vestigators. Ubbelohde[10] also observed a marked increase of the heat capacities below the melting point of *n*-tetradecane, *n*-pentadecane, *n*-hexadecane and *n*-octadecane Pitzer,[11] in studies of the heat capacities of ethylene dichloride and dibromide, found a gradual increase in the heat capacity of the crystals which he attributed to the beginning of rotation of the whole molecules about their long axes. From a study of the change of dielectric constant with temperature of some long-chain alkyl alcohols, amines and bromides, Hoffman and Smyth[12] observed that a marked increase in dielectric constant takes place below the melting point and attributed this to the gradual onset of molecular rotational freedom. This phenomenon has been termed "prerotation."[13] From X-ray studies, Müller[14] concluded that *n*-paraffin molecules tend to rotate about their longitudinal axes at temperatures below their melting points. The specific heat measurements on the normal paraffins, below their melting and transition temperatures, accord with the concepts of Pitzer, Hoffman and Smyth, and Müller. However, from the heat capacity data alone it can only be said that an abnormal energy-absorbing process occurs below the melting or transition temperatures and that the effect of this phenomenon is too large to attribute to heterophase premelting.

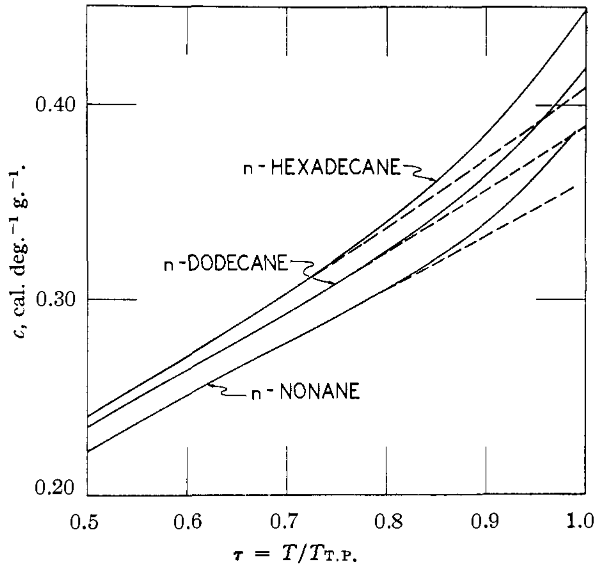

Fig. 2.—Specific heat *vs.* reduced-temperature curves for several *n*-paraffins.

BARTLESVILLE, OKLA.

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[11] K. S. Pitzer, THIS JOURNAL, **62**, 331 (1940).

[12] J. P. Hoffman and C. P. Smyth, *ibid.*, **71**, 431 (1949); *ibid.*, **71**, 3591 (1949); *ibid.*, **72**, 171 (1950).

[13] C. P. Smyth, *Trans. Faraday Soc.*, **42A**, 175 (1946).

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Thermodynamics of the In–In_2S_3 System

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The phase diagram for In–In_2S_3 (previously published) indicated the probable existence of four sulfides of indium, In_2S_3, In_3S_4, In_5S_6 and InS. In the present work each of these compounds was prepared by melting together the calculated amounts of indium metal and In_2S_3 under a helium atmosphere. Each compound was then reduced at various temperatures with hydrogen gas in a dynamic system so that the exit gases could be analyzed for hydrogen and hydrogen sulfide. From the equilibrium data obtained, free energies of reaction for each reduction were obtained. From these values, free energies of formation for each of the four sulfides of indium were calculated. Free energies of each reaction as a function of temperature are shown graphically.

