free energy change as a function of temperature can be calculated for the reaction

$$3InS(s) + 2In_2O_3(s) \rightleftarrows 7In(l) + 3SO_2(g)$$

This function indicates that a pressure of $SO_2(g)$ of one atmosphere over a mixture of InS and In_2O_3 should be observed at 1400°. Such a pressure was observed experimentally, and this served as a check on the above calculations.

Some deductions can be made from Fig. 1. The intersection of lines 3 and 4 at approximately 500°K. indicates that In_3S_4 is not stable at room temperature. This instability of In_3S_4 at room temperature was predicted by the phase diagram (1). The change in the slope of line 4 at about 1100°K. indicates that there is a phase change at this temperature, possibly because of the decomposition of In_2S_3 into some lower sulfide. With the data available at present, it is not possible to make any reliable conclusions concerning the stability of the various sulfides at high temperature.

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Summary.—Equilibrium data for the reduction of four sulfides of indium with hydrogen are given. Standard free energies of formation for the four sulfides are calculated to be: InS, −39.3; In_5S_6, −218; In_3S_4 − 139; and In_2S_3, −101 kcal./mole.

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The Heat Capacity of Chromium Carbide (Cr_3C_2)

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A Bunsen drop calorimeter has been constructed for the measurement of the heat capacities at high temperatures of substances of interest in the field of physical metallurgy. The operation and reliability of the instrument was checked by the use of pure alumina. The enthalpy of Cr_3C_2 was measured relative to 0° up to 915° with satisfactory agreement with former data. Entropy, enthalpy and free energy functions relative to 0°K. are tabulated at even temperature intervals.

Introduction

A general program has been initiated for the study of the high-temperature heat capacities of substances of interest to physical metallurgists. Accurate calorimetric data are essential for the determination of relative stabilities of phases and free energies of reactions at high temperatures, and these are of interest not only from the thermodynamic point of view but also for applications in calculations of the kinetics of phase transformations. For these reasons, a Bunsen drop calorimeter has been constructed, and will be used in the investigation of the properties of various compounds of alloying elements of steel, of liquid metals and of solid alloys.

Construction and Operation of the Calorimeter.—The principle of the Bunsen drop calorimeter is simple; in essence, it comprises the dropping of the sample in a capsule from the measured furnace temperature into a chamber surrounded by ice at 0°. The heat released melts ice to water at 0°, and the resulting volume change causes an intake of mercury from a reservoir which is weighed before and after the drop. In order to subtract out the effect of the capsule, a blank run must be made at the same temperature with the empty capsule. The apparatus has a natural calibration factor, depending only on the specific volumes of water, ice and mercury at 0°, and on the latent heat of fusion of ice; if these values were known sufficiently accurately, electrical calibration of the instrument would not be necessary. In the present work, we have relied on the elaborate electrical calibration of the calorimeter at the National Bureau of Standards[1-3] after which our instrument is patterned.[4]

The construction of the Bunsen calorimeter, shown in Fig. 1, and of the furnace and dropping mechanism will not be described in detail since, except for a few points of difference, they are similar to those described in reference 3. The filling of the present calorimeter with degassed water and mercury is facilitated by the provision of an auxiliary filling tube and valve for the water. The mercury-accounting system makes use of a precision bore glass stopcock in place of the metal valve of the N.B.S. instrument. Furthermore, it has been found possible to make use of a ground-glass taper joint on the calibrated capillary of the mercury-accounting system; this provision facilitates occasional cleaning of the capillary. The mercury used in the calorimeter was purified of oxidizable impurities by long-continued bubbling of air through the mercury, followed by filtration and distillation. The mercury and the water were degassed by the customary techniques prior to introduction into the calorimeter. In operating the instrument, a slow, constant flow of precooled helium is maintained within the calorimeter well in order to increase the thermal conductivity between the sample and the ice of the calorimeter. The capillary of the mercury-accounting system was calibrated *in situ* by separate experiments, and the level of the mercury in it is followed by a cathetometer which can be read to ±0.01 cm. The heat leak from the room into the calorimeter is measured by this capillary; it has an average value of 0.01 cal./min.

The furnace is wound with nichrome wire on an alumina tube, and has a massive core of nickel and alumina cylinders designed to minimize spatial and temporal variations of

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(1) D. C. Ginnings and R. J. Corrucini, *J. Research Natl. Bur. Standards*, **38**, R. P. 1796, 583 (1947).

(2) D. C. Ginnings and R. J. Corrucini, *ibid*, **38**, R. P. 1797, 593 (1947).

(3) D. C. Ginnings, T. B. Douglas and A. F. Ball, *ibid.*, **45**, R. P. 2110, 23 (1950).

