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VAPORIZATION KINETICS OF ZINC OXIDE SINGLE CRYSTALS

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ABSTRACT

The rates of vaporization of opposite basal faces of zinc oxide have been measured as functions of temperature. The average apparent enthalpies of vaporization for the reaction $\text{ZnO(s)} \rightarrow \text{Zn(g)} + \frac{1}{2} \text{O}_2(g)$ for the two faces were measured to be: zinc-rich (0001) face, 134.6 kcal/mole; oxygen-rich (0001) face, 140.8 kcal/mole. The differences between these values is greater than probable experimental error in the measurements, and both enthalpies are larger than the enthalpy of the equilibrium reaction, 110.5 kcal/mole in the temperature range studied.

The apparent entropies for the reaction were measured to be: (0001) face, 51.0 eu and (0001) face, 50.3 eu. These entropies, to within expected limits of error, are equal to each other and to the entropy of the equilibrium reaction in the same temperature, 48.0 eu.
I. INTRODUCTION

It has been known for some time that opposite crystallographic faces of crystals that have anisotropic arrangements of constituent atoms show different etching behavior and different rates of decomposition. Until recently, however, the rates of vaporization of the opposite faces of the only solid of anisotropic packing for which congruent vaporization had been studied, cadmium sulfide, were believed to be indistinguishable.\textsuperscript{1,2} Zinc oxide was then found, however, to vaporize about three times as fast from the zinc-rich (0001) face as from the oxygen-rich (000\overline{1}) face.\textsuperscript{3-5} And when cadmium sulfide\textsuperscript{5} was studied in a lower temperature range than that of the pioneering study, where a different mechanism probably governs the reaction, the opposite basal faces showed different vaporization rates. The temperature dependence of vaporization from these opposite faces was established for cadmium sulfide, but remains unclear for zinc oxide because of apparent interactions with a container material when zinc oxide was studied as a function of temperature.\textsuperscript{3}

Reliable determinations of temperature dependences of evaporation rates provides particularly important information for models describing the vaporization process,\textsuperscript{6} so additional measurements of temperature dependences of vaporization for anisotropic materials are of value.

For oxide materials the theoretical interest of vaporization data is complemented by an exceptional practical interest. Oxides are important structural materials for use at high temperature and their usability is partly determined by their vaporization rates. The present work is designed to measure (0001) and (000\overline{1}) face vaporization for zinc oxide as a function of temperature.
II. EXPERIMENTAL

The 3 M Company supplied the sliced and polished crystals of zinc oxide. The crystals were grown as hexagonal needles and cut with a diamond saw to expose basal slices of 1 mm thick by 8 mm diameter. The wafers were lightly polished with 600 grit SiC papers which left traces of Si on the surface of the crystal. Several crystals were ordered in an unpolished condition. No differences in the vaporization characteristics were observed between polished and unpolished crystals.

Observations by Mariano and Hanneman were used as a basis for determining the crystallographic polarity of the wafers. Mariano and Hanneman showed that the asymmetric nature of the crystal structure, along the c-axis, produces slightly different X-ray scattering factors for opposite orientations. They developed an etching technique that gave surface morphologies which could be correlated with X-ray data.

The samples were etched with 20 vol % HNO₃ for 20 min. The zinc-rich (0001) face developed hexagonal pits and the oxygen-rich (000̅1) face developed rough "hillocks." Etched surfaces of the prismatic face provided unambiguous identification of the polarity of the ZnO crystal because the apex of the large etch pits point toward the zinc surface. Care was taken to expose to free surface vaporization only the surface of the crystal that was not etched. This was especially important in the vaporization of the oxygen-rich (000̅1) surface, which is attacked considerably more than the zinc surface by the nitric acid solution.

Torsion-Langmuir and torsion effusion measurements were made with an apparatus whose operation and technique has been described. The torsion cells were constructed of 99.5% alumina encased in a molybdenum
cell holder. The cell holder was of a "dumbbell" shape to reduce its weight as much as possible. The cells were designed so that they could be used interchangeably for torsion-effusion and torsion-Langmuir studies. Care was taken to avoid leakage in a direction that would add to the moment. The orifice caps were thinned to the desired thickness, and the cells were then leak-tested by heating them with zinc oxide charges. No deflection was seen in the temperature range of interest. The cell assembly was suspended from a torsion fiber of .015" tungsten wire. The torsion constant of the wire was measured before any of the runs were made and checked repeatedly to insure that it remained constant. The force correction constants used for the Knudsen effusion were of the order of .58 for the .08 cm diameter orifice and .44 for the .15 cm diameter orifice. The force correction constants for the Langmuir study were of the order of .68 for the .40 cm orifice.

