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THE MECHANISM OF ZnO SINGLE CRYSTAL VAPORIZATION

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Peter P. Bihuniak
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THE MECHANISM OF ZnO SINGLE CRYSTAL VAPORIZATION

Peter P. Bihuniak

Inorganic Materials Research Division, Lawrence Berkeley Laboratory and Department of Materials Science and Engineering, College of Engineering; University of California, Berkeley, California

ABSTRACT

The abundance of vapor species from the reaction $\text{ZnO}_\text{s} + \text{Zn}_\text{g} + \frac{1}{2} \text{O}_2\text{g}$ in their first excited electronic states were compared for Knudsen equilibrium conditions at $1485^oK$ and Langmuir free surface vaporization conditions at $1640^oK$. The fractional occupancy of zinc atoms in the first excited $^3P$ state was found to be approximately the same under both Knudsen and Langmuir vaporization conditions. It was not possible to obtain meaningful results for the oxygen vapor.
I. INTRODUCTION

As a result of the kinetic theory of gases,\(^1,2\) the equilibrium flux, \(J\), of molecules or atoms of mass \(M\) leaving a solid surface whose temperature is \(T\) (in °K) may be expressed as

\[
J_{eq} \left( \frac{\text{moles}}{\text{cm}^2 \cdot \text{sec}} \right) = \frac{P_{eq}}{(2\pi R T)^{1/2}}
\]

where \(R\) is the gas constant and \(P_{eq}\) is the equilibrium pressure over the surface. This equilibrium flux is the maximum vaporization flux that can be emitted from a surface in vacuum.

\(P_{eq}\) is related to the standard entropy of vaporization, \(\Delta S^0_v\), and to the standard enthalpy vaporization, \(\Delta H^0_v\), by

\[
P_{eq} = P^0 \exp \left( \frac{\Delta S^0_v}{R} \right) \exp \left( \frac{-\Delta H^0_v}{RT} \right)
\]

where \(P^0\) is the standard pressure. Under nonequilibrium conditions (e.g., vaporization into a vacuum), it is convenient to introduce a vaporization coefficient, \(\alpha_v\), such that

\[
\alpha_v = \frac{J_{\text{observed}}}{J_{eq}} = \frac{P_{\text{observed}}}{P_{eq}}
\]

Searcy has proposed that oxide vaporization may be considered as a two-step process—the formation of a surface complex followed by desorption of this activated surface complex.\(^3\) He has shown that when \(\alpha_v = 1\), intermediates (those particles or surface states formed in mechanism steps prior to the final desorption) remain in equilibrium with the bulk phase and need not be introduced into the quantitative
description of the reaction kinetics. Hence, the rate limiting step may be considered as the overall reaction. That is, the kinetic expression for vaporization may be written as that of a single-step process for which the activation free energy, $\Delta G_v^*$, is the standard free energy of vaporization, $\Delta G_v^0$, and for which the frequency factor, $v$, for this step is $(2\pi MRT)^{-1/2}$. More concisely, when $\alpha_v=1$, the activated complex is identical with the product vapor and desorption is necessarily rate determining.

Searcy suggests that it is reasonable to assume $v = (2\pi MRT)^{-1/2}$ for all vaporization reactions if desorption is rate limiting. With this assumption, the apparent entropy, $\Delta S_v^*$, and apparent enthalpy, $\Delta H_v^*$, can be calculated. Then, if desorption is rate-limiting, the apparent enthalpy of vaporization must equal or exceed the equilibrium enthalpy and the apparent entropy should approximately equal that of the equilibrium process.

The vaporization of zinc oxide single crystals has been investigated, and has been found to show behavior consistent with expectations for a desorption limited process. Zinc oxide vaporizes to gaseous zinc atoms and oxygen molecules with no detectable ZnO molecules. For the vaporization of prismatic (1010) ZnO surfaces into a vacuum, Hoenig found $\Delta H_{298}^* = 140$ kcal/mole—23% higher than his measured enthalpy of the equilibrium reaction $\Delta H_{298}^0 = 114$ kcal/mole—and, $\Delta S_{v^*}(=52.2$ ev) $\approx \Delta S_v^0$. Galluzzo showed the apparent enthalpies of vaporization to be $\Delta H_{1428}^* = 134.6$ kcal/mole for the (0001) basal face and $\Delta H_{1428}^0 = 140.8$ kcal/mole for the (0001) face—21% and 27% higher than $\Delta H_{1428}^0 = 110$ kcal/mole. He measured the apparent entropies to be $\Delta S_{1428}^* = 51.0$ ev.
for the (0001) face and 40.3 eu for the (000$\overline{1}$) face—both values being within his experimental error of the equilibrium entropy, $\Delta S_{1428}^0 = 48.0$ eu.

