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A THERMODYNAMIC STUDY OF THE HAFNIUM - SULFUR SYSTEM BETWEEN HfS_2 (c) AND Hf_2S_3 (c)

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ABSTRACT

This study was concerned with determining the standard free energy change as a function of temperature for the reaction

$$2\overline{Hf}S_3(c) = 2Hf\overline{S}_2(c) + S_2(g)$$

where $\overline{Hf}S_3(c)$ is the metal-saturated trisulfide of hafnium and $Hf\overline{S}_2(c)$ is the sulfur-saturated disulfide.

The equilibrations were made by sealing sulfur and the appropriate sulfide in an evacuated silica capsule. The sulfur was melted and made to flow by gravity to the lower end of the capsule, the sulfide remaining in the upper end. The temperatures of the two ends were then set and controlled independently, thus fixing the sulfide temperature and the sulfur pressure. This data, combined with a knowledge of the initial and final compositions of the sulfides, permitted calculation of ΔG° for the above reaction as a function of T.

The system showed very slow reaction kinetics. For

this reason, probably none of the experimental runs attained true thermodynamic equilibrium, and an iterative technique was thus required to determine the equilibrium conditions. Because of the unavoidable uncertainties in the iterative technique and the usual uncertainties in temperature measurement, the resulting equation for ΔG^{o} as a function of T is more uncertain than desirable.

An independent estimate was made of ΔS^{o} for the reaction above. This estimated value, with its limits of uncertainty, is considerably closer to the value obtained in this study, again with its limits of uncertainty, than to the value obtained by previous investigators. A reason for the discrepancies between the results of this and the previous investigation is proposed. On the basis of the estimated value of ΔS^{o} and the consistent explanation for the discrepancies in the data, it is proposed that the equation of this study is more reliable than the equation of the previous workers.

The equation obtained in this study, for the above reaction is (with limits of uncertainty):

$$\Delta G^{o}(\pm 200 \text{ cal}) = 48{,}500(\pm 5000 \text{ cal}) - 48.4(\pm 5.3 \tfrac{\text{cal}}{^{o}\text{K}})\ T;$$

$$(919 - 969\ ^{o}\text{K}).$$

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The author wishes to express his appreciation to Dr. J. P. Hager and Dr. A. H. Larson for their guidance throughout the course of the investigation. He also would like to thank the National Science Foundation for providing the financial support for this study.

I. INTRODUCTION

A. OUTLINE OF THIS STUDY

This study was concerned with determining the standard free energy change as a function of temperature for the reaction

$$2\overline{Hf}S_3(c) = 2Hf\overline{S}_2(c) + S_2(g) \qquad (I\text{-}1)$$

where $\overline{Hf}S_3(c)$ is the metal-saturated trisulfide of hafnium and $Hf\overline{S}_2(c)$ is the sulfur-saturated disulfide.

The equilibrations were made by sealing sulfur and the appropriate sulfide in an evacuated silica capsule. The sulfur was melted and made to flow by gravity to the lower end of the capsule, the sulfide remaining in the upper end. The temperature of the two ends were then set and controlled independently, thus fixing the sulfide temperature and the sulfur pressure. This data, combined with a knowledge of the initial and final compositions of the sulfides, permitted calculation of ΔG^o for reaction (I-1) as a function of T.

Although the system behaved somewhat differently than

expected, leading to a less certain interpretation of data than desirable, a meaningful equation for ΔG^o as a function of T has been found. On the basis of criteria to be discussed, it is proposed that the data of this present study is more reliable than that of previous workers.[1]

B. EQUILIBRATION METHODS

Several methods are presently available for determining equilibrium properties of condensed phases. Of those discussed here, three involve equilibrium of the condensed phase(s) with a gaseous phase, and one involves the use of galvanic cells.

Examples of determinations of the free energies of various reactions using galvanic cells can be found in the literature.[2,3,4] References three and four are concerned with measuring the properties of solid phases using a solid CaF_2 electrolyte. Conceivably, this type of approach might be used to obtain the desired thermodynamic properties for reaction (I-1). This could not be done directly, however. A series of steps would be required. A cell of the type

$$Hf(c),\ HfF_2(c) \ \Big|\ CaF_2(c) \ \Big|\ HfS_x(c),\ HfF_2(c) \qquad (I\text{-}2)$$

might be proposed. The overall cell reaction with corresponding ΔG is

$$Hf(c) = \underline{Hf}_{in\ HfS_x} \qquad \Delta G = -2FE = RT\ \ln a_{Hf}.$$

Thus, the activity of hafnium in HfS_x can always be determined from such a cell. If HfS_x is the sulfide of highest $(S/Hf)_{molar}$ ratio, and if the data has been collected from mole fraction Hf = $\frac{1}{1+x}$ to zero, the Gibbs-Duhem equation can be utilized to calculate the activity of sulfur in HfS_x. With these two pieces of information, the standard free energy for the reaction

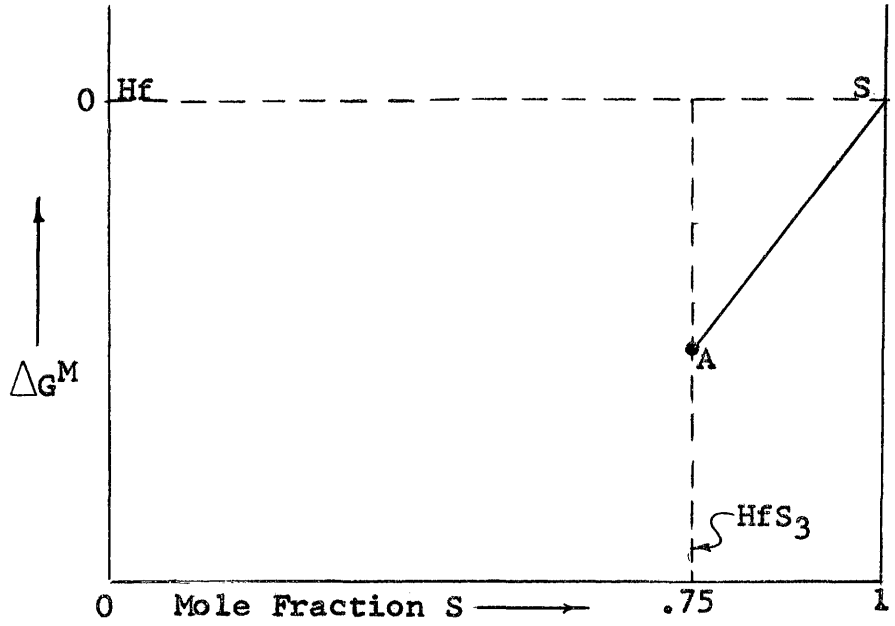
$$\frac{1}{1+x}\,Hf(c) + \frac{x}{1+x}\,S_{(Rh)} = \frac{1}{1+x}\,HfS_x(c)$$

can be calculated by

$$\Delta G^o = \Delta G^M = \frac{1}{1+x}\,\Delta\bar{G}_{Hf} + \frac{x}{1+x}\,\Delta\bar{G}_S =$$

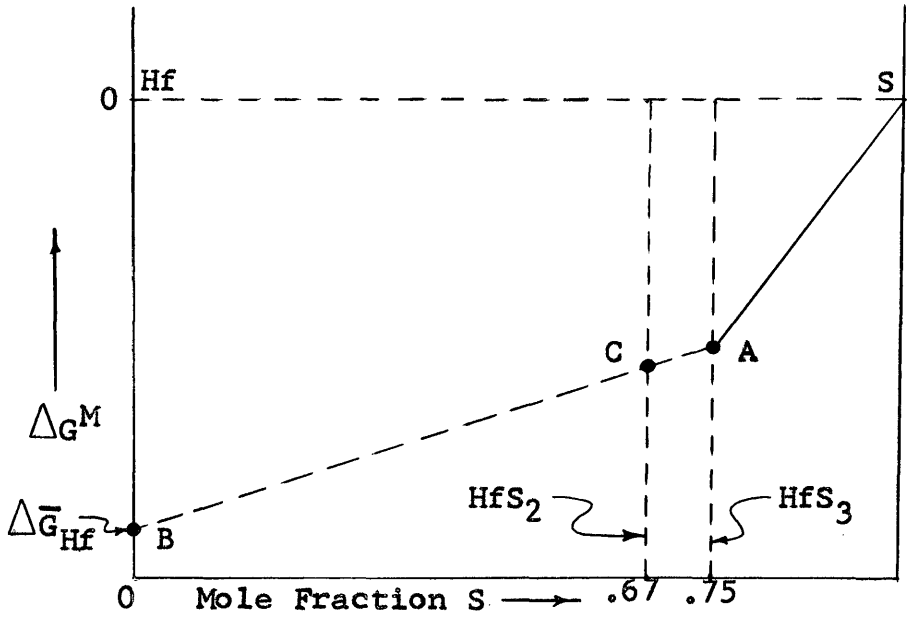
$$\frac{1}{1+x}\,RT\ \ln a_{Hf} + \frac{x}{1+x}\,RT\ \ln a_S$$

A plot of the form of Fig. 1 can then be started. The highest sulfide of hafnium reported in the literature is HfS_3.[1,5] This would then be the HfS_x used in the initial cell. The next lower sulfide reported is HfS_2.[1,5] If this were the HfS_x used in the next cell, the activity and hence the free energy of mixing of Hf in HfS_2 could be found. Referring to Fig. 2, point A is known from the cell using $\overline{HfS}_3$; point B is known from the cell using $Hf\bar{S}_2$; and point C, the integral free energy of mixing of HfS_2, is located by the intersection of the line A-B with the mole fraction 2/3.[6] If this procedure were carried out at a number of



Hypothetical ΔG^M vs. X_s for Hf Sulfides

Figure 1



Hypothetical ΔG^M vs. X_s for Hf Sulfides

Figure 2

different temperatures, ΔG° as a function of T could be determined for (I-1) from the resulting data. Properties of the compounds Hf_2S_3;[5] HfS;[5,7] and the lowest hafnium sulfide yet reported, Hf_2S,[7] could conceivably be obtained in a similar manner.

A technique of measuring $^{H_2S}/_{H_2}$ ratios above equilibrated samples has been used to determine equilibrium properties of reactions similar to (I-1).[8,9] The method consists of passing hydrogen over the sample at the given temperature, analyzing the gas for H_2S and H_2 at equilibrium, and calculating the sulfur potential of this gas mixture from the ratio $\frac{P_{H_2S}}{P_{H_2}}$ and the appropriate equilibrium constant. The process is shown schematically in Fig. 3. The reaction occurring in the furnace at temperature T_1 is

$$(\frac{1}{x-y})\ \overline{Hf}S_x(c) + H_2(g) = (\frac{1}{x-y})\ Hf\bar{S}_y(c) + H_2S \qquad (I\text{-}6)$$

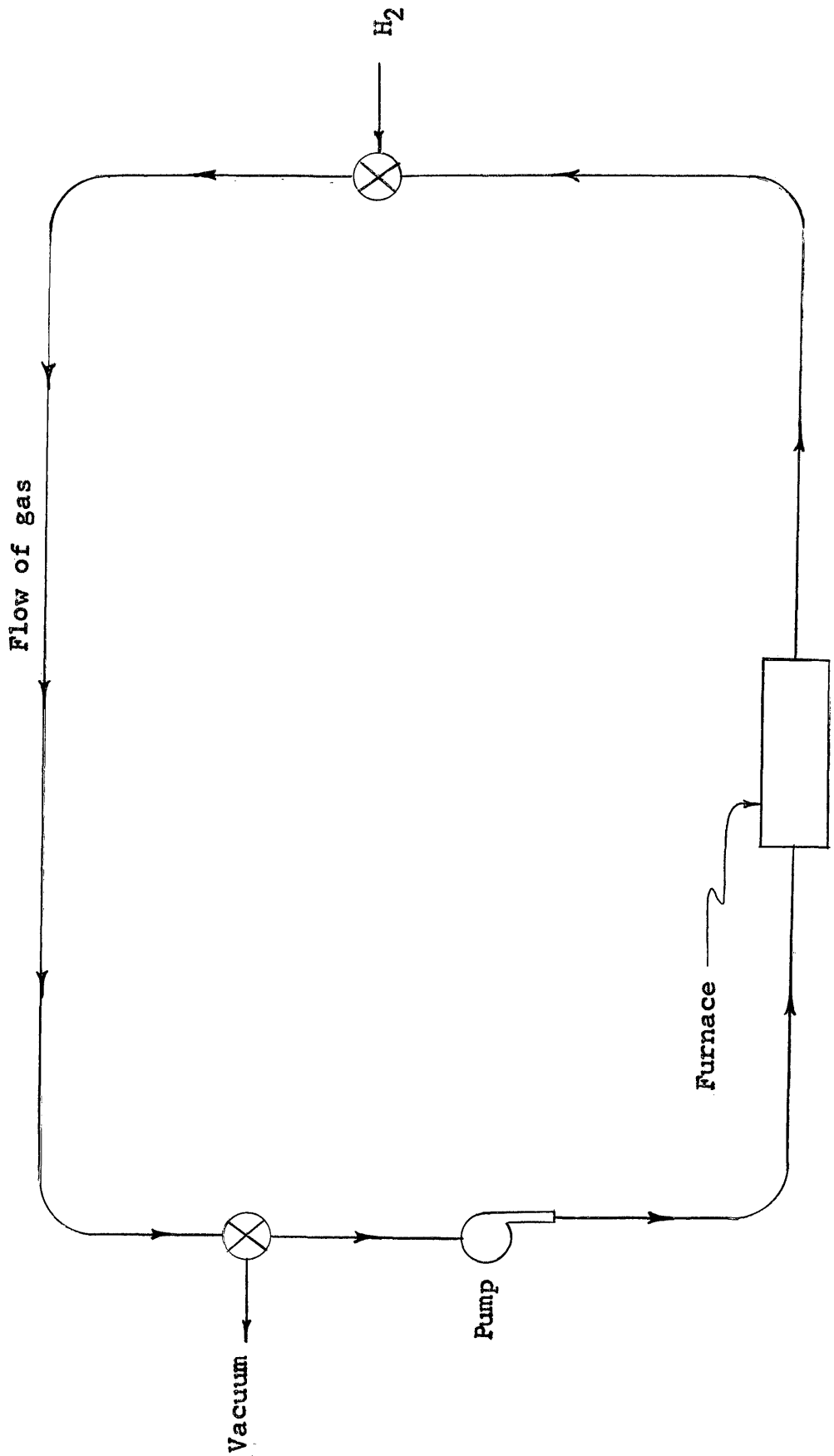
and is the summation of the two reactions

$$(\frac{1}{x-y})\ \overline{Hf}S_x(c) = (\frac{1}{x-y})\ Hf\bar{S}_y(c) + \tfrac{1}{2}S_2(g) \qquad (I\text{-}7a)$$

and

$$H_2(g) + \tfrac{1}{2}S_2(g) = H_2S(g). \qquad (I\text{-}7b)$$

According to reaction (I-7b), the circulating gaseous phase is required to carry sulfur. The pressure of the sulfur in the gas at the high reaction temperature T_1 is fixed by reaction (I-6) and its corresponding equilibrium $^{H_2S}/_{H_2}$ ratio.



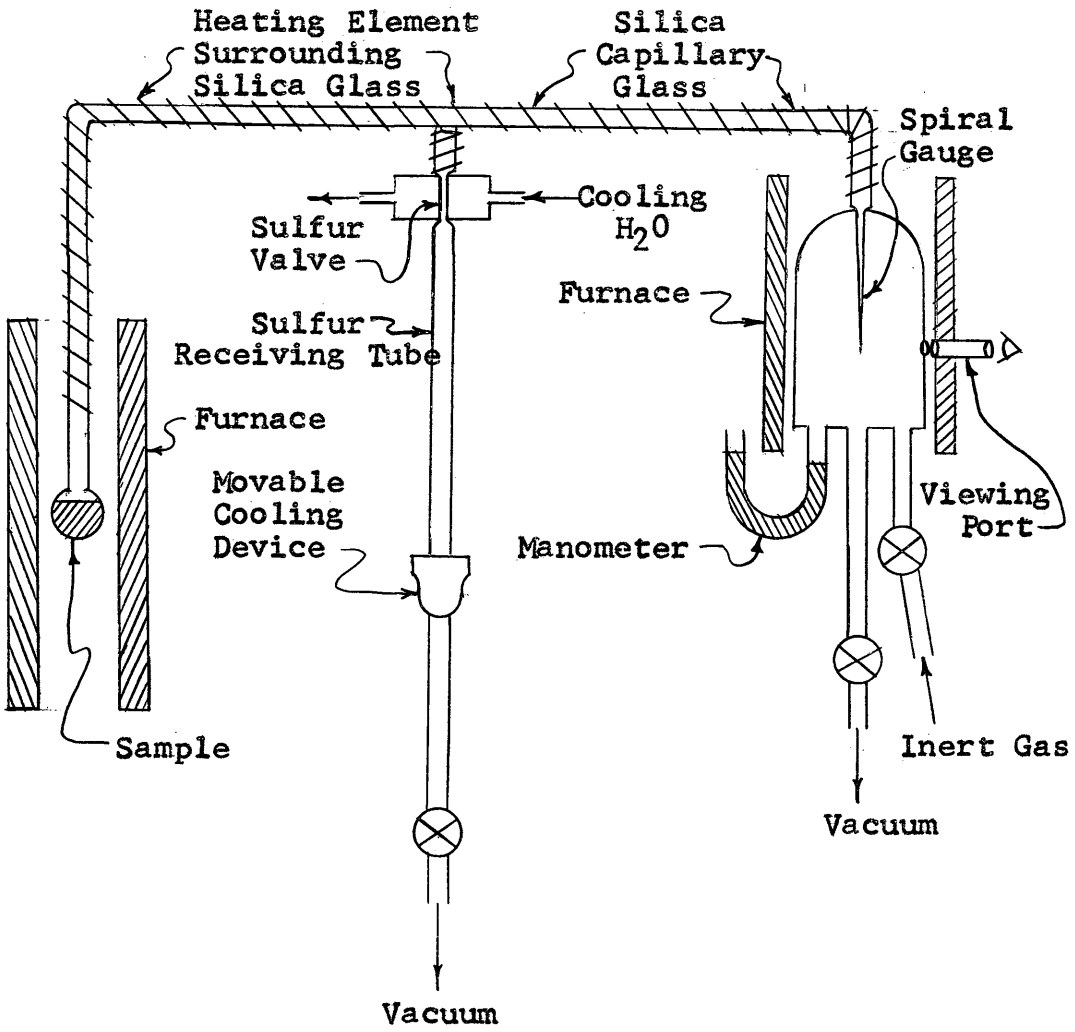
Schematic Diagram of Hydrogen Recirculation Apparatus