Published literature gives no values for the thermodynamic properties of the sulfides of indium. The phase diagram for the In–In_2S_3 system previously published[1] showed that the In–In_2S_3 system was quite complex, and indicated the probable existence of four sulfides of indium: In_2S_3, (In_3S_4), (In_5S_6) and InS. An attempt has been made to calculate the thermodynamic values of these compounds from the equilibrium constants obtained by reduction of these sulfides with hydrogen. The results help to give a more coherent picture of the In–In_2S_3 system, and agree well with the results of the thermal analysis.[1]

Experimental Part

The equilibrium values for the reduction of the sulfides of indium were determined in a dynamic system similar to the one previously described[2] which was modified to permit analysis of the exit gases for hydrogen and hydrogen sulfide. The charge of 10–12 g. of the various sulfides was suspended on washed and ignited asbestos in the Vycor reaction tube. The incoming gas passed into the reaction tube at a rate of 5–10 cc. per minute. The total volume of the exit gases was measured in a gas buret, and the mixture was then analyzed for H_2S and H_2. When the per cent. of H_2S in the exit mixture was high, the H_2S was removed by bubbling the mixture through 44% aqueous KOH solution. The volume of H_2 collected over the KOH solution was then determined, and the volume of H_2S was determined by difference. When the amount of H_2S in the exit mixture was small, titration with standard iodine solution, by means of a Tutwiler apparatus, provided the determination. In the case of the reduction of In_2S_3, where the value of the equilibrium constant ($K_e = p_{H_2S}/p_{H_2}$) was large, the equilibrium was approached from both sides, and separate determinations were made with pure H_2, pure H_2S, and mixtures of the two as incoming gases. In the case of all the other sulfides, where the value of the equilibrium constant was small, pure H_2 was

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[1] M. F. Stubbs, J. A. Schufle, A. J. Thompson and J. M. Duncan, THIS JOURNAL, **74**, 1441 (1952).

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the only incoming gas used. The In_2S_3 was prepared as previously described.[1] Table I gives equilibrium data for the system

$$3In_2S_3(s) + H_2(g) \rightleftharpoons 2In_3S_4(s) + H_2S(g) \text{ at } 960°$$

Table II gives a summary of the experimental results for this system at the seven different temperatures studied.

TABLE I

Inlet mixture	Rate of flow, cc./min.	Exit mixture H_2S (cc. at S.T.P.)	Exit mixture H_2 (cc. at S.T.P.)	K_e (P_{H_2S}/P_{H_2})
Pure H_2	5	7.82	23.58	0.33
Pure H_2	5	8.57	23.59	.36
Pure H_2	5	8.08	23.22	.35
Pure H_2	5	8.00	23.30	.34
Pure H_2	5	8.01	22.72	.35
Pure H_2	5	8.24	22.64	.36
Pure H_2	5	8.06	22.75	.35
Pure H_2S	5	7.89	23.16	.34
Pure H_2S	5	8.04	23.01	.35
Pure H_2S	5	7.93	21.99	.36
50% H_2S-H_2	5	7.53	23.22	.32
50% H_2S-H_2	5	7.84	23.12	.34
50% H_2S-H_2	5	7.62	23.24	.33
			Av. =	.35
			Stand. dev. =	.01

TABLE II

Temp., °K.	No. of trials	K_e (Dev. = stnd. dev.)	$\Delta F = -RT \ln K_e$ (cal. per $3In_2S_3$)
873	12	0.011 ± 0.001	7900
923	22	.019 ± .002	7300
973	14	.033 ± .002	6600
1022	10	.051 ± .003	6000
1075	9	.070 ± .002	5700
1127	11	.115 ± .006	4900
1181	20	.24 ± .01	3400
1233	13	.35 ± .01	2600

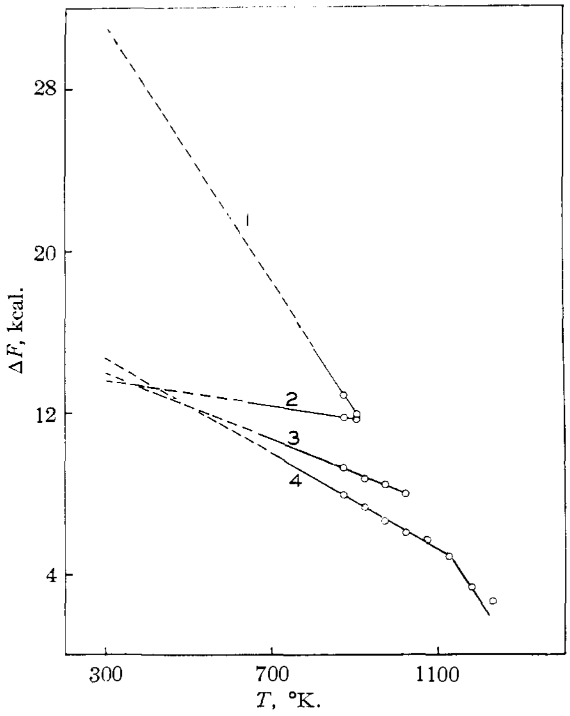

Fig. 1.

