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DETERMINATION OF THE STANDARD FREE
ENERGY OF FORMATION OF Zr_3S_2

BY

PETER E. OTTEN

A

THESIS

Submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the requirements for the
Degree of
MASTER OF SCIENCE IN METALLURGICAL ENGINEERING

Rolla, Missouri

1963

Approved by

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ABSTRACT

The Knudsen effusion method was used to find the equilibrium magnesium pressure for the reaction



By using known standard free energy data for the formation of magnesium sulfide and by using the equilibrium magnesium pressure, the standard free energy of formation of Zr_3S_2 was calculated and could be expressed by the equation

$$\Delta F^\circ = -139,800 + 49.13 T \quad \text{cal/mole}$$

in the temperature range 900 to 1100°C.

It was also found that Zr_3S_2 was the zirconium sulfide of lowest sulfur content.

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Dr. W. J. Kroll for the granting of a fellowship without which this graduate study would not have been possible and to Dr. A. H. Larson and Dr. A. W. Schlechten for their valuable guidance throughout this investigation.

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CHAPTER I

INTRODUCTION

The purpose of this investigation was to determine the standard free energy of formation of Zr_3S_2 . No quantitative data concerning the stability of the lower sulfides of zirconium are available in the literature.

The stability data were obtained by reducing magnesium sulfide with metallic zirconium to yield Zr_3S_2 and magnesium vapor. The equilibrium reaction pressure of the magnesium vapor was measured by means of the Knudsen effusion method and was used to calculate the free energy change for the reaction. By using known data for the standard free energy of formation of magnesium sulfide, the standard free energy of formation of Zr_3S_2 could be calculated. The reaction measurements were made in the temperature range 900 to 1100°C and at a pressure of approximately 10^{-3} mm Hg. X-ray diffraction methods were used to analyze the products of the reaction.

In addition, it was also the purpose of this investigation to determine the compound of lowest sulfur content in the zirconium - sulfur system.

CHAPTER II

REVIEW OF THE LITERATURE

Very few data can be found in the literature regarding the chemical properties of the zirconium sulfides, and almost none regarding their thermodynamic properties.

Larson¹ studied the two-phase region of Zr_3S_4 and ZrS_2 over a temperature range from 500 to 900°C. From these studies, he obtained thermodynamic data for this two-phase region.

Hahn and co-workers² studied the zirconium sulfide phases by means of x-ray diffraction methods. Among others they cited the compound Zr_3S_2 with a homogeneous phase region from $ZrS_{0.5}$ to $ZrS_{0.8}$. This homogeneous phase region is the one studied in this investigation.

Strotzer and co-workers³ also studied the zirconium sulfide phases and from x-ray diffraction studies they determined the compound Zr_4S_3 with a homogeneous phase region between the limits $ZrS_{0.5}$ to $ZrS_{0.9}$.

The most recent and accurate data for the standard free energy of formation of magnesium sulfide has been reported by Curlook and Pidgeon.⁴ They found that for the reaction



the standard free energy change can be expressed by the equation

$$\Delta F^\circ = -100,100 - 1.10 T \log T + 27.53 T \quad \pm 2500 \text{ cal} \quad (2)$$

for the temperature range 1180 to 1483°K.

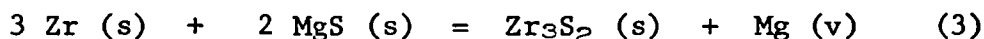
CHAPTER III

THEORETICAL CONSIDERATIONS

General.

One approach to the study of the thermodynamic stability of Zr_3S_2 , or more specifically, the standard free energy of formation of Zr_3S_2 would be to consider the reduction of a non-volatile metal sulfide phase by zirconium at high temperature.

The following reaction was considered:



The main reason for the choice of this particular reaction was that it could be studied conveniently by the Knudsen effusion method. The reasons for the amenability of this reaction to this method are:

- (1) The vapor pressures of MgS and Zr are extremely low;
- (2) The thermal stability of MgS is in the proper range in comparison with an estimated value for Zr_3S_2 ; and
- (3) Mg is relatively volatile.

However, the Knudsen method would not be applicable if the Zr_3S_2 phase were volatile. This aspect could only be determined by experiment.

To facilitate the attainment of equilibrium in the system, the reactants should be in a finely divided state and in intimate contact, which could be accomplished by grinding the reaction mixture and then pelletizing it in a small press.

Zirconium metal is available in a powder form, but the powder is normally mixed with water to prevent spontaneous combustion (since finely divided zirconium metal is highly pyrophoric). This method of packaging makes the use of zirconium metal useless for this investigation since each particle would be covered with a thin layer of zirconium oxide which would inhibit the solid-solid diffusion mechanism necessary for the above reaction. For these reasons zirconium hydride was used in this investigation as a source of metallic zirconium. Zirconium hydride is decomposed by heat into zirconium metal and hydrogen gas. It was decided that if zirconium hydride were mixed with magnesium sulfide and the mixture pelletized and heated in vacuum, the first reaction that would take place in the cell would be the decomposition of the hydride. The products of the first stage of reaction should be highly reactive zirconium metal and magnesium sulfide which should react in accordance with reaction (3).

After some preliminary runs, it was found that the time required for the decomposition of the zirconium hydride was about 15 minutes. X-ray diffraction patterns of samples showed the absence of zirconium hydride in the reaction mixture. However, the weight loss due to the evolution of hydrogen from the mixture had to be taken into account when measuring the weight loss of the cell. It was assumed that magnesium sulfide was not reduced by the evolved hydrogen.

The Knudsen effusion method.⁵

The effusion method or the Knudsen method of measuring vapor pressures is based upon the rate of effusion of the vapor of a substance through a small orifice into a vacuum. Due to the characteristics of the reaction employed in this investigation the Knudsen method was chosen for the experiments. The method consists of heating the material in a container having an orifice of known area. The experiment is carried out at a constant temperature and for a known length of time. The amount of vapor effused through the orifice is determined by the weight loss of the container after heating. By knowing the orifice area, temperature, time, amount of material effused through the orifice, and its molecular weight, the vapor pressure can be calculated from the following equation:

$$p = \frac{G}{At} \sqrt{\frac{2\pi RT}{M}}$$

where p = vapor pressure of the material

G = weight of the material effused

A = area of the orifice

t = time of the experiment

R = gas constant

T = absolute temperature

M = molecular weight of the material

Using the CGS system of units and the gas constant as 8.31×10^7 ergs per degree, the pressure is expressed in terms

of dynes per square centimeter. To obtain the pressure in atmospheres, these values are divided by the factor 1.013×10^6 dynes per square centimeter per atmosphere.