Figure 3

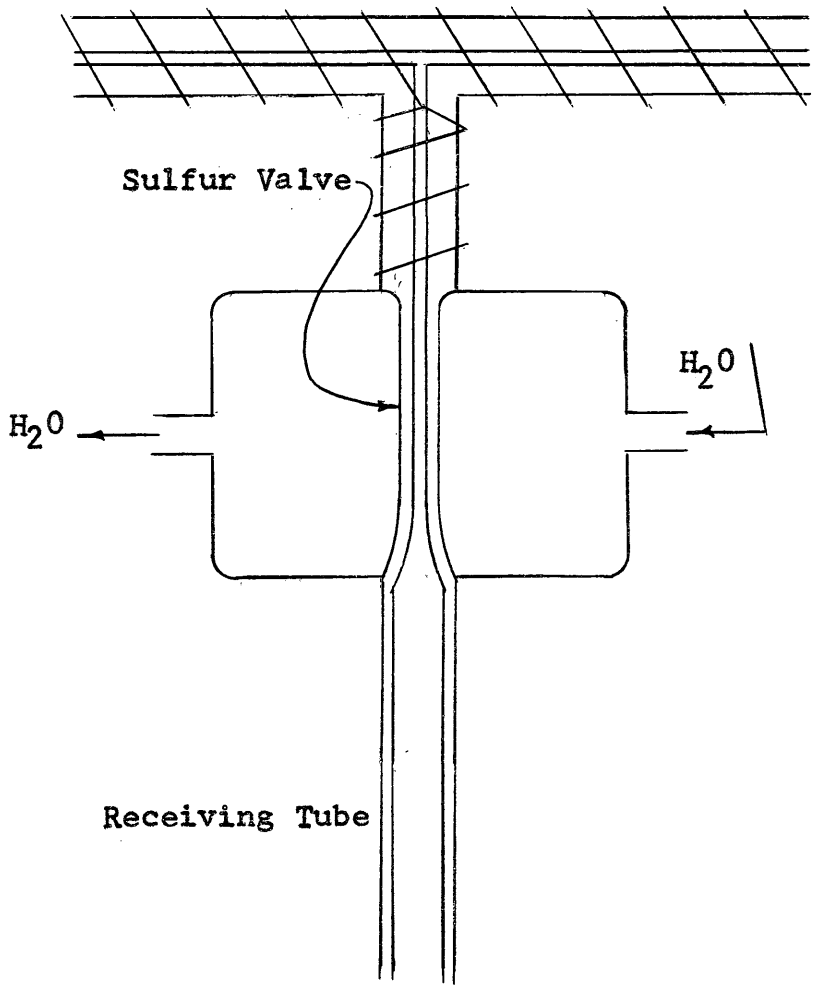
As this gas passes out of the hot zone into the recirculation glassware at nearly room temperature, the equilibrium constant for the gaseous phase [reaction (I-7b)] increases sharply, indicating a reaction between sulfur and hydrogen to form hydrogen sulfide. If the sulfur dictated by the sulfur potential of reaction (I-6) has a greater pressure than that in equilibrium with solid sulfur at room temperature, and if the gas phase is kinetically unable to react this excess sulfur at the lower temperature, sulfur will be deposited downstream from the furnace. This will effect a reduction of one or both of the sulfides and destroy the three phase equilibrium (solid-solid-gas). At the pressures of sulfur encountered in this study (about ½ atmosphere), sulfur deposition would certainly occur. This method can only be used where the equilibrium sulfur pressures are very small and within a few orders of magnitude of the sulfur pressure in equilibrium with solid sulfur at room temperature (2×10^{-11} atm @ 300°K). This value was calculated from data given in Kubaschewski and Evans.[10]

A technique of measuring equilibrium sulfur pressures for the systems $\overline{Ti}S_3 - Ti\overline{S}_2 - S_2$ and $\overline{Zr}S_3 - Zr\overline{S}_2 - S_2$ was used by Biltz, et al.[11,12] The same technique was used by Haraldsen, et al. for the system $\overline{Hf}S_3 - Hf\overline{S}_2 - S_2$.[1] A description of the apparatus is also given in Kubaschewski

and Evans[10], p. 145, 146, 147. The apparatus is shown schematically in Fig. 4. With the sample of HfS_3 or HfS_3 + HfS_2 of known $(S/Hf)_{molar}$ sealed in the sample tube, the entire apparatus is evacuated. The furnaces and heating elements are then brought up to temperature, the heating elements and gauge furnace being at a higher temperature than the sample furnace to prevent condensation of sulfur. As the heating is started, cold water is circulated past the position of the sulfur valve. Sulfur condenses into a vacuum-tight plug at this point and prevents sulfur vapor from distilling into the sulfur receiving tube. Thus, only a small amount of sulfur has been removed from the sample, and its change in $(S/Hf)_{molar}$ is therefore small. The sample continues to decompose until equilibrium is attained. At this point, the equilibrium sulfur pressure is measured by means of a calibrated Bodenstein-Johnson spiral gauge of vitreous silica (see references given by Haraldsen et al.,[1] p. 1292, and Kubaschewski and Evans,[10] p. 146, 409). This is a null device, and an inert gas is used to balance the effect of the hot sulfur gas, the pressure of the inert gas being measured by a conventional mercury manometer. After this pressure measurement is made, the sulfur valve is broken (i.e., cold water turned off) and the sulfur in the reaction space is allowed to distill into the sulfur



Overall View (a)



Enlargement of Sulfur Valve (b)

Schematic Diagram of Apparatus of Biltz, et al. and Haraldsen, et al.

Figure 4

receiving tube where it is again condensed by a movable cooling device containing a mixture of dry ice and alcohol. The cooling water is again turned on, the sample furnace is increased to a new temperature, and the same procedure is carried out again. This identical procedure can be carried out for a series of temperatures, thus permitting the equilibrium pressures at a number of temperatures to be obtained without disturbing the apparatus (i.e., changing the sample or breaking the seal). At the end of the series of temperature runs, the sulfur receiving tube contains one plug of sulfur for each run (the plug from run #2 being made closer to the sulfur valve than the plug for run #1, etc). This tube is removed and each plug of sulfur is weighed. Knowing the initial $(S/Hf)_{molar}$ this information permits the calculation of $(S/Hf)_{molar}$ after each temperature run. Thus, temperature, pressure, and composition data are all obtained. However, structure data (i.e., phases present) cannot be found after each temperature run. This is especially important at the lowest temperature studied when HfS_3 is used as starting material and at the highest temperatures when the two-phase mixture is the starting material. If the sample HfS_3 is not $\overline{HfS}_3$, that is the trisulfide of $(S/Hf)_{molar}$ in equilibrium with $Hf\overline{S}_2$ at the temperature in question, equilibrium might possibly be

attained before the phase $\overline{HfS}_2$ is formed. Thus, the pressure measured would not be that of reaction (I-1). Similarly, the phase $\overline{HfS}_3$ could disappear at the higher temperatures. These difficulties could be avoided at the low temperatures by having some knowledge of the $(S/Hf)_{molar}$ of $\overline{HfS}_3$, using this as a starting material, and by properly choosing the volume of the reaction space, having some knowledge of the expected equilibrium pressures. At higher temperatures, the difficulties could be avoided by again having some idea of the expected equilibrium pressures, having some knowledge of $(S/Hf)_{molar}$ for $\overline{HfS}_2$, and thus choosing the reaction volume so that $\overline{HfS}_3$ will not disappear.

Calibration of the gauge might possibly be another source of error. Unless calibration is made both before and after an experiment, there is no guarantee that the gauge has not changed during the experiment.

The presence of any gaseous species other than sulfur in the system under consideration would be another source of error in this method. Haraldsen, et al.,[1] p. 1287, state that TiS_3, ZrS_3, and HfS_3 are subject to sublimation, thus molecules of the type MeS_3 or Me_2S_6 are also in the gaseous phase and contribute an unknown amount to the total pressure measured by the gauge.

The method used in the present study eliminates the problems

of calibrating gauges and ignoring extraneous gaseous species. This method, described briefly in Part A of this chapter will be described in more detail in Chapter III.

The problem of extraneous species in the vapor phase is still present in this method; however, some quantitative estimate can be made as to its effects. The following relationship comes from the treatment in Swalin,[13] p. 81.

$$\frac{dP}{dP'} = \frac{V_{\text{condensed phase}}}{V_{\text{gas phase}}} \qquad \text{(I-8)}$$

P = vapor pressure of condensed phase

P' = pressure of inert gas in contact with condensed phase

V_x = molar volume of phase x

Assuming sulfur vapor to be an ideal gas at a temperature of 1000°K and a pressure of ½ atmosphere, $\frac{dP}{dP'} = 10^{-4}$. Thus, in order to change the sulfur pressure by 1 mm Hg, the pressure of $HfS_3(g)$ would have to change by 10,000 mm Hg. The effect of any extraneous gaseous species is, then, seen to be negligible.

Since the sulfur pressure is established in this method by setting the temperature of the sulfur, it is essential that the sulfur be absolutely pure and contain no dissolved species. Haraldsen, et al.,[1] p. 1287, state that HfS_3 is soluble in liquid sulfur to some extent. Their experiments

indicate that dissolved HfS_3 lowers the melting point of sulfur between .5 and 1°C; however, uncertainties involved in finding the melting point of sulfur make these figures rather uncertain.

Assuming the freezing point depression to be 1°C and knowing the normal freezing point of sulfur and its heat of fusion, the ratio of the vapor pressure of the sulfur containing dissolved HfS_3 to that of pure sulfur can be estimated. If the solution is sufficiently dilute so that the solvent (in this case, sulfur) can be treated as behaving ideally, the following expression results

$$d\ (\ln\ p) = -\ dX_B \qquad \text{(I-9)}$$

p = vapor pressure of solvent
X_B = mole fraction of solute

When data on freezing point depression is known, X_B can be estimated from

$$dT_{fp} = -\ \frac{RT^2_{fp}}{\triangle H_f}\ d\ X_B \qquad \text{(I-10)}$$

T_{fp} = normal freezing temp. of solvent
$\triangle H_f$ = heat of fusion of solvent.

These equations are developed in Barrow,[14] p. 495-501. Taking $\triangle T_{fp} = -\ 1°C$, $T_{fp} = 119°C$, $\triangle H_f = 360\ \frac{cal}{mole}$, X_B is found to be 1.18×10^{-3}. Using this result in equation (I-9),

$$\frac{P}{Po} = 10^{-\ .0005} = 1$$

P = vapor pressure of sulfur with dissolved HfS_3
Po = vapor pressure of pure sulfur.

Thus, the effect of dissolved HfS_3 on the pressure of sulfur is negligible.

A problem which is present in many procedures utilizing a gaseous phase which has species of different molecular weights is thermal segregation. This must be considered not only in this method but also in the two previous methods utilizing gases. In the method of this study, however, no thermal segregation can exist because of the "infinite reservoir" of molten sulfur in the lower end of the capsule (as described previously). Because the temperature of this reservoir is fixed, thus establishing the total sulfur pressure throughout the capsule, the pressure of each species of the gaseous sulfur directly above the molten sulfur is fixed (see Chapter IV for the thermodynamic treatment of this statement). At this position, the gaseous sulfur species are in equilibrium with each other and also with the "infinite" molten sulfur phase. Thus, any upset in the relative amounts of the species directly above the molten sulfur (such as depletion of the species $S_2(g)$ by thermal diffusion) would be corrected by effective evolution or condensation of the appropriate species by the molten phase. Any upsets in other regions of the capsule would be

transmitted back to the molten sulfur where they would be corrected by appropriate evaporation or condensation. Thus, the method of this study eliminates the difficulty of thermal segregation of the gaseous species. The sulfide in the method of Biltz, et al., and Haraldsen, et al. would also act as an "infinite" sulfur reservoir. Thus, thermal segregation would not be a problem in this method, either. However, in the method of hydrogen recirculation, the problem of thermal segregation still remains because there is no fixed value of PH_2 above the sample. Only the ratio $\frac{PH_2S}{PH_2}$ above the sample is fixed. Thus, hydrogen and the other gases in the mixture can exist in a state of thermal segregation.

In summary, galvanic cells could conceivably have been used for this study; however, much work of an exploratory nature would have been required. The hydrogen recirculation method could not have been used because of the high sulfur potentials encountered in this study. The method actually used eliminates many of the difficulties in the method of Biltz, et al., and Haraldsen, et al.

II. LITERATURE SURVEY

The only previous thermodynamic work on hafnium sulfides is that of Haraldsen, et al.[1] They studied reaction (I-1) by the method referred to in Chapter I and shown in Fig. 4. Their temperature controller kept variations in sulfide temperature down to no more than $\pm 0.1^{\circ}C$. A high vacuum of about 5×10^{-6} mm Hg was obtained in their system by means of an oil diffusion pump. Calibration of the spiral gauge was effected by measuring the pressure of molten sulfur at various temperatures. This calibration indicated the gauge to be accurate to ± 2 mm Hg in the range 6 to 704 mm Hg. The sulfur-pressure data obtained by Haraldsen, et al., is listed in Table 1. In Table 1, Ps_T is the <u>total</u> sulfur pressure (i.e., the sum of the pressures of the various gaseous sulfur species present), and Ps_2 is the pressure of the diatomic species.

Table 1

Data of Haraldsen, et al.

T (°K)	Ps_T (mm Hg)	Ps_2 (mm Hg)
873	4	4
923	30	29
943	80	77
963	147	139
973	199	186
993	485	428
1003	717	611

A least-squares treatment of this data gives, for reaction (I-1),

$$\Delta G^\circ = 66{,}270 - 65.5\ T\ (cal). \qquad (II\text{-}1)$$

The sulfur data used by Haraldsen, et al., is the same as will be used in this study and can be found in Kubaschewski and Evans,[10] p. 342.

Crystallographic data for HfS_3 was also determined by Haraldsen, et al.,[1] p. 1290. According to them, the monoclinic unit cell of HfS_3 is given by

a	b	c	β
5.100Å	3.594Å	8.992Å	98.16°.

Crystallographic data for HfS_3 has also been found by Grimmeiss, et al.,[15] p. 781. Their unit cell for HfS_3 is

a	b	c	β
5.08Å	3.58Å	8.96Å	98.4°.

McTaggart and Wadsley[5] have determined unit cell data for the compounds HfS_3, p. 450, and HfS_2, p. 452:

HfS_3	a	b	c	β
Monoclinic	5.08Å	3.58Å	8.96Å	98.4°

HfS_2	a	c
Hexagonal	3.635Å	5.837Å.

McTaggart and Wadsley[5] also report the densities and appearances of HfS_3, p. 450, and HfS_2, p. 452:

Compound	Appearance	Density (calculated)
HfS_3	bright light orange powder	5.70 g/cm^3
HfS_2	light purplish brown	6.03 g/cm^3

Unit cell data for Hf_2S_3, p. 453, has been determined by McTaggart and Wadsley[5]

Hexagonal	a	c
	3.635Å	5.839Å.

Franzen and Graham[7] have determined the lattice parameters of the compounds HfS, p. 377, and Hf_2S, p. 378:

HfS	a	c
Hexagonal	3.3748Å	3.4351Å

Hf_2S	a	c
Hexagonal	3.3736Å	11.7882Å.

The reactions

$$2TiS_3(c) = 2TiS_2(c) + S_2(g) \qquad \text{(II-2)}$$

and

$$2\overline{Zr}S_3(c) = 2Zr\bar{S}_2(c) + S_2(g) \qquad \text{(II-3)}$$

have been studied previously by Biltz, et al.[11,12] These workers used the method of Haraldsen, et al. These same reactions have been investigated by the method of this study.[16] It is of interest to compare the results of the two methods for all three similar reactions (I-1), (II-2), and (II-3) . For reaction (II-2), the following equations exist:

Biltz, et al.,[11] p. 105 $\Delta G^\circ = 35{,}800 - 39.9\ T$ (cal) (II-4a)

Present[16] $\Delta G^\circ = 40{,}200 - 44.8\ T$ (cal). (II-4b)

For reaction (II-3):

Biltz, et al.,[12] p. 257 $\Delta G^\circ = 47{,}000 - 39.1\ T$ (cal) (II-5a)

Present[16] $\Delta G^\circ = 59{,}650 - 50.0\ T$ (cal). (II-5b)

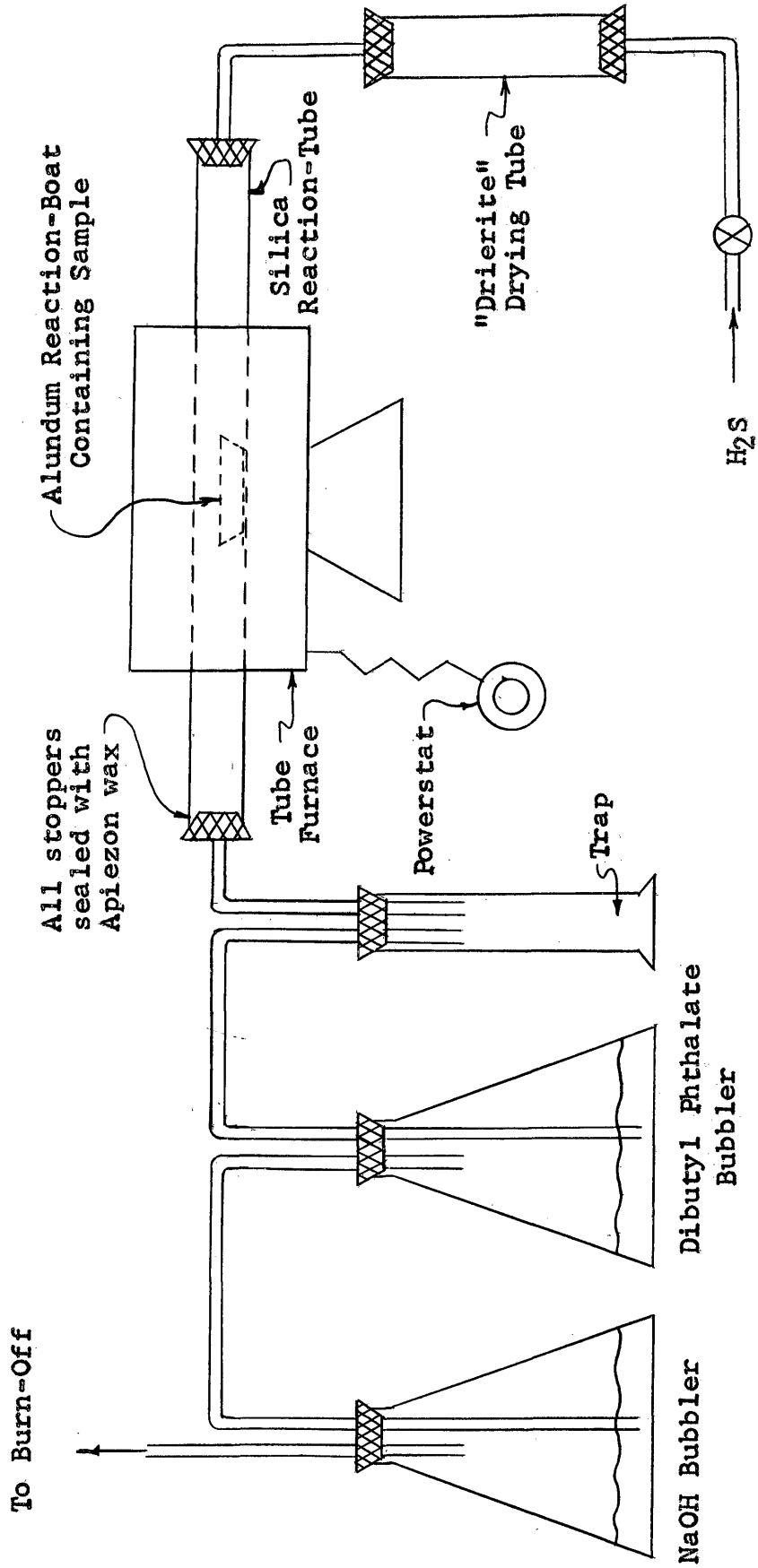
Both sets of data from Biltz, et al., have been reworked using more recent sulfur data (that found in Kubaschewski and Evans,[10] p. 342). Equations (II-4a) and (II-5a) were calculated using the raw data of Biltz, et al., the newer sulfur data, and a least squares treatment.

