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Vapor pressure and evaporation coefficient of cadmium oxide

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VAPOR PRESSURE AND EVAPORATION COEFFICIENT

OF CADMIUM OXIDE

BY

R. TOM COYLE, JR. — *1941* —

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THESIS

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Approved by

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Abstract

Knudsen effusion experiments were carried out on CdO in fused silica crucibles at temperatures of 918°K, 1008°K with orifice areas from 2.742×10^{-3} cm^2 to 30.52×10^{-2} cm^2. The experiments were made in a molybdenum-wire, resistance-heated vacuum furnace. Several orifice areas were used at each temperature and reciprocal pressure versus orifice area plots were made. These plots yielded an upper limit to the evaporation coefficient of 4.15×10^{-2}. An equilibrium constant for the vaporization reaction

$$CdO(s) = Cd(g) + 1/2O_2(g)$$
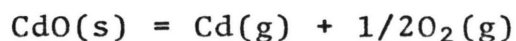
of

$$\log Keq = 11.12 - 1.952 \times 10^4 / T.$$

was obtained. Second and third law values of ΔH°_{298} were 91.1 ± 1.1 kcal/mole and 88.7 ± 0.9 kcal/mole respectively. A ΔS°_{298} of 54.1 ± 3.8 was determined by the second law method. The vapor pressure of silver was measured at 1210°K to check experimental techniques. Agreement with an accepted value was within 6.5 per cent.

Acknowledgement

The author wishes to acknowledge his indebtedness to Dr. Gordon Lewis for many helpful suggestions during this work. He would also like to express his appreciation for the generous assistance of Mrs. Frances G. Oesterling in assisting with some of the experiments. The author wishes to express his thankfulness to his Lord, Jesus Christ, for hope in the times of difficulty during this work.

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I.   Introduction

Cadmium oxide is an interesting compound because it is a solid at temperatures that are high enough to cause rapid vaporization of the solid. This behavior suggests that CdO might be useful as a subliming insulator, as discussed by Bartlett,[1] for use in lining rocket motors or in other applications where temperatures must be held below a critical value. The thermodynamic data for the vaporization reaction and the rate of vaporization, as influenced by the evaporation coefficient, are very important parameters in this type of application. The present study was conducted to further clarify the vaporization behavior of CdO.

II. Review of Literature

A review of the literature was conducted for three reasons: to determine the state of knowledge on the vaporization reaction of CdO, to determine the state of knowledge on the vaporization reaction of Ag, and to obtain information on the ways of analyzing Knudsen effusion results to obtain equilibrium and evaporation coefficient data.

The present experimental work on both CdO and Ag was done by a Knudsen effusion technique, which has been widely used and discussed -- see Margrave[15] or Hollahan[12] Briefly, the technique consists of determining the vapor pressure of a material by measuring the weight loss of vapor through an orifice in a crucible. A commonly used form of the Knudsen equation for a crucible with a knife-edge orifice is

$$P_K = \frac{m}{44.33at}\sqrt{\frac{T}{M}} \tag{1}$$

where P_K is the Knudsen pressure in atmospheres, m is the mass loss in grams, a is the orifice area in square centimeters, t is the effusion time in seconds, T is the temperature in Kelvin degrees and M is the molecular weight.

A. Vaporization Reaction of CdO

The equilibrium constant, standard enthalpy change and standard entropy change of a reaction can be determined when the reactants and products and their respective activities are known as a function of temperature, assuming that the change in heat capacity of the reaction is known. Therefore, experimental work concerning the products of the vaporization of CdO and the activities of the reaction components was sought in the literature.

Brewer and Mastick[2] predicted the complete dissociation of CdO by the reaction

$$CdO(s) = Cd(g) + \frac{1}{2} O_2(g). \qquad (2)$$
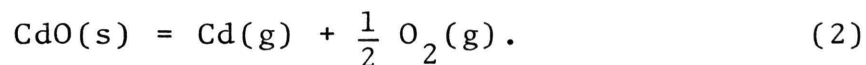
Later, both Gilbert and Kitchner,[5] and Glemser and Stocker[16] verified this prediction by showing the decrease in mass transfer when O_2 was introduced in the flow gas during a transpiration experiment.* Glemser and Stocker ran numerous experiments with various amounts of O_2 at several temperatures and established a $p_{O_2}^{-\frac{1}{2}}$ dependency for the Cd partial pressure. This O_2 dependency means that the cadmium bearing vapor species must be of the type $Cd_nO_{n-1}(g)$.[6] Thermodynamic data from sources other than the vaporization of CdO have been gathered[2,5,6] for reaction (2). These data give calculated thermodynamic values for reaction (2) that are in agreement with

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*This technique, like the Knudsen effusion technique, is well established and has been discussed by Margrave.[7] Briefly, transpiration involves passing a carrier gas over the sample at such a rate that saturation of the gas with vapor from the sample is insured, whereupon the weight of transported sample is used to calculate the vapor pressure.

experimental values, therefore reaction (2) is assumed to be correct.

A number of references[5,6,10,22] on the vapor pressure of CdO are found in the literature; however, Hinke[10] reported, in a study of the vapor pressure of CdO, that the older references were in considerable dis-agreement. Therefore, only the studies since Hinke's will be included in this discussion. These consist of studies by Hinke,[10] Uyeno,[22] Gilbert and Kitchner,[5] and Glemser and Stocker.[6] Their results are presented as a plot of log equilibrium constant versus reciprocal temperature in Figure 1. The results of the present work have been included for comparison. Uyeno's work was done by Knudsen effusion while the other three were done by transpiration.

The work of Glemser and Stocker appears to have been the most thorough of the four studies, having included numerous experiments with varied flow rates and using mixtures of H_2O, O_2, and Ar as the carrier gas. The apparatus consisted of a flow metering system for the carrier gas, a transpiration chamber in a resistance heated fur-nace and a condensation tube for weighing the amount of material transported by the carrier gas. The data of Gilbert and Kitchner, and of Hinke are in fair agreement with those of Glemser and Stocker; however, Uyeno's Knudsen effusion values, using a vacuum microbalance with fused silica crucibles, are much lower, probably due to errors in
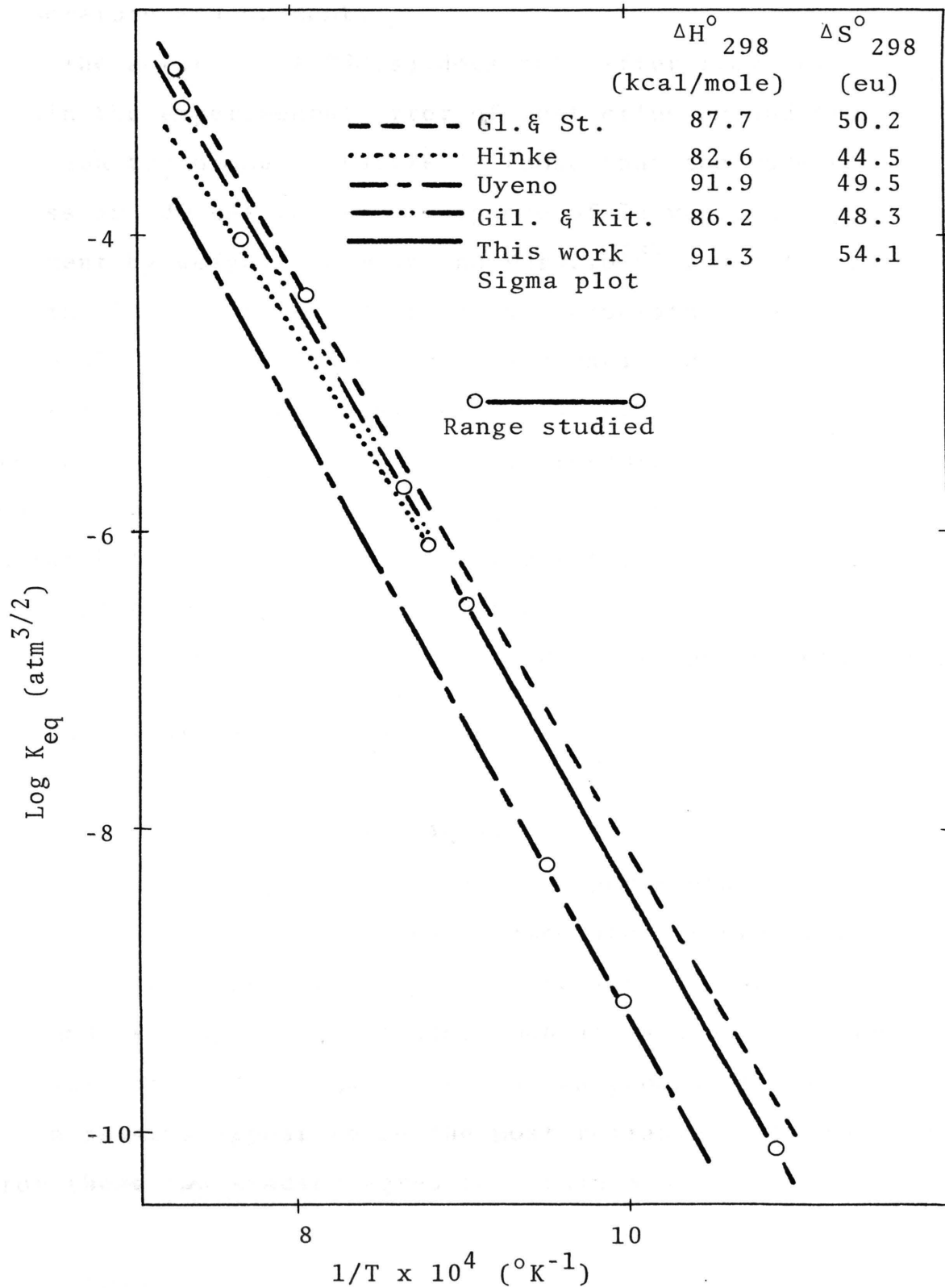
FIGURE 1. Comparison of vaporization studies on CdO.

temperature measurement.

The activity of CdO(s) does not differ from unity within the experimental error of most effusion and transpiration techniques. Faivre[4] found that the cadmium excess in CdO due to one atmosphere of Cd vapor was 0.5 per cent by weight. Cimino and Marezio[3] found the excess cadmium in CdO, prepared in air at temperatures of 500°C to 1000°C, to be 0.04 per cent, and Haul and Just[7] determined a cadmium excess of 0.044 per cent for CdO treated at 787°C at an O_2 partial pressure of 119 mm. Thus, according to Raoult's law, which states that for an infinitely dilute solution, the activity of the solvent is equal to its mole fraction, the activity is greater than 0.995, the mole fraction for 0.5 per cent excess cadmium.

B. Vaporization Reaction of Ag

The reaction

$$Ag(s) = Ag(g) \tag{3}$$

was used as a check on the present experimental technique since Ag vaporizes in the same temperature range as CdO and has a well-established vapor pressure. Nesmeyanov[19] has made a compilation of experimental data on the vapor pressure of silver, and has cited two groups of workers whose results appear to be the most reliable. The results from these two studies agree to within 3 per cent at 1200°K.

The data for solid silver from one of these groups,
McCabe, et.al,[16] can be expressed as

$$\log Pmm = 9.003 - \frac{14,250}{T} \qquad (4)$$

This work was done with Ag of 99.99 per cent purity
using three types of effusion cells: porcelain, tantalum,
and fused silica, all giving identical results.

C. Analysis of Effusion Data

Motzfeldt[18] and Whitman[24] have shown that the
Knudsen pressure obtained from the Knudsen equation is
not the equilibrium value but closely approaches it in
a properly designed cell when the orifice area approaches
zero. Hildenbrand and Hall[9] have used a form of
Motzfeldt's equation,

$$\frac{1}{P_K} = \frac{1}{P_e} + \frac{\beta Ca}{P_e} , \qquad (5)$$

to correct for the orifice area effect, where P_K is the
Knudsen pressure in atmospheres for an orifice of area, a,
in square centimeters, P_e is the equilibrium pressure in
atmospheres, C is the Clausing factor which is equal to
one for an ideal orifice, and

$$\beta = \frac{1}{\alpha A'} \qquad (6)$$

where α is the evaporation coefficient and A' is the
effective vaporizing area in square centimeters.

Hildenbrand and Hall performed effusion experiments
on BN and AlN using several orifice areas and plotted

$1/P_K$ versus $\underline{a}$ to obtain values of $P_{\underline{e}}$ and $\underline{\beta}$ in accordance with equation (5). Their corrected pressures were in excellent agreement with pressures calculated from reliable thermodynamic data, thus supporting the use of equation (5) to obtain equilibrium values. A further confirmation of this method of determining equilibrium pressures is found in the work of Hoenig[11] on ZnO, where the extrapolated values and the values calculated from thermodynamic data are in good agreement.

