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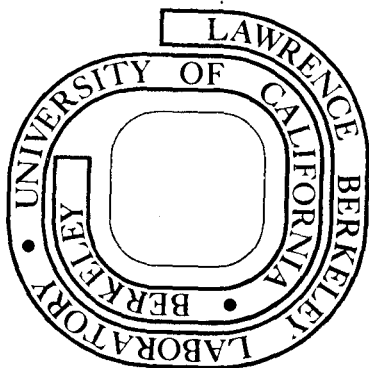
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USE OF THE LANGMUIR METHOD FOR KINETIC STUDIES OF
DECOMPOSITION REACTIONS: CALCITE

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ABSTRACT

The Langmuir method for measurement of vapor pressures has been tested for use in studies of decomposition reactions. The isothermal weight loss in vacuum from cleavage (10 $\bar{1}1$) planes of calcite (CaCO₃) single crystals was measured continuously at temperatures from 934 K to 1013 K. The reaction was first order until approximately 80% of a 1 mm slice had decomposed and had an apparent activation enthalpy of 205 KJ (49 kcal) per mole. Micrographic examination showed an approximately 30 μ thick layer, probably a metastable form of calcium oxide, separating the calcite from the growing layer of oriented stable calcium oxide. The 30 μ layer yielded a single X-ray diffraction peak which was displaced slightly from the strongest (220) peak of the oriented normal calcium oxide. Lower apparent activation enthalpies measured in previous studies of calcite decomposition in inert atmospheres are suggested to result either from partial diffusion control of the process or from catalysis of the direct formation of normal calcium oxide by carbon dioxide or a component of the system atmosphere. The ratio of the measured decomposition rate in vacuum to the maximum rate, which can be calculated from the Hertz-Knudsen-Langmuir equation, is shown to be a useful parameter in correlating and predicting decomposition reaction rates.

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The Knudsen effusion¹ and torsion-effusion² methods are used for thermodynamic studies of both congruent and incongruent vaporization. The related Langmuir³ and torsion-Langmuir⁴ methods are extensively used in studies of the kinetics of congruent vaporization. Determinations of weight losses in vacuum--in effect the Langmuir method--have frequently been used also in studies of incongruent vaporization, or decomposition, reactions.

Despite these experimental similarities, review articles on the kinetics of congruent vaporization⁵⁻⁹ and of decomposition reactions^{10,11} seem not to attempt a unified understanding of the two fields. In this study we initiate an attempt at unification by applying standard methods for study and interpretation of the kinetics of congruent vaporization to a decomposition reaction.

Langmuir or torsion-Langmuir studies carried out with single crystals in vacuum have merits in studies of both congruent and incongruent vaporization: (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 and in consequence increased uncertainty 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 understanding the reaction kinetics.

This last named parameter is our focus of attention. The ratio of the measured flux of vapor to the maximum flux predicted from the equilibrium dissociation on pressure by means of the Hertz-Knudsen-Langmuir

(H-K-L) equation³ should provide for endothermic decomposition reactions a valuable measure of the irreversibility of the rate limiting reaction step, just as it does for simple vaporization reactions¹¹ and for congruent dissociative vaporization reactions.^{6,12,13}

In addition to the benefit that may thus be attained in reaching a better understanding of the reaction mechanism, knowledge of the deviation of decomposition rates from the maximum possible rates makes it possible to predict reliably 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 reactions.

In a separate paper we plan to extend to decomposition reactions a modified form of transition state theory that we have already applied to congruent vaporization.¹³ The present paper reports the results of our experimental study of the decomposition of calcite (CaCO_3) single crystals by the Langmuir method in conjunction with scanning electron microscope and X-ray diffraction examination of the solid phase reaction products.

The kinetic results obtained in the present study differ significantly from those reported in the many previous investigations of calcite decomposition.¹⁴ In the discussion section we will suggest a

possible explanation for the difference, and we will compare the measured rate of carbon dioxide evolution to the maximum rate calculated by means of the H-K-L equation. A more complete consideration of possible reaction mechanisms will be presented in the theoretical paper.

