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THE KINETICS OF VAPORIZATION OF BARIUM SULFATE

Pirooz Mohazzabi

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THE KINETICS OF VAPORIZATION OF BARIUM SULFATE

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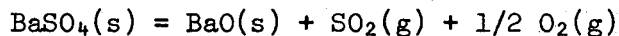
THE KINETICS OF VAPORIZATION OF BARIUM SULFATE

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ABSTRACT

Equilibrium vapor pressures of barium sulfate and free surface sublimation pressures of (002) face of its single crystals were both measured for the first time from a phase transformation temperature at 1422°K to 1540°K, using Torsion-effusion and Torsion-Langmuir techniques, respectively. The reaction was confirmed as



for both equilibrium and free surface conditions. Calculations by Second Law method yielded, for the reaction,

$$\Delta H_v^{\circ} = 138.9 \pm 1.9 \text{ Kcal}$$

$$\Delta S_v^{\circ} = 60.2 \pm 1.3 \text{ eu}$$

for the equilibrium studies, and

$$\Delta H_v^* = 136.4 \pm 2.9 \text{ Kcal}$$

$$\Delta S_v^* = 48.0 \pm 2.0 \text{ eu}$$

for the free surface sublimation studies.<sup>†</sup> Thus, within the experimental error,

---

<sup>†</sup> $\Delta H_v^{\circ}$ ,  $\Delta S_v^{\circ}$  are the standard enthalpy and entropy for the equilibrium reaction while  $\Delta H_v^*$ ,  $\Delta S_v^*$  are called the apparent activation enthalpy and entropy for the vaporization reaction.

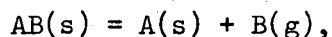
$$\Delta H_V^* = \Delta H_V^{\circ} \text{ but } \Delta S_V^* < \Delta S_V^{\circ}.$$

The rate of the free surface decomposition reaction was constant, within the experimental scatter in data, during the period of the measurements. This result indicates that effusion of the product gases through the porous product layer is not rate limiting even when the product layer thickness is as great as 1 mm. The simplest model consistent with these behaviors assumes that only 3% of the surface sites are active for the vaporization reaction.

## I. INTRODUCTION

An important factor in determining the usefulness of materials at high temperatures, especially in high vacuums, is the rate at which the materials vaporize. In recent years there has been a widespread interest in the problem of improving our understanding of kinetics of vaporization, both qualitatively and quantitatively.<sup>1-4</sup>

Although extensive and often advanced studies have been done<sup>5-7</sup> on incongruent vaporization reactions of the form



rarely have these studies exploited the full range of experimental techniques or methods of theoretical analyses that have been applied for studies of congruent vaporization. Recently, Beruto and Searcy<sup>8</sup> have shown that the torsion-Langmuir technique which was previously used only for studies of congruent vaporization, yields valuable new experimental information on calcite ( $CaCO_3$ ) decomposition. Furthermore, the kinds of theoretical analysis that have been used for studies of congruent vaporization also proved appropriate for interpretation of calcite decomposition, despite the expected complications introduced by formation of a porous product layer.

The rate of a congruent vaporization reaction is almost always analyzed in terms of its deviations from the Hertz-Knudsen-Langmuir equation,<sup>2</sup> but, although the equation predicts the maximum possible rates for incongruent vaporization as well, these reactions have not generally been analyzed in terms of the Hertz-Knudsen-Langmuir equation.

Most of the metals have been shown to have unit vaporization coefficient,  $\alpha_v$ , (that is to vaporize at the maximum possible rate predicted from equilibrium thermodynamic data and the Langmuir equation), which means that the desorption step is necessarily rate limiting.<sup>2</sup> A number of congruently vaporizing solids also show unit vaporization coefficients, for example, (111) faces of barium fluoride,<sup>9</sup> the arsenolite modification of  $\text{As}_4\text{O}_6$ ,<sup>10</sup> the (0001) faces of  $\text{LaF}_3$ ,<sup>11</sup> and polycrystalline white phosphorus.<sup>12</sup>

On the other hand, for those solids which show low vaporization coefficients, the interpretation of kinetics depends upon the relative magnitude of  $\Delta H_v^0$  and  $\Delta H_v^*$  and of  $\Delta S_v^0$  and  $\Delta S_v^*$ . Among solids with low vaporization coefficients are, for example, (0001) and (000 $\bar{1}$ ) faces of zinc oxide single crystal,<sup>13</sup> cadmium sulfide,<sup>3,14,15</sup> and ammonium halides.<sup>2</sup>

