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Low-Temperature Heat Capacity and High-Temperature Enthalpy of $TiAl_3$

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Low-Temperature Heat Capacity and High-Temperature Enthalpy of $TiAl_3$

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LOW-TEMPERATURE HEAT CAPACITY AND HIGH-TEMPERATURE ENTHALPY OF $TiAl_3$

by

J. M. Stuve[1] and M. J. Ferrante[1]

ABSTRACT

Thermodynamic properties were determined by the Bureau of Mines for the intermetallic compound, $TiAl_3$. Heat capacities were obtained from 5 to 303 K by adiabatic calorimetry. The derived value of $S_{298.15}$ is 22.08±0.07 cal/deg-mole. Enthalpies relative to 298 K were obtained from 298 to 1,413 K by copper-block drop calorimetry. No anomalous thermal behavior was noted in the temperature ranges investigated. Low- and high-temperature data were combined with a known enthalpy of formation at 298 K to give values of enthalpy of formation and Gibbs energy formation, 0 to 1,400 K.

INTRODUCTION

The present investigation of the intermetallic compound $TiAl_3$ was made in order to determine its thermodynamic stability over a range of temperature. This work was part of a Bureau of Mines program on the aluminothermic reduction of titanium dioxide.

The titanium-aluminum alloy system contains several stable compounds.[2] Among these, $TiAl_3$ has the highest aluminum content. Presented here for $TiAl_3$ are low-temperature heat capacities and the derived entropy at 298 K, as well as increments of enthalpy and entropy above 298 K. No previous similar data have been published.

The data were combined with a value for its standard enthalpy of formation as reported by Kubaschewski and Dench[3] to give enthalpies of formation and Gibbs energy of formation ($\Delta G°$) between 0 to 1,400 K.

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[1] Research chemist.

[2] Shunk, F. A. Constitution of Binary Alloys, Second Supplement. McGraw-Hill Book Co., Inc., New York, 1969, pp. 44-45.

[3] Kubaschewski, O., and W. A. Dench. The Heats of Formation in the Systems Titanium-Aluminum and Titanium-Iron. Acta Met., v. 3, July 1955, pp. 339-346.

MATERIALS[4]

Small ingots ranging from 3 to 10 grams were prepared by direct combination of high-purity titanium and aluminum metals in an arc-melting furnace. The resulting ingots were remelted and cast into larger, cigar-shaped pieces weighing about 30 grams each. To improve homogeneity the ingots were sealed in quartz tubes and evacuated to approximately 10^{-8} torr and back filled with sufficient argon to yield an internal pressure of about 1 atmosphere at 1,270 K. The sealed units were annealed approximately 100 hours at 1,270 K and then slowly cooled to room temperature over a period of 8 hours. X-ray phase analysis of the resulting ingots indicated the product to be essentially $TiAl_3$. Some ingots contained traces of a peritectic material consisting of $TiAl_3$ and $TiAl_2$. This mixture is formed when the titanium-rich composition of $TiAl_3$ is present. Sample selection for the calorimetric investigation above 298 K was made to obtain only single-phase $TiAl_3$ in order to avoid possible phase problems in this temperature range.

Metallographic and electron probe analyses of the annealed ingots confirmed phase evaluations by X-ray methods. No transformed or dendritic structures were observed. However, some random voids were noted along grain boundaries. The annealed ingots were ground to a fine powder (less than minus 100 mesh) prior to blending and analysis.

Table 1 lists the impurities present in the high- and low-temperature calorimetric samples. Corrections for the impurities were applied to the experimental heat capacity and enthalpy data.

TABLE 1. - Impurity analysis, ppm

High-temperature blend			
Oxygen	1,870	Manganese	100
Nitrogen	10	Silicon	1,400
Carbon	830	Vanadium	800
Low-temperature blend			
Oxygen	1,270	Silicon	680
Carbon	350	Vanadium	800

EXPERIMENTAL WORK

Low-Temperature Calorimetry

An adiabatically shielded calorimeter operating within the range of 5 to 315 K was used for low-temperature heat capacity measurements. Only an abbreviated description will be given because a detailed account is being prepared for another publication. Westrum[5] gives an excellent description of a very similar apparatus.

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[4] $TiAl_3$ samples used in this investigation were prepared by R. E. Siemens, research physicist, Albany Metallurgy Research Center, Albany, Oreg.

