

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Heat Capacity of Chromium Carbide ( $\text{Cr}_3\text{C}_2$ ) from 13 to 300°K.

BY WARREN DESORBO

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The heat capacity of chromium carbide ( $\text{Cr}_3\text{C}_2$ ) has been measured in the temperature range 13 to 300°K. The values of entropy, enthalpy and free energy have been determined and tabulated at integral values of temperature from 25 to 298.16°K. The entropy at 298.16°K. is given as  $20.42 \pm 0.05$  cal. deg.<sup>-1</sup> mole<sup>-1</sup> as compared with the value  $20.4 \pm 0.2$  obtained by Kelley with experimental measurements down to 53°K. For the purpose of extrapolating entropy below 13°K., three Debye functions,  $3D(300/T)$ , have been used.

## Introduction

A general program of determining the thermodynamic properties of various compounds of alloying elements of steels and the thermodynamic properties of various modifications of carbon has been initiated. Alloying elements in steels seem to have a marked effect upon the kinetics of phase transformations. Some of these factors are associated with the stability of the carbides of these elements. Thermodynamics has not been applied to the problem because there have been insufficient data to permit the calculation of reaction free energies. Since the new phases precipitate out in particle sizes of colloidal dimensions or smaller, it is also necessary to study size effects on low-temperature thermodynamic properties. This subject has received but little experimental attention. Chromium carbide,  $\text{Cr}_3\text{C}_2$ , is one of the few carbides whose heat capacity has been studied down to approximately 50°K.<sup>1</sup> In this work, the heat capacity data on this carbide, whose particle size distribution is also reported, have been extended down to 13°K. This study has provided a check on an entropy extrapolation used previously below 50°K.

## Apparatus

**Calorimeter.**—Measurements have been made with a Nernst type of vacuum calorimeter designed after that of H. L. Johnston and associates and referred to by them as a "solid calorimeter."<sup>2</sup> Minor modifications have been made. These pertain mostly to the design of the copper calorimeter container and to changes in the electrical circuits.

A copper calorimeter having a volume of approximately 99 cc. has been used. The calorimeter consists of two parts, a lower cylindrical can and a top cap, each spun separately from 0.020-in. OFHC copper sheet. Twelve radial copper fins (0.005-in.) were copper brazed along their outer edge to the inside wall of the cylindrical unit. This unit was then sealed vacuum tight by copper brazing to the upper cap. The thermocouple well, consisting of a small piece of copper tube closed at one end, was copper brazed to the bottom of the calorimeter. The outside of the calorimeter was wound with formex-insulated gold wire having a diameter of about 0.003-in. and containing 0.15% silver. The room temperature resistance of this winding, which serves both as a heater and as a resistance thermometer, is approximately 425 ohms. The two leads of this heater-thermometer wire terminate at two small insulated posts located at the shoulder of the calorimeter. This technique has ensured constancy of length of leads subsequent to the original calibration work. Thermal conductivity between the gold wire and the copper surface of the calorimeter has been markedly increased by the use of the formex-coated wire and the application of a General Electric Adhesive No. 7031. This improvement in the thermal conductivity has notably

reduced the  $A/E$  correction<sup>3</sup> which is associated with the super-heating of the gold heater wire during energy input.

The thermometer circuit is similar to that described by H. L. Johnston.<sup>2</sup> In the energy circuit, however, a finer adjustment of the voltage variation has been accomplished by means of a potential divider. Voltage increments of approximately 0.5 v. have been used and found to be both effective and convenient during operation. Standard resistors used in the thermometer and in the energy circuit had been previously calibrated at the U.S. Bureau of Standards.