This equation can be derived from the kinetic theory of gases. From the Maxwell-Boltzmann distribution laws which govern the distribution of molecular velocities, it has been proven that the arithmetical average velocity \bar{v} is given by the equation

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}} \quad (4)$$

where R is the gas constant, T is the absolute temperature and M is the molecular weight of the gas.

From the kinetic theory of gases it has been found that the total number of collisions of molecules with the walls of a container per unit area per unit time, with all speeds and from all directions is $\frac{1}{2}n\bar{v}$ where n is the number of molecules per unit volume and \bar{v} is the average speed of the molecules. But considering N as the total number of molecules, V the total volume, and m as the mass of a single molecule, the total mass m_t striking the walls per unit area per unit time is

$$m_t = \frac{1}{2} \frac{mN}{V} \bar{v} \quad (5)$$

however, the density ρ is

$$\rho = \frac{mN}{V} \quad (6)$$

and equation (5) becomes

$$m_t = \frac{1}{2} \rho \bar{v} \quad (7)$$

In order to obtain an expression for the density of a gas the equation of state of a perfect gas can be taken

$$pV = nRT \quad (8)$$

where p is the pressure, V is the volume, n is the number of moles of the gas, R is the gas constant, and T is the absolute temperature. Multiplying both sides of the equation by M , the molecular weight, and dividing by V , equation (8) becomes

$$pM = \frac{nM}{V} RT \quad (9)$$

and since nM/V is the density of the gas, (9) becomes

$$\rho = \frac{pM}{RT} \quad (10)$$

Combining equations (4), (7), and (10), one obtains

$$m_t = \frac{1}{2} \frac{pM}{RT} \sqrt{\frac{8RT}{\pi M}} \quad (11)$$

Solving for the pressure p in equation (11), one obtains an expression for p in terms of the total mass striking the walls of the container per unit area per unit time, the molecular weight of the vapor, and the absolute temperature. Hence equation (11) becomes

$$p = m_t \sqrt{\frac{2\pi RT}{M}} \quad (12)$$

But the mass m_t striking the walls of the container per unit area per unit time is

$$m_t = \frac{G}{At} \quad (13)$$

where A is the area of the orifice and t the total time at temperature T . Now (12) becomes

$$p = \frac{G}{At} \sqrt{\frac{2\pi RT}{M}} \quad (14)$$

The Knudsen effusion method gives accurate vapor pressure measurements under several ideal conditions. According to Dushman,⁶

"... let us consider the case in which molecules evaporating from a hot surface pass through a small orifice into another chamber in which they are condensed. If the pressure of residual gas in this 'cool' compartment is extremely low and the radius of the opening is less than L , the mean free path of the evaporating molecules in the 'hot' compartment, then the rate at which molecules pass through the hole is equal to the rate at which they strike this opening."

The general rule is that the mean free path of the vapor molecules at the pressure of effusion should be ten times greater than the diameter of the orifice.

Another condition is that the thickness of the wall of the cell at the orifice must be very small as compared to the radius of the orifice. Ideally, the orifice should have a knife-sharp edge, otherwise, correction factors must be applied.

Still other conditions are: The area of the sample contained

in the cell must be very much larger than the area of the orifice; the temperature of the orifice must be the same as that of the cell and the sample, and the temperature must be constant.

Thermodynamics.

The change in the standard free energy associated with a chemical reaction is related to its equilibrium constant by the following equation:

$$\Delta F^\circ = -RT \ln K_{eq}$$

where ΔF° is the standard free energy change, R is the gas constant, T is the absolute temperature and K_{eq} is the equilibrium constant.

According to the law of mass action, the equilibrium constant for reaction (3) would be given as

$$K_{eq} = \frac{(a_{Zr_3S_2})(a_{Mg})^2}{(a_{Zr})^3(a_{MgS})^2}$$

where a is the activity of each component. If zirconium, zirconium sulfide, and magnesium sulfide are pure solids at the equilibrium temperature, their activities are unity, and thus the expression for the equilibrium constant becomes

$$K_{eq} = a_{Mg}^2$$

Since the magnesium would be a vapor, its activity becomes equal

to its pressure, hence

$$K_{eq} = p_{Mg}^2$$

Substituting the latter into the expression for the free energy change, one obtains

$$\Delta F^\circ = -RT \ln p_{Mg}^2$$

The Gibbs-Helmholtz equation is given as

$$\Delta F^\circ = \Delta H^\circ - T \Delta S^\circ$$

where ΔF° is the standard free energy change of the reaction, ΔH° is the standard enthalpy and ΔS° is the standard entropy change of the reaction. Combining this equation with that relating the free energy change to the magnesium pressure, results in the following:

$$-RT \ln p_{Mg}^2 = \Delta H^\circ - T \Delta S^\circ$$

Rearranging terms and changing to common logarithms results in the linear equation

$$\log p_{Mg}^2 = -\frac{\Delta H^\circ}{4.574T} + \frac{\Delta S^\circ}{4.574}$$

which is of the form

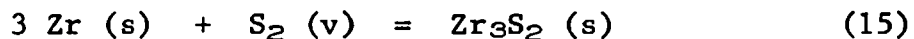
$$\log p_{Mg}^2 = \frac{A}{T} + B$$

where A is equal to $-\Delta H^\circ/4.574$ which is the slope of the line, and B is equal to $\Delta S^\circ/4.574$ which is the intercept of the line with the ordinate, at $1/T = 0$. Therefore, the average change over a small temperature change in enthalpy and in entropy of the reaction can be found by making a plot of $\log p_{\text{Mg}}^2$ versus $1/T$.

The standard free energy of the reaction can be calculated from these values. If one now takes the chemical reaction expressing the formation of magnesium sulfide from its elements, e.g.,



and one algebraically adds this reaction to (3), one obtains



and consequently, the standard free energy change for reaction (15) can be expressed as

$$\Delta F_T^\circ = \Delta F_T^\circ \text{ (Reaction 3) } + \Delta F_T^\circ \text{ (Reaction 14)}$$

This expression would therefore be the one for the standard free energy of formation of Zr_3S_2 at temperature T.

CHAPTER IV

THE APPARATUS

The basic pieces of equipment used in this investigation were: (1) an electrical resistance heated furnace, (2) a vacuum system, and (3) a Knudsen cell.