III. APPARATUS AND EXPERIMENTAL PROCEDURE

A. DESCRIPTION OF APPARATUS

1. Sulfide Preparation

The hafnium sulfides used in this study were prepared by two methods: one utilizing hydrogen sulfide and the other sulfur. A schematic diagram of the hydrogen sulfide method is shown in Fig. 5. A thoroughly dried alundum boat was used to hold the sample. The boat was placed in the furnace in a silica reaction tube. This tube was stoppered at both ends, and the stoppers were sealed with apiezon wax. The hydrogen sulfide was passed through a drying tube to remove any residual moisture before contacting the sample. After passing through the furnace, the hydrogen sulfide was passed through a trap. The function of this trap was to catch any liquid overflow from the next two flasks downstream. Such overflow occurred if the hydrogen sulfide flow stopped with the furnace at temperature. After passing through the trap, the hydrogen sulfide went through a dibutyl

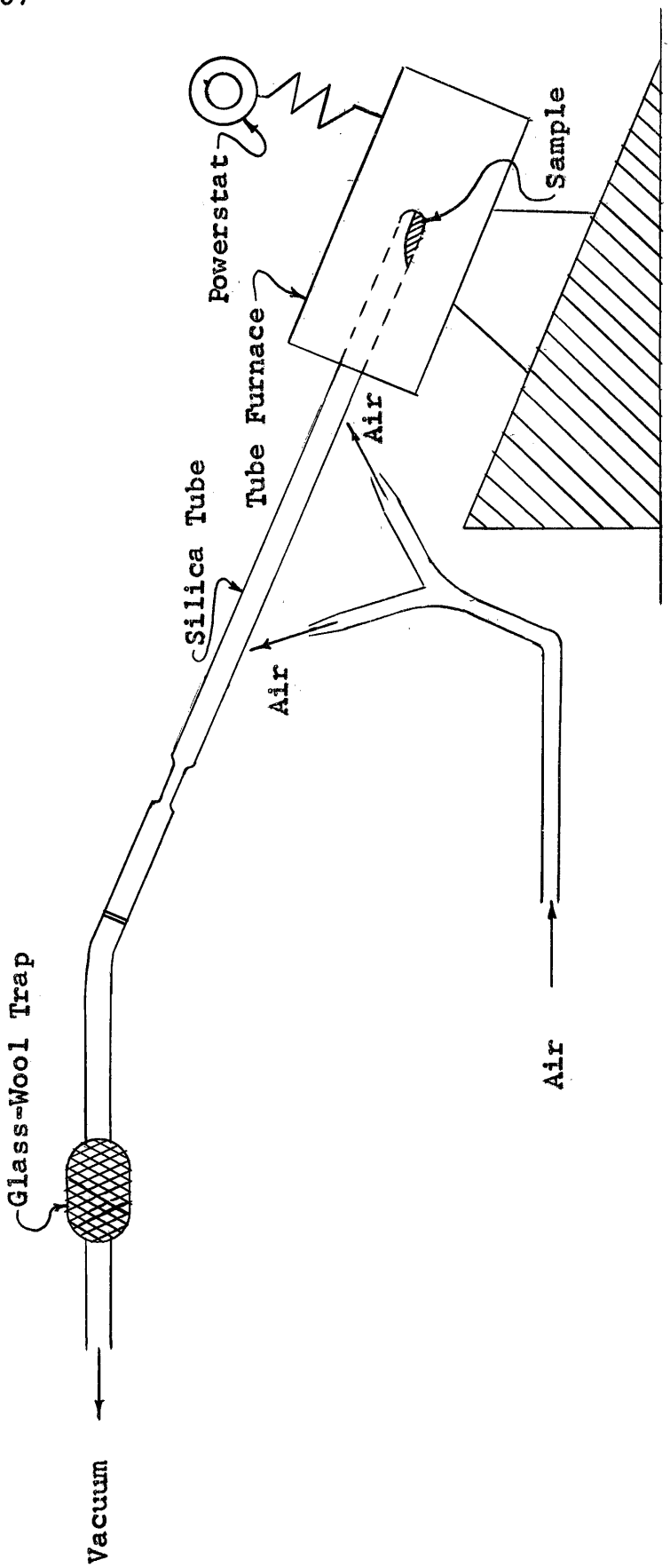


Schematic Diagram of Apparatus Used to Convert HfH_2 into HfS_2 Using H_2S

Figure 5

phthalate bubbler. The purpose of this bubbler was to prevent the back-diffusion of water-vapor from the sodium hydroxide bubbler, dibutyl phthalate having a relatively low vapor pressure at room temperature. This was apparently effective, as no visual oxidation of the downstream portion of the sample was ever noticed. The last bubbler contained a solution of sodium hydroxide. Its purpose was to dissolve as much hydrogen sulfide as possible. Any hydrogen sulfide passing through the last bubbler was burned in a natural-gas flame. Temperature control of the tube furnace was not critical, hence only a powerstat was used for its regulation. This tube furnace was about thirteen inches long. The outside diameter of the tube was about five and one-half inches; and the chamber, extending from end to end, had a diameter of about one and one-fourth inches.

A diagram of the sulfur method is shown in Fig. 6. Depending upon availability, either of two Welch rotary oil pumps was used to evacuate the system. One was capable of attaining a vacuum of less than five μ while the other attained a minimum pressure of about 75 μ. Upstream from the pump was a trap containing glass wool. Its function was to prevent any solid particles from contaminating the pump oil. The silica tube containing the sample and sulfur was connected to the pump by means of rubber vacuum tubing. Again



Schematic Diagram of Apparatus Used to Convert HfH_2 into HfS_2 Using Sulfur

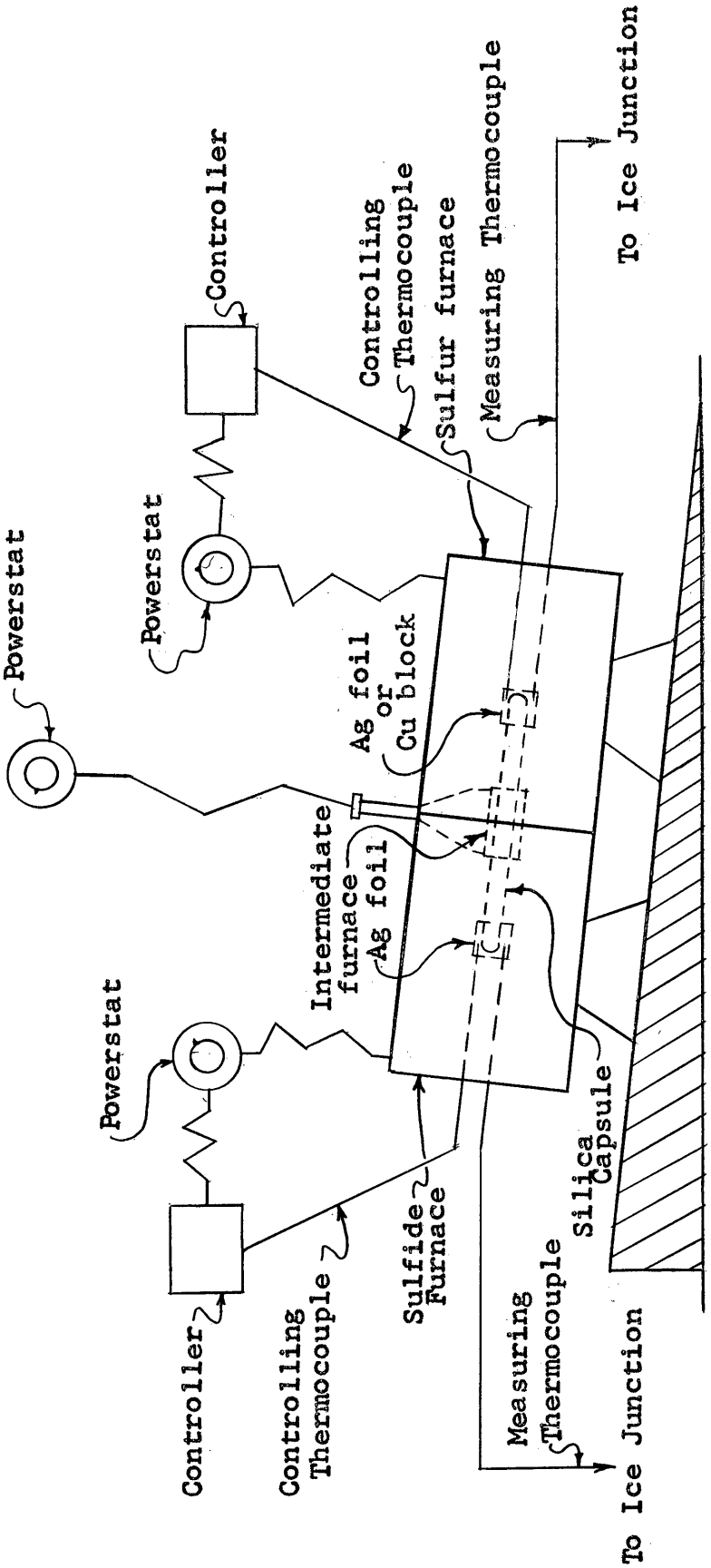
Figure 6

a tube furnace was used for heating, and its temperature was controlled by a powerstat. A slow air-flow was maintained on the portion of the silica tube outside the furnace to keep the sulfur from escaping from the tube into the vacuum-pump connections.

2. Equilibration

The hafnium sulfides prepared using the two previously described sets of apparatus were eventually (some were upgraded to make sulfides of higher $(^{S}/Hf)_{molar}$) sealed in evacuated capsules with sulfur, and the capsules were placed in the apparatus designed to yield equilibrium data for reaction (I-1). A diagram of this apparatus is shown in Fig. 7. The sulfide and sulfur furnaces were identical to the tube furnaces used in the sulfide syntheses described previously. Temperature setting and control were critical in the equilibrations, therefore, the furnaces received their electrical energy through powerstats which in turn were activated by controllers. The controllers were Barber-Colman model number 293C and were factory-calibrated for use with twenty-foot lengths of chromel-alumel wire as controlling thermocouple.

Two sets of this apparatus were used. One set (α) was used for equilibrations employing single-phase starting material, and the other (β) was used for equilibrations



Schematic Diagram of Equilibration Apparatus

Figure 7

using two-phase mixtures as starting material. They were identical in every respect except for intermediate furnaces and furnace partitions (both described below).

Because the two furnaces were butted together, an intermediate furnace was required where their ends came together to prevent sulfur condensation. These furnaces were made of alundum which had been wound with nichrome wire. The wire-wound surface was then covered with a paste of alundum cement and baked to dry. Since two furnace groups were used, two intermediate furnaces were required. The intermediate furnace in the group (α) used for equilibrations employing single-phase sulfides as starting materials will be described first. The alundum tube was about seven and three-eighth inches long and had an outside diameter of one and one-eighth inches and an inside diameter of about 5/8 inch. The intermediate furnace in the group (β) used for equilibrating two-phase mixtures had the following dimensions: approximately three and three-eighth inches long, an outside diameter of about 7/8 inch and a wall thickness of about 1/32 inch.

Each tube furnace had an end-piece of insulation approximately ½ inch in thickness. At the union of the two furnaces, there was an air space about 1/8 inch in thickness. Therefore, the total length not heated by the tube furnaces at the joint was about one and one-eighth inches, and the

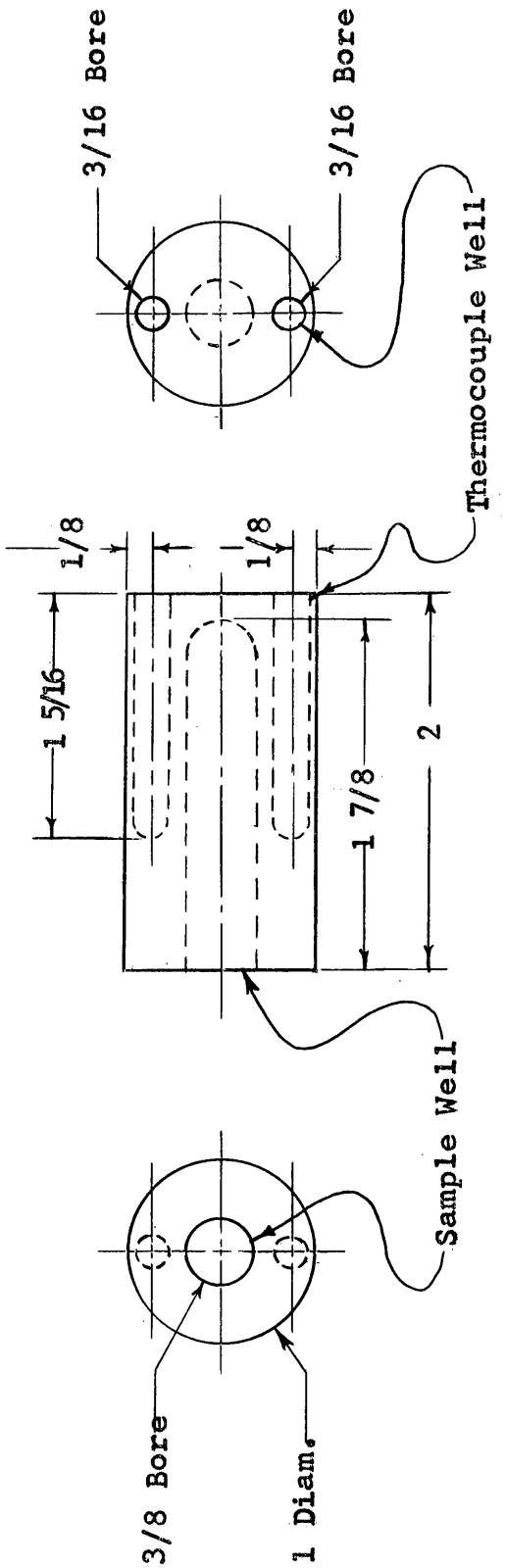
intermediate furnace provided heating not only in this "cold" zone but also on each side of it. Control of the temperature of this intermediate furnace was not critical, therefore it was controlled by a powerstat alone.

Each silica equilibration capsule was made so that, when in place in the furnace system, each of its ends extended slightly beyond the longitudinal center of its respective furnace. These silica capsules had an outside diameter of 9 mm and a wall thickness of 1 mm.

A piece of silver foil was wrapped around the end of the capsule containing the sulfide. This provided a length of about one and one-half inches with no temperature gradient, which provided a suitable constant-temperature volume for the sulfide. The measuring chromel-alumel thermocouple was placed within the wrappings of the silver foil, and its bead was placed as close to the longitudinal center of the sample as possible. The foil was pinched around the thermocouple to insure its constancy of position, and its position in the foil was not disturbed during the course of the experiments at a given sulfide temperature. The controlling chromel-alumel thermocouple was placed on the outside of the silver foil and held there with wire. Its position was not critical as long as it remained in the same place during any single run. Its bead was always placed as near to the

longitudinal center of the sample as possible so this point would dictate the controlling action.

Two methods of obtaining a zone of constant temperature were used on the sulfur end. One was the silver foil method described previously, and the other utilized a copper block. When the silver foil was used, the thermocouples were placed just as they were at the sulfide end. With the copper block, the thermocouples were placed in thermocouple wells bored in the block. Figure 8 shows the dimensions of the block. The block was always rotated in position until the plane through the two center lines of the thermocouple wells was parallel with the plane of tilt of the furnaces. The measuring and controlling thermocouples were always placed in the same wells for uniformity of the temperature measurement and control. The center of the sample well was placed as near the longitudinal center of the sulfur furnace as possible. A light oxide coating formed on the surface of the copper block during the course of each run. It was, however, very easily removed. The copper block could <u>not</u> be used at the sulfide end because the higher temperatures encountered there promoted the formation of too thick an oxide layer. Formation of such a thick layer of oxide (which occupied a greater volume than the volume of copper from which it formed) made it necessary to make the sample bore considerably



All dimensions in inches

Copper Block (Actual Size)

Figure 8

larger than 3/8" to prevent cracking of the silica capsule. However, when this was done, too large an air space existed between the silica and the copper to insure good heat transfer and reliable temperature measurement. The copper block was used on the sulfur end in arrangement β when two-phase mixtures were used as the starting material. Silver foil was used on the end of the capsules in the other apparatus, α (single-phase starting materials).

The furnace arrangement (see Fig. 7) was placed at an angle of about 6° from the horizontal. This was done to insure that the sulfur would all be in the end of the capsule which was in the sulfur furnace.

In order to minimize effects of thermal convection in the furnace-system chamber and to fix the capsule in the radial center of the chamber, two circular, bored, refractory discs were placed within the chamber, and one was placed at each end of the chamber. These were made of soft refractory brick, were 3/8 inch thick, 13/16 inch in diameter and had a 7/16 inch hole bored through the center. Of the two placed on the interior of the chamber, one was midway between the center joint and the sulfide end of the capsule, and the other was midway between the center joint and the sulfur end of the capsule. These partitions were used only in arrangement β. Glass wool was placed in the ends of the other

arrangement (∞) to decrease convection effects.

Temperature measurement of the sulfide and sulfur was effected by means of calibrated (calibration discussed later in this chapter) chromel-alumel measuring thermocouples. An ice-bath was used to fix the cold-junction temperature at 0° C. Its construction is shown in Figure 9.

The copper wires were attached to the proper (+ vs. -) terminals of a Leeds and Northrup potentiometer to determine temperature. This potentiometer was easily read to the nearest one-hundredth of a millivolt.

