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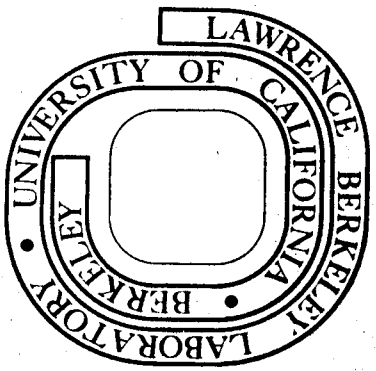

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THE KINETICS AND THERMODYNAMICS OF DECOMPOSITION OF BARIUM CARBONATE

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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, 252.1 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 are shown to be consistent with theoretical predictions if condensed phase diffusion or a surface step prior to desorption is rate limiting.

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INTRODUCTION

Nearly all of the many reported measurements of the kinetics of decomposition of calcite ($CaCO_3$) gave apparent enthalpies of activation approximately equal to the standard enthalpy of decomposition.[1] Recent measurements with single crystals in vacuum, however, yielded apparent enthalpies of activation about 20% higher than the standard enthalpy of decomposition.[2] It seems probable that, as contended by Hills[3] from analysis of transport data, vapor or heat transport rather than a chemical step have limited the calcite decomposition rate under the conditions of study that have usually been used.

There is, however, an alternate possibility. The decomposition rate of calcite in vacuum must be dependent, at least in part, on the rate of formation of a metastable form of calcium oxide, which was found in the vacuum study but may not be formed in air.[2] It seemed desirable to study a different carbonate reaction in vacuum to determine whether a metastable oxide product is formed in that reaction and to find whether or not the activation enthalpy is higher than the enthalpy of the equilibrium reaction.

Barium carbonate provides a particularly interesting subject for such a study because no previous measurements of either its rate of decomposition or of its equilibrium decomposition pressures have been reported. A single apparatus can be used to obtain both the kinetic and equilibrium data, and comparison of the two provides useful insight into the reaction mechanism.

EXPERIMENTAL

A torsion apparatus[4] described by Coyle[5] was used to measure the recoil force exerted by a vapor effusing into a vacuum from a small hole, and to measure the recoil force imparted to a sample surface by vaporizing molecules. In either kind of study, 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 vapor pressure can be calculated from the angle through which the cell is rotated by means of the formula[4]

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

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,[6,7] and ϕ is the angle through which the cell is rotated.

Witherite ($BaCO_3$) natural single crystals obtained from Hexham, England, were found by spectrographic analysis to contain 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 used for 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

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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 1.5K, 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 38μ 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 1023K. The low temperature crystallographic modification (witherite) is orthorhombic and the high temperature phase is hexagonal (aragonate-type).[1]

At the beginning of each run, the cells were heated at about 1100K until the ambient pressure in the furance fell to 5×10^{-5} Torr or less. Usually that pressure was reached in 1 to 1-1/2 hr. In any particular run from 10 to 16 points were taken with at least 15 min 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,[6] 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,[8] 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[9] 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 decomposition with two different orifice geometries. Several preliminary runs made with a 50μ wire agree, except for greater scatter, with the data obtained with the 38μ mil wire as long as the orifice geometry was constant. There was, however, a marked trend in observed pressures with effusion orifice size; higher pressures were obtained with smaller

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orifices. Equilibrium dissociation pressures were calculated from the effusion data by means of the Whitman-Motzfeld[10,11] equation

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

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 enhalpy and apparent entropy of decomposition 230.1±6.5 kJ and 58.6±3.7 J/deg.

