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VAPORIZATION AND THERMODYNAMIC PROPERTIES OF ZINC OXIDE

Berkeley, California

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VAPORIZATION AND THERMODYNAMIC PROPERTIES OF ZINC OXIDE

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ABSTRACT

The vaporization of zinc oxide has been investigated by (a) Knudsen weight-loss measurements, (b) mass spectrometric measurements of the vapors effusing from Knudsen cells containing either zinc oxide or a mixture of zinc and zinc oxide, and (c) measurements of the evaporation rates of zinc oxide in streams of helium and zinc vapors. Zinc oxide was found to vaporize by dissociation to zinc atoms and oxygen molecules only. The oxide sublimes congruently (i.e., to a vapor of the same overall composition as the solid) at a composition very close to the stoichiometric. From the measured ion currents of Zn^+ and O_2^+ during congruent sublimation, the relative efficiency of electron current production, σ_{O_2}/σ_{Zn}, is calculated to be 1.28. Limits for the dissociation energies of ZnO(g) and Zn_2O(g) are calculated to be $D^\circ_{298}(ZnO) \leqslant 66$ kcal and $D^\circ_{298}(Zn_2O) \leqslant 127$ kcal. The Knudsen effusion studies and mass spectrometer studies identify the main sublimation reaction as $ZnO(s) = Zn(g) + \frac{1}{2} O_2(g)$ at pressures in excellent agreement with pressures calculated from independent thermochemical data for the free energy of formation of zinc oxide and the vaporization of zinc metal. Transport experiments in which an inert carrier gas is passed over iron wool yield the same high rate of zinc oxide sublimation found by previous investigators when zinc vapor is passed over zinc oxide. The anomalously high

rate of zinc oxide transport in a stream of zinc vapor is thus demonstrated not to arise, as hypothesized by others, from a catalytic influence of zinc vapor on the sublimation process. The probable source of the high transport rate is reaction of water vapor and/or carbon dioxide with the metal to yield hydrogen and/or carbon monoxide, which reduces the zinc oxide to zinc vapor with regeneration of water vapor and/or carbon dioxide.

VAPORIZATION AND THERMODYNAMIC PROPERTIES OF ZINC OXIDE

I. INTRODUCTION

After examining the available data, Brewer and Mastick[1] concluded in 1951 that zinc oxide vaporized by decomposition to the gaseous elements under neutral conditions according to the reaction

$$ZnO(s) = Zn(g) + \frac{1}{2} O_2(g) \quad . \tag{1}$$

The zinc oxide phase has been reported by Brewer to sublime congruently, i.e., the ratio of zinc to oxygen atoms in the vapor phase is the same as the ratio of zinc to oxygen atoms in the condensed phase.[2] The composition for congruent sublimation is very close to the stoichiometric composition. In the same work, Brewer calculated a limit for the heat of dissociation of ZnO(g) to the gaseous atoms of $\Delta H^\circ_0 \lesssim 92$ kcal/mole.

Since the heat and entropy of reaction (1) are accurately known, the equilibrium zinc and oxygen pressures above zinc oxide can be calculated from the thermodynamic equilibrium constant

$$K = P_{Zn} \cdot P_{O_2}^{\frac{1}{2}} \quad . \tag{2}$$

Moore and Williams measured the rate of evaporation of zinc oxide in atmospheres of oxygen, nitrogen, and zinc gas by a transport method.[3] The evaporation rates of zinc oxide which they obtained in atmospheres of oxygen and nitrogen are in general agreement with the rates calculated from the thermodynamic data for zinc oxide -- although some of the weight losses obtained were so small as to be within the uncertainty of their balance measurements. However, the evaporation rate of zinc oxide which they measured in an atmosphere of zinc vapor is greater by a factor

of 100 than rates obtained in atmospheres of oxygen and nitrogen, and greater by a factor of 10^9 than the rate calculated from the thermodynamic data. Moore and Williams hypothesized that the zinc vapor somehow catalyzed the decomposition of zinc oxide.

Using a static system, Secco studied the evaporation rate of zinc oxide under varied partial pressures and varied total pressures of gas in the system.[4] He reported an equilibrium constant for the dissociation of solid zinc oxide to the gaseous elements greater than the equilibrium constant obtained from thermodynamic data by a factor of 10^8.

More recently, Pillay, using a transport method very similar to that used by Moore and Williams, investigated the rate of evaporation of zinc oxide in atmospheres of helium and zinc.[5] The evaporation rate, which he measured in pure helium, agrees with the rate calculated from thermodynamic data. However, the evaporation rate that he obtained when zinc vapor was passed over the zinc oxide was greater than the rate calculated from other data by a factor of 10^{10}, and was apparently independent of the zinc partial pressure in the system.

The anomalously high rates of evaporation of zinc oxide measured in the presence of zinc vapor have indicated a need for a greatly improved understanding of this system. This paper reports results of (a) Knudsen effusion measurements of the vapor pressure of zinc oxide, (b) a mass-spectrometric investigation of the vapor effusing from a Knudsen cell containing either zinc oxide or a mixture of zinc and zinc oxide, and (c) measurements of the rate of evaporation of zinc oxide in atmospheres of helium and zinc by a transport method. The experimental procedure and the results obtained in each of the three kinds of studies are described in sequence, and the implications of the various results will then be analyzed in a single discussion section.

II. KNUDSEN EFFUSION STUDIES

A. Method and Experimental Procedure

Measurements of the vapor pressure of zinc oxide were made by the Knudsen effusion method. When an appreciable fraction (approximately 15%) of a zinc oxide sample was sublimed, no solid residue other than zinc oxide remained. This observation demonstrates that the oxide evaporates to a vapor of the same overall composition as the solid, i.e., the system sublimes congruently. No detectable change was observed in the lattice parameter of the solid phase, nor any systematic change in the equilibrium constant for the dissociation of solid zinc oxide, during the evaporation of this sample. The composition of congruent sublimation can, therefore, be presumed close to the stoichiometric composition.

If more than one gaseous species is present in the effusing vapor, the partial pressures of these species cannot be established by this method alone, in which only the total weight loss is measured as a function of time. However, zinc oxide was shown in the mass-spectrometric study to evaporate to zinc atoms and oxygen molecules only. Since the ratio of zinc atoms to oxygen molecules in the vapor beam must therefore be 2, in this congruently subliming system, the partial pressures of oxygen and zinc in equilibrium with zinc oxide can be calculated from our Knudsen weight loss determinations, and these partial pressures can be compared with those calculated from the available thermodynamic data, by Eq. (2).

Polycrystalline zinc oxide (obtained from Johnson-Matthey Company) was used in all the experiments. Spectrographic examination of the zinc oxide showed the following impurities: 6 ppm (by weight) of silicon, 1 ppm of copper, 1 ppm of iron, and less than 1 ppm each of calcium, magnesium, and sodium.

One aluminum oxide and three quartz effusion cells were used. Each cell was degassed in a 10-hour experiment until the weight loss of the empty cell was less than 0.01 mg. The cells were weighed on an Ainsworth semimicrobalance with a reproducibility of 0.01 through 0.02 mg.

The aluminum oxide effusion cell was a crucible 1/2-in. i.d. by 11/16 in. deep, with an aluminum oxide lid in which a centered, cylindrical effusion orifice had been drilled. This cell was contained in a tantalum cell 9/10-in. i.d. by 7/8 in. deep, with a tantalum lid in which a centered 0.2-in.-diam. hole had been drilled. The tantalum cell was in turn contained in an open graphite crucible. The graphite and tantalum crucibles protected the effusion cell from residual gases in the furnace and increased the heat capacity of the cell assembly, so that minor power fluctuations did not produce significant temperature changes in the effusion cell. To avoid reduction of the aluminum oxide effusion cell by tantalum, the cell was separated from the bottom of the tantalum crucible by a ring made of 20-mil tungsten wire. A similar tungsten wire ring separated the effusion cell from the tantalum lid above it. The outside surface of the alumina cell was separated from the tantalum crucible by a 0.1-in. gap.

