THERMODYNAMIC PROPERTIES OF THE GROUP VIa SULFIDES:
CrS, Mo_2S_3 AND WS_2

by

JOHN PATRICK HAGER

B. S., Montana School of Mines
(1958)

M. S., School of Mines and Metallurgy
University of Missouri
(1960)

Submitted in Partial Fulfillment
of the Requirements for
the Degree of

DOCTOR OF SCIENCE

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

August, 1969

Signature of Author
Department of Metallurgy — Signature redacted

Signature of Professor
in Charge of Research — Signature redacted

10 July 1969

Signature of Chairman of
Departmental Committee on
Graduate Research — Signature redacted

THERMODYNAMIC PROPERTIES OF THE GROUP VIa SULFIDES: CrS, Mo_2S_3 and WS_2

by

John Patrick Hager

Submitted to the Department of Metallurgy on August 18, 1969, in partial fulfillment of the requirements for the degree of Doctor of Science.

ABSTRACT

The thermodynamic properties of the metal-saturated phase of the Group VIa sulfides have been determined through a study of the effect of gas composition on the sulfidizing action of $(H_2S_{(g)} + H_{2(g)})$ mixtures passed over heated metal samples. The following equations for the standard free energy of formation of $CrS_{(c)}$, $Mo_2S_{3(c)}$ and $WS_{2(c)}$ were obtained:

$$\Delta F^o_{CrS_{(c)}} (\pm 250) = -48{,}190\ (\pm 760) + 13.27(\pm 0.52)T;\ \text{cal/1/2 g-mole } S_{2(g)}\quad (1375\text{-}1570^oK)$$

$$\Delta F^o_{Mo_2S_{3(c)}} (\pm 220) = -41{,}730(\pm 890) + 17.39(\pm 0.59)T;\ \text{cal/1/2 g-mole } S_{2(g)}\quad (1365\text{-}1610^oK)$$

$$\Delta F^o_{WS_{2(c)}} (\pm 220) = -40{,}110(\pm 920) + 18.64(\pm 0.63)T;\ \text{cal/1/2 g-mole } S_{2(g)}\quad (1370\text{-}1565^oK)$$

An additional study of the thermodynamic properties of $Cu_2S_{(\gamma)}$ provided a means of evaluating the experimental technique.

The composition of the sulfide phase, in equilibrium with chromium at 1420°K, was determined to be stoichiometric chromous sulfide. By correlating the entropies of formation of the Group VIa sulfides with the entropies of formation observed for the refractory metal carbides, nitrides and oxides, estimated values of the entropy of formation at 298°K for the mono-, sesqui- and di-sulfide phases of the refractory metals were obtained.

Thesis Supervisor: Professor John F. Elliott
Title: Professor of Metallurgy

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Professor John F. Elliott for his counsel and assistance throughout the course of this study.

Special thanks is also expressed to Professor John Chipman and Dr. T. R. Meadowcroft, formerly Assistant Professor of Metallurgy, now Research Associate, The Steel Company of Canada, Hamilton, Ontario, for their interest and many helpful suggestions.

The following persons who have contributed to the successful completion of this project are also gratefully acknowledged:

Mr. Frank Woolley for many helpful discussions;

Mr. Theodore Strow for his assistance in chemical analyses;

Mr. George Prince and Mr. Walter Correia for their glassblowing services;

Miss Barbara Westdyke for her assistance in proofreading the manuscript;

Miss Catherine A. Walsh for her excellent preparation of the final manuscript;

The National Science Foundation for their financial support of this project.

I. INTRODUCTION

The Group VIa metals, Cr, Mo and W, are characterized by high melting points and, accordingly, are utilized as high-temperature materials. The compatibility of these metals, at high temperature, with sulfur-containing gases, liquids or solids is of practical interest. In addition, several compounds formed between sulfur and the VIa metals have found application as high-temperature lubricants and catalysts. Thermodynamic measurements on the Group VIa sulfides would provide valuable information concerning the stability of the VIa metals and their sulfides in various environments. Furthermore, thermodynamic measurements should provide additional information on the nature of the chemical bond between sulfur and the VIa metals.

The thermodynamic properties that are of greatest interest are the free energy, enthalpy and entropy of formation of the metal sulfide in the standard state from its elements in their assigned reference states. These properties can be obtained indirectly from calorimetric measurements, but more directly from high-temperature equilibrium measurements. Several methods that are available for high-temperature equilibrium measurement are reviewed in the next section. In Chapter II, specific references will be given to equilibrium studies based on the equilibrium methods described below.

A. Equilibrium Methods

One method is to measure the equilibrium dissociation sulfur pressure of the sulfide over a range of temperatures by means of an effusion cell. The effusing sulfur gas consists of several species, all of which contribute to the total dissociation sulfur pressure. From a knowledge of the thermodynamic relations between the various species, the dissociation pressure of diatomic sulfur vapor, which is the reference state for sulfur above 444.6°C, can be calculated. However, simultaneous vaporization of the metal sulfide will give spurious results as the total dissociation pressure cannot now be assumed equal to the dissociation sulfur pressure. Also, as a result of the dissociation of the sulfide, the surface of the sulfide may not represent the equilibrium conditions determined by the composition of the bulk phase. Consequently, the effusion sulfur pressure will not represent the equilibrium sulfur pressure for the bulk phase.

Another method consists of equilibration between the sulfide at one temperature and at one end of a capsule, and molten sulfur at a different temperature at the other end of the capsule. Equality is assumed between the total sulfur pressure between the two ends, but not between the different molecular species. From the temperature of the molten sulfur, the temperature of the sulfide, and the thermodynamic relations between the various molecular species, the partial pressure of diatomic sulfur vapor above the sulfide phase may be calculated. However, no convenient means are available for detecting the temperature of the sulfide for which the dissociation sulfur pressure is equal to the total sulfur pressure of the molten sulfur. Only by analysis of the sulfide, before and after equilibration in the capsule, can it be determined if the sulfide dissociation pressure was greater than or less than the pressure of the molten sulfur. Accordingly, a series of equilbration experiments are required, in order to estimate the temperature for equality of total sulfur pressure. Each experiment would have to be of sufficient duration for detection of any sulfur transfer.

Galvanic cell measurements provide another method of equilibrium measurement. However, a satisfactory electrolyte for transport of the sulfide ion[$S^=$] has not been developed. Accordingly, any galvanic cell would require an electrolyte which would transport the metal ion of the sulfide phase. In addition, the sulfide and electrolyte would have to be mutually insoluble. The applicability of galvanic cells at high temperature is further limited by the availability of compatible materials for construction of the cell.

One widely used equilibrium method is equilibration of the sulfide phase with a gas mixture of ($H_2S_{(g)}$ + $H_{2(g)}$). From known thermodynamic properties of $H_2S_{(g)}$, the equilibrium diatomic sulfur pressure for the sulfide can be calculated from the value of the equilibrium $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio and the temperature of the sample. Although the $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio is determined by analysis of the gas mixture at room temperature, the change in $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio, due to dissociation of $H_2S_{(g)}$ at the sample temperature, can be calculated from thermodynamic data available for the molecular species in the system H - S.

Equilibration between a sulfide phase and an ($H_2S_{(g)}$ + $H_{2(g)}$) mixture may be approached through several methods. The most direct method consists of recirculation of the gas mixture over the heated sulfide until the $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio remains constant. Equilibrium can be approached from both directions by adjusting the initial $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio. Another method consists of measuring the flow dependence of the $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio for hydrogen passed over the heated sulfide. Extrapolation of the $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio to zero flow rate is taken as the equilibrium ratio. Unfortunately, this is the condition for maximum thermal segregation of the gas mixture within the reaction system. However, both the recirculation and flow methods are limited to sulfide system that readily reach equilibrium with the gas phase. For slow reacting sulfides, an alternate method for approaching equilibration has been developed. This method is outlined in the following section.

B. Outline of this Study

The thermodynamic properties of Group VIa sulfides were determined by experimental investigation of the equilibrium $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio for the reaction

$$\frac{1}{Y}\,Me_XS_{Y(c)} + H_{2(g)} = \frac{X}{Y}\,Me_{(c)} + H_2S_{(g)} \qquad \text{(I-1)}$$

where Me = chromium, molybdenum or tungsten

Me_XS_Y = metal sulfide

The slow rate of reaction between the gas phase and the condensed phases discouraged direct equilibration with the gas phase. Consequently, an alternative procedure was developed.

Gas mixtures of varying $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio were prepared and passed over a metal sample at a fixed temperature. Samples of the same metal exposed to gas mixtures with a $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio greater than the equilibrium ratio for reaction (I-1) were sulfided on the surface, whereas samples exposed to gas mixtures with a $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio less than the equilibrium ratio for reaction (I-1) maintained a metallic surface. Accordingly, the $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio was adjusted until two ratios, differing only slightly, were obtained over which the surface changed from metallic to sulfide. The true equilibrium ratio was assumed to lie within this interval.

The amount of sulfur transferred from the gas phase to the metal surface was very small ($<$ 1 mg), but, nevertheless, it was sufficient to provide clear visual distinction between a metallic surface and a sulfided surface. However, the experimental method was limited to the study of the sulfide phase in equilibrium with the metal. The composition of the metal-saturated sulfide in reaction (I-1) was obtained from the literature or it was determined experimentally.

In addition to experiments on the metal-saturated VIa sulfides, supplementary experiments were conducted on cuprous sulfide. The equilibrium between $Cu_{(c)} + Cu_2S_{(\gamma)}$ and gas mixtures of $H_{2(g)} + H_2S_{(g)}$ had previously been studied by recirculation and flow methods. Comparison of the results obtained by these studies with those of the present study serve to establish the validity of the experimental technique.

II. LITERATURE SURVEY

A. Hydrogen-Sulfur System

A survey of available literature has been made, to obtain the most reliable thermodynamic data on gaseous species in the system hydrogen-sulfur. Accurate thermodynamic data are required for $H_2S_{(g)}$ and the species existing with $(H_2S_{(g)} + H_{2(g)})$ mixtures at high temperatures.

Equations for the ΔF_f° of $H_2S_{(g)}$, $HS_{(g)}$, $S_{(g)}$, $S_{6(g)}$ and $S_{8(g)}$ are given in Table I. The reference state for sulfur is $S_{2(g)}$ in the ideal gas state, and for hydrogen it is $H_{2(g)}$ in the ideal gas state. The equations for the ΔF_f° of $H_2S_{(g)}$, $HS_{(g)}$ and $S_{(g)}$ have been derived, by the method of least squares,[1] from tabulated ΔF_f° values given in the JANAF[2] thermochemical tables. The tabulated values of ΔF_f° $(HS_{(g)})$ have been adjusted by +3,650 cal, on the basis of Johns and Ramsay's[3] more recent determination of $D_o^\circ(HS_{(g)})$, from which the value $\Delta H_f^\circ(298.2°K) \doteq 35{,}650$cal was calculated. The equations for the ΔF_f° of $S_{6(g)}$ and $S_{8(g)}$ have been taken from Richardson and Jeffes.[4]

The literature has also been reviewed for thermodynamic measurements on the systems Cr-S, Mo-S, W-S and Cu-S, including the phase relations in these systems. The results are given in the following sections.

B. Chromium-Sulfur System

The results of x-ray studies on the phases in the system Cr-S have recently been reviewed by Jellinek[5] in a survey of the sulfides of the transition metals (see Table II). With the exception of CrS, all other chromium sulfides have narrow ranges of homogeneity separated by two phase

TABLE I

THERMODYNAMIC PROPERTIES OF SULFUR AND SULFUR-HYDROGEN GASES

Species	$\Delta F_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ$	Temperature Range
$H_2S_{(g)}$	$\Delta F_f^\circ = -21{,}570 + 11.79T$ cal ($\pm$ 200 cal)	900 - 1700°K
$HS_{(g)}$	$\Delta F_f^\circ = 20{,}070 - 3.70T$ cal ($\pm$ 3 Kcal)	900 - 1700°K
$S_{(g)}$	$\Delta F_f^\circ = 51{,}170 - 14.44T$ cal ($\pm$ 1 Kcal)	900 - 1700°K
$S_{6(g)}$	$\Delta F_f^\circ = -66{,}450 + 73.74T$ cal ($\pm$ 3 Kcal)	298 - 1300°K
$S_{8(g)}$	$\Delta F_f^\circ = -99{,}200 + 113.16T$ cal ($\pm$ 4 Kcal)	298 - 1300°K

TABLE II

PHASES IN THE Cr-S SYSTEM ACCORDING TO JELLINEK[5]

Phase	Homogeneity at 25°C	Symmetry
rh. Cr_2S_3	$CrS_{1.50}$	Rhombohedral
Tr. Cr_2S_3	$CrS_{1.45}$	Trigonal
Cr_3S_4	$CrS_{1.32}$ - $CrS_{1.27}$	Monoclinic
Cr_5S_6	$CrS_{1.18}$	Trigonal
Cr_7S_8	$CrS_{1.15}$ - $CrS_{1.14}$	Trigonal
CrS	Uncertain	Monoclinic
α-Cr	Very narrow	Cubic b.c.

regions. The homogeneity range and thermal stability of CrS is not well established.

In the first systematic study of the system Cr-S, Haraldsen[6] obtained an x-ray pattern for the phase CrS that contained a number of fairly strong additional lines which were indexed by means of a supercell. However, x-ray patterns obtained by Jellinek[7] showed that the supercell obtained by Haraldsen[6] was incorrect and that his "CrS" sample contained three phases: Cr_7S_8, CrS and Cr. For samples in the range $CrS_{1.10}$ - $CrS_{.68}$, Jellinek[7] was not able to obtain equilibrium but, rather, obtained three phases: Cr_7S_8, CrS and Cr. Konev, Bogacheva and Pavlova[8] found that the stoichiometric phase CrS was unstable at room temperature unless quenched in water from 800° to 1000°C. X-ray patterns showed lines for both Cr_5S_6 and Cr in slow-cooled samples, but only broadened CrS lines in water-quenched samples. However, Konev, Bogacheva and Pavlova[8] indexed their patterns with Haraldsen's[6] incorrect supercell of CrS, and it is not clear how this affects their conclusions. Accordingly, the composition of chromium sulfide in equilibrium with chromium metal in the temperature range of this study (1100 - 1300°C) is not apparent.

The only reported thermodynamic data are the heat capacity measurements of Fakidov and Grazhdankina[9] on Cr_5S_6 in the range 0 - 100°C.

C. Molybdenum-Sulfur System

Two molybdenum sulfide phases, MoS_2 and Mo_2S_3, are stable at high temperature. The existence of Mo_2S_3 as the sulfide phase in equilibrium with molybdenum, at temperatures of 850 - 1200°C, was established first by McCabe[10] and later by Stubbles and Richardson.[11] Gorokh, Rusakov and Savinskaya[12] also found that Mo_2S_3 was the lowest sulfide in the system Mo-S, at temperatures to 1400°C, and that on heating to 1600°C it dissociates, giving molybdenum and sulfur. Gorokh, Klokotina and Rispel,[13] studying the decomposition of MoS_2 by microscopic, chemical and x-ray analysis, found that under reducing conditions MoS_2 dissociated into Mo_2S_3 at temperatures to 1500°C. Similarly, Wildervanck and Jellinek[14] observed that hexagonal MoS_2, heated under vacuum above 1100°C, disproportionated into Mo_2S_3. Morimoto and Kullerud[15] found that reflection positions on x-ray powder patterns of Mo_2S_3, grown in equilibrium with Mo and also with MoS_2 in the range 700 - 925°C, gave identical results, thus indicating very limited solid solution over this temperature range. Schaefer, Larson and Schlechten[16] have shown, by chemical and x-ray analysis of sulfide phases equilibrated with known sulfur pressures, that the disulfide phase exhibits a solubility range of $MoS_{1.99}$ - $MoS_{2.23}$ at 1100°C. In addition, these investigators found that the solubility of sulfur in molybdenum was 1.49 atomic percent at 1100°C, and that Mo_2S_3 was stoichiometric when in equilibrium with MoS_2 at 1100°C. The results of structure determinations on MoS_2 and Mo_2S_3 are reviewed by Jellinek.[5]

Thermodynamic measurements on molybdenum sulfide were first reported by Parravano and Malquori.[17] The equilibrium $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio for the system $Mo_{(c)}$ - $MoS_{2(c)}$ at 800 - 1100°C was determined by extrapolating to zero flow rate the $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio resulting from passage of $H_{2(g)}$ over a mixture of Mo + MoS_2. However, McCabe[10] and Stubbles and Richardson[11] have shown that Mo_2S_3 and not MoS_2 is the sulfide in equilibrium with molybdenum. In addition, Richardson and Jeffes[4] have pointed out that the numerical value of the entropy of formation of MoS_2, calculated from Parravano and Malquori's[17] data, is suspiciously low. Accordingly, the thermodynamic properties of MoS_2, determined by Parravano and Malquori,[17] are not considered reliable. Similarly, Zelikman and Krein[18] have studied the reaction $MoS_{2(c)} + 2H_{2(g)} = Mo_{(c)} + 2H_2S_{(g)}$; however, since $MoS_{2(c)}$ cannot be in equilibrium with $Mo_{(c)}$, their results also appear to be spurious.

The equilibrium $S_{2(g)}$ pressure for the reaction $4/3\ Mo_{(c)} + S_{2(g)} = 2/3\ Mo_2S_{3(c)}$ was determined by McCabe[10] from weight loss measurements on Knudsen effusion cells containing $Mo_2S_{3(c)} + Mo_{(c)}$, together with the free energy of reaction $S_{2(g)} = 2S_{(g)}$, according to Richardson and Jeffes.[4] Their results are expressed in the following equation:

$$\Delta F^\circ_{f(2/3Mo_2S_3)} = -\ 96,800 + 41.8T \text{ cal}(\pm 10 \text{ Kcal})(1300\text{-}1425^\circ K) \qquad (II\text{-}1)$$

Correction of these results, due to more recent data[2] on the equilibrium $S_{2(g)} = 2S_{(g)}$, will be discussed in Chapter VI. Several runs were required, in order to obtain constant weight losses per unit time, indicating that considerable time was required to allow the sulfide and metal to adjust their compositions to the equilibrium values.

Stubbles and Richardson[11] studied the equilibria $1/3Mo_2S_{3(c)} + H_{2(g)} = 2/3Mo_{(c)} + H_2S_{(g)}$ and $2MoS_{2(c)} + H_{2(g)} = Mo_2S_{3(c)} + H_2S_{(g)}$

by equilibration of the condensed phases with a recirculating gas mixture of $H_2S_{(g)} + H_{2(g)}$. By introducing a small proportion of radio-sulfur into the stable sulfur used for synthesis of the sulfides, and incorporating and end-window Geiger-Müller counter in the gas circulation apparatus, the approach to equilibrium could be observed and the $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio could be measured without removing gas samples. Equilibration periods as long as 96 hours were required for $Mo_2S_3 + MoS_2$ samples, indicating slow diffusion of sulfur in molybdenum sulfide. The experimental results are given by the following equations:

$$\frac{1}{3} Mo_2S_{3(c)} + H_{2(g)} = \frac{2}{3} Mo_{(c)} + H_2S_{(g)}: 850 - 1200°C \qquad \text{(II-2)}$$

$$\Delta F^\circ_R = +21,270 - 6.4T\text{cal} \ (\pm\ 100\text{cal}) \qquad \text{(II-3)}$$

$$\Delta H^\circ_R = +21,270\text{cal} \ (\pm\ 1\text{Kcal}) \qquad \text{(II-4)}$$

$$\Delta S^\circ_R = +\ 6.4 \text{ cal/deg} \ (\pm\ 1 \text{ cal/deg}) \qquad \text{(II-5)}$$

$$2MoS_{2(c)} + H_{2(g)} = Mo_2S_{3(c)} + H_2S_{(g)}: 1000 - 1200°C \qquad \text{(II-6)}$$

$$\Delta F^\circ_R = +21,610 \text{ cal} - 8.23T\text{cal} \ (\pm\ 100\text{cal}) \qquad \text{(II-7)}$$

$$\Delta H^\circ_R = +21,610 \text{ cal} \ (\pm\ 2 \text{ Kcal}) \qquad \text{(II-8)}$$

$$\Delta S^\circ_R = +8.23 \text{ cal/deg} \ (\pm\ 2 \text{ cal/deg}) \qquad \text{(II-9)}$$

Stubbles and Richardson[11] found that equilibrium $S_{2(g)}$ pressures for $Mo_{(c)} + Mo_2S_{3(c)}$ derived from their results were larger by a factor of ten than those derived by McCabe[10] from Knudsen effusion measurements. This they assumed was most likely due to a very small vaporization coefficient for $S_{2(g)}$ from $Mo_2S_{3(c)}$, which McCabe[10] had assumed as being unity.

D. Tungsten-Sulfur System

The only phase in the system W-S which has been synthesized from the elements is the disulfide WS_2.[5] According to Ehrlich,[19] hexagonal WS_2 prepared from the elements is homogeneous over a small range of compositions from approximately $WS_{1.95}$ to $WS_{2.00}$. Similarly, Glemser, Sauer and König[20] found that for mixtures of composition $WS_{0.1}$ to $WS_{3.0}$ heated in quartz capsules under N_2 at 900°C only one thermally stable phase was formed, namely, WS_2. Samoilov and Rubinshtein[21] studied the composition and structure of WS_2 catalysts obtained by the decomposition of ammonium sulfotungstate at 400°C, followed by heating under N_2 to 600 - 1000°C. Their results show only one phase, WS_2, in the composition range $WS_{1.86}$ - $WS_{2.30}$; however, the parameters of the WS_2 lattice did not depend on the S/W ratio in the WS_2 catalysts, as would be expected for true solid solution within the WS_2 phase. Shchukarev, Morogova and Damen,[22] on the other hand, have shown quite clearly the absence of a homogeneity range in WS_2. In addition to an x-ray study of preparations of various S/W ratios, the results of which were in complete agreement with Ehrlich,[19] a series of isopiestic experiments were carried out. Two weighed WS_X preparations of different composition, where X was less than 2.0, were placed in a quartz ampoule, the ampoule evacuated, filled with $H_{2(g)}$, and then treated at 600°C for 200 hours. From weight measurements, it was observed that no transfer of sulfur took place, thus clearly indicating the absence of a region of homogeneity extending in the direction of higher metal content than that given by the formula WS_2. In addition, the absence of sulfur transfer between preparations containing very little sulfur and preparations of the composition $WS_{1.98}$ indicates the absence of intermediate compounds between W and WS_2. Similarly, Wildervanck and Jellinek[14] found that WS_2 heat treated at 1100°C has a hexagonal structure similar to that determined by Ehrlich.[19] In addition, no evidence could be found for the existence of a lower sulfide, such as W_2S_3.

Parravano and Malquori[17] have measured the quantity of $H_2S_{(g)}$ entrained in $H_{2(g)}$ passed over a $W\text{-}WS_2$ mixture at temperatures from 795 - 1065°C. By extrapolation, they have obtained the $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio at zero flow rate and have taken this as the equilibrium ratio, which, unfortunately, is the condition for maximum thermal segregation. By making an approximate correction for thermal segregation, and combining the corrected results with the free energy equation for $H_2S_{(g)}$, Richardson and Jeffes[4] have derived the following equation:

$$\Delta F^\circ_f(WS_{2(c)}) = -62{,}360 + 23.0T\text{cal}(\pm\ 10\ \text{Kcal})(298 - 1400°\text{K}) \qquad \text{(II-10)}$$

Cerny, Habes, Zelena and Erdos[23] have studied the equilibrium $1/2\ WS_{2(c)} + H_{2(g)} = 1/2\ W_{(c)} + HS_{(g)}$ by the emf measurements on the cell

$$W|WS_2|H_2S\ (1\ \text{atm})|KCl(0.1M)||KCl\ (0.1M)|H_2\ (1\ \text{atm})|Pt$$

in the temperature range 15 - 45°C, and by analysis of the $H_2S_{(g)}$ concentration in $H_{2(g)}$ passed over a W + WS_2 mixture at temperatures from 380 - 500°C. However, the results obtained are in poor agreement, as indicated by the following equations:

$$1/2\ WS_{2(c)} + H_{2(g)} = 1/2\ W_{(c)} + H_2S_{(g)} \tag{II-11}$$

$$\Delta F^\circ_R = 22{,}170 - 7.47\ T\ \text{cal};\ 288 - 318^\circ K \tag{II-12}$$

$$\Delta F^\circ_R = 19{,}070 - 1.20\ T\ \text{cal};\ 653 - 773^\circ K \tag{II-13}$$

It is doubtful whether equilibrium could have been established between the gas phase and W + WS_2 at the temperatures of this study. According to the calorimetric measurements of Hartmann and Wagner,[24] the heat of formation of $WS_{2(c)}$ is as follows:

$$\Delta H^\circ_f(WS_{2(c)}) = -\ 47.9\ \ \text{Kcal/gfw}\ (\pm\ 0.8\ \text{Kcal})\qquad T = 298^\circ K \tag{II-14}$$

Freeman,[25] according to a private communication from R. L. Nuttall, lists the $\Delta H^\circ_f(WS_{2(c)})$ at 298°K as -71.3 Kcal/gfw. The heat of formation of $WS_{2(c)}$ at 298°K, according to Rossini, Wagman, Evans, Levine and Jaffe,[26] is -46.3 Kcal/gfw.

E. Copper-Sulfur System

The sulfide phase in equilibrium with copper, at temperatures to 1067°C, is Cu_2S (chalcocite). By means of high-temperature x-ray and thermal analysis, three polymorphic forms of Cu_2S have been determined. Ueda[27] observed a phase change at 105°C for the transition from orthorhombic, α-Cu_2S, to hexagonal, β-Cu_2S, and another at 450°C for hexagonal, β-Cu_2S, to cubic, γ-Cu_2S. Djurle[28] found the α-Cu_2S to β-Cu_2S transition at 110°C, and the β-Cu_2S to γ-Cu_2S transition at 470°C. The phase diagram of the system Cu-S was studied by Wehefritz[29] between 300 and 450°C, by aid of radiographic investigations of the structure, coulometric titrations, emf measurements, and electrical conductivity measurements. The equilibrium temperature of β-Cu_2S and γ-Cu_2S was observed at 430°C($\pm$ 8°C), and the measured enthalpy of conversion was 110 cal/mole ($\pm$ 40 cal/mole). The composition of the phase in equilibrium with copper at 443°C was $Cu_{1.999}S$. Johannsen and Volmer[30] by means of microscopic analysis and cooling curves have found that the phase in equilibrium with copper at high temperature (to 1067°C) is stoichiometric Cu_2S, and that solid solution occurs only for an excess of S and Cu_2S. The measured heat of fusion for Cu_2S was 2700 cal/g-mole ($\pm$ 35 cal/g-mole).

The equilibrium $Cu_2S_{(\gamma)} + H_{2(g)} = 2Cu_{(c)} + H_2S_{(g)}$ has been studied by a series of investigators. Cox, Bachelder, Nachtrieb and Skapski[31] measured the equilibrium $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio by means of the recirculation method at temperatures from 700 to 1045°C. However, their circulation rate of 60 ml STP/min for a one inch-bore reaction tube may not have been sufficient to prevent thermal segregation. Sudo[32] measured the effluent $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio for $H_{2(g)}$ flow over a sample of $Cu_{(c)} + Cu_2S_{(\gamma)}$ at 725 - 875°C. The reaction chamber was especially designed to eliminate thermal segregation; however, the composition of the exit gas of a single-pass flow system will vary in a complicated manner, depending upon the flow rate, the rate of thermal diffusion, the rate of reaction and the design of the reaction bed, and it seems difficult to evaluate the linear extrapolation of the $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ values to zero flow rate in the absence of specific knowledge of the effects of these variables. Brooks[33] and Richardson and Antill[34] have measured the equilibrium $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio by the recirculation method, with a particular effort to eliminate the effect of thermal segregation. The results of the above series of investigations are tabulated in Table III. The equilibrium between $Cu_2S_{(\gamma)} + Cu_{(c)} + H_{2(g)} + H_2S_{(g)}$ also has been studied by Tanka, Watanabe and Kurihara[35] and Kihira and Sano,[36] but their results are not included in Table III. These results are badly scattered and in poor agreement with the more consistent results of the other investigators.

