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ABSTRACT

The sublimation 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 a gold-zinc alloy with zinc oxide, and (c) transpiration measurements in streams of helium and zinc vapors. Zinc oxide was found to sublime congruently by dissociation to zinc atoms and oxygen molecules only. Limits for the dissociation energies of ZnO(g) and $\text{Zn}_2\text{O(g)}$ are calculated to be $D_{298}^\circ(\text{ZnO}) \leq 66 \text{ kcal}$ and $D_{298}^\circ(\text{Zn}_2\text{O}) \leq 127 \text{ kcal}$. The probable source of the high transport rate reported in the literature for zinc oxide in zinc vapor is shown to be 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.

INTRODUCTION

After examining the data available in 1951, Brewer and Mastick¹ concluded that under neutral conditions zinc oxide sublimes congruently by decomposition to the gaseous elements according to the reaction

Brewer calculated a limit for the heat of dissociation of ZnO(g) to the gaseous atoms of $\Delta H^\circ_0 < 92$ kcal/mole.²

Moore and Williams measured the rate of sublimation of zinc oxide in atmospheres of oxygen, nitrogen, and zinc gas by a transport method.³ The sublimation rates which they obtained in streams of oxygen and nitrogen are in general agreement with the rates calculated from the thermodynamic data for reaction 1. However, the sublimation rates which they measured in an atmosphere of zinc vapor were 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 equilibrium constant for reaction 1. Moore and Williams hypothesized that the zinc vapor somehow catalyzed the decomposition of zinc oxide.

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

Pillay reinvestigated the rate of sublimation of zinc oxide by the transport method in atmospheres of helium and zinc⁵ and obtained results in essential agreement with those of Moore and Williams.

Moore and Williams quote Inghram and Drowart as reporting that no gaseous zinc oxide molecules are present in zinc oxide vapor that could account for the reported rates of vaporization that far exceed the maximum rates calculated by application of the Langmuir equation to thermodynamic data for reaction 1. The tentative explanations of the high sublimation rates given by Moore and Williams and by Secco both amount to proposals that decomposition of unstable intermediate reaction products yields higher concentrations of zinc and oxygen vapors than calculated for reaction 1. Both proposals require, therefore, the assumption that the equilibrium for reaction 1 can be shifted by catalysis. Such proposals are at variance with accepted theory and with the preponderance of experimental evidence. Further study that might yield a more acceptable explanation of the anomalous sublimation behavior appeared essential.

The present paper reports results of (a) Knudsen effusion measurements of the sublimation pressure of zinc oxide, (b) a mass spectrometric investigation of zinc oxide vapor under neutral and reducing conditions, and (c) new transport measurements.

KNUDSEN EFFUSION STUDIES

Method and Experimental Procedure

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 vapor has the same overall composition as the solid, i.e., the solid sublimes congruently. At 1000°C the composition of solid zinc oxide has been shown to differ from the stoichiometric composition by less than 10^{-2} at.% when the

gas with which the solid is held in contact is varied in composition from pure oxygen at 1 atm pressure to pure zinc vapor at 1 atm pressure.⁶

Zinc oxide was shown in the mass spectrometric study to sublime to zinc atoms and oxygen molecules only. Since the ratio of zinc atoms to oxygen molecules in the vapor beam must therefore be 2/1, the partial pressures of oxygen and zinc in equilibrium with zinc oxide can be calculated from Knudsen weight-loss determinations, and these partial pressures can be compared with those calculated from the available thermodynamic data for reaction 1.

Zinc oxide from Johnson-Matthey Company was used in all the experiments. Spectrographic examination showed 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 silica effusion cells were used. Each cell was degassed until the weight loss of the empty cell became less than 0.02 mg during a 10-hour heating. The cells were weighed on an Ainsworth semimicrobalance with a reproducibility of 0.01 to 0.02 mg.

The alumina effusion cell was a crucible 1.3 cm i.d. by 1.8 cm deep, which was fitted with an alumina lid which had a centered, cylindrical effusion orifice. This cell was contained in a tantalum cell 2.3 cm i.d. by 2.2 cm deep, with a tantalum lid in which a centered 0.5 cm-diam hole had been drilled. The tantalum cell was in turn contained in an open graphite crucible. The alumina cell was separated from the top and bottom of the tantalum crucible by rings made of 20-mil tungsten wire and from the side walls of the crucible by a 0.3-cm gap.

