$$N_3\left[\int_1^0 \frac{\bar{G}_2}{(1-N_2)^2}\,dN_2\right]_{\frac{N_1}{N_3},\frac{N_4}{N_3}\ldots=0} - \ldots$$

The only assumptions involved are: (1) that G is the molal value of an extensive function, and hence that the extended Gibbs–Duhem equation may be applied; G must be so chosen as to have zero value for each pure component; (2) that Henry's law is valid as a limiting law for all components at infinite dilution. The restrictions on the usefulness of the relation are discussed; departures from Henry's law at small finite concentrations must be such that $\bar{G}_2$ is proportional to $(1 - N_2)^2$ in the near vicinity of $N_2 = 1$, in order that the function to be integrated in the above equation be always finite.

It is shown that the above equation may be used as the basis of a new method for determining G for an n-component solution; this method involves the introduction of another miscible component and the experimental determination of $\bar{G}$ therefor in the new system of $n + 1$ components.

KEARNY, N. J. RECEIVED JUNE 22, 1949

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heat Capacities at Low Temperatures and Entropies of Zirconium, Zirconium Nitride, and Zirconium Tetrachloride

BY S. S. TODD[1]

A recent paper of Coughlin and King[2] presents high-temperature heat-content data for zirconium metal and its oxide (ZrO_2), nitride (ZrN), silicate ($ZrSiO_4$), and tetrachloride ($ZrCl_4$). The present paper gives low-temperature heat-capacity values and entropies at 298.16° K. for the metal, nitride, and tetrachloride, thus making possible free-energy calculations for the last two substances. Low-temperature heat-capacity and entropy values for the oxide and silicate have been reported by Kelley.[3,4]

Heat Capacities

The materials used in this investigation were identical with those described by Coughlin and King,[2] and repetition of the methods of preparation and tests of purity appears unnecessary. Correction was made for the hafnium contents, based upon the assumption that corresponding zirconium and hafnium compounds have the same molal heat capacity. This correction increased the measured heat-capacity values by the following amounts: Zr, 1.0%; ZrN, 0.7%; and $ZrCl_4$, 0.35%.

The measurements were made with previously described apparatus.[5] The results, expressed in thermochemical calories[6] (1 cal. = 4.1833 int. joules), are listed in Table I and plotted against

TABLE I

MOLAL HEAT CAPACITIES

T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.
Zr (mol. wt., 91.22)					
53.2	2.418	115.0	4.796	216.4	5.861
56.8	2.640	124.1	4.971	226.2	5.905
60.8	2.873	136.1	5.172	236.4	5.948
65.6	3.134	146.2	5.293	246.0	5.981
70.6	3.383	156.0	5.409	256.7	6.042
75.4	3.609	166.1	5.510	266.4	6.083
79.8	3.789	176.0	5.606	276.4	6.127
84.1	3.945	186.2	5.672	286.6	6.149
94.9	4.296	196.1	5.737	296.8	6.168
104.5	4.562	206.3	5.802	(298.16)	(6.186)
ZrN (mol. wt., 105.23)					
53.1	1.198	114.9	4.416	216.6	8.048
57.1	1.426	124.8	4.867	226.5	8.287
62.0	1.699	136.2	5.358	236.5	8.516
67.5	2.018	145.9	5.747	246.0	8.714
72.7	2.308	155.9	6.137	256.4	8.954
77.6	2.574	166.2	6.517	266.4	9.127
80.5	2.731	176.7	6.876	276.6	9.325
85.3	2.978	186.2	7.177	286.8	9.482
95.2	3.477	196.4	7.495	296.7	9.613
104.8	3.946	206.7	7.784	(298.16)	(9.655)
$ZrCl_4$ (mol. wt., 233.05)					
52.6	11.24	114.6	20.24	216.6	26.53
55.9	11.86	124.7	21.21	226.7	26.79
60.0	12.63	136.1	22.23	236.4	27.11
64.9	13.53	146.3	22.97	246.3	27.37
69.3	14.30	156.2	23.66	256.5	27.66
74.0	15.06	166.3	24.25	266.4	27.94
80.0	15.98	176.3	24.87	276.5	28.17
83.9	16.53	186.4	25.33	286.8	28.37
94.8	17.96	196.4	25.75	296.7	28.63
104.6	19.15	206.7	26.15	(298.16)	(28.65)

(1) Pacific Experiment Station, U. S. Bureau of Mines. Article not copyrighted.

(2) J. P. Coughlin and E. G. King, THIS JOURNAL, **72**, 2262 (1950).

(3) K. K. Kelley, (a) *ibid.*, **63**, 2750 (1941); (b) *Ind. Eng. Chem.*, **36**, 377 (1944).

(4) In this connection, it appears worth-while to record that Kelley's entropy values should be increased slightly to account for the now known hafnium contents of the materials. Recalculation gives $S^0_{298.16} = 12.12 \pm 0.08$ for ZrO_2 (monoclinic) and $S^0_{298.16} = 20.2 \pm 0.2$ for $ZrSiO_4$ (zircon).

(5) K. K. Kelley, B. F. Naylor, and C. H. Shomate, *U. S. Bur. Mines Tech. Paper*, 686 (1946).