If the desorption step is rate-determining as is suggested by these results, at least part of the excess energy of the activation (or, apparent) enthalpy over the equilibrium enthalpy must be associated with the vaporized products.

This "excess" energy may be carried off as translational, rotational, vibrational or internal energy of electronic excitation by the Zn atoms and $O_2$ molecules. Mar and Searcy$^7$ have shown for

$$2Ga \, N(s) \rightarrow 2Ga(g) + N_2(g)$$

where, $\Delta H^\circ_{1300}$ = 219 kcal/mole, and $\Delta H^\circ_{1300}$ = 173 kcal/mole, that the average vapor temperature, as measured from the kinetic energy of a known mass flux, is the same as the average surface temperature. If the "excess" 46 kcal/mole were distributed among rotational, vibrational and translational modes, the vapor temperature should be 3000$^\circ$ greater than the surface. They conclude that while substances which evaporate with "excess" energy may have excited internal states, that excess energy probably will not include excess translational energy. "Excess" rotational and vibrational energies are unlikely sources of 46 kcal/mole excitation. If that amount of energy is retained by the vapor species, electronic excitation must almost certainly be involved.

Similarly, in the case of ZnO vaporization electronic excitation would appear to be a likely source of the 30 kcal/mole retained by the vapor species. If all zinc atoms desorb from the surface in their $^3P$ first excited electronic state rather than their $^1S$ ground state, the vaporization reaction $ZnO(s) \rightarrow Zn(g) + \frac{1}{2}O_2(g)$ would require 9.3 kcal/mole.
"excess" energy. All $\text{O}_2$ molecules vaporizing in their first excited $^1\Delta_g$ state would require 22.6 kcal/mole of "excess" energy over their $^3\Sigma_g^-$ ground state.\textsuperscript{9} Entropy differences for excited Zn relative to the ground state atom should be +2.2 eu while for $\text{O}_2$, $\Delta S = -2.2$ eu. These excess energies are of the order of those observed by Galluzo and Hoenig.

The $^3P$ excited state of zinc atoms has two unpaired electrons, while the $^1S$ ground state has no unpaired electrons. On the other hand, the $^1\Delta_g$ excited state of an oxygen molecule has no unpaired electrons, while the $^3\Sigma_g^-$ ground state has two unpaired electrons. Badger, et al.\textsuperscript{10} have estimated the radiative half-life of isolated $^1\Delta_g \text{O}_2$ to be 45 minutes. Thus it should be possible to determine if zinc oxide vaporizes predominantly to excited atoms and/or molecules by comparing the concentrations of paramagnetic atoms and molecules in a vapor beam from free surface sublimation to the concentrations in the equilibrium vapor. It is the purpose of this study to make such comparisons using an inhomogeneous field magnet to deflect paramagnetic species from a vapor beam and a quadrupole mass spectrometer to determine the chemical composition of the undeflected species. While of obvious theoretical interest, such a study is also of practical importance as the useful life of oxides is often dependent upon vaporization rates.
II. EXPERIMENTAL

A. Materials

Zinc oxide crystals are of the hexagonal, wurtizite structure. Those used for the Langmuir experiments in this study were manufactured by the 3M Company. X-ray diffraction analysis confirmed the orientation of the crystals. A Taylor-Sinclair\textsuperscript{11} extrapolation on the X-ray data showed the best value of the room temperature C-axis lattice parameter to be 5.20 Å, the accepted value.

Zinc oxide crystals are polar—the (0001) face being Zn rich and the (0001) face O rich (see Fig. 1).\textsuperscript{12} Mariano and Hanneman\textsuperscript{13} have shown that crystal morphology is a useful criteria for evaluating polarity. They have suggested etching the edges of the basal crystals and noting the shape of the etch pits which point toward the Zn-rich face. Thermal etching during the course of the experiment makes the polarity obvious. Therefore, crystal polarity was determined after an experiment was conducted.

Zinc oxide powder used for the Knudsen equilibrium experiments in this study was manufactured by the Allied Chemical Company.