Aside from the information that may be obtained about reaction mechanisms from a systematic comparison of free evaporation data with those predicted by the Hertz-Knudsen-Langmuir equation, an entirely empirical evaluation of trends in these deviations may be of great value in itself.<sup>16</sup> Since there is a systematic deviation from the Hertz-Knudsen-Langmuir equation for various classes of congruently vaporizing solids, unknown rates of this kind of reaction can be predicted with higher confidence than almost any other type of reaction. This approach should be useful also for predicting rates of incongruently vaporizing solids.

As was mentioned earlier, Beruto and Searcy studied the vaporization of calcite. But a study of a second incongruently vaporizing solid



would be valuable. Studies of barium sulfate single crystals (barite), are of especial interest because (i) barite is from another class of compounds, (ii) its vaporization is more complex than that of calcite, in that it decomposes to two principal gaseous species, and (iii) no information is available for its vaporization above its phase transformation temperature.<sup>7</sup>

Available thermodynamic data indicated that barite should vaporize incongruently according to the equation



plus a negligible amount of  $\text{SO}_3$  in the temperature range of study.<sup>7</sup>

## II. EXPERIMENTAL

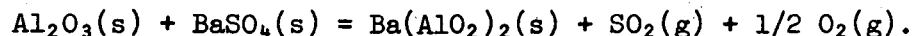
Torsion-effusion and torsion-Langmuir techniques<sup>17</sup> were used for measurements of equilibrium dissociation pressures and rates of dissociation in this work. The apparatus is essentially the same as the one described by R. T. Coyle.<sup>18</sup>

1. Sample Preparation: Barite single crystals collected approximately three miles from Stoneham, Logan Co., Colorado, were analyzed by the American Spectrographic Laboratories, Inc. They reported the following impurities as oxides of the elements:

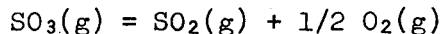
Sr	0.15%
Ca	0.005
Si	0.15
Mg	<0.001
Al	0.001
Cr	0.004

Some of the crystals were ground to powder for effusion runs, and some were cleaved with a razor blade on the (002) planes, which is a natural cleavage plane of barite. Then by grinding the rear side of these cleaved crystals, wafers of about 1.5 mm thickness were obtained.

2. Cell Preparation: One of the problems of concern was the possibility of reaction between barite and the material of the effusion cells at the temperatures of study.<sup>19</sup> For example, graphite could reduce barite to BaS. Molybdenum could be oxidized to its oxides. Alumina reacts with barite according to the following equation:



Platinum is a catalyst for the reaction



It was decided to try alumina cells because the solid state reaction rate between the cell and barite would probably become negligible as soon as a layer of  $\text{Ba}(\text{AlO}_2)_2$  was formed between the two materials. The results in alumina were checked by a heating in a platinum cell.

Knudsen cells were made with orifices  $1 \pm 0.01$  mm in diameter, and Langmuir cells were made with orifice diameters of  $4 \pm 0.01$  mm. To minimize the weight of the cell assemblies, a graphite cell holder was used. A protective molybdenum foil between the cells and the cell holder prevented reaction between the graphite and the alumina.

### 3. Calibrations:

(i) A flat part of the temperature profile of the furnace was found in which the vertical displacement of the cell of  $\pm 2.0$  cm gave a constant temperature to within  $1.5^\circ\text{K}$ , then the temperature inside a dummy graphite cell was measured to calibrate a second thermocouple placed 6 mm below the cell holder.

(ii) Tungsten torsion wire of 0.015" was used. The wire was calibrated by measuring its period of oscillations when it supported a brass disc with known moment of inertia.<sup>20</sup>

(iii) Finally the apparatus was calibrated by measuring in the apparatus the well known vapor pressure of tin<sup>21</sup>--two independent runs were made.

4. Barite Runs: Two independent Knudsen runs were made with barium sulfate powder, and three independent Langmuir runs were made in alumina cells using (002) faces of barium sulfate single crystals as

the vaporizing surfaces. In all of the cases, measurements were made at temperatures above  $1422^{\circ}\text{K}$ , the phase transformation temperature of barrite,<sup>7\*</sup> and below its melting point,  $1620^{\circ}\text{K}$ .<sup>†</sup> This range was chosen because the decomposition pressures were too low to be measured with satisfactory accuracy below the phase transformation temperature.