J. B. Wagner and C. Wagner[37] have determined the free energy change of the displacement reaction $2Cu_{(c)} + PbS_{(c)} = Cu_2S_{(\beta)} + Pb_{(c,\ell)}$ by emf measurements on the cell $Cu|CuBr|Cu_{1.98}S|(Cu_{1.98}S, PbS)|(PbCl_2 + 1\% KCl|Pb$ and have calculated a value of -22,607 cal for the standard free energy of formation of β-Cu_2S at 300°C.

TABLE III

RESULTS FROM PREVIOUS INVESTIGATORS FOR THE EQUILIBRIUM:

$Cu_2S_{(\gamma)} + H_{2(g)} = 2Cu_{(c)} + H_2S_{(g)}$

T, °K	ΔF°_R, cal	Investigator(s)
972	14,050	Cox, Bachelder, Nachtrieb and Skapski[31]
1069	14,770	
1071	14,870	
1168	14,960	
1273	15,830	
1273	15,640	
1317	15,420	
1000	14,250	Sudo[32]
1048	14,320	
1097	14,610	
1145	14,880	
934	14,060	Brooks[33]
937	14,050	
994	14,300	
1102	14,840	
1104	14,820	
1309	15,910	
1311	15,920	
1000	14,290*	Richardson and Antill[34]
1100	14,720	
1200	15,180	
1300	15,620	

* Richardson and Antill[34] did not tabulate their experimental results, but represented them by the equation

$$\Delta F^\circ_R = 9{,}840 + 4.45\ T\ \text{cal}$$

from which the following values are calculated.

III. APPARATUS AND EXPERIMENTAL PROCEDURE

The experimental method consisted of observing the sulfidizing action of ($H_2S_{(g)} + H_{2(g)}$) mixtures on metal samples at high temperature. By adjusting the composition of the gas mixture, it was possible to either sulfide the surface of a sample or have it remain metallic. Through a systematic variation of the $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio between samples of the same metal and at the same temperature, two limiting values of the gas ratio were obtained. These values which only differed slightly corresponded to the largest value of the gas ratio, for which the surface remained metallic, and to the smallest value of the gas ratio, for which the surface was sulfided. The equilibrium $P_{H_2S_{(g)}}/P_{H_2}$ ratio was assumed to lie within these two values. The temperature dependence of the equilibrium ratio was determined by repeating the systematic search procedure for several temperatures. A detailed description of the apparatus and the experimental procedure is given below.

A. Description of Apparatus

1. Furnace and Sample Loading Mechanism

A schematic view of the furnace and sample loading mechanism is shown in Fig. 1. Temperatures to 1350°C were obtained with a platinum-wound resistance furnace (A). The dimensions of the furnace tube were 35mm I.D. x 66 cm. An alumina support tube (B), with dimensions of 20 mm I.D. x 80 cm, was placed concentrically within the furnace tube and clamped in position. The ends of the support tube were fitted with water-cooling coils (L) to prevent overheating of the rubber stoppers (K). The alumina reaction tube (C), having the dimensions 6mm I.D. x 90 cm,

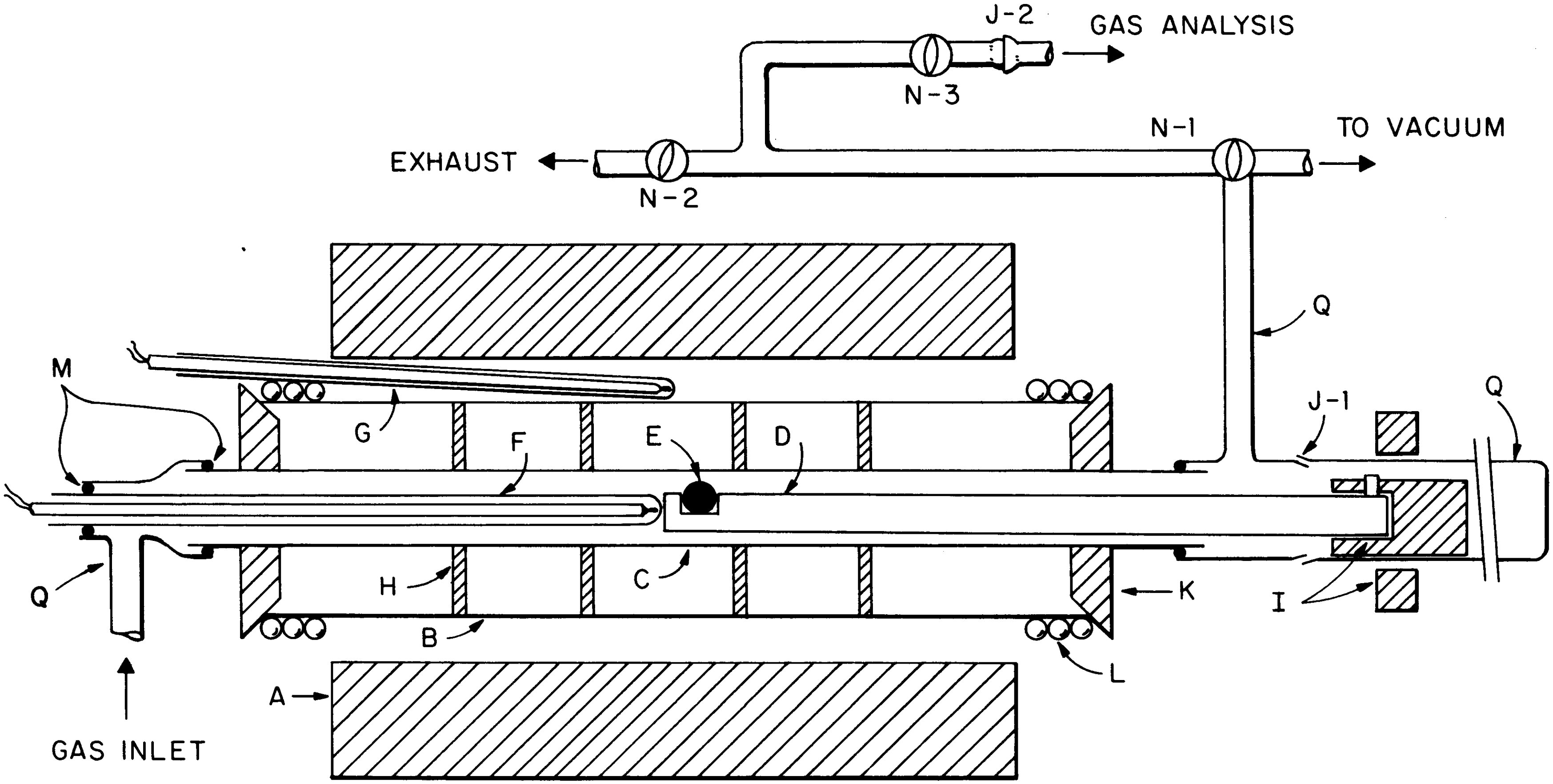

FIG. 1 - SCHEMATIC VIEW OF FURNACE AND SAMPLE LOADING MECHANISM; A, Pt-WOUND FURNACE; B, ALUMINA SUPPORT TUBE; C, ALUMINA REACTION TUBE; D, ALUMINA SAMPLE HOLDER; E, SAMPLE; F, MEASURING THERMOCOUPLE; G, CONTROLLING THERMOCOUPLE; H, ALUNDUM RADIATION SHIELD; I, MAGNETIC LOADING DEVICE; $J_{1,2}$, GLASS JOINTS; K, RUBBER STOPPER; L, COOLING COIL; M, WAX JOINTS; $N_{1,2,3}$, STOPCOCKS; Q, GLASS TUBING.

was supported at the ends by the stoppers (K), and was supported internally by the alundum radiation shields (H). Gas-tight connections at both ends of the reaction tube were made by air-cooled wax joints (M) between the alumina and glass tubing (Q). The sample (E) rested in a notch at the end of an alumina sample holder (D), having the dimensions 4.8mm O.D. x 60 cm. The sample holder could be inserted or removed from the reaction tube, without opening the reaction tube to the outside atmosphere, by means of the magnetic loading device (I). The magnetic loading device consisted of an iron plug machined to slide in the glass tubing and two external permanent magnets for moving the iron plug within the tubing. A ground-glass tapered joint (J-1) permitted convenient changing of the sample.

2. Temperature Control and Measurement

The temperature of the furnace was controlled by a Honeywell Brown Electronik controller actuated by a Pt-13% Rh/Pt thermocouple (G) placed between the furnace tube and the support tube. The on-off switch in the controller was shunted with a variable resistor to give a high-low control action. A control of ± 0.5°C was obtained during the course of a run (2 - 3 hours). The temperature of the sample was measured with a Pt-10% Rh/Pt thermocouple inserted in a 4mm O.D. alumina protection tube (F) and positioned against the end of the sample holder.

The temperature of the measuring thermocouple was determined from the emf reading and the standard conversion table.[38] At the completion of all the experimental runs, the measuring thermocouple was calibrated against the melting point of pure silver (960.8°C) and pure copper (1083°C), and found to be 16μv and 18μv low, respectively, relative to the standard table. Accordingly, all measuring thermocouple temperatures were corrected by + 1.5°C in the range 700 - 1000°C, and by + 1.4°C in the range 1000 - 1350°C. The combined uncertainty in the calibration correction, corresponding to the uncertainty in the melting point of the silver and copper, the imprecision of the potentiometer, and the absence of an additional calibration at the start of the experiments, was estimated as ± 0.8°C.

The correction between measuring thermocouple temperature and sample temperature was obtained from Fig. 2. The data points in Fig. 2 were calculated from the temperature gradient in the reaction tube, measured as a function of temperature, and the distance between the thermocouple element and the center of the sample ($\approx$10mm). The combined uncertainty in the correction taken from Fig. 2, corresponding to the uncertainty of ± 3mm in the thermocouple sample distance and the uncertainty in the temperature gradient was estimated as ± 2.5°C.

3. Gas Mixing System

A schematic view of the gas train is shown in Fig. 3. With the exception of short lengths of tygon tubing to connect the gas cylinders to the train and for connection (F) of the flow control bubblers (B), the gas train was of all-glass construction. Gas flow rates were measured with calibrated capillary flowmeters (A). The flow rate of gas through a capillary flowmeter was adjusted by the depth of immersion of the bubble tube within the flow control bubbler. The flow control bubblers were filled with tetrabromoethane (density, 3.0g/ml). A flow of gas through the bubbler was constantly maintained, not only to provide constant flow rates but to prevent contamination of the gas stream with tetrabromoethane.

The gas train was designed for delivery of pure $H_{2(g)}$, of

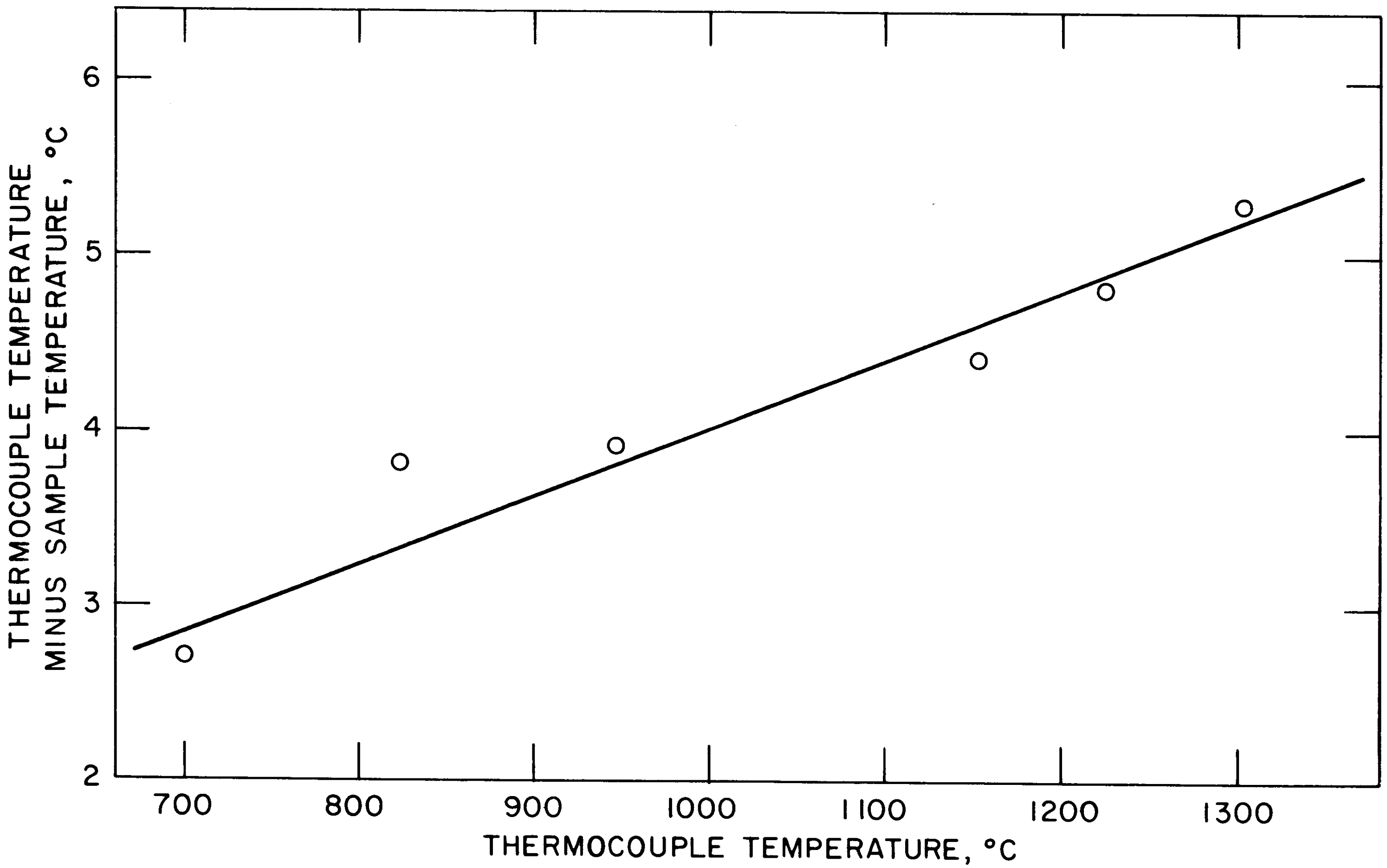

FIG. 2-CORRELATION BETWEEN THERMOCOUPLE AND SAMPLE TEMPERATURE

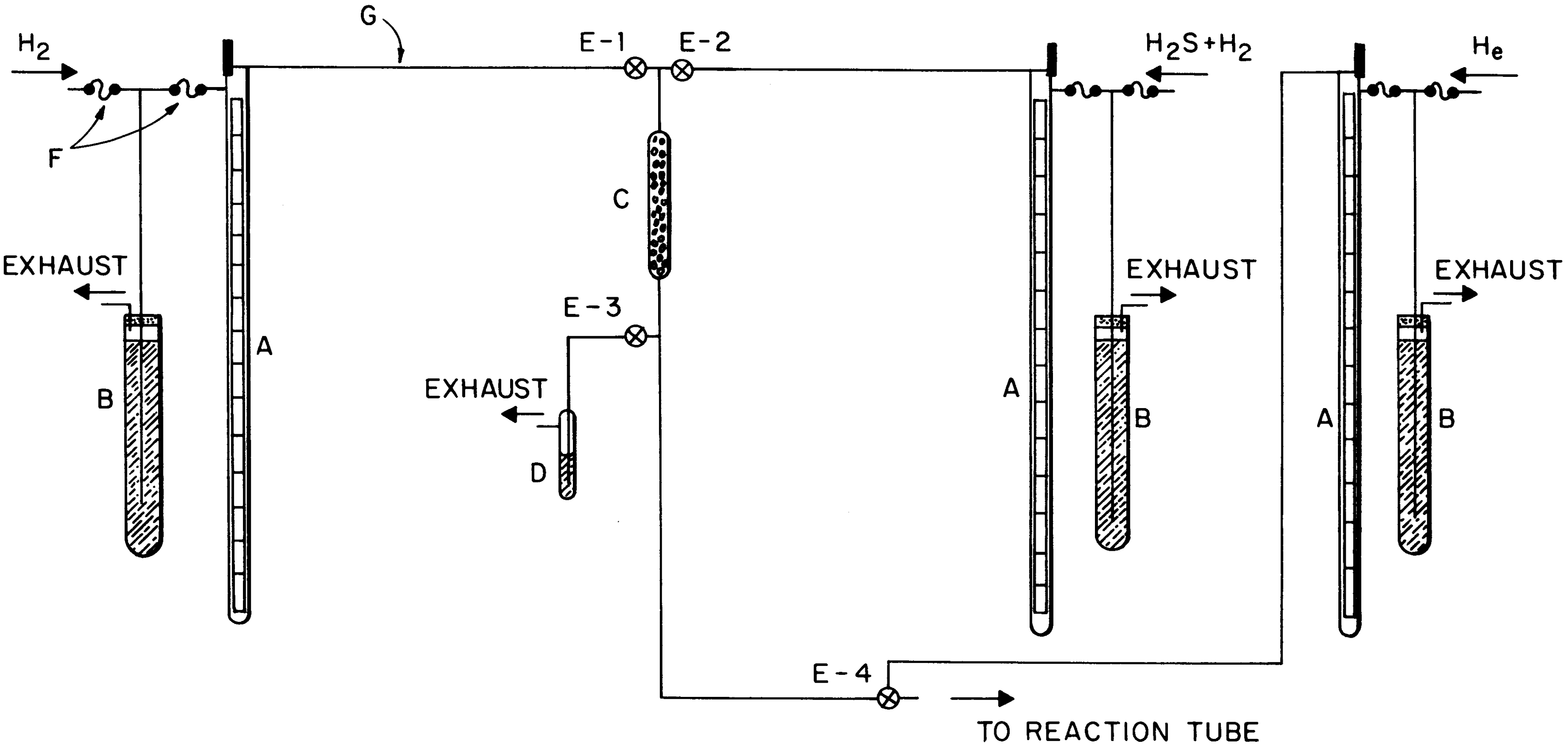

FIG. 3-SCHEMATIC VIEW OF GAS TRAIN; A, CAPILLARY FLOWMETER; B, FLOW CONTROL BUBBLER; C, MIXING COLUMN; D, BY-PASS BUBBLER; $E_{1,2,3,4}$ STOPCOCKS; F, TYGON TUBING; G, GLASS TUBING

mixtures of ($H_2S_{(g)} + H_{2(g)}$) of controlled composition, or of pure $He_{(g)}$ to the reaction tube. A gas mixture having the desired $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio was prepared by adjusting the flow rates of pure $H_{2(g)}$ and of the commercially prepared mixture of ($H_2S_{(g)} + H_{2(g)}$). To insure perfect mixing, the combined gas streams were passed through a mixing column (C) packed with porcelain beads. The by-pass bubbler (D) was provided, in order to allow the diversion of the gas stream from the reaction tube.

4. Gas Analysis Apparatus

The gas analysis apparatus is shown schematically in Fig. 4. The amount of $H_2S_{(g)}$ in an ($H_2S_{(g)} + H_{2(g)}$) mixture was determined by iodimetric titration in a 500 ml tutwiler burette (A). The volume of gas taken in for analysis was adjusted by the leveling bottle (C) containing an aqueous solution of soluble starch and potassium iodide. Then a standardized iodine solution was admitted slowly from the glass-stoppered calibrated reagent reservoir. The titration was continued to the starch-iodine endpoint.

Analyses of the gases were obtained by drawing a sample into the tutwiler burette (a) directly from the regulator of a tank of commercially prepared ($H_2S_{(g)} + H_{2(g)}$) mixture, (b) from stopcock E-4 (Fig. 3) for the prepared reaction gas, or (c) from joint J-2 (Fig. 1) for the effluent gas stream.

B. Experimental Procedure

1. Materials and Material Preparation

High-purity chromium was supplied by the Materials Research Corporation in the form of iodide-process crystallites (purity 99.997%).

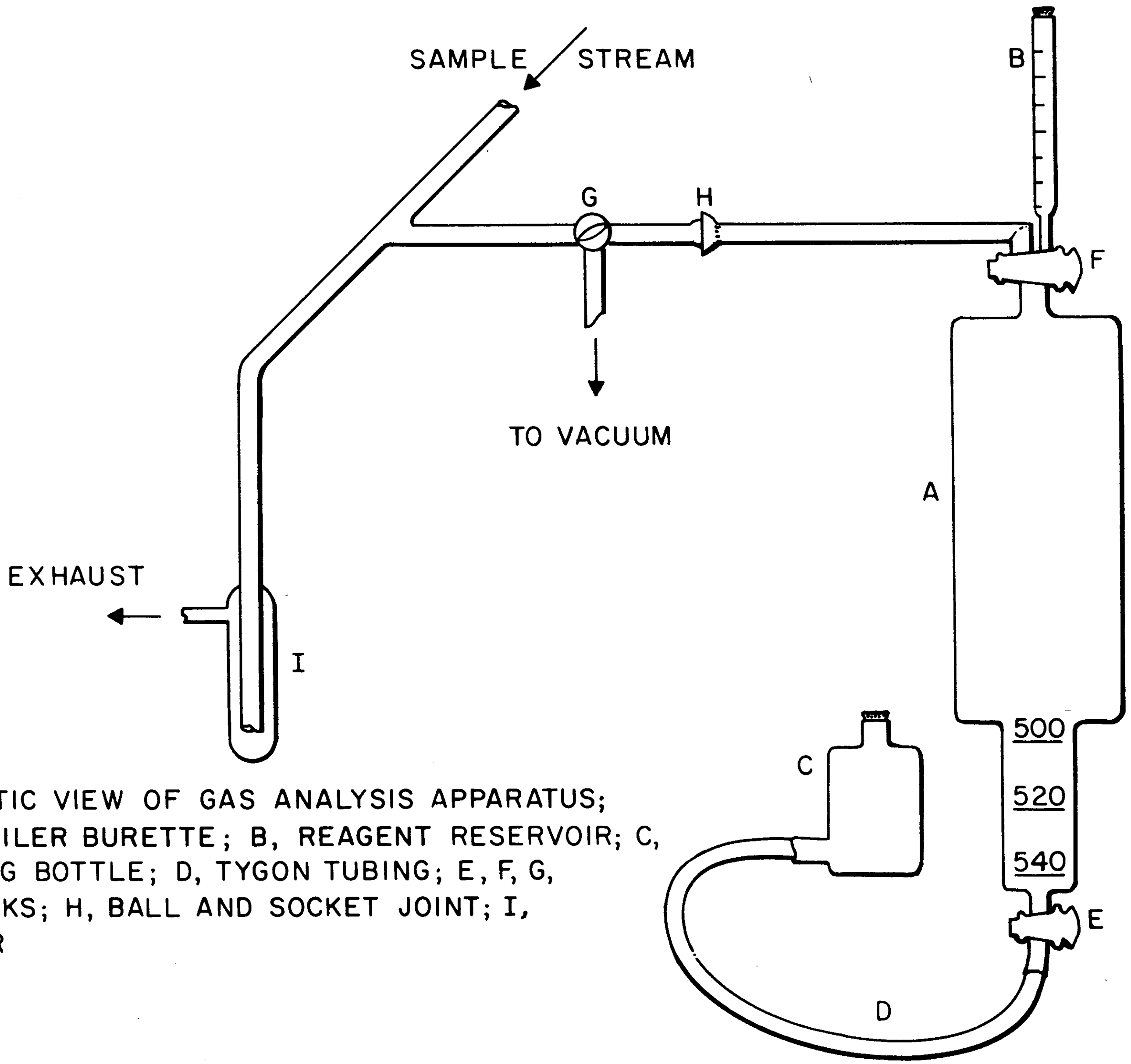

FIG. 4 - SCHEMATIC VIEW OF GAS ANALYSIS APPARATUS; A, TUTWILER BURETTE; B, REAGENT RESERVOIR; C, LEVELING BOTTLE; D, TYGON TUBING; E, F, G, STOPCOCKS; H, BALL AND SOCKET JOINT; I, BUBBLER

The crystallites were crushed with a porcelain mortar and pestle to give samples roughly in the shape of a rectangular parallelepiped 2mm x 2mm x 4mm. Samples of tungsten and molybdenum, approximately 3mm x 4mm long were cut from 0.005 inch annealed sheet (purity 99.95%) supplied by the General Electric Company. Similar sized samples of copper were cut from 0.005 inch annealed sheet (purity 99.9%) supplied by Baker and Adamson.

All of the gases were supplied by The Matheson Company. The hydrogen was ultra-high purity grade (99.999% H_2, <1ppm O_2, <0.5ppm H_2O) and the helium was high purity grade (99.995% He). The mixtures of ($H_2S_{(g)}$ + $H_{2(g)}$) were prepared from C.P. grade hydrogen sulfide (99.5% H_2S) and prepurified hydrogen (99.95% H_2, <20ppm O_2, <1ppm H_2O) and shipped in low pressure (200 psi) aluminum tanks. Use of aluminum tanks assured the stability of the mixtures over long periods of time. Chemical analysis of the ($H_2S_{(g)}$ + $H_{2(g)}$) tanks showed no detectable change of composition with time.

2. Flowmeter Calibration

The hydrogen and helium flowmeters were calibrated by measuring the rate of displacement of a soap bubble in a volumetrically-calibrated glass tube. The hydrogen flowmeter was calibrated at the start of the experimental study, again during the course of the experiments, and then at the completion of the experimental runs. No change in the calibration could be detected.

A modified technique was used for the direct calibration of the ($H_2S_{(g)}$ + $H_{2(g)}$) flowmeter. In-as-much as a stable soap bubble could not be formed in the presence of $H_2S_{(g)}$, a long coil of tygon tubing was inserted between the flowmeter and the bubble tube and purged with helium. Then helium was displaced by the flow of ($H_2S_{(g)}$ + $H_{2(g)}$), and the flow rate of the mixture was obtained with the passage of helium into the bubble tube. The ($H_2S_{(g)}$ + $H_{2(g)}$) flowmeter was calibrated for each of the following ($H_2S_{(g)}$ + $H_{2(g)}$) tanks, corresponding to the four metal-metal sulfide systems studied: 0.220% H_2S(Cr-CrS), 1.120% H_2S(Cu-Cu_2S), 10.75% H_2S (Mo-Mo_2S_3) and 42.36% H_2S(W-WS_2). The compositions were determined by the analytical procedure outlined in the next section.