Hildebrand and Hall[9] also used data they had obtained for $\underline{\beta}$ to estimate the upper limit for $\underline{\alpha}$ by assuming the effective vaporizing area to be equal to the cross-sectional area of the crucible. They had no way of checking the accuracy of this estimate, however. Hoenig performed Langmuir experiments on ZnO to determine the upper limit of $\underline{\alpha}$. Although he made no comparison between $\underline{\alpha}$ values obtained by Langmuir experiments and those obtained from $\underline{\beta}$ values, this is readily done, since both $\underline{\beta}$ and the cross-sectional area of the crucible are presented in his work. The upper limit of the evaporation coefficient of ZnO is found to be 10^{-3} to 10^{-2} for the Langmuir experiments and 1.4×10^{-2} as estimated from $\underline{\beta}$. For Be_3N_2, Hoenig's values of the upper limit of the evaporation coefficient are 10^{-3} and 5.1×10^{-3} respectively for the Langmuir and $\underline{\beta}$ values.

III. Statement of the Problem

The objective of this work was to determine the vapor pressure and evaporation coefficient of cadmium oxide at temperatures below 1150°K. Accomplishing this objective involved building a vacuum furnace, preparing Knudsen effusion crucibles and establishing experimental procedures for measuring and controlling the variables involved in the work. These variables were the weight loss of the Knudsen cell, its temperature, its orifice area and the length of time at the test temperature. Each of these factors will be discussed in more detail in the remainder of the thesis.

IV. Experimental Procedure

A. Vacuum Furnace

The Knudsen effusion experiments were conducted in the apparatus shown in Figure 2. It consisted of a resistance heated furnace with a molybdenum wire heating element and a vacuum system with an oil diffusion pump (with a water-cooled baffle) backed by a mechanical pump. The furnace power supply was manually operated and is shown in Figure 3. This furnace has been used up to 1250°K. The pressure in the furnace was dependent on the temperature and duration of the effusion run, being less than 1×10^{-5} torr for 900°K runs and less than 2×10^{-4} for 1100°K and 1200°K runs. The pressures were measured with the ionization gage shown in Figure 2.

B. Specimens

The fused silica crucibles used for the experiments are shown in Figure 4A. Knife-edged orifices were made by grinding the edges of the crucibles with a fine abrasive to the desired orifice area. The crucibles were then cleaned either by outgassing in the vacuum furnace or by boiling in a soap solution followed by two rinses in boiling distilled water and then outgassing in the vacuum furnace. After cleaning, they were charged with either 2.1 grams of 99.5 per cent CdO powder or 2.9 grams of 99.9 per cent Ag powder --

3 Al$_2$O$_3$ rods @ 120°

Power feed-thrus

6" x 2" Pyrex tee

O-Ring seal

Mo radiation shields

Water cooled stainless jacket

Al$_2$O$_3$ heating element supports

Mo heating element

SiO$_2$ crucible

Thermocouple

3 304 stainless rods @ 120°

To diffusion pump

Reference Plane

Al$_2$O$_3$ crucible pedistal

3 Al$_2$O$_3$ rods @ 120°

304 stainless plate

Ionization gage
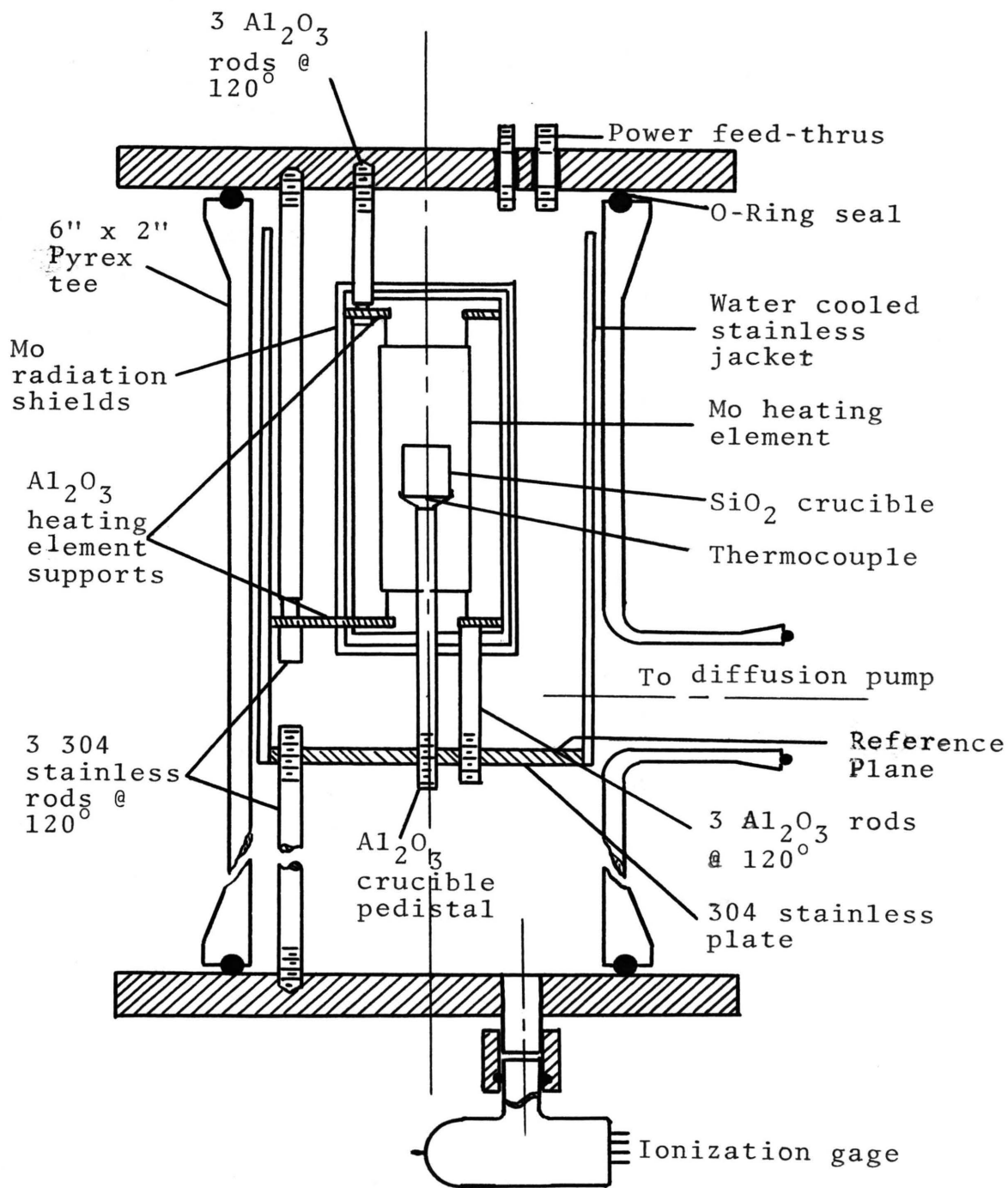
FIGURE 2. Vacuum furnace
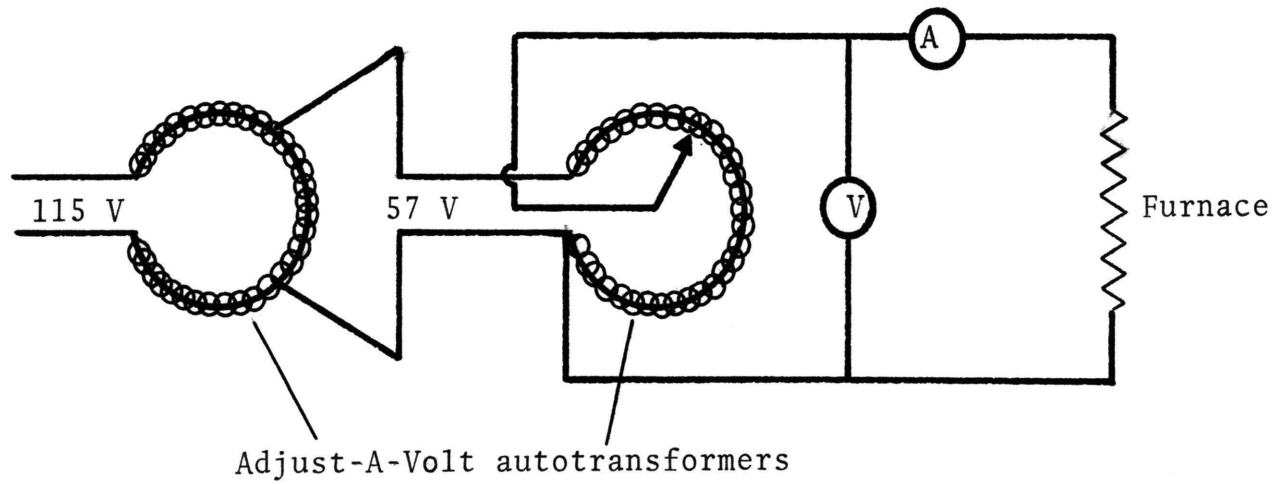
FIGURE 3. Furnace power supply

$\frac{7"}{8}$ D x $\frac{7"}{8}$
inside

Orifice

Fused silica

4A

Stainless
nuts and bolt

Pt foil

Chromel/alumel
thermocouple

Pt:10 Rh/Pt
thermocouple

4B

Protected
chromel/alumel
thermocouple

Fused
silica
crucible

CdO
or Ag

Chromel/alumel
thermocouple

4-bore
Al_2O_3 rod

4C
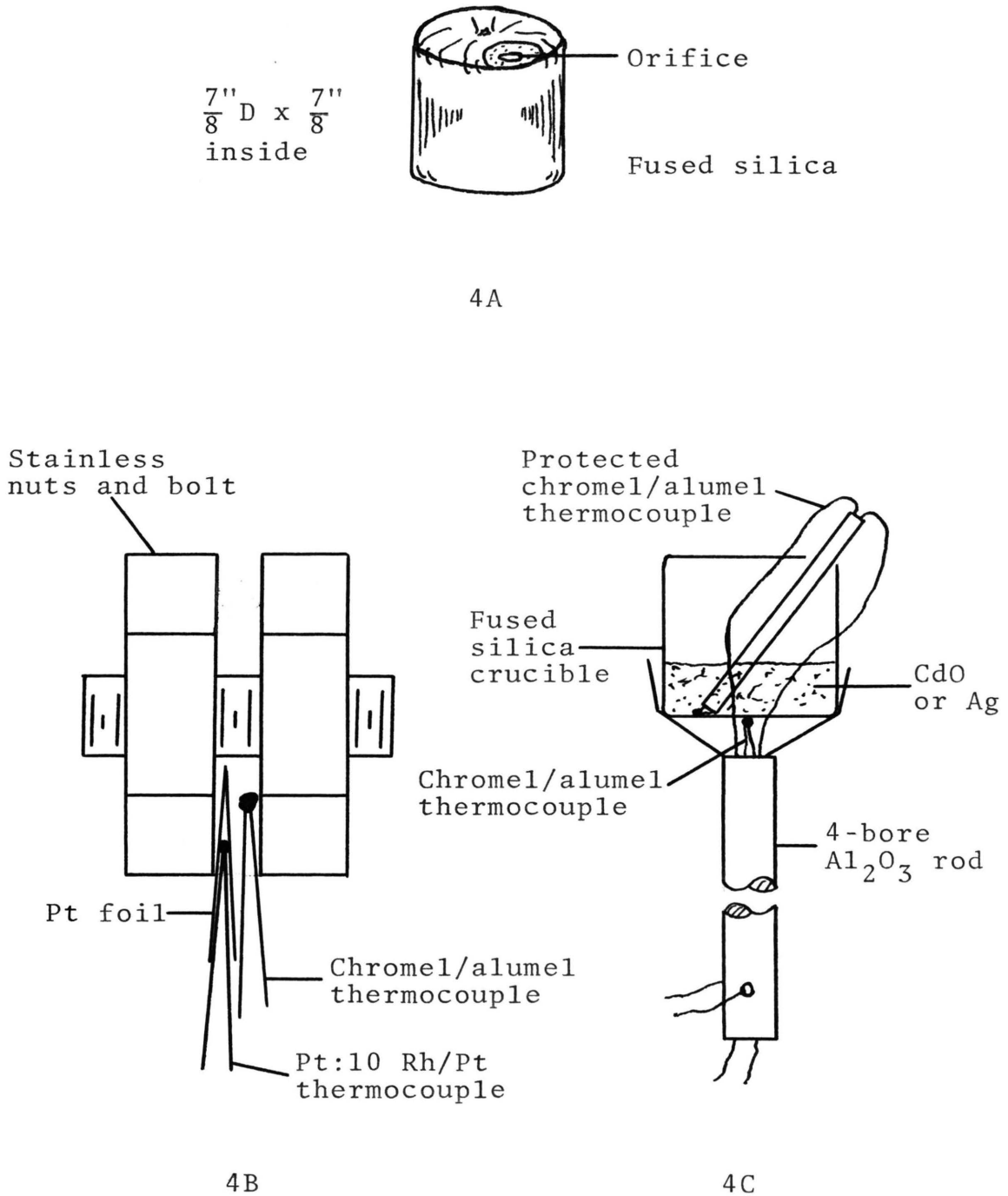
FIGURE 4. A) Knudsen effusion cell, B) Thermocouple
calibration setup, C) Sample temperature from
crucible bottom temperature setup.

the chemical analyses given by the supplier are given in Table 1 -- by gently vibrating the powder through the orifice. For the smallest orifice, the CdO was placed in the crucible by vacuum filling from a suspension of CdO powder in 99 mole per cent pure, spectroscopic grade acetone. The crucible was dried in an oven at 200°C and outgassed in the vacuum furnace to remove the acetone.