Another independent effusion run was made using platinum cells of 0.9 mm orifice diameter to compare the results with those of alumina cells. Again a graphite cell holder was used.

5. The barium oxide that formed in the Langmuir runs was examined by X-ray diffraction for metastable modifications of barium oxide.

6. J. A. Roberts, Jr. kindly helped with the ATLAS mass spectrometer to determine the ratios of  $\text{SO}_2$  to  $\text{SO}_3$ , both from effusion cells and from barite crystal wafers at the temperatures of study.

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\*The low temperature crystallographic modification of barite is orthorhombic, but its high temperature modification is unknown (see ASTM diffraction data cards of 1971).

†At the beginning of each experiment the cells were heated at high temperatures of the range for about 1.5 hour to allow for degassing. The total time for each run was about five to six hours.

### III. RESULTS

The torsion-effusion results of the tin runs are shown in Fig. 1. Least square analysis gave the following calculated thermodynamic values for the range of about 4125°K to 1550°K:

<u>Run #</u>	<u># of data pts</u>	<u><math>\Delta H_v^\circ</math>/Kcal</u>	<u><math>\Delta S_v^\circ</math>/eu</u>
1	23	73.8 ± 0.8	26.8 ± 0.5
2	13	71.9 ± 1.4	25.6 ± 1.0

and for the combined data, i.e., 36 data points

$$\Delta H_v^\circ = 73.1 \pm 0.7 \text{ Kcal/gm atom,}$$

$$\Delta S_v^\circ = 26.3 \pm 0.5 \text{ eu/gm atom.}$$

The values in (21) at the mid-point of the temperature range of this work (i.e. at 1490°K) is

$$\Delta H_{1490}^\circ = 70.7 \text{ Kcal/gm atom}$$

$$\Delta S_{1490}^\circ = 24.5 \text{ eu/gm atom}$$

Third law heat calculation for tin with 36 data points gave

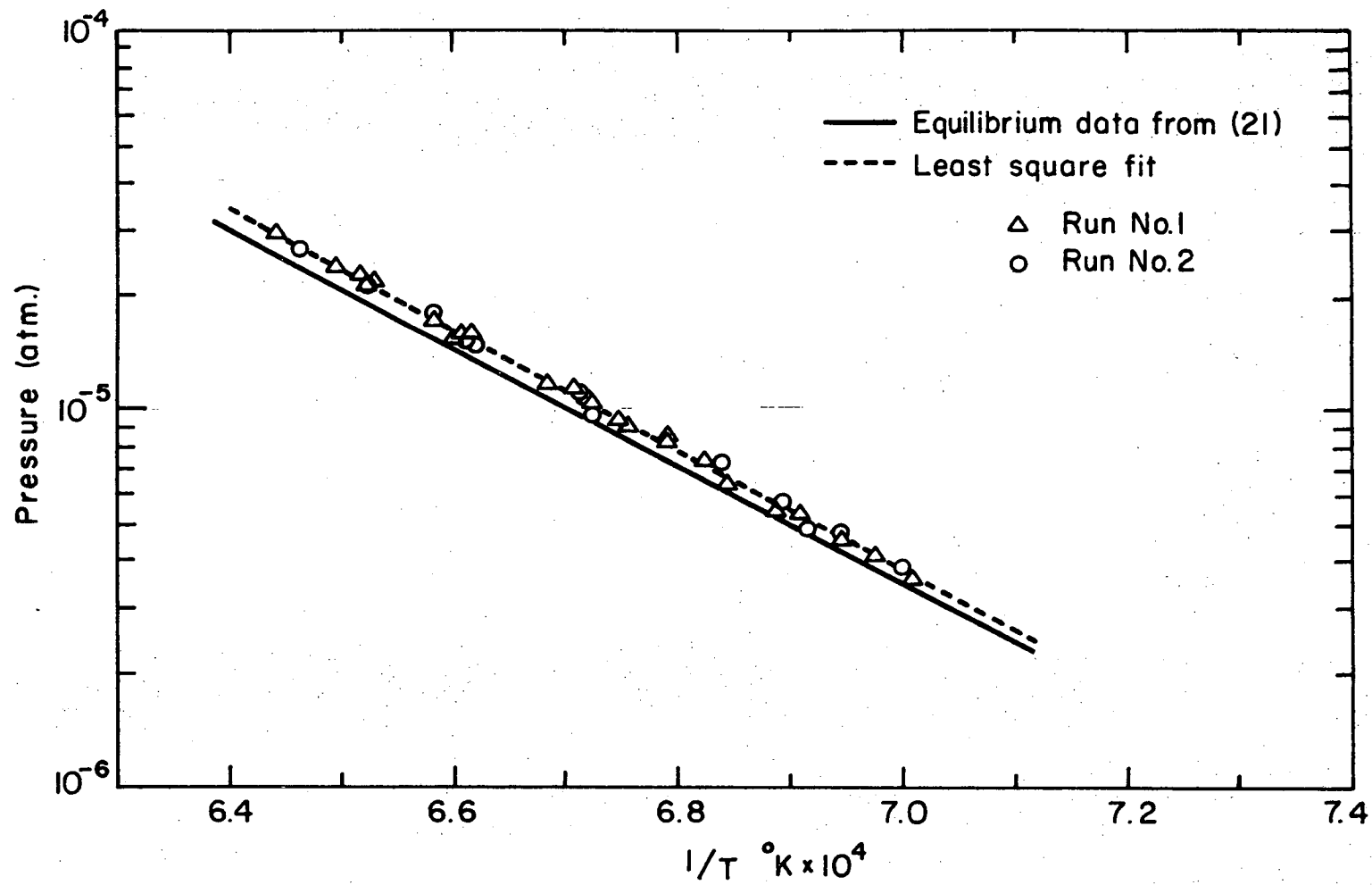
$$\Delta H_{298}^\circ = 71.7 \pm 0.1 \text{ Kcal/gm atom,}$$