Experiments were made to determine the weight loss of a sample of zinc oxide when heated in an aluminum oxide cell having no effusion orifice. In four experiments, an aluminum oxide plug was placed in the orifice of the effusion cell, and in one experiment, an aluminum oxide lid with no effusion orifice was used. The results are discussed in the next section (II-B).

Two of the quartz cells had the same dimensions as the aluminum oxide effusion cell. The third quartz cell was made larger to increase the sample area. This cell was 0.83-in. i.d. by 0.82 in. deep. The lids of all three cells were fused onto the crucibles to obtain gas-tight seals. The quartz cells were heated in a tantalum cell in an assembly like that already described for the aluminum oxide effusion cell. The effusion cell assembly was heated in a glass vacuum system by a 500-kc induction unit. During each vapor pressure experiment, the residual pressure inside the vacuum system was maintained below 1×10^{-5} mm Hg. A pyrex cold trap was located between the effusion cell and the diffusion pump. Liquid nitrogen was contained in this trap whenever the effusion cell was in the vacuum system.

The temperature of the cell was measured with an optical pyrometer focused on the orifice. Since the area of the orifice was small compared with the inside area of the cell, black-body conditions prevailed. The optical pyrometer used (Ser. No. 792636) had been calibrated by the National Bureau of Standards. The optical windows on the vacuum system, through which the pyrometer measurements were made, were calibrated for absorption and reflection losses, and appropriate corrections were applied to the temperature measurements.

No weight change was observed when an effusion cell containing a sample of zinc oxide was exposed to air. However, to reduce any possible pick-up of moisture by the finely divided sample to a minimum, the cell was allowed to cool 10 hours under high vacuum before the diffusion pump was turned off. Air, dried by having been passed over $Mg(ClO_4)_2$ and P_2O_5 and through a liquid N_2 cold trap, was admitted to the vacuum system. The effusion cell assembly was removed from the system and

stored over P_2O_5 for 8 hours before the cell was weighed. When the cell was handled in this manner, the weight change during storage for two days was within the reproducibility of the balance. Details of the equipment and the remainder of the procedure have already been reported by Searcy and McNees.[6]

B. Results

Vapor pressure data obtained with the aluminum oxide effusion cell are summarized in Table I. The weight losses given in column 3 have been reduced by 23.2% to correct for the observed weight losses when zinc oxide was heated in a cell with no effusion orifice. Since the rate of weight loss of the cell having an alumina plug in the effusion orifice was nearly identical to the rate of loss of the cell whose alumina lid had no effusion orifice, the loss was apparently the result of diffusion of zinc and oxygen through the walls of the alumina cell.

Vaporization from a Knudsen cell is a steady-state process in which the partial pressures of Zn and O_2 inside the Knudsen cell are related by

$$P_{Zn} = 2 \sqrt{\frac{M_{Zn}}{M_{O_2}}}\, P_{O_2}, \tag{3}$$

where M_{Zn} and M_{O_2} are the molecular weights of Zn and O_2 respectively. The equilibrium constant can be calculated from the weight loss of the effusion cell by the equation

$$K = \left[\frac{(2.63197 \times 10^{-8})\, w\, T^{\frac{1}{2}}}{a\, t\, k} \right]^{\frac{3}{2}}. \tag{4}$$

Derivations of these equations will be found elsewhere.[9, 10] The calculated equilibrium constants are tabulated in column 6 of Table I. The

Table I. ZnO vapor pressure measurements in Al_2O_3 Cell.

T (°K)	Time (min)	Weight loss (mg)	Area [a] ($cm^2 \times 10^3$)	Clausing [b] factor (k)	K ($\times 10^9$)
1341	266.6	5.45	8.517	.2550	27.3
1332	157.4	2.70	8.515	.2550	20.9
1374	163.6	7.26	8.521	.2550	89.0
1428	69.6	8.45	8.529	.2550	414.0
1404	120.9	9.42	8.525	.2550	210.0
1326	357.4	5.35	8.514	.2550	17.0
1282	704.8	3.90	8.509	.2550	3.73
1295	290.5	1.95	8.577	.2557	4.94
1368	142.7	4.26	8.587	.2557	48.2
1285	333.0	1.56	8.575	.2557	2.86
1324	225.5	2.43	8.580	.2557	10.2

[a] Corrected for thermal expansion.

[b] See references 7 and 8.

last four measurements were made with particles of quartz mixed with the zinc oxide sample. The reason for these four experiments, and the interpretation of the results, is discussed below.

The equilibrium constants given in Table I are shown plotted vs 1/T in Fig. 1, together with the equilibrium constants calculated from the thermodynamic data given in the report of Coughlin.[11]

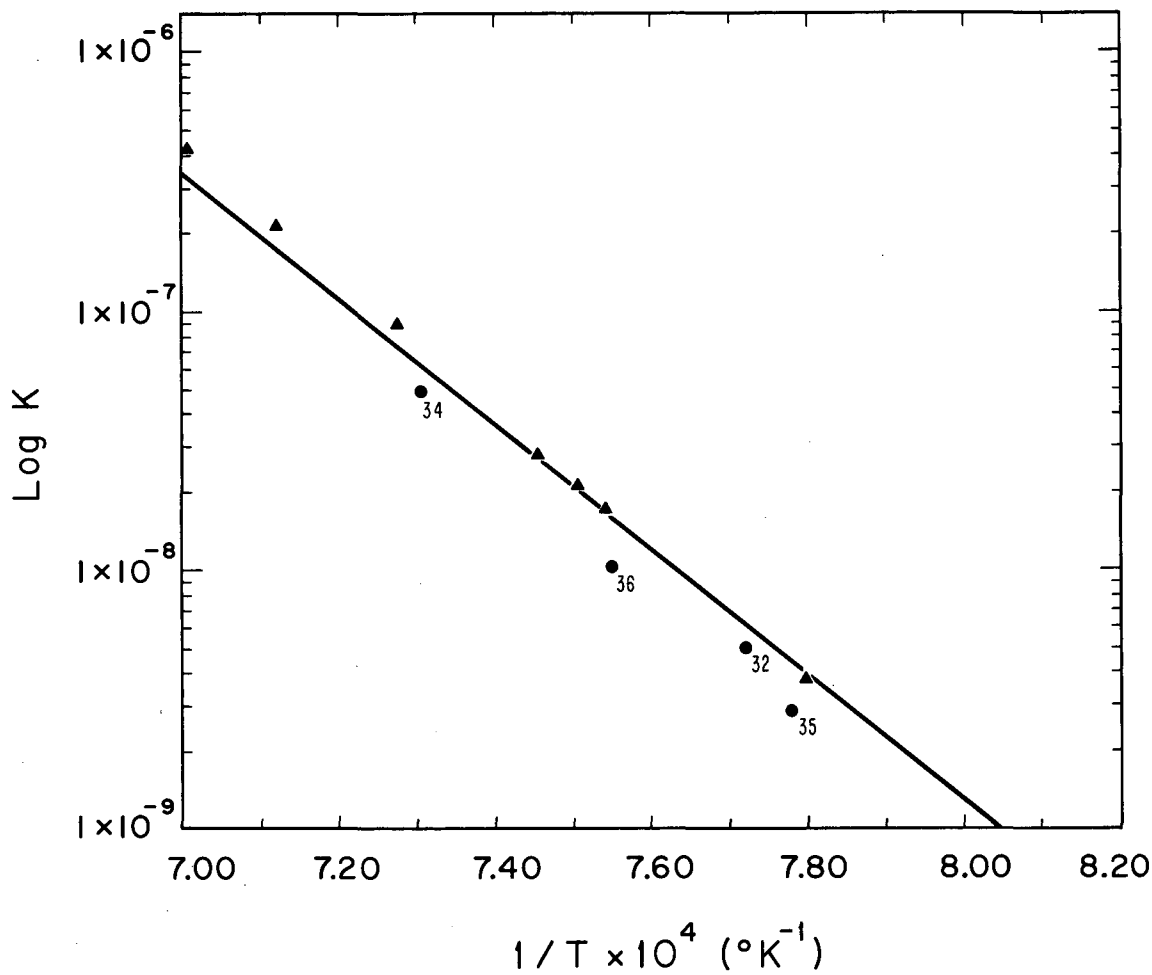
A summary of the vapor pressure data obtained from the three quartz effusion cells is given in Table II. The possibility that zinc oxide might escape through the walls of the quartz cells was not tested, because such an escape could not resolve the discrepancy already apparent between the low pressures measured in zinc oxide cells and the thermodynamically calculated partial pressures of zinc atoms and oxygen molecules. The first nine measurements listed in the table were made with the first quartz cell. The next five measurements were made with the second cell, and the following five measurements with the third. For the final two measurements, some crystals of aluminum oxide were mixed with the zinc oxide sample. The aluminum oxide crystals were very pure sapphire (obtained from the Aluminum Company of America).