In four experiments, an alumina plug was placed in the orifice of the effusion cell, and in one experiment a lid with no effusion orifice was used. The results are discussed in the next section.

Two silica cells had the same dimensions as the alumina cell. A third silica cell was 2.1 cm i.d. by 2.1 cm deep. The lid of each cell was fused to its crucible to obtain a gas-tight seal. The silica cells were heated in an assembly similar to that used for the alumina cell.

The effusion cell assembly was heated in a glass vacuum system by a 500-kc induction unit. During each experiment, the residual pressure inside the vacuum system was maintained below 1×10^{-5} Torr by means of an oil diffusion pump and liquid nitrogen trap. Temperatures were measured with a calibrated optical pyrometer focused on the cell orifice through a window of known transmissivity.

No weight change was observed when an effusion cell that contained a sample of zinc oxide was exposed to air. However, to reduce to a minimum any possible pick-up of moisture by the finely divided sample, the cell was allowed to cool 10 hours under high vacuum. Air, dried by passage over $\text{Mg}(\text{ClO}_4)_2$ 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. Weight changes of samples stored for two days were within the reproducibility of the balance. Additional descriptions of equipment and procedure have been given by Searcy and McNees.⁷

Results

Data obtained with the alumina cell are summarized in Table I. The weight losses given in column 3 have been reduced by 23.2% to correct

Table I. ZnO vapor pressure measurements in Al_2O_3 cell.

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

^aCorrected for thermal expansion. The Clausing factor⁸, was 0.2550 for the first 7 experiments and 0.2557 for the remaining 4.

for the observed weight losses when zinc oxide was heated in a cell with no effusion orifice or with a plugged orifice.

Pressures inside a cell can be calculated from the weight loss through an orifice by means of the Knudsen equation⁹ when account is taken of the fact that the partial pressures of Zn and O₂ inside the cell are related by

$$P_{\text{Zn}} = 2 P_{\text{O}_2} (M_{\text{Zn}}/M_{\text{O}_2})^{1/2}, \quad (2)$$

where M_{Zn} and M_{O_2} are the molecular weights of Zn and O₂. The calculated equilibrium constants are recorded in column 5 of Table I and plotted as functions of $1/T$ in Fig. 1. The last four measurements were made with particles of silica mixed with the zinc oxide sample. The reason for these four experiments, and the interpretation of the results, is presented in the discussion section.

The apparent equilibrium constants obtained from the three silica effusion cells are plotted vs $1/T$ in Fig. 2, together with an equilibrium line from thermochemical data.¹⁰ Nine measurements shown in Fig. 2 were made with the first silica cell. Five measurements were made with the second cell, and five measurements with the third. For the final two measurements, some crystals of alumina were mixed with the zinc oxide sample. The alumina crystals were very pure sapphire from the Aluminum Company of America.

MASS SPECTROMETRIC INVESTIGATION

Equipment and Procedure

A Nuclide Analysis Associates high temperature mass spectrometer was used to determine the vapor species in equilibrium with solid.

MUR-1760

Fig. 1

MUB:1761

Fig. 2

zinc oxide. Cells from the weight-loss studies served as the beam sources. A cell was nested inside a tantalum crucible fitted with a tantalum lid having a centered hole of larger diameter than the Knudsen cell orifice. Radiation from two tungsten filaments was used to produce cell temperatures up to 1000°C. Electron bombardment heating was necessary to obtain higher temperatures. Pressures between 1×10^{-7} and 7×10^{-7} Torr were maintained in the crucible region, and lower pressures were maintained in the analyzer region.

The temperature of the Knudsen cell was measured by a platinum, platinum-10%-rhodium thermocouple which was inserted in a recess drilled in the bottom of the tantalum crucible.

Results of Zinc Oxide Experiments

The three most abundant isotopes of zinc have mass numbers 64, 66, and 68 and relative abundances 0.489, 0.278, and 0.186, respectively. When zinc atoms are subjected to 70-volt-electron impact, some zinc atoms become doubly ionized. Since the mass-to-charge ratios of Zn^{64++} and O_2^{16+} are the same, the presence 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 32, were measured at each temperature. From a measurement of the Zn^{66+} ion current, the total ion current of Zn can be calculated from the relation $\text{I}_{\text{Zn}+} = \text{I}_{\text{Zn}^{66+}}/0.278$. The $\text{I}_{\text{Zn}^{66++}}/\text{I}_{\text{Zn}^{66+}}$ ratio was measured and assumed to be identical to the $\text{I}_{\text{Zn}^{64++}}/\text{I}_{\text{Zn}^{64+}}$ ratio in correcting the measurements at mass 32 for doubly ionized zinc.