[5] Westrum, E. F., Jr., G. T. Furukawa, and J. P. McCullough. Adiabatic Low-Temperature Calorimetry. Ch. 5 in Experimental Thermodynamics, v. 1, Calorimetry of Non-Reacting Systems, ed. by J. P. McCullough and D. C. Scott. Butterworths, London, 1968, pp. 133-214.

A calibrated platinum capsule thermometer was used for temperature measurements over the range 15 to 303 K. Below 15 K a NBS-calibrated germanium thermometer was used. These thermometers reproduce the International Practical Temperature Scale (IPTS) of 1968 to within a ±0.02 K limit of error. Precision potentiometric methods were used to determine temperature increments to a resoltuion of 0.001 K or less.

The sample container was a 90-ml gold-plated copper vessel fitted with a thermometer-heater assembly. The heat capacity of the container-thermometer-heater assembly ranged from 38 percent at 10 K to 33 percent of the gross heat capacity at 300 K. The low-temperature sample mass was 159.78 grams. Approximately 10^{-5} g-mole of helium gas was sealed with the sample to facilitate thermal response of the calorimeter-sample assembly.

All measurements of mass, time, resistance, and potential for both the low-temperature calorimetry and high-temperature calorimetry are traceable to NBS calibrations. Results are reported in terms of the defined calorie (1 calorie = 4.1840 joules). The 1969 table of atomic weights[6] was used to calculate a molecular weight of 128.8445 grams for $TiAl_3$.

Experimental heat capacities, corrected for curvature, are given in table 2. Extrapolation of heat capacity from the lowest temperature of measurement to 0 K was derived from the relation $C = AT + BT^3$. The absolute uncertainty of the corrected experimental data is estimated to be ±1 percent below 25 K; and ±0.3 percent, 50 to 300 K.

TABLE 2. - Experimental low-temperature heat capacities of $TiAl_3$(s)

T, K	Cp, cal/deg-mole	T, K	Cp, cal/deg-mole	T, K	Cp, cal/deg-mole
5.88	0.00618	41.31	1.062	127.15	12.873
6.36	.00797	43.64	1.264	132.22	13.441
6.84	.00935	48.36	1.755	133.67	13.592
7.33	.0104	53.15	2.329	139.51	14.179
8.01	.0126	61.84	3.533	141.42	14.362
8.78	.0151	66.75	4.274	148.32	15.003
9.54	.0177	70.48	4.814	155.60	15.618
10.30	.0211	73.22	5.266	162.85	16.180
11.06	.0248	75.97	5.701	171.09	16.773
11.84	.0286	78.74	6.144	180.34	17.365
12.64	.0328	81.76	6.637	189.24	17.890
13.62	.0381	84.78	7.122	198.29	18.388
14.83	.0457	87.83	7.614	207.86	18.826
16.23	.0540	90.96	8.088	217.48	19.261
17.72	.0670	94.20	8.566	226.47	19.605
19.17	.0806	96.93	8.960	236.12	19.959
20.63	.0985	97.45	9.032	245.56	20.260
22.27	.1256	100.38	9.432	254.80	20.543
24.04	.1598	104.21	9.991	264.58	20.824
26.38	.2169	108.49	10.574	274.64	21.092
29.21	.3101	112.82	11.150	284.43	21.341
32.30	.4414	117.09	11.682	294.18	21.552
35.56	.6275	122.13	12.301	303.23	21.731

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[6] International Union of Pure and Applied Chemistry, Division of Inorganic Chemistry, Commission on Atomic Weights. Atomic Weights of the Elements (1969). Pure and Appl. Chem., v. 21, 1970, pp. 97-108.

A graphic representation of the data is given in figure 1. No irregularity was observed over the temperature range studied. Smoothed values of heat capacity and other derived functions are listed at regular temperature intervals in table 3.