Analysis of the effluent gas stream of the reaction tube indicated an error in the flowmeter calibration curve for the 42.36% H_2S tank. The flow rate given by the calibration plot, logarithm of flow rate versus logarithm of pressure drop across capillary, as expressed in displacement of the manometer fluid (dibutyl phthalate), appeared to be 8% low. In addition, examination of the calibration plots, straight lines on the log-log graph, for pure H_2, 0.220% H_2S, 1.120% H_2S, 10.75 % H_2S and 42.36% H_2S, showed that only the gas containing 42.36% H_2S failed to give a theoretical slope of unity according to the Poiseiulle equation for laminar flow in circular tubes:[39]

$$\overline{v} = -\frac{\Delta P g_c D^2}{32\ \ell\ \mu} \qquad \text{(III-1)}$$

where $\overline{v}$ = average velocity, Ft/sec

ΔP = pressure drop, Lb/ft^2

g_c = dimensional constant, 32.77 $ft\text{-}Lb/Lb_f\text{-}sec^2$

D = diameter of capillary, ft

ℓ = length of capillary, ft

μ = absolute viscosity, Lb/ft-sec

Consequently, the calibration for the 42.36% H_2S mixture was redetermined by the following procedure.

Equation III-1 was simplified into the following form:

$$Q = \frac{T\,h}{\mu} \qquad \text{(III-2)}$$

where Q = flow rate, ml/sec

h = manometer reading, cm

μ = viscosity of the gas, centipoise

T = flowmeter constant (depending only on the dimensions of the capillary and the density of the manometer fluid)

The value of T for the ($H_2S_{(g)} + H_{2(g)}$) flowmeter was determined by calibrating the ($H_2S_{(g)} + H_{2(g)}$) flowmeter with pure $H_{2(g)}$ (μ = 89cp). Using the following equation, according to Wilke,[40] and a value of 128cp for the viscosity of hydrogen sulfide, the values of μ for the 0.220%, 1.120%, 10.75% and 42.36% H_2S mixtures were calculated.

$$\mu_{\text{mixture}} = \sum_{i=1}^{n} \frac{X_i \mu_i}{\sum\limits_{j=1}^{n} X_j \frac{1}{\sqrt{8}} \left(1 + \frac{M_i}{M_j}\right)^{-1/2} \left[1 + \left(\frac{\mu_i}{\mu_j}\right)^{1/2} \left(\frac{M_j}{M_i}\right)^{1/4}\right]^2} \qquad \text{(III-3)}$$

where (i,j) = components of the mixture

M = molecular weight, grams

μ = viscosity, g/cm-sec

Knowing T and μ, the calibration plots for the above gas mixtures were calculated from equation III-2. The calculated flow rates for the 0.220%, 1.120% and 10.75% H_2S mixtures were within ± 1.5% of the corresponding values from the direct calibration plots. However, the calculated flow rates for the 42.36% H_2S mixture were 7 to 9% greater than the values determined by direct calibration, indicating a loss of gas during direct calibration. Presumably the loss was due to adsorption of $H_2S_{(g)}$ by the tygon tubing. As a means for further verification of the calculated calibration plot for the 42.36% H_2S mixture, mixtures were prepared from the 42.36% H_2S tank and samples were taken at valve E-4 (Fig. 3). From the analyses and the known flow rates of hydrogen, the flow rates of the 42.36% H_2S mixture were calculated. The flow rates thus determined were within ± 1% of the corresponding values given by the calculated flowmeter calibration plot.

The direct calibration of the 0.220%, 1.120% and 10.75% H_2S mixtures was most likely subject to the same error as the 42.36% H_2S mixture. However, the agreement between measured and calculated flow rates and the agreement between measured and calculated gas compositions of prepared mixtures indicated that the uncertainty in the measured flow rates was less than ± 1.5%.

3. Gas Analysis Procedure

The tutwiler burette was prepared for analysis by filling the calibrated reagent reservoir and the bore of stopcock F (Fig. 4) connecting the reservoir to the bulb of the burette with standardized iodine solution, and by filling the leveling bottle and attached tygon tubing with leveling solution. The bore of stopcock E (Fig. 4) was filled with leveling solution and closed.

The burette was connected either to joint H (Fig. 4) or to joint

J-2 (Fig. 1), depending on the gas stream sampled. When connected to joint H, the bulb was first evacuated through stopcock G (Fig. 4) and then filled by turning stopcock G until the gas flow through bubbler I (Fig. 4) began to decrease. After the bulb was filled, at approximately barometric pressure, stopcock F was turned so that neither the reagent reservoir or gas inlet tube was connected to the burette bulb. When connected to joint J-2, the bulb was evacuated together with the reaction tube up to stopcock E-4 (Fig. 3). Stopcock N-3 (Fig. 1) was then closed, leaving the burette bulb under vacuum. The reaction tube was filled and the gas flow started through the reaction tube. At the desired time, a sample of the effluent stream was obtained by slowly opening stopcock N-2 until a decrease in the stream flow rate was observed. The sample bulb was filled to the pressure of the effluent stream, which in all cases was approximately barometric pressure.

The tutwiler burette and its gas sample were allowed to stand from 10 to 15 minutes to allow the gas sample to come to room temperature. The gas sample was then adjusted to 500 ml at the measured barometric pressure in the following manner. The leveling bottle was first clamped in a position corresponding to an equilibrium level for the solution in the bottle and burette, a short distance above the 500 ml calibration mark. Stopcock E was opened wide, allowing the leveling solution to enter and compress the gas sample. Stopcock F was then turned to a slightly opened position to allow the excess gas to escape. The rise of the leveling solution was watched very carefully and, when the meniscus reached the 500 ml calibration mark, stopcock E was closed. Stopcock F was then momentarily opened wide to adjust the sample to barometric pressure and then closed. The 500 ml gas sample was assumed to be free of moisture, in as much as the total time between opening stopcock E to introduce the leveling solution and the final closing of stopcock F was approximately 10 seconds.

With stopcock F still closed, the leveling bottle was then lowered to a position several feet below stopcock E. Stopcock E was then opened and the meniscus lowered to either the 520 or 540 ml calibration mark. Stopcock E was closed and the tygon tubing disconnected from the burette. By lowering the leveling solution, after the volume had been adjusted at barometric pressure, a partial vacuum was created in the burette bulb, which facilitated admission of the iodine solution through stopcock F.

The leveling solution was 50% water and 50% starch indicator solution by volume. This starch indicator solution was prepared by grinding 2 g of soluble starch and 10 ml water with a mortar and pestle and adding the paste to 1000 ml of boiling water. The solution was boiled until clear, cooled and 4 g of potassium iodide added. The sensitivity of the starch-iodine color is increased by the presence of the iodide ion; consequently, for titrations with dilute iodine solutions, the sensitivity of the end-point was improved by the presence of potassium iodide in the leveling solution.

The hydrogen sulfide in the gas sample was titrated with iodine solution according to the reaction

$$H_2S + I_2 = S + 2H^+ + 2I^- \qquad \text{(III-4)}$$

In the initial stage of titration, increments of approximately 0.5 ml of iodine solution were added. The entire burette was then shaken to give good mixing of the solution in the bulb. The ground glass stopper on top of the reagent reservoir was held in place to prevent spilling the iodine solution. As the end-point was approached, as witnessed by formation of a pink solution which cleared after several minutes of shaking, iodine solution was added in increments of approximately 0.05 ml. The end-point was taken at the appearance of a permanent blue color in the solution. The normality of the iodine solution was adjusted so that the titration volume of iodine solution was between 10 and 40 ml. For titration with iodine solutions more dilute than 0.008 N, a blank titration was made and the volume subtracted from the regular titration volume. The volumetric percent hydrogen sulfide was calculated from the following equation

$$\% \ H_2S = \frac{V \cdot N \cdot T \cdot 760}{0.44614 \cdot 273.2 \cdot P} \qquad \text{(III-5)}$$

where v = volume of iodine solution, ml

N = normality of iodine solution

T = room temperature (temperature of gas when volume was adjusted to 500 ml at barometric pressure), °K

P = barometric pressure, mm Hg

based on a sample volume of 500 ml.

Iodine solutions between 0.001 N and 0.4N were prepared in the following manner. Reagent grade resublimed iodine crystals were weighed in a large glass-stoppered weighing bottle and a preweighed amount of potassium iodide added. The addition of potassium iodide increased the solubility of the iodine, due to formation of the $[I_3^-]$ ion. For solutions weaker than 0.1N, 40 g of potassium iodide were added per liter of solution and for solutions stronger than 0.1N, (400/N)g of potassium iodide were added. Water was added to the weighing bottle and the iodine and potassium iodide were stirred into the solution. The contents of the weighing bottle were emptied into a one-liter volumetric flask, the weighing bottle and stirrer washed out into the flask, and the liquid level of the flask was brought up to volume. The solution was well mixed in the flask and then emptied into an amber glass bottle.

The iodine solutions were standardized against weighed amounts of primary standard As_2O_3 (purity 99.95%), according to the following reactions

$$As_2O_3 + 3H_2O = 2H_3AsO_3 \tag{III-6}$$

$$H_3AsO_3 + I_2 + H_2O = HAsO_4^{-2} + 2I + 4H^+ \tag{III-7}$$

The procedure followed for solution of the As_2O_3 in a properly buffered solution was that of Kolthoff and Belcher.[42] For each 100 ml of the prepared As_2O_3 solution, 5 ml of starch indicator solution was added and the solution then titrated to the appearance of the first permanent blue color in the solution. For iodine solution weaker than 0.01N, a blank titration was required. Each iodine solution was standardized by weighing out two to four samples of As_2O_3 for titration. The variance in normality between an individual standardization and the mean of the standardizations was within ±0.5%, relative to the mean standardization.

A series of analyses were made on four $(H_2S_{(g)} + H_{2(g)})$ tanks, with concentrations between 0.220% H_2S and 42.36% H_2S. Each tank was analyzed a minimum of three times, generally with duplicate analyses, before the tank was connected to the gas train and a single analysis after it was disconnected. For a given analysis, the variance between the individual analysis and the mean of the analyses on the tank was within ± 0.5%, relative to the mean analysis. This indicated a high precision in the analytical technique, and also that the analysis of the gas in the tanks did not change with time.

The systematic errors in the iodimetric titration of hydrogen sulfide have been discussed by Bethge,[41] Kolthoff and Belcher[42] and Sherman, Elvander and Chipman.[43] Their errors were assumed to have been eliminated by use of the analytical procedure discussed above. Loss of iodine by volatilization, and air oxidation of iodide to iodine were eliminated by titrating in a closed system. Partial oxidation of sulfide to sulfate, rather than to elemental sulfur, according to the reaction

$$S^{-2} + 4I_2 + 8OH^- = SO_4^{-2} + 8I^- + 4H_2O \qquad \text{(III-8)}$$

was prevented by preparing a leveling solution which was free of alkaline material. Furthermore, identical analyses were obtained with a regular neutral leveling solution and a leveling solution of pH1, substantiating the absence of reaction (III-8) in the normal titration procedure. The occlusion of iodine by elemental sulfur was eliminated by adding the iodine solution in small increments, forming a colloidal dispersion with the sulfur by addition of starch to the leveling solution, and by vigorous shaking of the burette after each addition of iodine solution. The use of the burette bulb for measuring the gas sample volume, as well as for the titration, eliminates the standard procedure followed for analyzing the H_2S concentration of a gas mixture. The gas sample is usually flushed from a volumetric sample bulb through an ammoniacal zinc or cadmium solution to remove the sulfide sulfur. The solution is then acidified to dissociate the metal sulfide and the liberated sulfide titrated with iodine. Consequently, the errors resulting from incomplete flusing of the sample bulb, evolution of gaseous hydrogen sulfide after acidification, and incomplete dissociation of the zinc or cadmium sulfide are eliminated. Furthermore, if the gas sample is flushed directly from the sample bulb through a standardized iodine solution and the excess iodine titrated with standardized thiosulfate, uncertainty exists as to whether the gas bubbles were completely reacted in their passage through the iodine solution. The systematic error in the gas sample volume, due to the inaccuracy of the calibration mark on the bulb of the tutwiler burette, was less than ± 0.1%. The systematic error in the volume of the calibrated reagent reservoir (9 ml) due to the inaccuracy of the calibration marks on the reservoir was less than ± 0.3%.

The total uncertainty in gas analysis was arbitrarily taken as the root of the sum of the squares of the random error in the analyses of the ($H_2S_{(g)} + H_{2(g)}$) tanks, the random error in the standardization of the iodine solutions, the systematic error in the gas sample volume, and the systematic error in the volume of the reagent reservoir and is given by the following equation

$$\delta(H_2S) = [(0.5)^2 + (0.5)^2 + (0.1)^2 + (0.3)^2]^{1/2} = \pm 0.8\% \approx 1\% \qquad \text{(III-9)}$$

where $\delta(H_2S)$ = uncertainty in hydrogen sulfide analysis expressed in relative percent

Consequently, the analyses of the effluent stream of the reaction tube, discussed in the next section, are assumed to have a relative accuracy of ± 1%.

4. Operating Procedure

An experimental run was started by disconnecting joint J-1 (Fig. 1), placing a metal sample in the notch of the sample holder E (Fig. 1), positioning the end of the sample holder on the lip of the reaction tube C (Fig. 1), and reconnecting joint J-1. With stopcocks N-2, N-3 (Fig. 1) and E-4 (Fig. 3) closed, the reaction tube and connecting glassware were evacuated through stopcock N-1 (Fig. 1). In the event that the effluent stream was to be sample during the run, stopcock N-3 was opened during evacuation but closed before gas was admitted to the reaction tube. With stopcock E-2 (Fig. 3) closed and stopcocks E-1 and E-3 (Fig. 3) opened, a flow of pure hydrogen was started and diverted through bubbler D (Fig. 3). With the vacuum disconnected, stopcock E-4 was slowly opened until a decrease in the hydrogen flow through bubbler D was observed, and the evacuated reaction tube filled with hydrogen. Stopcock N-2 was then opened and stopcock E-2 closed, directing the hydrogen flow through the reaction tube. At this point, a five-minute flush period began.

The sample holder was slowly pushed into position against the tip of the thermocouple protection tube F, while hydrogen was flowing. When the holder was in position, a ten-minute thermal equilibration period began. At the end of this period, stopcock E-2 was opened and the hydrogen sulfide plus hydrogen mixture was added to the pure hydrogen stream. The flow rates of the two gases, pure hydrogen and hydrogen sulfide plus hydrogen, were then adjusted to give the desired $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio for the gas mixture entering the reaction tube. The flow rates of the two gases were adjusted in such a way as not to exceed, in the process of adjusting the two flows, the precalculated value for the $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio. The volumetric flow rate of the mixture entering the reaction was 6 to 8 cm^3/sec. The area of the annulus between the thermocouple protection tube or the sample holder and the reaction tube was approximately 0.15 cm^2. Hence, on the basis of results by Richardson and Antill,[34] the linear velocity of the gas mixture in the reaction tube was more than adequate to prevent thermal segregation.

After exposure of the sample to the gas stream for a period of two to three hours, valve E-2 was closed terminating the addition of hydrogen sulfide to the gas stream. The hydrogen stream proceeded to flush the gas train and reaction tube of the hydrogen sulfide. After seven minutes of flushing, the sample holder was slowly withdrawn. When the sample holder was completely removed from the reaction tube, stopcock E-3 was opened to divert the flow through the bubbler, stopcocks N-2 and E-4 were closed, and the reaction tube was evacuated through stopcock N-1. The evacuated reaction tube was then filled with helium through stopcock E-4. Joint J-1 was disconnected, the exposed sample was removed and a new sample replaced.

A new metal sample was used for each run, so that the results of a sequence of runs could be inspected as desired. The decision of whether an exposed sample was sulfided or not sulfided was made by visual inspection of the sample. The exposed samples of molybdenum and tungsten were easily distinguished as having been sulfided by the gas mixture or not having been sulfided by the gas mixture. The sulfided samples of molybdenum and tungsten were characterized by the formation of a gray (Mo_2S_3) or brown (WS_2) coating on both sides of the metal sample. The exposed samples which were not sulfided retained the bright metallic appearance of the new, unexposed samples. The sulfide coatings on the sulfided samples of molybdenum and tungsten were not reduced when the samples were treated in a stream of pure hydrogen at the same temperature and for the same period of time as used for sulfidizing the samples. This meant that the sulfide coatings could not be reduced by the hydrogen stream during the period that the exposed samples were being removed from the reaction tube. Although this eliminated the possibility of error resulting from inadvertent reduction of the sulfide layer, it also eliminated the possibility of testing the reversibility of the sulfidizing reaction, i. e., studying the effect of gas ratio on the reduction of the sulfide to metal. The exposed samples of chromium were identified as being sulfided or not sulfided on the basis of the following observations. Chromium samples which were exposed to either pure hydrogen or to gas mixtures that were not sulfidizing were both characterized by a faint, gold-tinged appearance, presumably due to contamination by oxygen. On the other hand, sulfided samples were characterized by the black crystalline appearance of the sulfide layer formed on the surface of the sample in direct contact with the gas stream. The tinged appearance of the non-sulfided samples reduced somewhat the contrast between sulfided and non-sulfided samples, but did not appear to interfere with the formation of the sulfide. The reduction of the chromium sulfide by pure hydrogen was sufficiently fast that the reversibility of the formation of the chromium sulfide layer was established. The reversibility was established by first exposing a sample to a gas mixture with a $P_{H_2S(g)}/P_{H_2(g)}$ ratio slightly smaller than the determined equilibrium ratio and withdrawing the sample to confirm that no sulfide layer was formed. The sample was then re-exposed to a gas mixture with a gas ratio slightly greater than the equilibrium ratio, and the sample withdrawn to confirm that a sulfide layer was formed. Finally, the sample was re-exposed to a gas mixture with the original gas ratio and the sample was withdrawn to confirm that the sulfide was reduced back to metal. The rate of reduction of chromium sulfide by hydrogen, although sufficiently fast to study the reversibility of the formation of the sulfide, was not sufficiently fast to give inadvertent reduction of the sulfide during withdrawal of the samples under hydrogen. The exposed samples of copper were distinguished as sulfided or non-sulfided on the basis of the following observations. The sulfided samples were characterized by a black crystalline deposit on the surface of the sample. The samples which were not sulfided retained the bright metallic appearance of the new samples. However, the rate of reduction of the sulfide by hydrogen was quite high. Only by withdrawing the samples from the reaction tube at the maximum allowed rate was it possible to prevent the complete reduction of the sulfide layers. At the highest temperature studied, 1025°C, samples were withdrawn which showed a badly etched surface, indicating that the surface had been sulfided prior to withdrawal from the reaction tube. Consequently, the ability to distinguish between sulfided and non-sulfided samples was somewhat impaired at the higher temperatures.

The searching procedure followed for determining the small range of $P_{H_2S(g)}/P_{H_2(g)}$ ratios within which the true equilibrium value could be assumed to lie was as follows. The value of the gas ratio for the first experiment was that value which was considered most likely to be the equilibrium value, either on the basis of the experimental results at the other temperatures or, if this was the first temperature studied for the metal-metal sulfide system, from the estimated thermodynamic properties of the sulfide. If the first sample was sulfided by the gas mixture, the second sample was then exposed to a gas mixture with a smaller value for the gas ratio and, conversely, if the sample was not sulfided, the second sample was then exposed to a gas mixture with a larger value for the gas ratio. The value of the gas ratio for the second sample was taken midway between the value for the first sample and a value estimated as having a high probability of producing the opposite effect as the gas mixture of the first sample. Once two values of the gas ratio were obtained, one of which sulfided the metal sample and the other of which did not sulfide the metal sample, the following experiment was then taken at a value of the gas ratio midway between these two values. The procedure of halving the gas ratio interval was continued until a very small interval was obtained, as determined by the sensitivity of the flowmeters and the ability to distinguish between sulfided and non-sulfided samples. The control temperature of the furnace was then changed and the entire procedure repeated.

The value of the $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio for the gas entering the reaction tube was calculated from the flow rates of the pure hydrogen and the hydrogen plus hydrogen-sulfide mixture and the analyzed hydrogen sulfide content of the $(H_2S_{(g)} + H_{2(g)})$ tank. However, in order to assure the accuracy of the calculated ratios and the absence of contamination or leaks in the reaction tube, a series of hydrogen sulfide analyses were made on the effluent stream of the reaction tube, for runs where the sample was omitted. For runs using the 1.120% H_2S and 42.36% H_2S tanks, the analyzed gas ratio was within ± 1% of the calculated inlet gas ratio, relative to the calculated ratio. Analyses were not made for runs using the 10.75% H_2S tank, due to exhaustion of that tank at the completion of the equilibrium runs. However, the discrepancy in the $P_{H_2S(g)}/P_{H_2(g)}$ ratio between the analysed effluent stream and the calculated inlet stream was assumed to be within ± 1%, relative to the calculated inlet ratio, for all three tanks; 1.120% H_2S, 10.75% H_2S and 42.36% H_2S. For runs using the 0.220% H_2S tank, the analyzed gas ratio was within ± 4% of the calculated inlet ratio, relative to the calculated ratio.

5. Analysis of Sulfide Phase Composition

The compositions of the metal-saturated sulfides for the systems Cr-S, Mo-S, W-S, and Cu-S have been reviewed in Chapter II. For the temperatures of the study, 1100 - 1350°C for Cr-S, Mo-S and W-S, and 700 - 1025°C for Cu-S, the composition of molybdenum sulfide in equilibrium with molybdenum is stoichiometric Mo_2S_3, for tungsten sulfide satured with tungsten the composition is stoichiometric WS_2, and for copper sulfide in equilibrium with copper the phase is stoichiometric γ-Cu_2S. The composition of chromium sulfide in equilibrium with chromium had not been previously established. Accordingly, experiments were conducted to determine the composition of the metal-saturated chromium sulfide phase.

The experimental method consisted of x-ray, chemical and gravimetric analysis of sulfide layers formed on chromium samples exposed to a gas mixture with a $P_{H_2S(g)}/P_{H_2(g)}$ ratio only slightly greater than the determined equilibrium value. The analysis of x-ray diffraction patterns on material scraped from the surface of sulfided samples showed the presence of Cr, CrS and either or both Cr_5S_6 and Cr_7S_8. These results, similar to those of Jellinek[7] and Knoev, Bogacheva and Pavlova,[8] indicate that the CrS phase was in equilibrium with chromium at high temperature, 1147°C, but disproportionated upon cooling, according to either or both of the following reactions

$$6CrS_{(c)} = Cr_{(c)} + Cr_5S_{6(c)} \qquad \text{(III-10)}$$

$$8CrS_{(c)} = Cr_{(c)} + Cr_7S_{8(c)} \qquad \text{(III-11)}$$

The composition of the sulfide layer was obtained more directly by weight change measurements on chromium samples that were first sulfided and then treated with warm (70 - 90°C) concentrated nitric acid for selective dissolution of the sulfide layer. The experimental data and the calculated values for the molar Cr/S ratio for the sulfide phase are given in Appendix G. The mean value for the molar Cr/S ratio, from six samples, was 0.97 and the standard deviation for the determination of the molar Cr/S ratio was ± 0.05. Chemical analysis of the nitric acid leach solutions gave molar Cr/S ratios with greater scatter and consistently lower in chromium than those by gravimetric analysis. Disproportionation of the CrS phase during cooling would precipitate insoluble chromium particles, thus giving low results for chromium analysis of the leach solution. However, the results of the weight change measurements would be unaffected in as much as the precipitated chromium would be dispersed within the sulfide layer and would be physically removed from the sample during solution of the sulfide layer. Accordingly, the composition of the chromium sulfide phase in equilibrium with chromium metal was taken as stoichiometric chromous sulfide (CrS).

IV. REDUCTION OF EXPERIMENTAL DATA

A. Data Analysis - General Considerations

The experimental data for the systems $Cr_{(c)}$-$CrS_{(c)}$, $Mo_{(c)}$-$Mo_2S_{3(c)}$, $W_{(c)}$-$WS_{(c)}$ and $Cu_{(c)}$-$Cu_2S_{(\gamma)}$ are tabulated in Appendix A. For every system a series of experiments were conducted at each of several temperatures. Experiments in a given series differed only in the value of the $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio for the gas atmosphere, and whether the metal samples were sulfided at the end of the run or remained metallic. Each series is arranged in order of increasing $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio corresponding to the transition from metallic surfaces to sulfided surfaces. The two experiments in each series, which gave the highest $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio for which the sample surface remained metallic and the lowest $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio for which a sulfide layer formed on the metal sample, are used to calculate the thermodynamic properties of the metal sulfide.

The experimentally determined inlet gas ratio was calculated from the composition of the $(H_2S_{(g)} + H_{2(g)})$ mixture supplied from the tank and the ratio of mixing for the two gases, $(H_2S_{(g)} + H_{2(g)})$ and $(H_{2(g)})$, as obtained from the flowmeter readings. Therefore, calculations are required to establish the correction to be applied to the inlet $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio to correct for the dissociation of the $H_2S_{(g)}$ at the temperature of the sample.

B. Corrections for Dissociation of Hydrogen Sulfide

The extent of dissociation of $H_2S_{(g)}$ in the inlet mixture can be computed from a knowledge of the stoichiometry of the dissociation reactions, the equilibrium constant K_p for the dissociation reactions, and the composition of the inlet gas mixture. The dissociation of $H_2S_{(g)}$ into $H_{2(g)}$ and the species $S_{2(g)}$, $HS_{(g)}$, $S_{(g)}$, $S_{6(g)}$, and $S_{8(g)}$ is given by the following reactions:

$$H_2S_{(g)} = H_{2(g)} + 1/2\ S_{2(g)} \tag{IV-1}$$

$$H_2S_{(g)} = 1/2\ H_{2(g)} + HS_{(g)} \tag{IV-2}$$

$$H_2S_{(g)} = H_{2(g)} + S_{(g)} \tag{IV-3}$$

$$H_2S_{(g)} = H_{2(g)} + 1/6\ S_{6(g)} \tag{IV-4}$$

$$H_2S_{(g)} = H_{2(g)} + 1/8\ S_{8(g)} \tag{IV-5}$$

The equations for the standard free energy of reaction are as follows:

1. <u>For Dissociation into $S_{2(g)}$</u>

$$\Delta F^\circ_R = -\ \Delta F^\circ_f(H_2S_{(g)})$$

$$\Delta F^\circ_R = 21{,}570 - 11.79T, \text{ cal} \tag{IV-1-A}$$

2. <u>For Dissociation into $HS_{(g)}$</u>

$$\Delta F^\circ_R = \Delta F^\circ_f(HS_{(g)}) - \Delta F^\circ_f(H_2S_{(g)})$$

$$\Delta F^\circ_R = 41{,}640 - 15.49T, \text{ cal} \tag{IV-2-A}$$

3. For Dissociation into $S_{(g)}$

$$\Delta F^\circ_R = \Delta F^\circ_f(S_{(g)}) - \Delta F^\circ_f(H_2S_{(g)})$$

$$\Delta F^\circ_R = 72{,}740 - 26.23T, \text{ cal} \qquad \text{(IV-3-A)}$$

4. For Dissociation into $S_{6(g)}$

$$\Delta F^\circ_R = 1/6\ \Delta F^\circ_f(S_{6(g)}) - \Delta F^\circ_f(H_2S_{(g)})$$

$$\Delta F^\circ_R = 10{,}500 + 0.50T, \text{ cal} \qquad \text{(IV-4-A)}$$

5. For Dissociation into $S_{8(g)}$

$$\Delta F^\circ_R = 1/8\ \Delta F^\circ_f(S_{8(g)}) - \Delta F^\circ_f(H_2S_{(g)})$$

$$\Delta F^\circ_R = 9{,}170 + 2.36T, \text{ cal} \qquad \text{(IV-5-A)}$$

The equations for the ΔF°_f of $H_2S_{(g)}$, $HS_{(g)}$, $S_{(g)}$, $S_{6(g)}$ and $S_{8(g)}$ are from Table I. A rigorous treatment requires that dissociation into the various species be treated simultaneously. However, it will be shown later that the approach of treating the dissociation into each species sequentially will be valid within the limits of the experimental data. Also, the uncertainty in the corrected $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratios, due to the uncertainty in the above ΔF°_R equations, was less than ± 0.5% and has been neglected.