The equilibrium constants given in Table II are shown plotted vs 1/T in Fig. 2, together with an equilibrium line plotted from Coughlin's thermochemical data.[11]

III. MASS SPECTROMETRIC INVESTIGATION

A. Equipment and Procedure

A mass-spectrometric study was undertaken, in order to determine the molecular species present in the vapor effusing from a Knudsen cell that contains zinc oxide. A Nuclide Analysis Associates HT-6 mass



MUB-1760

Fig. 1. The equilibrium constant for the reaction $ZnO(s) = Zn(g) + \frac{1}{2} O_2(g)$ measured in alumina cells. The solid triangles are experimental determinations on zinc oxide alone. The line is plotted from the free energy of the reaction $ZnO(s) = Zn(g) + \frac{1}{2} O_2(g)$ that was calculated by Coughlin from the heats of formation of zinc oxide, the heat of vaporization of zinc, and from entropies and heat capacities. The numbered points were obtained when silica was added.

Table II. ZnO vapor pressure measurements in quartz cells.

T (°K)	Time (min)	Weight loss (mg)	Area [a] ($cm^2 \times 10^2$)	Clausing [b] factor (k)	K ($\times 10^9$)
1283	282.7	5.08	2.105	.3936	2.92
1315	216.8	6.87	2.106	.3936	6.97
1349	126.4	7.35	2.106	.3936	17.7
1253	485.1	2.19	2.105	.3936	0.362
1297	324.3	3.12	2.105	.3936	1.15
1329	244.3	4.53	2.106	.3936	3.15
1371	158.5	7.59	2.106	.3936	13.4
1292	375.8	2.09	2.105	.3936	0.506
1295	359.1	2.42	2.105	.3936	0.676
1291	293.9	4.23	1.527	.3760	3.65
1331	210.9	7.21	1.527	.3760	13.7
1260	463.4	3.22	1.527	.3760	1.20
1292	338.2	4.88	1.527	.3760	3.67
1295	303.2	4.59	1.527	.3760	3.95
1322	439.4	1.31	.1449	.3199	15.3
1358	408.3	2.20	.1412	.3173	39.8
1361	483.7	2.72	.1360	.3135	45.8
1282	524.3	0.52	.1327	.3111	3.40
1386	262.5	2.37	.1409	.3171	88.1
1289	415.3	1.90	2.105	.3936	0.377
1371	133.6	5.21	2.106	.3936	9.82

[a] Corrected for thermal expansion.

[b] See references 7 and 8.

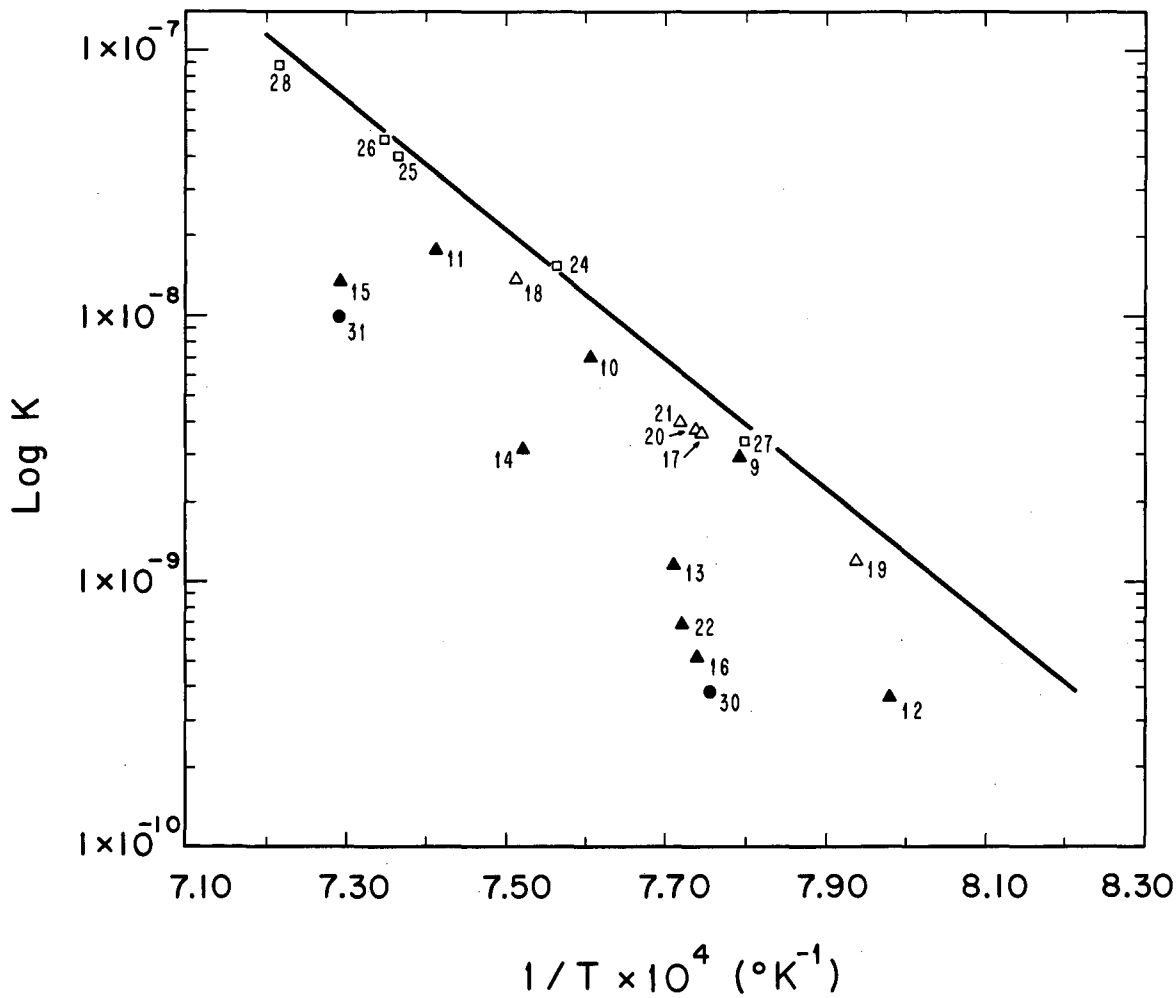


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Fig. 2. The apparent equilibrium constant for the reaction ZnO(s) = $Zn(g) + \frac{1}{2} O_2(g)$ measured in silica cells. The line is plotted from thermodynamic calculations of Coughlin. Points 24-28 were obtained with a cell that had a very small orifice.

□ = Quartz Cell III ▲ = Quartz Cell I

△ = Quartz Cell II ● = Quartz Cell I with some Al_2O_3 added.

spectrometer was used. Three mercury diffusion pumps maintained the vacuum between 1×10^{-7} and 7×10^{-7} mm in the crucible region, and between 1×10^{-8} and 1×10^{-7} mm in the analyzer region, of the mass spectrometer. Liquid nitrogen cold traps were employed on all three diffusion pumps.