while the value in reference (21) is 72.0 ± 0.4 Kcal.

The torsion-effusion and the torsion-Langmuir results of barium sulfate runs are shown in Fig. 2. Least square analysis gave the following calculated thermodynamic values in the temperature range of study, (about 1422°K to 1540°K):

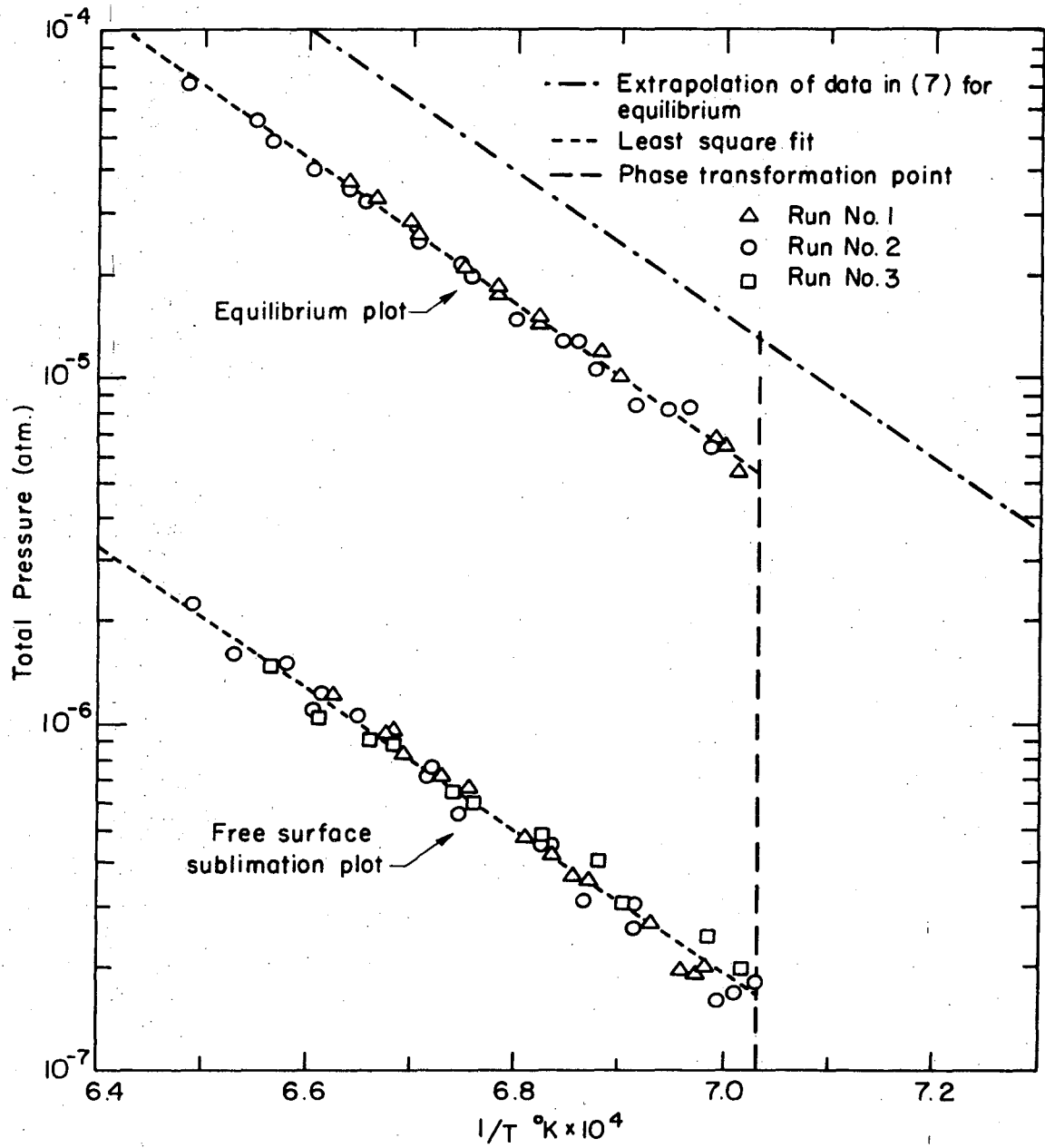
Torsion-effusion:

<u>Run #</u>	<u># of data pts</u>	<u><math>\Delta H_v^\circ</math>/Kcal</u>	<u><math>\Delta S_v^\circ</math>/eu</u>
1	14	148.2 ± 2.8	66.1 ± 1.9
2	17	142.5 ± 2.5	62.1 ± 1.7



XBL7211-7213

Fig. 1. Equilibrium Vapor pressures of tin.



XBL 7211-7214

Fig. 2. Equilibrium and free surface sublimation pressures of barium sulfate.

and for the combined data,

$$\Delta H_v^{\circ} = 143.7 \pm 2.0 \text{ Kcal/mole of BaSO}_4$$

$$\Delta S_v^{\circ} = 62.9 \pm 1.3 \text{ eu/mole of BaSO}_4.$$

Torsion-Langmuir: <sup>§</sup>

Run #	# of data pts	$\Delta H_v^*/\text{Kcal}$	$\Delta S_v^*/\text{eu}$
1	14	157.0 ± 3.7	61.5 ± 2.5
2	17	143.2 ± 4.0	52.1 ± 2.7
3	11 <sup>†</sup>	124.4 ± 4.0	39.5 ± 2.7

and for combined data, i.e. 42 data points

$$\Delta H_v^* = 141.1 \pm 3.0 \text{ Kcal/mole of BaSO}_4$$

$$\Delta S_v^* = 50.7 \pm 2.0 \text{ eu/mole of BaSO}_4. \text{ } ^{\ddagger}$$

Extrapolation of the equilibrium pressures obtained from data in (7) without correction for the unknown decrease in heat and entropy of decomposition at the transition temperature, 1422°K, gives

$$\Delta H_v^{\circ} = 143.4 \text{ Kcal/mole of BaSO}_4,$$

$$\Delta S_v^{\circ} = 65.4 \text{ eu/mole of BaSO}_4.$$

As can be seen from Fig. 2, the total pressures calculated from the low temperature data fall above the total pressures measured in this work by a factor of about 2.5.

§It is important to note that the steady state sublimation pressures did not show any time dependence.

†In this run 18 measurements were taken, but after 11 measurements, the pressures dropped suddenly, giving another parallel plot of log P vs 1/T. Upon opening the furnace and looking at the cells, this abrupt decrease in measured pressures was found to be due to displacement of one of the crystals in the cell.

‡Although the standard deviations are small in combined data, the real uncertainty is higher because of the deviations from run to run.