A Leeds & Northrup "White" double potentiometer, having a 100,000-microvolt range, has been used for the study of drift rates as well as for the measurement of the electrical energy input. A Wenner potentiometer, having a 10,000-microvolt range, has been used to measure the e.m.f. output of the standard thermocouple, and the auxiliary thermocouples. The latter thermocouples, consisting of two single junctions of copper and constantan wire, were patterned after those made at The Ohio State University Cryogenic Laboratory; they are described elsewhere.<sup>4</sup>

**Temperature Scale.**—The temperature scale has been established by a copper-constantan thermocouple No. 96 prepared and calibrated at The Ohio State University Cryogenic Laboratory. This thermocouple had been compared by Dr. H. L. Johnston's group against their standard copper-constantan thermocouple No. 80 (August, 1949). This standard thermocouple No. 80 had been previously calibrated against The Ohio State University Cryogenic Laboratory's primary standard which is a constant volume helium gas thermometer constructed by Rubin and co-workers.<sup>4</sup> According to Johnston,<sup>2</sup> the precision of these thermocouples, which are made from selected wire that has passed a severe temperature-gradient test, over a period of years amounts to approximately  $\pm 0.01$ °K. and is found to remain within the calibration accuracy of 0.02 to 0.03°K. Although the uncertainty in the absolute temperature measurements may amount to 0.02 to 0.05°K., the inaccuracy in determining the temperature interval during a heat capacity point determination may amount to 0.002 to 0.005°K.

**Procedure for Data Computation and Experimental Corrections.**—The method of data computation follows essentially the procedure cited by Johnston,<sup>2</sup> with the one exception that the corrections pertaining to the superheating of the calorimeter surface and to the radiation factors have been found small enough to be neglected in the liquid-hydrogen temperature region up to approximately 50°K. Although of small magnitude, the following experimental corrections have been accounted for: (a) gain or loss of thermal energy by conduction during equilibrium measurements; (b) superheating of the heater wire during energy input; (c) radiation from environment; (d) temperature drifts of the block; (e) potentiometer battery drifts; (f) heat generated through two leads connecting the gold wire to the copper pins of the upper block; and (g) heat developed in the 50,000-ohm resistor in the potential divider of the energy circuit. The same corrections have also been made in the calibration of the empty calorimeter.

**Preparation and Purity of Chromium Carbide.**—The sample of chromium carbide was prepared by D. L. Schwartz<sup>5</sup> of the Carbology Department of the General Electric Company. According to Schwartz: "Chromium

(1) K. K. Kelley, F. S. Boerick, G. E. Moore, E. H. Huffman and W. M. Bangert, U. S. Bureau of Mines Technical Paper 662 (1944).

(2) H. L. Johnston and E. C. Kerr, *THIS JOURNAL*, **72**, 4733 (1950).

(3) W. F. Giaque, Heat Capacity Calculations, unpublished.

(4) T. Rubin, H. L. Johnston and H. Altman, *THIS JOURNAL*, **73**, 3401 (1951).

(5) D. L. Schwartz, private communication.

oxide (75% Cr<sub>2</sub>O<sub>3</sub>) and lampblack (25%) were blended together dry and then carburized at 1525°C. in a hydrogen furnace. Time above 1400° was approximately 1.5 hours. Time above 1500° was estimated to be 30 minutes. Loss from reduction of the oxide was calculated to be 41%. The carbon content was found to be 13.2 ± 0.4%, and the chromium content was found to be 86.2%.<sup>6</sup> X-Ray analysis of the sample showed a pattern of Cr<sub>3</sub>C<sub>2</sub> with a small amount of metallic chromium. Spectroscopic analysis revealed the presence of traces of aluminum, copper, iron and magnesium.<sup>7</sup> The weight of the sample placed in the calorimeter was 164.067 g. (0.9112 mole).

**Particle Size Distribution of Chromium Carbide.**—Particle size distribution of the chromium carbide sample was studied by Walter.<sup>8</sup> These results on size distribution are presented in Fig. 1 where the frequency of distribution is plotted against the horizontal length of the particles. The curve contains two maxima, one at 0.8 μ, and the other at 3.2 μ. Walter has calculated the average particle size, with respect to surface area, to be 4.93 μ.