The molecular beam source was one of the quartz or aluminum oxide effusion cells from the Knudsen weight-loss studies. The cell was nested inside a tantalum crucible fitted with a tantalum lid having a centered hole of larger diameter than the Knudsen cell orifice. The tantalum crucible, 0.87-in. i.d. and 0.92 in. deep, was heated at 2200 °C in vacuo before it was put in the mass spectrometer. Six equally spaced pits drilled in the bottom of the crucible allowed it to be mounted on the tungsten support rods of the molecular beam source assembly. Two tungsten filaments heated by resistance surrounded the crucible. Radiation from the tungsten filaments was used to produce cell temperatures up to 1000 °C. Electron bombardment heating was necessary to obtain higher temperatures. A diagram of the molecular beam source assembly is given in Fig. 3

A shutter located between the Knudsen cell and the ion source allowed us to measure the background intensities. The molecular beam source assembly was mounted directly below the ionization region at a 60-deg angle to the vertical. The molecular beam from the Knudsen cell entered the ionization region through a system of slits.

The mass spectrometer output was recorded on a Minneapolis-Honeywell recorder having a chart speed of 1 in./min, and a full-scale deflection of 1 mV to 30 V, depending upon the sensitivity setting selected on the vibrating reed electrometer.

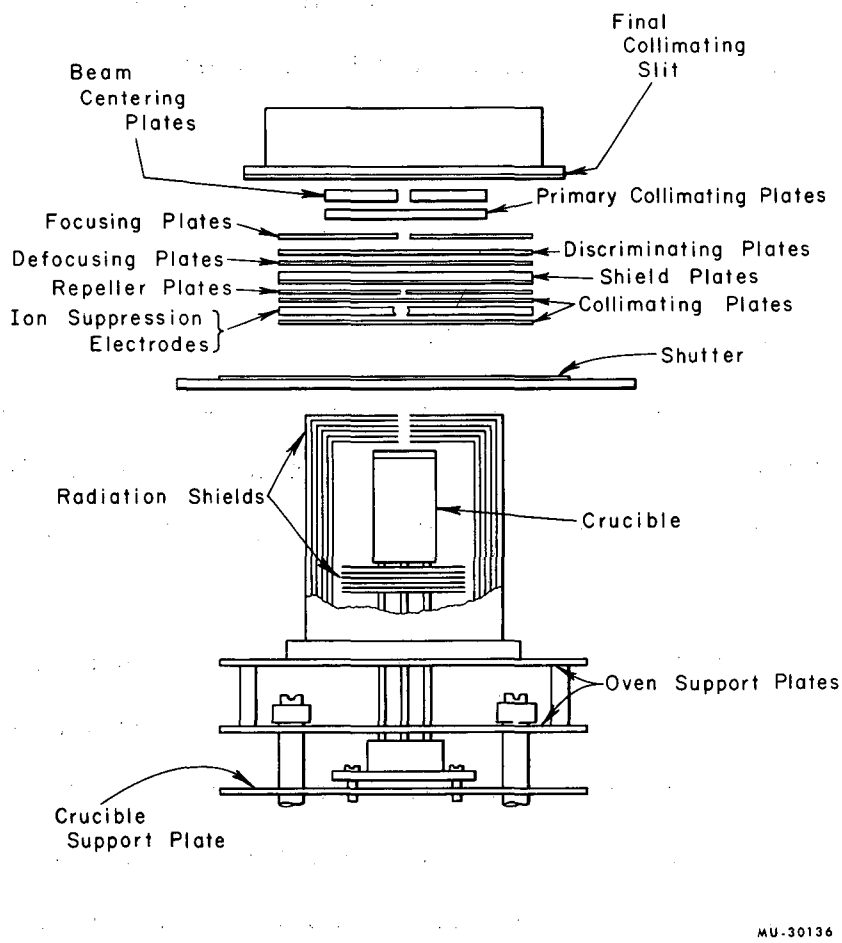

Fig. 3. Diagram of high-temperature molecular beam source assembly and Knudsen cell attachment.

The temperature of the Knudsen cell was measured by a platinum, platinum-10%-rhodium thermocouple. The thermocouple wires were introduced into the molecular beam source assembly through a glass seal, and the thermocouple bead was inserted in a hole drilled in the bottom of the tantalum crucible.

B. Results

1. Zinc Oxide Experiments

The quartz effusion cell used in this experiment was the second of the quartz cells used in the Knudsen effusion studies (Sec. II). The zinc oxide remaining from the Knudsen studies was replaced by a new sample.

The five isotopes of zinc occur at masses 64, 66, 67, 68, and 70, and the three most abundant are at masses 64, 66, and 68. For these isotopes, the relative abundances are 0.489, 0.278, and 0.186, respectively. When the zinc atoms are subjected to 70-volt electron impact in the ionization region, some zinc atoms become doubly ionized. Since the mass-to-charge ratios of $Zn^{64^{++}}$ and $O_2{}^{16^+}$ are the same, the pressures of $Zn^{64^{++}}$ in the ion beam interferes with measurements of the $I_{O_2}{}^+$. To overcome this difficulty, three ion currents, those for masses 66, 33, and 64, were measured at each temperature. From a measurement of the Zn^{66^+} ion current, the total ion current of Zn can readily be calculated from the relation

$$I_{Zn}{}^+ = I_{Zn}{}^+ \, 66/0.278 \, .$$

From a measurement of the ion current of $Zn^{66^{++}}$, the ratio $I_{Zn}66^{++}/I_{Zn}66^{+}$ can be obtained. This ratio should be the same as the $I_{Zn}64^{++}/I_{Zn}64^{+}$ ratio. The ion current of $Zn^{64^{++}}$ was then calculated from

$$\begin{aligned} I_{Zn}64^{++} &= (I_{Zn}64^{+})(I_{Zn}66^{++}/I_{Zn}66^{+}) \\ &= \frac{0.489}{0.278}\,(I_{Zn}66^{+})(I_{Zn}66^{++}/I_{Zn}66^{+}) \end{aligned} \tag{5}$$

This value for $I_{Zn}64^{++}$ was subtracted from the ion current measured at mass 32 to obtain that for $I_{O_2}{}^{+}$. The three ion currents at mass peaks 66, 33, and 32 were measured on several different days at several temperatures. The data obtained are given in Table III. Electron-emission currents of 0.3 and 1.2 mA were used. Since the ion current is not a linear function of the electron emission current, the ratio of the ion currents at the two values of the electron emission current was determined for each mass peak of interest. For $Zn^{66^{+}}$ the ratio of the ion currents was found to be 0.289, and for $Zn^{66^{++}}$ the ratio was 0.310. The ion currents given in column 8 of Table III are those corresponding to an electron emission current of 0.3 mA. The ratios of the P_{Zn}/P_{O_2} calculated from each set of ion measurements are given in column 9. These ratios were calculated from the measured ion currents, and the ionization cross sections given by Otvos and Stevenson,[13] from the relation

$$\frac{P_{Zn}}{P_{O_2}} = \frac{I_{Zn}{}^{+}}{I_{O_2}{}^{+}} \cdot \frac{\sigma_{O_2}}{\sigma_{Zn}} \cdot \frac{(E - A_{Zn}{}^{+})}{(E - A_{O_2}{}^{+})}, \tag{6}$$

where σ_{O_2} and σ_{Zn} are the ionization cross sections, $A_{Zn}{}^{+}$ and $A_{O_2}{}^{+}$

Table III. Mass-spectrometric data for zinc and oxygen.