Furnace construction,⁷

The electric furnace and the reaction tube are illustrated in Figure 1. The heated portion of the furnace consisted of an electric resistance made of chromel-A wire wound on an alumina core. The maximum temperature obtainable with this furnace was 1200°C. The resistance coil was coated with alundum cement and an alundum sleeve covered the entire core. This heating assembly was insulated by firebrick. The heating assembly and the firebrick were contained in a steel shell, and a steel plate was welded to the back of this shell. This steel plate also supported the heating assembly. A similar steel plate with a three inch round opening was welded to the front opening of the steel shell. To the front and back plates were attached casters to allow the furnace to travel on a horizontal set of tracks. Stops at both ends of the tracks limited the travel of the furnace. This arrangement provided a movable furnace for rapid heating and cooling of the reaction tube.

A mullite/zirco body reaction tube which was twenty-eight inches long and two and one-quarter inches in internal diameter was used to contain the Knudsen cell. One end of this tube was

hemispherically sealed. A brass flange three and one-half inches in diameter was attached to the other end of the tube. A vacuum-tight connection between the flange and the tube was maintained by a rubber gasket. A one-half inch internal diameter steel pipe was welded to the brass flange for connection to the vacuum system.

The reaction tube was supported by steel rings with centering screws. A copper water cooling coil was fitted to the exposed part of the reaction tube to prevent excessive heating of the flange gasket and to provide a cool region for condensation of the magnesium vapor that was evolved from the Knudsen cell.

The temperature of the furnace was measured with a Pt - Pt, 13% Rh thermocouple which was placed adjacent to the furnace heating element and outside the reaction tube. This thermocouple was connected to a Wheelco controller which controlled the temperature of the furnace to $\pm 5^{\circ}\text{C}$. A potentiometer was used to check the temperature readings indicated by the controller.

Before the experimental runs were made, a calibrated chromel-alumel thermocouple was placed inside the reaction tube in the same position normally occupied by the Knudsen cell. Comparisons between the inside and outside thermocouples were made and no appreciable difference was found. Therefore, it was assumed that the correct temperature of the Knudsen cell was given by the outside controlling thermocouple.

The vacuum system.

Connected to the above mentioned steel pipe was a five-eighths

internal diameter vacuum hose. This hose was also connected to the glass portion of the vacuum system. The hose gave the flexibility required for removing the brass flange to charge the reaction tube.

The glass portion of the vacuum system consisted of a one-half inch internal diameter Pyrex glass tube which was fitted with a two-way ground glass stopcock. On the furnace end of the stopcock was welded a one-quarter inch diameter Pyrex tube which was fitted with a three-way ground glass stopcock. The former served to disconnect the reaction tube from the vacuum system while the latter served to connect a McLeod vacuum gauge to the system and to release the vacuum.

The glass portion of the system was connected to an oil diffusion pump. This pump was connected directly via metal fittings to a mechanical vacuum pump.

The entire system was painted with Fisher "Sealit" paint to minimize leaks. A schematic diagram of the vacuum system is shown on Figure 2.

An instrument panel contained all the controls necessary to operate the furnace and the vacuum pumps, as well as a powerstat, the Wheelco controller and an ammeter.

The Knudsen cell.

The Knudsen cell was made of Vycor glass tubing having an outside diameter of 9 mm and a wall thickness of 1 mm. An eight inch long piece of this tubing was cut and flame-sealed at one

end. The tube was then heated at a spot about one inch from the sealed end, and by means of a curved-end steel rod, the glass was forced out at the heated spot forming a small bump. This bump was sanded down with emery cloth until an opening was obtained on the wall of the tube. This particular method of making the orifice provided a knife edge, see Figure 3.

With some practice, orifices ranging from 20 to 80 x 10⁻³ cm in diameter were made. The diameter of the orifice was measured under a microscope using a calibrated eyepiece. Several diameters were taken and the average was computed since the orifice was not exactly circular in shape. The Knudsen cell thus made was then ready to receive its charge of reaction mixture and to be sealed.

An alundum boat was used as a support for the Knudsen cells. Two charged cells were placed together in the boat for each run. A 10-gauge steel wire was attached to the boat to facilitate its insertion and removal from the reaction tube.