TABLE 3. - Low-temperature thermodynamic properties of $TiAl_3(s)$

T, K	Cp°	S°	$-(G^\circ-H^\circ_0)/T$	$H^\circ-H^\circ_0$,
	cal/deg-mole			cal/mole
5	[1](0.005)	(0.004)	(0.002)	(0.01)
10	.020	.012	.005	.07
15	.046	.025	.010	.23
20	.091	.043	.015	.56
25	.181	.072	.023	1.22
30	.340	.118	.035	2.48
40	.948	.289	.074	8.58
50	1.94	.601	.146	22.73
60	3.27	1.07	.26	48.58
70	4.77	1.68	.41	88.70
80	6.35	2.42	.62	144.3
90	7.91	3.26	.86	215.6
100	9.40	4.17	1.15	302.3
110	10.79	5.14	1.47	403.3
120	12.06	6.13	1.82	517.7
130	13.20	7.14	2.19	644.0
140	14.22	8.16	2.58	781.2
150	15.14	9.17	2.98	928.1
160	15.96	10.17	3.40	1,083.7
170	16.69	11.16	3.82	1,247.0
180	17.35	12.14	4.27	1,417.3
190	17.94	13.09	4.70	1,593.9
200	18.47	14.02	5.14	1,776.0
210	18.94	14.94	5.59	1,963.0
220	19.35	15.83	6.04	2,154.5
230	19.73	16.70	6.48	2,350.0
240	20.08	17.55	6.93	2,549.1
250	20.40	18.37	7.36	2,751.5
260	20.70	19.18	7.80	2,957.0
270	20.98	19.96	8.24	3,165.4
280	21.23	20.73	8.67	3,376.4
290	21.46	21.48	9.10	3,589.9
298.15	21.63	22.08	9.45	3,765.5
300	21.67	22.21	9.52	3,805.6

[1] Values in parentheses are extrapolations.

High-Temperature Calorimetry

A copper-block drop calorimeter was used to obtain high-temperature enthalpy data. This apparatus is described in detail elsewhere by Douglas