As mentioned earlier, an independent torsion effusion run was made with barium sulfate, using platinum cells. The total pressures obtained in this experiment were comparable to the total pressures obtained from alumina cells, but the slope of the plot was 12% lower. Since no temperature calibration was made for the platinum cells, the platinum cell data was not used for calculation of the heats and entropies. But the platinum cell run shows that the reaction between barium sulfate and alumina, in the alumina cell is negligible.

In calculations of the heat and the entropy of barium sulfate decomposition an equation of the form

$$\ln P = - \frac{2\Delta H_v^{o(*)}}{3R} \left( \frac{1}{T} \right) + \frac{2}{3} \left( \frac{\Delta S_v^{o(*)}}{R} - D \right) \quad (1)$$

has been used, (see Appendix 1), in which P is the total pressure measured, and D is a constant with the value -0.9740.

The deviation in heats and entropies for different independent torsion-Langmuir runs with barium sulfate are unusually high. These high deviations are probably not due to errors in experimentally measured quantities such as temperature, deflections or sample areas, because heats and entropies for torsion-effusion runs with tin and barium sulfate are much less scattered, and the tin data are in good agreement with the accepted values.

The heats and entropies measured for barium sulfate decomposition with either equilibrium or free surface vaporization techniques should be corrected by the amounts necessary to bring heats and entropies measured for tin under nearly identical experimental conditions into

exact agreement with the accepted values for tin. This is because the measured slope and intercept for tin are higher than the accepted values by 3.4% and 7.3%, respectively. The correction is made by multiplying each slope by ratio of the slope obtained for tin to the slope obtained for it from (21), and subtracting from each intercept the different of the two intercepts obtained from the sources mentioned, and then recalculating heats and entropies from these corrected values, using Eq. (1).

The corrected heats and entropies are as follows:

Torsion-effusion:

$$\Delta H_V^{\circ} = 138.9 \pm 1.9 \text{ Kcal/mole of BaSO}_4$$

$$\Delta S_V^{\circ} = 60.2 \pm 1.3 \text{ eu/mole of BaSO}_4.$$

Torsion-Langmuir:

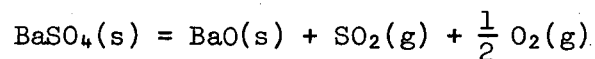
$$\Delta H_V^* = 136.4 \pm 2.9 \text{ Kcal/mole of BaSO}_4$$

$$\Delta S_V^* = 48.0 \pm 2.0 \text{ eu/mole of BaSO}_4.$$

No third law calculation is made for the barium sulfate data because high temperature free energy functions are not available, and the heat of transition from the low to high temperature crystal modification is unknown.

Despite the precaution exercised to protect the barium oxide formed in the decomposition reaction from hydrolysis, the X-ray studies on the surface of the Langmuir specimens showed nothing but a few diffraction lines which are expected for  $\alpha$  and  $\beta$  modifications of barium hydroxide-- it was not possible therefore to determine whether the oxide produced in the decomposition reaction was the stable crystalline form of barium oxide or an amorphous or metastable form.

In the mass spectrometer studies, the intensity of  $\text{SO}_2^+$  was found to be over two orders of magnitude higher than  $\text{SO}_3^+$ , both in the effusion case and for the free surface sublimation. Since the  $\text{SO}_3^+$  intensity increased with time in an unexplicable manner, a quantitative interpretation was not possible. However, the mass spectrometer studies confirmed the reaction



as the principal reaction for both the equilibrium and free surface sublimation.

#### IV. DISCUSSION

The direct measurements of barium sulfate dissociation pressure at the transition temperature between the low and high temperature modifications yielded values that were about 0.4 times the value predicted by combination of data for barium oxide, oxygen and sulfur dioxide with extrapolated thermodynamic data measured for barium sulfate at lower temperatures. The tin vapor pressure determinations in our apparatus in the same general temperature range as the barium sulfate pressure measurements, differed less than 10% from the values accepted by Hultgren and co-workers.<sup>21</sup> Furthermore, the measured heat of formation of barium sulfate is estimated to be uncertain by 5.0 Kcal,<sup>22</sup> and the extrapolations required estimation of heat capacity data for barium sulfate in the range from 1300°K to 1540°K. Accordingly, the direct dissociation pressure determinations of this study should be accepted as best describing the thermodynamics of the dissociation reaction at and above the transition temperature.

