

Heat Capacity and Enthalpy Measurements on Aluminum Carbide (Al_4C_3) From 15 to 1173 °K. Thermodynamic Properties From 0 to 2000 °K*

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Measurements of the heat capacity and relative enthalpy were made on aluminum carbide (Al_4C_3) from 15 to 1173 °K. The thermodynamic properties were calculated up to 2000 °K from the data by judicious extrapolation above 1173 °K. In conjunction with the heat-of-formation data on Al_4C_3 obtained by King and Armstrong and by Mah, second- and third-law analyses have been made of the thermodynamics of several high-temperature vapor-equilibrium reactions involving Al_4C_3 .

1. Introduction

The results of heat-capacity and enthalpy measurements on aluminum carbide, Al_4C_3 , in the range 15 to 1173 °K presented in this paper have been obtained in connection with a research program at the National Bureau of Standards to provide accurate thermodynamic and related data on the "light" elements and their compounds. No heat-capacity measurements on Al_4C_3 have been previously published, except for the relative enthalpy measurements in the range 273 to 693 °K by Satoh [1]¹ on a sample that contained only 74.74 percent Al_4C_3 , the impurities being 23.43 and 1.83 percent Al_2O_3 and SiO_2 , respectively. The work reported by Satoh is based on measurements at only three temperatures in the above temperature range.

Aluminum carbide, Al_4C_3 , is a yellow rhombohedral crystal of space group D_{3d}^5 with $a=8.53$ Å and $\alpha=22^\circ 28'$ [2]. Each carbon atom is surrounded by aluminum atoms and the shortest C—C distance is 3.16 Å [2], indicating that the carbon atoms are not bonded to one another. There are two structurally different carbon atoms, and the C—Al distance ranges from 1.90 to 2.22 Å. One of the carbon structures has six aluminum atoms at 2.17 Å, and the other has one aluminum atom at 1.90 Å, three at 1.94 Å, and one at 2.22 Å. On hydrolysis, Al_4C_3 yields methane. Other aluminum carbides that have been reported are $\text{Al}_2(\text{C}_2)_3$ [3] and Al_3C [4]. The carbide $\text{Al}_2(\text{C}_2)_3$, made by reacting acetylene with aluminum at 450 to 500 °C, yields acetylene on hydrolysis [3]. The carbide Al_3C , observed in the $\text{Al—Al}_2\text{O}_3\text{—Al}_4\text{C}_3$ phase investigations reported by Baur and Brunner [4], should yield CH_4 on hydrolysis.

2. Sample

The measurements of the low-temperature heat capacity and the high-temperature relative enthalpy were made on the same aluminum carbide sample kindly supplied by the Aluminum Company of America, ALCOA Research Laboratories, through the courtesy of George Long. The material had been prepared by heating a stoichiometric mixture of aluminum powder and lampblack in an atmosphere of argon to 1800 °C. Qualitative spectrochemical analyses were made on representative specimens of the sample by the Spectrochemistry Section of the National Bureau of Standards. The results are summarized in table 1.

TABLE 1. Spectrochemical analysis of the sample of aluminum carbide (Al_4C_3)

Element	%	Element	%	Element	%
Ag	—(?)	Hf	—	Sb	—
Al	>10	Hg	—	Se	—
As	—	In	—	Si	0.01–0.1
Au	—	Ir	—	Sn	—
B	—	La	—	Sr	—
Ba	—	Mg	0.001–0.01	Ta	—
Be	—	Mn	0.0001–0.001	Te	—
Bi	—	Mo	—	Th	—
Ca	0.0001–0.001	Nb	—	Ti	0.001–0.01
Cd	—	Ni	0.001–0.01	Tl	—
Ce	—	Os	—	U	—
Co	—	P	—	V	0.01–0.1
Cr	0.001–0.01(?)	Pb	—	W	—
Cu	0.001–0.01	Pd	—	Y	—
Fe	0.1–1.0	Pt	—	Zn	—
Ga	—	Rh	—	Zr	0.001–0.01
Ge	—	Ru	—		

—: Not detected.

Chemical analyses were performed by Rolf A. Paulson of the Applied Analytical Research Section of the National Bureau of Standards. These results are given in table 2. Specimens 1 and 2 were sampled from the original Al_4C_3 preparation

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¹ Figures in brackets indicate the literature references at the end of this paper.

as received. Specimen 3 was sampled from that portion of the Al_4C_3 preparation on which the low-temperature heat-capacity measurements had been completed. The percentage Al_4C_3 was determined by dissolving a sample in hot sulfuric acid. The evolved gases, taken to be CH_4 and H_2 , were burned and the combustion products collected. The amount of CO_2 collected was converted to Al_4C_3 and the excess H_2O over that attributable to CH_4 was reckoned to have been formed from H_2 released from the acid by free aluminum and iron. The insoluble residue from the hot sulfuric acid treatment was taken to be free carbon. Aliquot portions of the sulfuric acid solution were analyzed for total aluminum as Al_2O_3 by precipitating $\text{Al}(\text{OH})_3$ with ammonium hydroxide and igniting to Al_2O_3 . The excess of aluminum over that attributable to Al_4C_3 , free aluminum metal, and AlN was assumed to be Al_2O_3 in the original sample. The iron, determined in specimen 3 only, was analyzed colorimetrically using the thiocyanate-complex method on an aliquot portion of the sulfuric acid solution. The percentage AlN was determined by the Kjeldahl method on separate samples of the Al_4C_3 preparation.

analyses obtained in specimens 1 and 2 was normalized to yield 100 percent total analysis. The iron content, the chemical analysis for which was not made in specimens 1 and 2, was considered too small to contribute significantly to the results of the experimental data. In the processing of the heat-capacity data obtained at low temperatures, the chemical analysis obtained on specimen 3 was used, after normalizing to give a total analysis of 100 percent.

The corrections for the impurities were made assuming that the relative enthalpies were additive. The contributions from Al , Al_2O_3 , and AlN impurities were adjusted in accordance with the tabular values of thermodynamic functions obtained through the analysis of the literature data in connection with the light element research program [8]. The values for C were based mostly on the measurements of De Sorbo and Tyler [9]. The corrections for Fe were obtained primarily from the heat-capacity data reported by Simon and Swain [10] and by Kelley [11].

3. Low-Temperature Calorimetry

3.1. Apparatus and Method

The low-temperature heat-capacity measurements were made from about 18 to 380 °K in an adiabatic calorimeter similar in design to that described previously [12]. The calorimeter vessel, which was filled with sample as described in section 3.2 and sealed by means of a specially designed gold-gasket closure [13], was suspended within the adiabatic shield system by means of a Nylon string instead of the filling tube shown in the above reference. The adiabatic shield was controlled automatically by means of a combination of electronic and electro-mechanical equipment. Details of the design of the calorimeter used, its operation, and the automatic adiabatic control system will be described in a later publication.

The platinum resistance thermometer used in the measurements was calibrated in accordance with the International Practical Temperature Scale of 1948 [14]. The temperatures in degrees Kelvin (°K) were obtained by adding 273.15 deg to the temperatures in degrees Celsius (°C). Below 90 °K, the thermometer was calibrated on the NBS-1955 provisional scale which is numerically 0.01 deg lower than the former NBS-1939 provisional scale [15]. The resistance measurements were made by means of a Mueller bridge and a high sensitivity galvanometer to the nearest 0.00001 Ω . The temperatures were calculated from the resistance by inverse interpolation in a table of resistance given as a function of the temperature at closely spaced regular intervals.

The electrical power introduced into the calorimeter heater (100 Ω of constantan wire) was measured by means of a Wenner potentiometer in conjunction with a volt box, standard resistor, and saturated standard cells. A constant-current power supply stable to 10 ppm or better was used to facilitate the power measurements. The duration of each heating

TABLE 2. Chemical analysis of the sample of aluminum carbide (Al_4C_3)

Component	Percentage by weight		
	Specimen 1	Specimen 2	Specimen 3
Al_4C_3	94.9	94.8	94.8
Free Al	1.2	1.3	1.0
Free C	0.9	0.7	1.0
AlN	1.4	1.3	1.3
Al_2O_3	2.0	2.0	2.2
Free Fe			0.06
Total	100.4	100.1	100.36

The results of the chemical analysis agree with the usual composition found (of about 95% Al_4C_3) in samples prepared by the same method [5]. The small discrepancies in the analyses can be attributed to either uncertainties in the analytical methods or small inhomogeneities in the sample. The approximate summation of the analyses to 100 percent is an indication of the reliability of the analytical methods used. E. E. Hughes of the Applied Analytical Research Section, National Bureau of Standards, analyzed the gases generated by the action of an acid on the Al_4C_3 sample and found no acetylene or methylacetylene, indicating that $\text{Al}_2(\text{C}_2)_3$ was not present in the Al_4C_3 preparation. No effort was made to determine whether Al_3C was present.

M. v. Stackelberg et al. [6, 7] reported the conditions for formation and the crystal structure of the compound $\text{Al}_5\text{C}_3\text{N}$ ($\text{Al}_4\text{C}_3\text{-AlN}$). The results of the heat-capacity measurements presented in this paper were processed assuming that the nitrogen found in the chemical analysis came from AlN mixed with Al_4C_3 .

For the analysis of high-temperature relative-enthalpy measurements the average of the chemical

interval was measured by means of a high precision interval timer operated on 60-cycle frequency standard provided at the National Bureau of Standards. The 60-cycle frequency standard is based on a 100 kHz quartz oscillator which is stable to 0.5 ppm. The estimated uncertainty in the readings of the interval timer was not greater than ± 0.01 sec for any heating period, none of which was less than 2 min in these experiments.

3.2. Results

A sample of 153.8063 g mass was poured into the calorimeter vessel in a controlled-atmosphere box filled with argon gas (dew-point of -50 °C). At the same time, samples of the Al_4C_3 were sealed in test tubes under dry argon gas for chemical analysis. The calorimeter vessel plus the sample was evacuated and purged with dry helium gas several times. Finally, helium gas at a pressure of 5.8 cm Hg was sealed in the container with the sample. After completion of the measurements the calorimeter vessel was opened in the controlled-atmosphere box and additional samples taken for chemical analysis. As mentioned earlier, the analysis of the low-temperature heat data was based on the chemical analysis of the sample on which the measurements had been made (chemical analysis of specimen 3).