Consider first the dissociation into $S_{2(g)}$. From above

$$H_2S_{(g)} = H_{2(g)} + 1/2\ S_{2(g)} \tag{IV-1}$$

$$\Delta F^\circ_R = 21{,}570 - 11.79T, \text{ cal} \tag{IV-1-A}$$

For a given temperature (T), the equilibrium constant K_p is calculated by means of equation (IV-1-A) and the following equation

$$\Delta F^\circ_R = -RT \ln K_p \tag{IV-6}$$

where $$K_p = \frac{\left(P_{S_{2(g)}}{}^{1/2}\right)\left(P_{H_{2(g)}}\right)}{\left(P_{H_2S_{(g)}}\right)} \tag{IV-7}$$

By taking one mole of an inlet mixture, under the condition of constant total gas pressure P_T, bringing it to equilibrium at temperature (T) according to reaction (IV-1), and applying the equation

$$P_i = \frac{N_i}{\Sigma N_i} P_T \tag{IV-8}$$

the relations shown in Table IV are obtained, where

$N_{S_{2(g)}}$ = moles of $S_{2(g)}$ formed by dissociation of the $H_2S_{(g)}$ in the one mole of inlet gas mixture

$P_{H_2S_{(g)}}, P_{H_{2(g)}}$ = partial pressure of $H_2S_{(g)}$ and $H_{2(g)}$, respectively, in the inlet mixture

TABLE IV

STOICHIOMETRIC RELATIONS AND PARTIAL PRESSURE EXPRESSIONS FOR THE DISSOCIATION OF $H_2S_{(g)}$ INTO $H_{2(g)}$ PLUS $S_{2(g)}$

Species(i)	Moles of (i) in Inlet	Moles of (i) After $S_{2(g)}$ Formation	P_i
$H_2S_{(g)}$	$N_{H_2S_{(g)}} = \frac{P_{H_2S_{(g)}}}{P_T} \times 1$	$\frac{P_{H_2S_{(g)}}}{P_T} - 2N_{S_{2(g)}}$	$\frac{\left(\frac{P_{H_2S_{(g)}}}{P_T} - 2N_{S_{2(g)}}\right) P_T}{(1 + N_{S_{2(g)}})}$
$H_{2(g)}$	$N_{H_{2(g)}} = \frac{P_{H_{2(g)}}}{P_T} \times 1$	$\frac{P_{H_{2(g)}}}{P_T} + 2N_{S_{2(g)}}$	$\frac{\left(\frac{P_{H_{2(g)}}}{P_T} + 2N_{S_{2(g)}}\right) P_T}{\left(1 + N_{S_{2(g)}}\right)}$
$S_{2(g)}$	$\frac{0}{\Sigma N_i = 1}$	$\frac{N_{S_{2(g)}}}{\Sigma N_i = 1 + N_{S_{2(g)}}}$	$\frac{N_{S_{2(g)}} P_T}{\left(1 + N_{S_{2(g)}}\right)}$

The above expressions for P_i substituted in equation IV-7 give

$$K_p = \frac{\left[\dfrac{N_{S_{2(g)}} P_T}{1 + N_{S_{2(g)}}}\right]^{1/2} \left[\dfrac{\left(\dfrac{P_{H_{2(g)}}}{P_T} + 2N_{S_{2(g)}}\right) P_T}{\left(1 + N_{S_{2(g)}}\right)}\right]}{\left[\dfrac{\left(\dfrac{P_{H_2S_{(g)}}}{P_T} - 2N_{S_{2(g)}}\right) P_T}{\left(1 + N_{S_{2(g)}}\right)}\right]} \qquad \text{(IV-9)}$$

The solution of $N_{S_{2(g)}}$ from equation (IV-9) is best determined by a successive approximation procedure. As a first approximation, the expressions for $P_{H_{2(g)}}$ and $P_{H_2S_{(g)}}$ are replaced by the inlet values. The resulting equation is then first-order in $N_{S_{2(g)}}$ and can be readily solved. The second approximation of $N_{S_{2(g)}}$ is obtained by calculating the expressions for $P_{H_{2(g)}}$ and $P_{H_2S_{(g)}}$ using the first approximation value of $N_{S_{2(g)}}$. Finally, having computed the value of $N_{S_{2(g)}}$, the $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio corrected for dissociation of $H_2S_{(g)}$ into $S_{2(g)}$ is given by the following expression:

$$\left(\frac{P_{H_2S_{(g)}}}{P_{H_{2(g)}}}\right)_{(\text{corr.},\ S_{2(g)})} = \frac{\left(\dfrac{P_{H_2S_{(g)}}}{P_T} - 2N_{S_{2(g)}}\right)}{\left(\dfrac{P_{H_{2(g)}}}{P_T} + 2N_{S_{2(g)}}\right)} \qquad \text{(IV-10)}$$

Consider next the dissociation into $HS_{(g)}$. From previous equations

$$H_2S_{(g)} = 1/2\ H_{2(g)} + HS_{(g)} \qquad \text{(IV-2)}$$

$$\Delta F^\circ_R = 41{,}640 - 15.49T,\ \text{cal} \qquad \text{(IV-2-A)}$$

For a given temperature (T), the equilibrium constant K_p is calculated from equation (IV-2-A) and the following equation

$$\Delta F^\circ_R = -RT \ln K_p \qquad \text{(IV-6)}$$

where $$K_p = \frac{\left(P_{H_{2(g)}}{}^{1/2}\right)\left(P_{HS_{(g)}}\right)}{\left(P_{H_2S_{(g)}}\right)} \qquad \text{(IV-11)}$$

By taking the gas mixture, resulting from dissociation of $H_2S_{(g)}$ into $S_{2(g)}$, for one mole of inlet mixture and bringing it to equilibrium according to reaction (IV-2), at the same temperature (T) and constant total pressure (P_T), the relations shown in Table V are obtained, where

$N_{HS_{(g)}}$ = moles of $HS_{(g)}$ formed by dissociation of $H_2S_{(g)}$ according to reaction (IV-2)

$N_{S_{2(g)}}$ = moles of $S_{2(g)}$ as determined from equation (IV-9)

$P_{H_2S_{(g)}}$, $P_{H_{2(g)}}$ = partial pressure of $H_2S_{(g)}$ and $H_{2(g)}$, respectively, in the inlet mixture

TABLE V

STOICHIOMETRIC RELATIONS AND PARTIAL PRESSURE EXPRESSIONS FOR THE DISSOCIATION OF $H_2S_{(g)}$ INTO $H_{2(g)}$ PLUS $S_{2(g)}$ PLUS $HS_{(g)}$

Species(i)	Moles of (i) After $S_{2(g)}$ Formation	Moles of (i) After $S_{2(g)}$ + $HS_{(g)}$ Formation	P_i
$H_2S_{(g)}$	$\frac{P_{H_2S(g)}}{P_T} - 2N_{S_{2(g)}}$	$\frac{P_{H_2S(g)}}{P_T} - 2N_{S_{2(g)}} - N_{HS_{(g)}}$	$\frac{\left(\frac{P_{H_2S(g)}}{P_T} - 2N_{S_{2(g)}} - N_{HS_{(g)}}\right) P_T}{\left(1 + N_{S_{2(g)}} + 0.5N_{HS_{(g)}}\right)}$
$H_{2(g)}$	$\frac{P_{H_{2(g)}}}{P_T} + 2N_{S_{2(g)}}$	$\frac{P_{H_{2(g)}}}{P_T} + 2N_{S_{2(g)}} + 0.5N_{HS_{(g)}}$	$\frac{\left(\frac{P_{H_{2(g)}}}{P_T} + 2N_{S_{2(g)}} + 0.5N_{HS_{(g)}}\right) P_T}{\left(1 + N_{S_{2(g)}} + 0.5N_{HS_{(g)}}\right)}$
$S_{2(g)}$	$N_{S_{2(g)}}$	$N_{S_{2(g)}}$	
$HS_{(g)}$	$\frac{0}{\Sigma N_i = 1 + N_{S_{2(g)}}}$	$\frac{N_{HS_{(g)}}}{\Sigma N_i = 1 + N_{S_{2(g)}} + 0.5N_{HS_{(g)}}}$	$\frac{N_{HS_{(g)}} P_T}{\left(1 + N_{S_{2(g)}} + 0.5N_{HS_{(g)}}\right)}$

Substituting the above expressions for P_i into equation (IV-11) gives

$$K_p = \frac{\left[\frac{\left(\frac{P_{H_2(g)}}{P_T} + 2N_{S_2(g)} + 0.5N_{HS_{(g)}}\right) P_T}{\left(1 + N_{S_2(g)} + 0.5N_{HS(g)}\right)}\right]^{1/2} \left[\frac{N_{HS_{(g)}} P_T}{1 + N_{S_2(g)} + 0.5N_{HS_{(g)}}}\right]}{\left[\frac{\left(\frac{P_{H_2S_{(g)}}}{P_T} - 2N_{S_2(g)} - N_{HS_{(g)}}\right) P_T}{\left(1 + N_{S_2(g)} + 0.5N_{HS_{(g)}}\right)}\right]}$$

(IV-12)

The solution of $N_{HS_{(g)}}$ from equation (IV-12) is best determined by the same method of successive approximation as applied to equation (IV-9), except that the expressions for $P_{H_2(g)}$ and $P_{H_2S_{(g)}}$ used in the first approximation of $N_{HS_{(g)}}$ are the expressions in equation (IV-12) with the $N_{HS_{(g)}}$ term deleted. Finally, having computed the value of $N_{HS_{(g)}}$, the $P_{H_2S_{(g)}}/P_{H_2(g)}$ ratio corrected for dissociation of $H_2S_{(g)}$ into both $S_{2(g)}$ and $HS_{(g)}$ is given by the following expression:

$$\left(\frac{P_{H_2S_{(g)}}}{P_{H_2(g)}}\right)_{(corr., S_{2(g)}, HS_{(g)})} = \frac{\left(\frac{P_{H_2S_{(g)}}}{P_T} - 2N_{S_{2(g)}} - N_{HS_{(g)}}\right)}{\left(\frac{P_{H_2(g)}}{P_T} + 2N_{S_{2(g)}} + 0.5N_{HS_{(g)}}\right)} \qquad \text{(IV-13)}$$

Equations for correction of $P_{H_2S_{(g)}}/P_{H_2(g)}$, due to further dissociation into $S_{(g)}$, $S_{6_{(g)}}$ and $S_{8_{(g)}}$ can be similarly derived from equations (IV-3-A), (IV-4-A) and (IV-5-A). However, first approximation calculations, in which the $P_{H_2S_{(g)}}$ and $P_{H_2(g)}$ terms in K_p are assumed equal to the inlet mixture values, give results which indicate that these corrections are much less than 0.1% of the gas ratio. Furthermore, for the temperature range covered in the study, calculations from equations (IV-10) and (IV-13) show that corrections for dissociation into $S_{2(g)}$ and $HS_{(g)}$ are only significant for $P_{H_2S_{(g)}}/P_{H_{2(g)}} > 10^{-3}$. In addition, the correction for dissociation into $S_{2(g)}$ is several times that for dissociation into $HS_{(g)}$ (which is less than 0.50% of the gas ratio). Accordingly, the need of considering simultaneous dissociation into $S_{2(g)}$ and $HS_{(g)}$ is eliminated. Instead, the corrections have been made sequentially, considering dissociation into $S_{2(g)}$ first followed by dissociation into $HS_{(g)}$. The error in $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ (corr., $S_{2(g)}$), due to deletion of the effect of dissociation into $HS_{(g)}$ on the dissociation into $S_{2(g)}$, was less than 0.1% and has been neglected. Calculated corrections for gas mixtures of the $Mo_{(c)}$-$Mo_2S_{3(c)}$ and $W_{(c)}$-WS_2 systems are tabulated in Appendix B.

C. Thermodynamic Computations

The point of equilibrium between the gas phase and the metal-metal sulfide pair lies between the experimental point having the highest $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio for which a sulfide layer was not formed and the experimental point having the lowest $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio for which a sulfide layer was formed. These two points in each series of experiments, for a given temperature and a given metal-metal sulfide pair, are taken from Appendix A or, if the inlet $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio has been corrected for dissociation of $H_2S_{(g)}$, they are taken from Appendix B. The standard free energy of reaction for each of these two points is calculated for the reaction

$$\frac{1}{Y}\,Me_XS_{Y_{(c)}} + H_{2(g)} = \frac{X}{Y}\,Me_{(c)} + H_2S_{(g)} \qquad \text{(IV-14)}$$

where $Me_{(c)}$ = metal phase

$Me_XS_{Y(c)}$ = metal sulfide phase

by the following equation:

$$\Delta F^\circ_R = -RT \ln \frac{P_{H_2S(g)}}{P_{H_2(g)}} \tag{IV-15}$$

Accordingly, the true value of the standard free energy of reaction at the stated temperature lies within these two boundary values.

The variation of ΔF°_R with temperature is given by the equation

$$\Delta F^\circ_R = \Delta H^\circ_R - T\Delta S^\circ_R \tag{IV-16}$$

where ΔH°_R = standard heat of reaction

ΔS°_R = standard entropy change for the reaction

For the limited temperature range employed in this study, ΔH°_R and ΔS°_R are assumed to be constant. Equation (IV-16) thus gives the linear variation of ΔF°_R with temperature. A plot of the boundary values of ΔF°_R versus temperature shows that for each metal-metal sulfide system any number of straight lines can be drawn through the pairs of ΔF°_R values. However, further examination reveals that two ΔF°_R values, each at different temperatures, uniquely define the straight line of maximum slope which will pass within all of the pairs of ΔF°_R and, similarly, there are two other values of ΔF°_R which uniquely define the straight line of minimum slope which will pass within all of the pairs of ΔF°_R. In as much as there is no information available, either experimental or theoretical, regarding the position of the line representing the most probable value of ΔF_R° between each pair of ΔF_R° values, the best line through the points is arbitrarily taken as the line of average slope.

The value of ΔS_R° and ΔH_R° is determined from the following equations:

$$\Delta S_R^\circ = - \left(\frac{d\Delta F_R^\circ}{dT}\right) \tag{IV-17}$$

$$\Delta H_R^\circ = \Delta F_R^\circ - T\left(\frac{d\Delta F_R^\circ}{dT}\right) \tag{IV-18}$$

Since the best line through the ΔF_R° points is taken as the line of average slope, the best value of ΔS_R° and ΔH_R° is necessarily that value calculated by equations (IV-17) and (IV-18), respectively, from the line of average slope.

Finally, the values of the standard free energy, entropy and heat of formation of the metal sulfide according to the reaction

$$\frac{X}{Y}\,\mathrm{Me}_{(c)} + 1/2\ S_{2(g)} = \frac{1}{Y}\,\mathrm{Me}_X S_{Y(c)} \tag{IV-19}$$

are calculated by the following equation:

$$\Delta V^\circ_{f(1/Y\ \mathrm{Me}_X S_{Y(c)})} = \Delta V^\circ_{f(H_2S_{(g)})} - \Delta V_R^\circ \tag{IV-20}$$

where V = the free energy, entropy or enthalpy function

Thermodynamic computations, in addition to tabulation of experimental data for selected experiments, for the systems $Cr_{(c)}$-$CrS_{(c)}$, $Mo_{(c)}$-$Mo_2S_{3(c)}$, $W_{(c)}$-$WS_{2(c)}$ and $Cu_{(c)}$ - $Cu_2S_{(c)}$ are in Appendix C, D, E and F, respectively.

D. Estimation of Uncertainty

The uncertainties in the experimental results were evaluated by the methods outlined by Pantony.[44] With the exception of the uncertainty limits estimated for ΔS°_R and ΔH°_R, all others are estimated as being one standard deviation. The limits for ΔS°_R and ΔH°_R are estimated as being two standard deviations.

1. Uncertainty in experimental measurements

The total uncertainty in sample temperature, resulting from several independent errors in temperature, is given by the following equation:

$$\delta T = \left[(\delta T_{(calib)})^2 + (\delta T_{(grad)})^2 + (\delta T_{(drift)})^2\right]^{1/2} \qquad \text{(IV-21)}$$

where δT = combined uncertainty in sample temperature

$\delta T_{(calib)}$ = uncertainty in thermocouple calibration correction

$\delta T_{(grad)}$ = uncertainty between the thermocouple temperature and the sample temperature

$\delta T_{(drift)}$ = drift in control temperature during experiment

The total uncertainty in the $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio is calculated from the following equation:

$$\delta\left(\frac{P_{H_2S_{(g)}}}{P_{H_{2(g)}}}\right) = \left\{\left[\delta\left(\frac{P_{H_2S_{(g)}}}{P_{H_{2(g)}}}\right)_{(inlet)}\right]^2 + \left[\delta\left(\frac{P_{H_2S_{(g)}}}{P_{H_{2(g)}}}\right)_{(anal)}\right]^2\right\}^{1/2} \qquad \text{(IV-22)}$$

where $\delta \left(\dfrac{P_{H_2S_{(g)}}}{P_{H_{2(g)}}} \right)$ = combined uncertainty in inlet $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio

$\delta \left(\dfrac{P_{H_2S_{(g)}}}{P_{H_{2(g)}}} \right)_{(inlet)}$ = uncertainty between calculated inlet ratio and chemically analysed exit ratio

$\delta \left(\dfrac{P_{H_2S_{(g)}}}{P_{H_{2(g)}}} \right)_{(anal)}$ = uncertainty in chemical analysis of exit ratio

The estimated values for the various uncertainties in temperature and gas ratio are given in Chapter III.

2. Uncertainty in ΔF°_R

The total uncertainty in ΔF°_R includes the uncertainty between ΔF°_R, given by the equation of the average slope, and the experimental results, in addition to the uncertainty in the experimental results. The equation for the uncertainty in the experimentally-determined values of ΔF°_R is developed below:

$$\Delta F^\circ_{R_{(exp)}} = - RT \ln \frac{P_{H_2S_{(g)}}}{P_{H_{2(g)}}} \qquad \text{(IV-15)}$$

$$\delta \Delta F^\circ_{R_{(exp)}} = \left[\left(\frac{\partial \Delta F^\circ_{R_{(exp)}}}{\partial T} \right)^2 (\delta T)^2 + \left(\frac{\partial \Delta F^\circ_{R_{(exp)}}}{\partial \dfrac{P_{H_2S_{(g)}}}{P_{H_{2(g)}}}} \right)^2 \left(\delta \frac{P_{H_2S_{(g)}}}{P_{H_{2(g)}}} \right)^2 \right]^{1/2} \qquad \text{(IV-23)}$$

$$\delta\Delta F^\circ_{R_{(exp)}} = \left[\left(R \ln \frac{P_{H_2S_{(g)}}}{P_{H_{2(g)}}} \right)^2 (\delta T)^2 + \left(\frac{RT}{\frac{P_{H_2S_{(g)}}}{P_{H_{2(g)}}}} \right)^2 \left(\delta \frac{P_{H_2S_{(g)}}}{P_{H_{2(g)}}} \right)^2 \right]^{1/2} \tag{IV-24}$$

where $\delta\Delta F^\circ_{R_{(exp)}}$ = uncertainty in ΔF°_R calculated from experimental data

(δT), $\left(\delta \frac{P_{H_2S_{(g)}}}{P_{H_{2(g)}}} \right)$ = uncertainty in the temperature and gas ratio calculated from equations (IV-21) and (IV-22), respectively

The uncertainty between the value of ΔF°_R, calculated from the equation of the average slope and the value calculated from the experimental data, is computed from the following expression:

$$\delta\Delta F^\circ_{R_{(calc)}} = \left[\frac{\sum_{n=1}^{n=k} \left(\Delta F^\circ_{R_{(calc)}} - \Delta F^\circ_{R_{(exp)}} \right)^2_n}{k - 1} \right]^{1/2} \tag{IV-25}$$

where $\delta\Delta F^\circ_{R_{(calc)}}$ = uncertainty in ΔF°_R calculated from equation of the average slope

$\Delta F^\circ_{R_{(calc)}}$ = ΔF°_R calculated from equation of the average slope

$\Delta F^\circ_{R_{(exp)}}$ = ΔF°_R calculated from experimental results

k = number of experimental points

Finally, the combined uncertainty in ΔF°_R is determined from the equation:

$$\delta\Delta F^\circ_R = \left[\left(\delta\Delta F^\circ_{R_{(exp)}}\right)^2 + \left(\delta\Delta F^\circ_{R_{(calc)}}\right)^2\right]^{1/2} \tag{IV-26}$$

where $\delta\Delta F^\circ_R$ = total uncertainty in ΔF°_R, the value of ΔF°_R being given by the equation of the average slope

$\delta\Delta F^\circ_{R_{(exp)}}$, $\delta\Delta F^\circ_{R_{(calc)}}$ = uncertainties calculated from equations (IV-24) and (IV-25)

3. Uncertainty in ΔS°_R and ΔH°_R

The uncertainty in ΔS°_R and ΔH°_R is determined by the difference between the values of ΔS°_R and ΔH°_R from the equation of the average slope and the values from the equations of maximum and minimum slope. The uncertainty in the experimental points defining the lines of maximum and minimum slope is not included, since only two points define each line.

4. Uncertainty in ΔF°, ΔS° and ΔH° of formation of $Me_XS_{Y_{(c)}}$

The uncertainty in the ΔF°_f, ΔS°_f and ΔH°_f of $Me_XS_{Y_{(c)}}$ is calculated by the equation

$$\delta\Delta V^\circ_{f(Me_XS_{Y_{(c)}})} = \left[\left(\delta\Delta V^\circ_{f(H_2S_{(g)})}\right)^2 + (\delta\Delta V^\circ_R)^2\right]^{1/2} \tag{IV-27}$$

where V = the free energy, entropy or enthalpy function

The calculations of uncertainty in experimental results for the systems $Cr_{(c)}$-$CrS_{(c)}$, $Mo_{(c)}$-$Mo_2S_{3(c)}$, $W_{(c)}$-$WS_{2(c)}$ and $Cu_{(c)}$-$Cu_2S_{(\gamma)}$ are in Appendix C, D, E and F, respectively.

V. RESULTS

A. Chromium Sulfide

The thermodynamic properties of $CrS_{(c)}$, shown experimentally to be the metal-saturated chromium sulfide phase, have been determined through a high-temperature investigation of the equilibrium

$$CrS_{(c)} + H_{2(g)} = Cr_{(c)} + H_2S_{(g)} \tag{V-1}$$

The equilibrium $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio was not measured directly but, rather, two limiting values of the $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio were determined, within which the exact equilibrium value was assumed to lie. Consequently, two values of ΔF°_R for reaction (V-1) have been calculated for each experimental temperature. These are the limiting values within which the exact values of ΔF°_R lie. The results are tabulated in Appendix C, and are presented graphically in Fig. 5. Calculations to determine the linear variation of ΔF°_R with temperature and to estimate the uncertainty in the results are given in Appendix C. The equation for the standard free energy change of reaction (V-1) is:

$$\Delta F^\circ_R = 26{,}620 - 1.48T, \text{ cal } (\pm\ 150 \text{ cal})(1375 - 1570^\circ K) \tag{V-2}$$

where $$\Delta H^\circ_R = 26{,}620 \text{ cal } (\pm\ 750 \text{ cal}) \tag{V-3}$$

$$\Delta S^\circ_R = +\ 1.48 \text{ cal/deg } (\pm\ 0.5 \text{ cal/deg}) \tag{V-4}$$

Equation (V-2) combined with the equation for the standard free energy of formation of $H_2S_{(g)}$ from Table I gives the equation for the

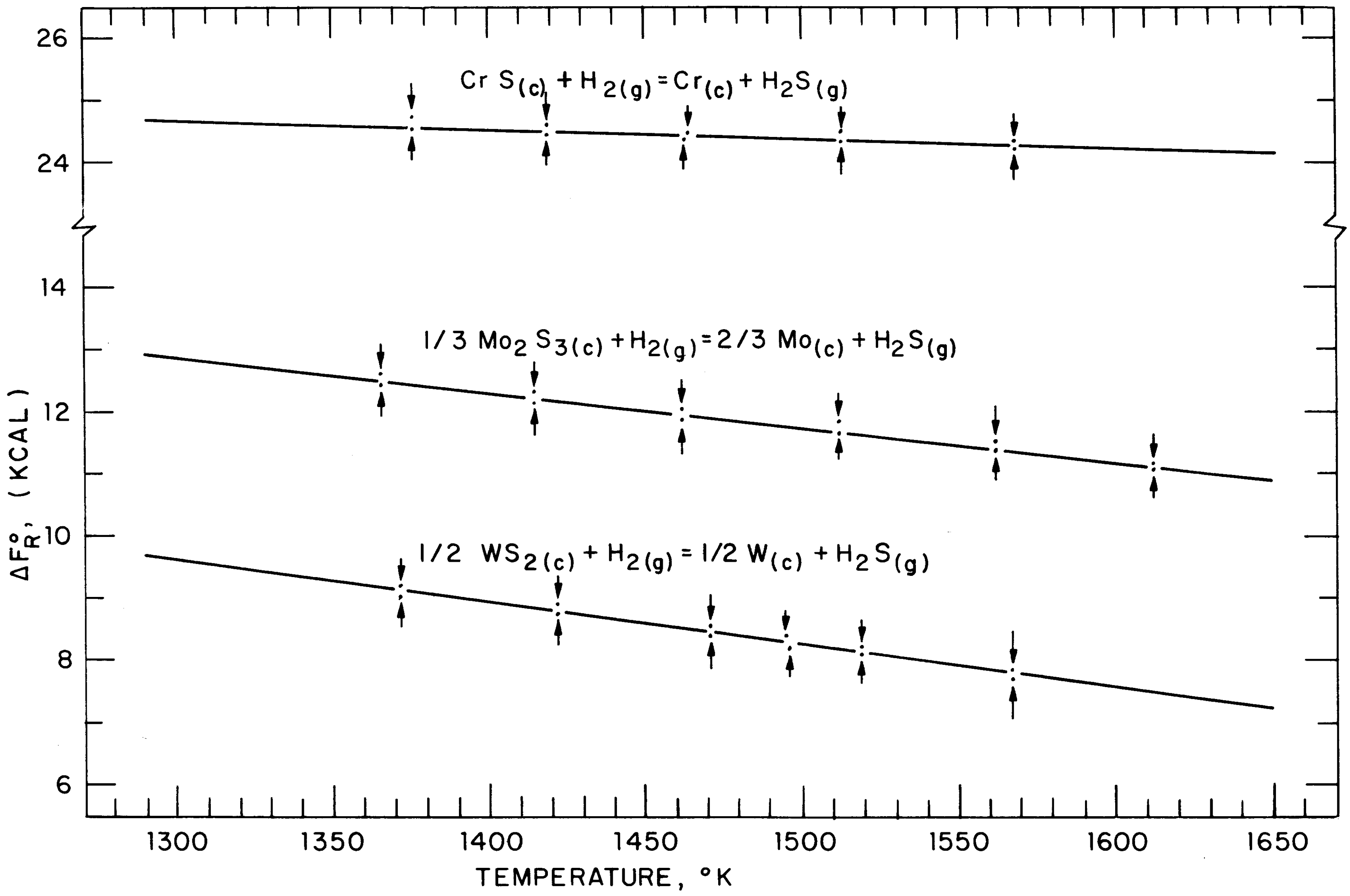

FIG. 5-FREE ENERGY CHANGE FOR REACTIONS (V-1) (V-5) (V-9); ARROWS INDICATING DIRECTION OF APPROACH TO EQUILIBRIUM

standard free energy of formation of $CrS_{(c)}$. The result, including the estimate of uncertainty, is calculated in Appendix C and is presented in Table VI.