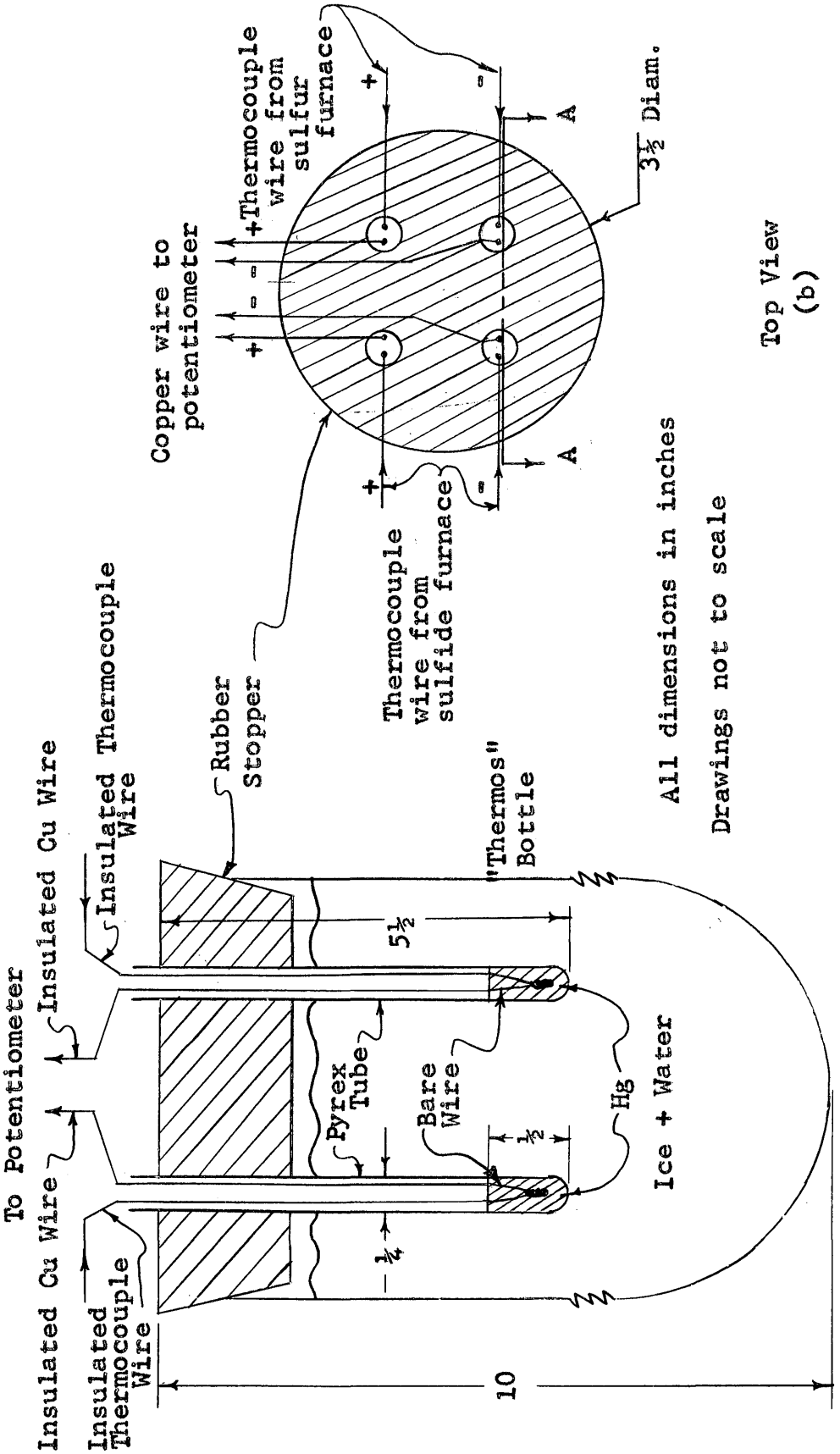
B. EXPERIMENTAL PROCEDURE

1. Chemicals

The hafnium hydride used in this study was purchased from Metal Hydrides Division of Ventron Corporation and was -325 mesh powder. Quantities from two different lot numbers were used. The analyses received with the two hydride shipments are given in Table 2. An x-ray diffraction pattern of the hydride showed $HfH_{1.98}$, $HfH_{1.70}$, and $HfH_{1.53}$ (A. S. T. M. Data).

The sulfur was special-high-purity from American Smelting and Refining Company and analyzed 99.999 + % S.

Hydrogen sulfide was purchased from the Matheson Company. It was C. P. grade, analyzing a minimum of 99.5% H_2S.



Ice Junction

Figure 9

TABLE 2

Analyses of HfH_2

LOT NO.	ELEMENT	AMOUNT
F-173	hydrogen nitrogen zirconium hafnium	1.10 wt. % .05 wt. % 1.26 wt. % balance (97.59%)
F-198	H_2	1.06 wt. %
	N_2	<10 ppm
	Ca	<50 ppm
	Cu	<50 ppm
	Al	<50 ppm
	Ni	<50 ppm
	Fe	12 ppm
	Mg	16 ppm
	Si	12 ppm
	Mn	<1 ppm
	Ti	125 ppm
	Zr	1.86 wt. %
	Hf	balance (97.04%)

Carbon disulfide used in leaching excess sulfur from sulfides prior to analysis was Fisher infra-red spectranalyzed CS_2.

2. Preparation of Hafnium Sulfides

The sets of apparatus for the two methods used were described previously and shown in Figs. 5 and 6. The method utilizing hydrogen sulfide will be described first.

The hafnium hydride to be used (Lot F-173) was well mixed with an approximately equal volume of sulfur. The purpose of this sulfur was to prevent oxidation of the hydride during the initial heat-up period when the boat and tube walls gave off any water vapor they had picked up between syntheses. Every precaution was taken to insure that this pickup would be minimum. Between syntheses, the silica reaction tube was kept stoppered, with no opening to the atmosphere or any other source of water vapor. The alundum boat was baked in air after each synthesis and cooled and stored in a desiccator between syntheses. The sulfur and hafnium hydride mixture was placed in the boat. The boat was filled to about three-fourths of capacity to allow for volume expansion. The loaded boat was then placed in the center of the reaction tube in the furnace. The system was then flushed with hydrogen sulfide for at least

two hours, the flow-rate of the H_2S being approximately 25 cm^3/min. At the end of this flushing period, with the same gas flow-rate maintained, heating of the furnace was begun. After about two hours, the furnace temperature was between 850 and 900° C. This temperature range was required to effect reasonably rapid production of HfS_2. Temperature was maintained in this range for two to three hours, at the end of which time it was decreased rapidly. After an hour of this rapid cooling, the system had reached room temperature. The hydrogen sulfide flow was then stopped, and the boat with its reaction product was removed from the reaction tube. The sulfide produced was inhomogeneous and graded in color from red to black. X-ray diffraction patterns showed that the only sulfides present were the disulfide and possibly some sesquisulfide. As listed previously, these two sulfides have nearly identical unit cells, making x-ray differentiation impossible. The previous investigators, McTaggart and Wadsley,[5] made no mention as to how they distinguished between these two sulfides. Color differences were of no value either, as the color of the disulfide varied between red and black, depending upon its composition and the lot number of the hydride used. The sesquisulfide was listed as being light yellow-brown by McTaggart and Wadsley,[5] p. 453; however, nothing but black material was ever seen when the

$(S/Hf)_{molar}$ was less than about 1.8. Analyses of leached samples of sulfide produced by this method yielded $(S/Hf)_{molar} = 1.9$ as an average. It was very difficult to produce oxide-free sulfide by this method. Very few synthesis runs yielded a product with no visual oxide (the oxide, HfO_2, is white). Many runs, however, yielded a product with visual oxide only at the upstream edge of the boat. In these cases, the entire upstream half of the product was discarded, and the remaining material was used. X-ray diffraction patterns of the material used indicated a very small amount of oxide present, certainly no more than 1 wt. %. This was calculated by comparing intensities of oxide peaks on the pure oxide pattern and on the sulfide patterns. This amount of oxide can be shown to produce a very small error in the analysis for $(S/Hf)_{molar}$ when at least a .2000 gram sample is analyzed and $(S/Hf)_{molar}$ is in the range of interest (i.e., $1.90 < (S/Hf)_{molar} < 2.95$). Using these figures, a sulfide having an actual analysis of $HfS_{1.90}$ would analyze as $HfS_{1.89}$ when contaminated with 1 wt. % of HfO_2. Similarly, a sulfide having an actual analysis of $HfS_{2.95}$ would analyze as $HfS_{2.93}$ with the given contamination. These represent the maximum effects of HfO_2 on the analyses. Since the content of HfO_2 was probably less than 1 wt. %, any extraneous effects on the analysis

of the sulfides caused by the presence of oxide were ignored.

This amount of oxide would also have negligible effect on the activities of the sulfides. Since the oxide concentration was so small, the sulfide activities would, for all practical purposes, remain unity. Since there was an "infinite" source for the sulfur vapor to draw from, the pressure of S_2 in the gaseous phase would be unaffected by the presence of oxygen. Even though some SO_2 might be formed, the pressure of S_2 would be restored by the "infinite" source. Thus, the equilibrium constant for reaction (I-1),

$$K = \frac{(^{a}Hf\overline{S}_{2(c)})^2 \quad (Ps_{2(g)})}{(^{a}\overline{Hf}S_{3(c)})^2},$$

would be unaffected by the presence of small amounts of oxide.

Since the sulfides produced by this method were rather inhomogeneous, they were given an opportunity to homogenize before they were used in equilibrations. If the disulfide was the desired starting material for the equilibrations, the sulfide from the synthesis furnace was sealed into a dried, evacuated, and gettered (described in Equilibration Procedure, this chapter) 13 mm O. D. silica capsule. The capsule with its charge was evacuated by one of the previously described pumps, and the portion containing the

sulfide was sealed-off using an oxygen-natural gas flame. This capsule was placed in the center of a tube furnace and was heated at about 700° C for about one week. At the end of this time, the sulfide was removed, analyzed, and encapsulated for equilibration use. If the desired starting material for the equilibrations was the trisulfide, the sulfide from the synthesis furnace was mixed with sulfur, and this mixture was encapsulated as described before. This mixture was heated for about one week at around 450° C. This was sufficient time and sulfur pressure to effect complete conversion of the disulfide to the trisulfide. The resulting trisulfide was then used in the equilibrations. During the course of the homogenations, no visual oxide was formed, and no increase in oxide content was indicated by x-ray diffraction.

Since a visual oxide crescent was formed in most of the synthesis runs utilizing H_2S, and since x-ray diffraction patterns of the retained sulfides showed a very small amount of HfO_2, some, if not all, of this retained sulfide had its lattice saturated with oxygen in solid-solution. Although the solid solubility of oxygen in the lattice was probably very small, thus having a negligible effect on the activity of the sulfide, its presence possibly could have explained the unexpected slow reaction rates encountered (this will be

discussed further in Chapter VI). On the basis of these uncertainties, it was decided that a different synthesis technique should be employed.

A 9 mm O. D. silica tube, closed at one end, was used as the reaction chamber in this method. This tube was dried under vacuum with an oxygen-natural gas flame. It was especially difficult to completely rid the silica glass of adsorbed water, even at high temperatures and under vacuum. The drying was done as completely as was practical. Enough HfH_2 (Lot F-198) to make .2 + grams of HfS_2 was placed in the capsule. A large excess of sulfur (greater than the amount required to make $(S/Hf)_{molar} = 2$) was then added. The tube was then "necked down" at the point where it would eventually be sealed off. This was done by rotating the tube about its longitudinal axis in the oxygen-natural gas flame and pulling gently on the two held ends when the glass started to soften. This caused the tube diameter to decrease in the region softened by the flame. In this way, a length of tube about ½ inch was obtained whose diameter had decreased from 9 mm to about 3 mm. At the end of the synthesis, the glass in this thin section was easily caused to flow together by the flame, hence sealing-off the capsule. The point along the tube at which this thin section was made was dictated by the length of tube required to extend slightly

beyond the centers of the furnaces of the equilibration apparatus (see Fig. 7).

After this necking-down procedure, the tube was attached to the vacuum pump by rubber vacuum tubing, and the system was evacuated for one hour. The pump capable of attaining a residual pressure of 5μ was used in all syntheses of this type. The end of the tube containing the material was then placed in the center of the tube furnace set on a slant as shown in Fig. 6, and heating was begun (the vacuum pump was running throughout the entire synthesis period). At the same time the heating was started, a slow flow of air was directed toward the portion of the tube outside the furnace. When the sulfur melted, it attained a relatively high vapor pressure (compared to its vapor pressure as a solid); and, because of the increased mean free path afforded by the vacuum, the sulfur vapor began to rapidly move to cooler regions. One stream of air, directed toward the end of the furnace from which the tube came, was designed to cool the tube enough to cause liquid sulfur, with its relatively high vapor pressure, to remain at the mouth of the furnace for a reasonable length of time (about 15 minutes). The other stream of air, directed further down the tube toward a point closer to the pump, was designed to condense any sulfur vapor which had not condensed by the time it got to that

position.

The furnace was heated slowly to about 900° C. Slow heating was required to prevent surging of sulfur and sulfide (hydride) out of the capsule. As the sulfur condensed in the air flow, it formed a plug in the capsule which had either a very small opening or no opening at all. When the plug was broken by the application of heat, any hydrogen or hydrogen sulfide which had formed behind the plug surged downstream carrying solid and liquid particles with it. A slow heating rate insured that hydrogen sulfide would be produced slowly and thus not be capable of building up a high pressure behind any plug which might have formed. The final temperature of about 900° C was attained approximately two hours after heat-up began. The material was allowed to heat at about 700° C for at least ½ hour during the heat-up period. Here, the temperature was low enough to allow the sulfide to increase in $(S/Hf)_{molar}$ and yet high enough to permit good kinetics. After this ½-hour period, the hydride was almost completely converted to sulfide. Heating from here to 900° C was rapid. The temperature was increased to 900° C to insure that all of the hydride was decomposed. However, with temperatures this high, the finely-divided sulfide began to sinter; therefore, the entire time from 700° C to 900° C and back down to 700° C was no more than ½

hour. Again the temperature was maintained at 600-700° C for about ½ hour. Then the furnace was opened, and the material was cooled rapidly. During this cooling period, the capsule was sealed-off as described before. The finished capsule contained disulfide at one end and sulfur at the final position of the air-streams and was ready for use in the equilibration apparatus.

The disulfide formed by this method had a $(S/Hf)_{molar}$ between 1.95 and 2.00. It contained no visual oxide, and x-ray diffraction patterns showed no oxide to be present.

Disulfides produced by this technique were also used in preparing mixtures of disulfide and trisulfide for equilibration. These mixtures were prepared in either of two ways. One way was to mix together two-phase samples which were produced by previous equilibrations employing capsules made by the sulfur-vacuum method. The other way was to make disulfide by the sulfur-vacuum method, seal this material into a dried, evacuated, and gettered (see below) 13 mm O. D. capsule, heat this at about 450° C for one week to produce trisulfide, and then decompose part of the trisulfide to disulfide by lowering the temperature to about 300° C for about 12 hours. The sulfide mixtures produced by both of these methods were leached with CS_2 to remove residual sulfur, analyzed to determine $(S/Hf)_{molar}$ and phases present,

and encapsulated as described below for use in the equilibration apparatus.

3. Equilibration Procedure

Preparation of one type of capsule used has already been described. This was the capsule made by combining sulfur with hafnium hydride under vacuum. Two other types of capsules were also used. These were capsules containing material made by the hydrogen sulfide technique and capsules made by mixing materials made by the sulfur-vacuum technique. These capsules were made in the same way. A 9 mm O. D. silica tube was closed at one end and dried with the oxygen-natural gas flame under vacuum. The desired sulfide was then placed in the closed end of the tube, and sulfur was placed on top of it. The tube was necked-down at the point giving the desired length of capsule. Several pieces of titanium sponge were placed in the tube beyond the neck, and the tube was then necked-down beyond the sponge. This gave a compartment containing titanium sponge, the compartment having a neck on each side. A length of 9 mm tube of about one inch existed beyond the neck furthest from the sample. This portion of the tube was attached to the vacuum pump via rubber vacuum hose. The pump capable of attaining a residual pressure of 75μ was used in making these capsules.

The capsules were evacuated for two hours, during which time further drying was attempted by running the flame up the capsule from the sample end, over the titanium and to the hose. Special care was taken not to heat the sulfide and thus change its composition. However, a small amount of the sulfur placed on top of the sulfide was vaporized and moved down the walls of the tube by the flame. It was hoped that this sulfur would provide effective gettering of adsorbed water vapor on the tube walls. At the end of the two-hour period, the capsule was sealed-off at the neck furthest from the sample. Thus, the compartment containing the titanium remained attached. This compartment was placed in a tube-furnace for the purpose of further reducing nitrogen and oxygen pressure in the capsule (this was the capsule-gettering process referred to previously). Because a volatile suboxide of titanium formed, special care was taken in placing the compartment in the furnace so that no suboxide would condense on the walls of the equilibration portion of the tube. The compartment was at a minimum temperature of 700° C for 24 hours. The maximum possible oxygen pressure remaining in the capsule would be dictated by the reaction

$$Ti\ (c) + O_2\ (g) = TiO_2\ (c). \qquad \text{(III-1)}$$

Calculations made from data taken from Kubaschewski and Evans[10] show that the equilibrium oxygen pressure of reaction

(III-1) is about 10^{-41} atmospheres at 700° C. Since no TiO_2 was seen in the compartment after gettering, the oxygen pressure approached a value less than 10^{-41} atmospheres. The only reaction product noticed was TiO which had formed as a thin black layer on the walls of the compartment. The pieces of titanium which were removed from the compartment showed very little sign of any chemical reaction. The metallic luster was only slightly dulled. No sign of the oxides Ti_2O_3 (violet) or Ti_3O_5 (blue) as reported in the summary given by Skinner, et al.,[17] pages 23 and 24, was seen. Also no evidence was seen of any TiN crystals. Skinner, et al.,[17] p. 60, report that in nitriding experiments found in the literature, no TiN crystals were found on the surface of the titanium after the experiments. Calculations made from data taken from Kubaschewski and Evans[10] for the reaction

$$2Ti\ (c) + N_2\ (g) = 2TiN\ (c) \qquad \text{(III-2)}$$

indicate that the residual nitrogen pressure in the capsules approached 10^{-27} atm. A tesla coil was used to check for residual gases in several capsules. No discharge was ever observed. According to Dushman,[18] p. 220-221, the discharge expected for air would have been red or pink in color; and the absence of such a discharge under vacuum conditions would indicate a residual air pressure of 10^{-6} atm. or less.

At the end of the 24-hour gettering period, the compartment containing the titanium was removed by applying the flame to the neck between the capsule and the compartment. The capsule thus made was sealed and ready to be used in the equilibration apparatus.

