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Author
Basu, Tushar Kanti.

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Tushar Kanti Basu
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THE KINETICS OF DECOMPOSITION OF BARIUM CARBONATE

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THE KINETICS OF DECOMPOSITION OF BARIUM CARBONATE

Tushar Kanti Basu

Inorganic Materials Research Division, Lawrence Berkeley Laboratory
and Department of Materials Science and Engineering,
College of Engineering; University of California,
Berkeley, California 94720

ABSTRACT

The equilibrium vapor pressure of barium carbonate and the vacuum decomposition kinetics of the (001) face of its single crystal were studied by use of torsion-effusion and torsion-Langmuir techniques respectively. The measured equilibrium pressures for the substance showed a strong dependence on effusion orifice area. The apparent activation enthalpy of decomposition for the reaction

$$BaCO_3(s) = BaO(s) + CO_2(g)$$
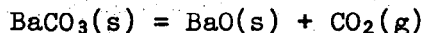
was found to be 54.0 Kcal, which is less than the enthalpy of the equilibrium reaction, 60.25 Kcal. The apparent entropy for the reaction was 12.8 eu. This entropy is also less than the entropy of the equilibrium reaction, 35.05 eu, in the temperature range studied.

The rate of the free surface decomposition reaction was constant, within the experimental scatter in data, during the period of the measurements, so the effusion of product gases through the porous product layer is not rate limiting. The ratio of the free surface decomposition pressure to the equilibrium decomposition pressure decreased in the temperature range of study from 2.4×10^{-4} at 1100°K to 1.9×10^{-4} at 1200°K.

I.   INTRODUCTION

Decomposition reactions, that is reactions of the type

$$AB(s) = A(s) + B(g)$$
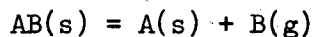
are of considerable practical importance in chemical processing of
minerals such as carbonates, hydroxides and hydrates. Extensive effort
has been devoted to the determination of the kinetics of decomposition
reactions, but almost all studies have been made with powdered or
granular samples and in inert atmospheres or low vacuum.

Recent work in our laboratory demonstrates that the Langmuir and
torsion-Langmuir methods for study of the kinetics of vaporization of
congruently vaporizing solids, are ideally suited for the study of decom-
position reactions.[1,2]

In particular, when information about the rate limiting surface
reaction step is sought, Langmuir and torsion-Langmuir studies of the
decomposition of single crystals in vacuum have several advantages:
(1) The possibility that intergranular gas phase diffusion may be slow
enough to influence the measured reaction rate is eliminated; (2) the
area and the morphology of the interface at which the reaction proceeds
can be precisely determined as a function of time. With powders there is
often considerable uncertainty about the effective area of reaction,
which contributes to uncertainty or disagreement about the nature of the
rate limiting process. (3) The ratio of the measured flux of gaseous
reaction product which leaves the reactant surface to the maximum possible
flux, which can be predicted from equilibrium data and the kinetic theory
of gases,[3] provides a valuable parameter for describing and understand-
ing the reaction kinetics.

The last named advantage is potentially important. The ratio of
the measured flux of vapor to the maximum flux predicted from the
equilibrium dissociation pressure by means of the Hertz-Knudsen-Langmuir
(H-K-L) equation[4] provides for endothermic decomposition reactions a
valuable measure of the irreversibility of the rate limiting reaction
step, just as it does for simple vaporization reactions[5] and for con-
gruent dissociative vaporization reaction.[6-8]

Knowledge of the deviation of decomposition rates from the maximum
possible rates makes it easier to predict unknown rates, whether or not
any mechanistic interpretation of the data is attempted.[6] Most simple
vaporization reactions and congruent dissociative vaporization reactions
occur either at their maximum possible rates or at rates only one or two
orders of magnitude lower, and the vaporization reactions of chemically
similar substances show generally similar deviations from their maximum
possible rates. In consequence, rates of vaporization can be predicted
when experimental measurements of the rates are unavailable with much
greater confidence than is possible for most classes of reactions.
Similar regularities can be expected for endothermic decomposition
reaction. But additional Langmuir or torsion-Langmuir studies are needed
to establish patterns of systematic deviations of measured decomposition
rates from predictions of the H-K-L equation.