C. Measurement of Variables.

The determination of vapor pressures by use of the Knudsen equation requires the measurement of four variables: weight loss, effusion time, orifice area, and temperature, plus a knowledge of the molecular weight of the vapor. The molecular weights of the vapor over CdO and Ag are known, and the other four variables are discussed below. The molecular weight of the vapor over Ag is the atomic weight of silver and the effective molecular weight of the vapor over CdO is calculated as discussed in Appendix A.

1. Temperature

The effusion temperature was measured with a chromel/alumel thermocouple and a L&N 8686 millivolt potentiometer. The chromel/alumel thermocouples were calibrated by comparing them with a platinum-10 per cent rhodium/platinum thermocouple which had been calibrated by the Rolla Station of the Bureau of Mines.

TABLE I. Analyses of materials used in effusion runs.

Ag - Fisher

Cu	0.001%
Cl	0.005%
Fe	0.002%
Other heavy metals as Pb	0.002%
Sulfate	0.05 %

CdO - B&A

Cl	0.002%
NO_3	0.005%
SO_4	0.2 %
Not ppt by H_2S	0.2 %
Cu	0.01 %
Pb	0.01 %
Fe	0.002%

The results are shown in Figures 5 and 6, along with the least squares straight lines for the data. The comparison was made by mounting the calibrated platinum-10 per cent rhodium/platinum thermocouple and the chromel/alumel thermocouple together in the fixture shown in Figure 4B. The piece of platinum foil served to protect the platinum thermocouple from contamination.

For effusion runs, the bead of the chromel/alumel thermocouple was placed in contact with the bottom of the crucible. This was verified visually before each run. The temperature obtained for the crucible bottom was corrected to the true sample temperature by a correction equation determined by using the setup in Figure 4C. The temperatures of both the bottom of the crucible and the sample were recorded for a series of temperatures. These data for CdO are shown in Figure 7, where the sample temperature minus the crucible bottom temperature is plotted as the ordinate, and the crucible bottom temperature is the abscissa. These results were fitted with a second degree least squares polynomial to obtain an analytical correction expression. All of the Ag effusion experiments were made at 1210°K. Using the apparatus in Figure 4C with Ag showed that 3.5K° must be added to the crucible bottom temperature to obtain the sample temperature.

For the CdO runs, the crucible was positioned in the furnace at a height (from the reference plane in
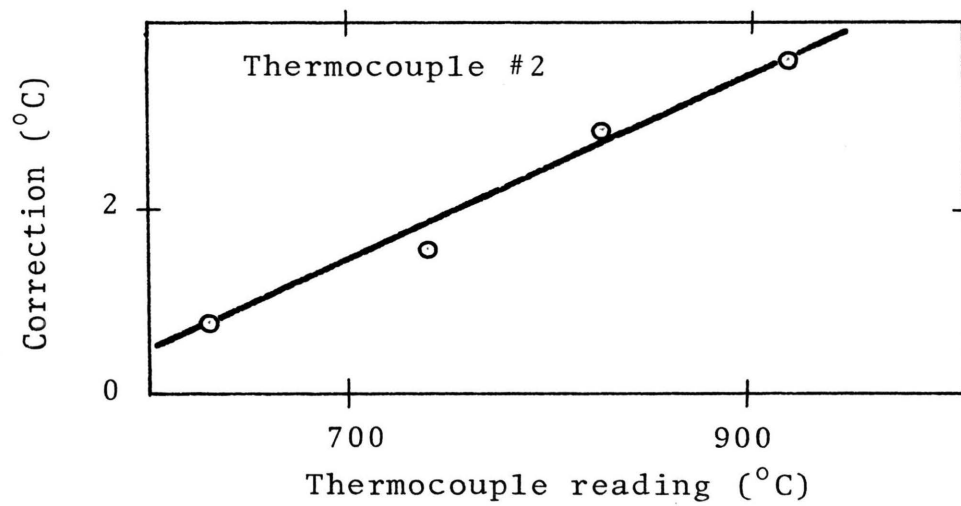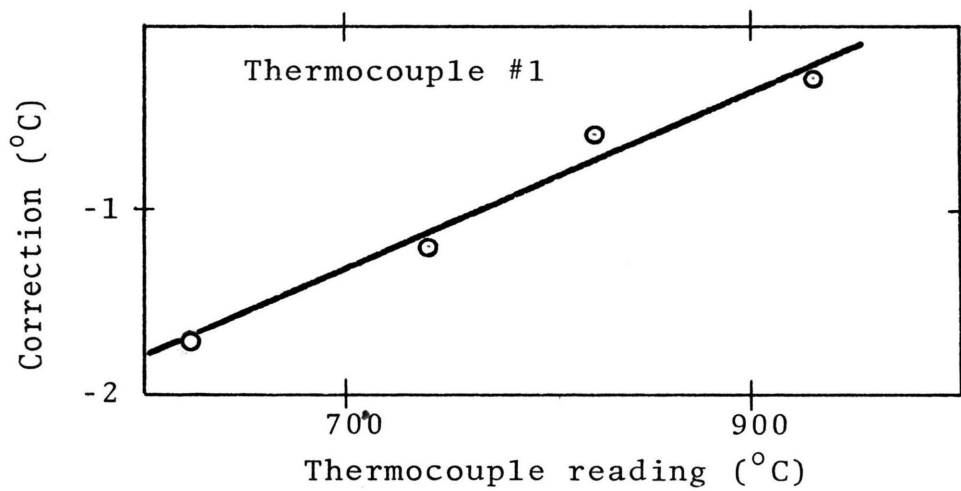
FIGURE 5.   Calibration of thermocouples #1 and #2.
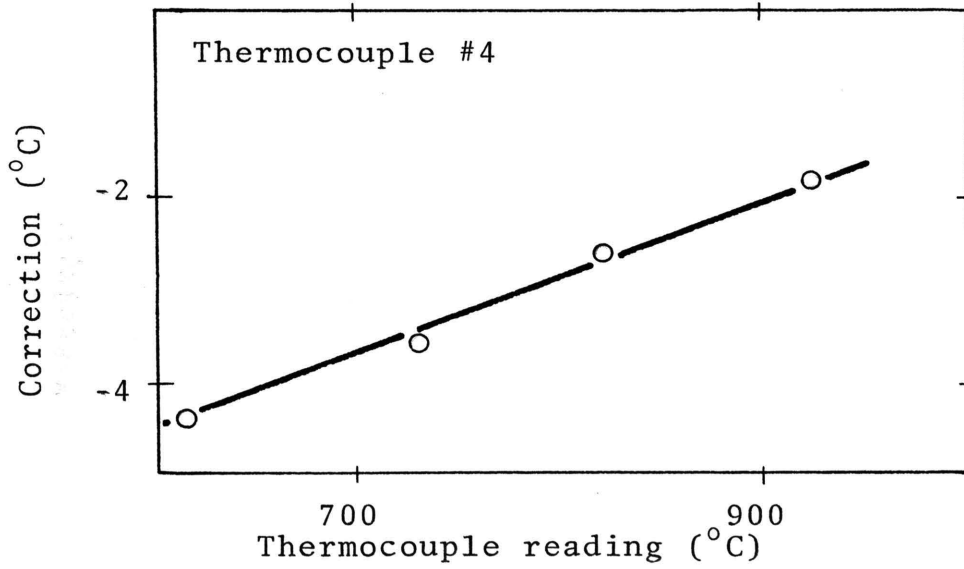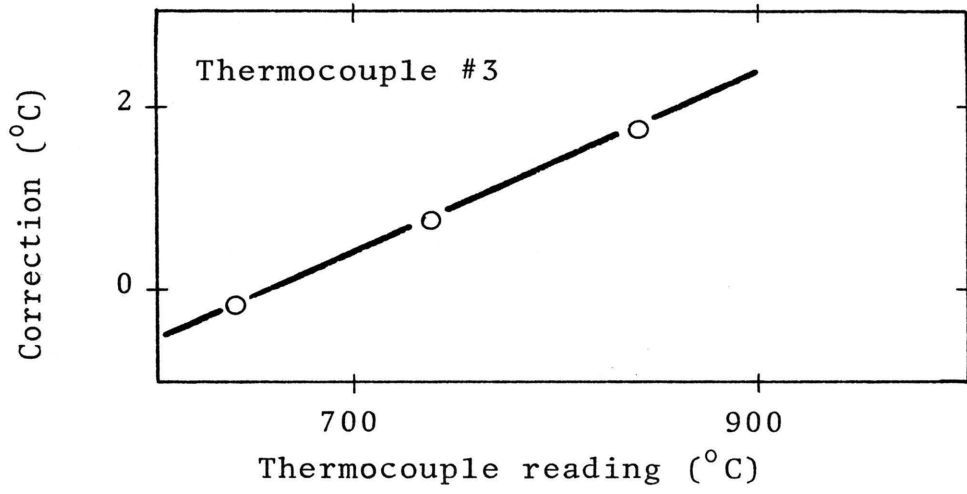
FIGURE 6. Calibration of thermocouples #3 and #4.
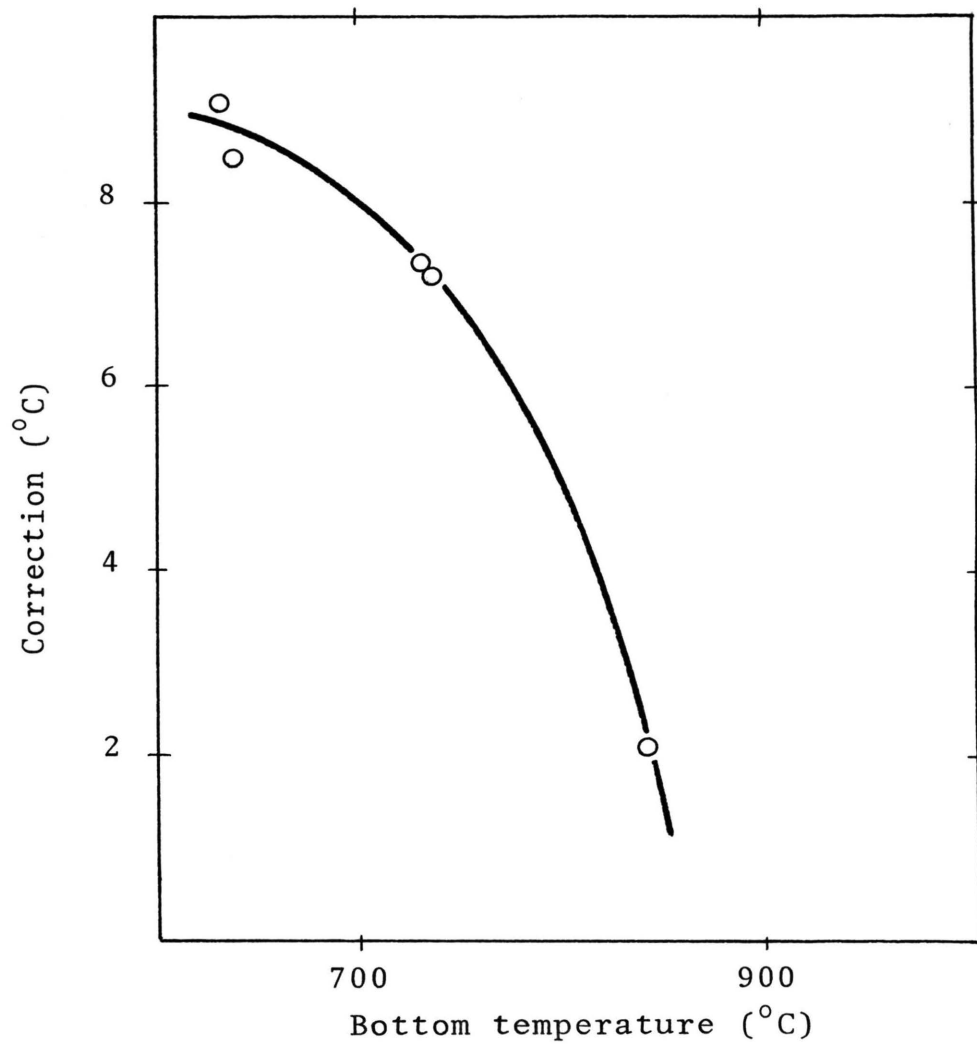
FIGURE 7. Correction to obtain the sample temperature from the crucible bottom temperature.

Figure 2) of 4 13/16 inches for the 918°K and 1008°K
runs and 4 3/4 inches for the 1107°K runs so that the
temperature difference between the top and bottom of
the cell would be less than 6K°, the top of the cell
being hotter, as can be seen from the data in Figure 8.
These data were obtained by using an alumel/chromel/
alumel differential thermocouple having one bead on
the bottom and the other bead on the top of the crucible.
For the silver runs at 1210°K, the crucible was posi-
tioned at a height of 4 3/4 inches which resulted in a
differential between the top and bottom temperature
of less than 6K°, the crucible top being hotter.

The power supply to the furnace was manually con-
trolled and the temperatures for all but runs 5 through
9 (see page 29) were maintained with $\pm$5K°. A temperature
of 918$\pm$10°K was maintained for these runs.