On the calorimeter vessel plus the sample ("gross"), 14 runs totaling 108 heat-capacity determinations were made and on the empty vessel ("tare"), 11 runs totaling 87 determinations were made. The experimental data of each of these two sets of measurements were fitted to empirical equations over selected, partially overlapping temperature intervals by the method of least squares using a digital computer. (A "set" of measurements consists of the observations of energy increments and the corresponding temperatures from about 18 to 380 °K on the empty vessel or on the vessel with sample. Measurements made during a given condition are classified as a "run" within the "set".) The empirical equations consisted of polynomials, the positive powers of temperature up to 4 being used below the inflection point in the heat capacity and powers from -4 to $+4$ in the region of the inflection point and above. Details of the computer routines used will be described in a later publication. Briefly, the overlapping equations for each set were joined at temperatures of the most favorable combinations of values of heat capacity and its first and second derivatives. The values of heat capacity obtained at regularly spaced integral temperatures by this process were smoothed by a 9-point cubic smoothing code [16] on the computer. (For the two sets of heat data obtained between 18 and 380 °K, a smooth function is defined and restricted to the following properties: (a) continuous derivatives, (b) monotonic increasing with not more than two inflection points, and (c) sigmoidal configuration of the heat-capacity curve.) The deviations of the observations of each set of measurements from the final smoothed values are shown in figures 1 and 2.

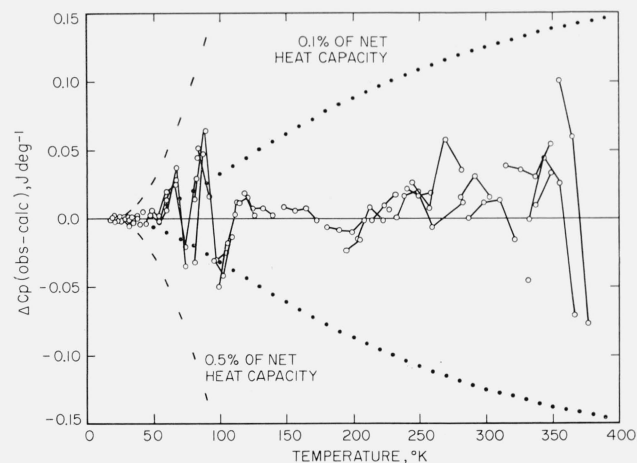


FIGURE 1. Deviations of the heat-capacity measurements on sample plus calorimeter vessel.

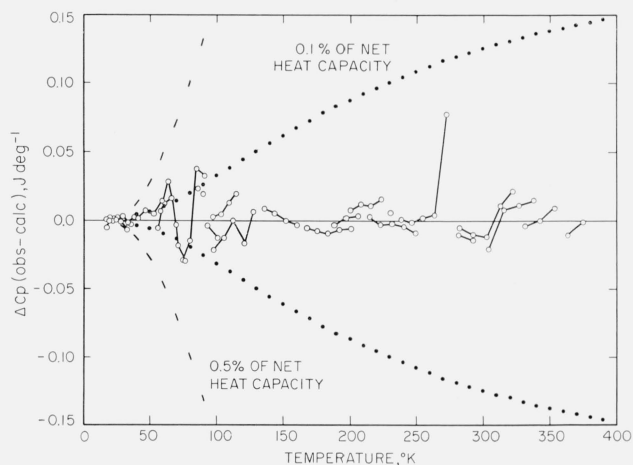


FIGURE 2. Deviations of the heat-capacity measurements on the empty calorimeter vessel.

The net values of heat capacity, obtained by differencing the above smoothed gross and tare values at corresponding temperatures, were corrected for the impurities and the helium exchange gas and again smoothed on the computer wherever necessary. These values were then converted to molal units using atomic weights based on carbon-12 [17]. A Debye heat-capacity function, fitted to the smoothed values at the lower temperatures, was used to obtain the values from 0 to 18 °K.

A consideration was given at this point regarding the use of a table of thermodynamic functions. Although the joule is a more fundamental unit of energy and its use is preferred, most scientists who use tables of thermodynamic functions are accustomed to the calorie as an energy unit. The values of heat capacity were converted, therefore, to the unit $cal\ deg^{-1}\ mol^{-1}$ using the relation: 1 defined calorie = 4.1840 J. These values of heat capacity from 0 to 390 °K were later combined with the high-

temperature heat data (see sec. 5) and the thermodynamic functions from 0 to 1200 °K (table 5) obtained in terms of the defined calorie. The hope

TABLE 3. Observed heat capacity of aluminum carbide (Al₄C₃)

Gram molecular weight=143.9594 g, $T \text{ deg K} = t \text{ deg C} + 273.15$

T		C _P		T		C _P	
RUN 1				RUN 7			
°K	J deg ⁻¹ mol ⁻¹	°K	J deg ⁻¹ mol ⁻¹	°K	J deg ⁻¹ mol ⁻¹	°K	J deg ⁻¹ mol ⁻¹
80.9304	19.039	47.9512	4.334	47.9512	4.334	47.9512	4.334
87.5349	22.750	53.8036	6.274	53.8036	6.274	53.8036	6.274
95.5198	27.145	60.2681	8.859	60.2681	8.859	60.2681	8.859
102.6529	31.166	67.1238	11.979	67.1238	11.979	67.1238	11.979
109.1860	34.903	74.4382	15.603	74.4382	15.603	74.4382	15.603
115.2630	38.389	82.5811	20.002	82.5811	20.002	82.5811	20.002
120.9611	41.644						
126.3603	44.702						
RUN 2				RUN 8			
83.3668	20.442	53.6690	6.221	53.6690	6.221	53.6690	6.221
83.7841	20.682	59.9095	8.700	59.9095	8.700	59.9095	8.700
92.0007	25.212	67.0407	11.949	67.0407	11.949	67.0407	11.949
99.2987	29.260	73.8189	15.264	73.8189	15.264	73.8189	15.264
105.9164	33.041	80.9261	19.085	80.9261	19.085	80.9261	19.085
112.1039	36.581	88.8040	23.473	88.8040	23.473	88.8040	23.473
118.3925	40.182	96.7037	27.812	96.7037	27.812	96.7037	27.812
125.2915	44.100	104.9602	32.491	104.9602	32.491	104.9602	32.491
132.5943	48.216	113.3395	37.293	113.3395	37.293	113.3395	37.293
140.0859	52.360						
148.2666	56.796	RUN 9					
156.8223	61.313	202.6976	83.252	202.6976	83.252	202.6976	83.252
165.0743	65.555	212.7334	87.532	212.7334	87.532	212.7334	87.532
173.0867	69.543	222.8071	91.600	222.8071	91.600	222.8071	91.600
181.1510	73.440	233.1927	95.614	233.1927	95.614	233.1927	95.614
189.9219	77.545	244.9902	99.979	244.9902	99.979	244.9902	99.979
199.0012	81.640	257.7564	104.411	257.7564	104.411	257.7564	104.411
		270.1210	108.507	270.1210	108.507	270.1210	108.507
		282.1421	112.178	282.1421	112.178	282.1421	112.178
RUN 3				RUN 10			
208.2596	85.650	228.2582	93.736	228.2582	93.736	228.2582	93.736
194.8391	79.768	238.8640	97.746	238.8640	97.746	238.8640	97.746
204.7784	84.152	249.4063	101.545	249.4063	101.545	249.4063	101.545
214.3612	88.195	260.0404	105.168	260.0404	105.168	260.0404	105.168
223.6167	91.931	282.9258	112.385	282.9258	112.385	282.9258	112.385
232.5986	95.409						
241.3449	98.662	RUN 11					
250.2226	101.831	287.5948	113.747	287.5948	113.747	287.5948	113.747
259.2433	104.929	299.1951	117.040	299.1951	117.040	299.1951	117.040
		310.6701	120.112	310.6701	120.112	310.6701	120.112
		322.1925	122.999	322.1925	122.999	322.1925	122.999
RUN 4				RUN 12			
19.4395	0.154	280.8853	111.785	280.8853	111.785	280.8853	111.785
21.2826	0.214	291.7646	114.978	291.7646	114.978	291.7646	114.978
23.1934	0.298	303.4013	118.188	303.4013	118.188	303.4013	118.188
26.1223	0.468	314.9180	121.232	314.9180	121.232	314.9180	121.232
28.9497	0.690	326.3407	124.053	326.3407	124.053	326.3407	124.053
31.8285	0.978	337.6879	126.647	337.6879	126.647	337.6879	126.647
34.7029	1.356	348.8494	129.087	348.8494	129.087	348.8494	129.087
37.9361	1.897						
RUN 5				RUN 13			
18.3556	0.125	332.8417	125.529	332.8417	125.529	332.8417	125.529
20.5917	0.194	344.3231	128.107	344.3231	128.107	344.3231	128.107
22.9086	0.286	355.7442	130.520	355.7442	130.520	355.7442	130.520
25.3911	0.425	367.1535	132.793	367.1535	132.793	367.1535	132.793
28.2211	0.628	RUN 14					
31.0744	0.900	332.3944	125.383	332.3944	125.383	332.3944	125.383
34.2214	1.292	338.2360	126.747	338.2360	126.747	338.2360	126.747
38.0580	1.925	349.3925	129.181	349.3925	129.181	349.3925	129.181
42.2987	2.823	354.7007	130.379	354.7007	130.379	354.7007	130.379
		365.6101	132.607	365.6101	132.607	365.6101	132.607
		376.3752	134.648	376.3752	134.648	376.3752	134.648
RUN 6							
32.2736	1.037						
35.9656	1.554						
39.9007	2.283						
44.3825	3.329						
48.7699	4.578						
53.7296	6.250						
60.1927	8.834						
67.1891	12.007						

is that eventually the joule would be the common energy unit in all scientific work. The thermodynamic functions of table 5 are, therefore, repeated in the appendix in terms of the joule.

Heat-capacity determinations usually require two series of measurements, one on the sample plus the calorimeter vessel and the other on the empty vessel. By conducting the two series of measurements under as identical conditions as possible, certain errors that occur equally in both measurements may be canceled in the final processing of the data. The data from both series of measurements are most useful in certain applications, such as in the numerical evaluation of the precision and accuracy of the original observations, in the correlation of the temperature scale, etc. These data are, however, not directly useful where the heat capacity of the substance is needed for the comparison of the precision and accuracy of measurements with other laboratories. The method used in processing the experimental data as outlined above yields the final smoothed values of heat capacity and the relation of these values with the original observations is linked through a somewhat tortuous path.