B. Molybdenum Sulfide

The thermodynamic properties of $Mo_2S_{3(c)}$ have been determined through a high-temperature investigation of the equilibrium

$$1/3\ Mo_2S_{3(c)} + H_{2(g)} = 2/3\ Mo_{(c)} + H_2S_{(g)} \qquad \text{(V-5)}$$

Two limiting values of ΔF°_R for reaction (V-5) have been calculated for each experimental temperature. The results are tabulated in Appendix D and are presented graphically in Fig. 5. Calculations to determine the linear variation of ΔF°_R with temperature and to estimate the uncertainty in the results are given in Appendix D. The equation for the standard free energy change of reaction (V-5) is:

$$\Delta F^\circ_R = 20{,}160 - 5.6T,\ \text{cal}\ (\pm\ 100\ \text{cal})(1365 - 1610°K) \qquad \text{(V-6)}$$

where

$$\Delta H^\circ_R = 20{,}160\ \text{cal}\ (\pm\ 880\ \text{cal}) \qquad \text{(V-7)}$$

$$\Delta S^\circ_R = 5.6\ \text{cal/deg}\ (\pm\ 0.57\ \text{cal/deg}) \qquad \text{(V-8)}$$

Equation (V-6) combined with the equation for the standard free energy of formation of $H_2S_{(g)}$ from Table I gives the equation for the standard free energy of formation of 1/3 $Mo_2S_{3(c)}$. The result, including the estimate of uncertainty, is calculated in Appendix D and is presented in Table VI.

TABLE VI

THE STANDARD FREE ENERGIES, ENTHALPIES AND ENTROPIES OF FORMATION OF THE SULFIDES

$CrS_{(c)}$, $Mo_2S_{3(c)}$, $WS_{2(c)}$, $Cu_2S_{(\gamma)}$ PER 1/2 GRAM-MOLE $S_{2(gas)}$

Sulfide	$\Delta F^\circ_f = A + BT$	ΔH°_f	ΔS°_f	Temperature Range
Group VIa:				
$CrS_{(c)}$	-48,190 + 13.27Tcal(±250cal)	-48,190cal(±760cal)	-13.27cal/deg(±0.52cal/deg)	1375-1570°K
1/3 $Mo_2S_{3(c)}$	-41,730 + 17.39Tcal(±220cal)	-41,730cal(±890cal)	-17.39cal/deg(±0.59cal/deg)	1365-1610°K
1/2 $WS_{2(c)}$	-40,110 + 18.64Tcal(±220cal)	-40,110cal(±920cal)	-18.64cal/deg(±0.63cal/deg)	1370-1565°K
Group Ib:				
$Cu_2S_{(\gamma)}$	-30,850 + 7.01Tcal(±220cal)	-30,850cal(±370cal)	- 7.01cal/deg(±0.36cal/deg)	970-1300°K

The standard state for the sulfides is the crystalline state at one atmosphere pressure and at the temperature designated. The reference state for the metals is the crystalline state at one atmosphere pressure and at the temperature designated, and for sulfur it is the ideal diatomic gas at one atmosphere pressure and at the temperature designated.

C. Tungsten Sulfide

The thermodynamic properties of $WS_{2(c)}$ have been determined through a high-temperature investigation of the equilibrium

$$1/2\ WS_{2(c)} + H_{2(g)} = 1/2\ W_{(c)} + H_2S_{(g)} \qquad \text{(V-9)}$$

Two limiting values for ΔF°_R for reaction (V-9) have been calculated for each experimental temperature. The results are tabulated in Appendix E and are presented graphically in Fig. 5. Calculations to determine the linear variation of ΔF°_R with temperature and to estimate the uncertainty in the results are given in Appendix E. The equation for the standard free energy change of reaction (V-9) is:

$$\Delta F^\circ_R = 18{,}540 - 6.85T\text{,cal } (\underline{+}100 \text{ cal}) \ (1370 - 1565°\text{K}) \qquad \text{(V-10)}$$

$$\text{where} \quad \Delta H^\circ_R = 18{,}540 \text{ cal } (\underline{+}\ 910 \text{ cal}) \qquad \text{(V-11)}$$

$$\Delta S^\circ_R = 6.85 \text{ cal/deg } (\underline{+}\ 0.61 \text{ cal/deg}) \qquad \text{(V-12)}$$

Equation (V-10) combined with the equation for the standard free energy of formation of $H_2S_{(g)}$ from Table I gives the equation for the standard free energy of formation of 1/2 $WS_{2(c)}$. The result, including the estimate of uncertainty, is calculated in Appendix E and is presented in Table VI.

D. Copper Sulfide

To serve as a check on the reliability of the experimental technique, the standard free energy of formation of $Cu_2S_{(\gamma)}$ was measured by means of a high-temperature investigation of the equilibrium

$$Cu_2S_{(\gamma)} + H_{2(g)} = 2Cu_{(c)} + H_2S_{(g)} \qquad \text{(V-13)}$$

using the same experimental procedure as was used for $CrS_{(c)}$, $Mo_2S_{3(c)}$ and $WS_{2(c)}$. Two limiting values of ΔF°_R for reaction (V-13) have been calculated for each experimental temperature. The results are tabulated in Appendix F and are presented graphically in Fig. 6, together with the results of other investigators (see Table III). Calculations to determine the linear variation of ΔF°_R with temperature and to estimate the uncertainty in the results are given in Appendix F. The equation for the standard free energy change of reaction (V-13) is:

$$\Delta F^\circ_R = 9,280 + 4.78T, \text{ cal } (\pm 100 \text{ cal})(970 - 1300°K) \qquad \text{(V-14)}$$

where $$\Delta H^\circ_R = 9,280 \text{ cal } (\pm\ 360 \text{ cal}) \qquad \text{(V-15)}$$

$$\Delta S^\circ_R = -4.78 \text{ cal/deg } (\pm\ 0.33 \text{ cal/deg}) \qquad \text{(V-16)}$$

Equation (V-14) combined with the equation for the standard free energy of formation of $H_2S_{(g)}$ from Table I gives the equation for the standard free energy of formation of $Cu_2S_{(\gamma)}$. The result, including the estimate of uncertainty, is calculated in Appendix F and is presented in Table VI.

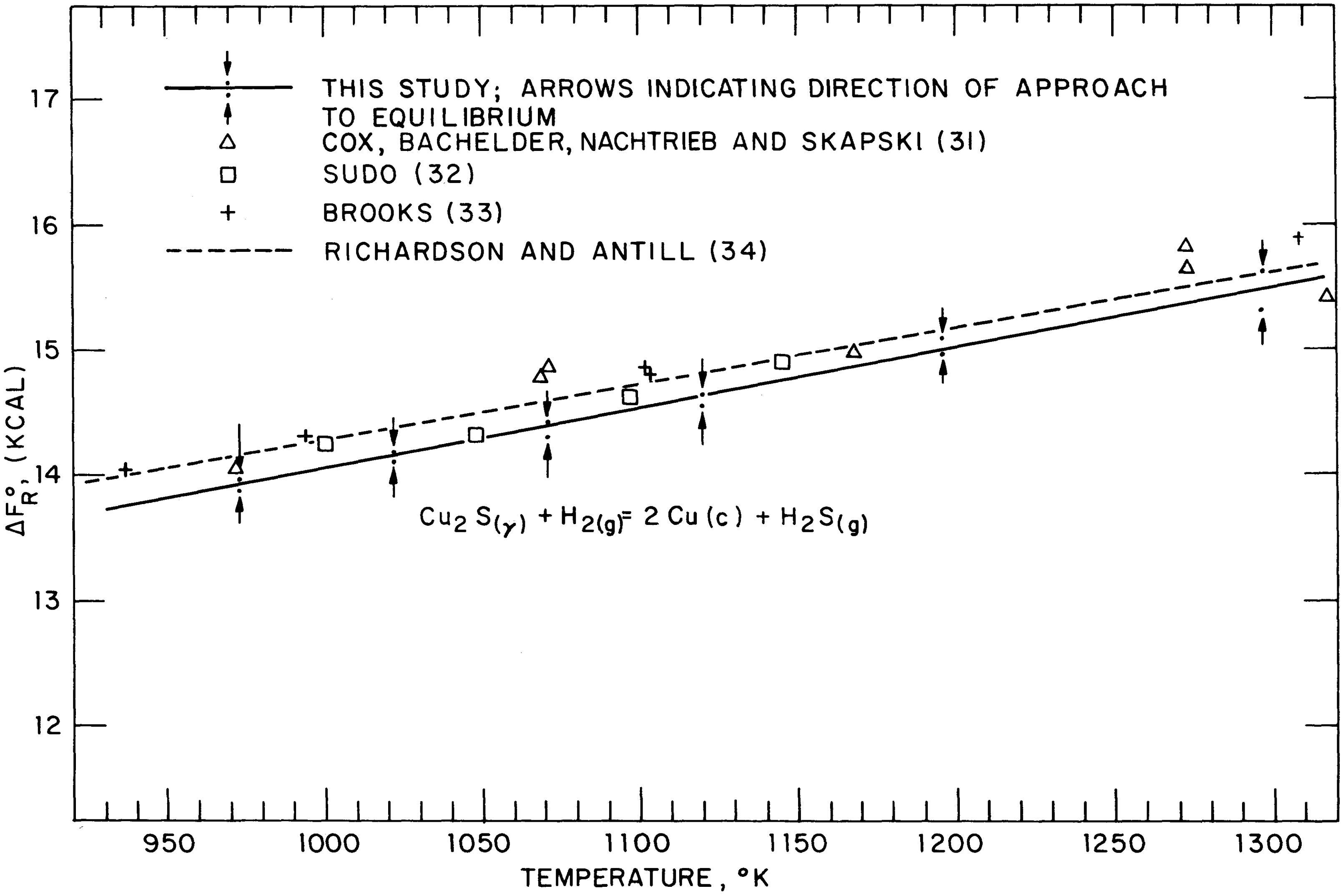

FIG. 6-FREE ENERGY CHANGE FOR REACTION (V-13)

VI. DISCUSSION

A. Evaluation of the Experimental Technique

One means of evaluating the experimental technique is by comparing equilibrium results obtained with the experimental method of this study against the results of other investigators for the same equilibrium measured by a different experimental technique. The equilibrium

$$Cu_2S_{(\gamma)} + H_{2(g)} = 2Cu_{(c)} + H_2S_{(g)} \qquad \text{(VI-1)}$$

was chosen, because the equilibrium $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio had been measured by several investigators using more classical experimental procedures.

The results of the experimental investigation of reaction (VI-1) are presented in Fig. 6 in the form of the limiting values of ΔF°_R for reaction (VI-1). The data of the equilibrium measurements of Cox, Bachelder, Nachtrieb and Skapski,[31] Sudo,[32] Brooks[33] and Richardson and Antill[34] are included for comparison. Of these four sets of measurements, the results of Cox, Bachelder, Nachtrieb and Skapski[31] and Sudo[32] are judged to be the least accurate. Cox, Bachelder, Nachtrieb and Skapski[31] measured the equilibrium $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio by the recirculation technique. However, their results are somewhat scattered and their flow-rate of 60 ml STP/min through a one-inch bore reaction tube may have been insufficient to prevent thermal segregation. Sudo[32] measured the effluent $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio for hydrogen passed over a heated sample of $Cu_2S_{(\gamma)} + Cu_{(c)}$, and extrapolated the gas ratio to zero flow-rate to obtain the equilibrium gas ratio. Unfortunately, this is also the condition for maximum thermal segregation in the reaction tube. Brooks[33] and Richardson and Antill[34] used the recirculation method with particular effort to eliminate the effects of thermal segregation. Their measurements are in good agreement. In addition, their results have been extrapolated by J. B. Wagner and C. Wagner[37] and combined with the standard free energy of formation of $H_2S_{(g)}$ to give the value -22,659 cal for the standard free energy of formation of $Cu_2S_{(c)}$ at 573°K, which is in good agreement with the value of -22,607 cal determined by J. B. Wagner and C. Wagner[37] from galvanic cell measurements.

The line drawn through the experimental results of this study gives values of ΔF°_R which are slightly less positive than those obtained by the other investigators. However, the line representing the results of this study is nearly parallel to the line representing the results of Richardson and Antill,[34] and, for that matter, the results of Brooks.[33] The difference in ΔF°_R at 1100°K, given by this study and by Richardson and Antill,[34] is (14,540 cal, this study, minus 14,740 cal, Richardson and Antill[34] = -200 cal) which is a little greater than the sum of the assigned uncertainties ($\pm$100 cal, this study, plus $\pm$ 30 cal, Richardson and Antill,[34] = $\pm$ 130 cal). On the other hand, the difference in ΔS°_R given by this study and by Richardson and Antil[34] is (4.78 cal/deg, this study, minus 4.45 cal/deg, Richardson and Antill[34] = 0.33 cal/deg) which is within the sum of the assigned uncertainties ($\pm$0.33 cal/deg, this study, plus $\pm$ 0.10 cal/deg, Richardson and Antill,[34] = $\pm$ 0.43 cal/deg). Consequently, it appears that the line representing the results of this study is subject to a systematic error of approximately 200 cal which has shifted the entire line downward to less positive values of ΔF°_R.

As observed in Chapter III, the rate of reduction of $Cu_2S_{(\gamma)}$ by pure hydrogen was rather high. If the rate of reduction was sufficiently fast, then samples which were only slightly sulfided by the gas stream, which is the case for samples exposed to mixtures with gas ratios only slightly greater than the equilibrium ratios, would be reduced by the hydrogen stream in the process of being withdrawn from the reaction tube. These samples would be interpreted erroneously as non-sulfided. Such an effect would explain the systematic error observed between the ΔF°_R values given by this study and those by the previous investigators. In Fig. 6, the data points indicated by the downward arrows correspond to the maximum values of the $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio for which the samples remained metallic at the experimental temperatures. If these samples were slightly sulfided by the gas stream, but inadvertently reduced during withdrawal from the reaction tube, then the equilibrium gas ratios were actually less than these experimental gas ratios. Accordingly, the arrows indicating these points should be pointed upward, which would place the line representing the values of ΔF°_R for reaction (VI-1) above these points and closer to the results of the other investigators.

Although the experimental method employed in this study was unable to measure the standard free energy change of reaction (VI-1) to better than 200 cal of the accepted ΔF°_R values, a somewhat better accuracy is expected for the application of the experimental technique to the study of the Group VIa sulfides. The observed rate of reduction of $CrS_{(c)}$, $Mo_2S_{3(c)}$ and $WS_{2(c)}$ by hydrogen was considerably less than that for $Cu_2S_{(\gamma)}$. Accordingly, the apparent error in the $Cu_2S_{(\gamma)}$ results, due to the inadvertent reduction of the sulfide layer on those samples exposed to a gas mixture with a $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio only slightly greater than equilibrium, was assumed to be eliminated. Furthermore, excellent agreement was obtained between the present results and those of Stubbles and Richardson[11] on $Mo_2S_{3(c)}$, which was the only previous investigation of the Group VIa sulfides to give apparently reliable results. The comparison will be discussed more fully in the next section.

The purpose of employing the present experimental technique was to eliminate the necessity of recirculating ($H_2S_{(g)} + H_{2(g)}$) mixtures for long periods of time, in order to obtain the equilibrium gas composition. In addition, two other disadvantages associated with the recirculation method were eliminated: namely, limitation to small sample volumes for gas analysis and possible contamination of the gas mixture and sample through continual circulation of the same gas volume. On the basis of the comparison of the results obtained with this method and those by other investigators using the recirculation method, the present experimental technique appeared to be entirely satisfactory as long as the rate of reduction of the sulfide phase was not so rapid as to cause removal of the sulfide layers during withdrawal of the sample from the reaction tube. On the other hand, the slow reaction rate between the sulfide and gas phase prevented an examination of the equilibrium ratio from the reverse direction; i. e., determining the gas ratios for which a sulfided sample would remain sulfided or be reduced to the metal phase. The rate of reduction of $CrS_{(c)}$ was sufficiently fast that the reversible formation of the $CrS_{(c)}$ layer was determined experimentally at one temperature. However, the sulfided surfaces of the molybdenum and tungsten samples were not easily reduced and the reversible formation of sulfide layers could not be studied.

B. Comparison of the Results for $CrS_{(c)}$, $Mo_2S_{3(c)}$ and $WS_{2(c)}$ with Those of Previous Studies

The thermodynamic measurements of previous investigators on the Group VIa sulfides have been reviewed in Chapter II. Their results may now be compared with those of this study.

1. Chromium Sulfide - $CrS_{(c)}$

Previous measurements have not been reported for the high temperature thermodynamic properties of chromous sulfide. The composition of the chromium sulfide phase in equilibrium with chromium at high temperature was determined experimentally to be stoichiometric $CrS_{(c)}$. Previous studies[5] of the phase relations in the Cr-S system had not established the exact composition of the metal-saturated chromium sulfide phase, but had postulated that it was chromous sulfide.

2. Molybdenum Sulfide - $Mo_2S_{3(c)}$

The equilibrium $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio for the reaction

$$1/3\ Mo_2S_{3(c)} + H_{2(g)} = 2/3\ Mo_{(c)} + H_2S_{(g)} \qquad \text{(VI-2)}$$

has been measured by Stubbles and Richardson[11] using the recirculation method. Their results for the thermodynamic properties of reaction (VI-2) together with the results of this study are given in Table VII. At 1500°K

TABLE VII

THERMODYNAMIC PROPERTIES FOR THE REACTION

$1/3\ Mo_2S_{3(c)} + H_{2(g)} = 2/3\ Mo_{(c)} + H_2S_{(g)}$

Investigation	$\Delta F^\circ_R = A + BT$	ΔH°_R	ΔS°_R
Stubbles and Richardson[11]	20,270-6.4Tcal($\pm$100cal) (1123-1573°K)	20,270cal($\pm$1Kcal)	6.4cal/deg($\pm$1.0cal/deg)
This Study	20,160-5.6Tcal($\pm$100cal) (1365-1610°K)	20,160cal($\pm$880cal)	5.6cal/deg($\pm$0.57cal/deg)

the difference in ΔF°_R is (11,760 cal, this study, minus 11,670 cal, Stubbles and Richardson[11] = 90 cal), which is well within the sum of the assigned uncertainties (± 100 cal plus ± 100 cal = ± 200 cal). These two sets of results are in good agreement.

The equilibrium diatomic sulfur pressure ($P_{S_{2(g)}}$) for the reaction

$$2/3\ Mo_2S_{3(c)} = 4/3\ Mo_{(c)} + S_{2(g)} \qquad \text{(VI-3)}$$

has been calculated by McCabe[10] from Knudsen cell measurements of the total dissociation sulfur pressure and Richardson and Jeffes'[4] data for the equilibrium

$$S_{2(g)} = 2S_{(g)} \qquad \text{(VI-4)}$$

Stubbles and Richardson[11] found that the $P_{S_{2(g)}}$ values calculated by McCabe[10] were less by a factor of ten than those derived from their results. Using more recent thermodynamic data[2] for reaction (VI-4), the equilibrium $P_{S_{2(g)}}$ values for reaction (VI-3) have been calculated from McCabe's[10] weight-loss data. However, the recalculated values of $P_{S_{2(g)}}$ for reaction (VI-3) are still a factor of two less than the corresponding values calculated from the results of this study or from those of Stubbles and Richardson.[11] In terms of ΔF°_R for reaction (VI-3), the values derived from the recalculated $P_{S_{2(g)}}$ values are approximately 1.5 Kcal more positive than the corresponding results given by this study or by Stubbles and Richardson.[11] Stubbles and Richardson[11] postulated that the low sulfur pressures obtained by McCabe[10] may be due to a very small vaporization coefficient for $S_{2(g)}$ from $Mo_2S_{3(c)}$.

3. Tungsten Sulfide - $WS_{2(c)}$

The thermodynamic properties of the reaction

$$1/2\ WS_{2(c)} + H_{2(g)} = 1/2\ W_{(c)} + H_2S_{(g)} \qquad \text{(VI-5)}$$

have been determined by Cerny, Habes, Zelena and Erdos[23] by galvanic cell measurements and by the analysis of the effluent $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio in a flow system. The galvanic cell was studied in the range 388-418°K and the flow system in the range 653-773°K. However, the values of ΔF°_R for reaction (VI-5) derived from the two sets of measurements are not consistent. At 1000°K the values differ by more than 3 Kcal. The equilibrium $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratios measured by Cerny, Habes, Zelena and Erdos[23] are a factor of four smaller than the corresponding values calculated from the extrapolated results of this study. Furthermore, it is unlikely that equilibrium between $WS_{2(c)} + W_{(c)} + H_{2(g)} + H_2S_{(g)}$ could have been established at the low temperatures of their measurements.

Parravano and Malguori[17] have also studied reaction (VI-5) by analyzing the hydrogen sulfide concentration in a hydrogen stream passed over a heated sample of $WS_{2(c)} + W_{(c)}$. By extrapolation, they have obtained the $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio at zero flow rate and have taken this as the equilibrium ratio. Richardson and Jeffes[4] have applied an approximate correction to their data for the error due to thermal segregation, and have combined the corrected results with the thermodynamic data for $H_2S_{(g)}$ to give the free energy equation for the formation of $WS_{2(c)}$ from $W_{(c)}$ and $S_{2(g)}$. Their result is given in Table VIII, together with the equation derived from this study (see Table VI). At 1400°K, the difference in the free energy of formation of $WS_{2(c)}$ given by the two equations is slightly greater than 2 Kcal, which is within the sum of the assigned uncertainties as a result of the large uncertainty assigned by Richardson and Jeffes.[4] The equation derived from this study has smaller assigned uncertainties, and also the

TABLE VIII

STANDARD FREE ENERGY CHANGE FOR THE REACTION

$W_{(c)} + S_{2(g)} = WS_{2(c)}$

Reference	$\Delta F^\circ_R = A + BT$	Temperature Range
Richardson and Jeffes[4]	-62,360+23.0Tcal(±10Kcal)	298-1400°K
This Study	-80,220+37.28Tcal(±440cal)	1370-1565°K

values of ΔH°_R and ΔS°_R are more consistent with the values derived for the other Group VIa sulfides (see Table VI).

An estimated value for the heat of formation of $WS_{2(c)}$ at 298°K was obtained from the experimental value for the heat of formation from $W_{(c)}$ and $S_{2(g)}$ at 1370-1565°K given in Table VI. In the absence of high-temperature heat capacity data for $WS_{2(c)}$, the value of ΔC_p for the formation of $WS_{2(c)}$ from $W_{(c)}$ and $S_{2(g)}$ was estimated as being zero. The value used for the heat of formation of $S_{2(g)}$ at 298°K was +30.84 Kcal.[2] The result is given in Table IX, together with the calorimetric values taken from the literature. The large uncertainty in the value estimated from the results of this study reflects the uncertainty in the estimated value of ΔC_p. It appears that the ΔH°_f value given by Freeman[25] may be spurious.

TABLE IX

HEAT OF FORMATION OF $WS_{2(c)}$ AT 298°K

Reference	$\Delta H^\circ_{f(298)} - WS_{2(c)}$	Uncertainty
Hartmann and Wagner[24]	-47.9 Kcal	± 0.8 Kcal
Rossini, et. al.[26]	-46.3 Kcal	?
Freeman[25]	-71.3 Kcal	± 0.2 Kcal
This Study	-49.4 Kcal	± 5 Kcal

C. Estimation of the Entropies of Formation of the Refractory Metal Sulfides

Krikorian[45] has shown that the entropies of formation of the refractory metal carbides, nitrides and oxides are equivalent if compared on the basis of the formation from the gaseous atoms. At 298°K, the average entropy of formation per 2 g-atoms of gaseous reactants was found to be -63.0 cal/deg (±1.0 cal/deg). It would be of practical interest to learn whether reasonable values for the entropy of formation of the Group VIa metal sulfides from crystalline metal and diatomic sulfur gas could be estimated, on the assumption that the average entropy of formation of the refractory metal sulfides per 2 g-atoms of gaseous reactants is also -63.0 cal/deg (± 1.0 cal/deg).

Estimated values for the entropy of formation of $CrS_{(c)}$, $Mo_2S_{3(c)}$ and $WS_{2(c)}$, according to the reaction

$$X/Y\ Me_{(c)} + 1/2\ S_{2(g)} = 1/Y\ Me_XS_{Y(c)} \qquad \text{(VI-6)}$$

can be calculated at 298°K from the following equation

$$\Delta S^\circ_f = \left(\frac{X+Y}{2Y}\right)(-63.0) + X/Y\left(S^\circ_{Me_{(g)}} - S^\circ_{Me_{(c)}}\right) + \left(S^\circ_{S_{(g)}} - 1/2S^\circ_{S_{2(g)}}\right) \qquad \text{(VI-7)}$$

where -63.0 = assumed entropy change for the reaction

$$\frac{2X}{X+Y}\,Me_{(g)} + \frac{2Y}{X+Y}\,S_{(g)} = \frac{2}{X+Y}\,Me_XS_{Y(c)}$$

$S^\circ_{Me_{(g)},Me_{(c)},S_{(g)},S_{2(g)}}$ = standard entropies of $Me_{(g)}$, $Me_{(c)}$, $S_{(g)}$, and $S_{2(g)}$ at 298°K

The entropies of formation of $CrS_{(c)}$, $Mo_2S_{3(c)}$ and $WS_{2(c)}$, calculated from equation (VI-7) and the standard entropies of $Cr_{(g)}$, $Cr_{(c)}$, $Mo_{(g)}$, $Mo_{(c)}$, $W_{(g)}$, $W_{(c)}$, $S_{(g)}$ and $S_{2(g)}$ (see Table X), are compared in Table XI with the experimental results of this study. The two sets of results are not directly comparable, since the experimental results were obtained in the range (1365-1610°K) and the estimated values were calculated at 298°K. However, the close agreement between the two sets of values indicates that the basic assumption, that the entropies of formation of the refractory metal sulfides are equivalent to the entropies of formation of the carbides, nitrides and oxides, if compared on the basis of the formation from the gaseous atoms, was correct. Accordingly, reasonable values for the standard entropy of formation of the refractory metal sulfides at 298°K can be estimated by assuming that the average entropy of formation per 2 g-atoms of gaseous reactants is -63.0 cal/deg ($\pm$ 1.0 cal/deg). The estimated standard entropies of formation of the mono-, sesqui- and di-sulfide phases of the Group IVa, Va and VIa metals are given in Table XII. Values for the standard entropies of the elements were taken from Table IX. Although the standard entropies of formation were calculated for the mono-, sesqui- and di-sulfide phases of each metal, this is not meant to imply that each metal-sulfur system will contain these three phases. The entropies of formation have been calculated per mole of rhombic sulfur, the reference state for sulfur at 298°K.