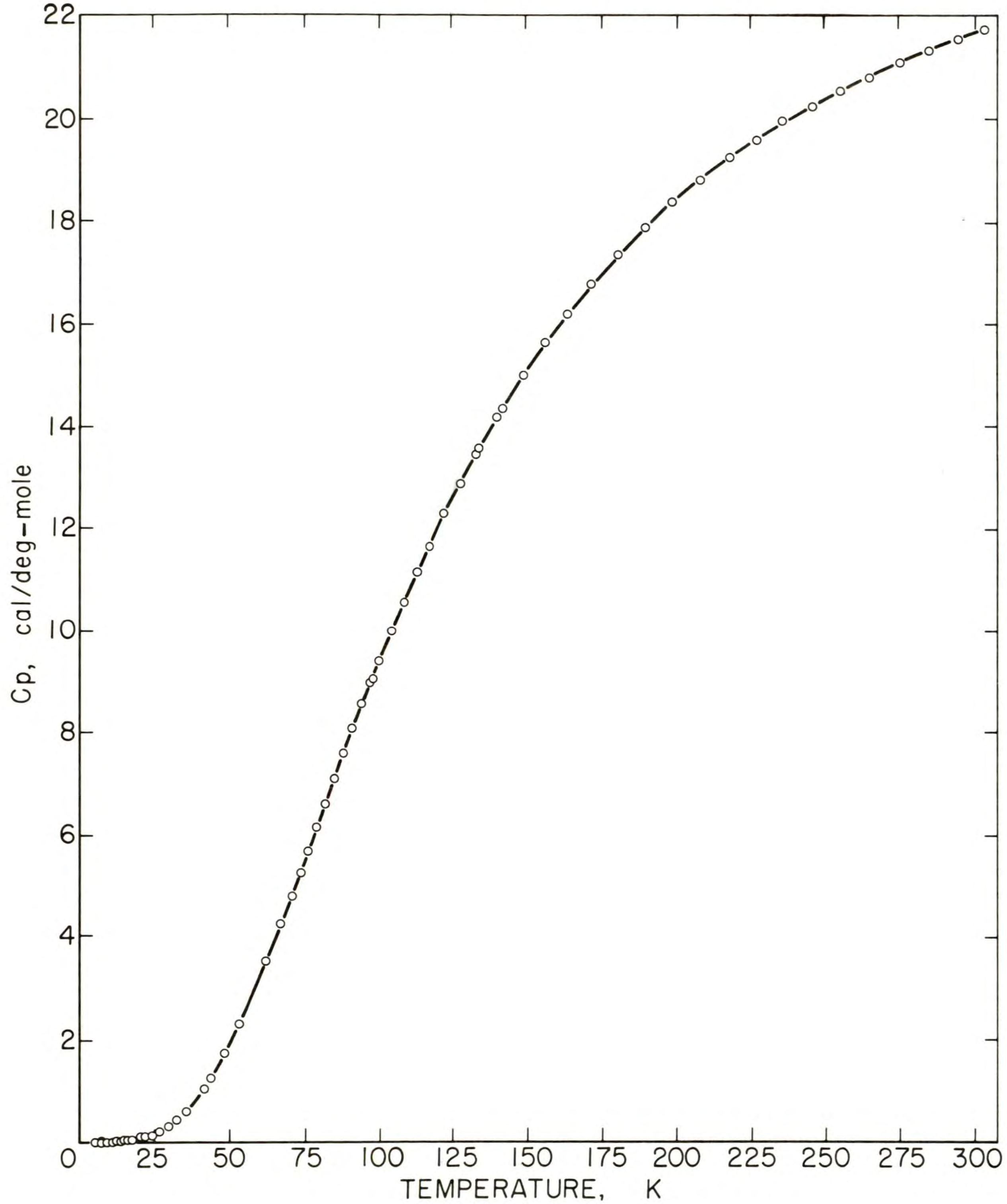

FIGURE 1. - Low-temperature heat capacity.

and King.[7] The present apparatus differs slightly by incorporating a more sensitive potentiometer system.

Ninety percent platinum-ten percent rhodium capsules were used as sample containers for the experimental determinations from ambient temperature up to 1,200 K. Above this temperature some reaction occurred between the sample and the Pt-Rh container. Measurements were extended to 1,400 K using silica glass containers. Three capsules were used to obtain 19 enthalpy determinations. The sample-capsule loading data are summarized below. The platinum-rhodium containers provided about 15 percent of the gross enthalpy, and the silica containers, about 43 percent.

Capsule	Composition	Sample mass, g	Capsule mass, g
1	90 pct Pt - 10 pct Rh.....	11.207	9.865
2	Silica glass..............	5.099	2.984
3	Silica glass..............	5.304	2.864

Experimental high-temperature enthalpy values, corrected to 100 percent of $TiAl_3$ are listed in table 4. Figure 2 shows the data expressed as the function $(H_T - H_{298.15})/(T - 298.15)$. The precision uncertainty is 0.1 percent, and the absolute uncertainty is estimated to be about 0.4 percent. Determinations were not extended beyond about 1,400 K because of the temperature limitation imposed by the silica capsules. As figure 2 shows, the two points near 1,400 K are well above the smooth curve. The most plausible explanation is that the alloy reacted with the silica container, although some melting due to undetected sample inhomogeneity might have occurred. The phase diagram does not indicate fusion at this low temperature. In any case, X-ray analysis of the final capsule contents indicated only the $TiAl_3$ phase.

TABLE 4. - Experimental enthalpies of $TiAl_3(s)$ above 298.15 K

T, K	$H - H_{298}$, cal/mole	T, K	$H - H_{298}$, cal/mole	T, K	$H - H_{298}$, cal/mole
401.5	2,320	706.7	9,710	1,194.5	22,449
449.0	3,430	805.7	12,204	1,218.8	23,119
503.3	4,722	905.3	14,772	1,293.3	25,229
604.4	7,187	1,005.6	17,431	1,411.7	28,936
604.4	7,192	1,007.1	17,450	1,413.2	28,949
705.7	9,694	1,009.9	19,966	-	-
705.9	9,713	1,102.5	19,975	-	-

Polynomial functions, determined with the aid of a computer, were fitted to the experimental enthalpy data.[8] These functions were used to

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[7] Douglas, T. B., and E. G. King. High-Temperature Drop Calorimetry. Ch. 8 in Experimental Thermodynamics, v. 1, Calorimetry of Non-Reacting Systems, ed. by J. P. McCullough and D. C. Scott. Butterworths, London, 1968, pp. 293-331.

[8] Justice, B. H. Thermal Data Fitting With Orthogonal Functions and Combined Table Generation. The FITAB Program. University of Michigan, Ann Arbor, Mich., COO-1149-143, 1969, 49 pp.