WEIGHT LOSS MEASUREMENTS

Weight losses from defined areas of a natural cleavage (10 $\bar{1}1$) selected face of calcite single crystals were measured continuously with a quartz microbalance in vacuum. The same apparatus and techniques that have been described by Leonard and Searcy¹⁵ were used except that the alumina parts that fit about the calcite crystals to define a limited area for vaporization were more carefully machined. As a consequence, decomposition was negligible from all of a calcite crystal slice except for the defined area of surface. The evaporation occurred through a short tubular alumina channel which had a cross-sectional area of 0.25 cm² and a channel length of 0.15 cm with a transmission probability of 0.83.¹⁶

No orifice correction was made for the decomposition of CaCO₃ because the flux of carbon dioxide produced by the decomposition reaction $\text{CaCO}_3(\text{s}) = \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ proved to be considerably lower than the maximum possible flux calculated by means of the H-K-L equation. In consequence, according to our recent work,¹⁷ the probability should be low that carbon dioxide molecules which return to the sample after collision with the orifice would cross the free energy barrier to recombine with calcium oxide.

The sensitivity of the balance was set at either 3×10^{-2} mg/div or 7.8×10^{-2} mg/div. To improve the constant temperature zone for studies at 830°K to 1020°K, tubular shields of 0.18 mm thick nickel were introduced into the quartz-walled tube furnace. This arrangement provided a 6 cm zone in which the temperature was constant within $\pm 1^\circ\text{C}$ at the decomposition temperatures.

Two chromel-alumel thermocouples were calibrated by measurements of the melting points of zinc and aluminum. The reference thermocouple then was calibrated throughout the experimental range by measuring its temperature against that of a couple mounted inside the sample holder. To test the reliability of this method of temperature determination and of microbalance calibration, the vapor pressure of zinc was measured in the range 500°K to 700°K by the Knudsen-effusion method. Measured pressures agreed to within 6% with the pressure curve recommended by Hultgren et al.¹⁸

Spectrographic analysis of the calcite single crystals showed them to contain as the only significant metallic elements other than calcium 0.025% strontium, 0.15% magnesium and 0.02% manganese. The samples, which weighed between 40 mg and 65 mg, were cleaved in order to expose (10 $\bar{1}$ 1) faces.¹⁹ Excessive heat loss due to rapid endothermic decomposition might result in surface cooling; i.e., in a temperature gradient which is perpendicular to the surface plane, but because the sample holder and cell were heated by radiation to their surfaces significant temperature gradients were not likely.²⁰ Rates of vaporization were independent of time during periods in which a significant fraction of the crystals were converted to a porous layer of calcium oxide. This

circumstance argues that surface cooling did not significantly lower surface temperatures. Most samples were 0.5 mm thick, but the same rate of decomposition was attained with a sample 1 mm thick. This result further supports the conclusion that temperature gradients within the sample were negligible.

The system could be pumped to 10^{-6} torr and the pressure rose to $5-6 \times 10^{-5}$ torr during the decomposition. The pressure was measured with an ion gauge at the opposite end of the system from the pumping port so these measured background pressures represent maximum values at the sample.

WEIGHT LOSS RESULTS

Representative data obtained with the quartz microbalance in vacuum are shown as data points in fig. 1. Data are plotted in terms of the fraction of undecomposed calcium carbonate, i.e. $1-w/w_0$ where w_0 refers to the equivalent number of mgs of CO_2 present in the sample at the initial experimental condition. The calcite decomposition occurred at a constant rate, without an appreciable induction period, until decomposition exceeded 80% of the initial weight. Typically the rate of decomposition reached 80% of the linear decomposition rate as soon as the temperature was stabilized at a constant value (i.e. within about 30 minutes), and visual examination of broken samples showed that this linear decomposition proceeds essentially in one dimension at an interface which moved from the surface of the crystal exposed to the vacuum toward the interior.

To determine if the non-linear period was due to a change in the rate limiting step when the calcium oxide layer becomes thick, we made

runs with a similar sample but with a doubled thickness. If the non-linear period resulted because the calcium oxide layer acted as a significant barrier to escape of the carbon dioxide vapor, the linear region should be of the same length as before. The results (fig. 2) show that the calcium oxide layer is not responsible for the deviation from linearity since linear decomposition was now observed for an oxide layer thickness nearly twice as great as before. Eventual deviation from linearity probably reflects a decrease in calcite surface area because the rate for the thicker sample again remained constant until decomposition was more than 80% complete. Fig. 3 shows the variation in the linear decomposition rate J (moles per sec per cm^2) with temperature in the range $903^\circ\text{K} - 1010^\circ\text{K}$.