To date the Langmuir method has been applied only to study the
decomposition of calcite[1] and the torsion-Langmuir method has been applied
only to study the decomposition of barium sulfate.[2] Barium carbonate has
been chosen as a substance to further test the applicability of torsion-
Langmuir technique. Though many studies have been made of the kinetics

of decomposition of calcite, no studies have been made of the decomposition of barium carbonate, which at the temperature of our decomposition studies has the aragonite-type structure.[9]

Thermodynamic data[9] indicated that barium carbonate should decompose according to the equation

$$BaCO_3(s) = BaO(s) + CO_2(g).$$
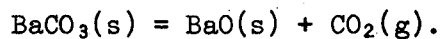
The equilibrium decomposition pressure was redetermined as part of the present study by the torsion-effusion technique in order to confirm the reliability of the thermodynamic data.

II. EXPERIMENTAL

The torsion-effusion technique[4] is a method for measuring directly the recoil force exerted by a vapor effusing into a vacuum from a small hole, and the torsion-Langmuir technique[4] is a method for measuring the recoil momentum imparted to a sample surface by vaporizing molecules. In applying both the methods, the cell is suspended in a vacuum furnace by a fine wire. Upon heating, vapor escapes through eccentrically placed orifices in the cell, thereby exerting forces which produce torque on the wire. In a cell with two anti-parallel orifices which are cylindrical, the individual torques resulting from effusion are additive. The angle through which the cell is turned is measured, and from this angle the vapor pressure can be calculated by means of the formula

$$P = 2\phi D/\Sigma qaf$$

where P is the vapor pressure to be measured, D is torsion constant of the wire, q is the perpendicular distance from the cell center to the axis of the effusing hole, a is the area of orifice, f is the force reduction factor due to finite orifice channel lengths, and ϕ is the angle through which the cell is rotated. Values for f have been tabulated by Freeman and Searcy[10] and by Schulz and Searcy.[11]

The apparatus is essentially the same as the one described by R. T. Coyle.[12]

A. Sample Preparation

Witherite (BaCO₃) single crystals obtained from Hexham, England, were analyzed by the American Spectrographic Laboratories, Inc. They reported the following impurities as oxides of the elements:

Sr	3.0%
Ca	0.035
Si	0.005
Mg	< 0.001
Al	0.001
Cu	< 0.001

The crystals were cut with a diamond saw along the (001) plane in order to obtain 1 mm thick wafers. The powdered barium carbonate of 99.9% purity was obtained from Mallinckrodt Chemical Works, St. Louis, Mo., for use in the equilibrium studies.

B. Cell Preparation

Two cylindrical alumina cells (99.5 purity) were mounted with their cylindrical axes horizontal in a graphite cell holder. The graphite cell holder was used because it is very light in weight. A protective molybdenum foil between cells and the cell holder prevented reaction between the graphite and alumina. The alumina cells were designed so that they could be used interchangeably for torsion-effusion and torsion-Langmuir studies. The torsion constant of the wire was 0.7219 dyne-cm-rad^{-1}. The moment arms were both 1.04 cm. Knudsen cells and Langmuir cells of different dimensions were used. Dimensions are shown in Table I.

Table I. Effusion geometries

Cell	Hole diameter			Lid thickness		
	(1)	cm	(2)	(1)	cm	(2)
Knudsen cell						
1	0.0820		0.0830	0.0863		0.0880
2	0.1002		0.1001	0.0787		0.0840
Langmuir cell						
3	0.2954		0.2954	0.0792		0.0797

C. Calibrations

A region of the furnace was found in which a vertical displacement of the cell of ± 2.0 cm gave a constant temperature to within 1.5°K, then the temperature inside a dummy graphite cell was measured to calibrate a second thermocouple placed 6 mm below the cell holder.

A tungsten torsion wire of 0.015" was used for suspending the cell assembly. The torsion constant of the wire was determined from its period of oscillation when it supported a brass disc with known moment of inertia. The constant was checked repeatedly to insure that it remained unchanged to within 5%.

Finally, the apparatus was calibrated with sodium chloride for which the equilibrium vapor pressure is well known.

D. Witherite Runs

Two independent effusion runs were made with barium carbonate powder and two Langmuir runs were made with (001) faces of barium carbonate single crystals as free vaporizing surfaces. In all cases, the pressures

were measured at temperatures above a phase transformation at 1023°K.
The low temperature crystallographic modification (witherite) is orthor-
hombic and the high temperature phase is hexagonal.[9]

At the beginning of each run, the cells were heated at about 1100°K
until the ambient pressure in the furnace fell to 5×10^{-5} torr or less.
Usually that pressure was reached in one to one and one-half hours. In
any particular run from ten to sixteen points were taken with at least
15 minutes being allowed after each temperature change in order to ensure
that equilibrium was reached. The effusion measurements were corrected
by the force-correction factor for finite channel lengths,[10] but factors
were not used for the torsion-Langmuir measurements; because the evapora-
tion coefficient is low, the condensation coefficient of molecules re-
turned to the surface after collision with wall should also be low,[6] and
these molecules should eventually escape.