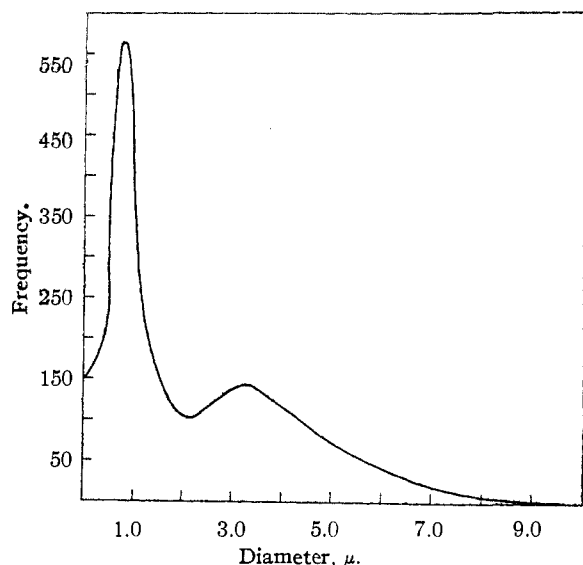


Fig. 1.—Size distribution curve Cr<sub>3</sub>C<sub>2</sub>.

### Experimental Results

Table I presents the heat capacity-temperature data of chromium carbide (Cr<sub>3</sub>C<sub>2</sub>). The temperature difference, ΔT, in the measurements has a value of approximately one degree at the lowest temperatures, increasing to approximately eight degrees at 180°K. Above the ice point, the value of ΔT is less than four degrees. The data of this research are expressed in terms of the defined thermochemical calorie equal to 4.1840 absolute joules. The values of the thermodynamic functions listed in Table II were obtained from a smooth curve of large graphs of heat capacity *versus* T, and heat capacity *versus* log T with the aid of Simpson's rule. The entropy at 298.16°K. is 20.42 ± 0.05 cal. deg.<sup>-1</sup> mole<sup>-1</sup>, of which 0.04 was obtained by extrapolating below 12.90°K. In this extrapolation, the heat capacity has been represented by three Debye functions, 3D (300/T).

(6) The carbon analysis was carried out by Dr. L. B. Pepkowitz of the Knolls Atomic Power Laboratory and the chromium analysis was carried out by Dr. E. H. Winslow of the General Electric Research Laboratory.

(7) The X-ray analysis was performed by Mrs. B. F. Decker, General Electric Research Laboratory; the spectroscopic analysis was performed by M. H. Steinmetz, Schenectady Works Laboratory.

(8) N. Walter, General Electric Research Laboratory, private communication.

TABLE I

MOLAL HEAT CAPACITY OF CHROMIUM CARBIDE (Cr<sub>3</sub>C<sub>2</sub>),  
Mol. wt. 180.05; sample, 0.9112 mole

Mean temp., °K.	C <sub>p</sub> , cal./deg.	Mean temp., °K.	C <sub>p</sub> , cal./deg.
12.90	0.121	148.84	13.33
13.82	.144	156.16	14.19
15.51	.148	162.84	14.80
17.66	.180	170.12	15.23
21.25	.214	177.87	16.09
23.16	.274	185.97	16.83
27.63	.311	193.60	17.38
29.82	.370	201.01	18.07
32.44	.476	208.14	18.54
35.22	.604	212.17	18.77
39.54	.812	218.88	19.23
42.18	.960	225.22	19.59
45.16	1.146	231.21	19.91
48.28	1.349	236.86	20.27
51.48	1.604	242.12	20.58
54.57	1.909	247.33	21.00
58.12	2.320	251.75	21.28
62.28	2.670	256.06	21.47
66.82	3.098	260.64	21.78
71.99	3.920	265.06	22.03
77.15	4.640	269.40	22.27
79.91	4.985	272.49	22.44
82.91	5.380	276.42	22.68
84.42	5.346	280.48	22.78
88.17	6.061	282.61	22.95
93.52	6.750	284.40	23.11
99.41	7.475	286.23	23.07
105.89	8.304	288.70	23.16
113.13	9.230	290.07	23.20
121.83	10.27	293.70	23.35
128.70	11.01	297.30	23.41
135.20	11.76	300.71	23.61
141.84	12.51		