2. Weight loss

The loss of CdO or Ag during an effusion run
was determined by weighing the crucible on a Sartorius
semi-microbalance before and after each run. The cru-
cibles increased in weight when exposed to the atmosphere
upon removal from the vacuum furnace. Therefore, to
avoid weighing errors due to variations in ambient con-
ditions, the following procedure was adopted for all
weighings. After a run, the vacuum furnace was allowed
to cool to 750°K before the diffusion pump was shut off.
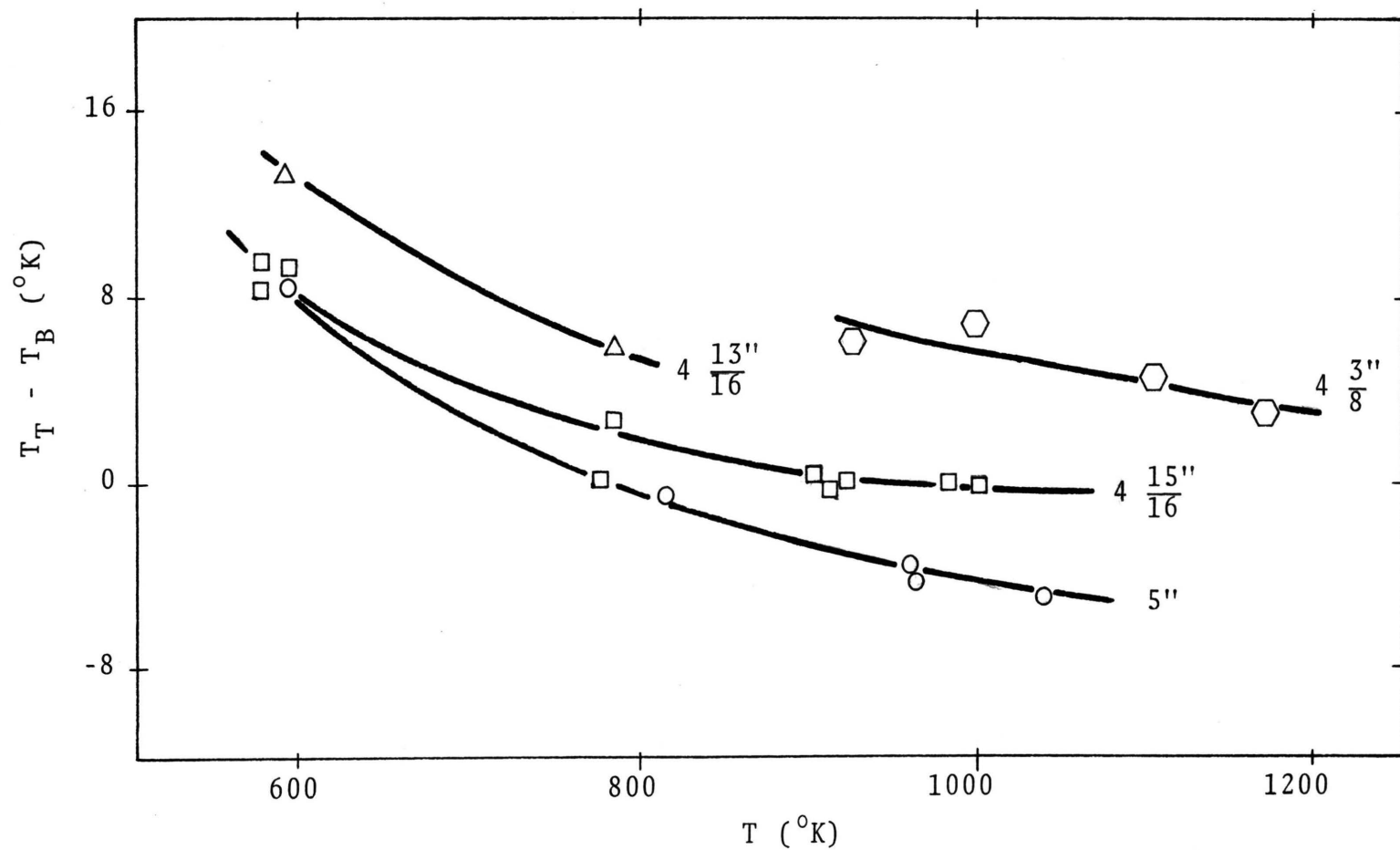
FIGURE 8. Temperature differential between the top, T_T, and bottom, T_B, of a crucible filled with CdO as a function of vacuum furnace temperature and position in the furnace.

At 640°K, the system was opened to the atmosphere and the crucible was immediately removed and placed in a desiccator containing $Mg(ClO_4)_2$. After setting in the desiccator for 67 ± 5 minutes, it was removed and placed on the balance. Its weight was determined by extrapolating a weight versus "time out of desiccator" curve to zero time. This procedure gave weights with a standard deviation of 79 micrograms or less, as shown in Figures 9 and 10.

A series of experiments were conducted to determine the rate of weight loss of the empty crucibles in the vacuum furnace. Figures 9 and 10 show the results of these weight loss experiments at 909°K, 1000°K and 1111°K. The rates of weight loss and the standard deviation of the experimental points from the straight line are also shown. These crucible weight loss corrections were less than one per cent of the total for CdO experiments. The correction for one of the Ag runs amounted to 1.5 per cent of the total weight loss, and was due to carbon deposition on the crucible. Each crucible was outgassed after it was filled to avoid any large initial weight losses due to adsorbed gases on the CdO. The crucible filled with Ag was not initially outgassed, but it showed no significant trends in pressure.

The time required for heating and cooling the crucible was sometimes a significant portion of the total time of the run; in such cases, end corrections were
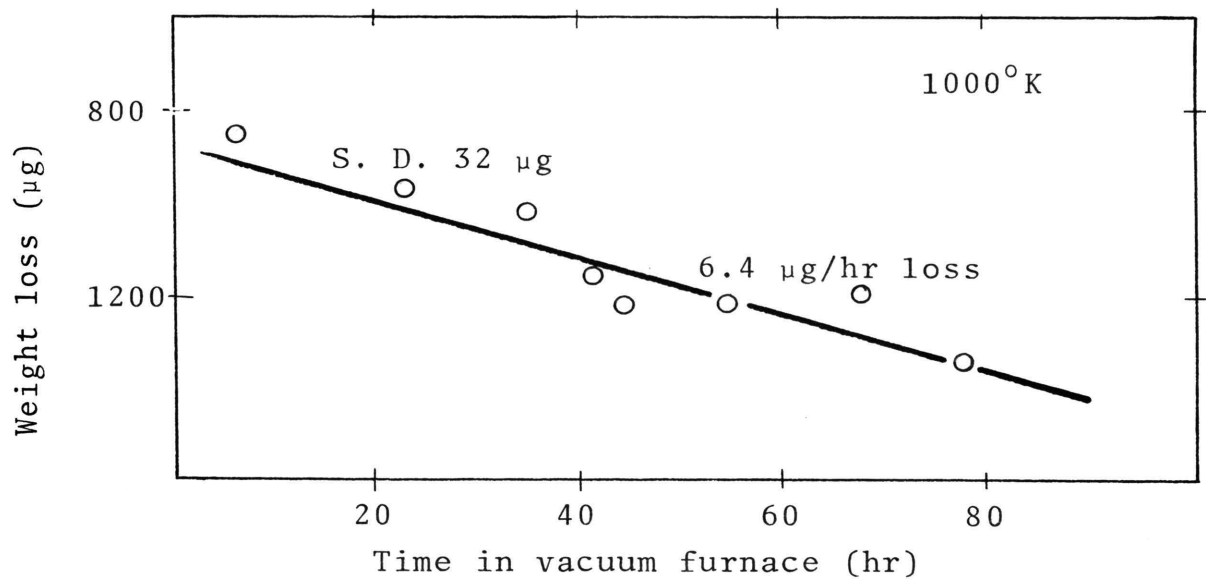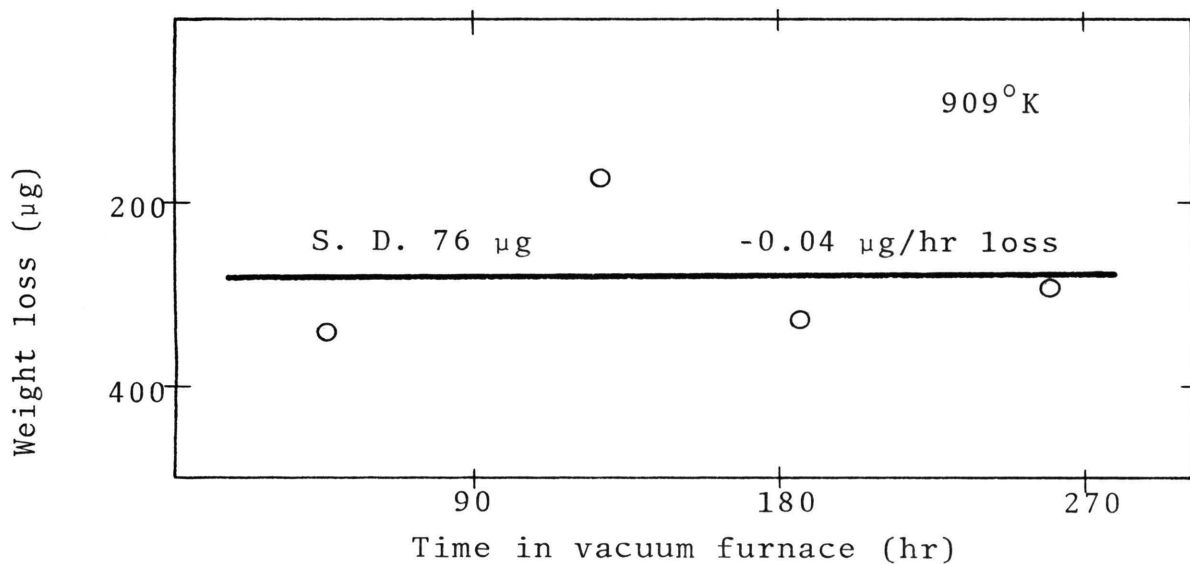
FIGURE 9. Weight loss of crucibles during effusion runs at 909°K and 1000°K.
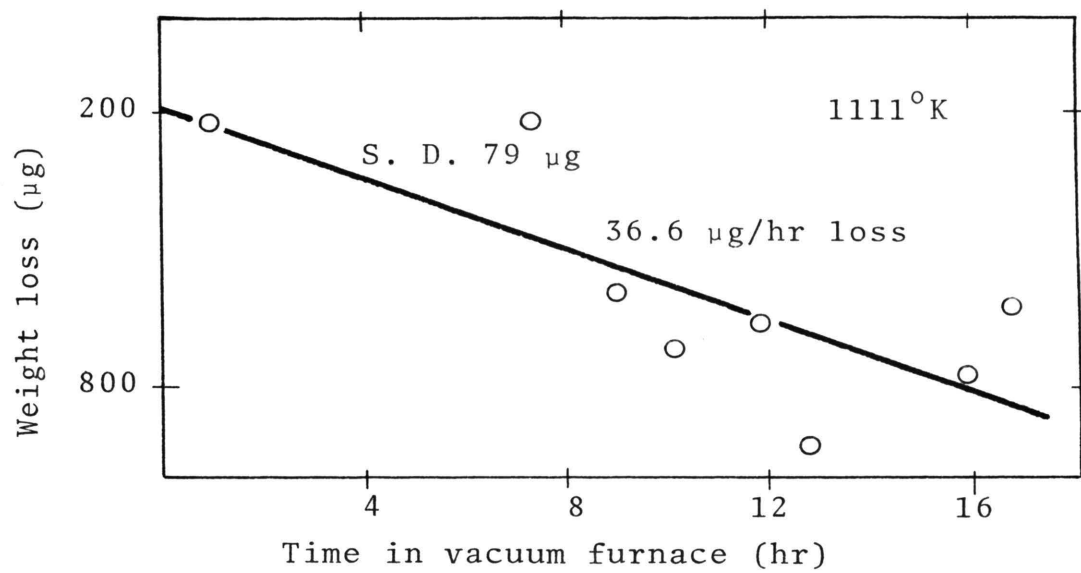
FIGURE 10. Weight loss of crucible during effusion
runs at 1111°K.

made. When the heating and cooling times were 1 per
cent of the total time, the temperature of the crucible
was measured at half-minute intervals during heating
and cooling to allow calculation of the weight losses
involved. For four of the runs this correction amounted
to 8 per cent of the total weight loss, which introduced
a maximum probable error in pressure of about 2 per
cent, because there is about 25 per cent error in the
end correction.

3. Orifice area

The orifice area of each crucible was deter-
mined by tracing a magnified photograph of the orifice
with a K&E compensating polar planimeter, which had
been tested on a $16cm^2$ area and found to be accurate
to $\pm.5$ per cent. The magnification was determined by
photographing an areal grid under the same magnification
as the orifice and measuring the area on the photograph.

The thermal expansion of the orifice during heating
to the effusion temperature was considered as a possible
source of error. White[23] has listed data on the thermal
expansion coefficient of fused silica. These can be used
to show that for a circular orifice of $3x10^{-2}$ cm^2 the
increase in area at 1100°K is less than 0.1 per cent,
which is negligible and indicates that the thermal expan-
sion is not a significant source of error. The change
in orifice area during effusion due to other causes

was determined by remeasuring the area of the crucible that had been used for the silver runs. The difference in the two area determinations was found to be 0.4 per cent; the same within experimental error. Therefore, it was concluded that orifice area does not change as the run progresses.