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

A scanning electron microscope and optical microscope both were used
to examine the various surfaces before and after partial decomposition
had taken place.

III. RESULTS

The torsion effusion results of sodium chloride are shown in Fig. 1. Least square analysis of the data yield the following calculated thermo-dynamic values given below:

Table II. Heats and entropies of vaporization

Run No.	No. of data pts	ΔH_v° Kcal	ΔS_v° eu
1	17	58.2 ± 0.78	41.0 ± 0.7
2	15	57.0 ± 0.68	38.9 ± 0.7

and the combined data gives:

ΔH_v° = 57.4 ± 0.7 Kcal/mole of NaCl

ΔS_v° = 39.4 ± 0.7 eu/mole of NaCl

The accepted values (13) at the midpoint of the temperature range over which this work was conducted is

ΔH_v° = 55.4 Kcal/mole of NaCl

ΔS_v° = 36.8 eu/mole of NaCl

Several initial runs were made for barium carbonate with a 2 mil diameter torsion wire. The data were somewhat scattered, and a 1-1/2 mil wire was substituted in hopes that the scatter would be reduced. Figure 2 shows the results obtained with this smaller wire using cells with two different orifice geometries. The data obtained with the 2 mil wire agree, except for greater scatter, with data obtained with the 1-1/2 mil wire as long as the orifice geometry was constant. There was, however, a marked trend in observed pressures with effusion orifice size, higher
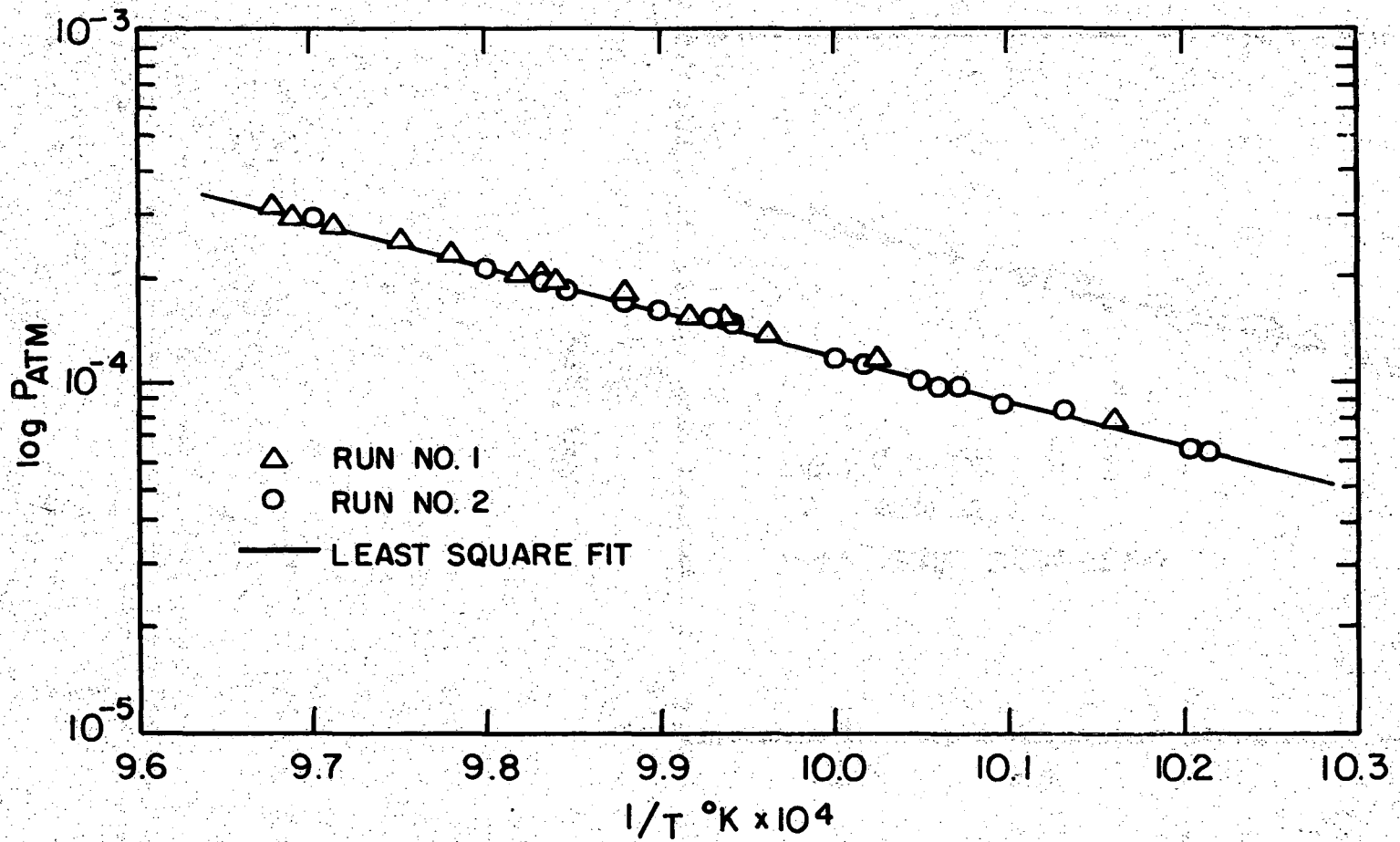
Fig. 1. Equilibrium vapor pressures of sodium chloride.
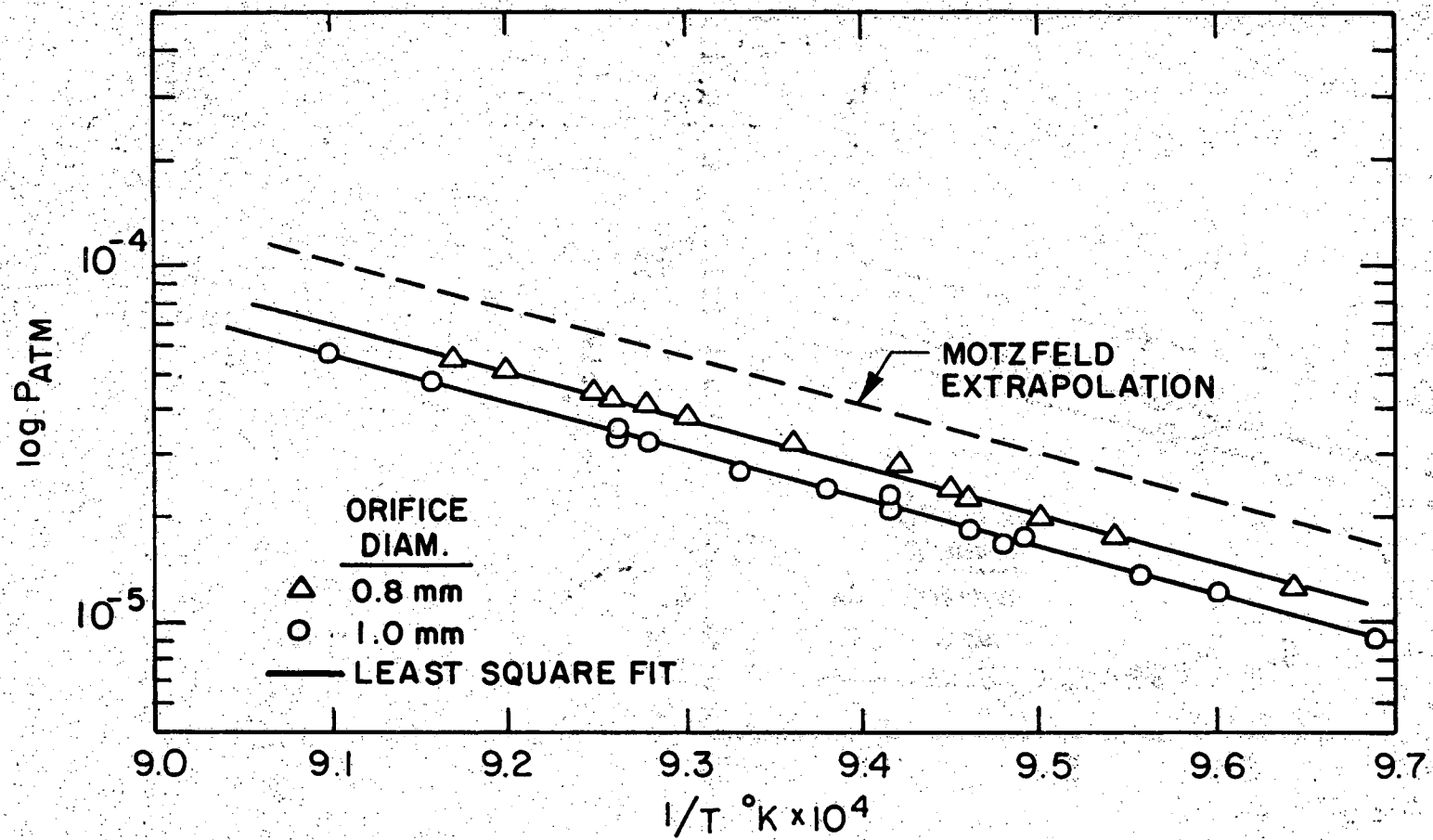
XBL 742-5644