TABLE II

THERMODYNAMIC FUNCTIONS OF CHROMIUM CARBIDE (Cr<sub>3</sub>C<sub>2</sub>) BASED ON THE SMOOTH CURVE OF HEAT CAPACITY

Temp., °K.	C <sub>p</sub> , cal./mole deg.	S <sup>0</sup> , cal./mole deg.	H <sup>0</sup> - H <sub>298</sub> <sup>0</sup> , cal./mole	(H <sup>0</sup> - H <sub>298</sub> <sup>0</sup> )/T, cal./mole deg.	-(F <sup>0</sup> - H <sub>298</sub> <sup>0</sup> )/T, cal./mole deg.
25	0.260	0.169	2.939	0.1175	0.051
50	1.473	0.648	19.441	0.3888	.259
75	4.292	1.737	91.453	1.2193	.517
100	7.545	3.397	239.62	2.3963	1.000
125	10.594	5.410	466.57	3.7325	1.678
150	13.48	7.595	767.52	5.1168	2.478
175	15.85	9.868	1135.45	6.4883	3.378
200	17.95	12.133	1558.13	7.7907	4.343
225	19.55	14.342	2027.92	9.0129	5.330
250	21.12	16.484	2535.99	10.1439	6.339
275	22.57	18.561	3082.85	11.2104	7.350
298.16	23.53	20.420	3621.09	12.1447	8.276

For comparison, these results and those of Kelley<sup>1</sup> are listed in Table III.

### Discussion of Results

The chromium carbide sample used in this study and that used by Kelley<sup>1</sup> have both been prepared at approximately the same temperature. The average particle size in each case may be, in all

TABLE III  
ENTROPY OF  $\text{Cr}_3\text{C}_2$  AT 298.16°K. (CAL./MOLE DEG.)

K. K. Kelley, <i>et al.</i>	
0-50.12°K. (extrap.)	0.56
50.12-298.16°K. (graph.)	19.79
$S_{298.16}^0$	$20.4 \pm 0.2$
This research	
0-12.90°K. (extrap.)	0.04
12.90-298.16°K. (graph.)	20.38
$S_{298.16}^0$	$20.42 \pm 0.05$

probability, of the same order of magnitude, although Kelley does not report quantitatively the particle size in his work. The maximum deviation between the heat capacity data of this research and that of Kelley's amounts to less than 0.1%, which is below the experimental accuracy of both investigations. Therefore, there appears to be no size effect between the two studies.

The heat capacity of  $\text{Cr}_3\text{C}_2$  can be described satisfactorily by three Debye functions,  $3D(470/T)$  in the range 30 to 100°K. Below 30°K., the average characteristic temperature for the  $\text{Cr}_3\text{C}_2$  lattice, calculated by employing three Debye functions, diminishes with decreasing temperature. At 13°K.,  $\theta_D = 294^\circ$ . The characteristic tempera-

ture,  $\theta_D = 470^\circ$ , is approximately of the same order of magnitude as the characteristic temperature of the chromium lattice, calculated from the experimental data of Anderson<sup>9</sup> with one Debye function, in the liquid nitrogen temperature region. This Debye function is  $1D(485/T)$ . The variation of  $\theta_D$  with temperature for chromium in the liquid hydrogen temperature region is not known. Estermann<sup>10</sup> has recently reported that the characteristic temperature of the chromium lattice has a constant value,  $\theta_D = 418^\circ$ , in the liquid helium temperature range.

**Acknowledgment.**—The author is grateful to The Ohio State University Cryogenic Laboratory staff for the numerous discussions on high precision calorimetric techniques. It is a pleasure to mention the kind cooperation and helpfulness of Mr. E. B. Warner, Jr., and Mr. C. M. Moehle in the construction and installation of the apparatus. The author also wishes to thank Mr. A. J. Peat for his assistance in taking data and calculations, as well as Mrs. M. N. Doyle and Mrs. E. L. Fontanella who also assisted with the calculations.