TABLE X

STANDARD ENTROPIES OF THE ELEMENTS AT 298°K, ACCORDING TO STULL AND SINKE[46]

ecies	$Cr_{(c)}$	$Cr_{(g)}$	$Mo_{(c)}$	$Mo_{(g)}$	$W_{(c)}$	$W_{(g)}$	$S_{(g)}$	$S_{2(g)}$	$S_{(rh)}$	$Ti_{(c)}$	$Ti_{(g)}$
98' 1/deg/gfw	5.70	41.64	6.83	43.46	8.04	41.55	40.09	54.51	7.62	7.33	43.07

ecies	$Zr_{(c)}$	$Zr_{(g)}$	$H_{f(c)}$	$H_{f(g)}$	$V_{(c)}$	$V_{(g)}$	$Nb_{(c)}$	$Nb_{(g)}$	$Ta_{(c)}$	$Ta_{(g)}$
98' 1/deg/gfw	9.29	43.32	10.91	44.64	7.01	43.55	8.73	44.49	9.90	44.24

TABLE XI

COMPARISON OF EXPERIMENTAL AND ESTIMATED VALUES FOR THE ENTROPY OF FORMATION OF THE GROUP VIa SULFIDES PER 1/2 g-MOLE $S_{2(g)}$

	ΔS°_f, cal/deg/1/2 g-mole $S_{2(g)}$	
Sulfide	This Study(1365-1610°K)	Estimated(298°K)
$CrS_{(c)}$	-13.27 (±0.52)	-14.2(±1.0)
$1/3Mo_2S_{3(c)}$	-17.39 (±0.59)	-18.6(±1.0)
$1/2WS_{2(c)}$	-18.64 (±0.63)	-17.7(±1.0)

TABLE XII

ESTIMATED STANDARD ENTROPIES OF FORMATION AT 298°K FOR THE MONO-, SESQUI- AND DI-SULFIDE PHASES OF THE REFRACTORY METALS

	ΔS°_f, cal/deg/g-atom $S_{(rh)}$		
Metal	Mono-sulfide	Sesqui-sulfide	Di-sulfide
Group IVa:			
Ti	5.2(±2.0)	3.8(±2.0)	3.1(±2.0)
Zr	3.5(±2.0)	2.7(±2.0)	2.2(±2.0)
H_f	3.2(±2.0)	2.5(±2.0)	2.1(±2.0)
Group Va:			
V	6.0(±2.0)	4.3(±2.0)	3.5(±2.0)
Nb	5.2(±2.0)	3.8(±2.0)	3.1(±2.0)
Ta	3.8(±2.0)	2.9(±2.0)	2.4(±2.0)
Group VIa:	[6.4(±3.0)]*		
Cr	5.4(±2.0)	3.9(±2.0) [2.2(±3.0]*	3.2(±2.0) [1.0(±3.0)]**
Mo	6.1(±2.0)	4.4(±2.0)	3.5(±2.0) [1.0(±3.0)]*
W	3.0(±2.0)	2.3(±2.0)	2.0(±2.0)

* Calculated by extrapolating the experimentally determined values of this study (see Table XI) to 298°K, assuming $\Delta C_p=0$, and combining with the entropy of formation of $1/2S_{2(g)}$ (see Table X).

** Calculated by extrapolating Stubbles and Richardson's[11] experimentally determined value of -18.66 cal/deg/1/2 g-mole $S_{2(g)}$ (1000-1200°C) to 298°K, assuming $\Delta C_p=0$, and combining with the entropy of formation of $1/2S_{2(g)}$ (See Table X).

VII. SUGGESTIONS FOR FURTHER WORK

A. Measurement of the Activity of Chromium in Cr-Mo and Cr-W Solid Solutions

By measuring the equilibrium $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio for the reaction

$$CrS_{(c)} + H_{2(g)} = \underline{Cr} + H_2S_{(g)} \qquad \text{(VII-1)}$$

where $\underline{Cr}$ = chromium dissolved in a solid solution of Cr-Mo or Cr-W

the activity of the dissolved chromium, relative to pure solid chromium, can be calculated as follows:

$$a_{\underline{Cr}} = \frac{\left(P_{H_2S_{(g)}}/P_{H_{2(g)}}\right)^{\circ}}{\left(P_{H_2S_{(g)}}/P_{H_{2(g)}}\right)^{*}} \qquad \text{(VII-2)}$$

where $a_{\underline{Cr}}$ = activity of the dissolved chromium

$\left(P_{H_2S_{(g)}}/P_{H_{2(g)}}\right)^{\circ}$ = equilibrium ratio for reaction (VII-1) for pure chromium (determined by this study)

$\left(P_{H_2S_{(g)}}/P_{H_{2(g)}}\right)^{*}$ = equilibrium ratio for reaction (VII-1) for chromium in the dissolved state

At 1300°C, chromium forms a continuous series of solid solutions with molybdenum whereas, with tungsten, two series of solid solutions which are separated by a miscibility gap. Activity measurements in the Cr-W system would provide additional information on the position of the miscibility gap.

From equation (VII-2) it is seen that, as the value of $a_{\underline{Cr}}$ decreases, the value of the $(P_{H_2S_{(g)}}/P_{H_{2(g)}})^{*}$ ratio increases. Calculations based on the free energy results for $CrS_{(c)}$, $Mo_2S_{3(c)}$ and $WS_{2(c)}$ show that the value of $\underline{a}_{\underline{Cr}}$ can be as low as 0.02 before the gas ratio is large enough to precipitate either $Mo_2S_{3(c)}$ or $WS_{2(c)}$. The equilibrium $(P_{H_2S_{(g)}}/P_{H_{2(g)}})^*$ ratio could be determined by the experimental technique employed in this study. Instead of pure chromium, samples of Cr-Mo or Cr-W alloy foil could be used. However, the possible formation of a mixed sulfide on the surface of the alloy foil cannot be discounted.

B. Investigation of the Sublimation of Tungsten Disulfide

In the course of this study, several experiments were conducted in which weight changes were recorded for sulfidization of tungsten samples according to the reaction

$$1/2\ W_{(c)} + H_2S_{(g)} = 1/2\ WS_{2(c)} + H_{2(g)} \qquad \text{(VII-3)}$$

The $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio for the gas mixture was adjusted so as to be only slightly greater than the determined equilibrium ratio. Samples exposed to the gas mixture for two to three hours showed a uniform coating of $WS_{2(c)}$. However, the weight change measurements revealed that the samples experienced a net loss of weight upon sulfidization. This indicated that sufficient $WS_{2(c)}$ had sublimed to more than offset the weight gain by the transfer of sulfur from the gas phase to the sample. The thermodynamics of the sublimation reaction could be obtained from a series of transpiration experiments, provided the stoichiometry of the reaction was first established by a mass spectrometric analysis of the gaseous molecules formed by sublimation.

Berkowitz, Chupka and Inghram[47] have found, from a mass spectrometric study of the gaseous species effusing from a Knudsen cell filled with $WO_{3(c)}$, that $WO_{3(c)}$ sublimes according to the following reaction

$$(4X + 5Y + 3)WO_{3(c)} = (WO_3)_{3(g)} + X(WO_3)_{4(g)} + Y(WO_3)_{5(g)} \qquad (VII\text{-}4)$$

From the relative ion current intensities of the largest ion peaks of $(WO_3)_{3(g)}$, $(WO_3)_{4(g)}$ and $(WO_3)_{5(g)}$ the values of X and Y were calculated to be 0.3 and 0.002, respectively. The sublimation of $WS_{2(c)}$ is anticipated to be similar to that for $WO_{3(c)}$.

By measuring the weight loss of a sample of powdered $WS_{2(c)}$ in a stream of $(H_2S_{(g)} + H_{2(g)})$ with a $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio, only slightly greater than the equilibrium ratio for reaction (VII-3), the effect of sulfur transfer in the transpiration experiment is eliminated. Consequently, the observed weight loss is due solely to the sublimation reaction. If the stoichiometry of the sublimation reaction has been established from a mass spectrometric study, the partial pressures of the molecular species formed by the sublimation of $WS_{2(c)}$ can be calculated from the value of the weight loss per unit volume of carrier gas. However, the value of the weight loss/unit volume of carrier gas must correspond to saturation of the carrier gas with the products of sublimation.

C. Study of the Higher Sulfides of Chromium Through $(H_2S_{(g)} + H_{2(g)})$ Equilibration

The thermodynamic properties of $CrS_{(c)}$, the sulfide in equilibrium with chromium, have been investigated in the present study. However, higher sulfide phases, $Cr_7S_{8(c)}$, $Cr_5S_{6(c)}$, $Cr_3S_{4(c)}$ and $Cr_2S_{3(c)}$ have been reported in the literature.[5] Thermodynamic studies have not been reported for any of these sulfide phases. Also, it is not clear whether all of these phases are stable above 1000°C.

On the basis of the results of this study, several conclusions can be drawn which indicate that a thermodynamic study of the higher sulfide phases can be made by means of equilibration with ($H_2S_{(g)} + H_{2(g)}$) mixtures. Most important, the values of the equilibrium $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio will be larger, not smaller, than the values encountered in this study (1 to 4×10^{-4}), and thus in a range amenable to experimental study. Also, the rate of reaction between the $CrS_{(c)}$ phase and the gas phase was sufficiently fast that equilibration should be readily attained by recirculation of the gas mixture over the heated sample. Furthermore, no deleterious side effects, such as formation of a highly volatile sulfide phase or a low temperature liquid phase, were observed.

An investigation of the variation of the equilibrium $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratio with composition, at constant temperature, would provide valuable information on the extent of the homogeneity ranges and the stability of the sulfide phases. In a composition region consisting of two sulfide phases, the gas ratio will remain constant with composition, whereas within the homogeneity range of a phase the gas ratio will increase with increasing sulfur concentration. Although the composition of the sulfide phase in equilibrium with chromium was determined experimentally to be stoichiometric $CrS_{(c)}$, the presence of solid solubility of sulfur in the $CrS_{(c)}$ phase, at higher sulfur pressures, could be detected.

REFERENCES

1. J. B. Scarborough, Numerical Mathematical Analysis, Johns Hopkins Press, Baltimore, 1958.

2. JANAF Thermochemical Tables, The Dow Chemical Company, Midland, Michigan; December 31, 1960 ($HS_{(g)}$), March 31, 1961 ($H_2S_{(g)}$) and June 30, 1961 ($S_{(g)}$).

3. J. W. C. Johns and D. A. Ramsay, "The Absorption Spectrum and Dissociation Energy of $HS_{(g)}$," Can. J. Phys., 39, 210 (1961).

4. F. D. Richardson and J. H. E. Jeffes, "The Thermodynamics of Substances of Interest in Iron and Steel Making," Part III - Sulfides, J. Iron and Steel Inst., 171, 165 (1952).

5. F. Jellinek, "Sulfides of Transition Metals," Arkiv fӧr Kemi., 20, 447 (1963).

6. H. Haraldsen, "Phase Relations in the System Cr-S," Z. Anorg. Allegem. Chem., 234, 372 (1937).

7. F. Jellinek, "The Structures of Chromium Sulfides," Acta Cryst., 10, 620 (1957).

8. V. N. Konev, N. G. Bogacheva and V. P. Pavlova, "The Problem of Chromium Sulfide Structure," Phy. Metals and Metallog., 9, No. 3, 139 (1960).

9. I. G. Fakidov and N. P. Grazhdankina, "Heat Capacity of Ferromagnetic Chromium Sulfide (Cr_5S_6)," Akad. Nauk. S.S.S.R. Ural Filial, 15, 60 (1954).

10. C. L. McCabe, "Sulfur Pressure Measurements of Molybdenum Sesquisulfide in Equilibrium with Molybdenum," J. Metals, 61 (Jan., 1955).

11. J. R. Stubbles and F. D. Richardson, "Equilibria in the System Molybdenum + Sulfur + Hydrogen," Trans., Faraday Soc., 56, 1460 (1960).

12. A. V. Gorokh, L. N. Rusakov and A. A. Savinskaya, "Synthesis and Characteristics of Molybdenum Sesquisulfide," Dokl. Akad. Nauk. S.S.S.R., 156, 541 (1964).

13. A. V. Gorokh, L. I. Klokotina and K. N. Rispel, "Behavior of Molybdenite and its Dissociation Products on Heating," Dokl. Akad. Nauk S.S.S.R., 158, 1183 (1964).

14. J. C. Wildervanck and F. Jellinek, "Preparation and Crystallinity of Molybdenum and Tungsten Sulfides," Z. Anorg. Allegem. Chem., 328, 309 (1964).

15. N. Morimoto and G. Kullerud, "The Mo-S System," Carnegie Institution of Washington Yearbook, *61*, 143 (1962).

16. S. C. Schaefer, A. H. Larson and A. W. Schlechten, "Sulfur Pressure Variation of Molybdenum Disulfide at 1100°C," *Trans.*, Met. Soc., AIME, *230*, 594 (1964).

17. N. Parravano and G. Malquori, "Reaction of MoS_2 and WS_2 with $H_{2(g)}$," *Att. Rendiconti Accad. Lincei.*, *7*, Series 6, 109, 189 (1928).

18. A. N. Zelikman and O. E. Krein, "Thermal Dissociation of Molybdenum Disulfide," *Zhur. Fiz. Khim.*, *29*, 2081 (1955).

19. P. Ehrlich, "Tungsten Sulfides," *Z. Anorg. Chem.*, *257*, 247 (1948).

20. O. Glemser, H. Sauer and P. König, "Sulfides and Selenides of Tungsten," *Z. Anorg. Chem.*, *257*, 241 (1948).

21. S. M. Samoilov and A. M. Rubinshtein, "Phase Composition and Crystalline Structure of WS_2 Catalysts," *Izvest. Akad. Nauk S.S.S.R.*; *Otdel. Khim. Nauk*, *1959*, 1905 (1959).

22. S. A. Shchukarev, M. P. Morozova and Kh. Damen, "The System W-WS_2," *Zhur. Obshchei Khim.*, *30*, 2102 (1960).

23. C. Cerny, M. Habes, M. Zelena and E. Erdos, "The Chemical Equilibrium of Reaction between Tungsten (IV) Sulfide and Hydrogen at Medium Temperatures," *Collection Czechoslov. Chem. Commun.*, *24*, 3836 (1959).

24. H. Hartmann and G. Wagner, "Heats of Formation of WS_2, V_2S_3, Nb_4S_7 and TaS_2 with a New High-Temperature Differential Calorimeter," *Abhandl. Braunschweig. Wiss. Ges.*, *14*, 13 (1962).

25. R. D. Freeman, *Thermodynamic Properties of Binary Sulfides*, Research Foundation Report No. 60, Oklahoma State University, Stillwater, Oklahoma, 1962.

26. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, *Selected Values of Chemical Thermodynamic Properties*, N. B. S. Circular 500, Washington, D. C., 1952.

27. R. Ueda, "X-ray and Thermal Studies on the Phase Transitions of Cuprous Sulfide," *J. Phy. Soc.*, Japan, *4*, 287 (1949).

28. S. Djurle, "X-Ray Study on the System Cu-S," *Acta Chem. Scand.*, *12*, 1415 (1958).

29. V. Wehefritz, "The System Copper-Sulfur," *Z. Physik. Chem. Neue Folge*, *26*, 339 (1960).

30. F. Johannsen and H. Vollmer, "The System Copper-Copper Sulfide," Z. Erzbergbau U. Metallhüttenw., 13, 313 (1960).

31. E. M. Cox, M. C. Bachelder, N. H. Nachtreib and A. S. Skapski, "The Influence of Temperature on the Affinity of Sulfur for Copper, Manganese and Iron," J. Metals, 1, 27 (1949).

32. K. Sudo, "Equilibrium in the Reduction of Solid Cuprous Sulfide by Hydrogen Gas," Sci. Rep. Res. Inst., Tohoku Univ., A2, 513 (1950).

33. A. A. Brooks, "A Thermodynamic Study of the Equilibrium $2Cu_{(c)} + H_2S_{(g)} = Cu_2S_{(\gamma)} + H_{2(g)}$," J. Am. Chem. Soc., 75, 2464 (1953).

34. F. D. Richardson and J. E. Antill, "Thermodynamic Properties of Cuprous Sulfide and its Mixtures with Sodium Sulfide," Trans., Faraday Soc., 51, 22 (1955).

35. T. Tanka, K. Watanabe and J. Kwihara, "Reduction Equilibrium of Cuprous Sulfide and Hydrogen," Mem. Fac. Eng. Hokkaido Univ., 8, Part 1, 14 (1950).

36. A. Kihira and K. Sano, "The Reduction Equilibrium of Cuprous Sulfide by Hydrogen," Mem. Fac. Eng. Nagoya Univ., 5, No. 1, 100 (1953).

37. J. B. Wagner and C. Wagner, "Determination of the Standard Free Energy of Formation of Cuprous Sulfide at 300°C," J. Electrochem. Soc., 104, 509 (1957).

38. H. Shenker, J. I. Lauritzen, Jr., R. J. Corruccini and S. T. Lonberger, Reference Tables for Thermocouples, N. B. S. Circular 561, Washington, D. C., 1955.

39. A. S. Foust, L. A. Wenzel, C. W. Clump, L. Maus and L. B. Andersen, Principles of Unit Operations, John Wiley & Sons, Inc., New York, 125, 1960.

40. C. R. Wilke, "A Viscosity Equation for Gas Mixtures," J. Chem. Phys., 18, 517 (1950).

41. P. O. Bethge, "The Volumetric Determination of Hydrogen Sulfide and Soluble Sulfides," Anal. Chim. Acta, 9, 129 (1953); 10, 113 (1954).

42. I. M. Kolthoff and R. Belcher, Volumetric Analysis - III, Titration Methods, Interscience Publishers, Inc., New York, 199, 1957.

43. C. W. Sherman, H. I. Elvander and J. Chipman, "Thermodynamic Properties of Sulfur in Molten Iron-Sulfur Alloys," Trans., Met. Soc. AIME, 188, 334 (1950).

44. D. A. Pantony, A Chemist's Introduction to Statistics, Theory of Error and Design of Experiment, Lecture Series 1961, No. 2, The Royal Institute of Chemistry, London, 1961.

45. O. H. Krikorian, "High Temperature Studies," Parts I, II and III, University of California Radiation Laboratory, UCRL-2888, April, 1955.

46. D. R. Stull and G. C. Sinke, *Thermodynamic Properties of the Elements*, Advances in Chemistry Series No. 18, American Chemical Society, Washington, D. C., 1956.

47. J. Berkowitz, W. A. Chupka and M. G. Inghram, "Polymeric Gaseous Species in the Sublimation of Tungsten Trioxide," *J. Chem. Phys.*, *27*, 85 (1957).

48. J. F. Elliott and M. Gleiser, *Thermochemistry for Steelmaking*, Vol. 1, Addison-Wesley Publishing Company, Reading, Massachusetts, 1960.

APPENDIX A

TABULATION OF EXPERIMENTAL DATA

The superscripts "M" and "S" attached to the run numbers indicate whether the sample surface was metallic or sulfided at the completion of the run. Temperatures are reported as corrected. Calculation of temperature corrections, due to thermal gradient in the reaction tube and calibration of the thermocouple, are outlined in Chapter III. The $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratios are the inlet ratios.

TABLE A-I

TABULATION OF EXPERIMENTAL DATA

SYSTEM: $Mo_{(c)} - Mo_2S_{3(c)}$

Run #	$T_{(corr)}$, °K	$P_{H_2S_{(g)}}/P_{H_{2(g)}}$
9-A-16^{M}	1612	$3.112x10^{-2}$
9-A-17^{S}	1612	$3.265x10^{-2}$
9-A-12^{M}	1562	$2.381x10^{-2}$
9-A-15^{M}	"	$2.472x10^{-2}$
9-A-13^{S}	"	$2.572x10^{-2}$
9-A-14^{S}	"	$2.686x10^{-2}$
9-A-8^{M}	1513	$1.704x10^{-2}$
9-A-7^{M}	"	$1.835x10^{-2}$
9-A-6^{M}	1512	$1.965x10^{-2}$
9-A-11^{S}	"	$2.085x10^{-2}$
9-A-9^{S}	"	$2.191x10^{-2}$
9-A-4^{M}	1462	$1.495x10^{-2}$
9-A-3^{M}	"	$1.590x10^{-2}$
9-A-5^{S}	"	$1.688x10^{-2}$
9-A-2^{S}	"	$1.767x10^{-2}$

SYSTEM: $Cr_{(c)} - CrS_{(c)}$

Run #	$T_{(corr)}$, °K	$P_{H_2S_{(g)}}/P_{H_{2(g)}}$
10-A-23^{M}	1567	$3.804x10^{-4}$
10-A-22^{M}	1568	$3.917x10^{-4}$
10-A-20^{M}	"	$4.064x10^{-4}$
10-A-21^{S}	"	$4.167x10^{-4}$
10-A-24^{S}	"	$4.300x10^{-4}$
10-A-8^{M}	1513	$2.690x10^{-4}$
10-A-9^{M}	"	$2.928x10^{-4}$
10-A-10^{S}	"	$3.040x10^{-4}$
10-A-7^{S}	"	$3.169x10^{-4}$
10-A-6^{M}	1464	$2.173x10^{-4}$
10-A-3^{M}	"	$2.225x10^{-4}$
10-A-5^{S}	1463	$2.285x10^{-4}$
10-A-4^{S}	1464	$2.389x10^{-4}$
10-A-1^{S}	1463	$2.582x10^{-4}$

TABLE A-I (Continued)

SYSTEM: Mo$_{(c)}$ - MO$_2$S$_{3(c)}$

Run #	$T_{(corr)}$, °K	$P_{H_2S(g)}/P_{H_2(g)}$
9-A-1^{S}	1463	2.013×10^{-2}
9-A-18^{M}	1415	1.251×10^{-2}
9-A-19^{S}	"	1.329×10^{-2}
9-A-20^{M}	1366	9.618×10^{-3}
9-A-21^{S}	"	1.034×10^{-2}

SYSTEM: Cr$_{(c)}$ - CrS$_{(c)}$

Run #	$T_{(corr)}$, °K	$P_{H_2S(g)}/P_{H_2(g)}$
10-A-12^{M}	1419	1.548×10^{-4}
10-A-15^{M}	"	1.609×10^{-4}
10-A-13^{M}	"	1.633×10^{-4}
10-A-11^{S}	"	1.708×10^{-4}
10-A-14^{S}	"	1.713×10^{-4}
10-A-18^{M}	1376	1.180×10^{-4}
10-A-17^{S}	"	1.275×10^{-4}

SYSTEM: W$_{(c)}$ - WS$_{2(c)}$

Run #	$T_{(corr)}$, °K	$P_{H_2S(g)}/P_{H_2(g)}$
11-A-14^{M}	1567	8.273×10^{-2}
11-A-15^{S}	"	8.696×10^{-2}
11-A-13^{M}	1519	6.592×10^{-2}
11-A-11^{S}	"	6.904×10^{-2}
11-A-12^{S}	"	7.199×10^{-2}
11-A-17^{M}	1495	5.989×10^{-2}
11-A-16^{S}	1496	6.431×10^{-2}
11-A-8^{M}	1471	4.665×10^{-2}
11-A-9^{M}	"	5.434×10^{-2}
11-A-10^{S}	"	5.709×10^{-2}
11-A-7^{M}	1422	4.282×10^{-2}
11-A-5^{S}	"	4.518×10^{-2}
11-A-6^{S}	1421	4.739×10^{-2}
11-A-4^{M}	1372	3.416×10^{-2}
11-A-3^{S}	"	3.640×10^{-2}
11-A-2^{S}	"	3.961×10^{-2}
11-A-1^{S}	"	4.331×10^{-2}

SYSTEM: Cu$_{(c)}$ - Cu$_2$S$_{(c)}$

Run #	$T_{(corr)}$, °K	$P_{H_2S(g)}/P_{H_2(g)}$
12-A-3^{M}	1298	1.999×10^{-3}
12-A-1^{M}	1297	2.341×10^{-3}
12-A-2^{S}	"	2.608×10^{-3}
12-A-16^{M}	1196	1.751×10^{-3}
12-A-15^{S}	"	1.852×10^{-3}
12-A-4^{M}	1120	1.276×10^{-3}
12-A-6^{M}	"	1.388×10^{-3}
12-A-8^{S}	"	1.451×10^{-3}
12-A-5^{S}	1119	1.513×10^{-3}
12-A-9^{M}	1071	1.141×10^{-3}
12-A-10^{S}	"	1.207×10^{-3}
12-A-11^{M}	1022	9.289×10^{-4}
12-A-10^{S}	"	9.697×10^{-4}
12-A-13^{M}	973	7.239×10^{-4}
12-A-14^{S}	"	7.580×10^{-4}

APPENDIX B

(See Chapter IV, Section B)

CORRECTION OF $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ RATIOS FOR DISSOCIATION OF $H_2S_{(g)}$

A. Calculation of Percent Correction for Dissociation into $S_{2(g)}$ and $HS_{(g)}$

$$H_2S_{(g)} = H_{2(g)} + 1/2\ S_{2(g)}$$

$$\Delta F^\circ_R = 21{,}570 - 11.79T = -RT \ln K_p$$

$$\log K_p = -\frac{4{,}714}{T} + 2.576$$

$$K_p = \frac{\left[\dfrac{N_{S_{2(g)}} P_T}{1 + N_{S_{2(g)}}}\right]^{1/2} \left[\dfrac{\left(\dfrac{P_{H_{2(g)}}}{P_T} + 2N_{S_{2(g)}}\right) P_T}{\left(1 + N_{S_{2(g)}}\right)}\right]}{\left[\dfrac{\left(\dfrac{P_{H_2S_{(g)}}}{P_T} - 2N_{S_{2(g)}}\right) P_T}{\left(1 + N_{S_{2(g)}}\right)}\right]}$$

$N_{S_{2(g)}}$ is determined for the following conditions:

T = sample temperature, °K

P_T = one atmosphere [experimentally P_T = 1 atm. ± 0.03 atm.; resulting error in $N_{S_{2(g)}}$ and $N_{HS_{(g)}}$ ($\approx \pm 3\%$) is neglected]

$P_{H_{2(g)}}, P_{H_2S_{(g)}}$ = calculated partial pressure of $H_{2(g)}$ and $H_2S_{(g)}$, respectively, in the inlet mixture.

$$\left(\frac{P_{H_2S_{(g)}}}{P_{H_{2(g)}}}\right)_{(\mathrm{corr.},\ S_{2(g)})} = \frac{\left(\frac{P_{H_2S_{(g)}}}{1} - 2N_{S_{2(g)}}\right)}{\left(\frac{P_{H_{2(g)}}}{1} + 2N_{S_{2(g)}}\right)}$$

$$H_2S_{(g)} = 1/2\ H_{2(g)} + HS_{(g)}$$

$$\Delta F^\circ_R = 41{,}640 - 15.49T = -RT \ln K_p$$

$$\Delta F^\circ_R = -\frac{9{,}100}{T} + 3.385$$

$$K_p = \frac{\left[\frac{\left(\frac{P_{H_{2(g)}}}{P_T} + 2N_{S_{2(g)}} + 0.5N_{HS_{(g)}}\right)P_T}{\left(1 + N_{S_{2(g)}} + 0.5N_{HS_{(g)}}\right)}\right]^{1/2}\left[\frac{N_{HS_{(g)}}P_T}{\left(1 + N_{S_{2(g)}} + 0.5N_{HS_{(g)}}\right)}\right]}{\left[\frac{\left(\frac{P_{H_2S_{(g)}}}{P_T} - 2N_{S_{2(g)}} - N_{HS_{(g)}}\right)P_T}{\left(1 + N_{S_{2(g)}} + 0.5N_{HS_{(g)}}\right)}\right]}$$

$N_{HS_{(g)}}$ is determined for the same conditions listed for $N_{S_{2(g)}}$.

$$\left(\frac{P_{H_2S_{(g)}}}{P_{H_{2(g)}}}\right)_{(\mathrm{corr.},\ S_{2(g)}, HS_{(g)})} = \frac{\left(\frac{P_{H_2S_{(g)}}}{1} - 2N_{S_{2(g)}} - N_{HS_{(g)}}\right)}{\left(\frac{P_{H_{2(g)}}}{1} + 2N_{S_{2(g)}} + 0.5N_{HS_{(g)}}\right)}$$

$$\begin{array}{l}\%\ \text{correction}\\ \text{(relative to}\\ \text{inlet ratio)}\end{array} = \frac{\left(\frac{P_{H_2S_{(g)}}}{P_{H_{2(g)}}}\right)_{(\mathrm{inlet})} - \left(\frac{P_{H_2S_{(g)}}}{P_{H_{2(g)}}}\right)_{(\mathrm{corr.})}}{\left(\frac{P_{H_2S_{(g)}}}{P_{H_{2(g)}}}\right)_{(\mathrm{inlet})}} \times 100$$

B. Tabulation of Corrections

The inlet $P_{H_2S_{(g)}}/P_{H_{2(g)}}$ ratios for the systems $Mo_{(c)}$-$Mo_2S_{3(c)}$, $W_{(c)}$-$WS_{2(c)}$ have been corrected by means of the equations given in Part A. Only those experiments selected for thermodynamic calculations have been included. The results are given in the following table.