To minimize the effect of any systematic errors of the system in temperature or pressure measurements, the heats and entropies measured for barium carbonate decomposition with either equilibrium or free surface vaporization techniques were 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[9] 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

X-ray diffraction studies on the surface of Langmuir specimens showed the layer of stable crystalline barium oxide which is formed on decomposition is in its normal structure (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 orthorhombic 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

In several obvious particulars the decomposition behavior of barium carbonate is similar to that for calcium carbonate:[2] Decomposition of each proceeds along a linear front and the decomposed carbonate is replaced by a layer of metal oxide plus pores with combined volumes equal to the volume of the initial carbonate. The porosities calculated from the relative molar volumes in each reaction are high--54% for calcium carbonate decomposition and 40% for barium carbonate. Both

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decompose at rates much lower than the maximum possible rates, which can be calculated from the Hertz-Knudsen-Langmuir equation;[2] calcium carbonate decomposes at 10^{-3} times the maximum rate and barium carbonate at 2×10^{-4} times the maximum rate. The rates of decomposition for both carbonates are independent of product layer thickness at least until thicknesses of 1 mm are reached.

But other features of the two reactions are very different, and in consequence, it is clear that the reaction mechanisms must be different. Important observational differences are: 1. Because the pores through the calcium oxide layer were too small to observe at 3000 magnifications, they must be less than 0.1μ in diameter, while pores through the barium carbonate averaged about 1μ diameter. 2. A 30μ thick layer of a metastable form of calcium oxide was found by micrographic and X-ray diffraction examination between the calcite and the growing layer of stable oxide; no intermediate solid layer was identifiable in barium carbonate decomposition. 3. For calcium carbonate decomposition the apparent activation enthalpy was found to be about 20% higher than the enthalpy of the equilibrium reaction and the apparent entropy of activation calculated by means of the Hertz-Knudsen-Langmuir equation was found to be almost the same as the entropy of the equilibrium reaction. But for barium carbonate decomposition both the apparent enthalpy and the apparent entropy of decomposition were significantly less than the equilibrium values.

The enthalpy observation for barium carbonate is particularly interesting because previously no carbonate has been known to have an enthalpy of decomposition smaller than the enthalpy of its equilibrium

reaction. However, it is the low apparent entropy of activation that is the more useful clue to the reaction mechanism.

Until recently it was commonly assumed that the rate limiting chemical process in a decomposition reaction must always be one that occurs on the surface of the reactant phase. But Searcy and Beruto[12] have shown that steady state decomposition rates for any particular reaction could depend, not only on the rate of a surface step of the gaseous component of the reaction, but also upon the rates of three additional necessary steps: Diffusion of the eventual gaseous reaction product along the interface between reactant and solid product, diffusion of the solid component of the reaction (here barium oxide) along the portions of reactant phase which are fronted by pores, and transfer of the solid reaction component from the reactant phase to the solid product phase across interfaces between the reactant phase and the solid product phase.

The simplest interpretation of the calcite data is that all steps of decomposition to the metastable calcium oxide are at equilibrium and that the difference between the apparent activation free energy for decomposition and the free energy of the equilibrium reaction is simply the free energy of formation of the metastable oxide.[12] Such an interpretation could not explain the barium carbonate rate data even if it were assumed that the immediate product of barium carbonate decomposition is a metastable barium oxide layer which is too thin to detect. The hypothetical metastable oxide would have to form from the stable oxide with an entropy change of -93 j/deg-mole (the apparent entropy of activation minus the entropy of the equilibrium reaction).

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This would be essentially an impossible entropy difference between a metastable solid and the corresponding stable solid.

The rate data for barium carbonate are also incompatible with either of the alternate assumptions: 1. that the slowest step is desorption of carbon dioxide or 2. that the slowest step is transfer of barium oxide across the interface between the carbonate and solid oxide phases with condensed phase diffusion and the surface steps of the carbon dioxide maintained at equilibrium with the barium oxide component of the barium carbonate phase.

The low apparent activation enthalpy measured for barium carbonate decomposition is sufficient evidence to eliminate desorption of carbon dioxide in excited states as the rate limiting step. Exactly the same arguments which have been applied in vaporization reactions[8] also 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 equilibrium reaction products and reactants, the activated complex cannot have acquired the minimum enthalpy content necessary for desorption to the gaseous product plus formation of the solid reaction product.