Temp. (°K)	Emission current (mA)	Electrometer sensitivity scale (V)	Mass No.	Peak height (divisions)	Background (divisions)	Net peak (divisions)	Ion current (x 10^8)	P_{Zn}/P_{O_2}
1316	1.2	10	66	85.0	19.5	65.5	1.90	
1317	1.2	1	33	64.0	16.0	48.0	0.148	
1320	0.3	30	32	72.5	60.5	12.0	3.60	0.90
1279	0.3	3	66	71.5	18.0	53.5	1.60	
1279	0.3	0.3	33	57.0	16.5	40.5	0.121	
1279	0.3	30	32	74.0	62.0	12.0	3.60	0.74
1249	1.2	10	66	39.0	8.5	30.5	0.886	
1247	1.2	1	33	29.0	7.0	22.0	0.068	
1249	0.3	30	32	33.5	27.0	6.5	1.95	0.76
1258	1.2	10	66	50.0	15.5	34.5	1.00	
1262	1.2	1	33	39.0	11.0	28.0	0.0866	
1265	0.3	30	32	40.0	34.0	6.0	1.80	0.95
1300	0.3	1	66	91.0	26.0	65.0	0.65	
1297	3.0	1	33	41.5	11.0	30.5	0.055	
1298	1.2	30	32	80.5	67.0	13.5	1.20	0.92

are the appearance potentials of the respective ions,[14] and E is the electron-ionizing voltage. When the values for these quantities are substituted into Eq. (6), it becomes

$$\frac{P_{Zn}}{P_{O_2}} = \frac{I_{Zn^+}}{I_{O_2^+}} \cdot \frac{6.58}{16.0} \cdot \frac{(70 - 9.5)}{(70 - 12.5)} \quad . \tag{6a}$$

As discussed by Searcy, Williams, and Schissel, systems that sublime congruently can be used to calculate relative ionization cross sections,[12] or if, as in this research, an electron multiplier is used, the relative current-production efficiency of the apparatus for the vapor species can be calculated. Since the Knudsen weight loss measurements demonstrated that the zinc and oxygen pressures are related by Eq. (3), the ratio of the current-production efficiency can be calculated from Eq. (6). This ratio is

$$\frac{\sigma_{O_2}}{\sigma_{Zn}} = \frac{(57.5)}{(60.5)} (2.86) \frac{I_{O_2^+}}{I_{Zn^+}} ,$$

$$\frac{\sigma_{O_2}}{\sigma_{Zn}} = 2.72 \frac{I_{O_2^+}}{I_{Zn^+}} . \tag{7}$$

Calculation of this ratio from ion currents given in Tables III and IV yields an average value for $\frac{\sigma_{O_2}}{\sigma_{Zn}}$ of 1.28. The relative ionization cross section calculated from the relationship given by Otvos and Stevenson is 0.411.[13] The first dynode of the electron multiplier is not equally sensitive to all atoms. From our data, it is not possible to conclude to what extent the difference between the ratio of current-production efficiency and the predicted ratio of ionization cross sections is due to imperfections in the Otvos and Stevenson theory, and to what extent it is due to difference in dinode response.

Table IV. Summary of mass spectrometric data obtained with aluminum oxide effusion cell.

Temp. (°K)	Emission current (mA)	Electrometer sensitivity scale (V)	Mass No.	Peak height (divisions)	Background (divisions)	Net peak (divisions)	Ion current (x 10^8)	P_{Zn}/P_{O_2}
1223	0.3	1	66	39.0	15.0	24.0	0.24	
1223	0.3	0.1	33	37.5	19.0	18.5	0.0185	
1222	0.3	10	32	34.0	30.5	3.5	0.35	1.17
1238	0.3	1	66	41.5	16.0	25.5	0.255	
1238	0.3	0.1	33	34.5	22.5	12.0	0.012	
1240	0.3	10	32	35.5	32.2	3.3	0.33	1.29

The vapors that effused from an aluminum oxide cell also were examined with the mass spectrometer. The aluminum oxide cell that had been used in the Knudsen effusion studies was filled with a new sample of zinc oxide for the mass spectrometric work. The data obtained with this alumina cell are given in Table IV.

In these experiments, the absolute temperature of the sample was estimated to be reliable only within ±40° of the measured temperature. Because the zinc oxide sublimes congruently and has a narrow composition range, this temperature uncertainty is not important in studies designed to determine relative ionization cross sections or composition of the vapor.

No gaseous zinc oxide molecules of any kind were detected. From the very low intensity of the background peak at mass 80, the ion current of $ZnO^+(g)$ can be estimated to be less than 2.8×10^{-12} at 1249 °K. At this temperature the measured ion currents of Zn^+ and O_2^+ were 3.2×10^{-8} and 1.8×10^{-8}, respectively. The equilibrium Zn and O_2 pressures above ZnO at this temperature, calculated from Coughlin's data,[11] are 1.6×10^{-6} atm and 5.6×10^{-7} atm, respectively. From pressures, measured ion currents, and ionization cross sections given by Otvos and Stevenson,[13] an upper limit of 1.2×10^{-10} atm was calculated for the pressure of ZnO(g). From these partial pressures, from free energy functions for Zn(g) and $O_2(g)$ given by Stull and Sinke,[15] and from estimated free energy functions for ZnO(g) given by Brewer and Chandrasekharaiah,[16] a limiting dissociation energy of ZnO(g) was calculated to be $D^\circ_{298} < 66$ kcal.

The ion current of $Zn_2O^+(g)$ was estimated to be less than 5.2×10^{-12} at 1258 °K from the very low intensity of the mass 148 peak.

The pressures of Zn and O_2 calculated from Coughlin's data at this temperature were 2.0×10^{-6} atm and 7.0×10^{-7} atm, respectively, while the corresponding measured ion currents were 3.60×10^{-8} and 1.65×10^{-8}. From these data, an upper limit of 1.3×10^{-10} atm was calculated for the pressure of $Zn_2O(g)$.

From these partial pressures, free energy functions for Zn(g) and $O_2(g)$ given by Stull and Sinke,[15] and estimated free energy functions for $Zn_2O(g)$, a limiting dissociation energy for $Zn_2O(g)$ of $D^\circ_{298} < 127$ kcal was calculated.

The possibility of fragmentation of any zinc oxide molecules was considered, but when the ionizing electron voltage was lowered to 45, 40, and 20 V, ions corresponding to ZnO, Zn_2O, or to polymers of these molecules, were still not observed. Furthermore, agreement with in-equilibrium constants calculated from the Zn^+ and O_2^+ intensities with the predictions from independent thermodynamic data precluded the possibility that an appreciable fraction of the Zn^+ peak was a product of fragmentation.

2. <u>Zinc-Plus-Zinc Oxide Experiments</u>

Since the very high evaporation rates of zinc oxide reported by other investigators[3-5] were obtained when excess zinc vapor was present, and since two of these investigators hypothesized that the excess zinc vapor somehow catalyzed the evaporation of the zinc oxide, a mass spectrometric investigation of the zinc-plus-zinc oxide system appeared desirable. The very high vapor pressure of liquid zinc, as compared with that of zinc oxide, precludes the use of a mixture of zinc oxide and zinc metal. However, a zinc-gold alloy that has a partial pressure of zinc considerably lower than the pressure of zinc above liquid zinc can be used successfully.

A 60%-gold-40%-zinc alloy was prepared as follows: A 10-mm-i.d. quartz tube, containing 1.9522 g of zinc and 8.8230 g of gold, was evacuated and sealed. This sealed quartz tube was heated in a furnace at 850 °C for four hours, after which the tube was removed and the alloy was quenched.

For the mass spectrometer experiment, a quartz effusion cell 11/16-in i.d. and 3/4 in. deep, with two compartments, was used. One compartment was an open, cup-shaped, quartz crucible, 5/16-in i.d. and 1/4 in. deep, which was centered on the bottom of the effusion cell. This compartment contained a zinc oxide sample. The region between the center crucible and the walls of the effusion cell formed the second compartment, which held 1.11 g of the gold-zinc alloy. In the quartz lid of the effusion cell was a centered, cylindrical effusion orifice. The quartz effusion cell was contained in a tantalum crucible as described in Sec. III-A. Heating was done solely by radiation from the filaments.

Since the activity of zinc in this gold-zinc alloy can be obtained from available thermodynamic data for the alloy,[17] the pressure of zinc above the alloy at a given composition and temperature can be calculated. From a measurement of the ion current of Zn^+ from the alloy at a known temperature, the sensitivity of the mass spectrometer for zinc can be calculated. The Knudsen cell was heated initially to about 430 °C, at which temperature the mass-66 peak became sufficiently intense for an accurate measurement of the ion current to be made. That the alloy did not change composition significantly during the measurements was indicated by the fact that the ion current of Zn^{66+} remained constant for more than three hours. The temperature was then raised to 533 °C and another measurement of the Zn^{66+} ion current was made. The ion current was observed to decrease with time during this measurement, an

indication that the composition of the alloy was changing. The ionizing electron voltage was 70 V and the electron emission current 1.2 mA. These results are summarized in Table V.