To meet the requirements for evaluating the precision of the observation and for comparing the results with other laboratories a "compromised" list of experimental data is given in table 3. The values of "observed molal heat capacity" given in the units of $J \text{ deg}^{-1} \text{ mol}^{-1}$ in table 3 were obtained by subtracting the smoothed tare heat capacity from the gross heat capacity at the observed temperatures (midtemperatures of the enthalpy increments). The tare heat capacities at the corresponding temperatures were obtained by interpolation in the table of smoothed tare heat capacities mentioned earlier. Corrections have been made for the impurities and for the helium gas. Curvature corrections were made wherever significant. These observed molal heat capacities are plotted in figure 3.

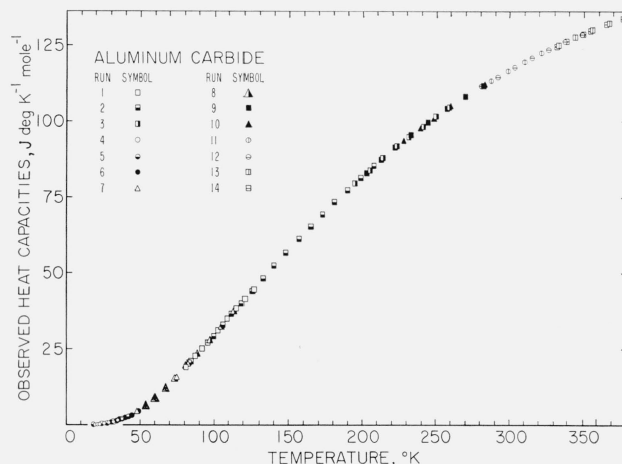


FIGURE 3. Observed values of the molal heat capacity of aluminum carbide.

4. High-Temperature Relative Enthalpy Measurements

4.1. Method and Apparatus

The relative enthalpy measurements were made from 273 to 1173 °K (0 to 900 °C) by the "drop" method using a Bunsen ice calorimeter. Details of the method have been described previously [18]. Briefly, the method involved suspending the samples sealed in a container (for the present measurements the container consisted mostly of the alloy Ni(80%)-Cr(20%)) in a furnace. When a constant, known temperature is attained, the container and its contents are dropped, with nearly free fall, into a Bunsen ice calorimeter in which is determined the heat evolved by the container plus sample in cooling to 273.15 °K. In order to account for the enthalpy of the container and the heat lost during the drop, a similar experiment is made with the empty container at the same furnace temperature. The difference between the two values of heat evolved in the ice calorimeter is a measure of the enthalpy change of the sample between 273.15 °K and the temperature in the furnace.

In the furnace used the sample is surrounded by a silver pipe 25 cm long and of 1.3 cm wall thickness, in order to minimize the temperature gradients around the sample and thus improve the accuracy of measuring its temperatures. Customarily, the temperature of this furnace (and hence that of the sample) is measured by a calibrated platinum resistance thermometer (precision, ± 0.002 deg) from 0 to 600 °C and by a calibrated Pt-Pt-10 percent Rh thermocouple (precision, ± 0.01 deg) at all temperatures. The routine simultaneous measurement by both instruments at and below 600 °C ensures that the thermocouple readings are consistent with the thermometer readings, which are more accurate. Unfortunately, shortly before the measurements on Al_4C_3 were begun, the thermometer suffered an accident and it was consequently necessary to use the thermocouple alone at all the temperatures.

Just before the measurements of the relative enthalpy of Al_4C_3 , similar measurements were carried out on a sample of Calorimetry-Conference standard sample of $\alpha\text{-Al}_2\text{O}_3$ in a silver container (six at 400, two at 600, and two at 700 °C), in order to check the overall accuracy. Compared with the smoothed values published earlier by the Bureau and recently slightly corrected [19], the mean enthalpies of the Al_2O_3 found at these three temperatures were respectively $+0.02 \pm 0.06$, -0.01 ± 0.01 , and -0.02 ± 0.01 percent higher. (The stated tolerances represent the standard deviations of the means.)

4.2. Results

All the high-temperature heat measurements were made on the same sample of aluminum carbide. The same identical container was used both with and without the sample, in order to preclude possible small differences in the relative enthalpy per unit

mass of different specimens of the container alloy. The results of the enthalpy measurements are summarized in table 4. The second and third columns give, in chronological order for each furnace temperature, the heats found in individual measurements on the container with sample and on the empty container, respectively. The values given have been corrected for small unavoidable differences in mass of the various parts of the container, and for the contribution of the impurities to the heats measured. The largest part of the latter correction above 873.15 °K, about -8 cal for the sample measured, was for the heat of fusion of the free aluminum present, and largely eliminated a small hump in a plot against temperature of the uncorrected net enthalpy of the sample near the melting point of this element, 932 °K.

TABLE 4. High-temperature enthalpy measurements on aluminum carbide (Al_4C_3)

Furnace temperature °K	Individual heat measurements ^a		$H_T - H_{273.15}$ of Al_4C_3 ^b	
	Sample + container	Container only	Mean observed	Obs.-caled., eq (1) ^c
	cal	cal	cal mol ⁻¹	cal mol ⁻¹
373.2	285.0 286.3 287.3 ----- 600.4 602.4 601.8 ----- 936.9 936.7 938.2 936.8 936.7 936.7	149.6 150.4 150.6 151.1 (306.8) ^e 310.1 309.8 311.1 310.2 475.2 475.5	2939 ^d	-8
473.2	----- 936.9 936.7 938.2 936.8 936.7 936.7	----- 475.2 475.5	6305	-27
573.2	1289.7 1288.9 1288.3 ----- 1648.0 1648.6 2021.1 2020.1 2405.4 2406.0 2808.8 2807.7 ^f 3213.1 ^f 3210.4 ^f ----- -----	648.0 647.9 ----- 826.8 825.9 1009.6 1009.9 1205.9 1205.3 1409.1 1409.1 1615.6 1617.4 1614.5 1616.9	9994	+6
673.2	----- 1289.7 1288.9 1288.3 ----- 1648.0 1648.6 2021.1 2020.1 2405.4 2406.0 2808.8 2807.7 ^f 3213.1 ^f 3210.4 ^f ----- -----	----- 648.0 647.9 ----- 826.8 825.9 1009.6 1009.9 1205.9 1205.3 1409.1 1409.1 1615.6 1617.4 1614.5 1616.9	13877	+49
773.2	----- 1648.0 1648.6 2021.1 2020.1 2405.4 2406.0 2808.8 2807.7 ^f 3213.1 ^f 3210.4 ^f ----- -----	----- 826.8 825.9 1009.6 1009.9 1205.9 1205.3 1409.1 1409.1 1615.6 1617.4 1614.5 1616.9	17794	-8
873.2	----- 2021.1 2020.1 2405.4 2406.0 2808.8 2807.7 ^f 3213.1 ^f 3210.4 ^f ----- -----	----- 1009.6 1009.9 1205.9 1205.3 1409.1 1409.1 1615.6 1617.4 1614.5 1616.9	21883	+4
973.2	----- 2405.4 2406.0 2808.8 2807.7 ^f 3213.1 ^f 3210.4 ^f ----- -----	----- 1205.9 1205.3 1409.1 1409.1 1615.6 1617.4 1614.5 1616.9	25980	-56
1073.2	----- 2808.8 2807.7 ^f 3213.1 ^f 3210.4 ^f ----- -----	----- 1409.1 1409.1 1615.6 1617.4 1614.5 1616.9	30289	+29
1173.2	----- 3210.4 ^f ----- -----	----- 1617.4 1614.5 1616.9	34543	+5

^a With all corrections applied, including those for the impurities in the sample. Sample mass = 6.650 g.

^b Molecular weight of $\text{Al}_4\text{C}_3 = 143.959$.

^c The final values of ($H_T - H_{273.15}$) (table 5) are smaller than those calculated from eq (1) by 11.5 cal mol⁻¹ at 373.15 °K and by 10 cal mol⁻¹ at each of the other temperatures in table 4.

^d The value found from the measurements with the adiabatic calorimeter is 2933.0 cal mol⁻¹.

^e Omitted from the mean because of inferior precision.

^f In these measurements 0.003 g of the sample had been removed, but these values have been corrected to a basis of the 6.650 g of sample present in the other measurements in this column.

Obviously no individual measurement in the third column of table 4 is uniquely associated with one in the second column. For each furnace temperature the difference between the averages for the two columns gives the mean observed net relative enthalpy of aluminum carbide shown on a mole basis in the fourth column. Using the method of least squares, these values (equally weighted) were used

TABLE 5. Thermodynamic functions for aluminum carbide (Al₄C₃) solid phaseGram molecular weight=143.9594 g, T deg K= t deg C+273.15

