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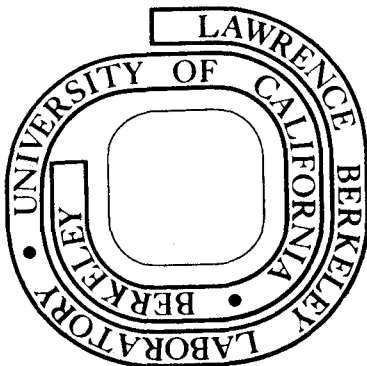Tushar Kanti Basu and Alan W. Searcy

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DISCLAIMER

THE KINETICS AND THERMODYNAMICS OF DECOMPOSITION OF BARIUM CARBONATE

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ABSTRACT

The equilibrium vapor pressure of barium carbonate and the vacuum decomposition rates of the (001) face of its single crystal were measured by torsion-effusion and torsion-Langmuir techniques, respectively. The rate of the free surface decomposition reaction was constant for product layers up to about 1 mm thickness. The apparent activation enthalpy of decomposition for the reaction

$$BaCO_3(s) = BaO(s) + CO_2(g)$$

is 225.9 KJ, which is less than the enthalpy of the equilibrium reaction, 251.1 KJ. The apparent activation entropy for the reaction is 53.5 J/deg. This entropy is also less than the entropy of the equilibrium reaction, 146.6 J/deg in the temperature range studied. These results prove that desorption of carbon dioxide cannot be 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.

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 the 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

$$BaCO_3(s) = BaO(s) + CO_2(g).$$
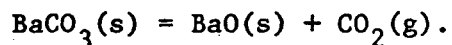
The equilibrium decomposition pressure was measured as part of the present study by the torsion-effusion technique in order to obtain thermodynamic data above a transition point at 1023°K.

<div align="center">EXPERIMENTAL</div>

The torsion-effusion technique 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 is a method for measuring the recoil force imparted to a sample surface by vaporizing molecules.[4] In either method, vapor escapes through eccentrically placed orifices in a rigid structure which is suspended from a fine wire, thereby exerting forces which produce a torque on the wire. The individual torques resulting from effusion are additive. The vapor pressure can be calculated from the angle through which the cell is rotated by means of the formula

$$P = 2\phi D / \sum_i q_i a_i f_i$$

where P is the vapor pressure to be measured, D is the torsion constant of the wire, q_i is the perpendicular distance from the cell center to the axis of an orifice i, a_i is the area of the orifice, f_i is the force reduction factor due to finite orifice channel lengths,[10,11] and ϕ is the angle through which the cell is rotated.

The apparatus is essentially the same as the one described by R. T. Coyle.[12,2]

Witherite ($BaCO_3$) single crystals obtained from Hexham, England, were analyzed by the American Spectrographic Laboratories, Inc., which reported the following impurities as oxides of the elements: 3.0% Sr, 0.035 Ca, 0.005 Si, <0.001 Mg, 0.001 Al, <0.001 Cu.

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

Two cylindrical alumina cells (99.5 purity) were mounted with their cylindrical axes horizontal in a light weight graphite cell holder. 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. Orifice and collimating geometries for the Knudsen cells and Langmuir cells are given in Table I.

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.

The cell assembly was suspended from a 1.5 mil diameter tungsten wire. 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%. The apparatus was calibrated with sodium chloride for which the equilibrium vapor pressure is well known.

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 orthorhombic and the high temperature phase is hexagonal (aragonite-type).[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 10 to 16 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 evaporation coefficient is low, the condensation coefficient of molecules returned to the surface after collision with a 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. A scanning electron

microscope and optical microscope both were used to examine the various

surfaces before and after partial decomposition had taken place.

RESULTS

Two torsion effusion measurements of sodium chloride yielded by

least square analysis ΔH_v^o = 243.5 ± 3.3 KJ, ΔS_v^o = 171.5 ± 2.9 J/deg, and

ΔH_v^o = 238.5 ± 2.8 KJ, ΔS_v^o 162.7 ± 2.9 J/deg for the standard molar heats

and entropies of vaporization. The combined data give ΔH_v^o = 240.2 ± 2.9

KJ, and ΔS_v^o = 164.8 ± 2.9 KJ. The accepted values (13) at the midpoint

of the temperature range over which this work was conducted are

ΔH_v^o = 231.8 KJ and ΔS_v^o = 153.9 J/deg.