The temperature was raised in steps to 986 °C. As the zinc evaporated, the composition of the alloy changed and the intensity of the Zn^{66+} peak decreased. When the temperature reached 956 °C, and the alloy became sufficiently depleted in zinc, the O_2^+ peak appeared. The variation of the ion current of O_2^+ with the ion current of Zn^+ is discussed more fully in Sec. V.

The calculations are summarized in Table VI for the partial pressures of zinc above the Au-Zn alloy of composition 40 mole % Zn, at the temperatures at which the mass spectrometer calibration measurements were made. The thermodynamic data given by Hultgren et al. were used in the calculations.[17] Since activity coefficients and partial molal free energies are known for the alloys only at 1048 °K, the calculation of the activity of Zn at 703 °K required some assumptions. For the process

$$Zn(\ell) = Zn\ (X_{Zn} = 0.4 \text{ in liquid alloy}),$$

the excess free energy is defined by the relation

$$\Delta\overline{F}_{Zn}^{Xs} = \Delta\overline{F}_{Zn} - RT\ \ell n\ X_{Zn} = RT\ \ell n\ \gamma_{Zn}\ ,$$

where $\Delta\overline{F}_{Zn}^{Xs}$ was assumed constant for the liquid from 1048 °K down to the temperature at which the activity was desired. For regular solutions, this assumption should be correct within experimental error; in the absence of enthalpy data, the regular solution approximation is the most reasonable one to apply. The liquidus temperature for the 40% zinc alloy lies at 950 °K.

Table V. Summary of mass spectrometric measurements on alloy composition 40 mole % Zn-60 mole % Au.

Temp (°K)	Electrometer sensitivity scale (V)	Mass No.	Peak height (divisions)	Background (divisions)	Net peak (divisions)	Ion current (x 10^8)
703	0.100	66	62.5	24.0	38.5	0.0385
704	0.030	33	75.0	65.5	9.5	0.00285
706	0.100	66	71.0	26.5	44.5	0.0445
705	0.030	33	73.5	62.5	11.0	0.00330
806	3.0	66	48.0	12.0	36.0	1.08
807	0.300	33	39.0	14.0	25.0	0.0750

Table VI. Summary of calculations for the equilibrium pressure of Zn above the Au-Zn alloy of composition $\bar{X}_{Zn} = 0.400$.

Temperature (°K)	Vapor pressure of pure zinc	Activity of zinc	Pressure of zinc over alloy
703	2.65×10^{-4}	1.06×10^{-3}	2.8×10^{-7}
704	2.73×10^{-4}	1.07×10^{-3}	2.9×10^{-7}
706	2.89×10^{-4}	1.09×10^{-3}	3.2×10^{-7}
705	2.80×10^{-4}	1.08×10^{-3}	3.0×10^{-7}
806	3.62×10^{-3}	2.8×10^{-3}	1.0×10^{-5}
807	3.73×10^{-3}	2.8×10^{-3}	1.0×10^{-5}

The entropy of fusion per gram atom was estimated to be 3 c.u. per gram atom. Then both ΔS_{fus} and ΔH_{fus} were assumed constant with temperature, and ΔF_{fus} at the desired temperature was calculated. $\Delta \bar{F}_{Zn}^{Xs}$ for the solid was then obtained. Since the excess free energy is, by definition,

$$\Delta \bar{F}_{Zn}^{Xs} = RT \ln \gamma_{Zn} ,$$

the activity of Zn in the alloy was thus known at the desired temperature.

The measured ion current is related to the pressure inside the Knudsen cell by

$$I^{+} = SP = S^{*} \frac{P}{T} , \qquad (8)$$

where S is the sensitivity as usually defined, and S^{*} is a constant independent of temperature. From a measurement of the ion current of a gaseous species at a known pressure and temperature, the constant S^{*} can be evaluated. The ion current measurements of Zn^{+} given in Table V were combined with the zinc pressures given in Table VII to obtain for S^{*} an average value of 3.50. The value given in Table V for $I_{Zn^{+}}$ at 806 °K was not used in this calculation, because the ion current was observed to decrease during that measurement. The pressure of Zn was calculated from each measurement of $I_{Zn^{+}}$ tabulated in Table VIII by means of Eq. (8).

From the measurements of the ion current for the mass-33 peak given in Table V, the ratios $I_{Zn^{66^{++}}}/I_{Zn^{66^{+}}}$ were calculated. The average value obtained for these ratios was 7.42×10^{-2}. This ratio was assumed to be constant, and the ion currents of $Zn^{64^{++}}$ were calculated from it by the relation

Table VII. Summary of pressure calculations from mass spectrometer data on the Zn + ZnO system.

Time	Temp (° K)	Gaseous species	I^+ (ion current) (x 10^8)	P (atm)	
0:0	849	Zn	7.12	1.73×10^{-5}	
4:48	991	Zn	19.0	5.40×10^{-5}	
7:35	1088	Zn	13.8	4.31×10^{-5}	
11:30	1185	Zn	0.809	2.74×10^{-6}	
11:55	1185	O_2	0.0		
12:50	1194	O_2	0.0		
13:31	1207	O_2	0.0		
13:55	1225	Zn	12.0	4.22×10^{-5}	
14:10	1229	O_2	0.0		
14:20	1229	O_2	0.022	1.8×10^{-7}	5.8×10^{-8}
14:30	1229	Zn	0.576	2.02×10^{-6}	
14:47	1229	O_2	0.043	3.5×10^{-7}	1.1×10^{-7}
15:10	1229	O_2	0.046	3.7×10^{-7}	1.2×10^{-7}
15:20	1230	Zn	0.396	1.39×10^{-6}	
16:00	1255	Zn	10.4	3.74×10^{-5}	
16:11	1257	O_2	0.0		
16:28	1257	O_2	0.189	1.57×10^{-6}	5.04×10^{-7}
16:35	1257	Zn	0.529	1.90×10^{-6}	
16:51	1258	O_2	0.281	2.33×10^{-6}	7.48×10^{-7}
17:01	1258	O_2	0.386	3.21×10^{-6}	1.03×10^{-6}
17:15	1258	Zn	0.518	1.86×10^{-6}	
17:31	1258	O_2	0.342	2.84×10^{-6}	9.12×10^{-7}
17:40	1258	O_2	0.357	2.96×10^{-6}	9.51×10^{-7}
17:55	1258	Zn	0.468	1.68×10^{-6}	
18:12	1259	Zn	0.400	1.44×10^{-6}	
18:50	1259	O_2	0.360	2.99×10^{-6}	9.61×10^{-7}

Table VIII. Summary of mass spectrometric data for the Zn + ZnO system.