MICROSCOPIC AND X-RAY DIFFRACTION MEASUREMENTS

Scanning electron microscope examination showed an approximately 30μ thick layer next to the calcite of different appearance from an outer layer that grew as the reaction proceeded. Optical microscope pictures taken at 400X showed for a total product layer about 300μ thick that the principal product had little visible texture. The interface between calcium oxide and the intermediate layer and the interface between that layer and the unreacted calcite crystal were very flat. Occasional cracks through the calcium oxide appeared to have formed during the cooling or handling operation after heating. The unreacted calcite itself was uncracked when removed from the furnace but developed cracks at distances of the order of 10μ apart. Both layers of reaction products had occasional channels of about 10μ diameter, which were usually either vertical or oriented at about 45° to the normal to the reaction surface

in the plane of the reproduction. Much more closely spaced pores of 2μ or smaller diameter could be seen in pictures taken with scanning electron microscope at 3000 magnification.

By sighting down into the larger pores, it was possible to observe that they extended completely through the product layer and into the unreacted calcite layer just below. This fact, plus the observation that flaps of the reaction product were displaced upward from the surface about these largest diameter pores, lead us to believe that they could be the result of explosive escape of small pockets of gas which were trapped within the calcite until the calcite layer above a pore became too thin to sustain the gas pressure.

The smaller diameter pores probably represent the largest of the pores produced by decomposition of the calcite, which has a molal volume of 37.2 cm^3 , to the calcium oxide reaction produce, for which the molal volume is 16.7 cm^3 . The calculated porosity is about 55% and the pores that were observed at 3000 magnification did not occupy more than the 30% of the projected surface area. Therefore the predominant pore area must have been less than 1μ in diameter.

The outer layer yielded an X-ray diffraction pattern in which the three strong lines have the spacing of the three strongest peak of the calcium oxide (NaCl structure type), powder pattern, but the most intense peak is the 220 rather than the 200 peak. We infer, therefore, that the outer layer is polycrystalline calcium oxide with the 110 crystallographic direction oriented preferentially normal to the exposed plane of calcite.²¹

Experiments were performed in which a fresh calcite sample was heated only until 4% of the total decomposition occurred. This procedure produced a 20 μ thick layer of transformation product. Scanning electron microscopic examination showed that this treatment resulted in a single layer of reaction product with a texture similar to that of the intermediate layer of the sample that had been heated for a longer period. This layer was also polycrystalline and oriented, but its only strong diffraction peak appears at 50.3° instead of at 53.9°, the position of the (220) peak for the outer layer of calcium oxide. Both the micrographic and X-ray evidence support earlier evidence from differential thermal analysis²² that a metastable modification of calcium oxide is sometimes a product of the decomposition reaction. A metastable oxide has been assumed to be a reaction intermediate in calcite decomposition by other investigators²³ but apparently this is the first visual identification of the metastable phase.

DISCUSSION

Previous investigators have concluded that the chemical decomposition of calcite to carbon dioxide gas and calcium oxide occurs on a definite boundary between the carbonate and calcium oxide phases,²³⁻²⁷ but it is recognized that the chemical step may not control the rate of the process.²⁸⁻³⁰

One reason for suspecting that other factors influence the observed decomposition rates is that the apparent order of the decomposition reaction has been variously reported as from 0.2 to 1 (see column 1 of Table I).^{28,31-40} Apparent reaction orders are expected to depend upon geometry; for example, if the rate controlling process for a

decomposition reaction occurs at a constant rate per unit area of a spherical interface, the change in surface area with time should yield an apparent reaction order of 0.67.⁴¹ But the range of apparent reaction orders reported for calcite decomposition seems too great to attribute only to differences in reaction geometries. It may be that differences in intra-particle and/or inter-particle diffusion influence the results and that the measured apparent activation enthalpies should not be attributed exclusively to a surface reaction step as has sometimes been supposed.^{14,42} Hills,^{29,30} who investigated the reaction with relatively large samples, has suggested that the reaction for large samples is controlled not by a chemical step at the interface, but by the transfer of heat to the reaction boundary and by the transfer of CO₂ away from it.