4. Time

The effusion time was measured with a Lab-Chron timer and was taken to be the time from turning on to turning off the furnace minus the time required for heating to the effusion temperature. The uncertainty in the effusion time was always less than 0.1 per cent.

V. Results and Discussion

A. Silver Runs

The vapor pressure of Ag was measured to provide a check on the accuracy of the apparatus and techniques. The effusion data and the resulting vapor pressures, P_{eq}, are presented in Table II, along with the accepted values of the vapor pressure of silver, $P_{calc.}$, which were obtained from equation (4). The percentage error between these two values is 6.5 on the average, which is good agreement for vapor pressure data and demonstrates that the experimental procedures are reliable.

A detailed discussion of the procedure for calculating P_{eq} is presented in Appendix A. Briefly, the effusion data were used to calculate a Knudsen pressure, P_K, using equation (1). Then equation (5) was used to find P_{eq} by calculating a value of β with equation (6). It is seen that β depends on the evaporation coefficient, α, for which Paul[20] has reported a value of unity, and the effective vaporizing area, which is the cross-sectional area of the Knudsen cell for a material with unit evaporation coefficient.

B. Cadmium Oxide Runs

The results of the Knudsen effusion runs on CdO are presented in Tables III and IV, and the details of the

TABLE II. Vapor pressure of Ag

T (°K)	Time (min)	Weight Loss (mg)	$P_K \times 10^6$ (atm)	$P_{eq} \times 10^6$ (atm)	$P_{calc} \times 10^6$ (atm)	Error (%)
1208.4	1066	195.16	$2.04 \pm 4\%$	$2.11 \pm 4\%$	2.139	1.4
1212.0	229	44.32	$2.09 \pm 4\%$	$2.15 \pm 4\%$	2.318	7.4
1213.6	186	35.80	$2.08 \pm 4\%$	$2.14 \pm 4\%$	2.400	10.8

TABLE III. Cadmium oxide Knudsen effusion data.

Run Number	Temp. ($°K$)	Time (min)	Wt.Loss (mg)	$P_K \times 10^6$ (atm)	$\Delta H°_{298}$ (kcal/mole)
Orifice Area $(cm^2) = 8.080 \times 10^{-2}$ $T_C = 918°K$					
1	903.2	1944.	17.29	.130	90.1
2	911.8	1740.	26.29	.222	89.5
3	918.7	1591.	30.03	.278	89.6
4	919.3	727.	9.23	.187	90.7
Orifice Area $(cm^2) = 1.249 \times 10^{-2}$ $T_C = 918°K$					
5	898.5	6495.	11.39	.166	89.0
6	920.9	9780.	36.86	.360	89.0
7	919.2	8709.	30.43	.334	89.1
8	923.7	8675.	36.22	.400	89.0
9	921.3	7660.	28.88	.360	89.1
Orifice Area $(cm^2) = 30.52 \times 10^{-2}$ $T_C = 918°K$					
10	920.9	542.	18.94	.136	91.7
11	917.5	605.	17.68	.114	91.8
12	919.0	461.	13.03	.110	92.1
Orifice Area $(cm^2) = 8.080 \times 10^{-2}$ $T_C = 1008°K$					
13	1009.4	62.5	19.91	4.69	89.7
14	1008.2	60.5	18.40	4.60	89.7
15	1013.5	61.0	19.01	4.74	90.0
Orifice Area $(cm^2) = 2.315 \times 10^{-2}$ $T_C = 1008°K$					
16	1006.3	207.5	21.85	5.63	88.9
17	1007.7	224.5	23.06	5.50	89.1
18	1006.5	574.5	48.49	4.53	89.6

Table III   Continued

Run Number	Temp. (°K)	Time (min.)	Wt. Loss (mg.)	$P_K 10^6$ (atm)	$\Delta H°_{298}$ (kcal/mole)
Orifice Area $(cm^2) = 2.743 \times 10^{-3}$ $T_C = 1008°K$					
19	1009.1	1581.	22.06	6.30	88.8
20	1008.4	1536.	18.34	5.76	89.0
21	1006.9	1290.	15.29	5.34	89.1
Orifice Area $(cm^2) = 30.52 \times 10^{-2}$ $T_C = 1008°K$					
22	1008.6	28.5	18.85	2.60	91.4
23	1006.9	20.5	11.25	2.13	91.9
24	1006.7	22.0	12.90	2.29	91.6
Orifice Area $(cm^2) = 5.721 . 10^{-2}$ $T_C = 1107°K$					
25	1106.5	31.5	101.49	69.7	89.3
26	1103.7	24.0	81.69	73.4	88.9
27	1111.3	20.0	59.04	62.1	90.0
Orifice Area $(cm^2) = 1.249 \times 10^{-2}$ $T_C = 1107°K$					
28	1109.9	21.0	21.56	99.6	88.4
29	1109.0	25.0	23.33	94.5	88.5
30	1111.5	20.0	19.69	96.0	88.6
Orifice Area $(cm^2) - 2.742 \times 10^{-3}$ $T_C = 1107°K$					
31	1110.8	82.5	18.25	103.	88.3
32	1107.0	96.0	18.32	89.3	88.5
33	1107.7	90.0	16.76	86.9	88.7

Table IV.   Data for Sigma plots and reciprocal pressure versus orifice area plots.

Run Number	$P_{KC} \times 10^6$ (atm)	$1/T \times 10^{-4}$ (°K^{-1})	$1/P_{KC} \times 10^5$ (atm^{-1})	$K \times 10^9$ (atm$^{3/2}$)	Sigma (eu)
	Orifice Area (cm^2)=8.080x10^{-2} T_C=918°K				
1	.220	11.07	45.5	.0170	37.0
2	.276	10.97	36.2	.0379	35.4
3	.272	10.89	36.8	.0533	34.69
4	.179	10.88	55.9	.0294	35.9
	Orifice Area (cm^2)=1.249x10^{-2} T_C918°K				
5	.332	11.13	30.1	.0244	36.3
6	.326	10.86	30.7	.0783	33.9
7	.320	10.88	31.2	.0698	34.1
8	.328	10.83	30.5	.0916	33.6
9	.321	10.85	31.2	.0784	33.9
	Orifice Area (cm^2)=30.52x10^{-2} T_C=918°K				
10	.124	10.86	80.9	.0183	36.8
11	.116	10.90	86.4	.0139	37.4
12	.107	10.88	93.9	.0133	37.4
	Orifice Area (cm^2)=8.080x10^{-2} T_C=1008°K				
13	4.51	9.91	2.22	3.68	26.1
14	4.57	9.92	2.19	3.57	26.1
15	4.04	9.87	2.47	3.74	26.0
	Orifice Area (cm^2)=2.315x10^{-2} T_C=1008°K				
16	5.91	9.937	1.69	4.84	25.5
17	5.55	9.923	1.80	4.68	25.6
18	4.74	9.935	2.11	3.50	26.2

Table IV. Continued

Run Number	$P_{KC}x10^6$ (atm)	$1/Tx10^{-4}$ (°K^{-1})	$1/P_{KC}x10^5$ (atm^{-1})	$Kx10^9$ (atm$^{3/2}$)	Sigma (eu)
	Orifice Area (cm^2)=2.743x10^{-2} T_C=1008°K				
19	6.10	9.910	1.64	5.73	25.2
20	5.70	9.917	1.76	5.01	25.5
21	5.50	9.931	1.82	4.47	25.7
	Orifice Area (cm^2)=30.52x10^{-2} T_C=1008°K				
22	2.55	9.914	3.92	1.51	27.8
23	2.19	9.931	4.56	1.12	28.4
24	2.38	9.933	4.20	1.26	28.2
	Orifice Area (cm^2)=5.721x10^{-2} T_C=1107°K				
25	70.6	9.038	.142	211.	17.8
26	79.5	9.060	.126	228.	17.7
27	56.1	8.998	.178	178.	18.2
	Orifice Area (cm^2)=1.249x10^{-2} T_C=1107°K				
28	92.9	9.010	.108	360.	16.8
29	90.2	9.017	.111	333.	16.9
30	86.1	8.997	.116	341.	16.9
	Orifice Area (cm^2)=2.742x10^{-3} T_C=1107°K				
31	94.2	9.002	.106	380.	16.7
32	89.2	9.033	.112	306.	17.1
33	85.4	9.028	.117	294.	17.2

calculations are given in Appendix A. Briefly, the vapor pressures, P_K, were calculated from the effusion data by equation (1) and then used to calculate equilibrium constants, K, for the vaporization reaction of CdO, which is shown in equation (2). A third law enthalpy of reaction (see Lewis and Randall[14], page 177) was calculated for each data point using the temperature in Table III, the corresponding K in Table IV and appropriate thermodynamic data (see Appendix A). These third law values are given in Table III under ΔH°_{298}.

The values of $1/T$ and Sigma listed in Table IV were used with the appropriate thermodynamic data (see Appendix A) to determine ΔH°_{298} by the Sigma plot method. The second law value is given in Figure 14 by the solid line.

The corrected pressure, P_{KC}, in Table IV was obtained by adjusting each of the values of P_K to one of the correction temperatures, T_C, 918°K, 1008°K, or 1107°K by using the relationship

$$P_{KC} = P_K \exp \left(\frac{\Delta H^\circ}{R} \left(\frac{1}{p}\right) \left(\frac{1}{T} - \frac{1}{T_C}\right) \right) \qquad (7),$$

where ΔH° is the heat of the vaporization reaction, R is the universal gas constant, and p is the exponent of the equilibrium constant's units, which is 3/2 for the vaporization reaction of CdO. The ΔH°_{298} obtained by Glemser and Stocker,[6] 87.66 kcal/mole, was used in this equation. The values of the reciprocal corrected

pressure, $1/P_{KC}$, in Table IV and the orifice area were used at the three values of Tc to find equilibrium pressures and evaporation coefficients. This was done by finding the intercept and slope of the reciprocal pressure versus orifice area curves and using equation (5).

    1.   Equilibrium pressures and evaporation coefficients.

    Plots of $1/P_{KC}$ versus orifice area for 918°K, 1008°K, and 1107°K are shown in Figures 11, 12 and 13, respectively, where the curve is a least squares straight line. It can be seen from these plots that the large orifice effusion data do not yield an equilibrium vapor pressure, P_{eq}. The intercept of the curve at zero orifice area gives the value of P_{eq} according to equation (5). This value is the same within experimental error as the P_{KC} value for the small orifice data at 1107°K and 1008°K, but it is significantly different from P_{KC} at 918°K. These extrapolated values will be used as the best values for P_{eq}, and are given in Table V. The standard deviations in these values and in the values of α were estimated with a method described by Hildebrand[8] and then used to calculate the probable errors given in the Table.