The capsule was placed in position in the furnace arrangement. The sulfide was packed as lightly as possible into its end of the capsule. A space always existed above the sulfide to permit as good gas-solid contact as possible. The cylinder of silver foil with its thermocouples in place was then placed over the sulfide end. Either silver foil or the copper block was placed over the sulfur end of the capsule. Care was taken during the capsule placement to shake as little sulfide as possible out of its zone of constant temperature. With the capsule in place, the furnace lids were closed, and the intermediate furnace and sulfur furnace were turned on and brought to temperature. When these reached the desired temperatures, the sulfide furnace was turned on and brought to temperature. This procedure was followed to insure that the trisulfide (if present) would not decompose during the heatup period. If the disulfide was used as the starting material, the capsule was left in the furnace arrangement for about one week. If the trisulfide or a mixture of disulfide and trisulfide was the

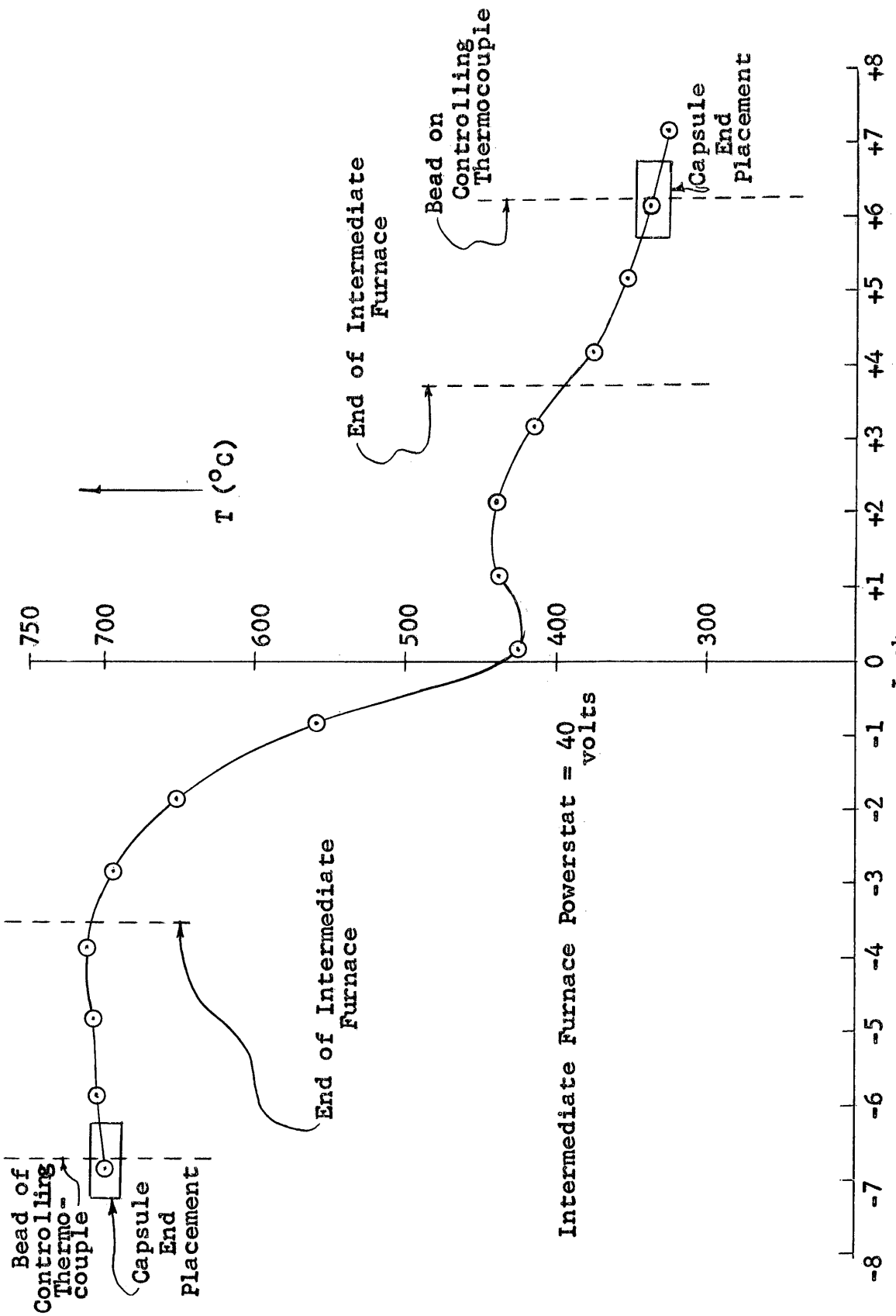
starting material, the capsule was left in for about two days. The temperatures of the two furnaces were measured periodically during the course of any run. At the end of the specified time, the capsule was removed from the arrangement and air-quenched. It took no longer than ½ min. to open the furnace, remove the capsule, and place it on the cooling brick. The capsule was cooled to room temperature in less than five minutes. The capsule was broken open, and the sulfide was leached with carbon disulfide to remove residual sulfur condensed from the gas phase and was then analyzed. Leaching was accomplished by pouring carbon disulfide over the sample, the sample being placed on filter paper and the filter paper being placed in a funnel. Carbon disulfide was poured over the sample several times to insure that all residual sulfur was removed. The analysis procedure will be described later.

The exact placement of the capsules in the furnace arrangements and the setting of the powerstats controlling the intermediate furnaces were determined by means of temperature profiles made on the arrangements. These profiles were made by pulling a thermocouple marked at one-inch intervals through a 13 mm O. D. silica tube which was approximately one inch shorter than the entire furnace arrangement. End-plugs were used on the furnace, but no intermediate

partitions were used. No silver foil was used. The profiles giving operating conditions of the two furnace groups used are shown in Figs. 10 and 11.

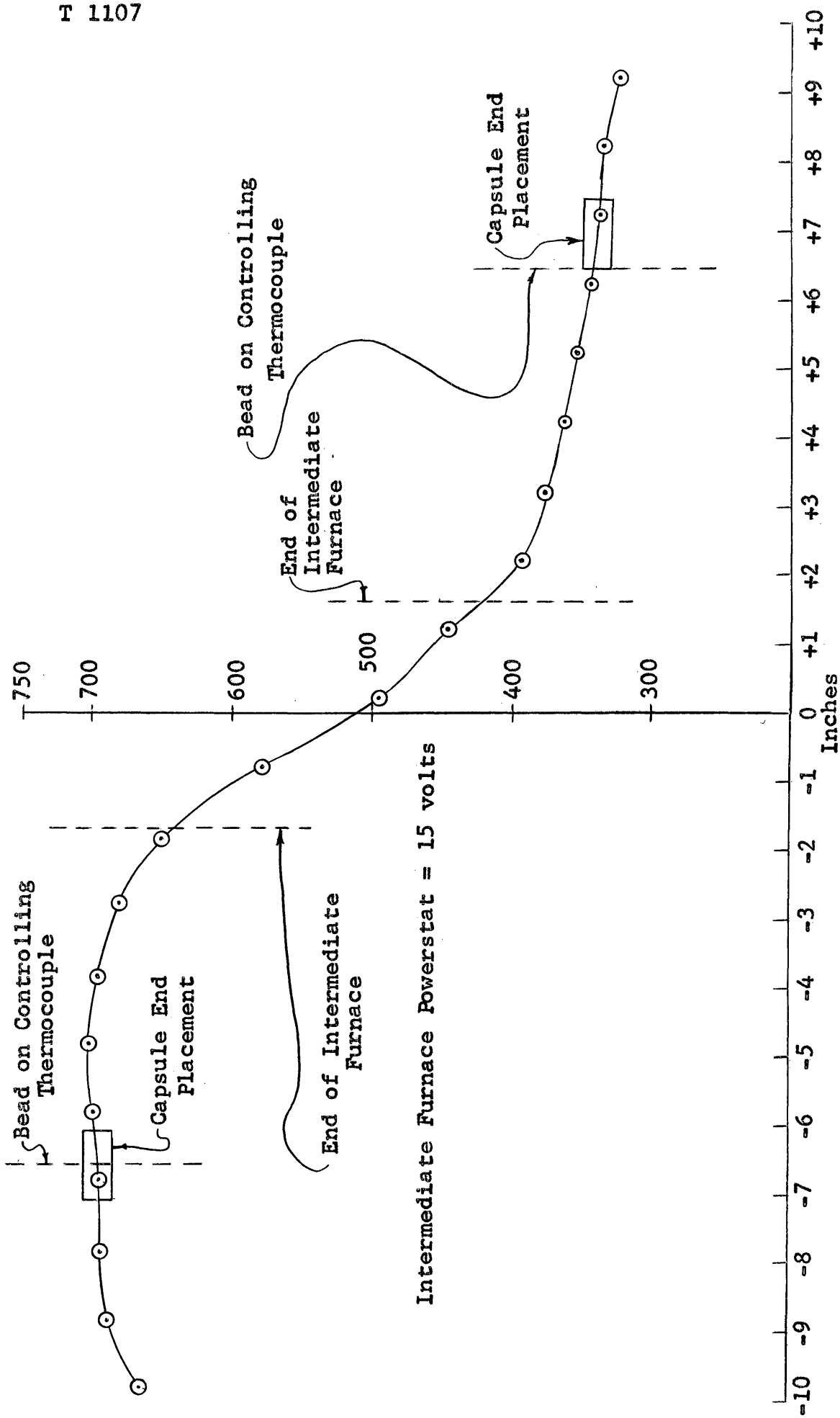
Table 3 summarizes the characteristics of the equilibration modifications. It will be noted that the data taken from group α resulted from single-phase starting material, and the data taken from group β resulted from two-phase starting material. The first set of runs made in arrangement β utilizing HfS_2 as the starting material yielded very inconsistent data. This set of runs did show, however, that the method of preparation made very little difference in the behavior of the sulfides kinetically (this will be discussed further in Chapter VI). Hence, mention of this series of runs is made here.

Thermocouples used in this study were standardized against the melting points of Pb, Zn, and Al. This was done by comparing them with a thermocouple which had been used to make cooling curves for these three metals. The metals were melted in graphite crucibles; and the thermocouple, surrounded by a 9 mm O. D. silica protection tube, was immersed in the melt. Melting point determinations made at two different times are listed in Table 4.



Profile of Furnace Arrangement Used for Equilibrations Using Single-Phase Sulfides as Starting Material (Runs 37-100)

Figure 10



Profile of Furnace Arrangement Used for Equilibrations Using Two-Phase Mixtures as Starting Material (Runs 2006-2017)

Figure 11

TABLE 3

Characteristics of Equilibration Modifications

DATA	FURNACE GROUP	HfH_2 LOT	STARTING MATERIAL	SYNTHESIS METHOD	RUN NUMBERS	SULFIDE END	SULFUR END	TEMP. PROFILE	SULFIDE THERMOCOUPLE	SULFUR THERMOCOUPLE
Consistent	α	F-173	$\overline{Hf}S_3$ or $Hf\overline{S}_2$	H_2S	37-100	Ag foil	Ag foil	Fig. 10	#1A	#2A
Not Consistent	β	F-198	$Hf\overline{S}_2$	Sulfur-vacuum	1000-1010	Ag foil	Ag foil	Fig. 11	#1A	#2A
Consistent	β	F-198	$\overline{Hf}S_3$ + $Hf\overline{S}_2$	Sulfur-vacuum	2006-2017	Ag foil	Cu block	Fig. 11	#1B	#2B

TABLE 4

Calibration of Standard Thermocouple

METAL	OBSERVED M. P. (°C)	LISTED M. P.[10] (°C)
Pb	327	327
Zn	418	419.5
Al	659	659
Pb	328	327
Zn	418	419.5
Al	658	659

This standard thermocouple was considered to have no inherent error on the basis of these determinations. Calibration of the measuring thermocouples was accomplished by comparing them with this standard couple. A measuring thermocouple and the standard couple were wrapped together in a piece of silver foil, their beads almost touching. The silver foil containing the couples was placed in the center of a tube-furnace which was activated through a controller. Several temperatures were set, and these were read on each thermo-couple, thus furnishing a comparison between the standard couple and the measuring couple in question. Table 5 gives the calibrations of the couples used in the data-gathering runs (see also Table 3).

TABLE 5

Calibration of Thermocouples used in Data-Gathering Runs

Calibration A of Measuring Thermocouples #1 and #2

(a)

RUN NUMBERS	THERMO-COUPLE #1A T(°C)	STD. COUPLE T(°C)	THERMOCOUPLE # 2A T(°C)	STD. COUPLE T(°C)
37-100	707 653.25	707 653.5	135.75 191.75 245.5 295.5 346 395.5 457.50	134.25 189.5 242.25 292.5 343.25 392.75 454.8

Calibration B of Measuring Thermocouples #1 and #2

(b)

RUN NUMBERS	THERMOCOUPLE #1B T(°C)	STD. COUPLE T(°C)	THERMOCOUPLE #2B T(°C)	STD. COUPLE T(°C)
2006-2017	721.25	721.5	351 401.5 451	348.5 399.5 449.5

These calibrations were made after the respective series of runs were completed. The uniformity of the thermodynamic data for these two sets of runs indicates that the thermocouples did not change appreciably during the course of the runs.

Temperature corrections were required not only to

correct readings in thermocouples but also to correct for the fact that the temperatures of the sulfide and sulfur were measured outside of the capsule. This latter correction was also found to be important. The bead of a calibrated thermocouple was placed at the closed end of an equilibration-length 9 mm O. D. silica tube. The bead was immersed in HfO_2 powder. The closed end was first placed at the sulfur end of the apparatus, and with the silver foil or copper block in place, actual run conditions were imposed. A series of "sulfur temperatures" were set, and measurements of these temperatures were taken by the thermocouple inside the tube and by the measuring thermocouple inside the foil or block. The inside thermocouple was then calibrated at the temperatures measured in the sulfur end. The closed end of the tube was then moved to the sulfide end where the same procedure was followed. In this way, the difference between measured and actual temperature was found. Table 6 shows the results of these temperature corrections for the data-collecting runs. The average values shown in Table 6 were subtracted from the measured values to determine actual sulfur and sulfide temperatures.

TABLE 6

Final Temperature Corrections

RUN NUMBERS	CORRECTED INSIDE SULFIDE T (°C)	CORRECTED FOIL T (°C)	FOIL T IS HIGH BY (°C)	CORRECTED INSIDE SULFUR T (°C)	CORRECTED FOIL T (°C)	FOIL T IS HIGH BY (°C)
37-100	695.75	699.75	4	(1) 140.25	142.5	2.25
	645	648.75	3.75	(2) 193.75	196.5	2.75
				(3) 242.25	245.75	3.5
				(4) 293	297.25	4.25
				(5) 343.25	348	4.75
(a)				(6) 395.25	399.5	4.25
				(7) 459.25	463.75	4.5
					Ave. of 2-5	4
		Ave.	4		Ave. of 5-7	4.5
2006-2017	695.5	700	4.5	345	347.25	2.25
				394.25	396.5	2.25
(b)				444.5	447.25	2.75
		Ave.	4.5		Ave.	2.5

On Figures 10 and 11, there is a temperature gradient across the regions labeled "capsule end placement". However, the profiles of these Figures were made with no silver foil or copper block. In actual equilibration runs with the silver foil and/or copper block in place on the ends of the capsule, there would be no measurable temperature gradients along these ends because of the high thermal conductivities of silver and copper. Thus, no corrections were necessary for longitudinal temperature gradients.

The leached sulfides were analyzed by room-temperature x-ray diffraction to determine the phases present and by combustion in air to determine $(S/Hf)_{molar}$. The combustion analysis is based on the following reaction:

$$HfS_x + (1 + x)O_2 \longrightarrow HfO_2 + xSO_2 \qquad \text{(III-3)}$$

where HfO_2 is the only condensed phase remaining at the end of the combustion. Franzen and Graham,[7] p. 377, also analyzed their hafnium sulfides by igniting in air and weighing as HfO_2. Thermodynamically, HfO_2 is the only hafnium compound which should exist. For the reaction

$$Hf(c) + O_2(g) = HfO_2(c) \qquad \text{(III-4)}$$

$\Delta G = -221{,}500$ cal at 600° C and $Po_2 = .21$ atm. This shows that if any oxides of hafnium exist with $(O/Hf)_{molar} < 2$, they would have been converted to HfO_2 under the combustion conditions used. There is always the possibility of volatile suboxides of hafnium forming during the oxidation process, however. A standard method for analysis of zirconium (and hafnium) is given in "Treatise on Analytical Chemistry."[23] After the zirconium (and/or hafnium) has been separated from its parent material, the procedure states that the precipitate (containing only salts of Zr and/or Hf) is to be ignited to constant weight at 800-1000°C and weighed as ZrO_2 (or HfO_2). Thus, any loss of hafnium due to volatilization as a suboxide must be negligible. For the reaction

$$HfO_2(c) + \tfrac{1}{2}N_2(g) = HfN(c) + O_2(g) \qquad \text{(III-5)}$$

ΔG = + 153,500 cal at 600° C, P_{O_2} = .21 atm. and P_{N_2} = .79 atm. This shows that no hafnium nitride would have formed under the combustion conditions. Data for these calculations was taken from Kubaschewski and Evans.[10] Thus, it can be stated with reasonable certainty that HfO_2 was the only condensed phase remaining after combustion.

The analysis procedure was as follows: The glazed-porcelain crucible used in the analysis was removed from the desiccator in which it was kept between analyses and was weighed. The balance used had a sensitivity of .0001 gram. Between .2 and .3 gram of sulfide was placed in the crucible, and the crucible with the sulfide in it was weighed. The sulfide was then heated in air in the crucible above a Fisher-burner for at least one hour. The sulfide temperature was always greater than 600° C during the one-hour combustion. Visually, the sulfide was converted to oxide in less than five minutes. The remaining combustion time insured complete oxidation. At the end of this one-hour period, the crucible was removed from the flame and placed in a desiccator for cooling. After ½ hour of cooling, the crucible had reached room temperature and was removed from the desiccator. The crucible with the oxide in it was weighed, and the oxide was then removed. The empty crucible was then weighed. This

process furnished the following information:

(1) wt. of sulfide sample

(2) wt. of oxide formed.

From the stoichiometry of reaction (III-3), the equation

$$x \text{ in } HfS_x = 6.56 \times \left[\frac{(\text{wt. } HfS_x)}{(\text{wt. } HfO_2)} - .848 \right] = (S/Hf)_{molar} \qquad \text{(III-6)}$$

was derived. In the derivation, the atomic weights used were as follows:

Hf	178.50
O_2	32.00
S	32.07

Thus, $(S/Hf)_{molar}$ was calculated using the results of the combustion analysis.

IV. REDUCTION OF EXPERIMENTAL DATA

A. GENERAL CONSIDERATIONS

Experimentally, two conditions were imposed on the system HfS_x-S. These were:

(1) fixed sulfide temperature
(2) fixed sulfur temperature

The number of degrees of freedom for the system S (1) = $S_T(g)$ is one. Since the temperature of S (1) was fixed, the pressure of $S_T(g)$ above S (1) was thus also fixed. This established the total sulfur pressure, Ps_T, throughout the capsule.

Gaseous sulfur, however, contains five different molecular species: S, S_2, S_4, S_6, and S_8. Equilibria between the species can be written as

$$2S(g) = S_2(g) \quad (a)$$
$$2S_2(g) = S_4(g) \quad (b) \qquad \text{(IV-1)}$$
$$3/2S_4(g) = S_6(g) \quad (c)$$
$$4/3S_6(g) = S_8(g) \quad (d)$$

Applying the phase rule to the phase $S_T(g)$: $F = 1 - 1 + 2 = 2$. Thus, if the temperature and pressure of the gaseous sulfur are both fixed, the composition of the phase is also fixed. In this study, Ps_T was fixed as stated previously. Also, at any given position in the capsule, T was fixed. It has been customary in thermodynamic data applied to systems of interest in metallurgy to use the gaseous sulfur species S_2 (ideal gas at 1 atm) as the standard state for gaseous sulfur. Therefore, in this study, Ps_2 was calculated knowing Ps_T and the temperature at which the gaseous sulfur contacted the sulfide (sulfide temperature).

In the system HfS_x - S, two types of equilibria are possible between the condensed phase (s) and the gaseous phase:

$$S_2(g) = 2\underline{S}_{(\text{in } HfS_x)} \qquad \text{(a)} \qquad \text{(IV-2)}$$

$$2\ \overline{Hf}S_3(c) = 2\ Hf\overline{S}_2(c) + S_2(g) \qquad \text{(b)}$$

Reaction (a) represents the equilibrium between the gaseous sulfur phase and the solid nonstoichiometric sulfide. If the phase rule is applied to this equilibrium, $F = 2 - 2 + 2 = 2$. Therefore, with both temperature and pressure fixed by the experimental conditions, the composition of the sulfide (i.e., x in HfS_x) was fixed.

Reaction (b) is the same as reaction (I-1) and was the equilibrium of primary concern for this study. For this

equilibrium, F = 2 - 3 + 2 = 1. This indicates that for any given temperature, the equilibrium sulfur pressure is fixed. Under the experimental conditions of fixed temperature and pressure, only one of the pressures at any given temperature corresponded to an equilibrium pressure for reaction (b). All of the other pressures established at the given temperature were equilibrium pressures for reaction (a). This situation can be shown schematically on a plot of Ps_T vs. x in HfS_x. In Fig. 12, a, b, and c are the equilibrium sulfur pressures for reaction (I-1) at temperatures T_1, T_2, and T_3 respectively.