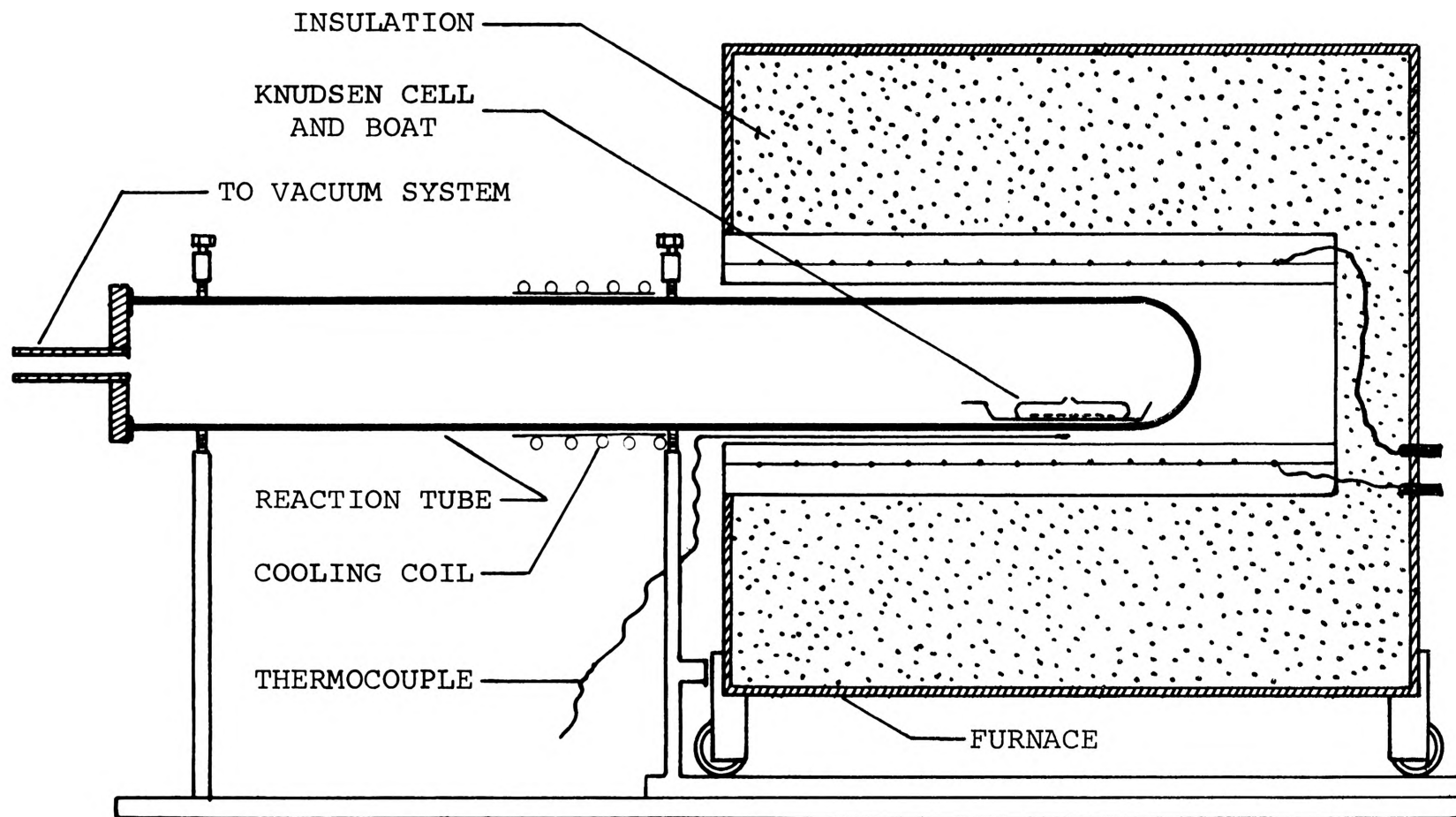


Fig. 1 - THE FURNACE AND THE REACTION TUBE

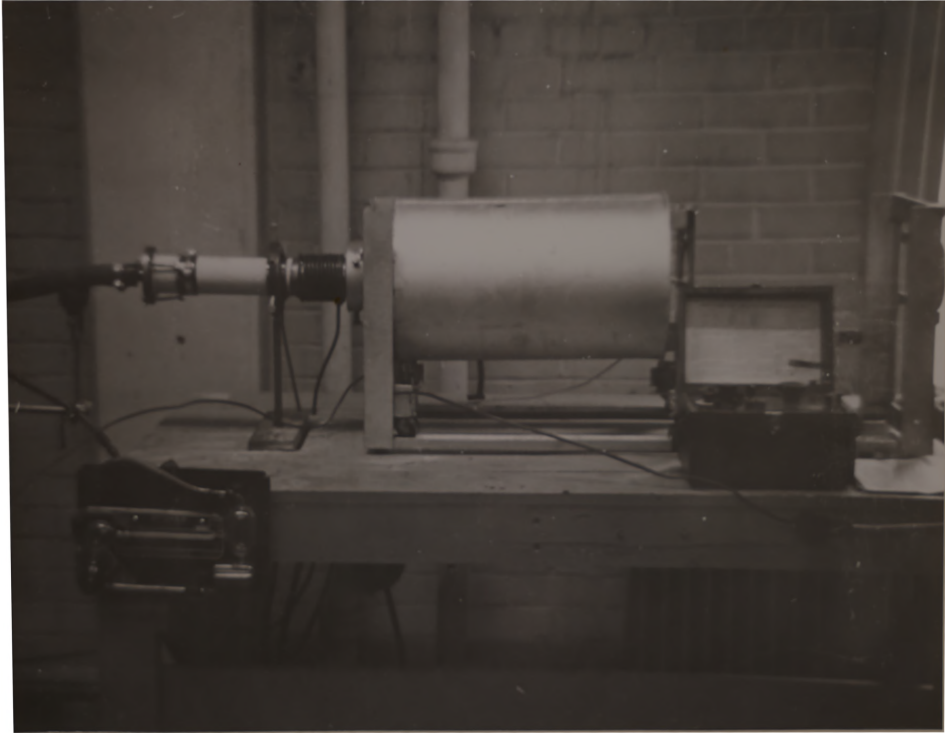


Fig. 1a - THE FURNACE AND THE REACTION TUBE

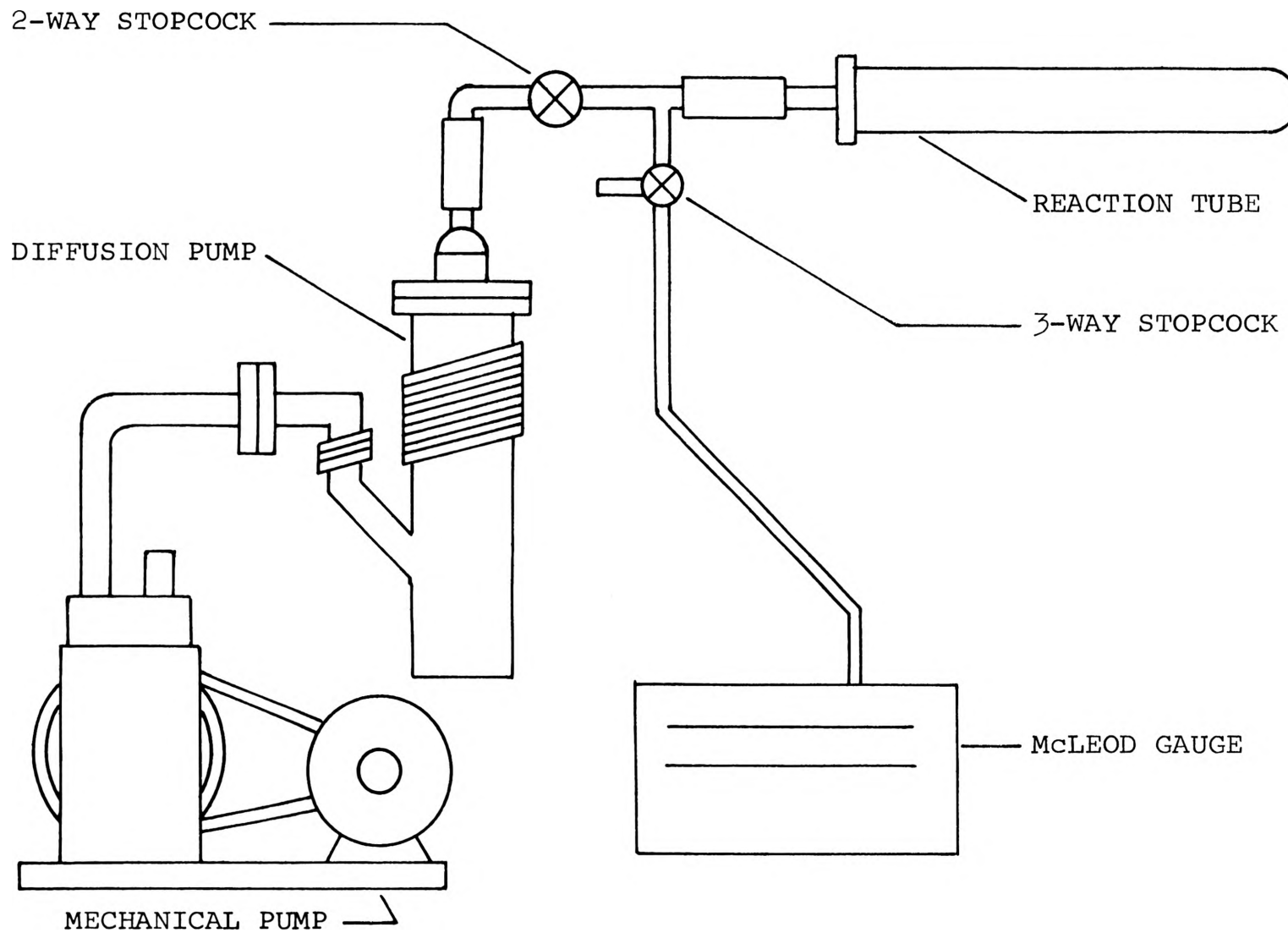


Fig. 2 - THE VACUUM SYSTEM

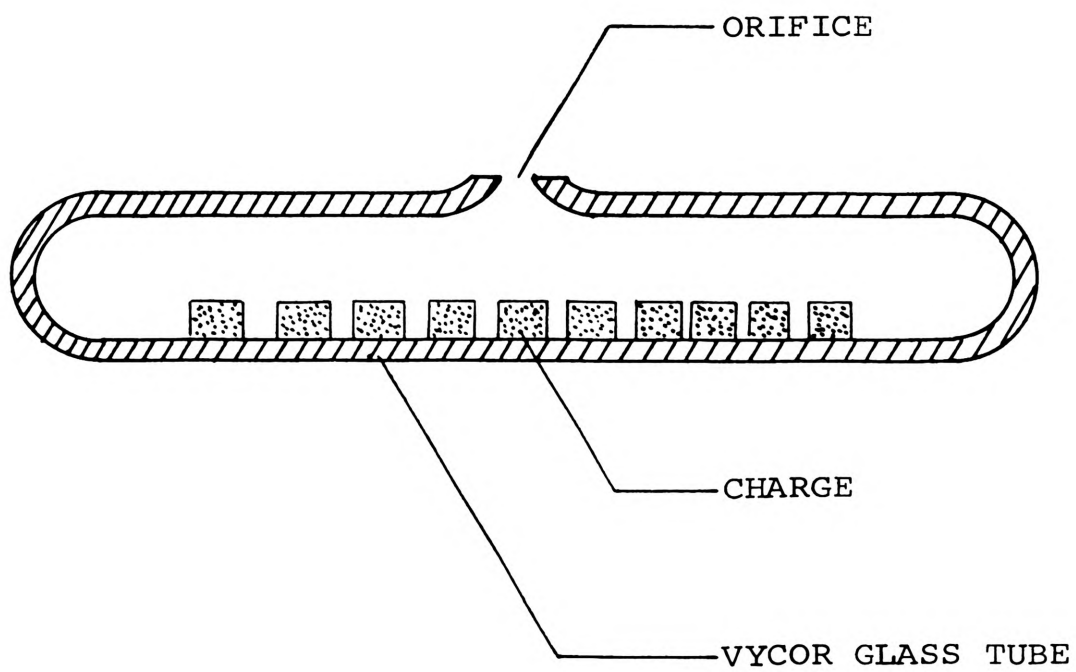


Fig. 3 - THE KNUDSEN CELL

CHAPTER V

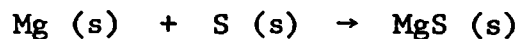
EXPERIMENTAL PROCEDURE

The following procedure was used in this investigation.

Preparation of the magnesium sulfide.

Magnesium sulfide was not available from commercial sources and had to be prepared for this investigation.

The simplest method to prepare magnesium sulfide is from its elements in accordance with the following reaction:



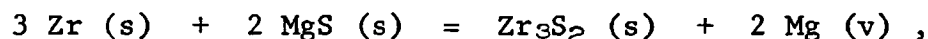
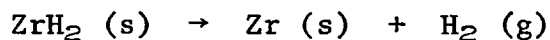
In this particular case, magnesium filings and sulfur powder were heated in a boat in a tube furnace under a stream of hydrogen sulfide. Various proportions of magnesium and sulfur were tried, as well as different temperatures. After each trial, a sample of the product was taken and analyzed by x-ray diffraction methods. The purest magnesium sulfide was obtained by reacting a mixture of 70 weight per cent magnesium and 30 weight per cent sulfur at 650°C for 18 hours. The reacted mixtures were cooled under a stream of hydrogen sulfide.

Three-gram batches were made at one time. Once made, the magnesium sulfide was ground to a fine powder and kept in a vacuum dessicator.

Preparation of the reaction mixture.

Assuming that the following reactions take place during the

experiment:



the following weight proportions were used to yield a stoichiometric reaction mixture:

71.4 weight % of ZrH_2

28.6 weight % of MgS .

The mixture of zirconium hydride and magnesium sulfide was pressed into pellets about 3/16 inch long in a 1/8 inch bore press. An average of 0.9 gram of pellets was charged into a Knudsen cell and the latter was flame sealed giving a cell about two inches long. The cell and its contents were then weighed.

The reaction.

Two Knudsen cells were charged for each run. These were placed side by side in a suitable sized alundum boat and were separated by means of a strip of asbestos to prevent possible sticking of the two cells during the run.

The boat was positioned in the reaction tube. The vacuum tight flange was attached and the system was evacuated until a total pressure of about 10^{-3} mm Hg was obtained. The furnace, which at this stage was separated from the tube, was turned on and allowed to attain the desired temperature. Once this was accomplished, the furnace was positioned for heating of the

reaction tube and the time recorded as zero.

Readings of the pressure in the system were taken with a McLeod gauge at one minute intervals in order to follow the evolution of hydrogen from the zirconium hydride. These readings were taken for the first fifteen minutes. From this time on readings were taken occasionally to serve as a check of the pressure, since the hydride was completely decomposed.