T	C_p^0	$(H_T^0 - H_0^0)$	$(H_T^0 - H_0^0)/T$	S_T^0	$-(G_T^0 - H_0^0)$	$-(G_T^0 - H_0^0)/T$
$^{\circ}\text{K}$	$\text{Cal deg}^{-1} \text{mol}^{-1}$	Cal mol^{-1}	$\text{Cal deg}^{-1} \text{mol}^{-1}$	$\text{Cal deg}^{-1} \text{mol}^{-1}$	Cal mol^{-1}	$\text{Cal deg}^{-1} \text{mol}^{-1}$
0.00	0.000	0.000	0.000	0.000	0.000	0.000
5.00	.001	.001	.000	.000	.000	.000
10.00	.005	.012	.001	.002	.004	.000
15.00	.017	.062	.004	.006	.021	.001
20.00	.041	.195	.010	.013	.065	.003
25.00	.095	.520	.021	.027	.162	.006
30.00	.188	1.207	.040	.052	.355	.012
35.00	.334	2.486	.071	.091	.707	.020
40.00	.549	4.667	.117	.149	1.299	.032
45.00	.833	8.094	.180	.230	2.236	.050
50.00	1.183	13.106	.262	.335	3.636	.073
55.00	1.603	20.042	.364	.467	5.628	.102
60.00	2.083	29.236	.487	.626	8.350	.139
65.00	2.612	40.956	.630	.814	11.939	.184
70.00	3.191	55.444	.792	1.028	16.532	.236
75.00	3.801	72.910	.972	1.269	22.265	.297
80.00	4.437	93.495	1.169	1.534	29.264	.366
85.00	5.089	117.31	1.380	1.823	37.648	.443
90.00	5.753	144.41	1.605	2.133	47.529	.528
95.00	6.424	174.85	1.841	2.462	59.007	.621
100.00	7.099	208.66	2.087	2.808	72.175	.722
105.00	7.776	245.84	2.341	3.171	87.117	.830
110.00	8.456	286.42	2.604	3.549	103.91	.945
115.00	9.138	330.41	2.873	3.939	122.62	1.066
120.00	9.819	377.80	3.148	4.343	143.32	1.194
125.00	10.499	428.60	3.429	4.757	166.07	1.329
130.00	11.175	482.79	3.714	5.182	190.92	1.469
135.00	11.843	540.34	4.002	5.617	217.91	1.614
140.00	12.503	601.21	4.294	6.059	247.10	1.765
145.00	13.154	665.35	4.589	6.509	278.51	1.921
150.00	13.795	732.73	4.885	6.966	312.20	2.081
155.00	14.427	803.29	5.183	7.429	348.19	2.246
160.00	15.048	876.98	5.481	7.897	386.50	2.416
165.00	15.658	953.75	5.780	8.369	427.16	2.589
170.00	16.258	1033.5	6.080	8.846	470.20	2.766
175.00	16.846	1116.3	6.379	9.325	515.62	2.946
180.00	17.424	1202.0	6.678	9.808	563.46	3.130
185.00	17.991	1290.5	6.976	10.293	613.71	3.317
190.00	18.546	1381.9	7.273	10.780	666.39	3.507
195.00	19.090	1476.0	7.569	11.269	721.51	3.700
200.00	19.622	1572.8	7.864	11.759	779.08	3.895
205.00	20.141	1672.2	8.157	12.250	839.11	4.093
210.00	20.649	1774.2	8.448	12.742	901.59	4.293
215.00	21.144	1878.6	8.738	13.233	966.52	4.495
220.00	21.628	1985.6	9.025	13.725	1033.9	4.700
225.00	22.101	2094.9	9.311	14.216	1103.8	4.906
230.00	22.564	2206.6	9.594	14.707	1176.1	5.113
235.00	23.016	2320.5	9.875	15.197	1250.8	5.323
240.00	23.459	2436.7	10.153	15.687	1328.1	5.534
245.00	23.893	2555.1	10.429	16.175	1407.7	5.746
250.00	24.317	2675.6	10.703	16.662	1489.8	5.959
255.00	24.732	2798.3	10.974	17.147	1574.3	6.174
260.00	25.136	2922.9	11.242	17.632	1661.3	6.389
265.00	25.530	3049.6	11.508	18.114	1750.6	6.606
270.00	25.914	3178.2	11.771	18.595	1842.4	6.824
273.15	26.151	3260.2	11.936	18.897	1901.5	6.961

TABLE 5. Thermodynamic functions for aluminum carbide (Al₄C₃) solid phase—ContinuedGram molecular weight=143.9594 g, T deg K= t deg C+273.15

T	C_P^0	$(H_T^0 - H_0^0)$	$(H_T^0 - H_0^0)/T$	S_T^0	$-(G_T^0 - H_0^0)$	$-(G_T^0 - H_0^0)/T$
$^{\circ}\text{K}$	<i>Cal deg⁻¹ mol⁻¹</i>	<i>Cal mol⁻¹</i>	<i>Cal deg⁻¹ mol⁻¹</i>	<i>Cal deg⁻¹ mol⁻¹</i>	<i>Cal mol⁻¹</i>	<i>Cal deg⁻¹ mol⁻¹</i>
275.00	26.288	3308.7	12.032	19.074	1936.6	7.042
280.00	26.651	3441.1	12.290	19.551	2033.1	7.261
285.00	27.005	3575.2	12.545	20.026	2132.1	7.481
290.00	27.351	3711.1	12.797	20.498	2233.4	7.701
295.00	27.695	3848.7	13.047	20.969	2337.1	7.922
298.15	27.909	3936.3	13.202	21.264	2403.6	8.062
300.00	28.035	3988.1	13.294	21.437	2443.1	8.144
310.00	28.694	4271.7	13.780	22.367	2662.1	8.587
320.00	29.314	4561.8	14.256	23.288	2890.4	9.032
330.00	29.894	4857.9	14.721	24.199	3127.8	9.478
340.00	30.439	5159.6	15.175	25.100	3374.3	9.925
350.00	30.952	5466.5	15.619	25.990	3629.8	10.371
360.00	31.435	5778.5	16.051	26.868	3894.1	10.817
370.00	31.893	6095.2	16.473	27.736	4167.1	11.262
373.15	32.032	6195.8	16.604	28.007	4254.9	11.403
380.00	32.324	6416.3	16.885	28.592	4448.8	11.707
390.00	32.726	6741.6	17.286	29.437	4738.9	12.151
400.00	33.104	7070.7	17.677	30.270	5037.5	12.594
425.00	33.973	7909.4	18.610	32.304	5819.8	13.694
450.00	34.746	8768.6	19.486	34.268	6652.1	14.782
475.00	35.439	9646.0	20.307	36.166	7532.7	15.858
500.00	36.064	10540.	21.080	38.000	8459.9	16.920
550.00	37.145	12371.	22.493	41.489	10448.	18.996
600.00	38.050	14252.	23.753	44.761	12605.	21.009
650.00	38.818	16174.	24.883	47.838	14921.	22.955
700.00	39.479	18132.	25.902	50.739	17386.	24.837
750.00	40.055	20120.	26.827	53.483	19992.	26.656
800.00	40.561	22136.	27.670	56.085	22732.	28.415
850.00	41.010	24175.	28.442	58.558	25599.	30.116
900.00	41.411	26236.	29.151	60.913	28586.	31.762
950.00	41.772	28316.	29.806	63.162	31688.	33.356
1000.00	42.099	30413.	30.413	65.313	34900.	34.900
1050.00	42.396	32525.	30.976	67.374	38218.	36.398
1100.00	42.669	34652.	31.502	69.353	41636.	37.851
1150.00	42.919	36792.	31.993	71.255	45152.	39.263
1200.00	43.150	38944.	32.453	73.087	48761.	40.634
1250.00	43.364	41106.	32.885	74.853	52460.	41.968
1300.00	43.563	43280.	33.292	76.557	56245.	43.265
1350.00	43.748	45463.	33.676	78.205	60114.	44.529
1400.00	43.922	47654.	34.039	79.799	64065.	45.760
1450.00	44.085	49855.	34.382	81.343	68093.	46.961
1500.00	44.239	52063.	34.708	82.841	72198.	48.132
1550.00	44.384	54278.	35.018	84.294	76377.	49.275
1600.00	44.521	56501.	35.313	85.705	80627.	50.392
1650.00	44.651	58730.	35.594	87.077	84947.	51.483
1700.00	44.774	60966.	35.862	88.412	89334.	52.549
1750.00	44.892	63208.	36.119	89.711	93787.	53.593
1800.00	45.004	65455.	36.364	90.978	98305.	54.614
1850.00	45.111	67708.	36.599	92.212	102884.	55.613
1900.00	45.213	69966.	36.824	93.416	107525.	56.592
1950.00	45.311	72229.	37.041	94.592	112226.	57.552
2000.00	45.406	74497.	37.249	95.741	116984.	58.492

 H_0^0 is the enthalpy of the solid at 0 °K and 1 atm pressure.

to determine the constants of the following empirical equation for Al_4C_3 :

$$H_T - H_{273.15} = 19771.1 + 47.5557T + 1.927(10^{-4})T^2 - 13452.4 \log_{10} T \text{ cal mol}^{-1} \text{ at } T \text{ }^\circ\text{K}. \quad (1)$$

(For consistency, the equation has more significant figures than the precision of the observations.) The deviations of the mean observed values from eq (1) are given in the last column. The final values of enthalpy from 373 to 1173 $^\circ\text{K}$, relative to 273 $^\circ\text{K}$ (table 5) are consistently lower than eq (1) by 10 cal mol^{-1} , an amount which is within the precision of the high-temperature measurements.

The heat measurements on the empty container were not smoothed separately because their temperature variation possesses an irregularity reflecting a well-known transition in the alloy 80 percent Ni-20 percent Cr in this temperature range.

5. Comparison of the Low- and High-Temperature Heat Data and the Calculation of Thermodynamic Functions

The low-temperature heat-capacity data overlap the high-temperature relative-enthalpy data in the range 273.15 to 380 $^\circ\text{K}$. Numerical integration of the smoothed values of the low-temperature heat-capacity yielded 2933 cal mol^{-1} for the enthalpy change between 273.15 and 373.15 $^\circ\text{K}$. The high-temperature relative enthalpy measurements (see table 4) give an average value of 2939 cal mol^{-1} and the enthalpy equation (eq (1)) gives 2947 cal mol^{-1} for this temperature interval. The smoothed values of heat capacity from the low-temperature measurements were merged with the values of heat capacity calculated from the relative enthalpy equation (eq (1)) in a manner such that the resultant enthalpy change from 273.15 to 373.15 $^\circ\text{K}$ would be about the average of the mean values determined by the two methods. After a process of adjusting and smoothing, the final values of heat capacity that were obtained yielded 2936 cal mol^{-1} for the enthalpy change of this temperature interval. In figure 4, the final selected values of heat capacity are compared with those from the low-temperature measurements and from the enthalpy equation (eq (1)) in the interval 270 to 390 $^\circ\text{K}$.

The relative-enthalpy equation (eq (1)) was used to extrapolate the thermodynamic properties up to 2000 $^\circ\text{K}$. The equation is of a form generally used for high-temperature heat capacities and is "well behaved" in terms of the configuration of the heat-capacity curve and the derivatives up to 2000 $^\circ\text{K}$ and higher. The various thermodynamic properties between 0 and 2000 $^\circ\text{K}$ given in table 5 were calculated from the heat capacities, using the standard thermodynamic relations [18], by numerical methods on the IBM 7094 computer.

Initially the various high-temperature vapor-equilibrium data involving Al_4C_3 were analyzed in order to obtain a guide for extrapolating the calorimetric data above 1200 $^\circ\text{K}$.

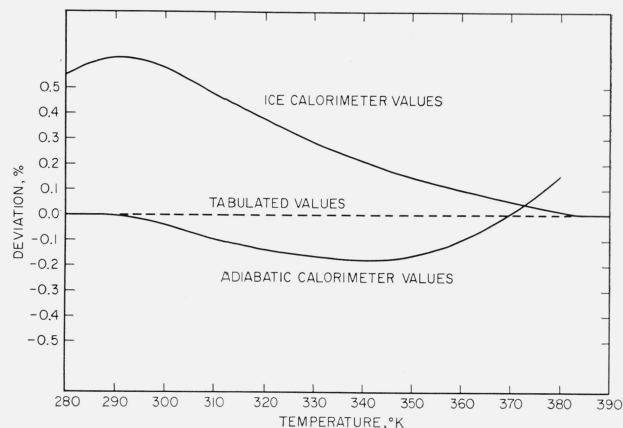


FIGURE 4. Comparison of the final selected values of heat capacity (table 5) with those of the low-temperature measurements and those derived from the enthalpy equation (eq (1)).