The studies of free surface vaporization rates for the reaction showed no measurable time dependence. Measured pressures in the free surface experiment remained about a factor of 0.03 below the pressures in the equilibrium studies. These observations are interesting to examine in light of the fact that in the time periods studied, the barium oxide layer on the sulfate surface grew to a thickness of nearly one millimeter.

Because of rapid hydrolysis of the barium oxide layer even when transfers of the samples were attempted in dried nitrogen, the form of the pores through the oxide layer could not be observed. But Beruto and

Searcy<sup>8</sup> found for calcite decomposition that most pores in the calcium oxide layer were of about  $2\mu$  diameter or less. Assuming similar pores for the barium oxide layer of this work, pore dimensions can be estimated. Theoretical calculations show that at the beginning of measurement, (after about 1.5 hour degassing at high temperatures), the oxide layer was about  $500\mu$  deep, while at the end it was about  $940\mu$  deep.\* Using the Dushman approximation for the Clausing factor<sup>#23</sup> at large values of  $l/a$ ,

$$K' = \frac{1}{1 + \frac{3}{8} \left( \frac{l}{a} \right)}$$

in which "l" is the length of the pores and "a" is the radius of the pores, the Clausing factors,  $K'$ , for the pores at the beginning and the end of the measurements are calculated to be about  $5.3 \times 10^{-3}$  and  $2.8 \times 10^{-3}$ , respectively.

If the gaseous molecules escaped from the pores by simple pore effusion, we would expect the pressures to be only about one-half as great at the end of the measurements as at the beginning. Because the pressures did not decrease with time, we conclude that the gaseous species probably escaped from pores by surface diffusion rather than pore effusion.

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\*The porosity of this layer was calculated to be about 48.3%.

#Since the force correction factors and the Clausing factors are similar in magnitudes,<sup>24</sup> for the purpose of this estimation, Clausing factors instead of force correction factors have been used.

It is interesting to note that since for large values of  $l/a$ ,  $K'$  becomes proportional to  $1/l$ , even if the pore diameters were considerably higher than those we assumed for the calculation, a decrease of a factor of about two in measured pressures would still be expected during the time of the measurements.

The ratio of the measured rates of free surface dissociation found in this study for barium sulfate decomposition and found by Beruto and Searcy for calcite decomposition are similar, about 0.03 and 0.02, respectively. The similarity in these values is probably fortuitous, however, in that experimental evidence suggests that the rate determining steps in the two reactions may well be different.

As was mentioned earlier, Searcy has developed a model<sup>2,13</sup> for vaporization reactions, in which a set of surface reactions are followed by the desorption step. He makes the provisional assumption that the rate of a vaporization reaction is controlled by the desorption step and compares the experimental results with the predicted results as a means of testing the assumption.

Thus he shows that for a desorption step to be rate limiting, the apparent heat of activation for vaporization,  $\Delta H_V^*$ , must be greater than or equal to the equilibrium heat of vaporization,  $\Delta H_V^O$ , and cannot be less than it. If  $\Delta H_V^* < \Delta H_V^O$  then a surface step rather than the desorption step must be rate limiting. On the other hand, if  $\Delta H_V^* > \Delta H_V^O$  and  $\Delta S_V^* \approx \Delta S_V^O$ , then he argues that the desorption step is probably rate limiting but the species leaving the surface in the case of free evaporation are either in excited states or leave excited sites on the surface. Unpublished theoretical analysis by Beruto and Searcy of

decomposition reaction kinetics indicates that these general conclusions apply also to those reactions.

Calcite shows the expected behavior for a desorption-limited reaction. Barium sulfate decomposition, however, shows a third type of behavior:<sup>2</sup>

$$\Delta H_V^* \approx \Delta H_V^0 \text{ and } \Delta S_V^* < \Delta S_V^0.$$

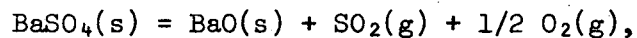
The simplest model that predicts the data for solids with this behavior is one in which only a fraction of the surface equal to the ratio of observed flux to the equilibrium flux is active in the vaporization process and desorption of the equilibrium reaction products is rate limiting. For barium sulfate, since  $\alpha_V = 0.030$ ,<sup>‡</sup> if this model is correct, only 3% of the exposed surface area is active. The observed behavior may reflect the fact that only a fraction of sites may be active in effecting the irreversible dissociation of surface complexes to SO<sub>2</sub> and O<sub>2</sub>.