After about 30 hours (depending on the run) the furnace was removed from the tube, the time was recorded and the tube allowed to cool to room temperature. When the reaction tube was cool, the vacuum system was shut off, the flange was removed and the boat containing the Knudsen cells was removed. The Knudsen cells were then weighed and the total weight loss was determined by the difference of the initial and final weight. This weight loss included the loss due to hydrogen evolution. The hydrogen loss was deducted from the weight loss of each run and the so called "corrected" weight loss was obtained.

The cells were then opened, the contents ground, and a sample taken for x-ray diffraction analysis.

CHAPTER VI

RESULTS AND CALCULATIONS

Silver vapor pressure measurements.

In order to check the accuracy of the pressure values obtained by using the Knudsen effusion method, samples of silver metal were used instead of the reaction mixture. The vapor pressure of silver was calculated from the equation^B

$$\log p_{\text{Ag}} = - \frac{14,260}{T} - 1.055 \log T + 12.23 \quad (\text{p in mm Hg})$$

and compared with the values obtained experimentally. These results are tabulated in Table 3. All runs were made at 1100°C. It can be observed that the values for the silver vapor pressure found experimentally varied somewhat with no definite pattern, being sometimes higher and sometimes lower than the calculated value. Since there was no such definite pattern, no correction factor was calculated, and it was assumed that the Knudsen cell would give accurate values for the magnesium vapor pressure.

Preliminary runs.

The runs performed prior to the ones using zirconium hydride and magnesium sulfide are presented here.

Magnesium sulfide powder and zirconium metal chips were used and a run was made at 1100°C. The chips had an average size of 1/16 inch. No evidence of reaction was found.

Magnesium sulfide and zirconium filings were used next. Again, no evidence of reaction was found.

Zirconium hydride was then used as the source of zirconium. The zirconium hydride and the magnesium sulfide were thoroughly mixed and placed in the Knudsen cell. Apparently, the rate of the reaction was too slow and again no appreciable weight loss was found. This was probably due to the fact that there was no intimate contact between the particles.

A run was made at 1100°C for 24 hours with pelletized magnesium sulfide, and a negligible weight loss (0.2 to 0.5%) was obtained. It was therefore assumed that no vaporization or decomposition of the magnesium sulfide occurred during the actual runs.

Final results.

Using zirconium hydride and magnesium sulfide powder compressed into pellets, as outlined in the procedure, appreciable reaction occurred. The resulting data are tabulated in Table 1.

The measured variables in the equation for the calculation of the magnesium vapor pressure

$$P_{\text{Mg}} = \frac{G}{At} \sqrt{\frac{2\pi RT}{M}}$$

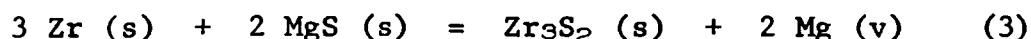
were the weight loss G , the area of the orifice A , the time t , and the temperature T . As was pointed out before, the measured weight loss included the loss due to the evolution of hydrogen. The weight loss due to the evolution of hydrogen from the zirconium hydride was found experimentally since zirconium hydride is

not a stoichiometric compound. It was found that zirconium hydride upon heating in vacuum (10^{-3} mm Hg) at 1000°C , lost on the average 2.21% of its weight. X-ray analyses performed on the residue proved it to be metallic zirconium. Hence, if the charge contained 71.4% of zirconium hydride by weight, the per cent weight loss of the charge due to hydrogen evolution would be:

$$(100)(0.714)(0.0221) = 1.57\%$$

By multiplying the original total weight of the charge and subtracting this figure from the measured weight loss, the corrected weight loss was obtained.

Since the expression for the equilibrium constant for the reaction



is

$$K_{\text{eq}} = p_{\text{Mg}}^2,$$

the logarithm of the square of the magnesium pressures (expressed in atmospheres) were plotted against corresponding values of the reciprocal of the absolute temperature. However, the plot shown on Figure 4 gives the average of the pressure values found for a specific temperature (see Table 2).

The slope of the line is equal to $-\Delta H^{\circ}/4.574$ and the intercept is equal to $\Delta S^{\circ}/4.574$.

Hence, from Figure 4,

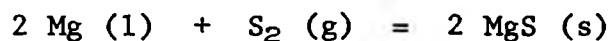
$$\text{slope} = - \frac{\Delta H^\circ}{4.574} = -1.29 \times 10^4$$

$$\text{intercept} = \frac{\Delta S^\circ}{4.574} = 0.44$$

Substituting these values in the Gibbs-Helmholtz equation, the following standard free energy equation for reaction (3) was obtained:

$$\Delta F^\circ = 59,000 + 2.01 T$$

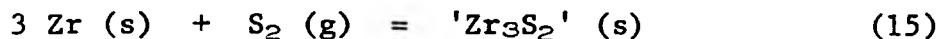
Since



where

$$\Delta F^\circ = 2 [-99,400 + 23.56 T]^*$$

Adding these two chemical equations algebraically, the following reaction is obtained



and

$$\Delta F^\circ = -139,800 + 49.13 T \quad (16)$$

*The data from Curlook and Pidgeon⁹ have been adjusted to fit a linear equation in the temperature range investigated.

for the temperature range 900 to 1100°C.

It should be mentioned at this point that the possibility of obtaining free energy data for the formation of Zr_3S_2 directly from its elements was explored. The reaction would be the same as (15). Using the Knudsen method, the problem would be one of measuring the sulfur pressure. However, using equation (16) and substituting in it

$$\Delta F^\circ = -RT \ln K_{eq} = 4.574 T \log p_{S_2}$$

one obtains

$$4.574 T \log p_{S_2} = - \frac{76,000}{5950} = -12.75$$

and

$$p_{S_2} = 1.78 \times 10^{-13} \text{ atm}$$

Hence it would be impossible to perform this experiment by the Knudsen method because of the extremely low pressure which would consequently require an extremely long period of time to obtain a measurable weight loss.

The possibility of using the Langmuir technique is also eliminated. The Langmuir technique is a modification of the Knudsen effusion method. The sample is placed in an open container and the area in the Knudsen formula becomes the effective area of the sample. However, this method enables one to measure pressures only as low as 10^{-10} atmospheres.