Figure 1 shows the results obtained for barium carbonate decompo-

sition with two different orifice geometries. Several preliminary runs

made with a 2 mil wire agree, except for greater scatter, with the data

obtained with the 1-1/2 mil wire as long as the orifice geometry was con-

stant. There was, however, a marked trend in observed pressures with

effusion orifice size; higher pressures were obtained with smaller

orifices. Equilibrium dissociation pressures were calculated from the

effusion data by means of the Whitman-Motzfeld[14,4] equation

$$P_{eq} = P_m \left(1 + \frac{fa}{\alpha A}\right) \qquad (1)$$

where P_m is the measured effusion pressure, α is the decomposition

pressure coefficient, and A is the effective vaporizing surface area.

From the slopes and intercepts of the calculated equilibrium curve

(Fig. 2) the standard molar heats and entropies of dissociation to

barium oxide and carbon dioxide gas were calculated to be 256.5 ± 7.5 KJ

and 153.6 ± 5 J/deg, respectively.

Torsion-Langmuir measurements for the (001) face are shown in Fig. 2. Least square analysis of the combined data yields for the apparent enthalpy and apparent entropy of decomposition 230.1 ± 6.7 KJ and 58.6 ± 3.7 J/deg.

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[13] for sodium chloride. The corrections were made by multiplying measured torsion-effusion and torsion-Langmuir carbon dioxide pressures by the ratio of accepted 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 molar values are:

Torsion-effusion: $\Delta H_d^o = 252.1 \pm 7.5$ KJ

$\Delta S_d^o = 146.6 \pm 5.0$ J/deg.

Torsion-Langmuir: $\Delta H_d^* = 225.9 \pm 6.7$ KJ

$\Delta S_d^* = 53.5 \pm 2.9$ J/deg

Extrapolation of equilibrium pressures obtained from room temperature calorimetric and heat capacity data in (9) to the same experimental range of this work gives $\Delta H_d^o = 257.7$ KJ and $\Delta S_d^o = 156.5$ J/deg 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 6 KJ/mole, a reasonable value, but the

uncertainty is of the order of 9 KJ.

X-ray diffraction studies on the surface of Langmuir specimens showed

the layer of stable crystalline barium oxide which is formed on decom-

position is in its normal structrue (NaCl-type) with the crystallites

randomly oriented relative to the carbonate surface. X-ray patterns

also showed that the undecomposed portion of the carbonate was reconverted

from the high temperature modification to a single crystal of the orthor-

hombic modification after heating. The surfaces after vaporization were

examined with the scanning electron microscope. Pores were observed to

be about 1μ in 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.

DISCUSSION

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 tempera-

ture 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 in thickness.

As stated earlier, most of the pores through the oxide layer are

of 10^{-3} mm. diameter. Dushman[15] provides an equation which predicts for Knudsen

flow the fraction K of molecules which, having entered one end of a

cylindrical channel of length, ℓ, and radius, a, will escape from the other end of the channel rather than return to the initial vapor source:

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

According to Eq. (2), the vaporization flux should decrease with increasing product layer thickness. For an oxide layer 1 mm thick and with pores of about 10^{-3} mm 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 measured flux is only about 2×10^{-4} times the flux which is obtained from an equilibrium source—the flux corresponding to the Whitman-Motzfeld extrapolated pressure.

The low activation enthalpy and entropies found for barium carbonate decomposition must reflect a markedly different rate limiting process from that which characterizes calcium carbonate decomposition.[1] 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 and the apparent enthalpy is approximately equal to the equilibrium value. 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. Both the metastable oxide and the stable outer oxide layer were, unlike the barium

oxide from barium carbonate decomposition, preferentially oriented relative to the underlying carbonate.

It has been shown for vaporization reactions that desorption cannot be rate limiting when the apparent activation enthalpies measured in free surface vaporization are substantially less than the enthalpies of the equilibrium vaporization reaction.[6] Exactly the same arguments apply for a decomposition reaction. The apparent activation enthalpy measures the difference between the enthalpy content of the activated complex in a reaction and the reactant. Unless that difference is at least as large as the enthalpy difference between reaction products and reactants, the activated complex cannot have acquired the minimum enthalpy content necessary for desorption plus formation of the solid reaction product to take place.

We can conclude that in barium carbonate decomposition some step other than desorption of carbon dioxide limits the reaction rate, while for calcium carbonate decomposition one possible interpretation[16] is that equilibrium is maintained between the carbonate and the metastable oxide product layer and that desorption of carbon dioxide at the maximum rate possible for that metastable equilibrium determines the reaction rate.