The entropy of Al_4C_3 was calculated from the ΔS° of the equilibrium reactions in which the ΔC_p° of the components was assumed to be zero. After consideration of the uncertainties in the values of S° calculated from the vapor-equilibrium data, the extrapolated values of eq (1) was found to be within the estimated uncertainties. Equation (1) was, therefore, used in the extrapolation. The details of this comparison and the subsequent refinements in the calculation, in which the ΔC_p° of the components are considered, are discussed in the following section (sec. 6).

6. Comparison of the Calorimetric and Vapor-Equilibrium Data

The calorimetric data obtained on Al_4C_3 and the results of extrapolating the thermodynamic properties to 2000 $^\circ\text{K}$ have been compared with vapor-equilibrium data on reactions involving Al_4C_3 . Intercomparisons were made of the results of thermodynamic analyses by three methods that are ordinarily used, depending upon the thermodynamic data available. The values of S° of Al_4C_3 and ΔH° and ΔS° of the various reactions that were obtained are intercompared. Vapor pressures calculated from calorimetric data are compared graphically with the observed values.

In method I the vapor-pressure data only were used, in which $\Delta C_p^\circ = 0$ is assumed for the reactions. Whenever the vapor-pressure equation only was given, the ΔS° of the reaction was calculated from the relations:

$$\Delta G^\circ = -RT \ln p^n \quad (2)$$

and

$$\left(\frac{\partial \Delta G^\circ}{\partial T}\right)_p = -\Delta S^\circ, \quad (3)$$

where n is the net number of moles of gaseous species produced in the reaction as written and R is the molal gas constant. When numerical values of the

vapor pressure were given, the relation

$$\frac{\Delta G^\circ}{T} = -R \ln p^n = \frac{\Delta H^\circ}{T} - \Delta S^\circ \quad (4)$$

was used and ΔH° and ΔS° obtained by the least squares method. Whenever both equation and numerical values were given, the values obtained through the least-squares analysis were selected for the comparison. The corresponding values of S° of Al_4C_3 were calculated, using the tables of thermodynamic properties recently issued from the National Bureau of Standards [8] containing values for the other substances in the reactions.

In method II, the ΔH° and ΔS° of the vapor equilibrium reactions were calculated taking into consideration the ΔC_p° of the components of the reaction involved. For Al_4C_3 the thermodynamic properties given in table 5 were used and for the other substances several of the appropriate sources of thermodynamic properties were used [8, 20]. The calculations of method II were carried out using a method suggested by Prosen [21] and illustrated by Otto [22]. Margrave [23] reported a similar method. The method involves the relation:

$$\frac{\Delta G_T^\circ}{T} - \Delta\psi = -R \ln K - \Delta\psi = \frac{\Delta H_*^\circ}{T} - \Delta S_*^\circ, \quad (5)$$

where

$$\Delta\psi = \frac{\Delta[(H_T^\circ - H_*^\circ)]}{T} - (S_T^\circ - S_*^\circ) \quad (6)$$

and the symbol * indicates the temperature at which the ΔH° and ΔS° are to be determined. For these calculations the temperature * was selected for purposes of the comparison at about the mid-temperature of the range of vapor-equilibrium data (at which the calculations of ΔH° and ΔS° were made assuming $\Delta C_p^\circ = 0$). The equilibrium constant K was taken to be the observed pressures of the gaseous species involved, raised to the appropriate power. The values of ΔH_*° and ΔS_*° were obtained by the least squares method.

In method III, the values of ΔH° and ΔS° of the reaction were calculated using the thermochemical and thermodynamic data on the components of the reactions [8, 20, 24, 25, 26]. For Al_4C_3 , Mah [25] reported -53.4 ± 2.0 kcal mol⁻¹ for the heat of formation (ΔH_f°) (298 °K) from combustion measurements on Al_4C_3 involving the reaction:



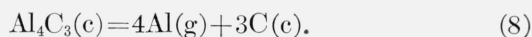
(Henceforth, any thermodynamic property at T °K will be symbolized, for example, by $\Delta H^\circ(T \text{ °K})$, and 298.15 °K will be abbreviated to 298 °K.) More recently King and Armstrong [26] obtained ΔH_f° (298 °K) = -49.7 ± 1.2 kcal mol⁻¹ from combustion measurements on a portion of the same Al_4C_3 preparation on which the present calorimetric results are being reported. Negligible amounts of $\delta\text{-Al}_2\text{O}_3$ were found in the combustion products by Mah [25],

but the experiments of King and Armstrong [26] showed from 50 to 75 percent $\delta\text{-Al}_2\text{O}_3$ which was corrected for the heat of transition to the α form. The somewhat purer sample used by Mah may be the reason for the negligible amounts of $\delta\text{-Al}_2\text{O}_3$ found in her experiments [27]. If $\alpha\text{-Al}_2\text{O}_3$ only were assumed to have been formed in the combustion reaction, the measurements of King and Armstrong [26] would yield $\Delta H_f^\circ(298 \text{ °K}) = -52.6 \pm 1.1$ kcal mol⁻¹. The earlier combustion measurements of Roth and colleagues [28, 29, 30] yield $\Delta H_f^\circ(298 \text{ °K}) = -46.2 \pm 6.2$ kcal mol⁻¹ when the recent thermochemical data [8, 24] are applied to their reported heat of reaction (-1036.7 ± 6.2 kcal mol⁻¹ for eq (7)). The value -49.7 ± 1.2 kcal mol⁻¹ obtained by King and Armstrong [26], was used in the calculations by method III. In the comparison of the vapor pressures of the various equilibrium reactions the value -53.4 ± 2.0 kcal mol⁻¹ obtained by Mah [25] was used also.

Table 6 shows the comparison of the calorimetric values of S° of Al_4C_3 with those calculated from the various vapor-equilibrium reactions assuming $\Delta C_p^\circ = 0$ (method I) and when the values of ΔC_p° of the reactions were considered (method II). The comparison of the values of ΔH° and ΔS° of the vapor-equilibrium reaction obtained from vapor-pressure (methods I and II) and calorimetric (method III) data is given in table 7. (Hereafter, the methods of calculation used to obtain the various thermodynamic quantities will be identified by the Roman numerals indicated above.)

The thermochemical and thermodynamic data were used to calculate the vapor pressure of the gaseous species of the vapor-equilibrium data. The activity coefficients of the components were assumed to be unity. The $\log_{10}p$ (observed or vapor-pressure equation obtained from least-square analysis) and $\log_{10}p$ (vapor pressures calculated from calorimetric data) are plotted in figure 5 for comparison.

The simplest vapor-equilibrium reaction analyzed is the dissociation of Al_4C_3 :



Meschi and Searcy [31] measured the vapor pressure of aluminum in the above reaction in the region from 1500 to 1800 °K by means of the Knudsen effusion method and by a torsion method. They reported for the reaction $\Delta H^\circ(1600 \text{ °K}) = 356 \pm 12$ kcal mol⁻¹ based on the vapor-pressure equation obtained from two of the runs by the torsion method. The values of ΔH° from each of the above two runs differed by 20 kcal mol⁻¹. The values of ΔH° and ΔS° for the reaction (eq (8)) were evaluated at 1650 °K, the midtemperature of the experimental range, using method I with the numerical data between 1600 and 1700 °K given only for the Knudsen effusion method. The results using method II are based on the same numerical values. (Meschi and Searcy [31] show a large number of observations in their plot but report only seven numerical values.

TABLE 6. Comparison of the entropy of aluminum carbide (Al_4C_3) obtained from the calorimetric measurements with those calculated from vapor-equilibrium data

Source	System or reaction	Temperature range	Temperature of S°	S_T°		
				Assuming $\Delta C_p^\circ = 0$	ΔC_p° from thermal data	Calorimetric data
Meschi and Searcy [31]-----	$\text{Al}_4\text{C}_3(\text{c}) = 4\text{Al}(\text{g}) + 3\text{C}(\text{c})$ -----	1500-1800	1650	e.u. ^a	e.u. ^a	e.u. ^{a, b}
Prescott and Hineke [36]-----	$4\text{AlN}(\text{c}) + 3\text{C}(\text{c}) = \text{Al}_4\text{C}_3(\text{c})$ $+ 2\text{N}_2(\text{g})$ -----	1774-1909	1850	99.8	99.5	87.1
Prescott and Hineke [37]-----	$2\text{Al}_2\text{O}_3(\text{c}) + 9\text{C}(\text{c}) = \text{Al}_4\text{C}_3(\text{c})$ $+ 6\text{CO}(\text{g})$ -----	1967-2293	2150	97.5	97.4	92.2
Brunner [38]-----	$2\text{Al}_2\text{O}_3(\text{c}) + 9\text{C}(\text{c}) = \text{Al}_4\text{C}_3(\text{c})$ $+ 6\text{CO}(\text{g})$ -----	1853-2253	2100	90.0	84.6	99.0
Grjotheim et al., [41]-----	$8\text{MgO}(\text{c}) + \text{Al}_4\text{C}_3(\text{c})$ $= 2\text{MgAl}_2\text{O}_4(\text{c}) + 3\text{C}(\text{c})$ $+ 6\text{Mg}(\text{g})$ -----	1324-1452	1400	58.0	57.3	98.0
				74.9	74.8	79.8

^a e.u. = cal deg⁻¹mol⁻¹.
^b Obtained from table 5.