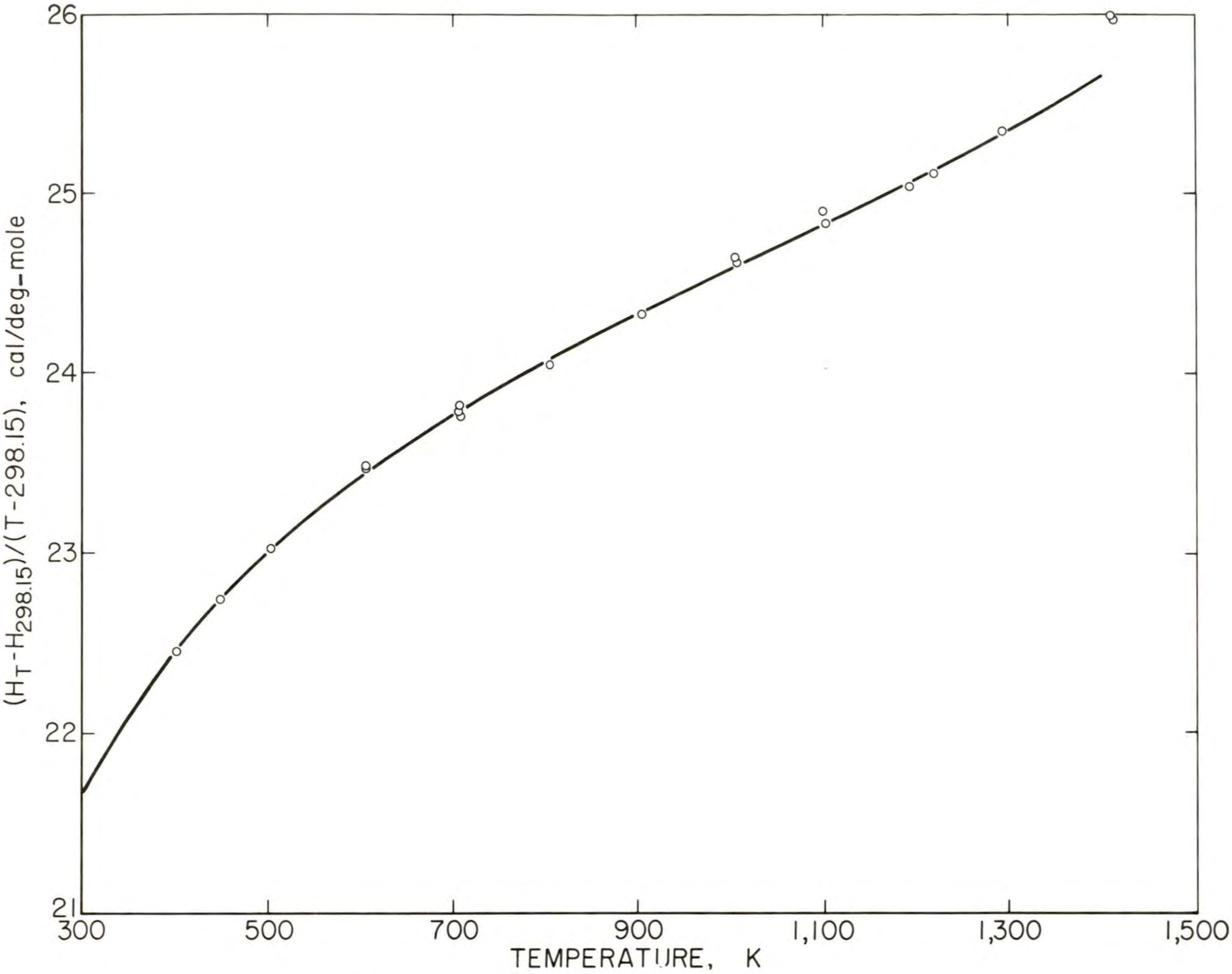

FIGURE 2. - High-temperature enthalpy function.

calculate values of Cp°, S°, $H°-H^\circ_{298}$, and $-(G°-H^\circ_{298})/T$ at regular temperature intervals. These appear in table 5.

The standard-form enthalpy equation derived by Kelley's method[9] is

$$H_T - H_{298.15} = 22.90\ T + 1.87 \times 10^{-3}T^2 + 2.12 \times 10^5 T^{-1} - 7{,}705/\text{cal mole.}$$

Excluding the two points above 1,400° K, the average percent deviation of this equation from the experimental enthalpy data is less than 0.2 percent in the range 298 to 1,400 K.

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[9] Kelley, K. K. Contributions to the Data on Theoretical Metallurgy. XIII. High-Temperature Heat-Content, Heat-Capacity, and Entropy Data for the Elements and Inorganic Compounds. BuMines Bull. 584, 1960, 232 pp.