(4) We take this opportunity of gratefully acknowledging the advice and helpful suggestions offered by Drs. D. C. Ginnings and T. B. Douglas of the National Bureau of Standards.

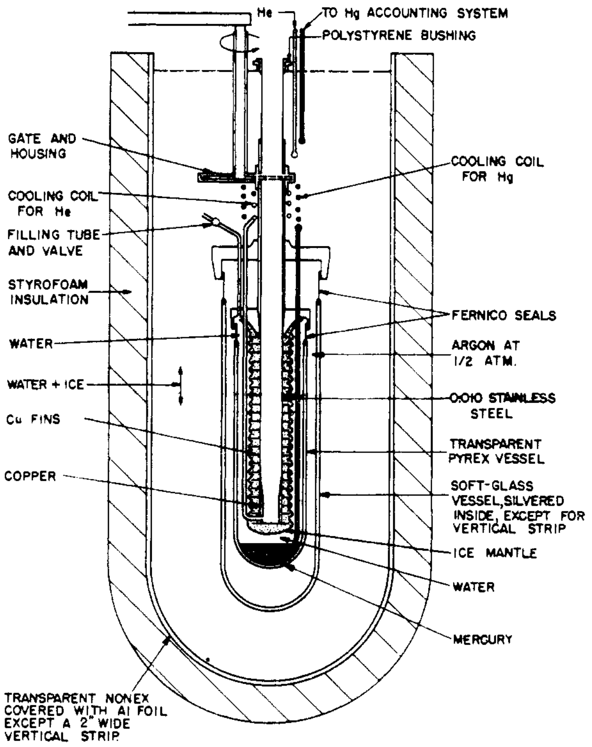

Fig. 1.—Calorimeter.

temperature. The temperature was maintained approximately constant simply by furnishing power stabilized by a Sorensen voltage regulator. The very large thermal capacity of the apparatus smoothed out all short-period fluctuations so that the furnace temperature followed only diurnal changes in its environment.[5] The average drift of furnace temperature at any one power setting is about three degrees over a period of weeks. The temperature is measured by a platinum–platinum, 10% rhodium alloy thermocouple and a Leeds and Northrup K-2 potentiometer. The assembly has been calibrated at the melting points of pure metals by the Temperature Standards section of the General Engineering and Consulting Laboratory of this Company, and a difference curve has been constructed for the thermocouple with standard calibration tables as the basis. Since the thermocouple is not in contact with the capsule, it is necessary to measure the small temperature difference that may exist between it and the capsule. This has been done by separate experiments as a function of furnace temperature by using a differential thermocouple, one leg of which was bound to the capsule. Since the temperature difference is of the order of 0.2°, a large percentage error in the determination of the difference produces only a small error in the absolute temperature.

The weight of mercury drawn in upon dropping the hot sample is corrected for the heat leak, and is plotted on a very expanded scale against the thermal e.m.f. of the measuring thermocouple. The very small range of temperature over which the furnace drifts at any one power setting is covered by at least four measurements, and the best straight line is drawn to fit the experimental points. The internal consistency, or reproducibility, of the measurements is measured by the scatter of the experimental points from the best straight line; the ± mean deviation of the points is computed as a measure of the precision of the data within one small temperature region. This is repeated at other furnace power settings, both for the empty, and for the full capsule containing a known weight of sample. Within any one small temperature region at which both the empty and full capsules were measured, a definite temperature is chosen and the net mercury intake due to the empty capsule is subtracted from that for the full capsule, and the difference is corrected to vacuum standard. The figures for the precision of the corrected weight of mercury that appear in the data tables are computed by adding the ±mean absolute deviations for the empty and full capsule determinations and dividing the sum by the net weight of mercury drawn in by the sample alone. Thus, this figure for precision is a measure of the reproducibility of the entire set of operations. The weight of mercury intake is converted to calories (1 calorie is defined as 4.1840 abs. joules[6]) through the use of the calibration factor[7] of 270.48 ± 0.03 abs. joules/g. Hg.

The errors that affect the accuracy of the final measurement lie in the measurement of the temperature of the sample, in the calibration factor of the calorimeter, and in the determination of the mass of mercury drawn in by the sample alone. The error in the calibration of the thermocouple and of the Leeds and Northrup potentiometer may be estimated as 0.1°. The temperature difference between thermocouple and capsule has been determined and has a maximum value of 0.2°; if the error here is 0.05°, the total error in the measurement of the capsule temperature may be about 0.15°. The error in the determination of the net mercury intake is the sum of the weighing error, which is negligible, the ±0.01 cm. error in reading the cathetometer, which introduces an uncertainty of 0.001 g. of mercury, and the error in the determination of the heat leak correction. Some of these uncertainties must be doubled since the net mercury intake is the difference between two numbers. The over-all accuracy of the cal./g. value, independently of the error of 0.15° in the temperature, is therefore estimated as 0.14% for an intake of ten grams.