TABLE 7. Comparison of the thermodynamics of vapor-equilibrium reactions of table 6 calculated by various methods

Reference	T	Calculations from vapor-equilibrium data				Calculations from calorimetric data		Difference (method II—calorimetric data)		
		Method I assuming $\Delta C_p = 0$		Method II ΔC_p from calorimetric data		ΔH_T°	ΔS_T°	$\delta\Delta H_T^\circ$	$\delta T\Delta S_T^\circ$	$\delta\Delta G_T^\circ$
		ΔH_T°	ΔS_T°	ΔH_T°	ΔS_T°					
Meschi and Searcy [31]-----	1650	kcal mol ⁻¹	cal deg ⁻¹ mol ⁻¹	kcal mol ⁻¹	cal deg ⁻¹ mol ⁻¹	kcal mol ⁻¹	cal deg ⁻¹ mol ⁻¹	kcal mol ⁻¹	kcal mol ⁻¹	kcal mol ⁻¹
Prescott and Hineke [36]-----	1850	345.2±27.3 ^a	117.5±16.4 ^a	345.6±27.3 ^a	117.8±16.4 ^a	351.1±2.1 ^{b, c}	130.2±0.3	-5.5	-20.5	+15.0
Prescott and Hineke [37]-----	2150	257.4±14.9	92.6±8.0	257.2±14.9	92.5±8.0	250.3±1.7	87.3±0.3	+6.9	+9.6	-2.7
Brunner [38]-----	2100	535.6±88.0	239.8±41.5	535.0±87.8	239.6±41.4	566.8±7.2	248.9±0.7	-31.8	-20.0	-11.8
Grjotheim et al., [41]-----	1400	467.6±3.4	209.4±1.7	466.1±3.4	208.7±1.6	567.6±7.2	249.3±0.7	-101.5	-85.3	-16.2
		297.2±6.5	172.4±4.7	297.2±6.5	172.3±4.7	301.3±4.7	167.5±0.3	-4.1	+6.7	-10.8

^a These figures following the ± symbols are standard deviations defined for the values of ΔH° by:

$$S_b = \left\{ \frac{S_y^2}{\sum x_i^2 - (\sum x_i)^2/k} \right\}^{1/2}, \text{ and of } \Delta S^\circ \text{ by: } S_a = \left\{ \frac{S_y^2 \sum x_i^2}{k \sum x_i^2 - (\sum x_i)^2} \right\}^{1/2},$$

where $S_y^2 = \sum \delta_i^2 / (k-2)$, δ_i the deviation of the experimental value from the "least-squared" value, k the number of observations, and $x_i = 1/T_i$ [42].

^b These figures following the ± symbols were obtained from the relation $(\sum \epsilon_i^2)^{1/2}$, where ϵ_i is the estimated uncertainty of the calorimetric data used.

^c These values of ΔH° are based on the ΔH_T° (298 °K) for Al_4C_3 reported by King and Armstrong [26].

The analysis is based on these seven values, which are unfortunately closely spaced in temperature and yield a poorer precision figure than that obtained by Meschi and Searcy using a larger number of observations.)

Earlier, Ruff and Jellinek [32] investigated the vapor equilibrium of the Al-C system and found as much as 14 percent of carbon in the gaseous products at 2543 °K. Zeeman [33] reported an analysis of the spectrum of AlC produced at 2423 °K in a graphite resistance furnace containing aluminum. On the other hand, a mass spectrometric analysis of the gaseous products from Al_4C_3 dissociation at 2100 °K by Chupka et al. [34] showed insufficient amounts of gaseous Al-C compounds to account for the large amounts of carbon found by Ruff and Jellinek [32]. Chupka et al. [34] found no molecular species of the

formula AlC treated by Zeeman [33]. The measurements of Ruff and Jellinek probably contained CO from oxygen contamination. Therefore, their results are not compared in tables 6 and 7.

The comparison of the vapor pressures of the Al_4C_3 dissociation equilibrium (fig. 5, curves B) shows that the observed values B'' [31] and those calculated from the calorimetric data B, B' are displaced very nearly parallel from each other. The close agreement (about 1.5%) of the values of ΔH° given in table 7 conforms with the agreement in the "slopes" of the vapor pressures. The displacement of the vapor-pressure curves is related to the deviations in the values of ΔS° . Thus

$$\delta\Delta S^\circ = \frac{\delta\Delta H^\circ}{T} + nR\delta \ln p = -\delta \left(\frac{\partial\Delta G^\circ}{\partial T} \right)_p \quad (9)$$

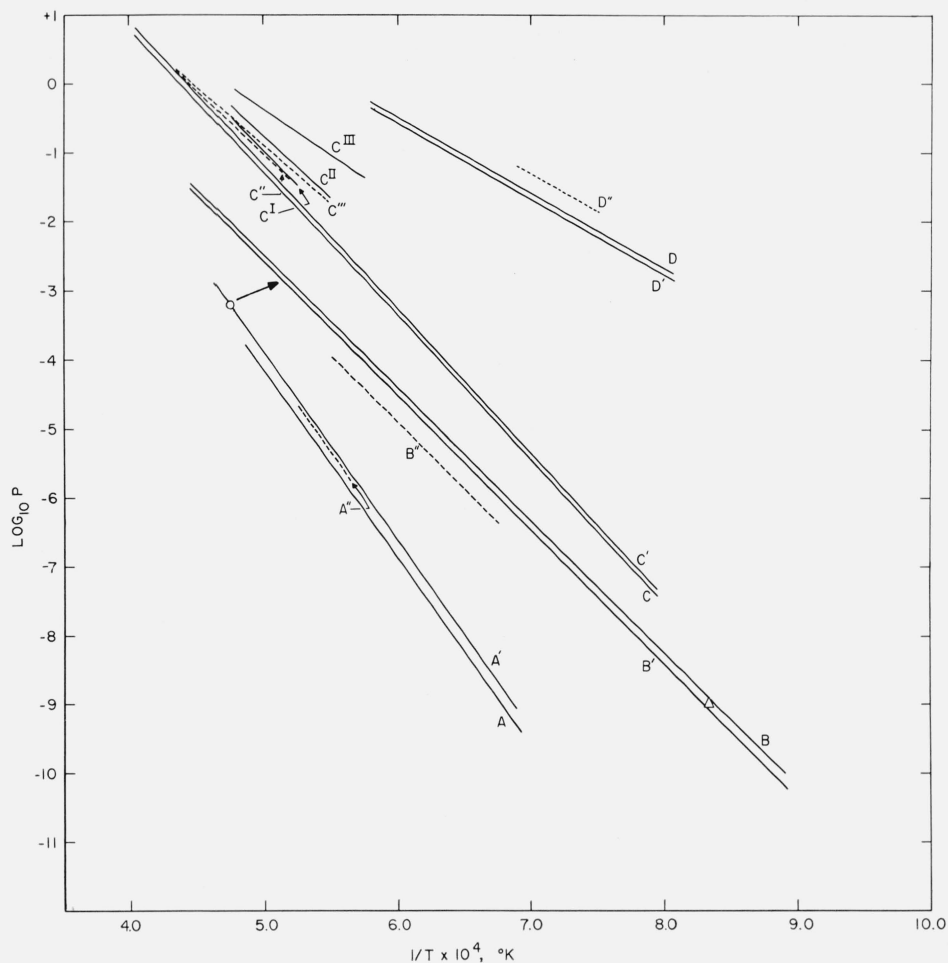


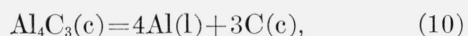
FIGURE 5. Comparison of vapor pressures ($\log_{10} p$ versus $1/T$) calculated from heat of formation and thermodynamic data with published values obtained in high-temperature equilibrium measurements.

- (a) $4\text{AlN}(c) + 3\text{C}(c) \rightarrow \text{Al}_4\text{C}_3(c) + 2\text{N}_2(g)$: A and A' calculation from thermal data,* A'' = Prescott and Hincke [36].
 (b) $\text{Al}_4\text{C}_3(c) \rightarrow 4\text{Al}(g) + 3\text{C}(c)$: B and B' = calculation from thermal data,* B'' = Meschi and Searcy [31],
 ○ = Chupka et al. [34], Δ = Campbell [35].
 (c) $2\text{Al}_2\text{O}_3(c) + 9\text{C}(c) = \text{Al}_4\text{C}_3(c) + 6\text{CO}(g)$: C and C' calculation from thermal data,*
 C'' = Prescott and Hincke [37], C''' = Brunner [38].
 C^I = $\text{Al}_4\text{O}_4(c) + 6\text{C}(c) \rightarrow \text{Al}_4\text{C}_3(c) + 4\text{CO}(g)$: Cox and Pidgeon [40].
 C^{II} = $2\text{Al}_2\text{O}_3(c) + 3\text{C}(c) \rightarrow \text{Al}_4\text{O}_4(c) + 2\text{CO}(g)$: [40].
 C^{III} = $\text{Al}_2\text{O}_3(c) + 3\text{C}(c) \rightarrow \text{Al}_2\text{OC}(c) + 2\text{CO}(g)$: [40].
 (d) $8\text{MgO}(c) + \text{Al}_4\text{C}_3(c) \rightarrow 2\text{MgAl}_2\text{O}_4(c) + 3\text{C}(c) + 6\text{Mg}(g)$: D and D' = calculation from thermal data, D'' = Grjotheim et al. [41].

*A, B, C, and D are based on the heat of formation of Al_4C_3 reported by King and Armstrong [26] and A', B', C', and D' on the value reported by Mah [25].

and $\delta\Delta G^\circ = -nRT\delta \ln p$, where n is the number of moles of the gas involved in the equilibrium and R is the molal gas constant. If $\delta\Delta H^\circ = 0$, then $\delta\Delta S^\circ = nR\delta \ln p$.

The single vapor-pressure value reported for the Al_4C_3 dissociation by Chupka et al. [34] is shown (fig. 5) to be over an order of magnitude lower than the calculated curve. Campbell [35] reported ΔG° (1193 °K) = 35.8 kcal mol⁻¹ for the reaction:



calculated from the activity coefficient obtained from the measurement of the vapor pressure of aluminum monofluoride over the Al_4C_3 -Al-C system and over pure aluminum at 1193 °K (920 °C). The value plotted in figure 5 was obtained after converting to the basis of aluminum vapor [8]. The agreement is fortuitously very close.

Prescott and Hincke [36] investigated the equilibrium reaction between aluminum carbide and nitrogen



in the region 1774 to 1909 °K. The Al_4C_3 sample was prepared by heating pellets of finely divided aluminum metal and graphite as high as 1880 °K. These pellets were mixed in stoichiometric proportion plus 10 percent excess of graphite. The equilibrium pressures were determined from time-pressure measurements obtained by means of a McLeod gage. M. v. Stackelberg et al. [6, 7] reported an intermediate compound, $\text{Al}_5\text{C}_3\text{N}$, similar in appearance and properties to Al_4C_3 , and pointed out that the equilibrium reaction investigated by Prescott and Hincke [36] possibly involved instead:



or



depending upon the degree of nitridation of Al_4C_3 to AlN. Since no thermodynamic data are available on $\text{Al}_5\text{C}_3\text{N}$, the comparison is based on the reaction given by eq (11). Methods I and II were applied with the numerical values of vapor pressures reported by Prescott and Hincke [36].