Fig. 2. Equilibrium pressure of barium carbonate.

pressures were obtained with smaller orifices. Figure 2 shows data for runs with the two different pairs of orifices. Additional data are summarized in Appendix A. Equilibrium pressures were calculated from the effusion data for barium carbonate by means of the Whitman-Motzfeld[14] equation:

$$P\ eq = P\ obs\ (1 + \frac{fa}{\alpha A})\qquad\qquad (1)$$

where P obs is the measured effusion pressure, a is the effusion orifice area, f is the associated orifice force factor, α is vaporization co-efficient and A is the effective vaporizing surface area. The pressures measured with the two different sets of orifices gave by the method of least squares two separate curves of log P vs 1/T. The data from these two smoothed curves at two different temperatures were substituted into Eq. (1) to obtain the equilibrium pressure as a function of temperatures. From the slopes and intercepts of the resulting equilibrium curve (Fig. 2) the following thermodynamic values were obtained:

ΔHv^{o} = 61.3 ± 1.8 Kcal/mole of $BaCO_3$

ΔSv^{o} = 36.7 + 1.2 eu/mole of $BaCO_3$

Torsion-Langmuir measurements for the (001) face are shown in Fig. 3. Least square analysis of the data yields the values of apparent enthalpy and apparent entropy of vaporization shown below:

Table III. Apparent heats and entropies of activation

Run No.	No. of data pts	ΔHv^{*} Kcal	ΔSv^{*} eu
1	12	55.7 ± 1.5	14.4 ± 0.7
2	14	54.2 ± 1.9	14.2 ± 0.5

and the combined data gives

$\Delta \overset{*}{H}v$ = 55.0 ± 1.6 Kcal/mole of $BaCO_3$

$\Delta \overset{*}{S}v$ = 14.0 + 0.9 eu/mole of $BaCO_3$

As seen in Fig. 3, two independent runs lead to consistent results with little experimental scatter.

The heats and entropies measured for barium carbonate decomposition with either equilibrium or free surface vaporization techniques should be corrected by the amounts necessary to bring heat and entropies measured for sodium chloride under nearly identical experimental conditions into exact agreement with the accepted values for sodium chloride. The corrections were made by multiplying measured torsion-effusion and torsion-Langmuir carbon dioxide pressures by the ratio of accepted (13) sodium chloride pressures to measured sodium chloride pressures at two different temperatures. The corrections in pressures were 5% or less in the range of study. From the slopes and intercepts of the resulting new curves of log P vs 1/T, corrected heats and entropies were calculated.

The corrected values are:

Torsion-effusion:

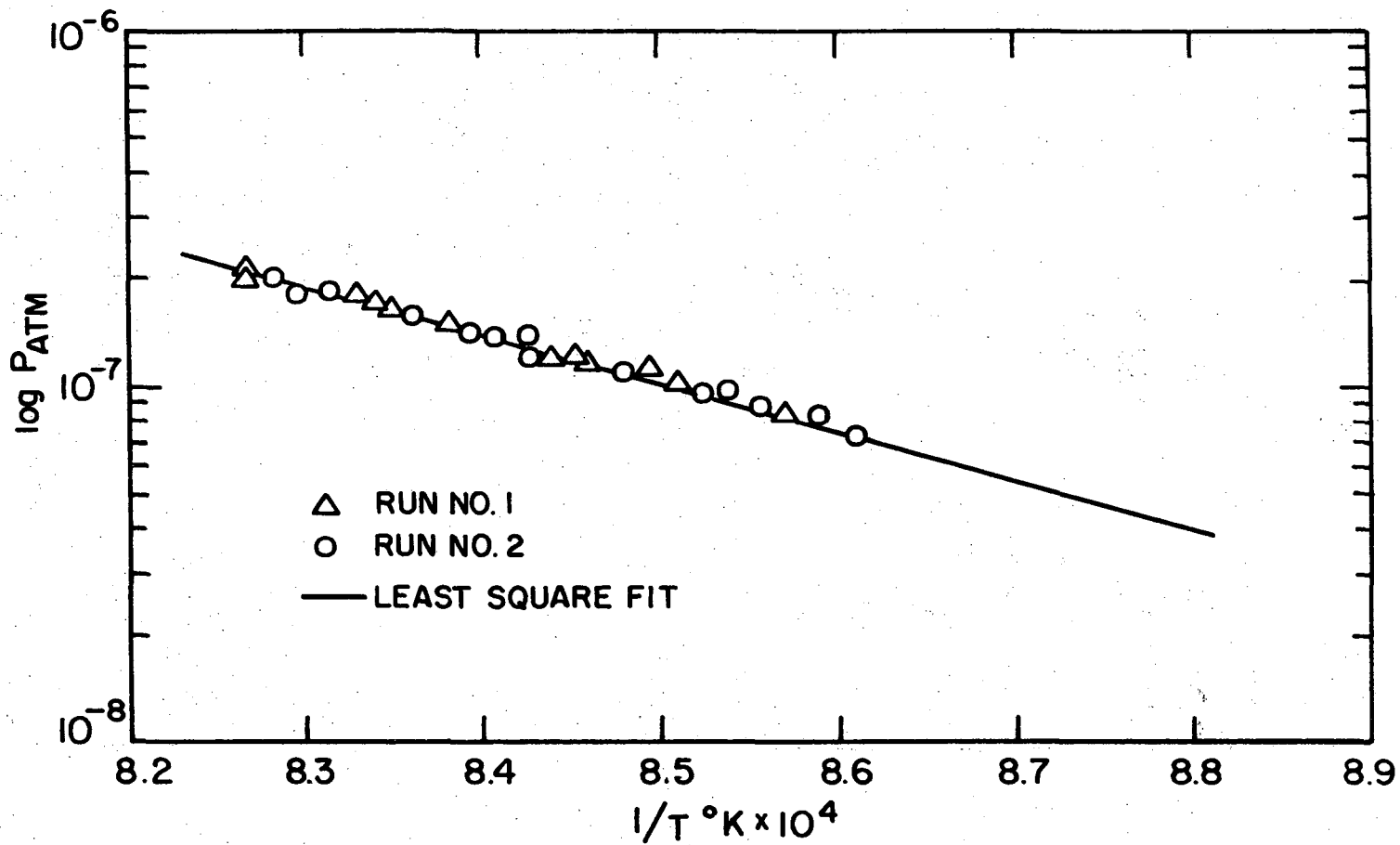$\Delta \overset{o}{H}v$ = 60.25 ± 1.8 Kcal/mole of $BaCO_3$

$\Delta \overset{o}{S}v$ = 35.05 ± 1.2 eu/mole of $BaCO_3$

Torsion-Langmuir:

$\Delta \overset{*}{H}v$ = 54.0 ± 1.6 Kcal/mole of $BaCO_3$

$\Delta \overset{*}{S}v$ = 12.8 ± 0.7 eu/mole of $BaCO_3$

Extrapolation of equilibrium pressures obtained from room temperature calorimetric and heat capacity data in (9) to the same experimental range of this work gives:

Fig. 3. Langmuir pressures of barium carbonate single crystals.

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$$\Delta \overset{\circ}{H}v = 61.6 \text{ Kcal/mole of } BaCO_3$$

$$\Delta \overset{\circ}{S}v = 37.4 \text{ eu/mole of } BaCO_3$$

if the unknown heat and entropy of the crystallographic transition at
1023°K are neglected. The two sets of equilibrium data are consistent
with an assumed heat of transition of 1.3 Kcal/mole, a reasonable value,
but the uncertainty is of the order of 2 Kcal.

No third law calculation was made from the barium carbonate 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.

X-ray diffraction studies on the surface of Langmuir specimens showed
the layer of stable crystalline BaO which is formed on decomposition is
in its normal structure (NaCl-type) with the crystallites randomly
oriented relative to the carbonates surface. X-ray patterns also showed
that the single crystal of orthorhombic barium carbonate was recovered
after heating.