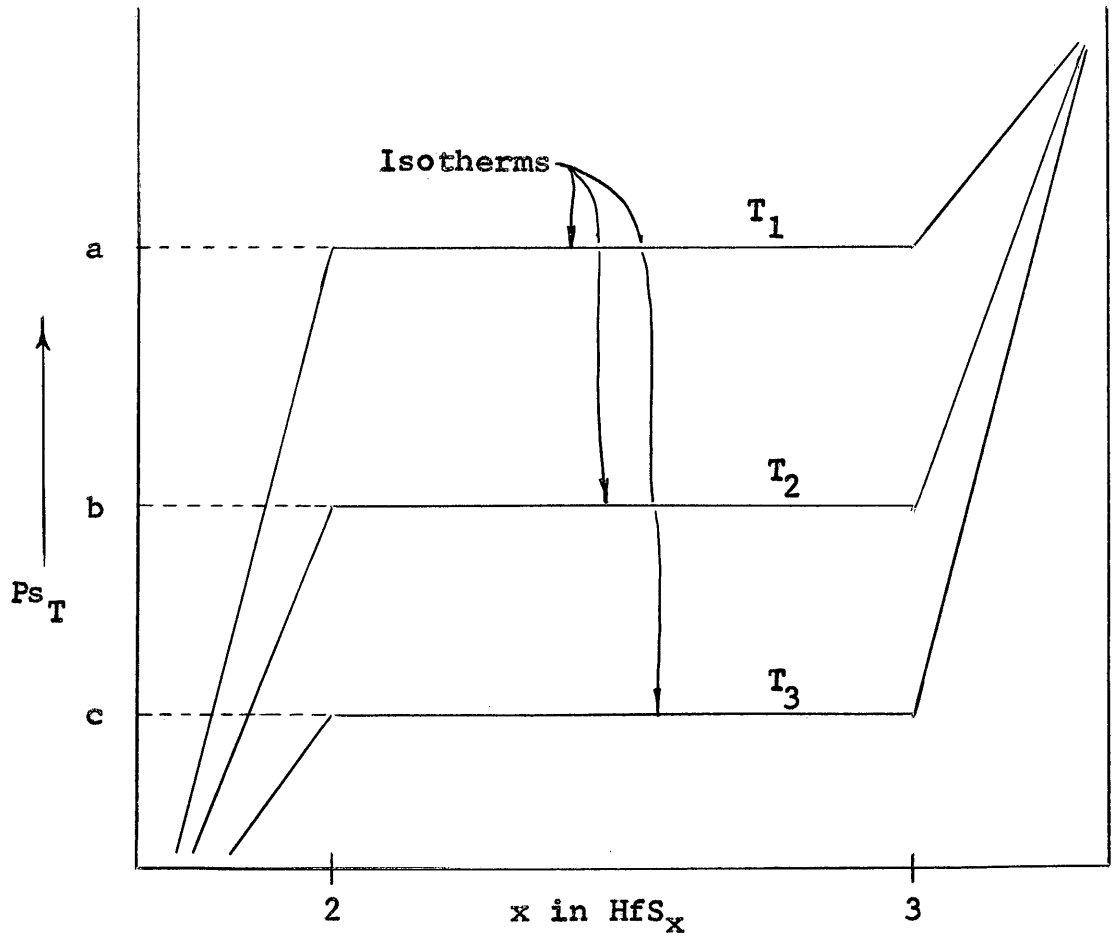
B. THERMODYNAMIC COMPUTATIONS

The total sulfur pressure in each capsule was calculated from data found in Kubaschewski and Evans.[10] The following equation was used:

$$\log_{10} Ps_T \text{ (mm Hg)} = \frac{-4,830}{T^{\circ} (^{\circ}K)} - 5.0 \log_{10} T^{\circ}(^{\circ}K) + 23.88 \quad \text{(IV-3)}$$

where T° is the temperature of the molten sulfur.

The pressure of diatomic sulfur was calculated from data on the following equilibria. This data was also taken from Kubaschewski and Evans.[10]



Schematic Diagram of Ps_T vs. x in HfS_x

Figure 12

$$
\begin{aligned}
&2S\ (g) = S_2\ (g) && \Delta G^\circ = 77{,}250 - 29.7T && (a)\\
&S_2\ (g) = \tfrac{1}{2}S_4\ (g) && \Delta G^\circ = -14{,}200 + 15.94T && (b)\\
&S_2\ (g) = 1/3S_6\ (g) && \Delta G^\circ = -21{,}240 + 23.1T && (c)\\
&S_2\ (g) = 1/4S_8\ (g) && \Delta G^\circ = -23{,}040 + 25.3T && (d)
\end{aligned}
\qquad \text{(IV-4)}
$$

T is the temperature of the gas. Utilizing the given ΔG° values and the relationship $\Delta G^\circ = -RT \ln K_{Eq}$, the pressures of all of the gaseous sulfur species can be written in terms of Ps_2. The total sulfur pressure is equal to the sum of the partial pressures of all of the species:

$$Ps_T = Ps + Ps_2 + Ps_4 + Ps_6 + Ps_8 \qquad (a)$$

$$\text{or} \quad Ps_T = f_1 (Ps_2)^{\frac{1}{2}} + Ps_2 + f_4 (Ps_2)^2 + f_6 (Ps_2)^3 + f_8 (Ps_2)^4, \qquad \text{(IV-5)} \quad (b)$$

where $Ps_n = f_n (Ps_2)^{n/2}$, and f_n is a temperature function.

$$\text{Let} \quad Ps_T - \left[f_1 (Ps_2)^{\frac{1}{2}} + Ps_2 + f_4 (Ps_2)^2 + f_6 (Ps_2)^3 + f_8 (Ps_2)^4 \right] = F. \qquad \text{(IV-6)}$$

When $F = 0$, equation (IV-5b) is satisfied, and the Ps_2 which makes $F = 0$ is the equilibrium Ps_2 sought. The value of Ps_2 which made $F = 0$ at any particular temperature T^* and sulfur pressure $\overset{*}{Ps}_T$ was found in the following manner:

(1) several values of Ps_2 arbitrarily chosen.

(2) F calculated for each of these values at $T = T^*$ and $Ps_T = \overset{*}{Ps}_T$.

(3) F vs. Ps_2 plotted.

(4) value of Ps_2 for which F = 0 on graph was the desired Ps_2.

The final equation (of the form of equation (IV-6)) for calculating F knowing the sulfur temperature T' and the sulfide temperature T (T is also the temperature of the gas contacting the sulfide) is

$$F = \frac{\left(10^{\frac{-4830}{T'} - 5.0 \log_{10} T' + 23.88}\right)}{760} - \left[\frac{(Ps_2)^{\frac{1}{2}}}{10^{\frac{8441}{T} - 3.25}} + Ps_2 + \frac{(Ps_2)^2}{10^{\frac{-6206}{T} + 6.96}} + \frac{(Ps_2)^3}{10^{\frac{-13926}{T} + 15.15}} + \frac{(Ps_2)^4}{10^{\frac{-20140}{T} + 22.12}}\right]. \quad \text{(IV-7)}$$

When a series of Ps_2 values with their corresponding T values are known for reaction (I-1), thermodynamic properties of the reaction can be calculated. The van't Hoff equation states:

$$\frac{d\,(\ln K_{eq})}{d\,(\frac{1}{T})} = \frac{-\Delta H^{\circ}}{R} \quad \text{(IV-8)}$$

For reaction (I-1),

$$K_{eq} = \frac{(Ps_{2(g)})\,(a_{HfS_{2(c)}})^2}{(a_{HfS_{3(c)}})^2} \quad \text{(IV-9)}$$

As stated previously, the standard state for $S_T(g)$ was taken

to be the ideal gaseous diatomic species at 1 atm pressure. It was assumed that the equilibrium Ps_2 values found in this study were sufficiently low to allow substitution of pressure for fugacity in the equilibrium constant for reaction (I-1). The standard state for $\overline{Hf}S_3(c)$ is hypothetical and was taken to be a compound with $(S/Hf)_{molar} = 3$ at the temperature in question. Similarly, the standard state for $Hf\overline{S}_2$ was the compound with $(S/Hf)_{molar} = 2$ at the given temperature. With these choices, the equilibrium constant for reaction (I-1) becomes

$$K_{Eq} = Ps_2(g) \qquad \text{(IV-10)}$$

Therefore according to equation (IV-8), if $\log_{10} Ps_2$ were plotted against $\frac{1}{T}$, the slope of the resulting line would be equal to $\frac{-\Delta H^o}{4.576}$. It can be shown that the intercept of such a plot (i.e., the value of $\log_{10} Ps_2$ when $\frac{1}{T} = 0$) is equal to $\frac{\Delta S^o}{4.576}$. The line on such a plot will be straight if there are no phase transformations in the temperature region investigated and if ΔH^o can be considered to be constant with temperature. If ΔH^o is constant with temperature, ΔS^o is also constant with temperature, and a linear equation of ΔG^o as a function of T can be obtained thus: $\Delta G^o = \Delta H^o - T\Delta S^o$. An equation of this form was obtained for reaction (I-1) using the procedure outlined above.

C. ESTIMATION OF UNCERTAINTY

The total uncertainty, δT, in both sulfide and sulfur temperatures resulting from independent experimental uncertainties is given by

$$\delta T = \pm \left[\delta T^2_{(\text{drift})} + \delta T^2_{(\text{standardization})} + \delta T^2_{(\text{calibration})} + \delta T^2_{(\text{grad})} + \delta T^2_{(\text{measure})} \right]^{\frac{1}{2}} \qquad \text{(IV-11)}$$

where $\delta T_{(\text{drift})}$ = uncertainty due to fluctuating control action;

$\delta T_{(\text{standardization})}$ = uncertainty in standard thermocouple standardization against the melting points of Pb, Zn, and Al;

$\delta T_{(\text{calibration})}$ = uncertainty in measuring thermocouple calibration against standard thermocouple;

$\delta T_{(\text{grad})}$ = uncertainty in measurement of temperature inside capsule vs. temperature in surrounding foil or block;

$\delta T_{(\text{measure})}$ = uncertainty in reading of potentiometer.

The uncertainty in sulfur temperature produces an uncertainty in the calculated total sulfur pressures which, with the uncertainty in sulfide temperature, produces an uncertainty in the pressure of diatomic sulfur in equilibrium with the sulfide.

Generally, if $Q = f(x, y, z, \ldots)$, then the most probable error in Q, δQ, is given by

$$\delta Q = \pm \sqrt{\left(\frac{\partial Q}{\partial x}\right)^2 e_x^2 + \left(\frac{\partial Q}{\partial y}\right)^2 e_y^2 + \left(\frac{\partial Q}{\partial z}\right)^2 e_z^2 + \ldots} \qquad \text{(IV-12)}$$

where e_x, e_y, and e_z are the errors in x, y, and z respectively.

From the van't Hoff equation,

$$\frac{d \ln Ps_2}{d(\frac{1}{T})} = \frac{-\Delta H^o}{R} \text{. Thus, } \Delta H^o = -R \left(\frac{d \ln Ps_2}{d(\frac{1}{T})}\right) .$$

Let $x = \dfrac{d \ln Ps_2}{d(\frac{1}{T})}$ = slope of plot of ln Ps_2 vs. $1/T$.

Then, $\Delta H^o = - Rx = f(x)$.

Applying equation (IV-12), $\left[\delta(\Delta H^o)\right]^2 = \left(\dfrac{\partial \Delta H^o}{\partial x}\right)^2 e_x^2$.

Thus, $\left[\delta(\Delta H^o)\right]^2 = (-R)^2 (e_x)^2$ where e_x is the uncertainty in the slope of a plot of ln Ps_2 vs. $\frac{1}{T}$.

Finally, $\delta(\Delta H^o) = \pm R\, e_x$. (IV-13)

Knowing that $\Delta G^o = \Delta H^o - T\Delta S^o = -R\, T \ln Ps_2$ and that $\Delta H^o = - R \dfrac{d \ln Ps_2}{d(\frac{1}{T})}$, ΔS^o can be found to be equal to

$$R \ln Ps_2 - \frac{R}{T} \frac{d \ln Ps_2}{d(\frac{1}{T})} .$$

Let $y = \ln Ps_2$ and $x = \dfrac{d \ln Ps_2}{d(\frac{1}{T})}$, then $\Delta S^o = R\, y - \frac{R}{T} x =$

g (y, T, x). Applying equation (IV-12) and the values of y and x given above,

$$\delta(\Delta S^o) = \pm \sqrt{R^2 e_y^2 + \left(\frac{-R}{T^2} \frac{d \ln Ps_2}{d(\frac{1}{T})}\right)^2 e_T^2 + \left(\frac{R}{T}\right)^2 e_x^2} . \qquad \text{(IV-14)}$$

where e_x = uncertainty in the slope of a plot of ln Ps_2 vs. 1/T

e_y = uncertainty in ln Ps_2

and e_T = uncertainty in temperature of sulfide (found by equation (IV-11)).

In a similar manner, the uncertainty in ΔG°, $\delta(\Delta G^\circ)$, can be found to be

$$\delta(\Delta G^\circ) = \pm \sqrt{(-R \ln Ps_2)^2 e_T^2 + (-R T)^2 e_y^2} \qquad \text{(IV-15)}$$

where e_T and e_y are as given previously.

An error analysis was also applied to the analyses for $(S/Hf)_{molar}$. The total uncertainty in the weight of a sample (oxide or sulfide) due to independent errors in weighing is given by

$$\delta W = \pm \sqrt{\delta W^2_{(balance)} + \delta W^2_{(crucible)} + \delta W^2_{(crucible + sample)}} \qquad \text{(IV-16)}$$

where $\delta W_{(balance)}$ = uncertainty in initial balancing of balance;

$\delta W_{(crucible)}$ = uncertainty in weighing of empty crucible;

$\delta W_{(crucible + sample)}$ = uncertainty in weighing of crucible with sample in it.

Using the value of δW calculated above and equation (III-6), the following relationship was derived for δx, the uncertainty in $(S/Hf)_{molar}$:

$$\delta x = \pm 6.56 \times \left[\frac{(\text{wt. } HfS_x) \pm \delta W}{(\text{wt. } HfO_2) \mp \delta W} - \frac{(\text{wt. } HfS_x)}{(\text{wt. } HfO_2)} \right] . \qquad \text{(IV-17)}$$

Curves of (wt. HfO_2) vs. δx were plotted for various values of (wt. HfS_x). These curves were then utilized with the analysis data to yield δx for the given sulfide sample analyzed.

V. RESULTS

The data collected in runs 37-100 are tabulated in Table 7. The sulfide and sulfur temperatures have been corrected by applying the data of Table 6a. The total sulfur pressure was calculated by utilizing equation (IV-3). This data is also shown in Fig. 13. Notice that the solid lines in Fig. 13 are similar to the isotherms of Fig. 12.

The data collected in runs 2006-2017 is tabulated in Table 8. Temperatures have been corrected by applying the data of Table 6b. The total sulfur pressures were calculated as before. This data is also shown in Fig. 14.

On Fig. 13, the equilibrium sulfur pressure for reaction (I-1) at 696° C lies between the pressure of run 61 and the pressure of run 98. At 646° C, the equilibrium pressure lies between the pressure of runs 55 and 100. The discussion of this interpretation of the data will be undertaken in Chapter VI.

TABLE 7

Data of Runs 37-100

SULFIDE T(°C)	RUN	SULFUR T(°C)	INITIAL x IN HfS_x	INITIAL PHASES PRESENT	x IN HfS_x AFTER EQUILIBRATION	PHASES PRESENT AFTER EQUILIBRATION	Ps_T (mm Hg)
646	43	276	2.95	$\overline{HfS_3}$	2.18±.01	$\overline{HfS_3}+Hf\overline{S}_2$	24
	44	266	2.95	$\overline{HfS_3}$	2.05±.02	$\overline{HfS_3}+Hf\overline{S}_2$	18
	52	186	2.95	$\overline{HfS_3}$	1.98±.02	$Hf\overline{S}_2$	1
	53	305	2.95	$\overline{HfS_3}$	2.58±.01	$\overline{HfS_3}+Hf\overline{S}_2$	52
	55	323	2.92	$\overline{HfS_3}$	2.80±.01	$\overline{HfS_3}+Hf\overline{S}_2$	79
	56	311	2.92	$\overline{HfS_3}$	2.41±.02	$\overline{HfS_3}+Hf\overline{S}_2$	60
	99	324	1.95	$Hf\overline{S}_2$	1.95±.02	$Hf\overline{S}_2$	81
	100	335	1.95	$Hf\overline{S}_2$	2.05±.02	$\overline{HfS_3}+Hf\overline{S}_2$	104
696	37	444.5	2.95	$\overline{HfS_3}$	2.91±.02	$\overline{HfS_3}$	740
	61	402.5	2.92	$\overline{HfS_3}$	2.77±.02	$\overline{HfS_3}+Hf\overline{S}_2$	382
	65	383.5	2.92	$\overline{HfS_3}$	2.33±.02	$\overline{HfS_3}+Hf\overline{S}_2$	274
	67	361.5	2.92	$\overline{HfS_3}$	1.95±.02	$Hf\overline{S}_2$	180
	68	368.5	2.92	$\overline{HfS_3}$	1.96±.02	$Hf\overline{S}_2$	206
	71	380.5	2.92	$\overline{HfS_3}$	2.13±.02	$\overline{HfS_3}+Hf\overline{S}_2$	259
	72	390.5	2.92	$\overline{HfS_3}$	2.30±.02	$\overline{HfS_3}+Hf\overline{S}_2$	309
	73A	433.5	1.90	$Hf\overline{S}_2$	2.89±.01	$\overline{HfS_3}$	627
	74A	369.5	1.90	$Hf\overline{S}_2$	1.97±.01	$Hf\overline{S}_2$	210
	83	372.5	1.90	$Hf\overline{S}_2$	1.95±.01	$Hf\overline{S}_2$	223
	85	376.5	1.90	$Hf\overline{S}_2$	1.95±.02	$Hf\overline{S}_2$	240

TABLE 7 (Continued)

SULFIDE T(°C)	RUN	SULFUR T(°C)	INITIAL x IN HfS_x	INITIAL PHASES PRESENT	x IN HfS_x AFTER EQUILIBRATION	PHASES PRESENT AFTER EQUILIBRATION	Ps_T (mm Hg)
696	87	386.5	1.90	$Hf\bar{S}_2$	$1.94\pm.01$	$Hf\bar{S}_2$	288
	90	411.5	1.91	$Hf\bar{S}_2$	$2.07\pm.02$	$\overline{Hf}S_3+Hf\bar{S}_2$	444
	91	423.5	1.91	$Hf\bar{S}_2$	$2.55\pm.02$	$\overline{Hf}S_3+Hf\bar{S}_2$	537
	92	416.5	1.91	$Hf\bar{S}_2$	$2.37\pm.02$	$\overline{Hf}S_3+Hf\bar{S}_2$	481
	96	406.5	1.95	$Hf\bar{S}_2$	$2.05\pm.01$	$\overline{Hf}S_3+Hf\bar{S}_2$	408
	97	403.5	2.95	$\overline{Hf}S_3$	$2.85\pm.02$	$Hf\bar{S}_3$	388
	98	405.5	1.95	$Hf\bar{S}_2$	$2.05\pm.02$	$\overline{Hf}S_3+Hf\bar{S}_2$	401