If $\Delta G^\circ < 0$ for the reaction



then ΔG° (eq (12)) $>$ ΔG° (eq (11)) and the observed vapor pressures according to eq (12) should be lower than those calculated from the thermal data for eq (11). On the other hand, ΔG° (eq (13)) $<$ ΔG° (eq (11)) so that the observed vapor pressures according to eq (13) should be higher than the calculated values based on eq (11). The plot of figure 5, curves A, shows that the observed vapor-pressures A'' lie midway between the calculated values A' and A (eq (11)) based on the heat of formation obtained by Mah [25] and by King and Armstrong [26], respectively. The agreement is shown to be reasonably good, so that ΔG° of the reaction represented by eq (14) is probably close to zero or compensating effects exist. (If the compound $\text{Al}_5\text{C}_3\text{N}$ were considered a mixture, the reactions represented by eqs (12) and (13) reduce to eq (11).)

In an earlier investigation, Prescott and Hincke [37] reported vapor-equilibrium measurements on the reaction between aluminum oxide and carbon in the region 1967 to 2293 °K



Calculations applying methods I and II were made with the numerical values that were reported.

Brunner [38] also investigated the equilibria of the Al_2O_3 -C reaction in the region 1853 to 2253 °K. The numerical values reported by Brunner are considerably more precise than those reported by Prescott and Hincke [37] for the reaction. Table 5 was extrapolated slightly above 2000 °K in order to compare the results reported by Prescott and Hincke [37] and by Brunner [38].

The divergent vapor-pressure values reported by various investigators for the Al_2O_3 -C reaction (see

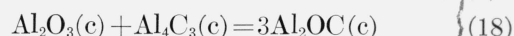
fig. 5, curves C) may be partially explained, depending upon the equilibrium reaction, on the basis of formation of aluminum oxycarbides. According to the phase diagram investigations reported by Foster, Long, and Hunter [27] and the survey of existing data on the Al-O-C system by Motzfeldt [39], Al_2O_3 and Al_4C_3 can not coexist at equilibrium. The equilibrium investigated by Prescott and Hincke [37] could be



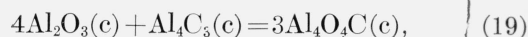
or



instead of the reaction represented by eq (15). At the upper temperatures (above 2100 °K) liquid phases may have been present. If $\Delta G^\circ < 0$ for the formation of the oxycarbides,



or



then the equilibrium represented by eq (17) should yield higher vapor pressures than those calculated according to eq (15). For eq (16), the relative values of vapor pressure with respect to eq (15) will depend on the relative values of ΔG_f° of the oxycarbides. Another equilibrium reaction possible, according to the phase diagram [27, 39], is



but for this reaction the observed vapor pressure should be lower than those calculated for eq (15). Prescott and Hincke [37] used an "excess" of Al_2O_3 ; the reactions given by eqs (16), (17), and (20) are possible depending upon the "excess". Brunner [38], on the other hand, used stoichiometric amounts of Al_2O_3 and C corresponding to eq (15) and his results are even higher than those of Prescott and Hincke [37].

Recently, Cox and Pidgeon [40] using a differential thermal analysis method reported results on the equilibrium reactions represented by eq (17),



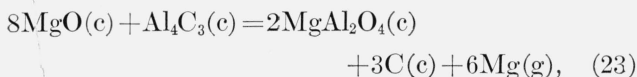
and



The measurements were made on each of three samples having Al_2O_3 to C molal ratios of 2:3, 2:6, and 2:9. Vapor-pressure equations of the form given by eq (4) were obtained by fitting the experimental data, corresponding to reactions represented by eqs (17), (21), and (22), respectively, by the method of least squares. (The numerical values, which were absent in the original paper, were kindly supplied by the authors.) These equations, plotted in figure 5, show that the vapor pressures observed by Cox and Pidgeon [40] are considerably higher than those calculated for the reaction given by eq (15). The vapor pressures corresponding to reaction (22) are fairly close to the values reported by Prescott

and Hincke [37]; the values for reaction (17) join at the lower temperatures with those obtained by Brunner [38]. The values for reaction (21) are higher than any of the other vapor pressures plotted for the Al-O-C system. Actually, of the three reactions reported by Cox and Pidgeon [40], only the reaction given by eq (17) is possible according to the phase diagrams [27, 39].

Recently, Grjothheim, Herstad, and Johannessen [41] reported vapor-equilibrium investigations by means of the transpiration method of the reaction:



in the range 1325 to 1450 °K. The observed vapor pressures are higher than the calculated values on the average by a factor of 2 (fig. 5, curves D), which corresponds to $\delta\Delta G^\circ$ (1400 °K) of about 12 kcal for the reaction given in eq (23). The uncertainty in the calorimetric data is considerably lower than 12 kcal and it is unlikely that the vapor-pressure measurements are in error by a factor of 2. The values of ΔH° (table 7) agree, however, within about 1.3 percent.

The comparisons of the results of thermodynamic analysis of high temperature vapor-equilibrium reactions show that the ΔH° of the reactions calculated from calorimetric data and by the second-law method using vapor-pressure data can agree within a few percent or better and within about the uncertainty of the calorimetric data. The vapor pressures and, therefore, the ΔG° of the reactions show systematic differences that are, in some cases, greater than the uncertainties in the calorimetric data or in the vapor-pressure determination. These differences are reflected in the values of $\delta\Delta G^\circ$ of table

$7 \approx \delta \log p$ of figure 5. These differences can be attributed partially to the deviations from unity of the activity coefficients of the components of the equilibrium reaction or the reactions being different from those as written. Also, because of the finite time involved in the experiments, possible kinetic effects can contribute to the deviations. For the second-law values of ΔH° , the standard deviation figures depend on the precision of the measurements and on the temperature distribution of observations. In method I, any departure from linearity of the $\log p$ versus $1/T$ relation increases the standard deviation figure. Wide divergences in ΔH° and ΔS° were found in the Al-O-C system; the need for further work on the system is indicated.

In the vapor-equilibrium reactions that were analyzed, the results obtained using method I and II were essentially the same, since in method I the ΔS° and ΔH° were evaluated at the mean temperature of the range of measurements (as should always be done) and also since the term given by eq (6) is small. In other equilibria or for wider ranges, this term may become important and should be used whenever a value or estimate of ΔC_p° is available.

The authors are indebted to Willis R. Thurber for all the measurements on the sample with the "drop" calorimeter, and to Rolf A. Paulson of the Analysis and Purification Section of the National Bureau of Standards for the chemical analyses on the samples. The processing of the heat measurements would not have been possible without the chemical analysis. The gift of the Al_4C_3 sample from the Aluminum Company of America, ALCOA Research Laboratories, through the courtesy of George Long, is gratefully acknowledged.

(Continued)

Appendix. Thermodynamic functions for aluminum carbide (Al₄C₃) solid phase

Gram molecular weight=143.9594 g, $T \text{ deg K} = t \text{ deg C} + 273.15$

T	C_p^0	$(H_T^0 - H_0^0)$	$(H_T^0 - H_0^0)/T$	S_T^0	$-(G_T^0 - H_0^0)$	$-(G_T^0 - H_0^0)/T$
$^{\circ}\text{K}$	$J \text{ deg}^{-1} \text{ mol}^{-1}$	$J \text{ mol}^{-1}$	$J \text{ deg}^{-1} \text{ mol}^{-1}$	$J \text{ deg}^{-1} \text{ mol}^{-1}$	$J \text{ mol}^{-1}$	$J \text{ deg}^{-1} \text{ mol}^{-1}$
0.00	0.000	0.000	0.000	0.000	0.000	0.000
5.00	.003	.003	.001	.001	.001	.000
10.00	.020	.051	.005	.007	.017	.002
15.00	.069	.259	.017	.023	.086	.006
20.00	.170	.817	.041	.054	.272	.014
25.00	.397	2.177	.087	.114	.679	.027
30.00	.786	5.052	.168	.218	1.488	.050
35.00	1.398	10.402	.297	.382	2.958	.085
40.00	2.299	19.525	.488	.624	5.436	.136
45.00	3.484	33.866	.753	.960	9.356	.208
50.00	4.950	54.838	1.097	1.401	15.215	.304
55.00	6.707	83.854	1.525	1.953	23.551	.428
60.00	8.716	122.33	2.039	2.621	34.937	.582
65.00	10.929	171.36	2.636	3.405	49.954	.769
70.00	13.351	231.98	3.314	4.302	69.175	.988
75.00	15.902	305.05	4.067	5.310	93.159	1.242
80.00	18.564	391.18	4.890	6.420	122.44	1.531
85.00	21.294	490.81	5.774	7.627	157.52	1.853
90.00	24.073	604.21	6.713	8.923	198.86	2.210
95.00	26.878	731.57	7.701	10.300	246.89	2.599
100.00	29.702	873.02	8.730	11.750	301.98	3.020
105.00	32.537	1028.6	9.796	13.268	364.50	3.471
110.00	35.381	1198.4	10.895	14.847	434.76	3.952
115.00	38.232	1382.4	12.021	16.483	513.06	4.461
120.00	41.085	1580.7	13.173	18.170	599.67	4.997
125.00	43.929	1793.3	14.346	19.905	694.84	5.559
130.00	46.755	2020.0	15.538	21.683	798.80	6.145
135.00	49.552	2260.8	16.746	23.500	911.74	6.754
140.00	52.314	2515.4	17.967	25.352	1033.9	7.385
145.00	55.037	2783.8	19.199	27.236	1165.3	8.037
150.00	57.719	3065.8	20.438	29.147	1306.3	8.708
155.00	60.361	3361.0	21.684	31.083	1456.8	9.399
160.00	62.959	3669.3	22.933	33.040	1617.1	10.107
165.00	65.513	3990.5	24.185	35.017	1787.3	10.832
170.00	68.022	4324.3	25.437	37.010	1967.3	11.572
175.00	70.485	4670.6	26.689	39.017	2157.4	12.328
180.00	72.902	5029.1	27.940	41.037	2357.5	13.097
185.00	75.273	5399.6	29.187	43.067	2567.8	13.880
190.00	77.598	5781.8	30.430	45.105	2788.2	14.675
195.00	79.873	6175.5	31.669	47.150	3018.8	15.481
200.00	82.098	6580.4	32.902	49.201	3259.7	16.298
205.00	84.271	6996.4	34.129	51.255	3510.8	17.126
210.00	86.394	7423.0	35.348	53.311	3772.2	17.963
215.00	88.466	7860.2	36.559	55.368	4043.9	18.809
220.00	90.492	8307.6	37.762	57.425	4325.9	19.663
225.00	92.471	8765.1	38.956	59.481	4618.2	20.525
230.00	94.407	9232.3	40.140	61.535	4920.7	21.394
235.00	96.300	9709.1	41.315	63.586	5233.5	22.270
240.00	98.154	10195.	42.480	65.632	5556.6	23.152
245.00	99.968	10691.	43.635	67.675	5889.9	24.040
250.00	101.74	11195.	44.779	69.713	6233.3	24.933
255.00	103.48	11708.	45.913	71.745	6587.0	25.831
260.00	105.17	12230.	47.037	73.770	6950.8	26.734
265.00	106.82	12760.	48.149	75.789	7324.7	27.640
270.00	108.42	13298.	49.251	77.801	7708.6	28.551
273.15	109.42	13641.	49.939	79.064	7955.7	29.126