    The slope of each of these plots can be used to determine a value of the evaporation coefficient, α, by using equations (5) and (6). However, the effective vaporizing area, A', is unknown, since effusion is
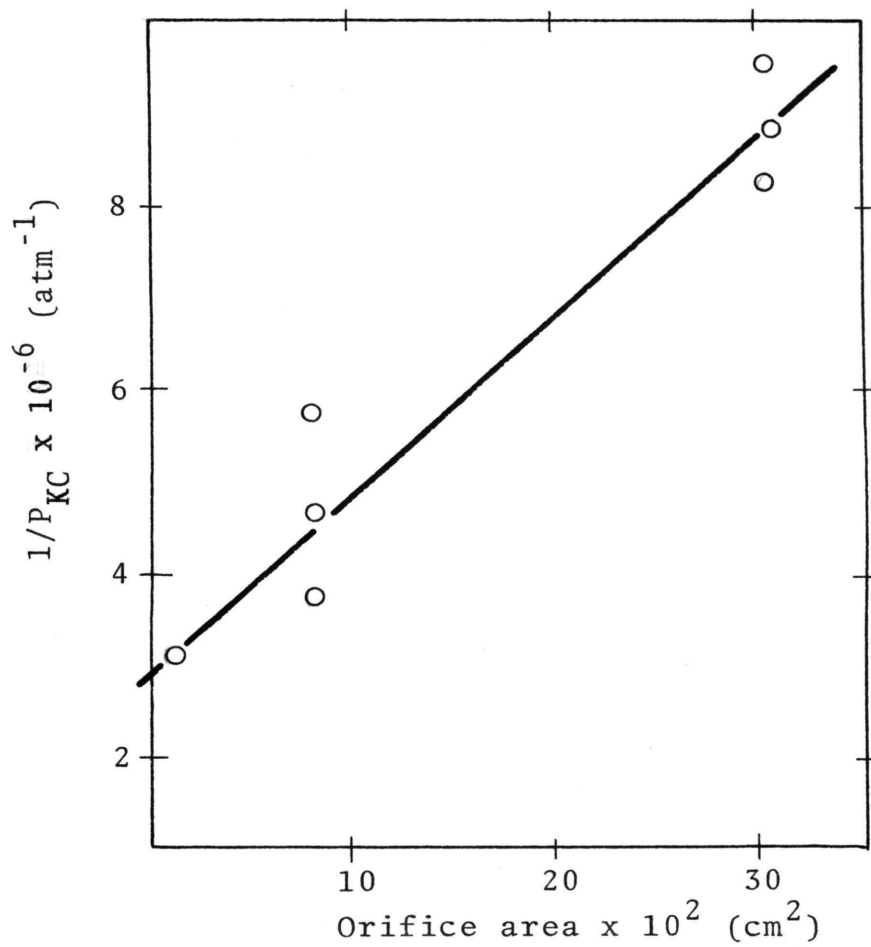
FIGURE 11. Determination of evaporation coeffieient and equilibrium pressure at 918°K.
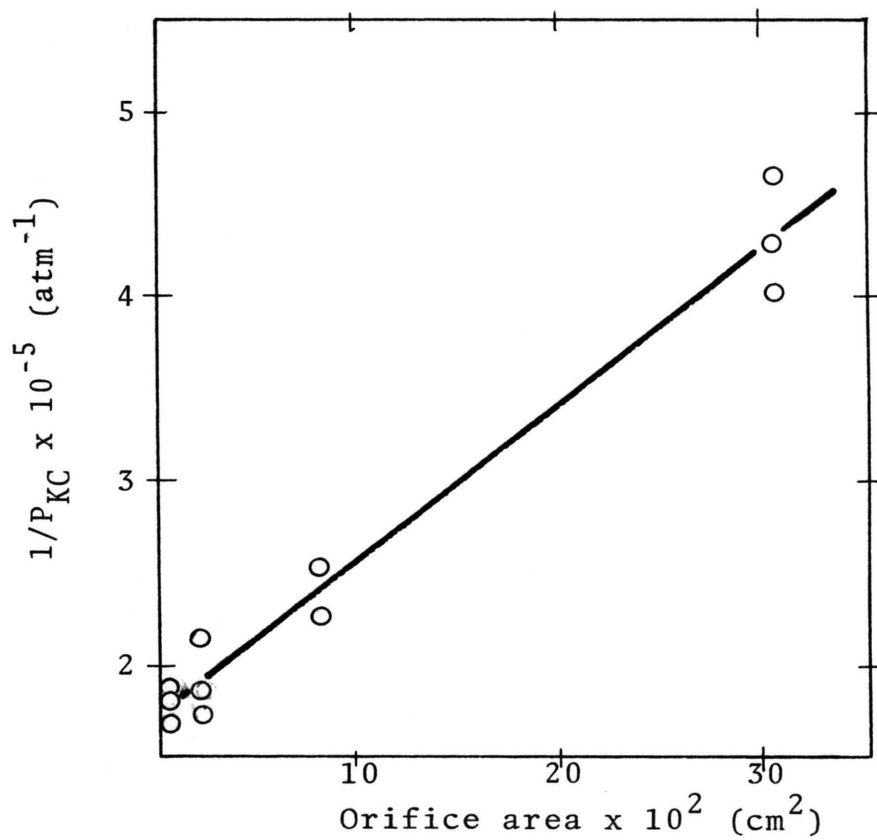
FIGURE 12. Determination of evaporation coeffieient and equilibrium pressure at 1008°K.
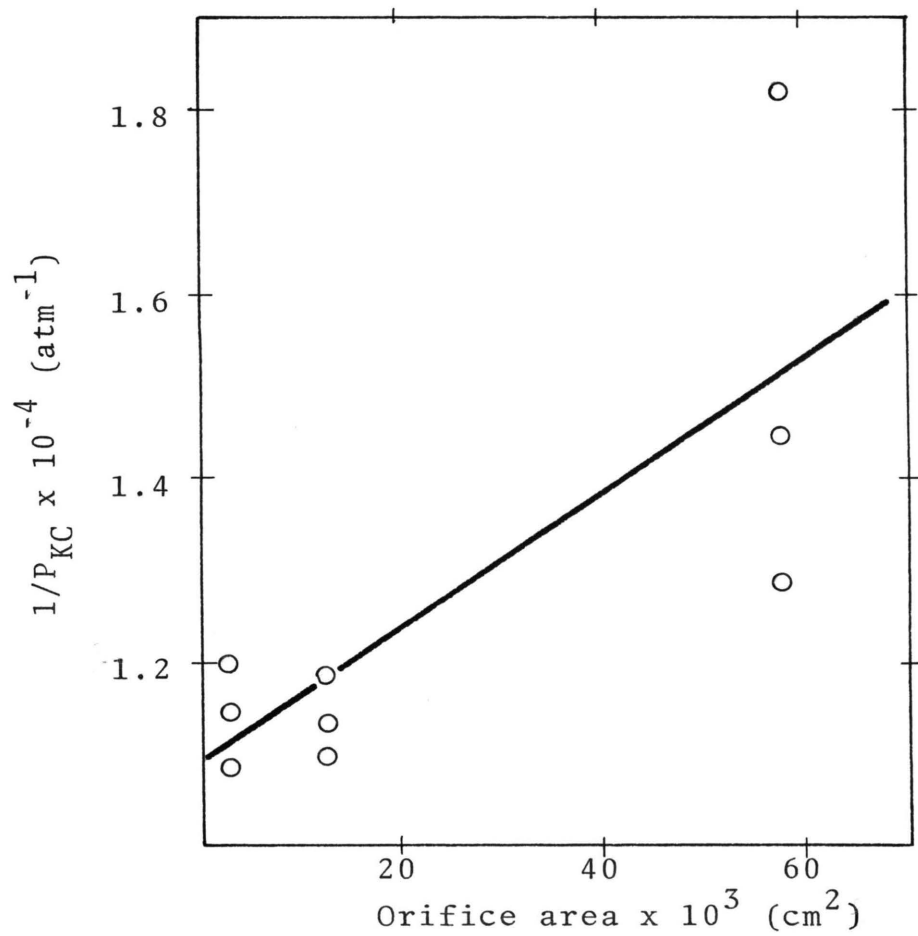
FIGURE 13. Determination of evaporation coefficient
and equilibrium pressure at 1107°K.

TABLE V. Equilibrium data for CdO from reciprocal pressure versus orifice area plots.

T_c (°K)	$P_{eq} \times 10^7$ (atm)	$K_{eq} \times 10^{10}$ (atm 3/2)	$Sigma_{eq}$ (eu)	Third Law $\Delta H°_{298}$ (kcal/mole)	α_{ul}
918	$3.54^{+}_{-}5.4\%$*	$.766^{+}_{-}8\%$	34.07	$88.8^{+}_{-}.9$	$3.70^{+}_{-}10.4\%$
1008	$59.7^{+}_{-}3\%$	$53.0^{+}_{-}4.5\%$	25.37	$88.9^{+}_{-}.9$	$5.03^{+}_{-}6.9\%$
1107	$9.37^{+}_{-}4.4\%$	$3280^{+}_{-}6.6\%$	16.98	$88.4^{+}_{-}.9$	$3.72^{+}_{-}22.9\%$

*All errors values are probably errors.

occurring from a porous powder. Therefore, only the upper
limit to the evaporation coefficient can be determined.
This is done by using the crucible cross-sectional area
as a lower limit for A'. Table V gives the value of
the evaporation coefficient upper limit, α_{ul}, for each
temperature. The average value of α_{ul} is 4.15×10^{-2}
which is in fairly good agreement with the 1.4×10^{-2}
value of α_{ul} calculated by the same method from Hoenig's
data on the chemically similar ZnO.

2. Thermodynamic data

The results of least square straight lines for
the Sigma versus $1/T$ data from Table IV and the $Sigma_{eq}$
versus $1/T_C$ data from Table V are shown in Figure 14.
The values of ΔH°_{298} and ΔS°_{298} shown in the figure were
obtained from the slope, ΔH°_{I}, and intercept, I, of each
curve in accordance with the relationship

$$Sigma = \frac{\Delta H^{\circ}_{I}}{T} + I \qquad (8)$$

and by use of the following two relationships (see
Appendix A),

$$\Delta H^{\circ}_{T} = \Delta H^{\circ}_{I} - 1.76T - 2.1 \times 10^{-4} T^2 - 1.64 \times 10^{-7} T^3 \qquad (9)$$

$$\frac{\Delta F^{\circ}_{T}}{T} = \frac{\Delta H^{\circ}_{I}}{T} + 1.76 \ln T + 2.1 \times 10^{-4} T + 8.2 \times 10^{-8} T^2 + I \qquad (10)$$

Clearly, the thermodynamic data obtained from the
$Sigma_{eq}$ data are more reliable. The procedure for
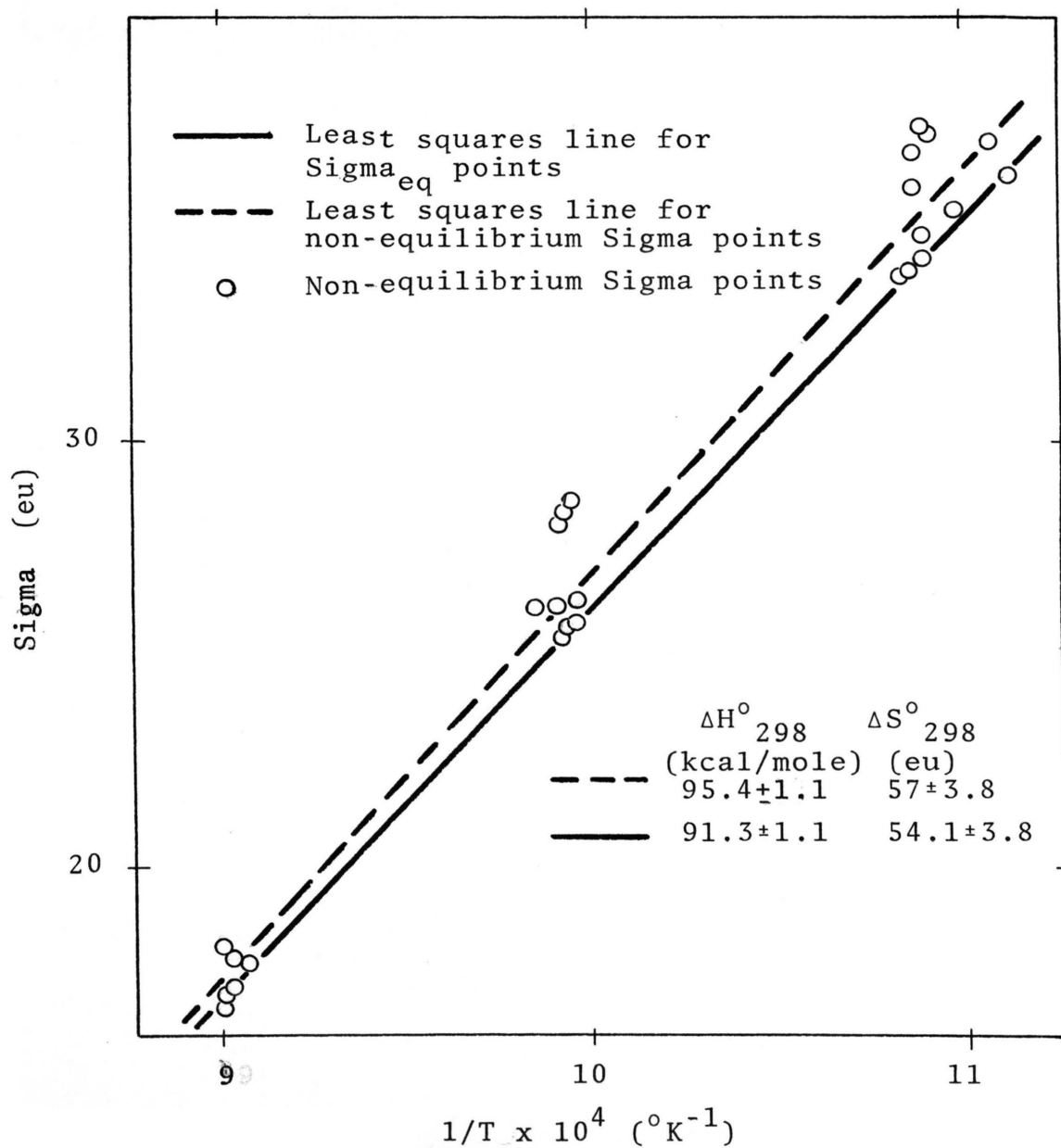
FIGURE 14. Sigma plot for determining ΔH^{o}_{298} and ΔS^{o}_{298}.

assigning the error to these values is shown in Appendix B.

The third law values of ΔH°_{298} listed in Table III show a dependence on orifice area, and are certainly not as reliable as those third law values from the equilibrium data in Table V. The procedure for assigning the error to the latter values is shown in Appendix B.

3. Discussion

Gilbert and Kitchner[5] have calculated a value of ΔH°_{298} for the vaporization reaction of CdO based on a calorimetric value of the enthalpy of formation of CdO, vapor pressure data for Cd and heat capacity data. They arrived at a value of 88.1kcal/mole. They also calculated a value of ΔS°_{298} for the reaction to be 51.45 eu. For the present work, the average value of the third law heat of reaction from Table V is 88.7 ± 0.9 kcal/mole which is in agreement with the above value within experimental error. The value of ΔH°_{298} from the Sigma plot method was 91.3 ± 1.1 kcal/mole which is a little higher than the third law value. The Sigma plot value of ΔS°_{298} was 54.1 ± 3.8 eu, which agrees with Gilbert and Kitchner's value within experimental error.