Equilibrium values for the system

$$5/2In_3S_4(s) + H_2(g) \rightleftharpoons 3/2In_5S_6(s) + H_2S(g)$$

were determined with the use of a sample of indium sulfide containing 73% indium (In_3S_4 = 72.95% In). The sample was prepared by mixing together the calculated amounts of In_2S_3 and In, and heating the mixture under a helium atmosphere in a Vycor reaction tube in an induction furnace to the molten state at 1050°. The melt was then cooled to 750° and held between 725–760° for 45 minutes to allow crystals of In_3S_4 to form in the equilibrium mixture. Table III gives equilibrium data for this system.

TABLE III

Temp., °K.	No. of trials	K_e (Dev. = stnd. dev.)	$\Delta F = -RT \ln K_e$ (cal. per $5/2In_3S_4$)
873	10	0.0049 ± 0.0002	9200
923	8	.0086 ± .0001	8700
973	10	.0131 ± .0002	8400
1023	12	.0199 ± .0003	8000

Equilibrium values for the system

$$In_5S_6(s) + H_2(g) \rightleftharpoons 5InS(s) + H_2S(g)$$

were obtained by using a prepared sample of indium sulfide containing 75.0% of indium (In_5S_6 = 74.9% In). The sample was prepared as described for In_3S_4 above. Table IV gives equilibrium data for this system.

TABLE IV

Temp., °K.	No. of trials	K_e (Dev. = stnd. dev.)	$\Delta F = -RT \ln K_e$ (cal. per mole In_5S_6)
873	12	0.0011 ± 0.0001	11,800
903	3	.0015 ± .0001	11,600

Equilibrium values for the system

$$InS(s) + H_2(g) \rightleftharpoons In(l) + H_2S(g)$$

were obtained with a sulfide containing 78.0% indium (InS = 78.16% In). The sample was prepared as described above for In_3S_4, except that after the mixture was melted it was held at 660–675° for one hour. Table V gives the equilibrium data for this system.

TABLE V

Temp., °K.	No. of trials	K_e (Dev. = stnd. dev.)	$\Delta F = -RT \ln K_e$ (cal. per mole InS)
873	23	0.0006 ± 0.0001	12,900
903	6	.0013 ± .0001	11,900

The experimental results are shown graphically in Fig. 1, where ΔF for the following reactions is plotted against temperature in °K.

Line 1: $InS(s) + H_2(g) \rightleftharpoons In(l) + H_2S(g)$
Line 2: $In_5S_6(s) + H_2(g) \rightleftharpoons 5InS(s) + H_2S(g)$
Line 3: $5/2In_3S_4(s) + H_2(g) \rightleftharpoons 3/2In_5S_6(s) + H_2S(g)$
Line 4: $3In_2S_3(s) + H_2(g) \rightleftharpoons 2In_3S_4(s) + H_2S(g)$

Extrapolation of these lines to 298°K. gives ΔF_{298} for these reactions as (1) 31.6, (2) 13.6, (3) 13.8, and (4) 14.9 kcal. From these values the standard free energies of formation of the four sulfides of indium are calculated to be: InS = −39.3; In_5S_6 = −218; In_3S_4 = −139; and In_2S_3 = −101 kcal./mole.

From heat capacity data for the various reactants and products, it was calculated that the ΔF for reaction 1 above is given by the equation

$$\Delta F = 42{,}700 + 3.83\ T \ln T - 1.94 \times 10^{-3}T^2 - 58.47\ T$$

From this equation and the one for the free energy of the reduction of In_2O_3 previously published,[2] the 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.

Acknowledgment.—The authors wish to express their appreciation to the Office of Naval Research for support of this work.

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.