As discussed by Searcy, Williams, and Schissel, systems that sublime congruently can be used to calculate relative ionization cross sections.¹¹

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. The Knudsen weight-loss measurements demonstrated that the zinc and oxygen pressures are related by Eq. (2). The ratio of the current-production efficiency measured in alumina cells was calculated to be 0.96 with an average deviation for two runs of about 0.04. The average of five runs in silica cells was 1.41 with an average deviation of 0.14. The relative ionization cross section calculated from the relationship given by Otvos and Stevenson is 0.411.¹² The difference in current production efficiency for measurements made in the two cells probably reflects some reaction of the oxygen of the beam from the alumina cell, which leaked, with tantalum of the collimating system. 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, to what extent it is due to differences in dynode response, and to what extent to selective reactions of the beam components with the tantalum collimators. For calculation of pressures from current intensities, determination of the rate of effusion from the cells by means of the weight-loss experiments coupled with knowledge that the oxide sublimes congruently at a Zn/O₂ molecule ratio of 2/1 allows calibration of the spectrometer intensities vs pressures for Zn and O₂ with an uncertainty of less than 20%.

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. From known pressures for Zn and O_2 , measured ion currents, and ionization cross sections given by Otvos and Stevenson,¹² 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 $\text{O}_2(\text{g})$ given by Stull and Sinke,¹³ and from estimated free energy functions for ZnO(g) given by Brewer and Chandrasekharaiah,¹⁴ a limiting dissociation energy of ZnO(g) was calculated to be $D_{298}^\circ < 66$ kcal.

The ion current of Zn_2O^+ was estimated to be less than 5.2×10^{-12} at 1258°K from the very low intensity of the mass 148 peak. The Zn and O_2 ion currents were 3.60×10^{-8} and 1.65×10^{-8} . An upper limit of 1.3×10^{-10} atm was calculated for the pressure of $\text{Zn}_2\text{O(g)}$.

From these partial pressures, free energy functions for Zn(g) and $\text{O}_2(\text{g})$ given by Stull and Sinke,¹³ and estimated free energy functions for $\text{Zn}_2\text{O(g)}$, a limiting dissociation energy for $\text{Zn}_2\text{O(g)}$ of $D_{298}^\circ < 127$ kcal was calculated. Free energy functions for $\text{Zn}_2\text{O(g)}$ were estimated to be identical with the functions by Cochran and Foster for Ga_2O .¹⁵

Gold-Zinc Alloy Plus Zinc Oxide Experiments

Since the very high sublimation rates of zinc oxide reported by other investigators³⁻⁵ 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 zinc 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 reduced zinc activity can be used successfully.

A 60%-gold-40%-zinc alloy was prepared as follows: A 1.0 cm i.d. silica tube, containing 1.9522 g of zinc and 8.8230 g of gold, was evacuated and sealed. This sealed tube was heated in a furnace at 1123°K for four hours, was removed, and was quenched.

For the mass spectrometer experiment, a silica effusion cell 1.7 cm i.d. and 1.9 cm deep, with two compartments, was used. One compartment was an open, cup-shaped crucible, 0.8 cm i.d. and 0.6 cm 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 lid of the effusion cell was a centered, cylindrical effusion orifice. The silica cell was contained in a tantalum crucible which was heated by radiation from the filaments.

The pressure of zinc above the alloy at a given composition and temperature can be calculated from thermodynamic data for the alloy.¹⁶ 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. At 703°K 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 at 703°K was indicated by the fact that the ion current of Zn^{66+} remained constant for more than three hours. When the temperature was raised to 806°K the Zn^{66+} ion current decreased with time of the measurement, an indication that the composition of the alloy was changing.

The temperature was raised in steps to 1229°K. The alloy was by this time depleted in zinc, and the O_2^+ peak appeared. The subsequent variations of the ion current of O_2^+ with the ion current of Zn^+ were followed until the ion ratios reached the ratio characteristic of the congruently subliming oxide.