Figure 4 is an optical photograph of a crystal after vaporization
from the (001) surface. It is apparent from the figure that the area of
vaporization remained substantially constant throughout the run. The
vaporized surfaces after vaporization were examined with the scanning
electron microscope (SEM). Figure 5 is an SEM photo taken at 1000X of
the product layer of barium oxide on the (001) face of barium carbonate.
The pores are about 1μ or smaller diameter. These pores result because
the decomposition of witherite, which has a molal volume of 44.5 cm^3,
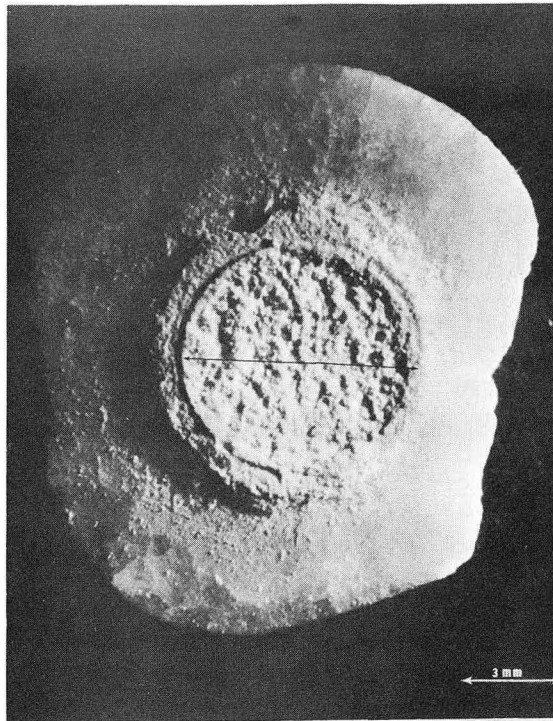yields barium oxide for which the molal volume is 26.8 cm^3.

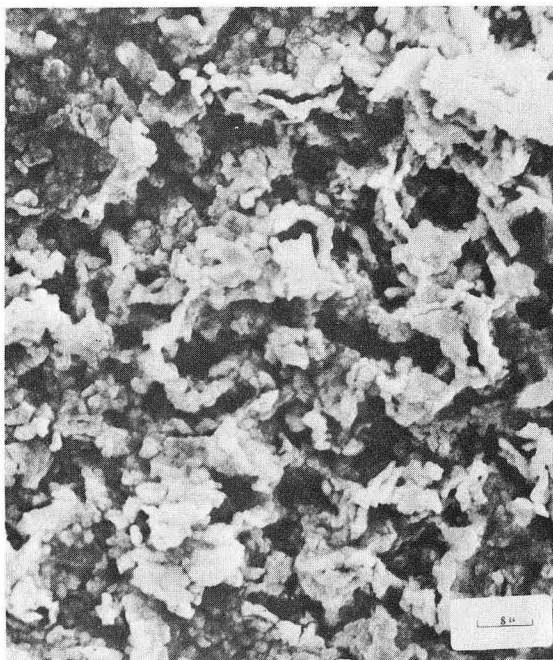Fig. 4. (001) face after decomposition (optical photograph).

Fig. 5. Scanning electron micrograph of center of Figure 4.

IV. DISCUSSION

The sodium chloride vapor pressure measurements in our apparatus in approximately the same temperature range as the barium carbonate pressure measurements differed by less than 5% from the values calculated from JANAF thermodynamic data.[13] Accordingly, the heat and entropy of decomposition of barium carbonate, when corrected as described above, can be accepted as best representing the thermodynamics of the barium carbonate dissociation reaction at temperatures above the barium carbonate phase transition.

Two aspects of the kinetic data are of special interest: the dependence of the decomposition rates on time of heating at constant temperatures and the dependence of the rate on temperature.

The rate of decomposition of barium carbonate at a fixed temperature proved to be independent of the quantity of carbon dioxide evolved until at least 80% of the barium carbonate had decomposed. This means that the rate was unaffected by barium oxide product layers up to some 1 mm (1000μ) in thickness.

As stated earlier, most of the pores through the oxide layer are of 1μ diameter or less. Dushman[15] provides an equation which correlates for Knudsen flow the fraction K of molecules which, having entered one end of a pore of length, ℓ, and radius, a, will escape from the end of the pore rather than return to the initial vapor source:

$$K = \frac{1}{1+\frac{3}{8}(\ell/a)} \tag{2}$$

According to Eq. (2), the vaporization flux should decrease with increasing product layer as K decreases with increasing ℓ. For an oxide layer 1000μ thick and about 1μ radius, the expected rate of escape of carbon dioxide should be reduced by a factor of about 1000 below the initial rate if the carbonate surface acts as an equilibrium source.