The design of the apparatus used in the present study reduces the heat transfer problem to a negligible source of error in the temperature and decomposition pressure range used; decomposition was limited to a single face of a calcite crystal; the interface was demonstrated to remain flat at 3000X magnification and essentially constant in area while advancing distances of the order of 0.8 mm into a 1 mm thick crystal; and decomposition was first order in time until some 80% complete. Gas phase inter-particle diffusion was eliminated as a possible rate limiting step by the reaction conditions employed. It seems unambiguously established that for these reaction conditions intra-particle diffusion does not influence the reaction rate in vacuum at least until the calcium oxide product layers are some 1 mm in thickness.

Discordant values from previous studies for the apparent reaction order and for apparent enthalpies of activation as well may reflect varying dependence of the decomposition rate on gas phase transport. Reported apparent enthalpies of activation for calcite decomposition range from 147 to 210 KJ per mole (see column 2 of Table I), with most values clustering near the enthalpy of the equilibrium decomposition reaction, 173.5 KJ. per mole (41.5 Kcal per mole) at 973°K. The apparent activation enthalpy was found from the temperature dependence of vaporization flux in the present study to be 205 KJ. per mole (49 Kcal per mole) at 973°K, about 18% higher than the equilibrium reaction enthalpy. That apparent activation enthalpies are sensitive to sample size for powdered samples is demonstrated by results reported by Gallagher and Johnson⁴⁰ since our own experimental investigation was completed. They measured decomposition rates of calcite powdered samples heated in oxygen as functions of sample size as well as temperature. They programmed a computer to give the best possible fit of the experimental data to each of the most widely discussed mechanisms for decomposition reactions. Their calculated activation enthalpies were insensitive to the assumed mechanism, but dependent on sample size. An apparent activation enthalpy of 190 KJ was found for a 32 mg powder sample and 208 KJ for a 1 mg sample.

Even the largest of the samples used by Gallagher and Johnson is smaller than samples commonly used in studies of calcite decomposition. It may well be that with the large samples and protective atmospheres or relatively poor vacua employed for most studies of calcite decomposition, transport of carbon dioxide away from the outer sample surfaces or

diffusion of carbon dioxide becomes rate limiting so that essentially complete equilibrium between calcite and its ultimate decomposition products, carbon dioxide and the stable modification of calcium oxide, is established in the centers of the powdered or granular samples.

Because gas phase diffusion is proportional to the partial pressure gradients, the overall decomposition rate in portions of a sample in which equilibrium carbon dioxide pressures are approached would be roughly proportional to the equilibrium pressure independent of temperature and thus show approximately the same apparent activation enthalpy as the enthalpy of the equilibrium reaction. Near the outer portion of a sample mass, the escape of carbon dioxide into the surrounding system would reduce the carbon dioxide pressure below the equilibrium value. There, a solid state or surface reaction of high activation free energy, such as that which apparently determines the rate of decomposition under the conditions of this study, could determine the decomposition rate. For a fixed pressure of background gas and fixed external reaction conditions experimental activation enthalpies would then, as found by Gallagher and Johnson, be characteristic of the activated solid state process for sufficiently small samples, but approach the enthalpy of the equilibrium reaction for large samples. Depending on the effectiveness of convective diffusion and other transport processes that remove carbon dioxide from the samples, measurements of different investigators would yield activation enthalpies more or less equal to the enthalpy of the equilibrium reaction. It is also possible that carbon dioxide or a component of the furnace atmosphere may catalyze direct formation of the stable modification of calcium oxide.

Figure 3 provides a comparison of the steady state flux, J^* , of carbon dioxide, measured for calcite as a function of temperature, to the maximum possible flux, J_{\max} , calculated from the free energy of the equilibrium reaction by means of the H-K-L equation:³

$$J_{\max} = \frac{P_{\text{eq}}}{(2\pi MRT)^{1/2}} = \frac{\exp(-\Delta G_d^0/RT)}{(2\pi MRT)^{1/2}} \quad (1)$$

where P_{eq} is the equilibrium carbon dioxide pressure, M is the molecular weight, R is the gas constant, and ΔG_d^0 is the standard Gibbs free energy of the equilibrium decomposition reaction at the temperature T .