Since the ΔH°_{298} determined by the second law method is higher by about 3 kcal, this could indicate that there is a systematic error in the data. A systematic

error of 28 per cent in K_{eq} over a temperature range of 189°K can cause an error in ΔH°_{298} of 3 kcal/mole; thus, it is suspected that a temperature dependent systematic error of this magnitude may have been introduced over the temperature range studied.

The fact that the vapor pressures for Ag were slightly lower than the accepted values and the above difference in the second law and the third law heats indicate that the values of K_{eq} for CdO are probably low. A least squares fit of the values of log K_{eq} and $1/T_C$ from Table V gives

$$\log K_{eq} = 11.12 - \frac{1.952 \times 10^4}{T} . \qquad (11)$$

The values of K_{eq} from this equation are probably not more than 50 per cent less than the true equilibrium values. This limit is chosen because of the uncertainty in the difference between the second and third law enthalpies which gives rise to the 28 per cent systematic error mentioned above.

A value of ΔH°_{298} calculated by the third law method from the present data is increased 0.5 kcal/mole by a value of K_{eq} which is 25 per cent low at 1000°K. Thus it is reasonable to expect that the true value of ΔH°_{298} is about this much less than indicated by this work. This gives a value of 88.2 kcal/mole, compared to Gilbert and Kitchner's calculated value of 88.1 kcal/mole.

This calculated value by Gilbert and Kitchner is probably the most accurate ΔH°_{298} for the vaporization of CdO.

Since the ΔS°_{298} from a second law treatment is inexact, there is little question that Gilbert and Kitchner's value of 54.45 eu is the best available value for the vaporization of CdO.

VI.   Summary and Conclusions

Knudsen effusion runs were made on Ag and CdO. The Ag runs were made at 1210°K and the CdO runs at 918°K, 1008°K, and 1107°K. For the CdO runs, a series of orifice areas were used at each temperature so that equilibrium values and evaporation coefficients could be obtained from reciprocal pressure versus orifice area plots. Values of ΔH°_{298} for the CdO vaporization reaction were calculated by the second and third law methods and compared to a value calculated by Gilbert and Kitchner. A value of ΔS°_{298} was determined by the second law method and compared with the value from Gilbert and Kitchner's calculation. The following conclusions were drawn:

1. The value of the vapor pressure of Ag at 1210°K obtained in this work is in good agreement with the accepted value, approximately 7 per cent lower.

2. A value of ΔH°_{298}, determined by the third law method, of 88.7 ± 0.9 kcal/mole, and a second law value of 91.1 ± 1.1 kcal/mole indicated that there is a temperature dependent systematic error and that the best value for ΔH°_{298} is the one calculated by Gilbert and Kitchner of 88.1 kcal/mole.

3. The upper limit of the evaporation coefficient over the temperature range of 918°K to 1107°K is 4.15×10^{-2} ± 13 per cent.

4. The equilibrium constant is given by the expression

$$\log K_{eq} = 11.12 + 1.952 \times 10^4 / T$$

for the range 918°K to 1107°K, and is probably no more

than 50 per cent below the true equilibrium values.

5. A value of ΔS°_{298} of 54.1 ± 3.8 eu was determined

by the second law method as compared to Gilbert and Kitchner's

calculated value of 51.45 eu. Because of the uncertainty

in second law determinations of ΔS°_{298} the latter is probably

the best value available in the literature.

VII. Recommendations for Future Work

As a follow-up to this work, it would be interesting to prepare Langmuir samples for determining the evaporation coefficient and comparing the results with the value obtained in this work. It would also be very interesting to study the effect on the evaporation coefficient of minor additions of In^{3+} or Ag^{1+} as the effect of these additions on the defect structure has been studied by Cimino and Marezio.[3]

To ensure the absence of systematic error in the experimental procedure, it would be good practice to run a material of known vapor pressure, such as Ag, over a series of temperatures.

Apparently no mass spectrometric work has been done on the vapor species above CdO, and it is generally accepted that only $Cd(g)$ and $O_2(g)$ are present. It would be interesting to see if species of the type $Cd_nO_{(n-1)}(g)$ other than $Cd (g)$ are present in trace amounts by studying the mass spectrum.

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Appendix A

DETAILS OF THE CALCULATIONS ON CdO AND Ag

A. Calculations for CdO

The data from the effusion runs on CdO(s) were analyzed by the program in Figure A1 on an IBM 360 Digital Computer. The purposes of this program were:

a. To calculate a vapor pressure for each set of data.

b. To provide data for a Sigma versus reciprocal temperature plot.

c. To provide data for plots of reciprocal pressure versus orifice area at 918°K, 1008°K, and 1107°K.

d. To provide a value of $\Delta H°_{298}$ for each data point by the third law method.

Each section of the program will be discussed in the following paragraphs.

1. Symbols

The symbols describing the input data are given in Table A1, along with symbols describing the output, and other symbols used in the program.

2. Calculation of temperatures

The input millivolt data, <u>XM(I)</u>, were first converted to centigrade by an expression fitting the chromel/ alumel values in the Handbook of Chemistry & Physics to the nearest 0.05°. Next, the data were corrected by a calibration expression obtained by comparing the thermocouple with a platinum-10 per cent rhodium/platinum thermocouple.

Figure Al.   Knudsen effusion program

```
    KNUDSEN PRESSURES FOR CADMIUM OXIDE
    DIMENSION XM(50),T(50),P(50),XLR(50)
11  READ(1,100) NO,NT,N1,N2,N3,N4,IT,NS,IV,IDNO
    READ (1,101) WLO,CORRC,TIME,XMW,AREA,(XM(I),I=1,N4)
    WRITE(3,100) NO,NT,N1,N2,N3,N4,IT,NS,IV,IDNO
    WRITE(3,101) WLO,CORRC,TIME,XMW,AREA,(XM(I),I=1,N4)

    CONVERSION FROM MILLIVOLTS TO TEMP IN CENTIGRADE

    DO 9 I=1,NT
    T(I)=9.698298+24.87683*XM(I)-0.008592464*XM(I)**2
 9  T(I)=T(I)+0.001550103*XM(I)**3

    CALIBRATION CORRECTION

    GO TO (1,2,3,4),NO
 1  DO 5 I=1,NT
 5  T(I)=T(I)-4.65669+0.004772*T(I)
    GO TO 18
 2  DO 6 I=1,NT
 6  T(I)=T(I)-5.7602+0.01025*T(I)
    GO TO 18
 3  DO 7 I=1,NT
 7  T(I)=T(I)-6.335+0.00963*T(I)
    GO TO 18
 4  DO 8 I=1,NT
 8  T(I)=T(I)-9.6533 +.008478*T(I)

    SAMPLE TEMP FROM CRUCIBLE BOTTOM TEMP AND CHANGE TO KELVIN

18  DO 30 KL=1,NT
30  T(KL)=T(KL) +222.19 + 0.190*T(KL)-0.000151*T(KL)**2

    CORRECTION FOR CRUCIBLE WEIGHT LOSS

    KCORC=CORRC
    GO TO(25,26,27),KCORC
25  CORRC=0.0
    GO TO 23
26  CORRC=.85316E-05*TIME/60.
    GO TO 23
27  CORRC=.47352E-04*TIME/60.
23  WLO=WLO-CORRC

    HEATING AND COOLING END CORRECTIONS

    TC=912.
    PC=.351E-06
    PS=PC
    TS=TC
```

Figure A1. Continued

```
    A=N2
    K1=N1
    K2=N2
    IF(0.5-A)29,21,21
21  WLT=WLO
    GO TO 24
29  XYZ=1.
22  DO 10 L=1,2
    DO 12 I=K1,K2
    P(L)=PS*EXP (29418.*(1./TS-1./T(1)))
12  XLR(I)=44.33*P(I)*AREA*(SQRT(XMW/T(I)))*60.
    BRAK1=0.0
    BRAK2=0.0
    MN=K1+1
    NN=K1+2
    LAST=K2-1
    FUNA=XLR(K1)
    FUNB=XLR(K2)
    DO 13 J=MN,LAST,2
13  BRAK1=BRAK1+XLR(J)
    LAST=K2-2
    DO 14 J=NN,LAST,2
14  BRAK2=BRAK2+XLR(J)
    TI=IT
    TI=TI/100.
    SIMP=TI/3.0*(FUNA+4.0*BRAK1+2.0*BRAK2+FUNB)
    IF(2-K1)16,16,15
15  SIMPC=SIMP
    GO TO 17
16  SIMPH=SIMP
17  K1=K2+1
10  K2=N3
    CORRT=SIMPH+SIMPC
    WRITE (3,104) SIMPC,SIMPH,CORRT
    WLT=WLO-CORRT

    CALCULATION OF KNUDSEN PRESSURE

24  PK=(WLT/(AREA*TIME*60.*44.33))*SQRT (T(N4)/XMW)

    TEST TO SEE IF THE CORRECT PRESSURE WAS USED IN END
    CORRECTIONS.

    IF(0.5-A)33,31,31
33  IF(0.05-ABS((PK-PS*EXP(29418.*(1./TS-1./T(N4))))/PK))34,
    131,31
```

Figure Al. Continued

```
 34 PS=PK
    TS=T(N4)
    K1=N1
    K2=N2
    XYZ=XYZ+1.
    IF(16.-XYZ)40,22,22
 40 WRITE (3,41)
 41 FORMAT(4X43HCORR PROC DOES NOT WORK FOR THIS DATA POINT)
    GO TO 11
 31 WRITE(3,103) T(N4),AREA
103 FORMAT(4X13HEFFUSION TEMPF11.5,4X12HORIFICE AREAF10.5)
    WRITE(3,105) WLO,WLT,PK

    CALCULATION OF EQUILIBRIUM CONST FROM KNUDSEN PRESSURE

    XKEQ=3.74*SQRT((PK/4.74)**3)

    CALCULATION OF THIRD LAW HEAT OF REACTION

    H298=1.985*ALOG(XKEQ)-114.04-8.542E-03*T(N4)+1.6785E-06
   1*T(N4)**2
    H298=H298+9.78*ALOG(T(N4))+3004./T(N4)
    H298=-T(N4)*H298

    ADJUSTMENT OF KNUDSEN PRESSURE

    IF(1050.-T(N4))35,36,36
 35 XTC=1107.
    GO TO 39
 36 IF(950.-T(N4))37,38,38
 37 XTC=1008.
    GO TO 39
 38 XTC=918.
 39 PKC=PK*EXP(29418.*(1./T(N4)-1./XTC))
    PKCI = 1./PKC
    WRITE (3,106) XKEQ,H298,XTC,PKC
    WRITE (3,201) PKCI

    CALCULATION OF SIGMA FOR SIGMA PLOT

    DA=-1.76
    DB=-0.42E-03
    DC=-4.905E-07
    SIGMA=-1.985*ALOG(XKEQ)+DA*ALOG(T(N4))+0.5*DB*T(N4)
    SIGMA=SIGMA+1./6.*DC*T(N4)**2
    RECIP=1./T(N4)
    WRITE(3,107) SIGMA,RECIP
    IF(IV-NS)11,20,20
100 FORMAT(10I7)
101 FORMAT(6F11.5)
104 FORMAT(4X6HSIMPC=,E12.5,4X6HSIMPH=,E12.5,4X6HCORRT=
   1,E12.5)
```

Figure Al. Continued

```
105 FORMAT(4X4HWLO=,E12.5,4X4HWLT=,E12.5,4X3HPK=,E18.8)
106 FORMAT(4X3HKEQ,E13.4,4X4HH298,F7.0,4X4HTEMP,F5.0,4X
   13HPKC,E12.4)
107 FORMAT(4X6HSIGMA=,E18.8,10X6HRECIP=,E18.8///)
201 FORMAT (4X,7HPKCI=   ,F18.4)
 20 STOP
    END
```

Table A1

Symbols used in the Computer Program

AREA   Orifice area.

CORRC   Number indicating the nominal temperature of the
            run.

CORRT   Weight loss during heating and cooling.

DA,DB,DC   The parts of ΔC_p for the reaction related to
            T^0, T^1, T^2 terms respectively.

H298   Heat of vaporization at 298°K, determined by
            Third Law method.

IDNO   Identification number for data set.

IT   Time interval used in Simpson integration (X100).

IV   Has value of one.

N1   Has value of one.

N2   Number of cooldown temperatures (must be odd).

N3   Number of heatup plus cooldown temperatures
            (must be even).

N4   Designation number of effusion temperature.

N0   Thermocouple identification number.

N5   Zero for last data set, otherwise, two.

NT   Number of temperatures in the data set.

PC   Vapor pressure of CdO at temperature TC.

PK   Knudsen effusion pressure.

PKC   Vapor pressure at temperature XTC

PKCI   Reciprocal of PKC.

RECIP	Reciprocal of effusion temperature.
SIGMA	Values to be used in Sigma plot.
SIMPC	Weight loss during cooling.
SIMPH	Weight loss during heating.
T	Temperature
TC	Temperature at which the CdO vapor pressure is known.
TIME	Effusion time.
WLO	Crucible weight loss, observed.
WLT	Crucible weight loss, corrected.
XKEQ	Equilibrium constant.
XLW	Mass loss rate from orifice.
XM	Temperature data in millivolt form.
XMW	Molecular weight of effusing gas.
XTC	Correction temperature for vapor pressure data.