B. Apparatus

The apparatus is pictured in Fig. 2\textsuperscript{14} to consist of three chambers. The sample is heated via a molybdenum resistance alumina furnace (see Figs. 3 and 4). Temperatures were measured with a Pt-Pt + 10% Rh thermocouple cemented to the sample cell. The equilibrium vapor was obtained from zinc oxide powder heated in an alumina Knudsen effusion cell equipped with a slit orifice measuring 0.016 in. wide by 0.20 in. long by 0.10 in. deep.
For free surface measurements, a single crystal wafer cut to expose a basal (0001) or (0001) surface was mounted on an alumina holder and covered by a slit orifice measuring 0.016 in. wide by 0.20 in. long by 0.010 in. deep. The vapor from the Knudsen cell or free surface orifice is collimated into a ribbon-shaped beam (about 0.4 mm thick) which passes between the pole pieces of an inhomogeneous-field magnet (capable of producing a 16 kG field with a 55 kG/m field gradient) to enter the ionization region of an EAI Quad 250 quadrupole mass filter. The apparatus is housed in a stainless steel vacuum system. A mechanical pump (Kinney KTC-21), two 6-in. diameter mercury diffusion pumps and an Ultek titanium sublimation pump evacuate the system.

The inhomogeneous field magnet acts as a selector—deflecting paramagnetic molecules or atoms out of the path of the original beam. Thus, the apparatus measures the paramagnetism of collimated vaporized molecules/atoms (a molecular beam) by comparing the measured intensities of the beam with the deflecting i.f. magnet on and off.

C. Procedure

First, the sample (zinc oxide single crystal or powder) was heated sufficiently to obtain an easily detectable signal. Calculations based upon Galluzo's zinc oxide single crystal vapor pressure measurements indicated that 1200°C would result in a good molecular beam.

Beam presence was noted by observing isotopic mass intensities on the EAI QUAD mass filter oscilloscope. Isotopic masses observed were:

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<th>% abundance</th>
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<tr>
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<td>64</td>
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When the presence of the molecular beam was confirmed, the left half of the adjustable collimating slit was centered. Next, the alumina sample cell collimating slit was aligned along the centered half of the adjustable collimating slit by sighting through the chamber windows. Then the right half of the adjustable collimating slit was centered to the same spacing.

Intensity readings were taken at 0.010 in. interval positions of the adjustable detector collimating slit to obtain the molecular beam intensity profile. The total distance traversed was 0.100 in. At each position four intensity readings were taken—two with the i.f. magnet off and two with the i.f. magnet on. The circuitry was such that integrated intensities were plotted over a time span of 11 seconds.

The average of the two integrated intensity readings was plotted versus slit position when the i.f. magnet was on and when the i.f. magnet was off. Partial plugging of the sample cell collimating slit and, in the case of the Knudsen effusion experiments, partial sintering of the powder sample resulted in intensity variations during the course of the experiments. To correct for this, data were plotted as a percent of the maximum integrated intensity.

The difference in the integrated intensity profile with the i.f. magnet on and off is a measure of the abundance of paramagnetic vaporized species. The Knudsen effusion experiments provided reference paramagnetic abundances for both Zn and O₂ species. As previously discussed, the difference in paramagnetic quantities between the equilibrium situation and free surface vaporization is the crucial data.
III. RESULTS

Unfortunately, it was not possible to obtain intensity readings for the vaporized O\textsubscript{2} species. A constant high background intensity that could not be reduced sufficiently with the Ti sublimation pump completely masked the vapor beam signal.

Isotopic mass unit 64 was selected to monitor the vaporized zinc abundance. The data for the Knudsen equilibrium experiments are shown in Table I. They represent the averages of five experiments conducted at 1480\degree\textsubscript{K} where the data from each individual experiment were adjusted so that the measured integrated intensity maxima corresponded to the central slit position. Graph I is a plot of the relative integrated intensity—with the maximum data point normalized to 100—versus slit position when the i.f. magnet was on and when the i.f. magnet was off. The area between the two curves is a measure of the abundance of first excited state zinc atoms in the vapor beam. Under equilibrium conditions, one would expect 13\% occupancy of the first excited state at the experimental temperature.\textsuperscript{18}

The data for the free surface vaporization of species are shown in Table II and plotted in Graph II. They represent the averages of 10 experiments conducted at 1640\degree\textsubscript{K}. Two zinc oxide single crystals were used. The polarity of the crystals had little effect on the measured integrated intensities so the data were averaged without regard to crystal polarity.