The apparatus was calibrated with zinc oxide whose equilibrium vaporization behavior is well known. Vaporization occurs by the congruent reaction

\[ \text{ZnO}(s) = \text{Zn}(g) + \frac{1}{2} \text{O}_2(g). \quad (1) \]

Temperatures were measured with a platinum/platinum-10% rhodium thermocouple inserted into a dummy cell of molybdenum of roughly the same weight as the cell assembly. Temperature profiles were run previous to the vaporization studies. Two thermocouples, one in contact with the cell assembly and the other inserted in the dummy cell, were moved up and down the furnace. A region about 5 cm long was found in
which the temperature was constant to 1.5°C. All thermocouples were calibrated using the melting point of copper as a reference point (1083°C).
III. RESULTS

The torsion effusion results as shown in Fig. 1 showed an orifice area dependence. Extrapolation to zero orifice by means of the Motzfeld equation puts the experimental plot of pressure above the accepted thermocouple data by a factor of about two.

Torsion Langmuir measurements for the zinc-rich (0001) face were more reproducible than for the oxygen-rich (000\overline{1}) face. As seen in Fig. 2, two independent runs lead to consistent results with little experimental scatter. The reason for the difference between faces can be seen by comparing profiles. Figure 3 is a photograph of a crystal after vaporization from the (0001) surface. The cross sectional view shows vaporization took place with little undercutting of the orifice cap. The white arrows in the photograph show the size and position of the orifice. The area of vaporization remained substantially constant throughout the run.

On the (000\overline{1}) face, as can be seen from the cross sectional view of Fig. 4, there is much undercutting. In fact, there was vaporization to some extent from the whole crystal face. Again the white arrows show the size and position of the orifice on the crystal. Clearly the effective area of vaporization of this oxygen face is ill-defined and increasing with time.

A run was made in which the effective area of vaporization of an oxygen face was determined more accurately. The crystal was held in the furnace at approximately the temperature range of interest until its rate of vaporization had become constant, a process that required about 1 hour for each face. The crystal was removed from the furnace and the
diameter of its thermally etched surface was measured to be .44 cm. The crystal was again placed in the furnace and heated to the temperature of interest. Only a few points were taken to establish the temperature dependence in order to minimize the time of heating and therefore minimize the change in effective area of vaporization. The run was completed in 2-1/2 hours. The diameter of the vaporized surface after this period was .46 cm. For the calculation of the pressures from the deflections, the average diameter (.45 cm) was used.

For the zinc-rich (0001) face the total pressure is given as a function of temperature by

\[
\log P = 8.25404 - 2.02536 \times 10^4 (1/T)
\]

and for the oxygen-rich face by

\[
\log P = 8.24929 - 2.11946 \times 10^4 (1/T).
\]

Least squares analysis of the data yield raw values of the apparent enthalpy and apparent entropy of vaporization. These quantities were calculated for each face exactly as though equilibrium pressures were being measured for reaction 1. For the zinc-rich face the data yielded \( \Delta H^* = 139,023 \text{ cal} \) and \( \Delta S^* = 54.48 \text{ eu} \) over the temperature range 1400-1537°K. For the oxygen-rich face at 1460-1550°K the values are \( \Delta H^* = 145,480 \text{ cal} \) and \( \Delta S^* = 54.73 \text{ eu} \).

This method of calculation implies the tentative assumption that desorption is rate determining. If, for example, the formation of
activated zinc oxide molecules in a self adsorbed surface layer is assumed to be rate limiting, the calculated apparent enthalpy of activation would be about \( 2/3 \) that calculated by the assumption used.

As mentioned previously, the Motzfeld extrapolated data for the zinc oxide equilibrium data was higher than the accepted thermochemical data of Coughlin. The difference between Coughlin's data and the extrapolation probably represents a systematic error inherent in the experiments, and the Langmuir data should be adjusted to correct for this systematic error. The enthalpy from the extrapolated curve was about 2 kcal higher than the accepted enthalpy. Langmuir enthalpies were corrected by multiplying then the ratio of the slope of the thermochemical data to the slope of the extrapolated data. Pressures of Langmuir studies were corrected by multiplying them by the ratio of pressures calculated from the thermochemical data to measured pressures at the midpoint of the Langmuir temperature range.