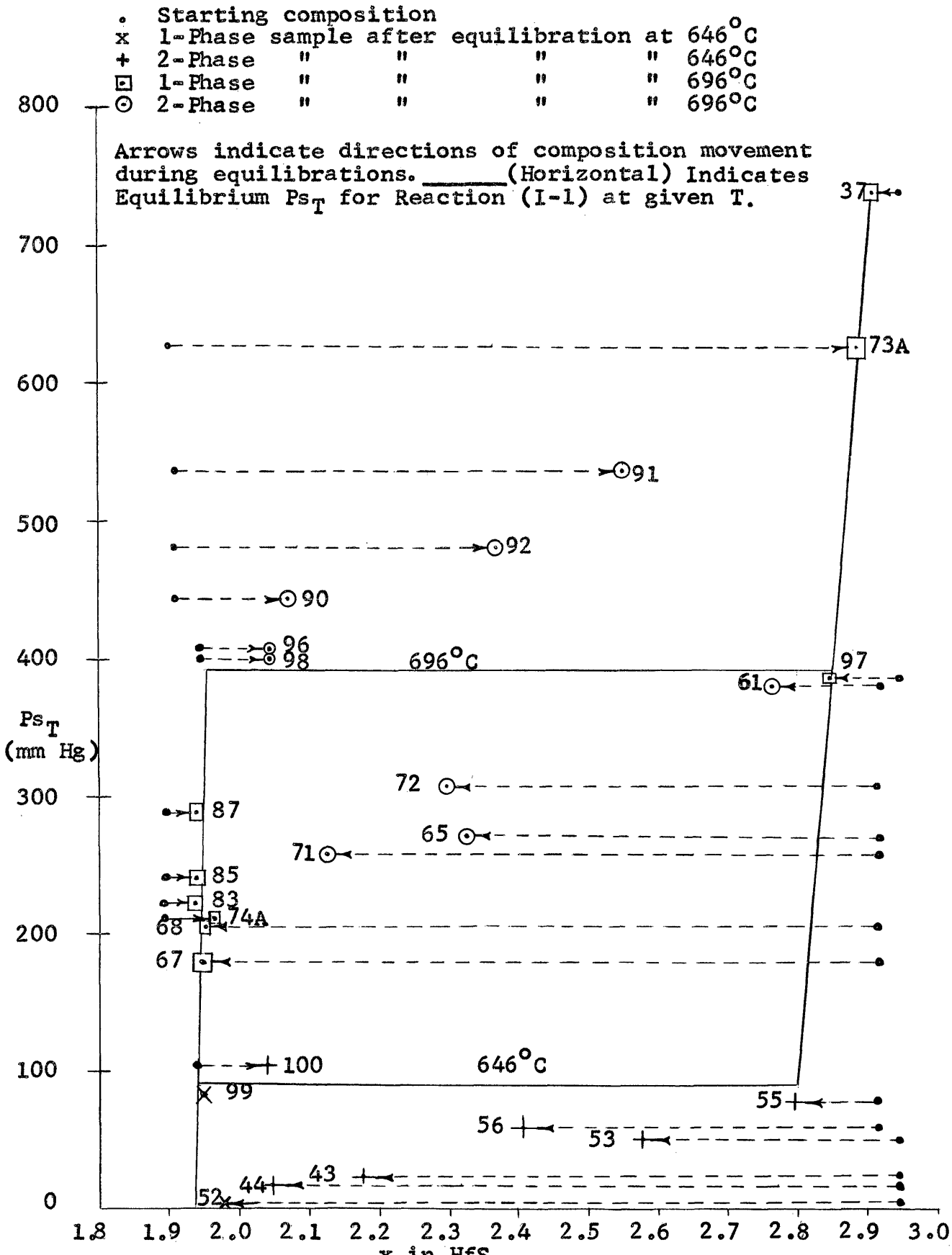
TABLE 8

Data of Runs 2006-2017

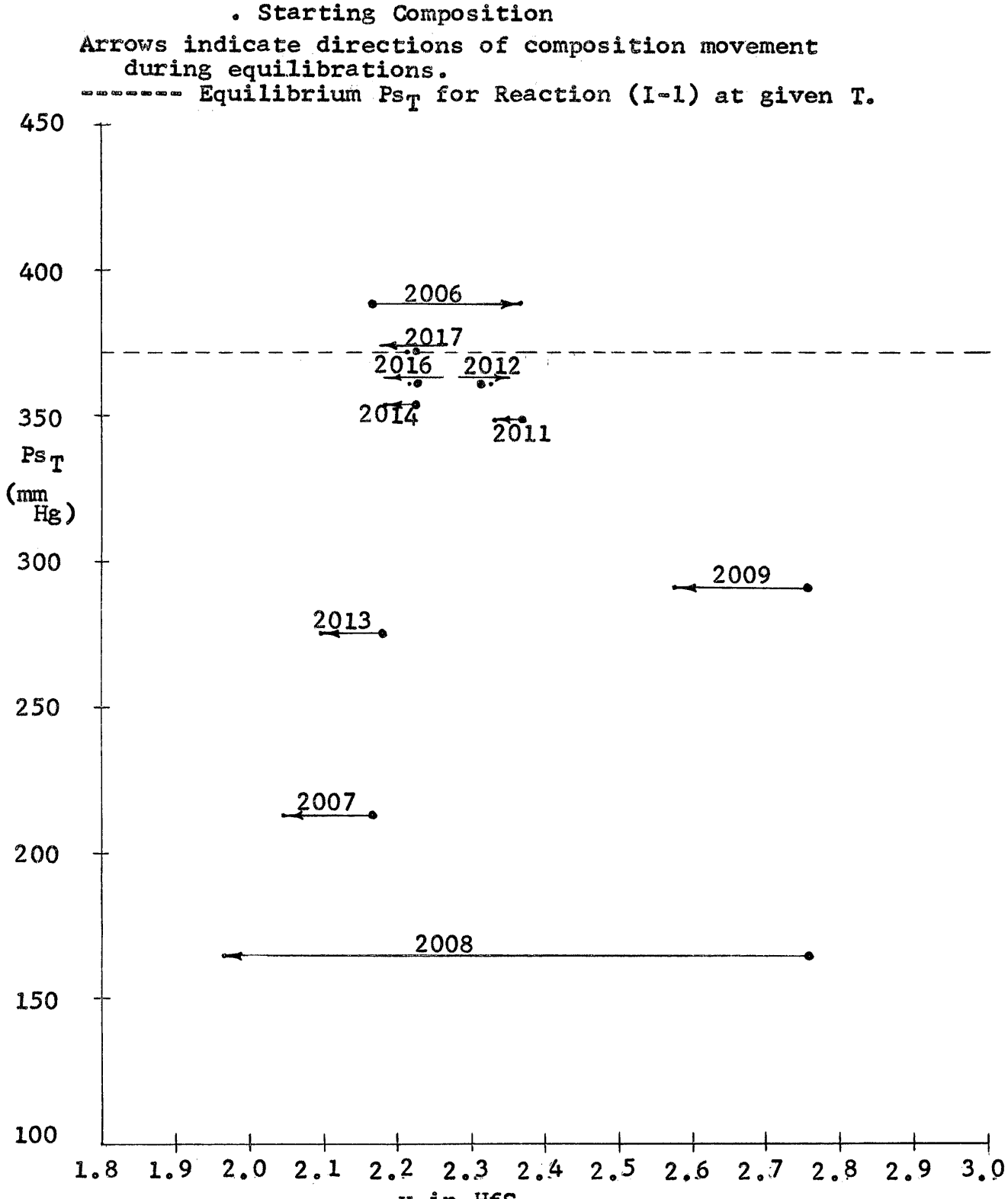
SULFIDE T(°C)	RUN	SULFUR T(°C)	INITIAL x IN HfS_x	INITIAL PHASES PRESENT	x IN HfS_x AFTER EQUILIBRATION	PHASES PRESENT AFTER EQUILIBRATION	Ps_T (mm Hg)
696	2006	403.5	$2.17\pm.01$	$\overline{Hf}S_3+Hf\bar{S}_2$	$2.37\pm.02$	---	388
	2007	371	$2.17\pm.01$	$\overline{Hf}S_3+Hf\bar{S}_2$	$2.05\pm.01$	---	217
	2008	357	$2.76\pm.02$	$\overline{Hf}S_3+Hf\bar{S}_2$	$1.97\pm.01$	---	164
	2009	387	$2.76\pm.02$	$\overline{Hf}S_3+Hf\bar{S}_2$	$2.58\pm.02$	---	291
696	2010	387	$2.76\pm.02$	$\overline{Hf}S_3+Hf\bar{S}_2$	$2.51\pm.02$	$\overline{Hf}S_3+Hf\bar{S}_2$	291
	2011	397	$2.37\pm.02$	$\overline{Hf}S_3+Hf\bar{S}_2$	$2.34\pm.01$	---	348
	2012	399	$2.32\pm.02$	$\overline{Hf}S_3+Hf\bar{S}_2$	$2.33\pm.01$	---	360
	2013	384	$2.18\pm.02$	$\overline{Hf}S_3+Hf\bar{S}_2$	$2.10\pm.02$	---	275
	2014	398	$2.23\pm.01$	$\overline{Hf}S_3+Hf\bar{S}_2$	$2.19\pm.02$	---	353
	2016	399	$2.23\pm.01$	$\overline{Hf}S_3+Hf\bar{S}_2$	$2.22\pm.01$	---	360
	2017	401	$2.23\pm.01$	$\overline{Hf}S_3+Hf\bar{S}_2$	$2.22\pm.02$	---	372

On Fig. 14, the equilibrium pressure at 696° C lies between the pressures of runs 2014 and 2006. This data will also be discussed in Chapter VI.

The boundaries of the equilibrium pressure ranges with their corresponding uncertainties are tabulated in Table 9.



Data of Runs 37-100
Figure 13



Data of Runs 2006-2017
Figure 14

TABLE 9

Preliminary Equilibrium Data for Reaction (I-1)

RUN	T(°C)	Ps_T (atm)	Ps_2(atm)
55	646±2	.104±.004$_5$	.098±.004
100	646±2	.137±.006	.125±.005
61	696±2	.503±.017	.435±.015
98	696±2	.528±.017$_5$	.453±.015
2014	696±2	.464±.016	.406±.014
2006	696±2	.510$_5$±.017	.441±.015

The uncertainties in temperature were calculated by assuming all of the independent uncertainties except $\delta T_{(measure)}$ in equation (IV-11) to be ± 1° C. The uncertainty in reading the potentiometer, $\delta T_{(measure)}$, was taken to be ± ½° C. This total uncertainty was then applied to both sulfide and sulfur temperatures. Equation (IV-3) was used to calculate the uncertainties in the total sulfur pressure. The uncertainties in the pressures of diatomic sulfur were found by combining the uncertainties in sulfide temperature, T, and Ps_T in such a way that the values of Ps_2 calculated from equation (IV-7) were the maximum distance apart.

In determining the value of Ps_2 in each range to be used in the least-squares treatment of the data, the average

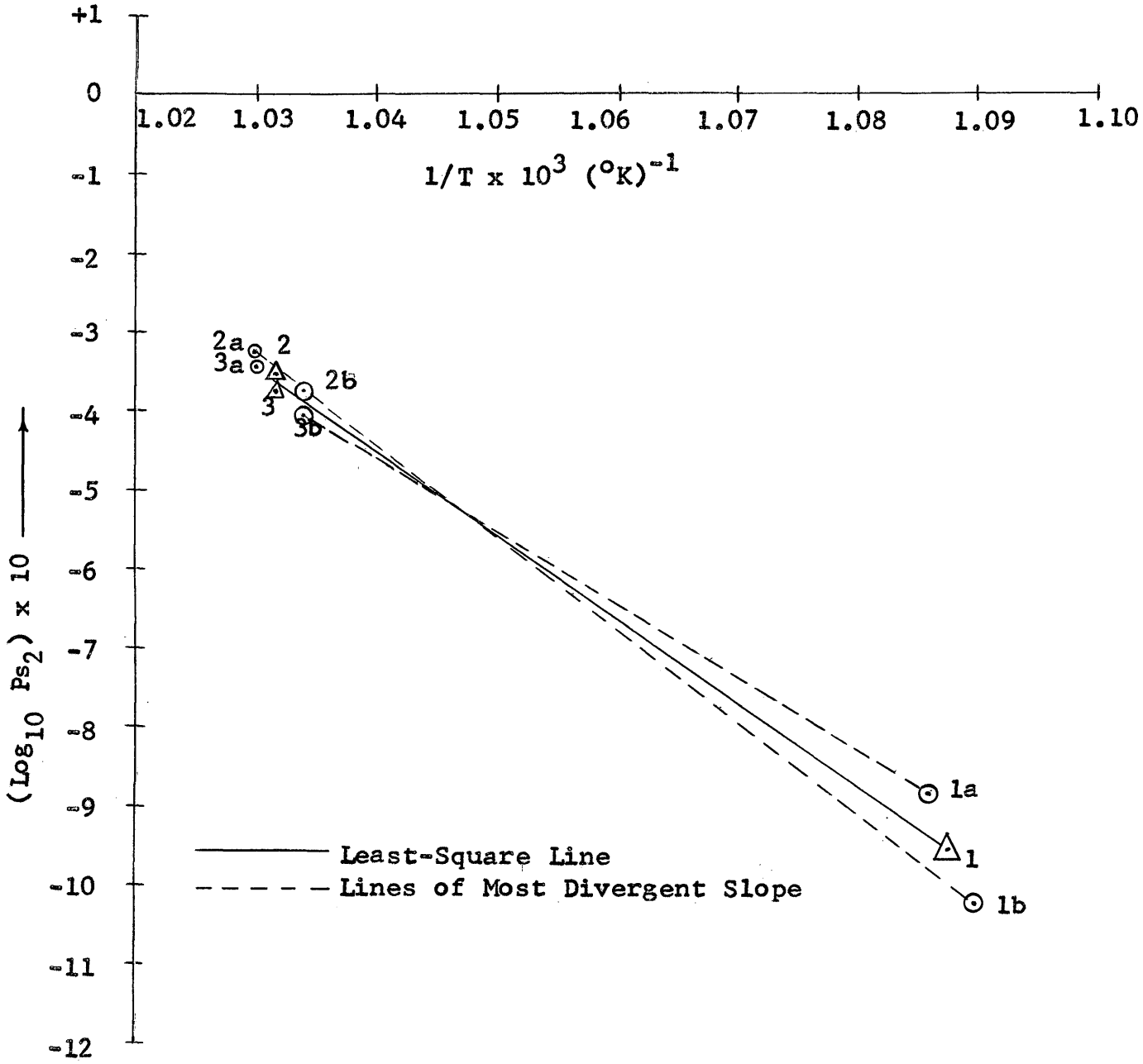
was taken of the two most divergent pressures in the range, and this value with its uncertainty was considered to be the best value obtainable from the data. These divergent values along with the final point calculated in each case are tabulated in Table 10.

TABLE 10

Equilibrium Data for Reaction (I-1)

POINT NO.	T(°K)	AVE. T(°K)	Ps_2 (atm)	AVE. Ps_2 (atm)	POINT NO. OF AVE. Ps_2
1a	921	919	.094	.112±.018	1
1b	917	±2	.130		
2a	971	969	.420	.444±.024	2
2b	967	±2	.468		
3a	971	969	.392		3
3b	967	±2	.456	.424±.032	

A plot of $\log_{10} Ps_2$ vs. 1/T is shown in Fig. 15. The solid line is a least-squares fit of the points 1, 2, and 3 (Table 10). The dashed lines are the lines of most divergent slope which can be drawn through the points 1a, 1b, 2a, 2b, 3a, and 3b (Table 10). The line of maximum (negative) slope is 1b-2a, and the line of minimum (negative) slope is 1a-3b. The slope



Equilibrium Data for Reaction (I-1)
(See Table 10)

Figure 15

of the solid line is -10,600 °K. The slope of line 1b-2a is -11,600 °K. The slope of 1a-3b is -9,200°K. Therefore, the uncertainty in $\frac{d \log_{10} Ps_2}{d (\frac{1}{T})}$ is about ±1100 °K. Thus, e_x in equations (IV-13) and (IV-14) was taken to be ±1100 °K. e_y in equations (IV-14) and (IV-15) was calculated for each of the ranges above and was found to be ±.0704 for point 1, ±.0235 for point 2, and ±.0329 for point 3. Values for $\delta(\Delta S^\circ)$ and $\delta(\Delta G^\circ)$ were thus calculated for each of the three points, and the respective averages of the three values obtained in each case were taken to be the uncertainties in ΔS° and ΔG°.

The least-squares equation of the line 1-2-3 is:

$$\log_{10} Ps_2 = 10.58 - 10{,}600 \left(\frac{1}{T}\right). \qquad \text{(V-1)}$$

Therefore, for reaction (I-1),

$$\Delta H^\circ = 48{,}500 \text{ cal and } \Delta S^\circ = 48.4 \frac{\text{cal}}{^\circ K}.$$

Applying the uncertainty equations of Chapter IV to the uncertainty values given here, the final equation for reaction (I-1) expressing ΔG° as a function of T is

$$\Delta G^\circ \ (\pm 200 \text{ cal}) = 48{,}500 \ (\pm 5{,}000 \text{ cal}) - 48.4 \ (\pm 5.3 \frac{\text{cal}}{^\circ K}) \ T; \quad (919\text{-}969\ ^\circ K). \qquad \text{(V-2)}$$

The uncertainties in determining $(S/Hf)_{molar}$ were calculated by utilizing the graphs calculated from equation (IV-17) with δW, the total weighing uncertainty, equal to

±.0002 gram. This value of δW was calculated by assuming all of the independent weighing errors in equation (IV-16) to be ±.0001 gram. With this weighing uncertainty, an analysis weight of HfS_x not less than about .2 gram was required to keep $|\delta x| < .02$.

Room temperature x-ray diffraction patterns made on hafnium trisulfide and hafnium disulfide are presented in Tables 11 and 12 respectively. The 2θ values of the present study are compared with those calculated from unit cell data given by McTaggart and Wadsley[5] and Haraldsen, et al.[1] These unit cell dimensions are listed in Chapter II of this report.

The 2θ and relative intensity values presented in Tables 11 and 12 are representative of the many patterns obtained during the course of the study. The values of 2θ and I/I_o were found to change slightly with $(S/Hf)_m$. However, no systematic study was made of these variations.