If the interface transfer step for the barium oxide were the slowest of the four steps that are required for the steady state reaction, the chemical potential of the barium oxide component of the barium carbonate phase would rise and the chemical potential of the carbon dioxide component of the barium carbonate would fall until the reaction fluxes of barium oxide leaving the carbonate phase and of carbon dioxide

leaving the carbonate phases are equilized by the increased driving force for barium oxide escape and the decreased driving force for carbon dioxide escape. With the very well justified assumption that the integral-free energy of formation of the barium carbonate during steady state decomposition is negligibly different from its equilibrium value, Searcy and Beruto's solution for CO_2, the steady state molar flux of carbon dioxide, then is

$$J_{CO_2} = \left(k_i k_{CO_2}\right)^{1/2} \tag{2}$$

where k_i is the rate constant for the interface transfer of the barium oxide and k_{CO_2} is the rate constant for diffusion of CO_2 or for a surface step of carbon dioxide, whichever is slower.

If it is now assumed that the slowest step for the carbon dioxide reaction component is the final step of desorption, Eq. (2) becomes

$$J_{CO_2} = \left[\frac{nkT}{6h} \exp\left(\Delta S_i^*/R\right) \exp\left(-\Delta H_i^*/RT\right)\right]^{1/2} \left[\frac{P^o \exp\left(\Delta S_v^o/R\right) \exp\left(-\Delta H_v^o/RT\right)}{(2\pi MRT)^{1/2}}\right]^{1/2} \tag{3}$$

where n is the number of moles of BaO per unit area of the first monolayer of barium oxide along the barium carborate-barium oxide interface, k is the Boltzmann constant, h is the Planck constant, ΔS_i^* and ΔH_i^* are the molar activation entropy and enthalpy of the interfacial step, P^o is the standard pressure of the gas (1 atm, expressed, however, in consistent units), R is the gas constant, M is the molecular weight of carbon dioxide and ΔS_v^o and ΔH_v^o are the standard entropy and enthalpy of the equilibrium reaction.

6 1 5 0 0 4 4 0 0 0

The first bracketed expression in Eq. (3) is the value for k_i obtained by means of absolute reaction rate theory.[13] The second bracketed expression is obtained by assuming that the rate constant for a desorption that produces a gas which is at thermal equilibrium is independent of the chemical potential of the adsorbed gas; then because in the derivation of Eq. (2), the activity of a gas was defined as unity when the gas is at its equilibrium pressure, the rate constant for desorption is identical to the expression for the flux of the gas which would be produced by the gas when present at its equilibrium decomposition pressure.

The temperature dependences of terms of Eq. (3) other than those in $\exp(-\Delta H/T)$ are negligible compared to the temperature dependence of the terms in $\exp(-\Delta H/T)$. In consequence, if an interface transfer step for barium oxide coupled with desorption of carbon dioxide determines the decomposition rate the quantity

$$\left[\frac{nkT}{6h}\exp\left(\Delta S_i^*/R\right)\right]^{1/2}\left[\frac{P^o \exp\ \Delta S_v^o/R}{(2\pi MRT)^{1/2}}\right]^{1/2} \qquad (4)$$

should have the same value as J_{CO_2} calculated from the intercept of a linear extrapolation of $\ln J_{CO_2}$ vs $1/T$ to $1/T = 0$.

From the crystal structure of barium oxide n is known to be about 1.3×10^{-9} moles/cm^2, $\exp\left(\Delta S_i^*/R\right)$ should be of the order of 1, and ΔS_v^o is known from the equilibrium measurements to be about 147 J/deg. The calculated value of expression 3 is 2×10^5 moles/cm^2-sec while J_{CO_2} calculated from the extrapolation of experimental data is 1×10^2. The calculated value of the second bracketed term of Eq. (3) should be in

error by a factor of 3 at worst. The value calculated for the term inside the first bracket would have to be in error by a factor of 10^6 to reconcile the mechanism under consideration with the experimental data. Such a large aggregate error in estimation of the factors that make up that term seems highly unlikely and we conclude that the interface transfer step coupled with desorption is almost certainly not rate limiting.

The slowest step in the decomposition of barium carbonate in the temperature range of this study must be the condensed phase diffusion of one of the reaction components or a surface step of the carbon dioxide, prior to desorption; these remaining possibilities could give the observed apparent enthalpies and entropies of activation. We have initiated experimental and theoretical studies in our laboratory on the effects on the net rates of decomposition reactions of background pressures of the product gases. Our theoretical analysis suggests that the pressure dependence of reaction rates should be different when the slowest step is one of the solid reaction component from when the slowest step is one for the gas reaction component.