(9) C. T. Anderson, *THIS JOURNAL*, **59**, 488 (1937).

(10) I. Estermann, S. A. Friedberg and J. E. Goldman, *Phys. Rev.*, **87**, 582 (1952).

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

## Polarography of Tellurium(VI)<sup>1a</sup>

BY ELINOR NORTON, R. W. STOENNER AND A. I. MEDALIA<sup>1b</sup>

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The polarographic reduction of tellurium(VI) at the dropping mercury electrode has been investigated in a variety of media. Several media were found to be suitable for the analytical determination of this element. The half-wave potentials and diffusion current constants in these media have been obtained. The reduction of tellurium(VI) at the dropping electrode has been found coulometrically to proceed to the -2 state. It was found that selenium(VI) was not reduced at the dropping electrode in any of the media here reported.

Reduction of tellurium(VI) at the dropping mercury electrode has not previously been reported. At the conclusion of a thorough study of the polarography of tellurium and selenium in the +4 and -2 states,<sup>2a</sup> Lingane and Niedrach state<sup>2b</sup> that "The +6 states of selenium and tellurium are not reduced at the dropping electrode under any of the conditions investigated." However, it is shown in the present work that under a variety of conditions, samples of telluric acid prepared by several different procedures do exhibit well-defined (though irreversible) waves, suitable for the analytical determination of this element.

### Experimental

**Materials.**—Three samples of telluric acid were used. Sample A was prepared by the method of Gilbertson<sup>3</sup> ( $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2$ ) from elementary tellurium (Amend C.P.) in which only traces of other elements were detectable spectrographically. Sample B was prepared from this same lot of elementary tellurium by the procedure of Meyer and

Franke<sup>4</sup> ( $\text{Ba}(\text{ClO}_3)_2$ ), which was the procedure that had been employed by Lingane and Niedrach.<sup>5</sup> Sample C was telluric acid as received from Varlacoid Chemical Co.

Analyses were carried out by three different methods. (1) Reduction of a solution in 1 *N* hydrochloric acid at the boiling point to elementary tellurium by addition of hydrazine hydrochloride and sulfur dioxide.<sup>6</sup> Contrary to the statement of Lehner and Hornberger, reduction of telluric acid to the metal was not complete after the time of five minutes recommended by these authors, as established by the further formation of tellurium metal on treatment of the hot filtrate with sulfur dioxide or with metallic magnesium. In order to obtain complete reduction, it was found necessary to pass sulfur dioxide through the solution at the boiling point for a time of two hours, following the initial addition of hydrazine hydrochloride. A similar observation has been made by Niedrach.<sup>7</sup> (2) Reduction of tellurium(VI) to tellurium(IV) in concentrated hydrochloric acid, sweeping the chlorine gas thus formed into a solution of potassium iodide, and titrating the liberated iodine with thiosulfate. (3) Titration with alkali in the presence of glycerol (50%) with phenolphthalein as indicator. Since the end-point was not very sharp with 0.1 *N* reagent, the accuracy of this determination was limited to  $\pm 0.5\%$ . Samples A and B were analyzed by all three methods; each determination

(1) (a) Research carried out under the auspices of the U. S. Atomic Energy Commission; (b) Chem. Dept., Boston Univ., Boston, Mass.

(2) (a) J. J. Lingane and L. W. Niedrach, *THIS JOURNAL*, **70**, 4115 (1948); (b) **71**, 198 (1949).

(3) L. I. Gilbertson, *ibid.*, **55**, 1460 (1933).

(4) J. Meyer and W. Franke, *Z. anorg. Chem.*, **193**, 191 (1930).

(5) J. J. Lingane and L. W. Niedrach, *THIS JOURNAL*, **70**, 1997 (1948).

(6) V. Lehner and A. W. Hornberger, *ibid.*, **30**, 387 (1908).

(7) L. W. Niedrach, Ph.D. Thesis, Harvard University, 1948.