With a correction for the temperature difference between the Langmuir and Knudsen experiments, the area between the beam intensity profiles for the Langmuir free surface vaporization is 1.5 times greater.
than the corresponding area for the Knudsen equilibrium experiments. At 1640°K, one would expect 18% occupancy of the $^3p$ state under equilibrium conditions. The data indicate 27% $^3p$ occupancy under free surface conditions at 1640°K.
IV. DISCUSSION

Before examining the implications of the results, it might be best to consider some of the experimental limitations and difficulties. The most persistent problem throughout the experimentation was the high background intensity. In an attempt to overcome this, the chopper frequency was increased to 50 hertz, the system was baked out (at 350°C) for several days, and a Ti sublimation pump was installed. The results were still inadequate for any meaningful measurements on the vaporized O₂ species.

Although it was possible to make measurements on the zinc atoms, it was necessary to choose a collimating slit width (0.050 in.) wider than the specimen cell width (0.016 in.). Correspondingly, to obtain a distinguishable beam intensity profile the total traverse of the detector collimating slit had to be increased. As the deflection of paramagnetic species by the inhomogeneous field magnet is not large, the net effect of increasing the collimating slit width is to increase the signal resolution with respect to the background but to decrease the ability of the i.f. magnet to separate paramagnetic species from non-paramagnetic species. Preliminary experiments under Knudsen conditions indicated that a collimating slit width of 0.020 in. gave good paramagnetic resolution. Unfortunately, with Langmuir conditions such a slit width was too narrow to permit signal distinction from the background. A collimating slit width of 0.050 in. gave a satisfactory signal, but a paramagnetic resolution of questionable effectiveness.

After the experiments, the crystals were examined and appeared to have been incompletely masked by the sample cell lid. Further, the
back of the cell lid showed some zinc oxide deposition. The evidence indicates that free surface vaporization conditions were not completely attained.

The results indicate that, in the case of zinc oxide, electronic excitation of the zinc atom cannot account for the observed "excess" enthalpy of vaporization. On a molar basis, the observed 1.5 times increase in paramagnetic first excited state abundance in the Langmuir experiments over the Knudsen experiments would account for less than 1 Kcal of excess energy. Standard deviations greater than the difference between the two curves on either of the Langmuir or Knudsen plots prohibit quantitative conclusions. However, regardless of experimental difficulties it seems apparent that electronic excitation of zinc atoms cannot account for the excess enthalpies measured by Galluzzo and Hoenig.

It may be speculated that as a result of some step prior to desorption, oxygen molecules are preferentially receiving and desorbing with the majority of the excess enthalpy. Supportive evidence for this would be Galluzzo's measured excess enthalpies. He found there to be 30 Kcal/mole excess enthalpy for the (0001)--oxygen rich--basal face and 24 Kcal/mole excess enthalpy for the zinc rich (0001) face. Although the same number of zinc atoms and oxygen molecules vaporize regardless of which basal face is vaporizing, the evidence might suggest that oxygen molecules are preferentially excited. Consequently, it is unfortunate that oxygen measurements could not be made.
V. ACKNOWLEDGMENTS

The author is indebted to David Meschi and Professor Alan Searcy for their constant guidance.

The alumina parts were fabricated by Will Lawrence. Emery Kozak provided technical assistance throughout this work.

This work was performed under the auspices of the U. S. Atomic Energy Commission.
VI. REFERENCES


3. ibid.


5. C. L. Hoenig, Vapor Pressure and Evaporation Studies of Stannic Oxide, Zinc Oxide, and Beryllium Nitride (Ph. D. thesis), University of California, Berkeley, April 1964.


Fig. 1

Zinc face

Zinc
Oxygen

Oxygen face

Zinc
Oxygen

C-axis

XBL 725-6341
Fig. 2. Inhomogeneous-magnetic-field molecular beam apparatus.
Fig. 3. Furnace and specimen cell assembly.
Fig. 4. Furnace power supply and thermocouple schematic.
TABLE I  Knudsen condition

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TABLE II  Langmuir condition

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XBL725-6345
GRAPH I  Knudsen condition

Relative Integrated Intensity

Slit Position

XBL 725-6346
GRAPH II  Langmuir condition

-21-

Relative Integrated Intensity

Slit Position

i.f. magnet off

i.f. magnet on

XBL725-6347
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