Time	Temp (° K)	Electrometer sensitivity scale (V)	Mass No.	Peak height (divisions)	Background (divisions)	Net peak (divisions)	Ion current (x 10^8)
0:0	849	3.0	66	91.0	25.0	66.0	1.98
4:48	991	10.0	66	68.0	15.0	53.0	5.30
7:35	1088	10.0	66	47.0	8.5	38.5	3.85
7:45	1092	0.300	33	30.5	12.0	18.5	0.0556
11:30	1185	1.0	66	39.0	16.5	22.5	0.225
11:50	1185	0.100	33	42.5	28.5	14.0	0.014
11:55	1185	3.0	32	48.5	48.5	0.0	0.0
12:50	1194	3.0	32	48.5	48.5	0.0	0.0
13:31	1207	3.0	32	49.0	49.0	0.0	0.0
13:55	1225	10.0	66	38.5	5.0	33.5	3.35
14:10	1229	3.0	32	49.5	49.0	0.5	0.015
14:20	1229	3.0	32	51.0	49.5	1.5	0.045
14:30	1229	1.0	66	30.5	14.5	16.0	0.160
14:47	1229	3.0	32	54.0	52.0	2.0	0.060
15:03	1229	0.100	33	34.5	26.5	8.0	0.0080
15:10	1229	3.0	32	55.5	53.5	2.0	0.060
15:20	1230	1.0	66	24.5	13.5	11.0	0.110
16:00	1255	10.0	66	32.5	3.5	29.0	2.90
16:11	1257	3.0	32	50.0	49.0	1.0	0.030
16:22	1257	0.100	33	40.5	27.5	13.0	0.013
16:28	1257	3.0	32	64.5	57.5	7.0	0.210
16:35	1257	0.300	66	97.5	48.5	49.0	0.147
16:51	1258	3.0	32	70.5	60.5	10.0	0.300
17:01	1258	3.0	32	75.0	61.5	13.5	0.405
17:15	1258	0.300	66	96.0	48.0	48.0	0.144
17:31	1258	3.0	32	77.0	65.0	12.0	0.360
17:40	1258	3.0	32	77.0	64.5	12.5	0.375
17:55	1258	1.0	66	26.0	13.0	13.0	0.130
18:12	1259	0.300	66	81.0	44.0	37.0	0.111
18:50	1259	3.0	32	76.5	64.0	12.5	0.375

$$I_{Zn^{64^{++}}} = I_{Zn^{66^{+}}} (7.42 \times 10^{-2}) \left(\frac{0.489}{0.278}\right) . \qquad (9)$$

The ion currents for O_2^+ were obtained by subtraction of the $Zn^{64^{++}}$ ion currents calculated by Eq. (9) from the ion currents given in Table VIII for the mass-32 peak. The pressures of O_2 were then calculated from the O_2^+ ion currents by Eq. (6). Results of the pressure calculations are summarized in Table VII.

No gaseous zinc oxide molecules of any kind were detected. From measurements of the background intensities at mass 80 and mass 148, upper limits for the pressure of ZnO(g) and Zn_2O(g) were calculated. A summary of the data appears in Table IX.

IV. TRANSPORT STUDIES

A. Apparatus and Procedure

The Knudsen effusion experiments and the mass spectrometric investigation indicated that zinc oxide vaporized by dissociation to zinc atoms, and oxygen molecules at rates to be expected from the known thermodynamic data. Re-examination of the influence of zinc vapor on zinc oxide in a tube furnace seemed necessary to reveal the cause of the earlier, anomalous tube furnace results.

The experimental apparatus was deliberately designed to be similar to that used by Moore and Williams,[3] and by Pillay.[5] Polycrystalline zinc oxide from the same lot of material used in the Knudsen and mass spectrometric studies was pressed into disks 1/2 in. in diameter and 1/10 in. thick. Three of these disks were placed in a previously degassed alumina boat which, in turn, was placed in a horizontal mullite tube of a resistance furnace. The mullite tube was 1-in. i.d. with a 1/8-in. wall thickness. The alumina boat, 1-1/2 in. long, 7/8 in. wide

Table IX. Calculation of limits for P_{ZnO} and P_{Zn_2O}.

Temp (° K)	I_{Zn}^+ (x 10_8)	P_{Zn}	$I_{Zn_2O}^+$ (ion current)	P_{Zn_2O}	I_{ZnO}^+ (ion current)	P_{ZnO}
1185	0.907	3.07×10^{-6}	$<11.6 \times 10^{-12}$	$<1.8 \times 10^{-9}$		
1185	0.860	2.91×10^{-6}			$<2.04 \times 10^{-11}$	$<5.7 \times 10^{-9}$
1151	0.919	3.02×10^{-6}	$<11.6 \times 10^{-12}$	$<1.7 \times 10^{-9}$		
1151	0.919	3.02×10^{-6}			$<2.04 \times 10^{-11}$	$<5.6 \times 10^{-9}$
1123	1.27	4.08×10^{-6}			$<1.84 \times 10^{-11}$	$<4.9 \times 10^{-9}$
997	1.67	4.77×10^{-6}	$<17.4 \times 10^{-12}$	$<2.25 \times 10^{-9}$		

and 1/4 in. deep, held the zinc oxide disks at midpoint between the top and bottom of the mullite tube. To one end of the mullite tube a ground glass joint was sealed. A rubber stopper, through which a gas outlet tube and a porcelain thermocouple protection tube were sealed, was placed in the other end.

Helium obtained from the U.S. Bureau of Mines was used as the carrier gas. The analysis furnished by the supplier showed no oxygen and a dew point of -60°C. Helium from the cylinder was first passed through a $Mg(ClO_4)_2$ drying tube, then through a quartz tube filled with copper turnings at 450°C. The gas was then passed through a variable-area flowmeter (made by Fischer and Porter Company). A liquid nitrogen cold trap was located between the flowmeter and the furnace tube to remove any remaining condensable gases.

Four experiments were performed in this tube furnace. In the first experiment, the alumina boat containing the zinc oxide disks was placed in the end of the mullite tube. The furnace was heated to the desired temperature, during which time it was purged with helium. When the desired furnace temperature was obtained, the alumina boat was pushed into the center of the hot zone by the porcelain thermocouple protection tube No. 2.

The evaporation rate of zinc oxide in the presence of flowing zinc vapor was determined. The procedure was the same as that just described, except that as soon as the alumina boat had been pushed to the center of the heated tube, the ground-glass joint was unsealed and an aluminum oxide crucible containing some zinc metal was placed in the cool region of the mullite tube near the ground-glass joint. The joint was immediately resealed, and after the system had been flushed with helium for an hour,

the crucible containing the zinc was slowly pushed into the hotter position of the mullite tube by the porcelain thermocouple protection tube. The thermocouple inside this protection tube was used to monitor the temperature of the zinc. The flow rate of zinc vapor was, thus, controlled by the temperature of the zinc metal and the rate of helium flow through the tube. The approximate flow rate of zinc vapor was calculated from the weight loss of the alumina crucible containing zinc, in the known time of heating.

The zinc metal (purity at least 99.999%) used in this experiment was obtained from Johnson-Matthey Company. Since any dissolved hydrogen in the zinc could reduce the zinc oxide and cause an unexpectedly high weight loss of zinc oxide, the zinc metal used for this experiment was first melted under vacuum in the open alumina crucible used to contain the zinc in the tube furnace. Residual pressure in the vacuum system was less than 1×10^{-5} mm.

Two tube furnace experiments were performed in which the zinc metal was replaced by iron wire (analytical grade). Iron has a negligible vapor pressure at the temperature at which it was heated (approximately 600°C).

A new mullite furnace tube and new porcelain thermocouple protection tubes were used for these experiments to ensure that zinc from the previous experiments would not affect the results. The procedure then followed was the same as that used in the experiment with zinc metal, except that no container was used for the iron. The iron wire was handled only with rubber gloves or forceps. The wire was wound into a small wad, inserted into the end of the mullite tube, and pushed into the hotter portion of the furnace tube by thermocouple protection

tube No. 2, and the temperature of the iron was monitored with thermocouple No. 2. In the third and fourth experiments 14.6955 and 18.0330 g of iron were used, respectively. All weighings for these tube furnace experiments were performed on a balance accurate to ±0.2 mg.

B. Results

The results of these experiments are given in Table X. The rates of weight loss of the zinc oxide sample are given in column 8. In column 9 are given the rates of weight loss of the zinc oxide calculated from thermodynamic data on the basis that zinc oxide evaporates by dissociation to zinc atoms and oxygen molecules.

V. DISCUSSION

Equilibrium constants for sublimation of zinc oxide to zinc gas and oxygen gas were calculated from Knudsen weight-loss experiments in quartz effusion cells, and are plotted vs 1/T in Fig. 2. Points are labeled by run numbers in boths Figs. 1 and 2 to indicate the sequence in which the points were obtained. Equilibrium constants calculated from measurements made with quartz cell I were lower than the constants calculated from Coughlin's data.[11] Furthermore, the constants decreased after each high temperature experiment, i.e., after experiments 11 and 15. The sample was stirred before experiment 22 was made, but stirring had little effect on the apparent pressure. Since this behavior was not observed with the aluminum oxide effusion cell (Fig. 1), some kind of interaction between the cell and the sample appeared responsible. To determine whether the quartz or the alumina was causing the strange behavior, aluminum oxide was mixed with the zinc oxide in quartz cell I, and experiments 30 and 31 were performed. The apparent equilibrium

Table X. Summary of tube furnace experiments.