Results and Calculations

Thermodynamic data given by Hultgren et al.¹⁶ were used to calculate the partial pressure of zinc at 703°K. The current-production efficiency at mass 66 was then calculated from this pressure and from the measured current intensity. Activity coefficients and partial molal free energies are known for the alloy only at 1048°K. The regular solution approximation was used for both the solid and liquid alloy to calculate the activity of Zn at 703°K. The liquidus temperature for the 40% zinc alloy lies at 950°K. The entropy of fusion per gram atom of alloy was estimated to be 3 e.u., and both ΔS_{fus} and ΔH_{fus} were assumed constant with temperature. The calculation led to $P_{\text{Zn}} = 2.8 \times 10^{-7}$ for the 40% zinc alloy at 703°K.

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

$$I^+ = SP = S^* \frac{P}{T}, \quad (3)$$

where S is the sensitivity as usually defined, and S^* is a constant independent of temperature. From I^+ and P at 703°K , S^* was calculated to be 3.50. As the temperature was subsequently raised and the composition of the alloy changed, the pressure of Zn was calculated from each measurement of I_{Zn^+} by means of Eq. (3).

From the measurements of the ion current for the mass-33 peak made during the calibration with the alloy at 703°K , the ratios $I_{\text{Zn}66^{++}}/I_{\text{Zn}66^+}$ were evaluated as 7.42×10^{-2} . Ion currents for O_2^+ were calculated from the total intensity measured at mass 32 by the method previously described. Results of the pressure calculations are summarized in Table II. Equilibrium constants calculated from these pressure determinations are summarized in Table III.

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 $\text{Zn}_2\text{O(g)}$ were calculated. At 1151°K the pressure of Zn(g) calculated from the measured ion current was 3.02×10^{-6} atm. The upper limits for the pressures of ZnO(g) and $\text{Zn}_2\text{O(g)}$ were 5.6×10^{-9} and 1.7×10^{-9} atm, respectively.

TRANSPORT STUDIES

Apparatus and Procedure

The Knudsen effusion experiments and the mass spectrometric investigation indicated that zinc oxide sublimes by dissociation to zinc atoms,

Table II. 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 x 10 ⁻⁵
4:48	991	Zn	19.0	5.40 x 10 ⁻⁵
7:35	1088	Zn	13.8	4.31 x 10 ⁻⁵
11:30	1185	Zn	0.809	2.74 x 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 x 10 ⁻⁵
14:10	1229	O ₂	0.0	
14:20	1229	O ₂	0.022	5.8 x 10 ⁻⁸
14:30	1229	Zn	0.576	2.02 x 10 ⁻⁶
14:47	1229	O ₂	0.043	1.1 x 10 ⁻⁷
15:10	1229	O ₂	0.046	1.2 x 10 ⁻⁷
15:20	1230	Zn	0.396	1.39 x 10 ⁻⁶
16:00	1255	Zn	10.4	3.74 x 10 ⁻⁵
16:11	1257	O ₂	0.0	
16:28	1257	O ₂	0.189	5.04 x 10 ⁻⁷
16:35	1257	Zn	0.529	1.90 x 10 ⁻⁶
16:51	1258	O ₂	0.281	7.48 x 10 ⁻⁷
17:01	1258	O ₂	0.386	1.03 x 10 ⁻⁶
17:15	1258	Zn	0.518	1.86 x 10 ⁻⁶
17:31	1258	O ₂	0.342	9.12 x 10 ⁻⁷
17:40	1258	O ₂	0.357	9.51 x 10 ⁻⁷
17:55	1258	Zn	0.468	1.68 x 10 ⁻⁶
18:12	1259	Zn	0.400	1.44 x 10 ⁻⁶
18:50	1259	O ₂	0.360	9.61 x 10 ⁻⁷

Table III. Equilibrium constants for the vaporization reaction

T (°K)	P _{Zn} (atm)	P _{O₂} (atm)	K' (From measured pressures)	K eq. (From thermo-dynamic data ¹⁰)
1229	1.39 x 10 ⁻⁶	1.2 x 10 ⁻⁷	4.8 x 10 ⁻¹⁰	6.0 x 10 ⁻¹⁰
1229	2.02 x 10 ⁻⁶	1.1 x 10 ⁻⁷	6.7 x 10 ⁻¹⁰	6.0 x 10 ⁻¹⁰
1259	1.44 x 10 ⁻⁶	9.61 x 10 ⁻⁷	1.4 x 10 ⁻⁹	1.7 x 10 ⁻⁹
1258	1.68 x 10 ⁻⁶	9.51 x 10 ⁻⁷	1.6 x 10 ⁻⁹	1.7 x 10 ⁻⁹
1258	1.86 x 10 ⁻⁶	9.12 x 10 ⁻⁷	1.8 x 10 ⁻⁹	1.7 x 10 ⁻⁹
1258	1.90 x 10 ⁻⁶	7.48 x 10 ⁻⁷	1.6 x 10 ⁻⁹	1.7 x 10 ⁻⁹
1257	1.90 x 10 ⁻⁶	5.04 x 10 ⁻⁷	1.5 x 10 ⁻⁹	1.6 x 10 ⁻⁹