TABLE 11

X-Ray Diffraction Data of Hafnium Trisulfide

RUN #97 THIS STUDY $(S/Hf)_m$=2.85		McTAGGART AND WADSLEY[5]	HARALDSEN, ET AL.[1]
DEGREES 2θ	I/I_o	DEGREES 2θ	DEGREES 2θ
10.0	VVSt	10.0	10.0
		17.6	17.6
19.1	W		
20.0	VSt	20.0	20.0
21.4	W	21.6	21.4
25.0	VW	24.8	24.8
26.8	VW	26.8	26.8
27.2	VW		
28.4	VW	28.8	28.6
30.2	St	30.2, 30.6	30.2, 30.6
32.1	M	32.2	32.0
35.7	W	35.8	35.6
38.4, 38.7	VW	38.4, 38.6	38.2
39.5	VW	39.6	39.4
40.7	VSt	40.8	40.6
44.0	W	44.0	43.8
45.2	VW	45.5	45.2
46.4	W	46.5	46.2
48.2	W	48.3	48.1
50.9	W	51.0, 51.2	50.8
57.2	VW	57.5, 57.6	57.2
60.6	VW	60.4	60.4
62.7	M	63.0	62.6
63.6	VW	63.5, 63.6, 63.7, 63.8	63.4, 63.6
65.5	VW	65.8	65.4
74.7	W	74.4, 74.8	74.4, 74.6

TABLE 12

X-Ray Diffraction Data of Hafnium Disulfide

RUN #67 THIS STUDY	$(S/Hf)_m$=1.95	McTAGGART AND WADSLEY[5]
DEGREES 2θ	I/I_o	DEGREES 2θ
15.1	VSt	15.2
28.4	M	28.4
30.6	M	30.6
32.3	St	32.3
42.2	St	42.2
46.6	M	46.7
50.3	M	50.2
52.8	M	52.8
55.5	M	55.6
58.8	VW	58.6
60.0	VW	60.0
61.0	W	61.0
63.6	W	63.8
67.6	W	67.6
71.0	W	71.0
		71.2
78.0	VW	78.2

VI. DISCUSSION

A. INTERPRETATION OF THE DATA

The actual-data points of Fig. 13 bear virtually no resemblance to the schematic diagram of the same plot shown in Fig. 12. Fig. 12 was drawn for systems at equilibrium. Because of the extremely slow reaction rates encountered in the system $HfS_3(c)$ - $HfS_2(c)$ - $S_2(g)$, it is doubtful that any of the data points obtained in this study represent equilibrium conditions. The points obtained, however, do give a trend toward the schematic of Fig. 12. The solid lines of Fig. 13, while supported directly by less than half of the data points (i.e., runs 67, 68, 83, 85, 87, 97, 73A, 37, and 99), are supported by the trend of all the data points. The solid lines of Fig. 13 were drawn to conform to the general shape of the isotherms of Fig. 12. The solid horizontal lines labeled 696° C and 646° C of Fig. 13 represent the equilibrium total sulfur pressures for reaction (I-1) at those temperatures (the positioning of these lines

is discussed below). Above the horizontal line at a given temperature, say 696° C, only hafnium trisulfide should have been the reaction product. Runs above the pressure of the horizontal at 696° C which were of disulfide starting material (i.e., runs 98, 96, 90, 92, 91, and 73A) with but one exception (run 73A) were two phase mixtures (disulfide + trisulfide) after equilibration. It will be noted that, in general, the further the sulfur pressure of a given run was above the sulfur pressure of the horizontal line, the greater was the change in composition of the sulfide. This trend suggests a kinetic phenomenon. It was inferred from the trend that all of these disulfide-starting-material runs above the horizontal at 696° C which developed the trisulfide phase during the equilibration period would have, if given sufficient time, been completely converted to the trisulfide. Thus, their equilibrium curve would be represented by the sloping solid line through runs 73A and 37. Runs below the horizontal at 696° C which were of trisulfide starting material (i.e., runs 97, 61, 72, 65, 71, 68, and 67) should have produced, during equilibration, only disulfide. Two runs, 68 and 67, did produce only disulfide. Three runs, 72, 65, and 71, produced two-phase mixtures of disulfide and trisulfide; and one run, 97, remained trisulfide. Again, the trend can be seen. Generally, the further the pressure

of a given run below the pressure of the horizontal, the greater was the change in the composition of the sulfide. Again, inferring from the trend, if a run below the horizontal line at 696° C of trisulfide starting material formed any disulfide during the equilibration period, it was assumed that, given sufficient time, only the disulfide phase would have remained. Thus, the sloping solid line through points 67, 83, and 85 was established. These two sloping solid lines just described are further supported by runs 74A, 83, 85, and 87 (disulfide starting material) and run 37, (trisulfide starting material). These two lines may not represent equilibrium conditions exactly but are the best lines that can be constructed with the data obtained in this study.

At 696° C, with disulfide starting material, the lowest pressure at which any trisulfide was formed was the pressure of run 98. This indicates that the equilibrium pressure (Ps_T) for reaction (I-1) must lie below the pressure of run 98. Again at 696° C and with trisulfide starting material, the highest pressure at which any disulfide formed was the pressure of run 61. Thus, the equilibrium pressure (Ps_T) of reaction (I-1) must lie above the pressure of run 61. Combining this with the data discussed immediately above, the equilibrium total sulfur pressure at 696° C for reaction

(I-1) must lie somewhere between the pressures of runs 98 and 61 (or more accurately, between the most divergent pressures of their respective regions of uncertainty). Thus, the solid horizontal line labeled 696° C was drawn between the pressures of runs 98 and 61, and these were the pressures used in calculating ΔG° for reaction (I-1) at 696° C.

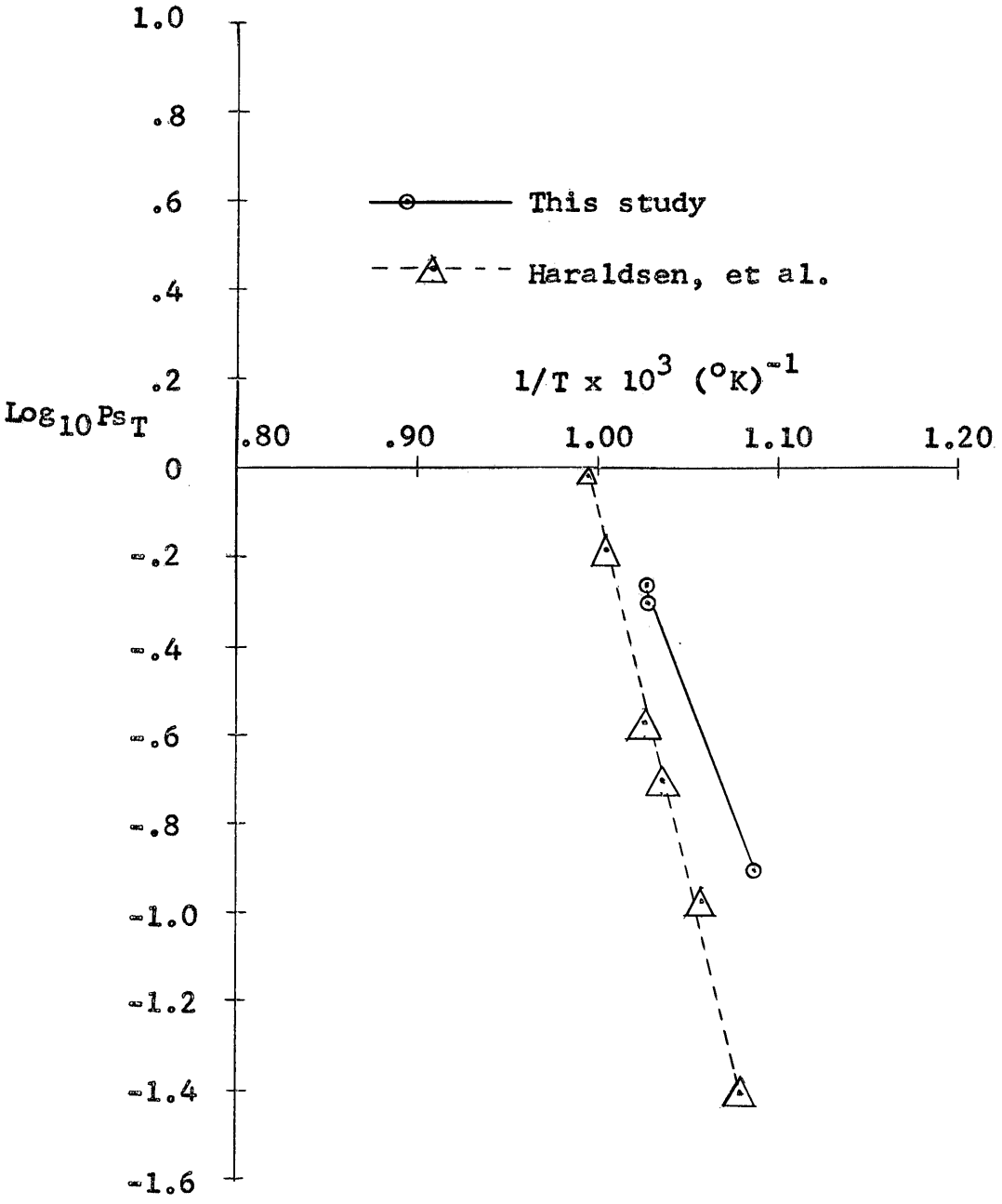
The previous discussion was entirely on runs at 696° C. A similar discussion could be made on the runs at 646° C. All of the points at 646° C show the trends previously discussed. While there are not as many data points at 646° C to support the conclusions as there were at 696° C, all of the points obtained are consistent. The runs at 696° C showed that this method yielded consistent data, therefore fewer runs were required at 646° C to establish with certainty the equilibrium total sulfur pressure of reaction (I-1).

The data of runs 2006-2017 requires a different interpretation from that of runs 37-100. All of the starting materials were mixtures of trisulfide and disulfide. For a given run, if the composition, $(^{S}/Hf)_{molar}$, decreased, then the equilibrium total sulfur pressure for reaction (I-1) was above the pressure of that run. Similarly, if $(^{S}/Hf)_{molar}$ increased, the equilibrium pressure (Ps_T) for reaction (I-1) was below the pressure of that run. Following this

reasoning, the equilibrium total sulfur pressure for reaction (I-1) at 646° C was found to lie between runs 2014 and 2006. The runs of intermediate pressure (2016, 2012, and 2017) between runs 2014 and 2006 changed only by $(S/Hf)_{molar} = \pm.01$. A change of this size was within the limits of uncertainty of the analysis technique and thus gave no real information on change in $(S/Hf)_{molar}$.

B. EVALUATION OF THE EXPERIMENTAL TECHNIQUE

As discussed in Chapter I, the method of the present study eliminated several experimental difficulties inherent in the method of Haraldsen, et al.[1] However, the discrepancy in the equations obtained for ΔG° for reaction (I-1) (compare equation (II-1) with equation (V-2)) apparently comes from a source not mentioned in Chapter I. The difference in the two sets of data (this study vs. Haraldsen, et al.) is best seen in a plot of $\log_{10} Ps_T$ vs. $1/T$. This plot has been made in Fig. 16. For simplicity, a straight line has been drawn through the points of each set of data. Theoretically, there is no reason for the lines to be straight; but because the species $S_2(g)$ makes up the predominant part of the sulfur gas (greater than 80%) under the conditions of temperature and pressure encountered in these studies and because a plot of $\log Ps_2$ vs. $\frac{1}{T}$ would be linear,



$Log_{10} Ps_T$ vs. 1/T for This Study and for Haraldsen, et al.

Figure 16

the lines do not deviate markedly from linearity. Fig. 16 shows that the pressures obtained by Haraldsen, et al., at any given temperatures are lower than the pressures obtained in this study at the same respective temperatures. The plot also shows that the two lines start to converge at low values of $\frac{1}{T}$ (high T). Haraldsen, et al.,[1] p. 1285, state that in the region 66.7 - 75.0 atomic-% sulfur, constant pressures were obtained "very rapidly" for increasing temperatures (i.e., decomposition of $\overline{Hf}S_3$). This statement, coupled with the comparisons made in Fig. 16 and the kinetic difficulties encountered in this study suggest that the previous investigators did not allow sufficient time for equilibrium to occur before making final pressure measurements.

In Chapter II, mention was made of studies of the systems $\overline{Ti}S_3(c) - Ti\overline{S}_2(c) - S_2(g)$ and $\overline{Zr}S_3(c) - ZrS_{2(c)} - S_2(g)$ in which the method of this study was employed. Kinetic difficulties were encountered in neither of these two systems, with equilibrium being attained in less than 48 hours. As stated in Chapter III, oxide contamination was at first suspected as being the cause of the relatively slow kinetics encountered in this study. It was thought that impurity oxide ions in solid solution in the sulfide lattice were hindering the rate of sulfide-ion diffusion in the lattice. Thus, the sulfur-vacuum sulfide-synthesis technique described

in Chapter III was utilized in an attempt to produce oxide-free sulfide. No detectable (visually or by x-ray diffraction) oxide was formed by this method. However, the results of runs 1000-1010 (made in the manner of runs 37-100 and mentioned in Table 3) and runs 2006-2017 indicate that no kinetic advantage was gained by this synthesis technique. On the basis of the evidence obtained, therefore, no explanation for the kinetically-deviant behavior of the system of this study from the similar systems of Ti and Zr is obvious.

C. COMPARISON OF RESULTS OF THIS STUDY WITH THOSE OF PREVIOUS STUDIES

As given previously, the equations for ΔG° for reaction (I-1) as a function of temperature are

Haraldsen, et al.[1]: $\Delta G^\circ = 66{,}270 - 65.5T$ (cal) (VI-1)

This study: ΔG° ($\pm$200 cal) = 48,500 ($\pm$5,000 cal) $- 48.4$ ($\pm 5.3 \frac{\text{cal}}{^\circ\text{K}}$) T. (VI-2)

Even with the rather large uncertainties in the equation of this study, it is apparent that the two equations are significantly different. The reason proposed to explain this difference was given previously. A criterion which has not as yet been discussed exists which makes the equation of this study appear more probable than the equation of Haraldsen,

et al. This criterion will now be discussed.

Krikorian,[19] in his work on refractory metal carbides, has stated that the entropies of formation of solid metal carbides from their gaseous elemental constituents according to the reaction

$$\left(\frac{x}{x+y}\right) Me\ (g) + \left(\frac{y}{x+y}\right) C\ (g) = \left(\frac{1}{x+y}\right) Me_x\ C_y\ (c) \qquad (VI\text{-}3)$$

should be nearly the same for all metal carbides at the same temperature. His Table I, p. 79, gives values of ΔS°_{298} for reactions of the type (VI-3) for a number of metal carbides. The constancy of the values obtained is very good (64 ± 2 e.u.), if the exceptions of CaC_2, Mn_3C, and Fe_3C are ignored. These exceptions are explained by the fact that CaC_2 contains a different type of bonding from that found in the other metal carbides in the table, and Fe_3C and Mn_3C have possible magnetic entropy contributions which are not present in the other carbides. Krikorian also found the same type of agreement within groups of metal oxides and nitrides. Thus, at least for oxides, nitrides, and carbides, ΔS° at a given temperature for reactions of this type (VI-3) should be nearly constant within each group (oxides, nitrides, or carbides), barring radical differences in bonding and sources of entropy contribution.

Hager and Elliott[20] have reevaluated Krikorian's calculations in the light of more recent data. They found that

ΔS°_{298} for reactions of the type

$$\left(\frac{x}{x+y}\right) Me\ (g) + \left(\frac{y}{x+y}\right) X\ (g) = \left(\frac{1}{x+y}\right) Me_x X_y\ , \qquad \text{(VI-4)}$$

where Me is a refractory metal and X is C, N, O, or S, is constant and is equal to -35.5 ($\pm$ 1) e.u. Thus, while Krikorian had separate groups (oxides, nitrides, and carbides) of constant ΔS°_{298} for reactions of the type (VI-4), the newer data indicate that all of these groups along with the sulfides can be put into one group with constant ΔS°_{298} for reaction (VI-4).

Using -35.5 e.u. for reaction (VI-4) with S substituted for X and the appropriate data for the elements, ΔS°_{298} for reactions of the type

$$2\ \overline{Me}S_3\ (c) = 2\ Me\overline{S}_2\ (c) + S_2\ (g) \qquad \text{(VI-5)}$$

can be calculated. The data on entropies of the elements was taken from Stull and Sinke[21] and Kelley and King.[22] For reaction (I-1), ΔS°_{298} was calculated to be 44.70 e.u. In order to calculate ΔS° for reaction (I-1) at the temperatures of this study, some data on $\Delta \overline{C}p$ for reaction (I-1) is required. Hager and Elliott[20] used $\Delta \overline{C}p = 2.7\ \frac{cal}{^\circ K}$ for reactions of the type

$$\frac{x}{y}\ Me(c) + \tfrac{1}{2}\ S_2(g) = \frac{1}{y}\ Me_x\ S_y(c).$$

This value was calculated using data for MoS_2. Using this value, $\Delta \overline{C}p$ for reaction (I-1) was calculated to be -5.4 e.u.

Using the Neumann-Kopp Rule (Swalin,[13] p. 60) for estimating heat capacities, $\Delta\bar{C}p$ was calculated to be -3.0 $\frac{cal}{^oK}$. Using a value (assumed to be constant with temperature) intermediate between these, -4.0$\frac{cal}{^oK}$, ΔS^o for reaction (I-1) at the representative temperature of 950° K was calculated to be 40.1 e.u. The value of $\Delta\bar{C}p$ used was considered to have an uncertainty of $\pm$ 3 $\frac{cal}{^oK}$. This led to an uncertainty in the calculated ΔS^o value of $\pm$3.7 e.u. A comparison of the available ΔS^o values for reaction (I-1) is shown in Table 13.

TABLE 13

Comparison of ΔS^o_{950} for Reaction (I-1)

SOURCE	ΔS^o_{950} (e.u.)
Haraldsen, et al.	65.5
This study	48.4 ($\pm$5.3)
Estimated	40.1 ($\pm$3.7)

With the rather uncertain estimate of $\Delta\bar{C}p$ for reaction (I-1), the estimated value of ΔS^o for reaction (I-1) is clearly seen to be best approached by the ΔS^o obtained in this study.

It is interesting to compare estimated ΔS^o values for reactions (II-2) and (II-3) with those of Biltz, et al.[11,12] and with those obtained utilizing the method of this study.[16]

This comparison is made in Table 14.

TABLE 14

(a)

Comparison of ΔS°_{820} for Reaction (II-2)

SOURCE	ΔS°_{820} (e.u.)
Biltz, et al.	39.9
Method of this study	44.8
Estimated	40.7 ($\pm$3.0)

(b)

Comparison of ΔS°_{1070} for Reaction (II-3)

SOURCE	ΔS°_{1070} (e.u.)
Biltz, et al.	39.1
Method of this study	50.0
Estimated	44.7 ($\pm$3.8)

Considering the magnitude of the uncertainties inherent in the estimated values, the comparisons of Table 14 yield little or no information as to reliability of experimental data.

The foregoing kinetic considerations coupled with the ΔS° estimations indicate the equation of ΔG° as a function

of temperature for reaction (I-1) obtained in this study is more reliable than that obtained by Haraldsen, et al.

VII. CONCLUSIONS

Because of the slow kinetics encountered, time allowed the investigation of only two temperatures, namely 919 and 969° K. However, one of these temperatures, 969° K was studied in two different ways, and the results obtained by the two methods were in close agreement (regions of uncertainty overlapped). The slow kinetics offered a reasonable explanation for the differences between the data of this study and that of Haraldsen, et al.[1] On the basis of this explanation and the estimated value of ΔS° for the reaction of this study, it is proposed that the conclusions drawn here (in the form of ΔG° as a function of T) are more reliable than those of Haraldsen, et al.

For the reaction

$$2\ \overline{Hf}S_3(c) = 2\ Hf\overline{S}_2(c) + S_2(g)\ , \qquad \text{(VII-1)}$$

the data of this study yield

$$\Delta G^{\circ}\ (\pm 200\ \text{cal}) = 48{,}500\ (\pm 5{,}000\ \text{cal}) - 48.4\ (\pm 5.3\ \tfrac{\text{cal}}{^{\circ}\text{K}})\ T; \qquad (919 - 969\ ^{\circ}\text{K}). \qquad \text{(VII-2)}$$

VIII. SUGGESTIONS FOR FURTHER WORK

Time permitted the investigation of thermodynamic properties of reaction (I-1) at only two different temperatures. It would be very desirable to study more temperatures. The method of this study utilizing the single-phase starting material seemed consistent and therefore could be recommended for use. However, it is doubtful that the limits of uncertainty could be reduced by use of this method. Therefore, another experimental approach would be better. Of those discussed in Chapter I, the method utilizing galvanic cells seems the most attractive. Much time would be required in this method, however, making preliminary studies of the high-temperature behavior of mixtures of the appropriate hafnium sulfide and hafnium fluoride. However, in order to determine with certainty equilibrium conditions for reaction (I-1), it appears that some method such as the one utilizing galvanic cells is required.

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