TABLE I
Experimental data

temp.	time	weight of charge	weight loss	correct wt.loss	orifice area	pressure
$^{\circ}\text{K}$	10^5 sec	g	g	g	10^{-3} cm^2	10^{-5} atm
1173	1.11	0.9340	0.0278	0.0131	3.32	0.57
1173	1.11	0.9500	0.0254	0.0105	4.22	0.36
1173	1.54	0.8752	0.0265	0.0128	3.32	0.40
1173	1.54	0.8769	0.0284	0.0146	3.12	0.47
1173	1.10	0.8293	0.0249	0.0119	2.37	0.71
1173	1.10	0.7461	0.0229	0.0112	2.83	0.57
1223	0.86	0.6283	0.0243	0.0145	3.52	0.76
1223	0.86	0.6509	0.0253	0.0151	3.32	0.85
1223	0.86	0.6689	0.0243	0.0138	2.21	1.15
1223	0.86	0.7684	0.0290	0.0169	2.83	1.10
1273	1.76	1.3006	0.0533	0.0329	2.38	1.29
1273	1.76	1.1697	0.0520	0.0336	1.96	1.59
1273	0.90	0.8754	0.0375	0.0238	1.96	2.21
1273	0.90	0.8916	0.0383	0.0243	2.37	1.87
1273	0.91	0.6713	0.0295	0.0190	2.83	1.19
1273	0.91	0.5815	0.0289	0.0199	2.83	1.26
1373	1.41	1.2545	0.0607	0.0410	3.85	1.29
1373	1.41	1.3563	0.0628	0.0415	3.12	1.61
1373	1.00	0.6777	0.0372	0.0265	3.32	1.36
1373	1.00	0.7198	0.0386	0.0273	3.32	1.40
1373	0.88	0.7697	0.0387	0.0266	3.85	1.34
1373	0.88	0.7313	0.0368	0.0253	3.85	1.29

TABLE II
Calculated values of $\log K_{eq}$

temp.	1/T	P _{Mg}	log K_{eq}	
°K	°K ⁻¹	10 ⁻⁵ atm		
1173	8.53 x 10 ⁻⁴	0.57	-10.488	
1173	"	0.36	-10.888	
1173	"	0.40	-10.796	
1173	"	0.47	-10.654	
1173	"	0.71	-10.298	
1173	"	0.57	-10.488	average: -10.602
1223	8.18 x 10 ⁻⁴	0.76	-10.238	
1223	"	0.85	-10.142	
1223	"	1.15	-9.880	
1223	"	1.10	-9.918	average: -10.044
1273	7.85 x 10 ⁻⁴	1.29	-9.778	
1273	"	1.59	-9.598	
1273	"	2.21	-8.910	
1273	"	1.87	-9.456	
1273	"	1.19	-9.848	
1273	"	1.26	-9.798	average: -9.731
1373	7.29 x 10 ⁻⁴	1.29	-9.778	
1373	"	1.61	-9.586	
1373	"	1.36	-9.732	
1373	"	1.40	-9.706	
1373	"	1.34	-9.746	
1373	"	1.29	-9.778	average: -9.720

TABLE III

Silver vapor pressure measurements

wt. loss	time	orifice area	pressure
g	sec	cm ²	mm Hg
0.0082	2.23×10^4	7.06×10^{-4}	0.0319
0.0163	2.16×10^4	8.13×10^{-4}	0.0379
0.0101	2.10×10^4	9.07×10^{-4}	0.0324
0.0131	2.16×10^4	12.55×10^{-4}	0.0371
			average: 0.0348

Calculated $p_{Ag} = 0.0339$ mm Hg

$$\text{per cent deviation} = \frac{0.0348 - 0.0339}{0.0339} \times 100 = 2.7\%$$

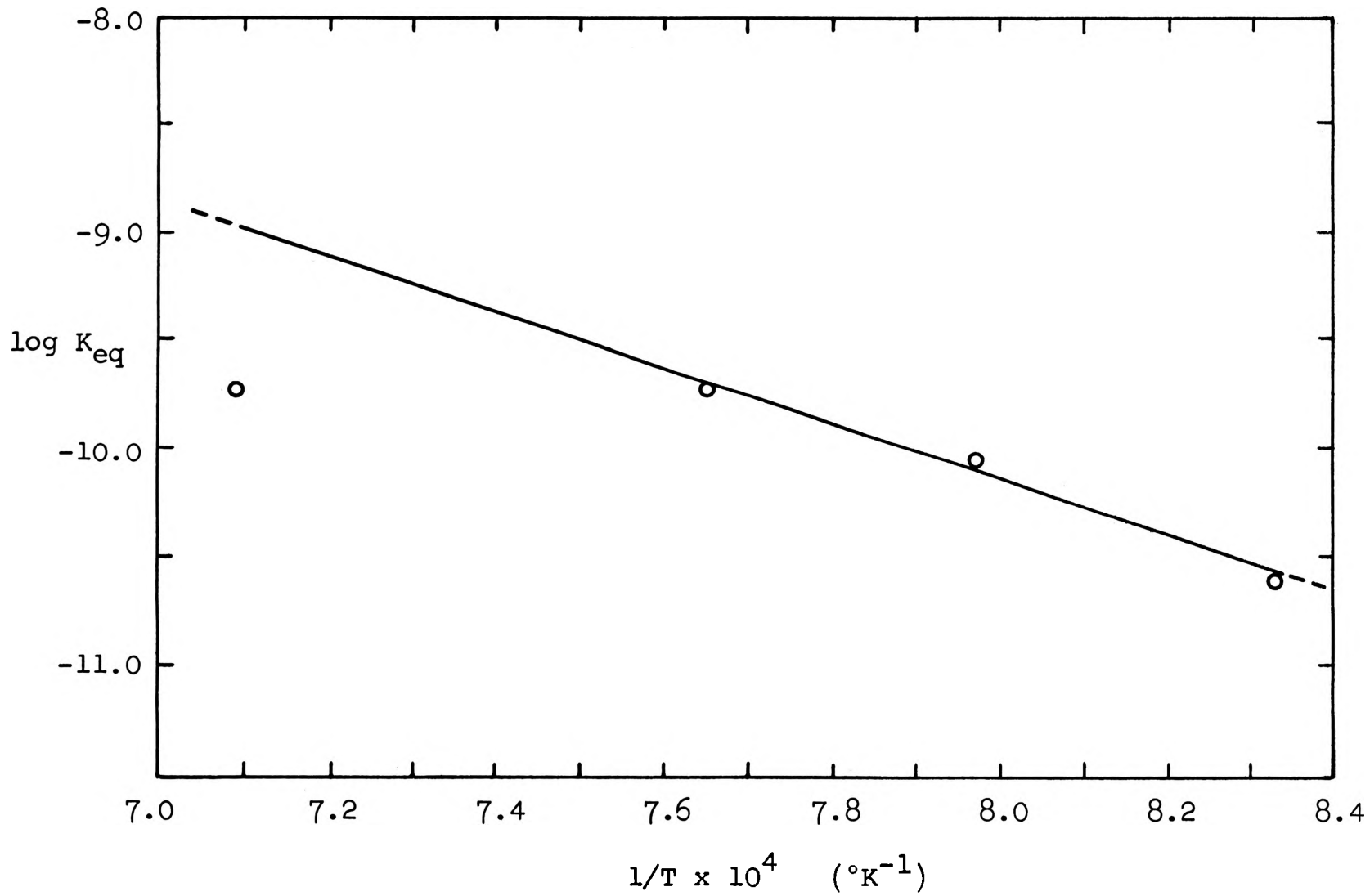


Fig. 4 - RELATIONSHIP BETWEEN $\log K_{eq}$ AND $1/T$ FOR THE REACTION
 $3 \text{ Zr} + 2 \text{ MgS} = \text{Zr}_3\text{S}_2 + 2 \text{ Mg (v)}$