Besides the instrumental errors, the sample itself may cause trouble in two respects. First, the purity of the substance should be high and known, and should remain constant; that is, there should be no decomposition, oxidation, loss by volatilization, etc. This depends on the characteristics of the substance itself and on the technique used in sealing it within the capsule. Second, since the enthalpy of the substance is measured relative to its state at 0°, the condition of the substance at this temperature should be reproducible independently of the furnace temperature from which it is dropped. This requirement may not be met by some solids having a transition within the temperature range investigated.

Experimental Results on Pure Alumina.—Measurements on high-purity α-alumina (corundum), furnished by the National Bureau of Standards[8] were undertaken in order to establish the reliability and accuracy of the entire operation. The experimental results on 11.6463 g. of Al_2O_3 are listed in Table I. The temperatures are those of the capsule and sample, and the figures for precision, or reproducibility, of the net mercury intake were computed as described above. Our values of enthalpy referred to 0° are given in the third column and are compared with corresponding values interpolated from the smoothed data of the National Bureau of Standards.[2] The per cent. discrepancy at each of the six temperatures is listed in the next column, and is regarded as a measure of the accuracy of the present data. However, in evaluating these deviations, consideration must be given to the small error involved in the graphical interpolation of the smoothed N.B.S. data, and to the probable discrepancy between "true" enthalpies and smoothed enthalpies in the N.B.S. data. Column 7 of Table I contains these probable discrepancies, interpolated at our temperatures from the discrepancies given in Table II of reference 2. Taking

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(5) At the present time, a more elaborate temperature controller is being used.

(6) F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, This Journal, **74**, 2699 (1952).

(7) T. B. Douglas and J. L. Dever, *Natl. Bur. Standards*, Reprint 1406, Jan. 10, 1952.

(8) Our thanks are due to Dr. Leo Epstein of the Knolls Atomic Power Laboratory who kindly furnished us this alumina, formerly obtained by him from the National Bureau of Standards.

these into account, the probable deviation of our enthalpy values from the "observed" enthalpies of the National Bureau of Standards is in no case larger than 0.2% and is generally smaller. This is regarded as satisfactory agreement, and hence as a check on the reliability of the present instrument.

TABLE I

EXPERIMENTAL RESULTS ON PURE ALUMINA, 11.6463 G.

t, °C.	Net Hg intake, g. and % precision		Ht_0, cal./g.	N.B.S. Ht_0 cal./g.	% Dev. from N.B.S. data	N.B.S. data % deviation of obsd. from smooth
40.10	1.3239	±0.05	7.347	7.340	+0.10	−0.03
127.6	4.6268	± .08	25.679	25.679	.0	+ .04
174.1	6.5765	± .07	36.500	36.440	+ .17	+ .09
254.6	10.1735	± .10	56.464	56.292	+ .27	+ .06
343.8	14.2990	± .06	79.361	79.552	− .24	− .04
512.8	22.6876	± .02	125.918	125.871	+ .02	− .04

TABLE II

EXPERIMENTAL RESULTS ON Cr_3C_2

Temp., °C.	Net Hg intake, g. and % precision		$H^0 - H^0_{273.16}$, cal./g. mole	$S^0 - S^0_{273.16}$, cal./g. mole deg.
24.3_5	0.3976	±0.24	557.1_1	1.953
161.2_5	2.9239	± .09	$4,094._4$	11.66
307.1_4	6.0302	± .03	$8,442._5$	20.28
406.7_3	8.2262	± .02	$11,51_6$	25.12
524.9_1	10.9687	± .09	$15,35_4$	30.32
561.1	11.7623	± .06	$16,46_5$	31.68
586.7	12.3647	± .08	$17,30_7$	32.68
657.6	14.0745	± .07	$19,70_1$	35.36
733.7	15.9661	± .05	$22,34_8$	38.10
836.6	18.6537	± .07	$26,11_0$	41.66
914.5	20.6731	± .06	$28,93_6$	44.12