TABLE B-I

CORRECTIONS FOR DISSOCIATION OF $H_2S_{(g)}$

SYSTEM: $Mo_{(c)}$ - $Mo_2S_{3(c)}$

Run #	$T_{(corr)}$, °K	$P_{H_2S_{(g)}}/P_{H_{2(g)}}$ (inlet)	% Correction for $H_2S_{(g)} = H_{2(g)} + 1/2 S_{2(g)}$	% Correction for $H_2S_{(g)} = 1/2 H_{2(g)} + HS_{(g)}$	$P_{H_2S_{(g)}}/P_{H_{2(g)}}$ (Corrected)
9-A-16^M	1612	3.112×10^{-2}	1.29	0.55	3.055×10^{-2}
9-A-17^S	"	3.265×10^{-2}	1.51	0.55	3.198×10^{-2}
9-A-15^M	1562	2.472×10^{-2}	0.69	0.36	2.446×10^{-2}
9-A-13^S	"	2.572×10^{-2}	0.70	0.36	2.545×10^{-2}
9-A-6^M	1512	1.965×10^{-2}	0.36	0.20	1.954×10^{-2}
9-A-11^S	"	2.085×10^{-2}	0.36	0.20	2.073×10^{-2}
9-A-3^M	1462	1.590×10^{-2}	0.0	0.0	1.590×10^{-2}
9-A-5^S	"	1.688×10^{-2}	0.0	0.0	1.688×10^{-2}
9-A-18^M	1415	1.251×10^{-2}	0.0	0.0	1.251×10^{-2}
9-A-19^S	"	1.329×10^{-2}	0.0	0.0	1.329×10^{-2}
9-A-20^M	1366	9.618×10^{-3}	0.0	0.0	9.618×10^{-3}
9-A-21^S	"	1.034×10^{-2}	0.0	0.0	1.034×10^{-2}

Table B-I (Continued)

SYSTEM: $W_{(c)} - WS_{2(c)}$

Run #	$T_{(corr)}$, °K	$P_{H_{2(g)}}/P_{H_{2(g)}}$ (inlet)	% Correction for $H_2S_{(g)} = H_{2(g)} + 1/2S_{2(g)}$	% Correction for $H_2S_{(g)} = 1/2H_{2(g)} + HS_{(g)}$	$P_{H_{2(g)}}/P_{H_{2(g)}}$ (Corrected)
11-A-14^{M}	1567	8.273×10^{-2}	2.51	0.39	8.033×10^{-2}
11-A-15^{S}	"	8.696×10^{-2}	2.68	0.39	8.429×10^{-2}
11-A-13^{M}	1519	6.592×10^{-2}	1.27	0.25	6.491×10^{-2}
11-A-11^{S}	"	6.904×10^{-2}	1.36	0.25	6.793×10^{-2}
11-A-17^{M}	1495	5.989×10^{-2}	0.90	0.15	5.924×10^{-2}
11-A-16^{S}	1496	6.431×10^{-2}	0.98	0.20	6.355×10^{-2}
11-A-9 ^{M}	1471	5.434×10^{-2}	0.64	0.15	5.391×10^{-2}
11-A-10^{S}	"	5.709×10^{-2}	0.68	0.16	5.661×10^{-2}
11-A-7 ^{M}	1422	4.282×10^{-2}	0.30	0.10	4.265×10^{-2}
11-A-5 ^{S}	"	4.518×10^{-2}	0.33	0.11	4.498×10^{-2}
11-A-4 ^{M}	1372	3.416×10^{-2}	0.0	0.0	3.416×10^{-2}
11-A-3 ^{S}	"	3.640×10^{-2}	0.0	0.0	3.640×10^{-2}

APPENDIX C
(See Chapter IV, Sections C and D)

ANALYSIS OF CHROMIUM SULFIDE DATA

The standard free energy change for the reaction

$$CrS_{(c)} + H_{2(g)} = Cr_{(c)} + H_2S_{(g)}$$

is calculated from the experimental data, selected from Appendix A, according to the equation

$$\Delta F^\circ_R = - RT \ln \frac{P_{H_2S(g)}}{P_{H_2(g)}}$$

The results are tabulated below.

TABLE C-I

EXPERIMENTAL DATA AND CALCULATED VALUES OF ΔF°_R FOR $CrS_{(c)} + H_{2(g)} = Cr_{(c)} + H_2S_{(g)}$

Run #	$T_{(corr)}$, °K	$P_{H_2S(g)}/P_{H_2(g)}$ (inlet)	log K_p	ΔF°_R, cal
10-A-20^M	1568	4.064×10^{-4}	-3.3911	24,336
10-A-21^S	"	4.167×10^{-4}	-3.3802	24,256
10-A-9^M	1513	2.928×10^{-4}	-3.5334	24,467
10-A-10^S	"	3.040×10^{-4}	-3.5171	24,349
10-A-3^M	1464	2.225×10^{-4}	-3.6527	24,463
10-A-5^S	1463	2.285×10^{-4}	-3.6411	24,379
10-A-13^M	1419	1.633×10^{-4}	-3.7870	24,587
10-A-11^S	"	1.708×10^{-4}	-3.7675	24,460
10-A-18^M	1376	1.180×10^{-4}	-3.9281	24,737
10-A-17^S	"	1.275×10^{-4}	-3.8945	24,527

The best values of ΔF°_R are taken from the equation of the average slope. The equation of the average slope is calculated as follows:

(Maximum slope defined by experiments 10-A-3^M and 10-A-21^S)

$$\Delta S^\circ_{R_{(max)}} = -\left(\frac{d\Delta F^\circ_R}{dT}\right)_{(max)} = -\frac{(24,463 - 24,256)}{(1464 - 1568)}$$

$$\Delta S^\circ_{R_{(max)}} = 1.98 \text{ cal/deg}$$

$$\Delta H^\circ_{R_{(max)}} = \Delta F^\circ_{R_{(max)}} - T\left(\frac{d\Delta F^\circ_R}{dT}\right)_{(max)}$$

$$\Delta H^\circ_{R_{(max)}} = 24,463 + (1464)(1.98)$$

$$\Delta H^\circ_{R_{(max)}} = 27,361 \text{ cal}$$

(Minimum slope defined by experiments 10-A-17^S and 10-A-20^M)

$$\Delta S^\circ_{R_{(min)}} = -\left(\frac{d\Delta F^\circ_R}{dT}\right)_{(min)} = -\frac{(24,527 - 24,336)}{(1376 - 1568)}$$

$$\Delta S^\circ_{R_{(min)}} = 0.99 \text{ cal/deg}$$

$$\Delta H^\circ_{R_{(min)}} = \Delta F^\circ_{R_{(min)}} - T\left(\frac{d\Delta F^\circ_R}{dT}\right)_{(min)}$$

$$\Delta H^\circ_{R_{(min)}} = 24,527 + (1376)(0.99)$$

$$\Delta H^\circ_{R_{(min)}} = 25,889 \text{ cal}$$

For average slope

$$\Delta S^\circ_R = 0.99 + \frac{(1.98 - 0.99)}{2}$$

$$\Delta S^\circ_R = 1.48 \text{ cal/deg}$$

$$\Delta H^\circ_R = 25{,}889 + \frac{(27{,}361 - 25{,}889)}{2}$$

$$\Delta H^\circ_R = 26{,}620 \text{ cal}$$

$$\underline{\Delta F^\circ_R = 26{,}620 - 1.48T \text{ cal: } (1375\text{-}1570°K)}$$

The equation for the ΔF°_f of $CrS_{(c)}$ according to the reaction

$$Cr_{(c)} + 1/2\ S_{2(g)} = CrS_{(c)}$$

is determined as follows

$$\Delta F^\circ_{f(CrS_{(c)})} = \Delta F^\circ_{f(H_2S_{(g)})} - \Delta F^\circ_R$$

$$\Delta F^\circ_{f(H_2S_{(g)})} = -21{,}570 + 11.79T \qquad \text{(TABLE I)}$$

$$\Delta F^\circ_{f(CrS_{(c)})} = -21{,}570 + 11.79T - (26{,}620 - 1.48T)$$

$$\underline{\Delta F^\circ_{f(CrS_{(c)})} = -48{,}190 + 13.27T \text{ cal:} (1375\text{-}1570°K)}$$

UNCERTAINTY ANALYSIS

A. Uncertainty in T and $P_{H_2S(g)}/P_{H_2(g)}$

$$\delta T = \left[(\delta T_{(calib)})^2 + (\delta T_{(grad)})^2 + (\delta T_{(drift)})^2 \right]^{1/2}$$

Estimated:
(Chapter III)

$$\delta T_{(calib)} = \pm\, 0.8°K$$

$$\delta T_{(grad)} = \pm\, 2.5°K$$

$$\delta T_{(drift)} = \pm\, 0.5°K$$

$$\delta T = [(0.8)^2 + (2.5)^2 + (0.5)^2]^{1/2}$$

$$\delta T = \pm\, 2.7°K$$

$$\delta \frac{P_{H_2S(g)}}{P_{H_2(g)}} = \left\{ \left[\delta \frac{P_{H_2S(g)}}{P_{H_2(g)}}_{(inlet)} \right]^2 + \left[\delta \frac{P_{H_2S(g)}}{P_{H_2(g)}}_{(anal)} \right]^2 \right\}^{1/2}$$

Estimated:
(Chapter III)

$$\delta \frac{P_{H_2S(g)}}{P_{H_2(g)}}_{(inlet)} = \pm\, 4\%$$

$$\delta \frac{P_{H_2S(g)}}{P_{H_2(g)}}_{(anal)} = \pm\, 1\%$$

$$\delta \frac{P_{H_2S(g)}}{P_{H_2(g)}} = [(4)^2 + (1)^2]^{1/2}$$

$$\delta \frac{P_{H_2S(g)}}{P_{H_2(g)}} = \pm 4.1\%$$

B. Uncertainty in ΔF°_R

$$\delta \Delta F^\circ_{R(exp)} = \left[\left(R\ln \frac{P_{H_2S(g)}}{P_{H_2(g)}}\right)^2 (\delta T)^2 + \left(\frac{RT}{\frac{P_{H_2S(g)}}{P_{H_2(g)}}}\right)^2 \left(\delta \frac{P_{H_2S(g)}}{P_{H_2(g)}}\right)^2\right]^{1/2}$$

$$\delta \Delta F^\circ_{R(exp)} = \left[(R\ln 2.225\text{x}10^{-4})^2 (2.7)^2 + \left(\frac{R \text{ x } 1464}{2.225\text{x}10^{-4}}\right)^2 (0.041\text{x}2.225\text{x}10^{-4})^2\right]^{1/2}$$

$$\delta \Delta F^\circ_{R(exp)} = \pm 127 \text{ cal}$$

$$\delta \Delta F^\circ_{R(calc)} = \left[\frac{\sum_{n=1}^{n=k} \left(\Delta F^\circ_{R(calc)} - \Delta F^\circ_{R(exp)}\right)_n^2}{k-1}\right]^{1/2}$$

Run #	$\Delta F^\circ_{R(exp)}$, cal	$\Delta F^\circ_{R(calc)}$, cal	$\left(\Delta F^\circ_{R(calc)} - \Delta F^\circ_{R(exp)}\right)$ cal
10-A-20^{M}	24,336	24,300	- 36
10-A-21^{S}	24,256	24,300	44
10-A-9^{M}	24,467	24,380	- 87
10-A-10^{S}	24,349	24,380	31
10-A-3^{M}	24,463	24,450	- 13
10-A-5^{S}	24,379	24,450	71
10-A-13^{M}	24,587	24,520	- 67
10-A-11^{S}	24,460	24,520	60
10-A-18^{M}	24,737	24,580	-157
10-A-17^{S}	24,527	24,580	53

$$\delta \Delta F^\circ_{R_{(calc)}} = \left[\frac{52502}{9}\right]^{1/2}$$

$$\delta \Delta F^\circ_{R_{(calc)}} = \pm\ 76 \text{ cal}$$

$$\delta \Delta F^\circ_R = \left[\left(\delta \Delta F^\circ_{R_{(exp)}}\right)^2 + \left(\delta \Delta F^\circ_{R_{(calc)}}\right)^2\right]^{1/2}$$

$$\delta \Delta F^\circ_R = [(127)^2 + (76)^2]^{1/2}$$

$$\underline{\Delta F^\circ_R = \pm\ 148 \text{ cal} \approx \pm\ 150 \text{ cal}}$$

C. Uncertainty in ΔS°_R and ΔH°_R

$$\delta \Delta S^\circ_R = \Delta S^\circ_{R_{(max)}} - \Delta S^\circ_R = \Delta S^\circ_R - \Delta S^\circ_{R_{(min)}}$$

$$\delta \Delta S^\circ_R = 1.98 - 1.48$$

$$\underline{\delta \Delta S^\circ_R = \pm\ 0.5 \text{ cal/deg}}$$

$$\delta \Delta H^\circ_R = \Delta H^\circ_{R_{(max)}} - \Delta H^\circ_R = \Delta H^\circ_R - \Delta H^\circ_{R_{(min)}}$$

$$\delta \Delta H^\circ_R = 27{,}361 - 26{,}620$$

$$\underline{\delta \Delta H^\circ_R = \pm\ 741 \text{ cal} \approx \pm\ 750 \text{ cal}}$$

D. Uncertainty in ΔF_f°, ΔS_f° and ΔH_f° of $H_2S_{(g)}$

$$\delta\Delta F^\circ_{f(H_2S_{(g)})} = \pm 200 \text{ cal} \quad \text{(TABLE I)}$$

$$\delta\Delta H^\circ_{f(H_2S_{(g)})} = \pm 100 \text{ cal} \quad \text{(Ref.48)}$$

At constant temperature for $\delta\Delta F_f^\circ$, independent of $\delta\Delta H_f^\circ$

$$\delta\Delta S_f^\circ = [(1/T)^2(\delta\Delta F_f^\circ)^2 + (1/T)^2(\delta\Delta H_f^\circ)^2]^{1/2}$$

For T = 1500°K

$$\delta\Delta S^\circ_{f(H_2S_{(g)})} = [(1/1500)^2(200)^2 + (1/1500)^2(100)^2]^{1/2}$$

$$\delta\Delta S^\circ_{f(H_2S_{(g)})} = \pm 0.15 \text{ cal/deg}$$

E. Uncertainty in ΔF_f°, ΔS_f° and ΔH_f° of $CrS_{(c)}$

$$\delta\Delta F^\circ_{f(CrS_{(c)})} = \left[(\delta\Delta F_R^\circ)^2 + \left(\delta\Delta F^\circ_{f(H_2S_{(g)})}\right)^2\right]^{1/2}$$

$$\delta\Delta F^\circ_{f(CrS_{(c)})} = [(150)^2 + (200)^2]^{1/2}$$

$$\underline{\delta\Delta F^\circ_{f(CrS_{(c)})} = \pm 250 \text{ cal}}$$

$$\delta\Delta S^\circ_{f(CrS_{(c)})} = \left[(\delta\Delta S_R^\circ)^2 + \left(\delta\Delta S^\circ_{f(H_2S_{(g)})}\right)^2\right]^{1/2}$$

$$\delta\Delta S^\circ_{F(CrS_{(c)})} = [(0.5)^2 + (0.15)^2]^{1/2}$$

$$\underline{\delta\Delta S^\circ_{f(\mathrm{CrS}_{(c)})} = \pm\ 0.52\ \mathrm{cal/deg}}$$

$$\delta\Delta H^\circ_{f(\mathrm{CrS}_{(c)})} = \left[(\delta\Delta H^\circ_R)^2 + \left(\delta\Delta H^\circ_{f(\mathrm{H_2S}_{(g)})}\right)^2\right]^{1/2}$$

$$\delta\Delta H^\circ_{f(\mathrm{CrS}_{(c)})} = [(750)^2 + (100)^2]^{1/2}$$

$$\underline{\delta\Delta H^\circ_{f(\mathrm{CrS}_{(c)})} = \pm\ 757\ \mathrm{cal} \approx \pm\ 760\ \mathrm{cal}}$$

APPENDIX D

(See Chapter IV, Sections C and D)

ANALYSIS OF MOLYBDENUM SULFIDE DATA

The standard free energy change for the reaction

$$1/3\ Mo_2S_{3(c)} + H_{2(g)} = 2/3\ Mo_{(c)} + H_2S_{(g)}$$

is calculated from the corrected experimental data in Appendix B, according to the equation

$$\Delta F^\circ_R = -\ RT\ \ln \frac{P_{H_2S_{(g)}}}{P_{H_{2(g)}}}$$

The results are tabulated below:

TABLE D-I

EXPERIMENTAL DATA AND CALCULATED VALUES OF ΔF°_R FOR $1/3Mo_2S_{3(c)} + H_{2(g)} = 2/3Mo_{(c)} + H_2S_{(g)}$

Run #	$T_{(corr)}$, °K	$P_{H_2S_{(g)}}/P_{H_{2(g)}}$ (corrected)	log K_p	ΔF°_R, cal
9-A-16^M	1612	3.055×10^{-2}	-1.5150	11,175
9-A-17^S	"	3.198×10^{-2}	-1.4951	11,027
9-A-15^M	1562	2.446×10^{-2}	-1.6115	11,516
9-A-13^S	"	2.545×10^{-2}	-1.5943	11,397
9-A-6^M	1512	1.954×10^{-2}	-1.7091	11,826
9-A-11^S	"	2.073×10^{-2}	-1.6834	11,651
9-A-3^M	1462	1.590×10^{-2}	-1.7986	12,029
9-A-5^S	"	1.688×10^{-2}	-1.7726	11,861
9-A-18^M	1415	1.251×10^{-2}	-1.9027	12,324
9-A-19^S	"	1.329×10^{-2}	-1.8765	12,155
9-A-20^M	1366	9.618×10^{-3}	-2.0169	12,607
9-A-21^S	"	1.034×10^{-2}	-1.9855	12,411

The best values of ΔF°_R are taken from the equation of the average slope.

The equation of the average slope is calculated as follows:

(Maximum slope defined by experiments 9-A-20^{M} and 9-A-13^{S})

$$\Delta S^\circ_{R_{(max)}} = -\left(\frac{d\Delta F^\circ_R}{dT}\right)_{(max)} = -\frac{(12,607 - 11,397)}{(1366 - 1562)}$$

$$\Delta S^\circ_{R_{(max)}} = 6.17 \text{ cal/deg}$$

$$\Delta H^\circ_{R_{(max)}} = \Delta F^\circ_{R_{(max)}} - T\left(\frac{d\Delta F^\circ_R}{dT}\right)_{(max)}$$

$$\Delta H^\circ_{R_{(max)}} = 12,607 + (1366)(6.17)$$

$$\Delta H^\circ_{R_{(max)}} = 21,035 \text{ cal}$$

(Minimum slope defined by experiments 9-A-21^{S} and 9-A-16^{M})

$$\Delta S^\circ_{R_{(min)}} = -\left(\frac{d\Delta F^\circ_R}{dT}\right)_{(min)} = -\frac{(12,411 - 11,175)}{(1366 - 1612)}$$

$$\Delta S^\circ_{R_{(min)}} = 5.03 \text{ cal/deg}$$

$$\Delta H^\circ_{R_{(min)}} = \Delta F^\circ_{R_{(min)}} - T\left(\frac{d\Delta F^\circ_R}{dT}\right)_{(min)}$$

$$\Delta H^\circ_{R_{(min)}} = 12,411 + (1366)(5.03)$$

$$\Delta H^\circ_{R_{(min)}} = 19,283 \text{ cal}$$

For average slope

$$\Delta S^\circ_R = 5.03 + \frac{(6.17 - 5.03)}{2}$$

$$\Delta S^\circ_R = 5.6 \text{ cal/deg}$$

$$\Delta H^\circ_R = 19{,}283 + \frac{(21{,}035 - 19{,}283)}{2}$$

$$\Delta H^\circ_R = 20{,}160 \text{ cal}$$

$$\underline{\Delta F^\circ_R = 20{,}160 - 5.6T \text{ cal:}(1365\text{-}1610^\circ K)}$$

The equation for the ΔF°_f of 1/3 $Mo_2S_{3(c)}$, according to the reaction

$$2/3\ Mo_{(c)} + 1/2\ S_{2(g)} = 1/3\ Mo_2S_{3(c)}$$

is determined as follows:

$$\Delta F^\circ_{f(1/3Mo_2S_{3(c)})} = \Delta F^\circ_{f(H_2S_{(g)})} - \Delta F^\circ_R$$

$$\Delta F^\circ_{f(H_2S_{(g)})} = -\ 21{,}570 + 11{,}79T \qquad \text{(TABLE I)}$$

$$\Delta F^\circ_{f(1/3Mo_2S_{3(c)})} = -21{,}570 + 11.79T - (20{,}160 - 5.60T)$$

$$\underline{\Delta F^\circ_{f(1/3Mo_2S_{3(c)})} = -41{,}730 + 17.39T \text{ cal:}(1365\text{-}1610^\circ K)}$$

UNCERTAINTY ANALYSIS

A. Uncertainty in T and $P_{H_2S_{(g)}}/P_{H_2(g)}$ ($\delta T = \pm\ 2.7^\circ K$ Appendix C)

$$\delta\frac{P_{H_2S_{(g)}}}{P_{H_2(g)}} = \left\{\left[\delta\frac{P_{H_2S_{(g)}}}{P_{H_2(g)}}\ _{(inlet)}\right]^2 + \left[\delta\frac{P_{H_2S_{(g)}}}{P_{H_2(g)}}\ _{(anal)}\right]^2\right\}^{1/2}$$

Estimated:
(Chapter III)

$$\delta \frac{P_{H_2S(g)}}{P_{H_2(g)}}_{\text{(inlet)}} = \pm 1\%$$

$$\delta \frac{P_{H_2S(g)}}{P_{H_2(g)}}_{\text{(anal)}} = \pm 1\%$$

$$\delta \frac{P_{H_2S(g)}}{P_{H_2(g)}} = [(1)^2 + (1)^2]^{1/2}$$

$$\delta \frac{P_{H_2S(g)}}{P_{H_2(g)}} = \pm 1.4\%$$

B. Uncertainty in ΔF°_R

$$\delta\Delta F^\circ_{R(\text{exp})} = \left[\left(R\ln \frac{P_{H_2S(g)}}{P_{H_2(g)}}\right)^2 (\delta T)^2 + \left(\frac{RT}{\frac{P_{H_2S(g)}}{P_{H_2(g)}}}\right)^2 \left(\delta \frac{P_{H_2S(g)}}{P_{H_2(g)}}\right)^2\right]^{1/2}$$

$$\delta\Delta F^\circ_{R(\text{exp})} = \left[(R\ln 1.59\text{x}10^{-2})^2 (2.7)^2 + \left(\frac{R \text{ x } 1462}{1.59\text{x}10^{-2}}\right)^2 (0.014\text{x}1.59\text{x}10^{-2})^2\right]^{1/2}$$

$$\delta\Delta F^\circ_R = \pm 46 \text{ cal}$$

$$\delta\Delta F^\circ_{R(\text{calc})} = \left[\frac{\sum_{n=1}^{n=k} \left(\Delta F^\circ_{R(\text{calc})} - \Delta F^\circ_{R(\text{exp})}\right)_n^2}{k - 1}\right]^{1/2}$$

Run #	$\Delta F^\circ_{R(exp)}$,cal	$\Delta F^\circ_{R(calc)}$,cal	$\left(\Delta F^\circ_{R(calc)} - \Delta F^\circ_{R(exp)}\right)$cal
9-A-16^M	11,175	11,130	- 45
9-A-17^S	11,027	11,130	103
9-A-15^M	11,516	11,410	-106
9-A-13^S	11,397	11,410	13
9-A-6 ^{M}	11,826	11,700	-126
9-A-11^S	11,651	11,700	49
9-A-3 ^{M}	12,029	11,970	- 59
9-A-5 ^{S}	11,861	11,970	109
9-A-18^M	12,324	12,230	- 94
9-A-19^S	12,155	12,230	75
9-A-20^M	12,607	12,510	- 97
9-A-21^S	12,411	12,510	99

$$\delta\Delta F^\circ_{R(calc)} = \left[\frac{91372}{11}\right]^{1/2}$$

$$\delta\Delta F^\circ_{R(calc)} = \pm\ 91\ \text{cal}$$

$$\delta\Delta F^\circ_R = \left[\left(\delta\Delta F^\circ_{R(exp)}\right)^2 + \left(\delta\Delta F^\circ_{R(calc)}\right)^2\right]^{1/2}$$

$$\delta\Delta F^\circ_R = [(46)^2 + (91)^2]^{1/2}$$

$$\underline{\delta\Delta F^\circ_R = \pm\ 102\ \text{cal} \approx \pm\ 100\ \text{cal}}$$

C. Uncertainty in ΔS°_R and ΔH°_R

$$\delta\Delta S^\circ_R = \Delta S^\circ_{R(max)} - \Delta S^\circ_R = \Delta S^\circ_R - \Delta S^\circ_{R(min)}$$

$$\delta\Delta S^\circ_R = 6.17 - 5.6$$

$$\underline{\delta\Delta S^\circ_R = \pm\ 0.57 \text{ cal/deg}}$$

$$\delta\Delta H^\circ_R = \Delta H^\circ_{R(\max)} - \Delta H^\circ_R = \Delta H^\circ_R - \Delta H^\circ_{R(\min)}$$

$$\delta\Delta H^\circ_R = 21{,}035 - 20{,}160$$

$$\underline{\delta\Delta H^\circ_R = \pm 875 \text{ cal} \approx \pm\ 880 \text{ cal}}$$

D. Uncertainty in ΔF°_f, ΔS°_f and ΔH°_f of $H_2S_{(g)}$

$\delta\Delta F^\circ_{f(H_2S_{(g)})} = \pm\ 200$ cal (TABLE I)

$\delta\Delta S^\circ_{f(H_2S_{(g)})} = \pm\ 0.15$ cal/deg (Appendix C)

$\delta\Delta H^\circ_{f(H_2S_{(g)})} = \pm\ 100$ cal (Ref. 48)