Appendix. Thermodynamic functions for aluminum carbide (Al₃C₃) solid phase—Continued

Gram molecular weight = 143.9594 g, T deg K = t deg C + 273.15

T	C_p^0	$(H_T^0 - H_0^0)$	$(H_T^0 - H_0^0)/T$	S_T^0	$-(G_T^0 - H_0^0)$	$-(G_T^0 - H_0^0)/T$
$^{\circ}\text{K}$	$J \text{ deg}^{-1} \text{ mol}^{-1}$	$J \text{ mol}^{-1}$	$J \text{ deg}^{-1} \text{ mol}^{-1}$	$J \text{ deg}^{-1} \text{ mol}^{-1}$	$J \text{ mol}^{-1}$	$J \text{ deg}^{-1} \text{ mol}^{-1}$
275.00	109.99	13844.	50.341	79.805	8102.7	29.464
280.00	111.51	14397.	51.419	81.800	8506.7	30.381
285.00	112.99	14959.	52.487	83.787	8920.6	31.301
290.00	114.44	15527.	53.542	85.765	9344.5	32.223
295.00	115.87	16103.	54.587	87.733	9778.3	33.147
298.15	116.77	16469.	55.239	88.969	10057.	33.730
300.00	117.30	16686.	55.620	89.693	10222.	34.073
310.00	120.06	17873.	57.655	93.584	11138.	35.930
320.00	122.65	19087.	59.646	97.437	12093.	37.792
330.00	125.08	20325.	61.592	101.25	13087.	39.657
340.00	127.36	21588.	63.493	105.02	14118.	41.524
350.00	129.50	22872.	65.349	108.74	15187.	43.392
360.00	131.53	24177.	67.159	112.42	16293.	45.258
370.00	133.44	25502.	68.925	116.05	17435.	47.122
373.15	134.02	25923.	69.472	117.18	17803.	47.709
380.00	135.24	26846.	70.647	119.63	18614.	48.983
390.00	136.93	28207.	72.325	123.16	19828.	50.840
400.00	138.51	29584.	73.960	126.65	21077.	52.692
425.00	142.14	33093.	77.866	135.16	24350.	57.294
450.00	145.38	36688.	81.528	143.38	27832.	61.850
475.00	148.28	40359.	84.966	151.32	31517.	66.351
500.00	150.89	44099.	88.198	158.99	35396.	70.792
550.00	155.42	51760.	94.110	173.59	43715.	79.481
600.00	159.20	59629.	99.381	187.28	52740.	87.900
650.00	162.42	67671.	104.11	200.15	62429.	96.045
700.00	165.18	75863.	108.38	212.29	72743.	103.92
750.00	167.59	84183.	112.24	223.77	83647.	111.53
800.00	169.71	92617.	115.77	234.66	95111.	118.89
850.00	171.59	101150.	119.00	245.01	107104.	126.01
900.00	173.26	109772.	121.97	254.86	119603.	132.89
950.00	174.77	118474.	124.71	264.27	132583.	139.56
1000.00	176.14	127247.	127.25	273.27	146023.	146.02
1050.00	177.39	136086.	129.61	281.89	159904.	152.29
1100.00	178.53	144984.	131.80	290.17	174207.	158.37
1150.00	179.57	153937.	133.86	298.13	188916.	164.27
1200.00	180.54	162940.	135.78	305.80	204015.	170.01
1250.00	181.43	171989.	137.59	313.18	219491.	175.59
1300.00	182.27	181082.	139.29	320.32	235329.	181.02
1350.00	183.04	190215.	140.90	327.21	251518.	186.31
1400.00	183.77	199386.	142.42	333.88	268047.	191.46
1450.00	184.45	208592.	143.86	340.34	284903.	196.48
1500.00	185.10	217830.	145.22	346.61	302077.	201.38
1550.00	185.70	227101.	146.52	352.68	319560.	206.17
1600.00	186.28	236400.	147.75	358.59	337343.	210.84
1650.00	186.82	245728.	148.93	364.33	355417.	215.40
1700.00	187.34	255082.	150.05	369.91	373773.	219.87
1750.00	187.83	264461.	151.12	375.35	392406.	224.23
1800.00	188.30	273864.	152.15	380.65	411306.	228.50
1850.00	188.74	283290.	153.13	385.82	430468.	232.69
1900.00	189.17	292738.	154.07	390.85	449886.	236.78
1950.00	189.58	302207.	154.98	395.77	469552.	240.80
2000.00	189.98	311696.	155.85	400.58	489461.	244.73

H_0^0 is the enthalpy of the solid at 0 °K and 1 atm pressure.

7. References

- [1] S. Satoh, *Sci Papers Inst. Phys. Chem. Research (Tokyo)* **34**, 50 (1938).
- [2] M. v. Stackelberg and E. Schnorrenberg, *Z. physik. Chem.* **B27**, 37 (1934).
- [3] J. F. Durand, *Bull. Soc. Chim.* **35**, 1141 (1924).
- [4] E. Baur and R. Brunner, *Z. Elektrochem.* **40**, 154 (1934).
- [5] George Long, private communication, June 21, 1960.
- [6] M. v. Stackelberg, E. Schnorrenberg, R. Paulus, and K. F. Spiess, *Z. physik. Chem.* **A175**, 127 (1935).
- [7] M. v. Stackelberg and K. F. Spiess, *Z. physik. Chem.* **A175**, 140 (1935).
- [8] Preliminary Report on the Thermodynamic Properties of Selected Light-Element and Some Related Compounds, National Bureau of Standards Report No. 6928, July 1, 1960.
- [9] W. DeSorbo and W. W. Tyler, *J. Chem. Phys.* **21**, 1660 (1953).
- [10] F. Simon and R. C. Swain, *Z. physikal. Chem.* **28B**, 189 (1935).
- [11] K. K. Kelley, *J. Chem. Phys.* **11**, 16 (1943).
- [12] R. B. Scott, C. H. Meyers, R. D. Rands, Jr., F. G. Brickwedde, and N. Bekkedahl, *J. Res. NBS* **35**, 39 (1945) RP 1661.
- [13] G. T. Furukawa, M. L. Reilly, and J. H. Piccirelli, *J. Res. NBS* **68A** (Phys. and Chem.) No. 4, 381 (1964).
- [14] H. F. Stimson, *J. Res. NBS* **65A** (Phys. and Chem.) No. 3, 139 (1961).
- [15] H. J. Hoge and F. G. Brickwedde, *J. Res. NBS* **22**, 351 (1939) RP1188.
- [16] E. T. Whittaker and G. Robinson, *The Calculus of Observations. A Treatise on Numerical Mathematics*, pp. 285-316, 4th ed. (Blackie and Sons, London, 1944).
- [17] IUPAC revises atomic weight values, *Chem. Eng. News* **39**, 42 (1961).
- [18] G. T. Furukawa, T. B. Douglas, R. E. McCoskey, and D. C. Ginnings, *J. Res. NBS* **57**, 67 (1956) RP2694.
- [19] D. C. Ginnings, *J. Phys. Chem.* **67**, 1917 (1963).
- [20] J. Hilsenrath, C. W. Beckett, W. S. Benedict, L. Fano, H. J. Hoge, J. F. Masi, R. L. Nuttall, Y. S. Touloukian, and H. W. Woolley, *Tables of thermal properties of gases*, NBS Circ. 564, November 1, 1955.
- [21] E. J. Prosen, private communication.
- [22] E. M. Otto, *J. Electrochem. Soc.* **111**, 88 (1964).
- [23] J. L. Margrave, *J. Phys. Chem.* **64**, 288 (1960).
- [24] JANAF Thermochemical Data, The Dow Chemical Company, Thermal Laboratory, Midland, Mich.
- [25] A. D. Mah, Bureau of Mines RI 6415, 1964.
- [26] R. C. King and G. T. Armstrong, *J. Res. NBS* **68A**, (Phys. and Chem.) No. 6, 661 (1964).
- [27] L. M. Foster, G. Long, and M. S. Hunter, *J. Am. Ceram. Soc.* **39**, 1 (1956).
- [28] A. Meichsner and W. A. Roth, *Z. Elektrochem.* **40**, 19 (1934).
- [29] W. A. Roth, U. Wolf and O. Fritz, *Z. Elektrochem.* **46**, 42 (1940).
- [30] W. A. Roth, *Z. Elektrochem.* **48**, 267 (1942).
- [31] D. J. Meschi and A. W. Searcy, *J. Phys. Chem.* **63**, 1175 (1959).
- [32] O. Ruff and E. Jellinek, *Z. anorg. allgem. Chem.* **97**, 312 (1916).
- [33] P. B. Zeeman, *Can. J. Phys.* **32**, 9 (1954).
- [34] W. A. Chupka, J. Berkowitz, C. F. Giese, and M. G. Inghram, *J. Phys. Chem.* **62**, 611 (1958).
- [35] C. S. Campbell, *Met. Soc. Conf.* **7**, 412 (1961).
- [36] C. H. Prescott, Jr., and W. B. Hincke, *J. Am. Chem. Soc.* **50**, 3228 (1928).
- [37] C. H. Prescott, Jr., and W. B. Hincke, *J. Am. Chem. Soc.* **49**, 2753 (1927).
- [38] R. Brunner, *Z. Elektrochem.* **38**, 55 (1932).
- [39] K. Motzfeldt, *Tek. Ukeblad.* **109**, 1137 (1962).
- [40] J. H. Cox and L. M. Pidgeon, *Can. J. Chem.* **41**, 671 (1963).
- [41] K. Grjotheim, O. Herstad, and K. Stahl-Johannessen, *Z. anorg. allgem. Chem.* **328**, 267 (1964).
- [42] M. G. Natrella, *Experimental statistics*, (National Bureau of Standards Handbook, No. 91), U.S. Government Printing Office, Washington, D.C., 20402, 1963.

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