and oxygen molecules at rates to be expected from the known thermodynamic data. Re-examination of the influence of zinc vapor on zinc oxide sublimation 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 Williams³ and by Pillay.⁵ Zinc oxide powder was pressed into disks 1.3 cm in diam and 0.3 cm thick. Three of these disks were placed in a degassed alumina boat which, in turn, was placed in a horizontal mullite tube in a resistance furnace. The tube was 2.5 cm i.d. with a 0.3 cm wall thickness. The boat was 3.8 cm long, 2.2 cm wide, and 0.6 cm deep. To one end of the tube a ground-glass joint was sealed. To this joint were sealed a gas inlet tube and a thermocouple protection tube. A rubber stopper, through which a gas outlet tube and a porcelain thermocouple protection tube were introduced, was placed in the other end.

Helium obtained from the U. S. Bureau of Mines was the carrier gas. The analysis furnished by the supplier showed no oxygen and a dew point of -60°C . The helium passed in sequence through a $\text{Mg}(\text{ClO}_4)_2$ drying tube, a silica tube filled with copper turnings at 450°C , a variable-area flowmeter, and a liquid nitrogen cold trap before entering the furnace tube.

In an initial experiment, the boat containing the disks was placed in the gas inlet end of the tube. A helium flow was maintained while the furnace was heated to 1056°C . The boat was then pushed with the thermocouple protection tube into the center of the hot zone.

For determination of the sublimation rate of zinc oxide in excess zinc vapor the procedure was the same as that just described, except

that as soon as the 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 tube near the 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 a hotter section of the tube by the thermocouple protection tube. The thermocouple inside this protection tube was used to monitor the temperature of the zinc. 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. Upon heating, any hydrogen that might be dissolved in the zinc might be evolved and react with the zinc oxide to yield water vapor and zinc gas. Accordingly, the zinc metal was melted in an open alumina crucible at a pressure of less than 10^{-5} Torr prior to use. This procedure should reduce the hydrogen content to a negligible level.

For two experiments the zinc was replaced in the tube furnace by iron wire (analytical grade). Iron has a negligible vapor pressure at the temperature to which it was heated (approximately 600°C). A new furnace tube and a new thermocouple protection tube were used for these experiments to ensure that zinc from the previous experiments would not affect the results.

The iron wire (which was handled only with rubber gloves or forceps) was wound into a small wad, inserted into the inlet end of the mullite tube, and pushed into the hotter portion of the tube by thermocouple protection tube.

The results of these experiments are given in Table IV. The rates of loss of the zinc oxide sample are given in column 8. In column 9 are given the rates of loss of the zinc oxide calculated on the assumption that zinc oxide sublimes by dissociation to zinc atoms and oxygen molecules.

DISCUSSION

Points in both Figs. 1 and 2 are labeled by run numbers to indicate the sequence of experiments in the Knudsen weight-loss studies. Equilibrium constants calculated from measurements made with silica cell I were lower than the constants calculated from Coughlin's data.¹⁰ Furthermore, the calculated 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 alumina effusion cell (Fig. 1), some kind of interaction between one kind of cell and zinc oxide appeared responsible. To determine whether the silica or the alumina caused the strange behavior, alumina powder was mixed with the zinc oxide in silica cell I, and experiments 30 and 31 were performed. The apparent equilibrium 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 silica were mixed with the zinc oxide sample in the alumina cell. The apparent equilibrium constants measured after this addition (experiments 32, 34, 35, and 36) are lower than the constants measured in runs in which zinc oxide was exposed to alumina only (Fig. 1).

Table IV. 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)	Rate of measured loss of ZnO (g/hr)	Rate of loss of ZnO expected for reaction 1 (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}

X-ray diffraction showed no evidence of reaction products. Perhaps the surface of the zinc oxide acquired a coating of silica, which lowered the sublimation rate of the zinc oxide. Surface diffusion is the probable mechanism of such transport because surface diffusion is known to change catalytic activity at concentrations well below those at which bulk reactions occur,¹⁷ and the partial pressures of $\text{SiO}_2(\text{g})$ and $\text{SiO}(\text{g})$ were both less than 10^{-11} atm, too low for significant vapor transport.