These corrected data, which corresponded to the crucible bottom temperature, were then corrected by an expression which related the crucible bottom and the CdO sample temperatures. This expression also converted the temperature to °K.

3. Weight corrections

The observed weight loss, WLO, was corrected for the weight loss of the SiO_2 crucible and also for the loss of CdO which occurred during heating and cooling the crucible to and from the effusion temperature.

Crucible weight loss rate expressions from Figures 9 and 10 for the three nominal effusion temperatures were used. CORRC determined which correction was used. The correction was the product of the weight loss rate and the effusion time and was subtracted from WLO.

The correction for weight losses during the time of heating and cooling were used only in cases where this time was more than 1% of the total effusion time. This correction involved two Simpson rule integrations, one for heating and one for cooling. These integrations are of the type:

$$\int (XLR) \, dt \tag{1}$$

where t is time in minutes and XLR is the rate of mass loss in grams/minute, which is a function of time. XLR is determined by the Knudsen equation, using an approximate

value of the pressure, PS, at the temperature, TS, in a
form of equation (7) on page 33 to estimate vapor pressures.
Later in the program at statement 33, a check is made to
determine the agreement between the approximated pressure
and P_K. If they disagreed by more than 5 per cent, P_K and
the effusion temperature were substituted for PS and TS.
An iterative procedure was then used for a maximum of 16
times to achieve agreement. The heating and cooling
weight losses were subtracted from WLO to give WLT, from
which the Knudsen pressure, P_K , is calculated.

4. Calculation of equilibrium constant

The escaping tendency of $O_2(g)$ from an effusion
cell is greater than that for $Cd(g)$ because of the differ-
ence in molecular weight, as can be seen from the Knudsen
equation. Since $CdO(s)$ retains its stoichiometric com-
position during effusion, the following expression results
from the effusion equations for $Cd(g)$ and $O_2(g)$:

$$P_{Cd}/P_{O_2} = 2 \ (M_{Cd}/M_{O_2})^{\frac{1}{2}} \tag{2}$$

Using this and the fact that the activity of $CdO(s)$ is
unity, within experimental error, the expression for the
equilibrium constant is:

$$K_{eq} = 3.74 \ (P_K/4.74)^{3/2} \tag{3}$$

Also, from (2), the effective molecular weight of the vapor
in the cell is found to be 91.37, which is the molecular
weight used in the calculation of P_K.

5. Calculation of third law enthalpy of reaction

Enthalpies of reaction, ΔH°_{298} can be obtained from equilibrium constants by the third law method (see Lewis and Randall, page 177) by the expression:

$$\Delta H^\circ_{298} = -T(R\ln K_{eq} + \Delta FEF) \qquad (4)$$

where $\underline{\Delta FEF}$ is the change in free energy function in going from reactants to products. The value of $\underline{\Delta FEF}$ was obtained by a least squares fit of $\underline{FEF}$ data on $1/2O_2(g)$ and $Cd(g)$, (Stull and Sinke)[2], which gave the following expressions:

$$FEF(Cd(g)) = 38.06 + 5.61 \times 10^{-3}T - 1.0714 \times 10^{-6}T^2 \qquad (5)$$

$$FEF(1/2O_2(g)) = 23.057 + 3.940 \times 10^{-3}T - 6.072 \times 10^{-7}T^2 \qquad (6)$$

and by calculating the following $\underline{FEF}$ for $CdO(s)$:

$$FEF(CdO(s)) = 52.93 - 9.78\ln T - 1.01 \times 10^{-3} - 3004/T \qquad (7)$$

The value of $\underline{FEF}$ for $CdO(s)$ was obtained by using the expression:

$$FEF = -S^\circ_{298} - \int_{298}^{T} C_p/T + 1/T \int_{298}^{T} C_p \, dT \qquad (8)$$

where S°_{298} was found by Millar[17] to be 13.17 eu and Kelley[13] estimated the heat capacity of $CdO(s)$ to be

$$C_p(CdO(s)) = 9.78 + 2.02 \times 10^{-3}T \quad (298-2086^\circ K) \qquad (9)$$

6. Adjustment of Knudsen pressure

In order to make plots of reciprocal pressure versus orifice area, each of the effusion pressures, $\underline{P_K}$, was adjusted to 918, 1008, or 1107°K. The corrected pressure was obtained by using a value of 87.66 for ΔH°_{298}, the $\underline{P_K}$

value, and the effusion temperature in a form of equation
(7) on page 33.   This created an error in pressure of
less than 1 per cent at all but two data points.   The
larger of the two errors was 2.5 per cent.

   7.   Calculation of Sigma

   In order to determine values of ΔH°_{298} and ΔS°_{298}
by the Sigma plot method, the following equation is used:

$$\text{Sigma} = \Delta H^\circ_I/T + I \tag{10}$$

(Lewis and Randall page 175).

where

$$\Delta H^\circ_T = \Delta H^\circ_I + \Delta aT + \tfrac{1}{2}bT^2 + 1/3\Delta cT^3 \tag{11}$$

$$\Delta F^\circ_T/T = \Delta H^\circ_I/T - \Delta a\ln T - \tfrac{1}{2}\Delta bT - 1/6\Delta cT^2 + I \tag{12}$$

and

$$\text{Sigma} = R\ln K_{eq} + \Delta a\ln T + \tfrac{1}{2}\Delta bT + 1/6\Delta cT^2 \tag{13}$$

The Δa, Δb, Δc terms correspond to the change in the T^0,
T^1, and T^2 terms of the heat capacity expressions in going
from reactants to products.   The value for the heat capacity
of CdO(s) given in equation (9) on page 58 was used to-
gether with a value of C_p for Cd(g) of 4.97 cal/$^\circ$K/$_{mole}$ and
a value of C_p for O_2(g) fitted from Stull and Sinke's[21]
data to the equation:

$$C_p(O_2(g)) = 6.106 + 3.20 \times 10^{-3}T - 9.8 \times 10^{-7}T^2 \tag{14}$$

B.   Calculations for Ag.

   The same procedures, with slight modifications to be
mentioned below, were used to compute the vapor pressure

of Ag(s). For the Ag runs, the $\underline{K}_{eq}$, third law $\Delta H°_{298}$, cor-
rected pressure, and values of Sigma were not calculated.
Since all runs were made at a nominal temperature of 1210°K,
only one correction value was needed to get Ag sample tem-
peratures from crucible bottom temperatures: this was
3.5 K°, which was added to the bottom temperature. In the
first Ag run, a crucible weight correction for a gain of 2.73
mg. was made, and for the last two runs, corrections of
0.32 mg. and 0.26 mg. were made for gains in crucible weight.
The expression in equation (4) on page 7 was used to
determine the mass loss rate, XLR, for the heating and cool-
ing corrections. The vapor pressure used in this expression
was obtained from McCabe, et al.[16] and was corrected to
give the Knudsen pressure by use of equation (5) on page 7.

Appendix B. Error Analysis

A. Errors in ΔH°_{298} and ΔS°_{298} from the Sigma plot.

The equilibrium constants used in the plots were derived from vapor pressures that had been corrected to one of three temperatures. For this reason, there is no temperature error, rather, all of this error is transferred to the pressure values in the correction process.

The expression for Sigma is

$$\text{Sigma} = -R\ln K_{eq} + \Delta a \ln T + \frac{1}{2}\Delta bT + \frac{1}{6}\Delta cT^2 \quad (1)$$

where Δa, Δb, and Δc are the terms describing the change in heat capacity between reactants and products. The error in Sigma is due to the error in $\ln K_{eq}$, Δa, Δb, and Δc. From Table V on page 38 it is seen that error in P_{eq} is 4.2 per cent, and it can be readily shown from the relation

$$K_{eq} = 3.74 \left(\frac{P_{eq}}{4.74}\right)^{\frac{3}{2}} \quad (2)$$

which is developed in Appendix A, that the error in K_{eq} is 3/2 the error in P_{eq}, i.e., 6.3 per cent. The errors in Δa, Δb, and Δc, are found by adding the errors produced in the a, b, and c terms of the expression for heat capacity,

$$C_p = a + bT + cT^2. \quad (3)$$

The probable errors in the heat capacity expressions for CdO, O_2, and Cd, were taken as 5 per cent, 0.5 per cent, and 0.5 per cent, respectively. This yields absolute error values for dΔa, dΔb, and dΔc of 0.528, 1.02×10^{-2} and 2.46×10^{-9}, respectively. The expression for d(Sigma) from above is found to be:

$$d(Sigma) = Rd(lnK_{eq}) + lnTd\Delta a + \frac{1}{2}Td\Delta b + \frac{1}{6}T^2 d\Delta c \quad (4)$$

Evaluation of this expression gives a d(Sigma$_{1000}$) of 3.65 at 1000°K.

In finding a value of ΔH_I° from the slope in a Sigma plot, one is interested not in absolute values of Sigma, but in the relative accuracy of one value with respect to another. The relationship for ΔH_I° which expresses this is:

$$\Delta H_I = (Rln (\frac{K_{eq1}}{K_{eq2}}) + \int_{T_1}^{T_2} Sigma_T dT) / (\frac{1}{T_1} - \frac{1}{T_2}) \quad (5)$$

where Sigma is the first derivative with respect to T of the heat capacity terms in Sigma. Evaluation of the integral gives:

$$\Delta a \; ln (\frac{T_2}{T_1}) + \frac{1}{2} \Delta b(T_1 - T_2) - \frac{1}{6} \Delta c(T_2^2 - T_1^2). \quad (6)$$

Thus, there are errors in ΔH_I° due to K_{eq}, Δa, Δb, and Δc. dΔH_I° can be written:

$$d\Delta H_I^\circ = (1/(\frac{1}{T_1} - \frac{1}{T_2})) \sqrt{A^2 + B^2} \quad (7)$$

where:

$$A^2 = (\ln(\frac{T_2}{T_1}) \; d\Delta a)^2 + ((\frac{1}{2})(T_2 - T_1) d\Delta b)^2 \qquad (8)$$

and:

$$B^2 = ((\frac{1}{6}) (T_2^2 - T_1^2) d\Delta c)^2 + (2R(\frac{dK_{eq}}{K_{eq}}))^2 \qquad (9)$$

Evaluation of this expression for the interval from 918°K to 1107°K gives an error in ΔH_I of $\pm$1.1 kcal/mole.

The value of the intercept, I, is used to find $\Delta S°_{298}$ from equations (11) and (12) in Appendix A. Since the C_p terms in equation (11) make only a small contribution, the expression,

$$\Delta S°_{298} = \frac{\Delta H°_T}{1000} + \text{Sigma}_{1000} \qquad (10)$$

serves to evaluate the error at 1000°K. This error in $\Delta S°_{298}$ is written:

$$d\Delta S°_{298} = \sqrt{(\frac{d\Delta H°_I}{1000})^2 + (d(\text{Sigma}_{1000}))^2} \qquad (11)$$

From the value of $d\Delta H_I$ and $d(\text{Sigma}_{1000})$, a value of $\pm$ 3.8 e.u. is obtained for $d\Delta S°_{298}$.

B. Errors in ΔH°_{298} by third Law.

The expression for finding ΔH°_{298} by the third Law
method is:

$$\Delta H^\circ_{298} = -T \ (\Delta FEF + R\ln K_{eq}) \qquad (12)$$

where $\underline{\Delta FEF}$ is the change in free energy function, $\underline{FEF}$,
between reactants and products. The $\underline{FEF}$ for CdO was
determined from the entropy and heat capacity data, given
in Appendix A by the expression

$$FEF = -S^\circ_{298} - \int_{298}^{T} \frac{C_p}{T} \, dT + \frac{1}{T} \int_{298}^{T} C_p \, dT \qquad (13)$$

A 5 per cent error in C_p for CdO and a 2.5 per cent error
in its entropy give an error of $\pm.832$ in its $\underline{FEF}$ at $1000°K$.
The percent error in the $\underline{FEF}$'s of O_2 and Cd were taken as
0.5 per cent, and resulted in an absolute error in $\underline{FEF}$
of 0.87. The absolute error in $R\ln K_{eq}$ is found to be
0.19. Since the error in ΔH°_{298} is

$$d\Delta H^\circ_{298} = \sqrt{(T \ d(R\ln K_{eq}))^2 + (T \ d\Delta FEF)^2}, \qquad (14)$$

the total error in ΔH°_{298} is $\pm 0.87 \text{kcal/mole}$ at $1000°K$.

Vita

The author was born in Memphis, Tennessee, on August 20, 1940. He then lived in Fort Smith, Arkansas and later Paducah, Kentucky, where he attended elementary school for two years. He then lived in St. Louis, where he attended public schools until June, 1958. In September, 1958, he was admitted to the Missouri School of Mines and Metallurgy where he received a Bachelor of Science Degree in Ceramic Engineering in June, 1962. He worked for McDonnell Aircraft Corporation in St. Louis, Missouri until September, 1964, when he was admitted to the University of Missouri at Rolla for graduate work. In September, 1966, he was admitted to the University of California at Berkeley for graduate work.

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