The corrected apparent enthalpies and entropies for reaction 1 are then for the zinc-rich face, \( \Delta H^* = 134,600 \text{ cal} \) and \( \Delta S^* = 51.0 \text{ eu} \), and for the oxygen-rich face \( \Delta H^* = 140,800 \text{ cal} \) and \( \Delta S^* = 50.3 \text{ eu} \). These values can be compared to the enthalpy and entropy of the equilibrium reaction,\(^{10,11} \Delta H = 110,750 \text{ cal} \) and \( \Delta S = 48.0 \text{ eu} \). For the zinc-rich (0001) face, the evaporation coefficients are .0086 at \( 1428^\circ \text{K} \), and .0122 at \( 1515^\circ \text{K} \). For the oxygen-rich (000\( \bar{1} \)) face, the evaporation coefficients are .0019 at \( 1428^\circ \text{K} \), and .0029 at \( 1515^\circ \text{K} \).
IV. DISCUSSION

The rates of vaporization of single crystals have been assumed to be controlled by reactions that occur on specific surface sites or by the advancement of ledges across the exposed surface planes. However, Searcy has called attention to the fact that rates of vaporization of substances that occur at the maximum possible rates consistent with the given vapor pressures must be limited by the rate of desorption from the self-adsorption layer. He developed a model for vaporization in which a surface reaction is assumed to be followed by a desorption reaction. He showed that if desorption is rate determining, the apparent enthalpy of the vaporization reactions must equal or exceed the equilibrium enthalpy and the apparent entropy should be approximately equal to the entropy of the equilibrium process.

Leonard and Searcy found apparent entropies for the cadmium-rich (0001) face vaporization of cadmium sulfide that are near the entropy of the equilibrium reaction. Wang finds similar results for the zinc-rich (111) face of cubic zinc sulfide. The present study yields apparent entropies of vaporization for both (0001) and (0001) faces of zinc oxide that are within expected experimental error of the entropy of the equilibrium reaction.

These apparent entropies are all calculated on the assumptions (a) that the appropriate frequency factor for the rate determining step is the factor from gas phase kinetics that relates pressure to flux at a plane, (b) that every portion of the exposed surface constitutes an equally probable source of the molecules that vaporize.
If a surface reaction step rather than desorption is rate determining, a frequency factor such as $kT/h$ per molecule of activated complex would be expected to be appropriate and only particular surface sites such as kinks or ledge sites might be active sites for the reaction. Because translational modes are not excited, the entropy of reactions on bound surface sites are expected to be lower than the apparent entropies if desorption is rate controlling.

If a surface step is rate determining, only accidentally would the product $kT/h \times n^* \exp (\Delta S^*/R)$ per particle be equal to $(2\pi mRT)^{-1/2} \exp (\Delta S^*/R)$ per particle for the equilibrium reaction. But if desorption is rate determining, the entropy calculated by the method used would be the difference in entropy between the vapor molecules that leave the surface (presumably in internally activated states) and the entropy that their components have when bound in the bulk condensed phase. This entropy difference should be approximately the same as for the equilibrium reaction. The near agreement between the calculated apparent activation entropies and the entropy of the equilibrium reaction, therefore, is circumstantial evidence, but not of course proof, that desorption limits the rate of vaporization of both basal surfaces of zinc oxide.

A desorption-limited vaporization mechanism is compatible with the experimental evidence that Somorjai and coworkers found with cadmium sulfide that the vaporization is catalyzed by light and is inhibited by a flux of sulfur that impinges on the surface. Desorption rates would be expected to be a function of the ratio of metal to non-metal atoms on the self-adsorbed layer. The ratio of metal to non-metal atoms in the self-adsorption layer may sometimes be very different from the
ratio in the crystal lattice, and impingement of atoms from the vapor would almost certainly influence the ratio. In semiconductors the ratio is probably a sensitive function of light quanta of energy sufficient to excite electrons across the band gap.

On the other hand, the fact that vaporization rates on opposite zinc oxide faces are similar seems inconsistent with a mechanism such as that proposed by Hirth and Munir for cadmium-rich face vaporization\textsuperscript{17} of cadmium sulfide. Their mechanism assumes that the spacing between crystal ledges plays a critical role in determining the extent to which the measured vaporization rate falls below the maximum possible rate. Leonard and Searcy\textsuperscript{5} have shown that opposite basal faces of both zinc oxide and cadmium sulfide have very different structures. If the ledge concentration is critical in fixing the vaporization rate, these different structures imply dissimilar ledge spacings. Great dissimilarity in vaporization behavior might be expected.
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7. The 3M Co., Electrical Products Division, Minneapolis, Minn.
   Note: Zinc oxide single crystals are no longer available from 3M.
Figure 1. Equilibrium pressure of zinc oxide.
Figure 2. Langmuir pressures of zinc oxide single crystals.
Figure 3. (0001) face after vaporization.

(a) Top view

(b) Cross sectional view
Figure 4. (000\overline{1}) face after vaporization.

(a) Top view

(b) Cross sectional view
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