The very low decomposition pressure coefficient for barium carbonate can account for the fact that the 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 pressure
coefficient, α. In this study α was   smaller than estimated
minimum values of a/ℓ.

ACKNOWLEDGMENTS

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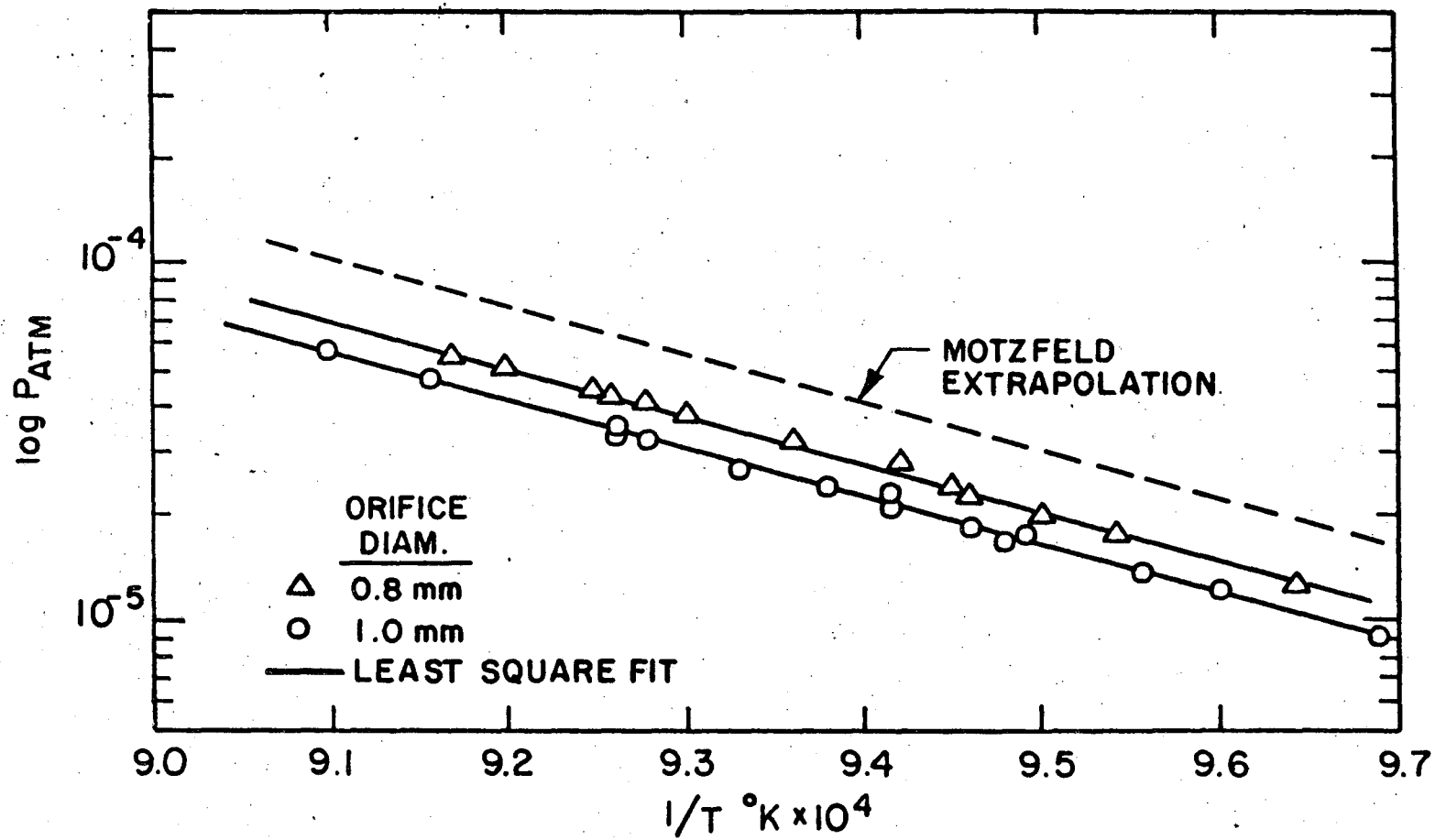Table I. Orifice and collimator