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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.

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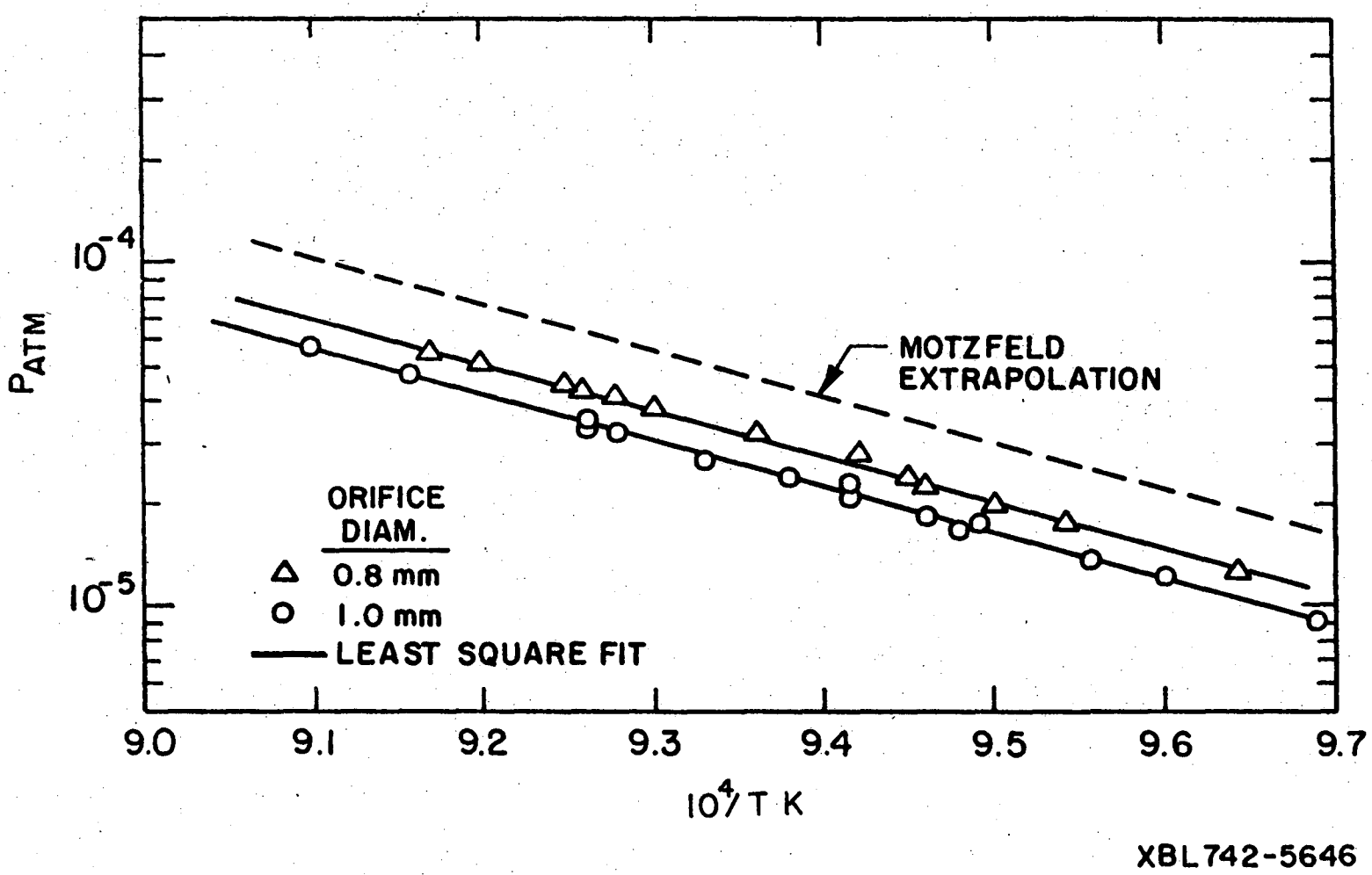
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Fig. 1