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<sup>‡</sup>This is the value of  $\alpha_V$  at the mid-point of the temperature range. The value varies within 2.3% of its value over the entire temperature range.

APPENDIX 1

In the steady state effusion through the orifice of a Knudsen cell in which barium sulfate decomposes according to the equation



the flux of  $\text{SO}_2$  molecules must be twice the flux of  $\text{O}_2$  molecules, so

$$J_{\text{SO}_2} = 2J_{\text{O}_2} .$$

But since according to the kinetic theory of gases

$$J = \frac{P}{(2\pi MRT)^{1/2}}$$

then

$$\frac{P_{\text{SO}_2}}{(2\pi M_{\text{SO}_2} RT)^{1/2}} = \frac{2P_{\text{O}_2}}{(2\pi M_{\text{O}_2} RT)^{1/2}}$$

$$\therefore P_{\text{SO}_2} = 2P_{\text{O}_2} \left( \frac{M_{\text{SO}_2}}{M_{\text{O}_2}} \right)^{1/2}$$

On the other hand, since



$$P_{\text{total}} = P_{\text{SO}_2} + P_{\text{O}_2}$$

then

$$P = P_{\text{O}_2} \left[ 2 \left( \frac{M_{\text{SO}_2}}{M_{\text{O}_2}} \right)^{1/2} + 1 \right]$$

∴

$$P_{\text{O}_2} = \frac{P}{\left[ 2 \left( \frac{M_{\text{SO}_2}}{M_{\text{O}_2}} \right)^{1/2} + 1 \right]} \quad (1)$$

and

$$P_{\text{SO}_2} = \frac{P}{\left[ \frac{1}{2} \left( \frac{M_{\text{O}_2}}{M_{\text{SO}_2}} \right)^{1/2} + 1 \right]} \quad (2)$$

The equilibrium constant,  $K_{\text{eq}}$ , for the reaction is given by

$$K_{\text{eq}} = P_{\text{SO}_2} \times P_{\text{O}_2}^{1/2}$$

Substituting for  $P_{\text{SO}_2}$  and  $P_{\text{O}_2}$  from equations (1) and (2), and manipulating the result gives

$$K_{eq} = \frac{2 \left( \frac{M_{SO_2}}{M_{O_2}} \right)^{1/2}}{\left[ 2 \left( \frac{M_{SO_2}}{M_{O_2}} \right)^{1/2} + 1 \right]^{3/2}} \times P^{3/2} = CP^{3/2}$$

where

$$C = \frac{2 \left( \frac{M_{SO_2}}{M_{O_2}} \right)^{1/2}}{\left[ 2 \left( \frac{M_{SO_2}}{M_{O_2}} \right)^{1/2} + 1 \right]^{3/2}}$$

On the other hand we have<sup>2</sup>

$$\ln K_{eq} = - \frac{\Delta H_v^{\circ}}{R} \left( \frac{1}{T} \right) + \frac{\Delta S_v^{\circ}}{R}$$

Substitution for  $K_{eq}$  into this equation gives

$$\ln C + \frac{3}{2} \ln P = - \frac{\Delta H_v^{\circ}}{R} \left( \frac{1}{T} \right) + \frac{\Delta S_v^{\circ}}{R}$$

which upon manipulation gives

$$\ln P = - \frac{2\Delta H_v^{\circ}}{3R} \left( \frac{1}{T} \right) + \frac{2}{3} \left( \frac{\Delta S_v^{\circ}}{R} - D \right) \quad (3)$$

where  $D = \ln C$ , and has the value of  $-0.9740$ .

Note that for the free surface sublimation we again use Eq. (3) but we replace  $\Delta H_v^{\circ}$  and  $\Delta S_v^{\circ}$  by  $\Delta H_v^{*}$  and  $\Delta S_v^{*}$ , respectively. Therefore, as a matter of brevity, we write

$$\ln P = - \frac{2\Delta H_v^{\circ(*)}}{3R} \left( \frac{1}{T} \right) + \frac{2}{3} \left( \frac{\Delta S_v^{\circ(*)}}{R} - D \right) .$$

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