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

Figure Captions

Fig. 1. Equilibrium pressure of barium carbonate. Dashed line is the
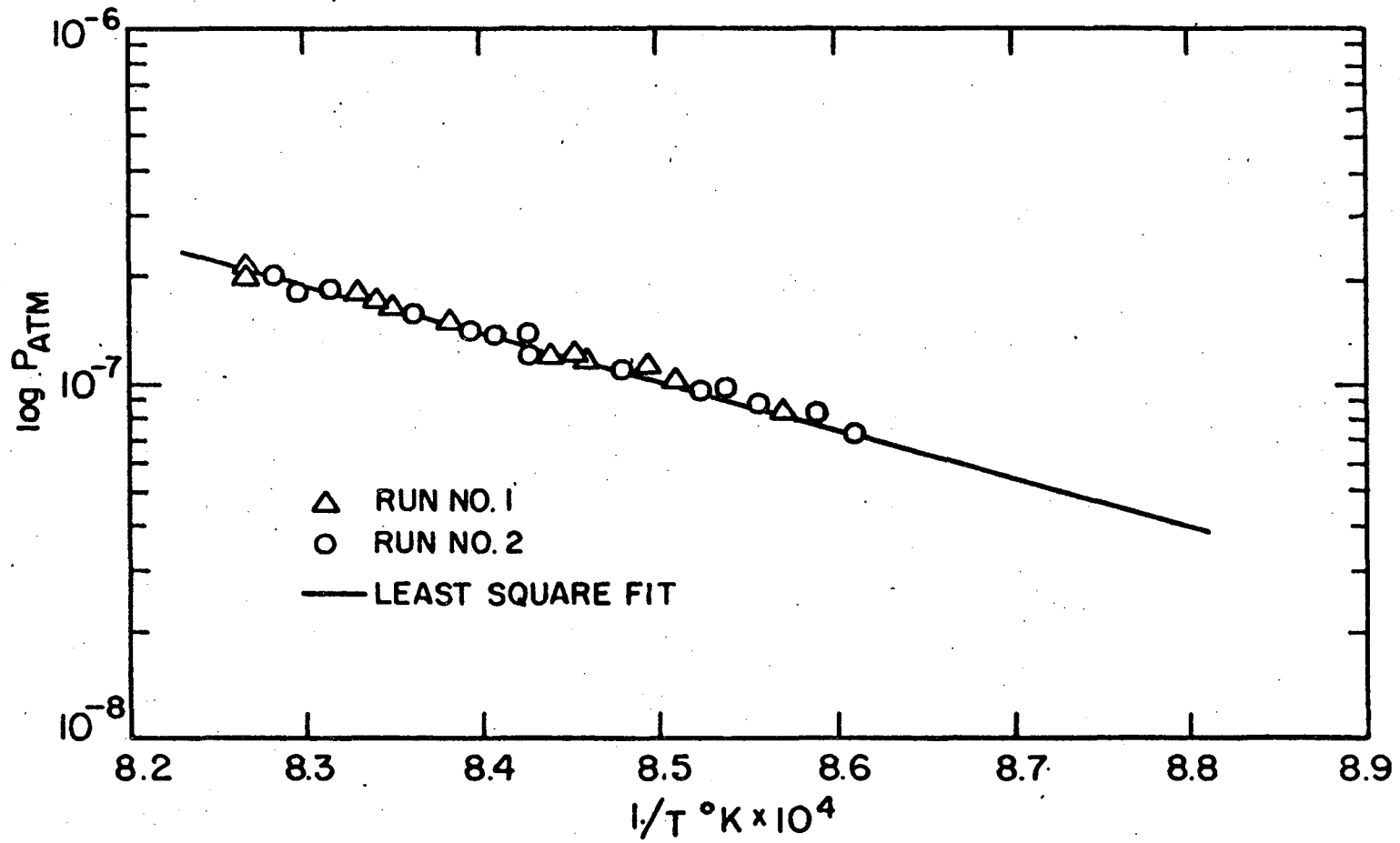equilibrium pressure calculated by means of the Whitman-
Motzfeld extrapolation.

Fig. 2. Langmuir pressures from decomposition of barium carbonate
single crystals.

MOTZFELD EXTRAPOLATION.

ORIFICE DIAM.
△ 0.8 mm
○ 1.0 mm
—— LEAST SQUARE FIT

$1/T \ ^{\circ}K \times 10^4$

$\log P_{ATM}$

10^{-4}

10^{-5}

9.0   9.1   9.2   9.3   9.4   9.5   9.6   9.7

XBL742-5646

Fig. 1

XBL742-5645

Fig. 2

-16-