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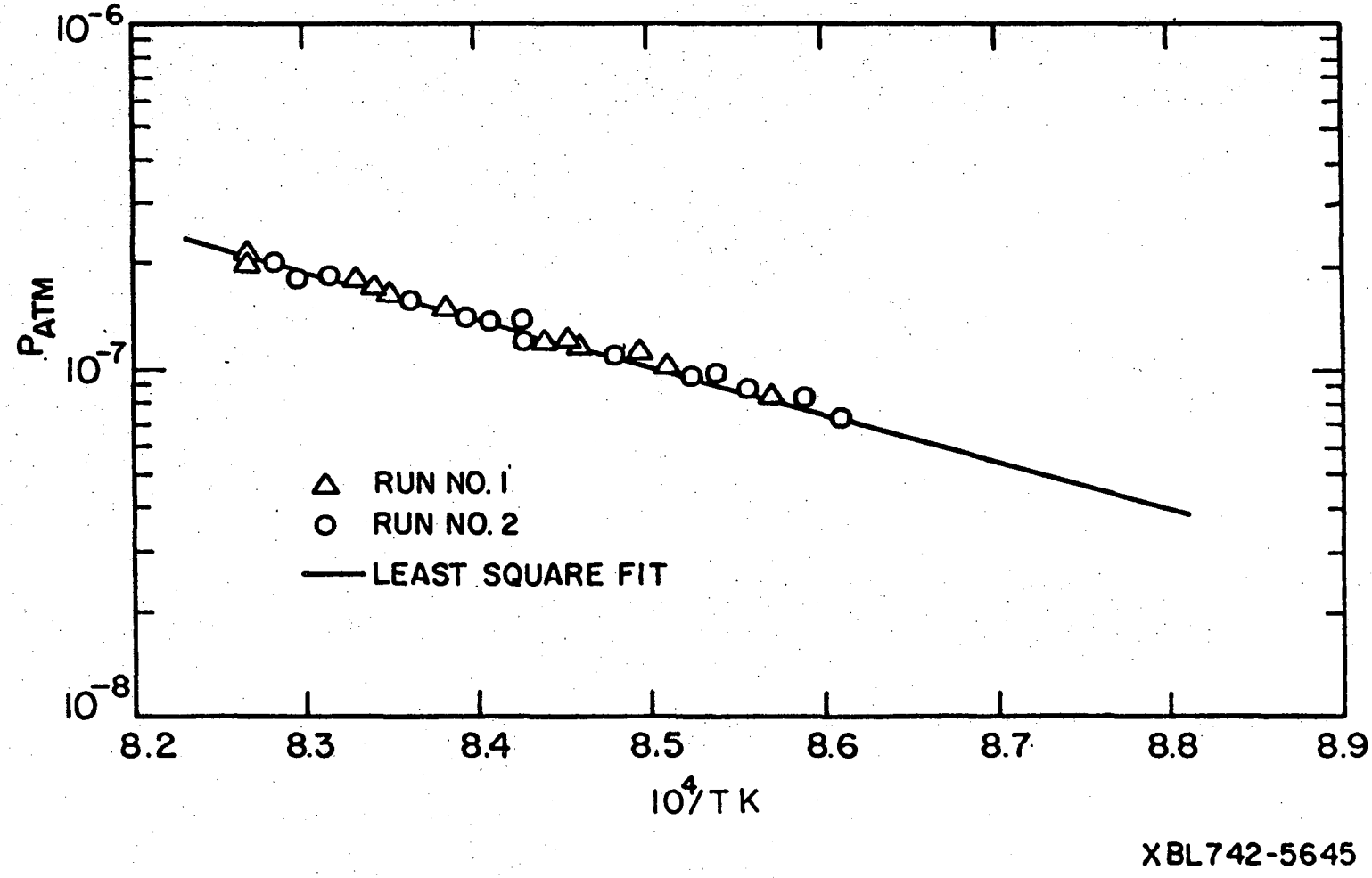

Fig. 2

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