. ASD-TDR-62-765 to Wright Air Development Division, August, 1962.
(9) Pears, C.D., Private Communication, May 21, 1962.
(10) Prophet, H., Unpublished work cited in the JANAF Tables, edited by D.R. Stull, Dow Chemical Company, Midland, Mich.
(11) Westrum, E.F., Feick, G., J. Chem. Eng. Data 8, 193 (1963).

Thermodynamic Activities of Cadmium and Zinc in Binary Mercury-Rich Amalgams

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Thermodynamic activities, as determined from e.m.f. data, are presented for solute cadmium and zinc in their respective mercury-rich amalgams. The calculated activities are relative to a standard state of the saturated amalgam at the temperature of measurement. Concentration cell potentials were measured at 50.0, 70.2, and 93.2° C. for various amalgam concentrations up to the equilibrium solubility. Values of the equilibrium solubilities for these amalgam systems were determined at the same temperatures.

MANY OF THE theoretical correlations for diffusion phenomena in binary solutions require the use of thermodynamic activity data to correct for the departure from ideal solution behavior. Thus, the thermodynamic activities presented in this paper were determined in the course of studying diffusional behavior in cadmium and zinc amalgam systems.

MATERIALS AND APPARATUS

All materials used in this research were ACS Reagent Grade or better. Amalgams were prepared by dissolving solute zinc or cadmium directly in mercury. Compositions were established by gravimetric preparation with an estimated relative accuracy of better than 0.0001 per cent (7); absolute accuracy was limited only by the residual

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