For simple vaporization reactions, the ratio of the flux measured for free surface vaporization in vacuum J_L to the maximum flux calculated from the H-K-L equation J_{\max} is called the vaporization coefficient α_v .⁵⁻⁸ Because values of α_v for one substance can be readily predicted from values of α_v for chemically similar substances, it is possible to predict reliably the rates of vaporization of materials for which no measurements are available.⁶ The corresponding ratio α_d , which may be called a decomposition coefficient, should have similar predictive value.

For decomposition reactions, however, the possibility, often realized in practice,^{10,11} that a metastable solid phase product will be formed must be considered.

A metastable solid forms only if the kinetic barrier to its formation is smaller than that to formation of the stable solid. Suppose, for example, that α_d^* is the ratio of the measured to maximum flux when a metastable oxide is the direct product of the measured reaction. Then if the flux of gaseous product produced in a decomposition directly to

the stable oxide could somehow be measured, that flux J_d would be less than J^* . And for the direct decomposition reaction, the corresponding decomposition coefficient α_d would be smaller than α_d^* and might have a very different temperature dependence.

Any empirical correlation of values of decomposition coefficients, therefore, should so far as possible, take into account any systematic differences in behavior between decomposition reactions that yield metastable solid products from those that do not and should, so far as possible, include an effort to understand and predict whether metastable solid reaction products are produced or are to be expected for any particular decomposition reaction.

The evidence of the present research is strong that the decomposition of calcite in vacuum yields a metastable oxide as the initial product. Furthermore, this metastable oxide is almost certainly not in equilibrium with the stable modification of calcium oxide, as is the kind of active oxide which has been suggested in some mechanistic interpretations of the decomposition kinetics data.^{14,23,42} The observation by Rao, et al.²² of an exothermic process when the initial product of calcite decomposition is heated shows that the initial decomposition reaction produces a condensed phase product that is not at equilibrium with the stable oxide because exothermic processes that occur during heating are necessarily irreversible.⁴⁴ And the micrographic and X-ray data of the present research show that that initial product is almost certainly a distinct layer of metastable oxide that separates the undecomposed calcite from the stable oxide which is the eventual principal condensed phase reaction product. Thus it is almost certainly α_d^* rather

than α_d that has been measured in the present study. The measured α_d^* approach unity as the temperature is increased as do α_v values for many of the substances for which data are available; the value found for α_d^* is 1.2×10^{-3} at 934°K and is 1.8×10^{-3} at 1013°K .

Because the X-ray pattern for the metastable intermediate layer yielded only a single peak, little can be directly concluded about its structure, except that the displacement of that peak from the strongest (220) peak of the oriented calcium oxide that forms the outer product layer implies that the metastable phase probably has a nearest neighbor calcium to oxygen distance some 5% greater than does the normal oxide. But because the X-ray data for the stable calcium oxide layer shows it to be oriented relative to the (10 $\bar{1}$ 1) calcite face, the metastable phase from which the stable phase is formed must also be oriented and probably grows epitaxially on the calcite surface. Irreversible transformation to the stable oxide probably occurs when the cumulative strains consequent to lattice mismatch exceed a critical level.

It may be that on other faces of calcite crystals the conditions for epitaxial growth of the metastable oxide are significantly more or less favorable. On some faces the stable oxide might form directly, but the evidence of the exothermic reaction reported by Rao et al. implies that the metastable oxide is a direct product for the decomposition of powders as well as for decomposition restricted to (10 $\bar{1}$ 1) crystal faces. We hope to investigate the decomposition rates on other calcite crystal faces and to examine the effect of particle size, of temperature, and of carbon dioxide pressures on the quantity of metastable oxide produced in calcite decomposition.

We think that this test study of calcite decomposition confirms our hope and expectation that the Langmuir experimental method for determination of evaporation rates of single crystals would yield less ambiguous data for the chemical step of the process than can readily be obtained by studies of decomposition of powdered or granular samples in inert atmospheres. We are strengthened in our belief that systematic organization of kinetic data for decomposition reactions in terms of their deviations from the maximum possible rates, which are predictable from equilibrium data, will prove to be as useful in correlating and predicting the rates of the chemical step of decomposition reactions as it has already proved to be for vaporization reactions.