But barium carbonate clearly does not act as an equilibrium source of carbon dioxide when the decomposition is carried out in vacuum because the temperature dependence of carbon dioxide evolution is different from the temperature dependence of the equilibrium vaporization reaction. It is noteworthy that while most, and perhaps all, of the apparent activation enthalpies reported for decomposition reactions are either equal to the enthalpies of the equilibrium decomposition reaction or are larger,[5] the apparent activation enthalpy found for barium carbonate is smaller.

The low activation enthalpy is one of several items of evidence that the kinetics of barium carbonate decomposition are very different from the kinetics of calcium carbonate decomposition. Calcium carbonate, in the form of calcite single crystals, was found to decompose in vacuum by a process for which the apparent activation enthalpy is greater than the enthalpy of the equilibrium decomposition reaction.[1] Furthermore, a thin layer of a metastable form of calcium oxide was shown to be the direct product of the decomposition of calcite while no such metastable product could be detected in the present study. An additional important difference between barium carbonate and calcium carbonate decomposition in vacuum is that calcium carbonate was found to decompose in the experimental temperature range at a rate about 1/50 the maximum possible rate,

which can be calculated from substitution of equilibrium dissociation pressure into the Langmuir equation,[3] while for barium carbonate the observed rate was much lower, about 1/5000 the maximum possible rate.

The ratio of the observed flux J_L to the maximum possible flux Jm i.e. $J_L/Jm = P_L/P$ eq $= \alpha_d$, the decomposition coefficient, provides a useful measure of the irreversibility of a decomposition reaction.[16] For barium carbonate α_d, the decomposition coefficient was found to be 1.8×10^{-4} at the midpoint of the working temperature range (i.e. $1066°K$). When the effective surface area of samples in the effusion cell is assumed to be the cross-sectional area of the cell, a value $\alpha_d = 10^{-3}$ is calculated from the Whitman-Motzfeld equation (Eq. (1)). Since the effective area for decomposition inside the cell can be larger than cross-sectional area by an unknown amount, this second value is an upper limit which is consistent with the value calculated from the torsion-Langmuir data.

The very low decomposition coefficient for barium carbonate can account for the fact that substantial reduction in carbon dioxide flux predicted by Dushman's relation to result from the porous oxide layer is not observed. Searcy and Beruto[16] have derived an expression that shows that for an irreversible decomposition reaction a porous layer will measurably reduce the rate only when the ratio a/ℓ for the pores becomes as small as the value of the decomposition coefficient, α_d. In this study α_d was always smaller than estimated minimum values of a/ℓ.

No attempt to identify the slow reaction step or steps, will be made in this thesis because published theories[5] for analysis of the kinetics of decomposition reactions do not address the possibility that slow

processes at the reactant-vapor and reactant-solid product interfaces may both simultaneously influence the reaction rate. The analysis of Searcy and Beruto shows that low apparent activation enthalpies such as encountered in the present study can result when processes at these two different interfaces are both irreversible. A discussion of this possibility should await publication of their analysis.

ACKNOWLEDGEMENTS

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APPENDIX A
Table IV. Carbon-dioxide partial pressures from effusion
measurements for the reaction $BaCO_3(s) = BaO(s) + CO_2(g)$

Conditions	T(°K)	CO_2 partial pressure (atm x 10^{-5})
Alumina cell	1089	5.04
Diam. of torsion wire	1057	2.26
= 0.002"	1009	0.28
Orifice diam. = 1 mm	1067	2.90
	1021	0.69
	1044	1.59
	1022	0.68
	1048	1.80
	1006	0.36
	1027	1.00
	1060	2.34
	1004	0.32
Alumina cell	1092	4.82
Diam. of torsion wire	1080	3.78
= 0.015"	1098	5.61
Orifice diam. = 1 mm	1062	2.21
	1066	2.33
	1042	1.32
	1046	1.33
	1031	0.91
	1053	1.73
	1080	3.24
	1072	2.58
	1079	3.11
	1054	1.57
	1062	1.86
	1040	1.18
Alumina cell	1090	5.64
Diam. of torsion wire	1086	5.02
= 0.015"	1080	4.37
Orifice diam. = 0.8 mm	1052	1.97
	1079	4.13
	1077	4.05
	1056	2.28
	1075	3.63
	1047	1.67
	1067	3.19
	1037	1.31
	1061	2.82
	1058	2.37
	1090	5.61