CHAPTER VII

DISCUSSION OF EXPERIMENTAL ERRORS

The equation for the measurement of pressure by the Knudsen method involved the measurement of four variables, i.e., temperature, time, area of the orifice of the cell, and weight of the material effused. This gave rise to four sources of possible error.

The weight of the magnesium vapor effused through the orifice of the cell was obtained by the weight loss of the cell and its contents. This weight loss was small (in the order of 0.03 grams) and the balance used weighed only to the nearest 0.1 mg. Collecting the magnesium condensate was a practical impossibility since it was very difficult to control the temperature of the reaction tube outside of the region where the cell was placed.

Perhaps the error of greatest magnitude was associated with the zirconium hydride dissociation. The weight of hydrogen evolved from the hydride at the beginning of each run had to be subtracted from the weight loss of the cell in an amount proportional to the quantity of zirconium hydride present in the cell. Since zirconium hydride is a non-stoichiometric compound, the weight loss of hydrogen for a given amount of zirconium hydride could not be calculated from its chemical formula but had to be determined by actual measurements.

The temperature of the furnace was controlled $\pm 5^{\circ}\text{C}$ from the temperature selected. This could not be avoided due to the

characteristics inherent to the controlling mechanism. The controller turned the furnace on and off via a relay. This caused the furnace to be held at an average temperature. Also at the beginning of each run, a drop of about 500°C was experienced in the temperature of the furnace when it was positioned on the reaction tube which was at room temperature. It took the furnace 15 minutes to reach the preset temperature again, and this time was assumed to be negligible in comparison with the time of each run which was in the order of 30 hours.

The area of the orifice of the Knudsen cell was measured under a microscope with a calibrated eyepiece. The orifices were never perfectly circular due to the nature of the method used in making them. Four to six readings of the diameter of the opening were taken and the average was used to calculate the area of the orifice. It was also observed that in the higher temperature runs the area of the orifice changed somewhat since the sharp edge was slightly corroded by the magnesium vapor being effused through the orifice.

It was assumed that all the reactants were in their standard states of unit activity. The magnesium sulfide, although pure as far as it was possible to tell from the x-ray diffraction data could have some magnesium oxide in it which would alter the nature of the reaction. The zirconium hydride decomposed into metallic zirconium and hydrogen at the beginning of each run, and although active zirconium was left to react with the magnesium sulfide, the question remains whether there was or was not any sulfur dissolved

in the zirconium thus reducing its activity. The activity of the magnesium vapor was assumed to be equal to its partial pressure, but this would only hold true if the magnesium vapor behaved as an ideal gas.

In the higher temperature runs (1100°C) it was noticed after each run that the Vycor cell had been attacked by the magnesium vapor. This was not true in the case of the lower temperature runs. This attack would cause a change in the weight loss determinations of the cell after the run since the magnesium vapor, instead of effusing through the opening could react with the walls of the cell with possible formation of some magnesium silicide or silicate. This could account for the discrepancy encountered in the graph of $\log K_{eq}$ versus $1/T$ at the 1100°C temperature.

The rate of the reaction taking place inside the Knudsen cell had to be fast enough to maintain an equilibrium magnesium vapor pressure within the cell, even though the magnesium vapor was continuously being removed from the cell. Otherwise, a steady state pressure would be attained which would give erroneous values of a low magnitude.

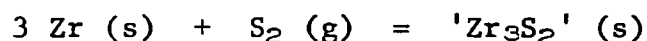
It was also assumed that the values of ΔH° and ΔS° did not vary with temperature over the range 900 to 1100°C.

CHAPTER VIII

CONCLUSIONS

The Knudsen effusion method gave satisfactory data in this investigation. This method could be used with other reactions where one vapor phase is present, provided that the area of the orifice of the cell is in the proper proportion to the mean free path of the evaporating molecules.

In this investigation, it was found that for the reaction



the standard free energy change could be expressed as

$$\Delta F^\circ = -139,800 + 49.13 T \quad \text{cal/mole}$$

over the temperature range 900 to 1100°C.

It was also found that the phase of the lowest sulfur content in the zirconium - sulfur system between 900 and 1100°C is Zr_3S_2 . This fact is evidenced by the attainment of equilibrium in the presence of the zirconium metal phase. Even though the phase was identified as Zr_3S_2 by x-ray diffraction methods, according to previous investigators the sulfur content could vary from $\text{ZrS}_{0.5}$ to $\text{ZrS}_{0.8}$. Consequently, the composition of the Zr_3S_2 phase encountered in this investigation was probably $\text{ZrS}_{0.5}$.

CHAPTER IX

RECOMMENDATIONS FOR THE IMPROVEMENT OF THE APPARATUS

Although the equipment used in this investigation performed fairly satisfactorily, some refinements could be introduced.

According to Theobald,¹⁰ a condenser for the metallic vapor should be introduced in the reaction tube in order to collect the condensate, weigh it and compare it to the weight loss of the cell. He also suggests the use of a steel crucible to contain the reaction mixture. Although Vycor glass tubing was a satisfactory material for runs up to 1000°C, it was not so above this temperature because the contents reacted with the glass. A tantalum crucible could be used for this purpose.

A McLeod gauge was used in this investigation. This gauge provides an adequate measurement of the pressure inside the system. However, the use of this gauge introduced some leaks in the system because the nature of the gauge required excessive rubber connections for its free operations. This could be avoided by using an all glass ionization vacuum gauge welded to the vacuum system.

The use of ground glass stopcocks is imperative.

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- ⁹ Curlook and Pidgeon, loc. cit.
- ¹⁰ Theobald, op. cit., p. 81.

VITA

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