TABLE 5. - Thermodynamic properties of $TiAl_3(s)$

$[Ti(\alpha,\beta) + 3\ Al(s,l) = TiAl_3(s)]$

T, K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	-ΔHf°	-ΔGf°	Log Kf
	cal/deg-mole			kcal/mole			
0	0	0	∞	-3.766	34.6±1.2	34.6±1.2	∞
100	9.40	4.17	38.80	-3.463	34.8	34.5	75.41
200	18.47	14.02	23.97	-1.990	35.1	34.1	37.31
298.15	21.63	22.08	22.08	0	35.3	33.6	24.66
300	21.67	22.21	22.08	.040	35.3	33.6	24.50
400	23.11	28.67	22.95	2.287	35.5	33.0	18.06
500	23.97	33.92	24.63	4.644	35.6	32.4	14.18
600	24.57	38.35	26.56	7.073	35.8	31.8	11.57
700	25.04	42.17	28.52	9.554	36.1	31.1	9.70
800	25.46	45.54	30.44	12.079	36.4	30.3	8.29
900	25.87	48.57	32.29	14.645	36.9	29.6	7.18
[1]933.5	26.01	49.51	32.89	15.514	37.0	29.3	6.86
933.5	26.01	49.51	32.89	15.514	44.8	29.3	6.86
1,000	26.31	51.31	34.06	17.253	45.1	28.2	6.16
1,100	26.81	53.84	35.74	19.909	45.5	26.5	5.26
[2]1,156	27.13	55.18	36.65	21.419	45.7	25.5	4.82
1,156	27.13	55.18	36.65	21,419	46.7	25.5	4.82
1,200	27.41	56.20	37.35	22.619	46.8	24.7	4.50
1,300	28.14	58.42	38.89	25.396	47.0	22.8	3.84
1,400	[3](29.04)	(60.54)	(40.36)	(28.253)	(47.2)	(21.0)	(3.27)

[1] Melting point of Al.

[2] Transition point of Ti, α→β.

[3] Values in parentheses are extrapolations.

ENTHALPIES AND GIBBS ENERGIES OF FORMATION

Thermodynamic properties of $TiAl_3$ over the temperature range 0 to 1,400 K are listed in table 5. Values of enthalpy of formation and Gibbs energy of formation were calculated by combining the entropy and enthalpy data resulting from this investigation with the standard enthalpy of formation at 298 K reported by Kubaschewski and Dench.[10] Kubaschewski and Dench determined enthalpies of formation of various Ti-Al compositions by direct reaction calrimetry. Their data yielded a value of -35.3 kcal/mole for $TiAl_3$ at 298 K. Other auxiliary data were also needed for calculating the derived values given in table 5. Enthalpy and entropy data for aluminum and titamium above 298 K were taken from Hultgren and coworkers[11] and for aluminum and titanium below 298 K, from the JANAF tables.[12] These auxiliary data were corrected to the

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[10] Work cited in footnote 3.

[11] Hultgren, R. Dept. of Materials Science and Engineering, University of California, Berkeley, Calif. Private communications, September 1966 and May 1968. Available upon request from J. M. Stuve or M. J. Ferrante , Bureau of Mines, Albany, Oreg.

[12] Stull, D. R., and H. Prophet. JANAF Thermochemical Tables. 2d ed., Nat. Standard Reference Data Service, NBS, 37, 1971, 1141 pp.

International Practical Temperature Scale of 1968.[13] The uncertainty in the formation data given in table 5 is determined principally by the uncertainty in the 298 K enthalpy of formation value reported by Kubaschewski and Dench. The uncertainties related to impurities and phase composition in the present investigation are less significant.

DISCUSSION

The data in table 5 indicate considerable entropy decrease in the formation of $TiAl_3$ from the elements. The entropy change is -5.7 cal/deg-mole at 298 K and increased to -8.3 at 933 K, the melting point of aluminum. This is evidence that $TiAl_3$ shows a substantial deviation from the Neumann-Kopp rule, which is frequently used to estimate high-temperature heat capacities of alloys.

At all temperatures of investigation, $TiAl_3$ exhibits a high degree of chemical stability. By taking into account the work of Kubaschewski and Dench, it is estimated that TiAl and $TiAl_2$ would have stabilities per gram atom at least as great as that of $TiAl_3$.