(6) E. F. Mueller and F. D. Rossini, *Am. J. Phys.*, **12**, 1 (1944).

temperature in Fig. 1. Molecular weights accord with the 1947 International Atomic Weights. The sample masses employed were: Zr, 396.79 g.; ZrN, 303.10 g.; and $ZrCl_4$, 185.15 g.

The heat-capacity curves appear normal in all respects, but it is of interest to note that below about 125° K. the molal heat capacity of the nitride becomes progressively lower than that of the metal, reaching a value half that of the metal at 53° K.

Entropies

The entropies at 298.16° K. were calculated in the usual manner. The measured portions, between 51.00° and 298.16° K., were obtained by numerical integration of plots of C_p against log T, using Simpson's rule. The portions below 51.00° K. were obtained by extrapolation, employing the empirical Debye and Einstein functions listed below. (The temperature range of representation of the measured values and the maximum deviation are indicated in parentheses.)

Zr: $D(252/T)$(53°–120°K., 1.0%)
ZrN: $D(360/T) + E(673/T)$(53°–298°K., 1.7%)
$ZrCl_4$: $D(73.0/T) + 2E(167/T) + 2E(414/T)$(53°–200°K., 1.0%)

The entropy results are listed in Table II.

TABLE II

MOLAL ENTROPIES, CAL./DEG.

	Zr	ZrN	$ZrCl_4$
0–51.00°K. (extrap.)	1.002	0.413	8.12
51.00–298.16°K. (meas.)	8.277	8.880	36.39
$S^\circ_{298.16}$	9.28 ± 0.08	9.29 ± 0.05	44.5 ± 0.5

The extrapolated values for zirconium, zirconium nitride, and zirconium tetrachloride are, respectively, less than 11, 5, and 19% of the total values at 298.16° K. The entropies of zirconium and zirconium nitride at 298.16° K. are virtually identical, as was found previously for titanium and titanium nitride.[7,8] The entropy value for zirconium is 0.2 unit lower than the previously accepted value, 9.5 ± 0.6,[9] which was based upon a single heat capacity measurement. There are no previous values for the other two substances.

Related Thermal Data.—The heats of formation of zirconium nitride and tetrachloride have been given as $\Delta H_{298.16} = -82{,}200$ and $\Delta H_{298.16} = -230{,}000$ cal./mole, respectively.[10] The present entropy values, in conjunction with 45.77 for nitrogen and 53.31 for chlorine, yield $\Delta S^\circ_{298.16} = -22.88$ and $\Delta S^\circ_{298.16} = -71.4$ for the respective entropies of formation. In turn, the free energies of formation are $\Delta F^\circ_{298.16} = -75{,}400$ for the nitride and $\Delta F^\circ_{298.16} = -208{,}700$ for the tetrachloride. The free energy of formation of monoclinic zirconium oxide[3b] may be revised using $\Delta H_{298.16} = -258{,}200$[10] and $\Delta S^\circ_{298.16} = -46.17$, yielding $\Delta F^\circ_{298.16} = -244{,}400$ cal./mole.

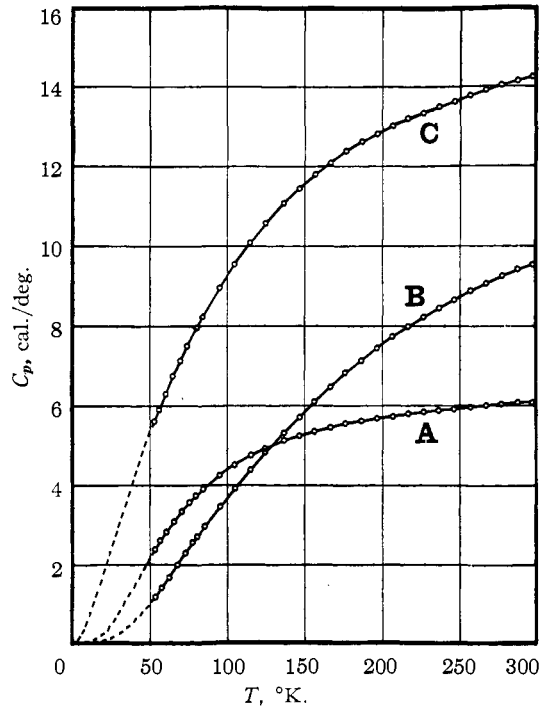

Fig. 1.—Heat capacities: A, Zr; B, ZrN; C, $ZrCl_4$ (values plotted for 1/2 mole).

Summary

The heat capacities of zirconium metal, zirconium nitride, and zirconium tetrachloride were measured throughout the temperature range 51° to 298° K.

Entropies and free energies of formation at 298.16° K. were calculated.

BERKELEY, CALIFORNIA RECEIVED DECEMBER 23, 1949

(7) K. K. Kelley, *Ind. Eng. Chem.*, **36**, 865 (1944).
(8) C. H. Shomate, THIS JOURNAL, **68**, 310 (1946).
(9) K. K. Kelley, U. S. Bur. Mines Bull., 434 (1941).
(10) National Bureau of Standards, Selected Values of Chemical Thermodynamic Properties, Series I, Table 56, June 30, 1949.