If the hypothesis that silica reduces the rate of sublimation of zinc oxide is correct, an increase in the ratio of sample surface area A to orifice area a might allow equilibrium to be attained in fused silica cells. Silica cell III was designed to have an A/a ratio 48 times as great as that in cell I. Small amounts of condensate of zinc oxide were deposited in the effusion channel of silica cell III during the experiments, and we estimate the total uncertainty in the equilibrium constant may be as high as 19%. However, the apparent equilibrium constants calculated from experiments made with cell III clearly agree well with constants calculated for the alumina cell, and with constants calculated for reaction 1, dissociation to $\text{Zn}(\text{g})$ plus $\frac{1}{2} \text{O}_2(\text{g})$.

The mass spectrometer studies give further support to the conclusion that reaction 1 describes the sublimation of zinc under neutral conditions and furthermore give evidence that reaction 1 remains the equilibrium sublimation reaction in the presence of excess zinc vapor. No peaks that could be attributed to zinc oxide molecules were observed. Furthermore, in the experiments in which a gold-zinc alloy was heated with zinc oxide, the partial pressures calculated for zinc atoms and oxygen molecules

yielded equilibrium constants for reaction 1 that were in excellent agreement with the constant calculated from thermochemical data for zinc oxide and sublimation data for zinc (Table III).

Zinc pressures as high as those used in the tube furnace experiments (10^{-3} atm or more) could not be used in our mass spectrometer experiments; the highest zinc partial pressure used 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,⁵ and Secco found high rates of sublimation when the only source of zinc was the zinc oxide dissociation reaction itself. The zinc pressures in our mass spectrometer, therefore, should have been high enough to induce any effects that might have increased the rate of weight loss from zinc oxide.

Our mass spectrometric study of zinc-plus-zinc oxide did not reveal even low concentrations of gaseous molecules such as ZnO , ZnO_2 , Zn_2O , or polymers thereof. Furthermore, the product $P_{\text{Zn}} \times P_{\text{O}_2}^{1/2}$ remained equal to the calculated equilibrium constant, while the zinc-to-oxygen pressure ratio varied from as high as about 15/1 to about 2.8/1, the ratio dictated for steady-state effusion by equation 3. This fact appears to preclude the possibility that significant fractions of the zinc ion intensities measured in the spectrometer experiments were contributed by fragmentation of undetected zinc oxide molecules.

The explanation of the conflicting data reported by other investigators was revealed by our tube furnace experiments. The tube furnace design and procedure were deliberately similar to those used by Pillay⁵ and by Williams.³ The sublimation rate of zinc oxide in an atmosphere of flowing

helium (Table IV) was, within the limits of uncertainty, that calculated for the dissociation reaction. In the presence of zinc vapor, the rate 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

and

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 zinc. Iron has negligible volatility at the temperature of our experiments but can reduce water to hydrogen and carbon dioxide to carbon monoxide. The sublimation rates of zinc oxide measured when iron was heated in the gas stream were comparable to those obtained when zinc had been present. Furthermore, after each experiment the iron was severely oxidized.

The purification to which our carrier gas was subjected was as rigorous as the procedures followed in the earlier studies of Moore and Williams and of Pillay. We conclude that the increase in sublimation rate, attributed by Moore and Williams to a catalytic effect of zinc

vapor on the sublimation of zinc oxide, in fact was caused by a reaction of hydrogen and/or carbon monoxide with the zinc oxide. In Secco's static experiments a trace of water and of a reducing agent coupled with a small temperature gradient would account for the high observed zinc oxide transport. On the other hand, in our mass spectrometer experiments the background pressures of water and CO_2 were too low to cause significant reactions.

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FIGURE LEGENDS

Fig. 1. The equilibrium constant for the reaction $\text{ZnO(s)} = \text{Zn(g)} + \frac{1}{2} \text{O}_2\text{(g)}$ 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 $\text{ZnO(s)} = \text{Zn(g)} + \frac{1}{2} \text{O}_2\text{(g)}$ 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.

Fig. 2. The apparent equilibrium constant for the reaction $\text{ZnO(s)} = \text{Zn(g)} + \frac{1}{2} \text{O}_2\text{(g)}$ 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.

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