Experimental Work on Cr_3C_2.—The chromium carbide used in this work is the same material employed by DeSorbo[9] in an investigation of the low-temperature heat capacity. The carbide was prepared by D. L. Schwartz, Carboloy Company, Detroit, by firing chromium oxide and lampblack in a hydrogen furnace at 1525°. The carbon content was found to be 13.2 ± 0.4% (theoretical 13.3), and the chromium content was 86.2% (theoretical 86.66). X-Ray analysis by Mrs. B. F. Decker revealed a small amount of metallic chromium. Spectroscopic analysis showed traces of aluminum, copper, iron and magnesium. The weight of the material used in these experiments was 8.3140 g., corrected to vacuum standard. The platinum capsule used weighed 12.1380 g., and the necessary blank runs with the empty capsule were carried out first. The capsule was then filled and sealed under 1 atmosphere of pure argon by cold welding followed by arc welding; separate experiments have shown that the weight change of the capsule due to this sealing technique is restricted to 1 mg. or less. The results are shown in Table II, in which column 1 lists the sample temperatures obtained as described above. Column 2 shows the mercury intake, corrected to vacuum, due to the sample alone; the mercury intake caused by the empty capsule is roughly one third of that due to the sample. The reproducibility figures of column 2 apply to the over-all measurement except for error in the temperature, as described above. The remaining columns show the enthalpy per mole and entropy per mole per degree of Cr_3C_2 referred to 273.16°K. The entropy was calculated directly from the enthalpy data by the relation

$$S^0 - S^0_{273.16} = \frac{H^0 - H^0_{273.16}}{T} + \int_{273.16}^{T} \frac{H^0 - H^0_{273.16}}{T} \, d \ln T$$

The molecular weight of Cr_3C_2 was taken as 180.05.

The molar enthalpy data can be fitted by the method of Shomate[10] by the empirical equation

$$H_T - H_{273.16} = 26.19T + 4.74 \times 10^{-3}T^2 + 4.72 \times 10^5 T^{-1} - 9237$$

in which T is the absolute temperature °K. In deriving the numerical parameters, the value of $C_p = 22.46$ cal./mole deg. obtained by DeSorbo[9] at 273.16°K. was used. The average deviation of this equation from the measured values is ±0.4% and the maximum deviation is 0.9% at 297.5°K. The corresponding heat capacity equation is then

$$C_p = 26.19 + 9.48 \times 10^{-3}T - 4.72 \times 10^5 T^{-2}$$

TABLE III

COLLECTED VALUES OF THERMODYNAMIC FUNCTIONS FOR Cr_3C_2, CAL./G. MOLE DEG.

Temp., °K.	$(H^0 - H^0_0)/T$	$S^0 - S^0_0$	$-(F^0 - H^0_0)/T$
25	0.1175	0.169	0.051
50	0.3887	0.648	0.259
100	2.395	3.396	1.000
150	5.115	7.592	2.477
200	7.788	12.13	4.341
300	12.17	20.54	8.363
400	15.44	27.77	12.33
500	18.11	34.18	16.07
600	20.12	39.68	19.56
700	21.70	44.49	22.79
800	22.98	48.71	25.73
900	24.10	52.64	28.54
1000	25.15	56.26	31.11
1100	26.12	59.70	33.58
1200	27.03	62.91	35.87

The only other data with which the present work may be compared are those of Moore and Kelley,[11] who employed a drop calorimeter in which the temperature rise of a large metal block is measured. Their enthalpy values are referred to 25°, and after correction has been made for the difference in reference state it is seen that the present enthalpy data lie somewhat below theirs. The maximum disparity occurs at 970°K. where the percentage discrepancy is 1.2%. It is believed that this disparity reflects more on differences in the nature of the samples than on calorimetric technique. The presence of residual Cr_2O_3 is particularly effective in raising the apparent heat capacity of the sample. Because the present sample of carbide was prepared at a much higher temperature than that of Moore and Kelley, and because higher temperatures favor the formation[12] of Cr_3C_2 and CO, the present sample probably has the lower oxide content. The low-temperature values of heat capacity for this sample[9] are also somewhat lower than those of Kelley and Moore[13] in the low-temperature range.

In Table III are collected smoothed values of $(H^0 - H^0_0)/T$, $(S^0 - S^0_0)$, and $-(F^0 - H^0_0)/T$ at even values of absolute temperature. The results of DeSorbo[9] have been incorporated in order to have all quantities referred to 0°K.

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[9] W. DeSorbo, THIS JOURNAL, **75**, 1825 (1953).

[10] C. H. Shomate, *ibid.*, **66**, 928 (1944).

[11] G. E. Moore and K. K. Kelley, *Bur. of Mines Tech. Paper* No. 662, 10 (1944).

[12] K. K. Kelley and F. S. Boericke, *ibid.*, 28 (1944).

[13] K. K. Kelley and G. E. Moore, *ibid.*, 6 (1944).