System studied	Time (hr)	Temp (° C)	He flow rate (cm^3/min)	Wt. of Zn transported (g)	P_{Zn}	Wt. loss of ZnO (mg)	Wt. loss of ZnO (g/hr)	Calc. rate of loss of ZnO (g/hr)
ZnO	44.4	1056	77.0	-	-	3.8	8.56×10^{-5}	1.31×10^{-4}
ZnO + Zn	19.97	1019	64.8	3.0046	1.45×10^{-2}	387.6	1.94×10^{-2}	3.7×10^{-12}
ZnO + Fe	22.8	1019	75.8	-	-	128.7	5.64×10^{-3}	5.79×10^{-5}
ZnO + Fe	26.3	1006	65.2	-	-	152.8	5.81×10^{-3}	3.72×10^{-5}

constants calculated from these two experiments continued to decrease. This fact implies that alumina has no effect on the zinc oxide evaporation.

Next, some particles of fused quartz were mixed with the zinc oxide sample in the alumina cell. The apparent equilibrium constants calculated from experiments 32, 34, 35, and 36, made after this addition, are lower than the constants calculated from measurements made with zinc oxide in alumina in the absence of silica (Fig. 1).

X-ray diffraction showed no evidence of phases other than zinc oxide in the sample after long heating in silica, but silica must, in some manner, reduce the evaporation rate of zinc oxide. Although the partial pressures of SiO_2(g) and SiO(g) are both less than 10^{-11} atm at the highest temperature used in these experiments, apparently the surface of the zinc oxide acquired a coating by either vapor deposition or surface diffusion, which lowered the evaporation rate of the zinc oxide. Surface diffusion is the more probable source of transport of silica, because surface diffusion is known to change catalytic activity at concentrations well below those at which bulk reactions occur.

If the hypothesis that silica reduces the rate of evaporation of zinc oxide is correct, an increase in the ratio of sample surface area $\underline{A}$ to orifice area $\underline{a}$ might allow equilibrium to be attained in quartz cells. Quartz cell III was designed to have an A/a ratio 48 times as great as that in cell I. Because small amounts of condensate of zinc oxide were deposited in the effusion channel of quartz cell III during the experiments, we estimate the total uncertainty in the equilibrium constant may be as high as 19%. The apparent equilibrium constants calculated from the five experiments made with quartz cell III certainly agree well with the constants calculated from Coughlin's data. The conclusion from the

alumina cell data, that the weight loss for zinc oxide is described by the reaction

$$ZnO(s) = Zn(g) + \frac{1}{2} O_2(g),$$

is therefore supported by the study with the quartz cell having a small ratio of orifice area to sample area.

As discussed in Sec. III-B, the partial pressures of zinc above the zinc-plus-zinc oxide systems were calculated from the measured ion currents by means of a calibration of the I_{Zn^+} from an alloy of known composition. The relative ionization cross section 1.28 for oxygen was then used to calculate the oxygen partial pressures from oxygen ion intensities. When the alloy was first heated in the spectrometer, only zinc ion intensities were detected. However, as the zinc vaporized from the alloy, the composition changed, the ion current of Zn^+ decreased, and the ion current of oxygen became detectable. Measurements of corresponding zinc and oxygen intensities at successively lower zinc concentrations and successively higher temperatures are summarized in Table XI. In column 4 are given the equilibrium constants calculated from the pressures for the dissociation reaction

$$ZnO(s) = Zn(g) + \frac{1}{2} O_2(g). \tag{10}$$

The equilibrium constants calculated from Coughlin's data for the reaction are given in column 5. For experiments of this type, the agreement between columns 4 and 5 is excellent. Pressures calculated from mass spectrometer ion currents are usually estimated to be correct to within only a factor of 2.

Although Pillay, in his tube furnace experiments, used zinc partial pressures between 10^{-1} and 10^{-3} atm,[5] such high zinc pressures

Table XI. Equilibrium constants for the vaporization reaction $ZnO(s) = Zn(g) + \frac{1}{2} O_2(g)$.

T (° K)	P_{Zn}	P_{O_2}	K'	K eq.
1229	1.39×10^{-6}	1.2×10^{-7}	4.8×10^{-10}	6.0×10^{-10}
1229	2.02×10^{-6}	1.1×10^{-7}	6.7×10^{-10}	6.0×10^{-10}
1259	1.44×10^{-6}	9.61×10^{-7}	1.4×10^{-9}	1.7×10^{-9}
1258	1.68×10^{-6}	9.51×10^{-7}	1.6×10^{-9}	1.7×10^{-9}
1258	1.86×10^{-6}	9.12×10^{-7}	1.8×10^{-9}	1.7×10^{-9}
1258	1.90×10^{-6}	7.48×10^{-7}	1.6×10^{-9}	1.7×10^{-9}
1257	1.90×10^{-6}	5.04×10^{-7}	1.5×10^{-9}	1.6×10^{-9}

could not be used in our mass spectrometer experiments. The highest zinc partial pressure which was measured in the spectrometer for the zinc-plus-zinc oxide systems was 5×10^{-5} atm. However, Pillay found no variation of the evaporation rate of zinc oxide with the partial pressure of zinc in the system. Since our mass spectrometric study of zinc-plus-zinc oxide did not reveal any gaseous zinc oxide molecules such as ZnO, ZnO_2, Zn_2O, or polymers thereof, and since the zinc and oxygen partial pressures were observed to vary in accordance with the thermodynamic equilibrium constant over the pressure range 1229°K through 1259°K, in order to attribute the high rate of evaporation of zinc oxide, obtained by other investigators,[3-5] to some effect of zinc vapor upon zinc oxide, one would have to assume the partial pressures vary as predicted by the equilibrium constant over a low-pressure range, but are higher than the equilibrium values when zinc pressures are high. Since such a hypothesis is a violation of the laws of thermodynamics, an explanation was sought elsewhere.

The explanation of the conflicting data reported by other investigators was revealed by our tube furnace experiments. The tube furnace and procedure were deliberately similar to those used by Pillay,[5] and Williams.[3] The evaporation rate of zinc oxide in an atmosphere of flowing helium (Table X) was, within the limits of uncertainty, equal to the value calculated from the equilibrium constant for the dissociation reaction (Eq. 10). In the presence of zinc vapor, the apparent rate of evaporation of zinc oxide in our tube furnace was increased, just as reported by Williams and by Pillay. One possible explanation, first suggested by D. D. Cubicciotti,[18] remained to be tested. This was that, despite the traps, water vapor was present in the tube furnaces in sufficient concentration to produce the observed zinc oxide volatilization. The reaction

sequence could be

$$Zn(\ell) + H_2O(g) \overset{800\,^\circ K}{=} ZnO(s) + H_2(g) ,$$

and

$$H_2(g) + ZnO(s) \overset{1273\,^\circ K}{=} Zn(g) + H_2O(g) .$$

Our calculations showed that if water vapor were present this set of reactions could produce the observed behavior, and so could the corresponding equilibrium involving CO_2 and CO. To test the possibility that water or CO_2 caused the observed behavior, iron wire was substituted for liquid zinc. Iron has negligible volatility at the temperature of our experiments, but can reduce water to hydrogen and carbon dioxide to carbon monoxide. The evaporation rates of zinc oxide obtained when iron wire was heated in the gas stream were comparable to those obtained when zinc had been present. Furthermore, after each experiment the iron wire was severely oxidized. The oxidation of the iron, together with the high evaporation rate of zinc oxide when iron was present, demonstrates that the weight loss of zinc oxide was caused by the presence of water vapor and/or carbon dioxide in the helium gas streams. The contamination may have resulted from degassing of the furnace parts.

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