E. Uncertainty in ΔF°_f, ΔS°_f and ΔH°_f of $1/3\ Mo_2S_{3(c)}$

$$\delta\Delta F^\circ_{f(1/3Mo_2S_{3(c)})} = \left[(\delta\Delta F^\circ_R)^2 + \left(\delta\Delta F^\circ_{f(H_2S_{(g)})}\right)^2\right]^{1/2}$$

$$\delta\Delta F^\circ_{f(1/3Mo_2S_{3(c)})} = [(100)^2 + (200)^2]^{1/2}$$

$$\underline{\delta\Delta F^\circ_{f(1/3Mo_2S_{3(c)})} = \pm\ 224 \text{ cal} \approx \pm\ 220 \text{ cal}}$$

$$\delta\Delta S^\circ_{f(1/3(Mo_2S_{3(c)})} = \left[(\delta\Delta S^\circ_R)^2 + \left(\delta\Delta S^\circ_{f(H_2S_{(g)})} \right)^2 \right]^{1/2}$$

$$\delta\Delta S^\circ_{f(1/3Mo_2S_{3(c)})} = [(0.57)^2 + (0.15)^2]^{1/2}$$

$$\underline{\delta\Delta S^\circ_{f(1/3Mo_2S_{3(c)})} = \pm\ 0.59 \text{ cal/deg}}$$

$$\delta\Delta H^\circ_{f(1/3Mo_2S_{3(c)})} = \left[(\delta\Delta H^\circ_R)^2 + \left(\delta\Delta H^\circ_{f(H_2S_{(g)})} \right)^2 \right]^{1/2}$$

$$\delta\Delta H^\circ_{f(1/3Mo_2S_{3(c)})} = [(880)^2 + (100)^2]^{1/2}$$

$$\underline{\delta\Delta H^\circ_{F(1/3Mo_2S_{3(c)})} = \pm\ 886 \text{ cal} \approx \pm\ 890 \text{ cal}}$$

APPENDIX E

(See Chapter IV, Sections C and D)

ANALYSIS OF TUNGSTEN SULFIDE DATA

The standard free energy change for the reaction

$$1/2WS_{2(c)} + H_{2(g)} = 1/2W_{(c)} + H_2S_{(g)}$$

is calculated from the corrected experimental data in Appendix B, according to the equation

$$\Delta F^\circ_R = - RT \ln \frac{P_{H_2S(g)}}{P_{H_2(g)}}$$

The results are tabulated below:

TABLE E-I

EXPERIMENTAL DATA AND CALCULATED VALUES OF ΔF°_R FOR

$1/2WS_{2(c)} + H_{2(g)} = 1/2W_{(c)} + H_2S_{(g)}$

Run #	$T_{(corr)}$, °K	$P_{H_2S(g)}/P_{H_2(g)}$ (corrected)	log K_p	ΔF°_R, cal
11-A-14^{M}	1567	8.033×10^{-2}	-1.0951	7,855
11-A-15^{S}	"	8.429×10^{-2}	-1.0742	7,705
11-A-13^{M}	1519	6.491×10^{-2}	-1.1877	8,254
11-A-11^{S}	"	6.793×10^{-2}	-1.1679	8,119
11-A-17^{M}	1495	5.924×10^{-2}	-1.2274	8,395
11-A-16^{S}	1496	6.355×10^{-2}	-1.1969	8,196
11-A-9^{M}	1471	5.391×10^{-2}	-1.2683	8,538
11-A-10^{S}	"	5.661×10^{-2}	-1.2471	8,396
11-A-7^{M}	1422	4.265×10^{-2}	-1.3701	8,912
11-A-5^{S}	"	4.498×10^{-2}	-1.3470	8,764
11-A-4^{M}	1372	3.416×10^{-2}	-1.4670	9,213
11-A-3^{S}	"	3.640×10^{-2}	-1.4395	9,037

The best values of ΔF°_R are taken from the equation of the average slope. The equation of the average slope is calculated as follows:

(Maximum slope defined by experiments 11-A-4^M and 11-A-11^S)

$$\Delta S^\circ_{R(\max)} = -\left(\frac{d\Delta F^\circ_R}{dT}\right)_{(\max)} = -\frac{(9{,}213 - 8{,}119)}{(1372 - 1519)}$$

$$\Delta S^\circ_{R(\max)} = 7.46 \text{ cal/deg}$$

$$\Delta H^\circ_{R(\max)} = \Delta F^\circ_{R(\max)} - T\left(\frac{d\Delta F^\circ_R}{dT}\right)_{(\max)}$$

$$\Delta H^\circ_{R(\max)} = 9{,}213 + (1372)(7.46)$$

$$\Delta H^\circ_{R(\max)} = 19{,}451 \text{ cal}$$

(Minimum slope defined by experiments 11-A-5^S and 11-A-14^M)

$$\Delta S^\circ_{R(\min)} = -\left(\frac{d\Delta F^\circ_R}{dT}\right)_{(\min)} = -\frac{(8{,}764 - 7{,}855)}{(1422 - 1567)}$$

$$\Delta S^\circ_{R(\min)} = 6.24 \text{ cal/deg}$$

$$\Delta H^\circ_{R(\min)} = \Delta F^\circ_{R(\min)} - T\left(\frac{d\Delta F^\circ_R}{dT}\right)_{(\min)}$$

$$\Delta H^\circ_{R(\min)} = 8{,}764 + (1422)(6.24)$$

$$\Delta H^\circ_{R(\min)} = 17{,}636 \text{ cal}$$

For average slope

$$\Delta S^\circ_R = 6.24 + \frac{(7.46 - 6.24)}{2}$$

$$\Delta S^\circ_R = 6.85 \text{ cal/deg}$$

$$\Delta H^\circ_R = 17{,}636 + \frac{(19{,}451 - 17{,}636)}{2}$$

$$\Delta H^\circ_R = 18{,}540 \text{ cal}$$

$$\underline{\Delta F^\circ_R = 18{,}540 - 6.85T \text{ cal: } (1370\text{-}1565°K)}$$

The equation for the ΔF°_f of $1/2WS_{2(c)}$, according to the reaction

$$1/2W_{(c)} + 1/2S_{2(g)} = 1/WS_{2(c)}$$

is determined as follows:

$$\Delta F^\circ_{f(1/2WS_{2(c)})} = \Delta F^\circ_{f(H_2S_{(g)})} - \Delta F^\circ_R$$

$$\Delta F^\circ_{f(H_2S_{(g)})} = -\ 21{,}570 + 11.79T \qquad \text{(TABLE I)}$$

$$\Delta F^\circ_{f(1/2WS_{2(c)})} = -\ 21{,}570 + 11.79T - (18{,}540 - 6.85T)$$

$$\underline{\Delta F^\circ_{f(1/2WS_{2(c)})} = -40{,}110 + 18.64T \text{ cal: } (1370\text{-}1565°K)}$$

UNCERTAINTY ANALYSIS

A. Uncertainty in T and $P_{H_2S(g)}/P_{H_2(g)}$

$$\delta T = \pm 2.7^\circ \qquad \text{(Appendix C)}$$

$$\delta \frac{P_{H_2S(g)}}{P_{H_2(g)}} = \pm 1.4\% \qquad \text{(Appendix D)}$$

B. Uncertainty in ΔF°_R

$$\delta\Delta F^\circ_{R(exp)} = \left[\left(R\ln \frac{P_{H_2S(g)}}{P_{H_2(g)}}\right)^2 (\delta T)^2 + \left(\frac{RT}{\frac{P_{H_2S(g)}}{P_{H_2(g)}}}\right)^2 \left(\delta \frac{P_{H_2S(g)}}{P_{H_2(g)}}\right)^2\right]^{1/2}$$

$$\delta\Delta F^\circ_{R(exp)} = \left[(R\ln 5.391\text{x}10^{-2})^2 \ (2.7)^2 + \left(\frac{R \text{ x } 1471}{5.391\text{x}10^{-2}}\right)^2 (0.014\text{x}5.391\text{x}10^{-2})^2\right]^{1/2}$$

$$\delta\Delta F^\circ_{R(exp)} = \pm 44 \text{ cal}$$

$$\delta\Delta F^\circ_{R(calc)} = \left[\frac{\sum_{n=1}^{n=k} \left(\Delta F^\circ_{R(calc)} - \Delta F^\circ_{R(exp)}\right)^2_n}{k - 1}\right]^{1/2}$$

Run #	$\Delta F^\circ_{R(exp)}$, cal	$\Delta F^\circ_{R(calc)}$, cal	$\left(\Delta F^\circ_{R(calc)} - \Delta F^\circ_{R(exp)}\right)$ cal
11-A-14^{M}	7,855	7,800	- 55
11-A-15^{S}	7,705	"	95
11-A-13^{M}	8,254	8,140	-114
11-A-11^{S}	8,119	"	21
11-A-17^{M}	8,395	8,300	- 95
11-A-16^{S}	8,196	8,290	94
11-A-9^{M}	8,538	8,460	- 78
11-A-10^{S}	8,396	"	64
11-A-7^{M}	8,912	8,800	-112
11-A-5^{S}	8,764	"	36
11-A-4^{M}	9,213	9,140	- 73
11-A-3^{S}	9,037	"	103

$$\delta\Delta F^\circ_{R(calc)} = \left[\frac{83331}{11}\right]^{1/2}$$

$$\delta\Delta F^\circ_{R(calc)} = \pm\ 87\ \text{cal}$$

$$\delta\Delta F^\circ_R = \left[\left(\delta\Delta F^\circ_{R(exp)}\right)^2 + \left(\delta\Delta F^\circ_{R(calc)}\right)^2\right]^{1/2}$$

$$\delta\Delta F^\circ_R = [(44)^2 + (87)^2]^{1/2}$$

$$\underline{\delta\Delta F^\circ_R = \pm\ 98\ \text{cal} \approx \pm\ 100\ \text{cal}}$$

C. Uncertainty in ΔS°_R and ΔH°_R

$$\delta\Delta S^\circ_R = \Delta S^\circ_{R(max)} - \Delta S^\circ_R = \Delta S^\circ_R - \Delta S^\circ_{R(min)}$$

$$\delta \Delta S^\circ_R = 7.46 - 6.85$$

$$\underline{\delta \Delta S^\circ_R = \pm\ 0.61 \text{ cal/deg}}$$

$$\delta \Delta H^\circ_R = \Delta H^\circ_{R_{(max)}} - \Delta H^\circ_R = \Delta H^\circ_R - \Delta H^\circ_{R_{(min)}}$$

$$\delta \Delta H^\circ_R = 19{,}451 - 18{,}540$$

$$\underline{\delta \Delta H^\circ_R = \pm\ 911 \text{ cal} \approx \pm\ 910 \text{ cal}}$$

D. Uncertainty in ΔF°_f, ΔS°_f and ΔH°_f of $H_2S_{(g)}$

$\delta \Delta F^\circ_{f(H_2S_{(g)})} = \pm\ 200$ cal (TABLE I)

$\delta \Delta S^\circ_{f(H_2S_{(g)})} = \pm\ 0.15$ cal/deg (Appendix C)

$\delta \Delta H^\circ_{f(H_2S_{(g)})} = \pm\ 100$ cal (Ref.48)

E. Uncertainty in ΔF°_f, ΔS°_f and ΔH°_f of $1/2WS_{2(c)}$

$$\delta \Delta F^\circ_{f(1/2WS_{2(c)})} = \left[(\delta \Delta F^\circ_R)^2 + \left(\delta \Delta F^\circ_{f(H_2S_{(g)})} \right)^2 \right]^{1/2}$$

$$\delta \Delta F^\circ_{f(1/2WS_{2(c)})} = [(100)^2 + (200)^2]^{1/2}$$

$$\underline{\delta \Delta F^\circ_{f(1/2WS_{2(c)})} = \pm\ 224 \text{ cal} \approx \pm\ 220 \text{ cal}}$$

$$\delta\Delta S^\circ_{f(1/2WS_{2(c)})} = \left[(\delta\Delta S^\circ_R)^2 + \left(\delta\Delta S^\circ_{f(H_2S_{(g)})}\right)^2\right]^{1/2}$$

$$\delta\Delta S^\circ_{f(1/2WS_{2(c)})} = [(0.61)^2 + (0.15)^2]^{1/2}$$

$$\underline{\delta\Delta S^\circ_{f(1/2WS_{2(c)})} = \pm\ 0.63 \text{ cal/deg}}$$

$$\delta\Delta H^\circ_{f(1/2WS_{2(c)})} = \left[(\delta\Delta H^\circ_R)^2 + \left(\delta\Delta H^\circ_{f(H_2S_{(g)})}\right)^2\right]^{1/2}$$

$$\delta\Delta H^\circ_{f(1/2WS_{2(c)})} = [(910)^2 + (100)^2]^{1/2}$$

$$\underline{\delta\Delta H^\circ_{f(1/2WS_{2(c)})} = \pm\ 916 \text{ cal} \approx \pm\ 920 \text{ cal}}$$

APPENDIX F

(See Chapter IV, Sections C and D)

ANALYSIS OF COPPER SULFIDE DATA

The standard free energy change for the reaction

$$Cu_2S_{(\gamma)} + H_{2(g)} = 2Cu_{(c)} + H_2S_{(g)}$$

is calculated from the experimental data, selected from Appendix A, according to the equation

$$\Delta F^\circ_R = - RT \ln \frac{P_{H_2S(g)}}{P_{H_2(g)}}$$

The results are tabulated below:

TABLE F-I

EXPERIMENTAL DATA AND CALCULATED VALUES OF ΔF°_R FOR $Cu_2S_{(\gamma)} + H_{2(g)} = 2Cu_{(c)} + H_2S_{(g)}$

Run #	$T_{(corr)}$, °K	$P_{H_2S(g)}/P_{H_2(g)}$ (inlet)	log K_p	ΔF°_R, cal
12-A-1^{M}	1297	2.341×10^{-3}	-2.6306	15,619
12-A-2^{S}	"	2.608×10^{-3}	-2.5837	15,338
12-A-16^{M}	1196	1.751×10^{-3}	-2.7567	15,091
12-A-15^{S}	"	1.852×10^{-3}	-2.7324	14,956
12-A-6^{M}	1120	1.388×10^{-3}	-2.8576	14,643
12-A-8^{S}	"	1.451×10^{-3}	-2.8383	14,549
12-A-9^{M}	1071	1.141×10^{-3}	-2.9427	14,423
12-A-10^{S}	"	1.207×10^{-3}	-2.9183	14,304
12-A-11^{M}	1022	9.289×10^{-4}	-3.0320	14,185
12-A-12^{S}	"	9.697×10^{-4}	-3.0134	14,097
12-A-13^{M}	973	7.239×10^{-4}	-3.1403	13,982
12-A-14^{S}	"	7.580×10^{-4}	-3.1203	13,893

The best values of ΔF°_R are taken from the equation of the average slope. The equation of the average slope is calculated as follows:

(Maximum slope defined by experiments 12-A-6^M and 12-A-14^S)

$$\Delta S^\circ_{R(max)} = -\left(\frac{d\Delta F^\circ_R}{dT}\right)_{(max)} = -\frac{(14{,}643 - 13{,}893)}{(1120-973)}$$

$$\Delta S^\circ_{R(max)} = -\ 5.11\ \text{cal/deg}$$

$$\Delta H^\circ_{R(max)} = \Delta F^\circ_{R(max)} - T\left(\frac{d\Delta F^\circ_R}{dT}\right)_{(max)}$$

$$\Delta H^\circ_{R(max)} = 14{,}643 + (1120)(-5.11)$$

$$\Delta H^\circ_{R(max)} = 8{,}921\ \text{cal}$$

(Minimum slope defined by experiments 12-A-15^S and 12-A-11^M)

$$\Delta S^\circ_{R(min)} = -\left(\frac{d\Delta F^\circ_R}{dT}\right)_{(min)} = -\frac{(14{,}956 - 14{,}185)}{(1196-1022)}$$

$$\Delta S^\circ_{R(min)} = -\ 4.44\ \text{cal/deg}$$

$$\Delta H^\circ_{R(min)} = \Delta F^\circ_{R(min)} - T\left(\frac{d\Delta F^\circ_R}{dT}\right)_{(min)}$$

$$\Delta H^\circ_{R(min)} = 14{,}956 + (1196)(-4.44)$$

$$\Delta H^\circ_{R(min)} = 9{,}645\ \text{cal}$$

For average slope

$$\Delta S^\circ_R = -\ 4.44 + \frac{(-5.11 + 4.44)}{2}$$

$$\Delta S^\circ_R = -\ 4.78 \text{ cal/deg}$$

$$\Delta H^\circ_R = 9{,}645 + \frac{(8{,}921 - 9{,}645)}{2}$$

$$\Delta H^\circ_R = 9{,}280 \text{ cal}$$

$$\underline{\Delta F^\circ_R = 9{,}280 + 4.78T \text{ cal:}(970\text{-}1300°K)}$$

The equation for the ΔF°_f of $Cu_2S_{(\gamma)}$, according to the reaction

$$2Cu_{(c)} + 1/2S_{2(g)} = Cu_2S_{(\gamma)}$$

is determined as follows:

$$\Delta F^\circ_{f(Cu_2S_{(\gamma)})} = \Delta F^\circ_{f(H_2S_{(g)})} - \Delta F^\circ_R$$

$$\Delta F^\circ_{f(H_2S_{(g)})} = -21{,}570 + 11.79T \qquad \text{(TABLE I)}$$

$$\Delta F^\circ_{f(Cu_2S_{(\gamma)})} = -\ 21{,}570 + 11.79T - (9{,}280 + 4.78T)$$

$$\underline{\Delta F^\circ_{f(Cu_2S_{(\gamma)})} = -\ 30{,}850 + 7.01T \text{ cal: } (970\text{-}1300°K)}$$

UNCERTAINTY ANALYSIS

A. Uncertainty in T and $P_{H_2S_{(g)}}/P_{H_{2(g)}}$

$\delta T = \pm\ 2.7°K$ (Appendix C)

$$\delta \frac{P_{H_2S(g)}}{P_{H_2(g)}} = \pm\ 1.4\% \qquad \text{(Appendix D)}$$

B. Uncertainty in ΔF°_R

$$\delta\Delta F^\circ_{R(exp)} = \left[\left(R\ \ln \frac{P_{H_2S(g)}}{P_{H_2(g)}}\right)^2 (\delta T)^2 + \left(\frac{RT}{\frac{P_{H_2S(g)}}{P_{H_2(g)}}}\right)^2 \left(\delta \frac{P_{H_2S(g)}}{P_{H_2(g)}}\right)^2\right]^{1/2}$$

$$\delta\Delta F^\circ_{R(exp)} = \left[(R\ \ln 1.388\text{x}10^{-3})^2 (2.7)^2 + \left(\frac{R \text{ x } 1120}{1.388\text{x}10^{-3}}\right)^2 (0.014\text{x}1.388\text{x}10^{-3})^2\right]^{1/2}$$

$$\delta\Delta F^\circ_{R(exp)} = \pm\ 47 \text{ cal}$$

$$\delta\Delta F^\circ_{R(calc)} = \left[\frac{\sum_{n=1}^{n=k}\left(\Delta F^\circ_{R(calc)} - \Delta F^\circ_{R(exp)}\right)^2_n}{k-1}\right]^{1/2}$$

Run #	$\Delta F^\circ_{R(exp)}$,cal	$\Delta F^\circ_{R(calc)}$,cal	$\left(\Delta F^\circ_{R(calc)} - \Delta F^\circ_{R(exp)}\right)$cal
12-A-1^{M}	15,619	15,480	-139
12-A-2^{S}	15,338	"	142
12-A-16^{M}	15,091	15,000	- 91
12-A-15^{S}	14,956	"	44
12-A-6^{M}	14,643	14,630	- 13
12-A-8^{S}	14,549	"	81
12-A-9^{M}	14,423	14,400	- 23
12-A-10^{S}	14,304	"	96
12-A-11^{M}	14,185	14,170	- 15
12-A-12^{S}	14,097	"	73
12-A-13^{M}	13,982	13,930	- 52
12-A-14^{S}	13,893	"	37

$$\delta\Delta F^\circ_{R_{(calc)}} = [\frac{75812}{11}]^{1/2}$$

$$\delta\Delta F^\circ_{R_{(calc)}} = \pm\ 83 \text{ cal}$$

$$\delta\Delta F^\circ_R = \left[\left(\delta\Delta F^\circ_{R_{(exp)}}\right)^2 + \left(\delta\Delta F^\circ_{R_{(calc)}}\right)^2\right]^{1/2}$$

$$\delta\Delta F^\circ_R = [(47)^2 + (83)^2]^{1/2}$$

$$\underline{\delta\Delta F^\circ_R = \pm\ 95 \text{ cal} \approx \pm\ 100 \text{ cal}}$$

C. Uncertainty in ΔS°_R and ΔH°_R

$$\delta\Delta S^\circ_R = \Delta S^\circ_{R_{(max)}} - \Delta S^\circ_R = \Delta S^\circ_R - \Delta S^\circ_{R_{(min)}}$$

$$\delta\Delta S^\circ_R = -\ 5.11 + 4.78$$

$$\underline{\delta\Delta S^\circ_R = \pm\ 0.33 \text{ cal/deg}}$$

$$\delta\Delta H^\circ_R = \Delta H^\circ_{R_{(max)}} - \Delta H^\circ_R = \Delta H^\circ_R - \Delta H^\circ_{R_{(min)}}$$

$$\delta\Delta H^\circ_R = 8{,}921 - 9{,}280$$

$$\underline{\delta\Delta H^\circ_R = \pm\ 359 \text{ cal} \approx \pm\ 360 \text{ cal}}$$

D. Uncertainty in ΔF°_f, ΔS°_f and ΔH°_f of $H_2S_{(g)}$

$\delta\Delta F^\circ_{f_{(H_2S_{(g)})}} = \pm\ 200$ cal (TABLE I)

$\delta\Delta S^\circ_{f_{(H_2S_{(g)})}} = \pm\ 0.15$ cal/deg (Appendix C)

$\delta\Delta H^\circ_{f_{(H_2S_{(g)})}} = \pm\ 100$ cal (Ref. 48)

E. Uncertainty in ΔF°_f, ΔS°_f and ΔH°_f of $Cu_2S_{(\gamma)}$

$$\delta\Delta F^\circ_{f(Cu_2S_{(\gamma)})} = \left[(\delta\Delta F^\circ_R)^2 + \left(\delta\Delta F^\circ_{f(H_2S_{(g)})}\right)^2\right]^{1/2}$$

$$\delta\Delta F^\circ_{f(Cu_2S_{(\gamma)})} = [(100)^2 + (200)^2]^{1/2}$$

$$\underline{\delta\Delta F^\circ_{f(Cu_2S_{(\gamma)})} = \pm\ 224 \text{ cal} \approx \pm\ 220 \text{ cal}}$$

$$\delta\Delta S^\circ_{f(Cu_2S_{(\gamma)})} = \left[(\delta\Delta S^\circ_R)^2 + \left(\delta\Delta S^\circ_{f(H_2S_{(g)})}\right)^2\right]^{1/2}$$

$$\delta\Delta S^\circ_{f(Cu_2S_{(\gamma)})} = [(0.33)^2 + (0.15)^2]^{1/2}$$

$$\underline{\delta\Delta S^\circ_{f(Cu_2S_{(\gamma)})} = \pm\ 0.36 \text{ cal/deg}}$$

$$\delta\Delta H^\circ_{f(Cu_2S_{(\gamma)})} = \left[(\delta\Delta H^\circ_R)^2 + \left(\delta\Delta H^\circ_{f(H_2S_{(g)})}\right)^2\right]^{1/2}$$

$$\delta\Delta H^\circ_{f(Cu_2S_{(\gamma)})} = [(360)^2 + (100)^2]^{1/2}$$

$$\underline{\delta\Delta H^\circ_{f(Cu_2S_{(\gamma)})} = \pm\ 374 \text{ cal} \approx \pm\ 370 \text{ cal}}$$

APPENDIX G

(See Chapter III, Section B, Part 5)

GRAVIMETRIC ANALYSIS OF CHROMIUM SULFIDE LAYERS

The composition of a chromium sulfide layer was determined by first measuring the weight change accompanying formation of the layer, to give the weight of sulfide sulfur $[S^{-2}]$, and then measuring the weight change accompanying dissolution of the sulfide layer in acid, to give the weight of chromium sulfide. The weight of sulfided chromium $[Cr^{+n}]$ was obtained by difference. All weight measurements were made with a microbalance and the molar Cr/S ratio was calculated from the following equation

$$\text{molar Cr/S} = \frac{\text{Wt}[Cr^{+n}],\ \text{mg}/52.01,\ \text{mg}}{\text{Wt}[S^{-2}],\ \text{mg}/32.07,\ \text{mg}} \tag{G-1}$$

The measured weight changes, the calculated values for the molar Cr/S ratio, the mean value for the molar Cr/S ratio, and the standard deviation for the determination of the molar Cr/S ratio are given in the following table.

TABLE G-I

DATA FOR DETERMINATION OF MOLAR Cr/S RATIO FOR Cr_XS_Y PHASE IN EQUILIBRIUM WITH CHROMIUM AT 1420°K

[For T = 1420°K, equilibrium $P_{H_2S(g)}/P_{H_2(g)} = 1.68 \times 10^{-4}$]

Sample #	$T_{(corr)}$, °K	$P_{H_2S(g)}/P_{H_2(g)}$ (inlet)	Exposure Time, hr.	$Wt[S^{-2}]$, mg	Wt. Sulfide, mg	$Wt[Cr^{+n}]$ mg	Molar Ratio Cr/S
$10\text{-}A\text{-}25^S$	1420	1.91×10^{-4}	6-1/2	1.602	4.124	2.522	0.97
$10\text{-}A\text{-}26^S$	"	1.91×10^{-4}	6-1/2	0.656	1.644	0.988	0.93
$10\text{-}A\text{-}28^S$	"	1.98×10^{-4}	10	2.813	7.261	4.448	0.98
$10\text{-}A\text{-}29^S$	"	1.98×10^{-4}	10	1.461	4.003	2.542	1.07
$10\text{-}A\text{-}30^S$	1422	1.96×10^{-4}	7-1/2	2.256	5.753	3.497	0.96
$10\text{-}A\text{-}31^S$	"	1.96×10^{-4}	7-1/2	1.113	2.772	1.659	0.92

$$\overline{Cr/S} = 0.97$$

$$S_{Cr/S} = \sqrt{\frac{\sum_{n=1}^{k} (\delta Cr/S)_n^2}{k - 1}} = \pm 0.05$$

BIOGRAPHICAL NOTE

The author was born on October 2, 1936, in Miles City, Montana. He received his primary and secondary education in Big Timber, Montana. He entered the Montana School of Mines (presently the Montana College of Mineral Science and Technology), Butte, Montana, in September, 1954, and received a Bachelor of Science Degree in Metallurgical Engineering in June, 1958.

In September, 1958, he was enrolled as a graduate student at the School of Mines and Metallurgy of the University of Missouri (presently the University of Missouri at Rolla), Rolla, Missouri, and in June, 1960, received the degree of Master of Science in Metallurgical Engineering. His Master's thesis was entitled, "A Thermodynamic Study of the System PbO-PbS".

He entered the Graduate School of the Massachusetts Institute of Technology in September, 1960, as a candidate for the degree of Doctor of Science, with a major in Metallurgy and a minor in Chemistry. From July, 1961 to June, 1964 he was an Instructor in the Department of Metallurgy. While at M. I. T., he has published a paper entitled, "Thermodynamic Properties of the Silver-Silicon System," in the _Transactions of the Metallurgical Society_, A.I.M.E., _227_, 1000 (1963).

His industrial experience includes summer employment with Kaiser Aluminum Company, Union Carbide Corporation (Metals Research Laboratory), Battelle Memorial Institute, and AVCO Corporation (Research and Advanced Development Division).

The author is a member of the Tau Beta Pi Association, the Society of Sigma Xi and the American Institute of Mining, Metallurgical and Petroleum Engineers.

The author is married to the former Mary Anna McCloskey, and has three children.