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TABLE I. Some experimental values for the thermal decomposition of CaCO_3

Apparent activation enthalpy of KJ/Mole (Kcal/mole)	Apparent reaction order	Sample		Atmosphere	Ref.
		Form	Wt. (mg)		
147-176 (35-42)	0.58-0.74	Powder	500	10^{-2} torr	28
173 (41.2)	-	-	300-450	N_2	31
205 (49)	0-1	Powder	-	-	32
170 (40.6)	0.67	-	455	Air	33
180 (42.9)	0.22	-	-	-	34
159 (38)	1	Powder	-	CO_2 pumped off intermittently	35
180-193 (43-46)	~ 0.7	Pellet and powder	1000	-	36
155-163 (37-39)	0.3	Powder	-	CO_2 pumped off intermittently	37
172-210 (41-50)	0.2-0.53	Small blocks	18434	Vacuum not reported N_2	38,39
190-208 (45.3-49.7)	0.5	Powder	1-32	O_2	40
205 (49)	1	Slice of single crystals	35-70	$10^{-5} \div 10^{-6}$ torr	This work

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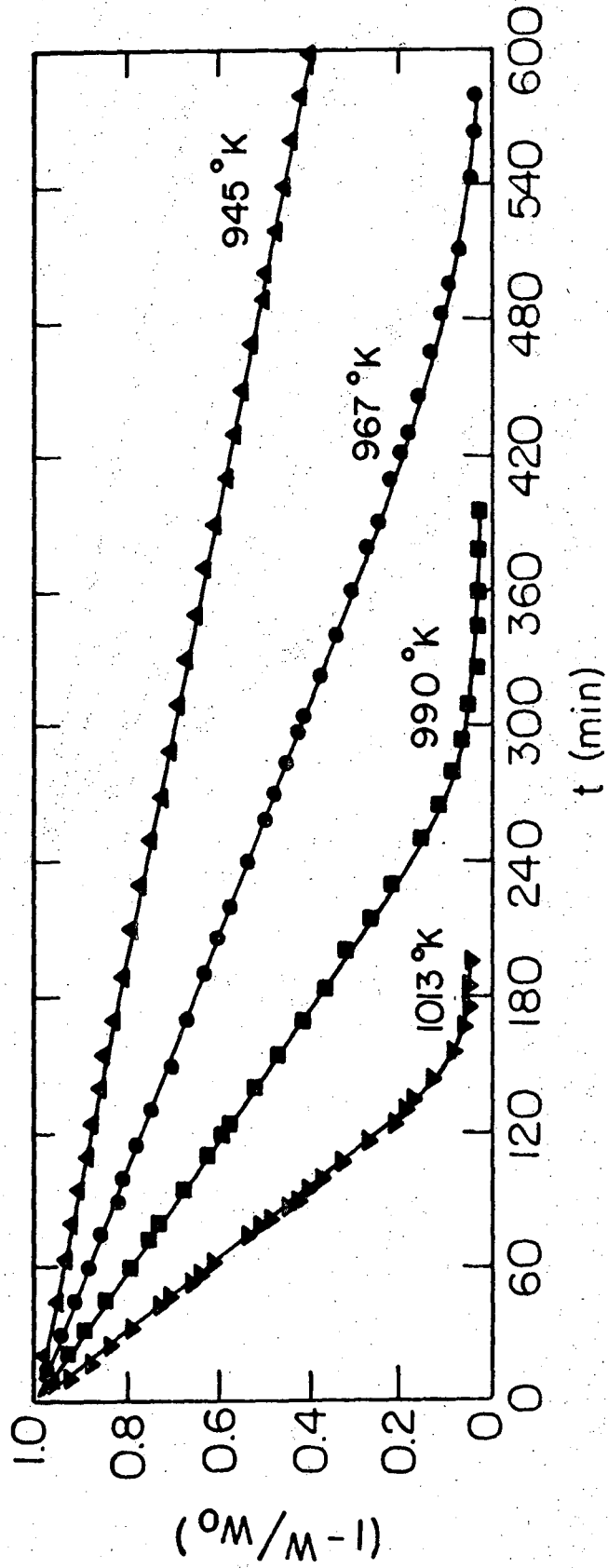
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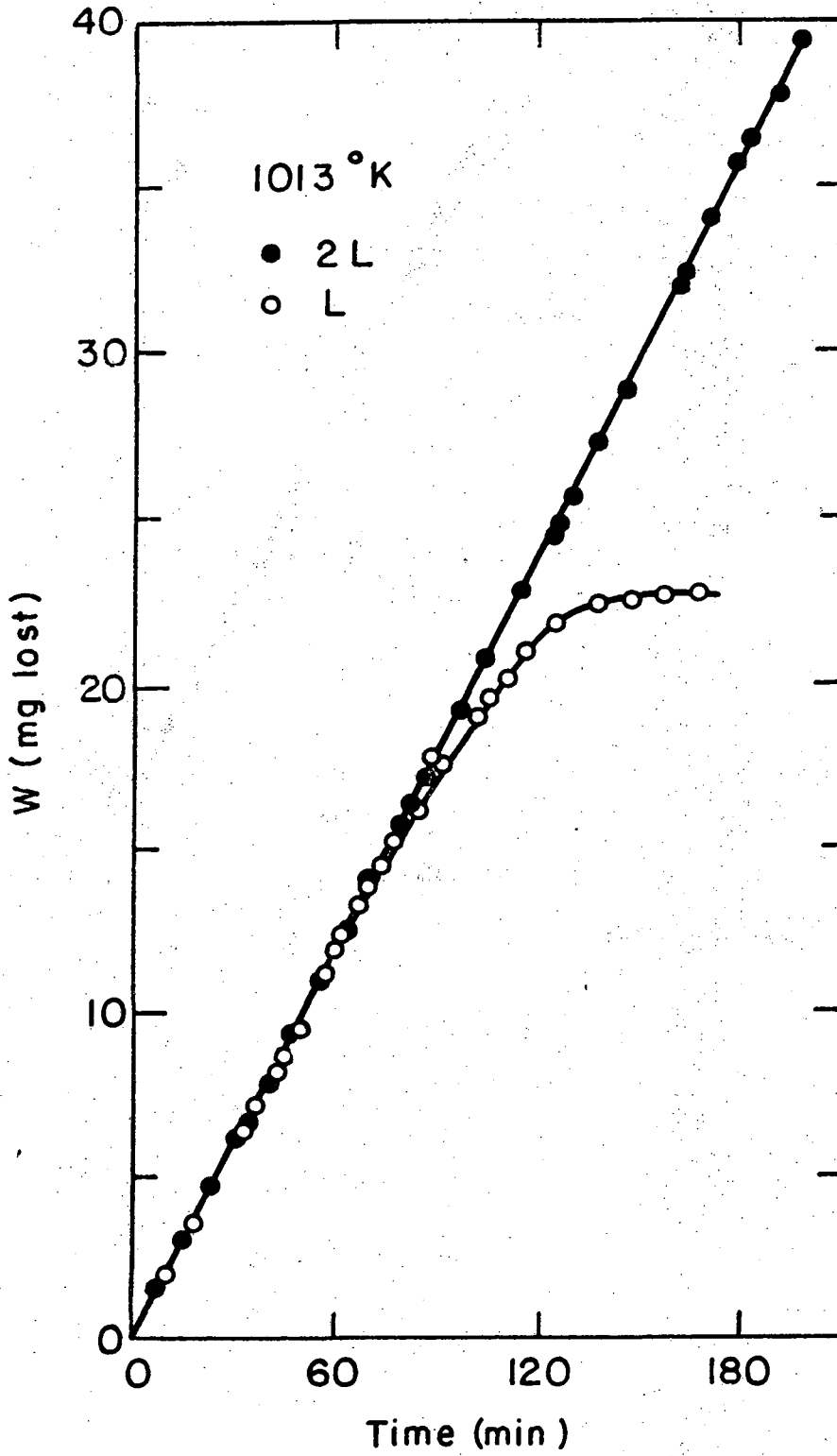
FIGURE CAPTIONS

- Fig. 1. Typical values of $1 - w/w_0$, where w_0 is the initial CO_2 content and w is the weight of CO_2 lost plotted as functions of time at several temperatures.
- Fig. 2. The weight lost as a function of time by a calcite crystal approximately 0.5 mm thick (L) and by a crystal approximately 1 mm thick (2L).
- Fig. 3. Plots of measured flux from the $(10\bar{1}1)$ face of a calcite crystal decomposed in vacuum (lower curve) and of the maximum possible flux calculated from the equilibrium dissociation pressure by means of the Langmuir equation (upper curve).



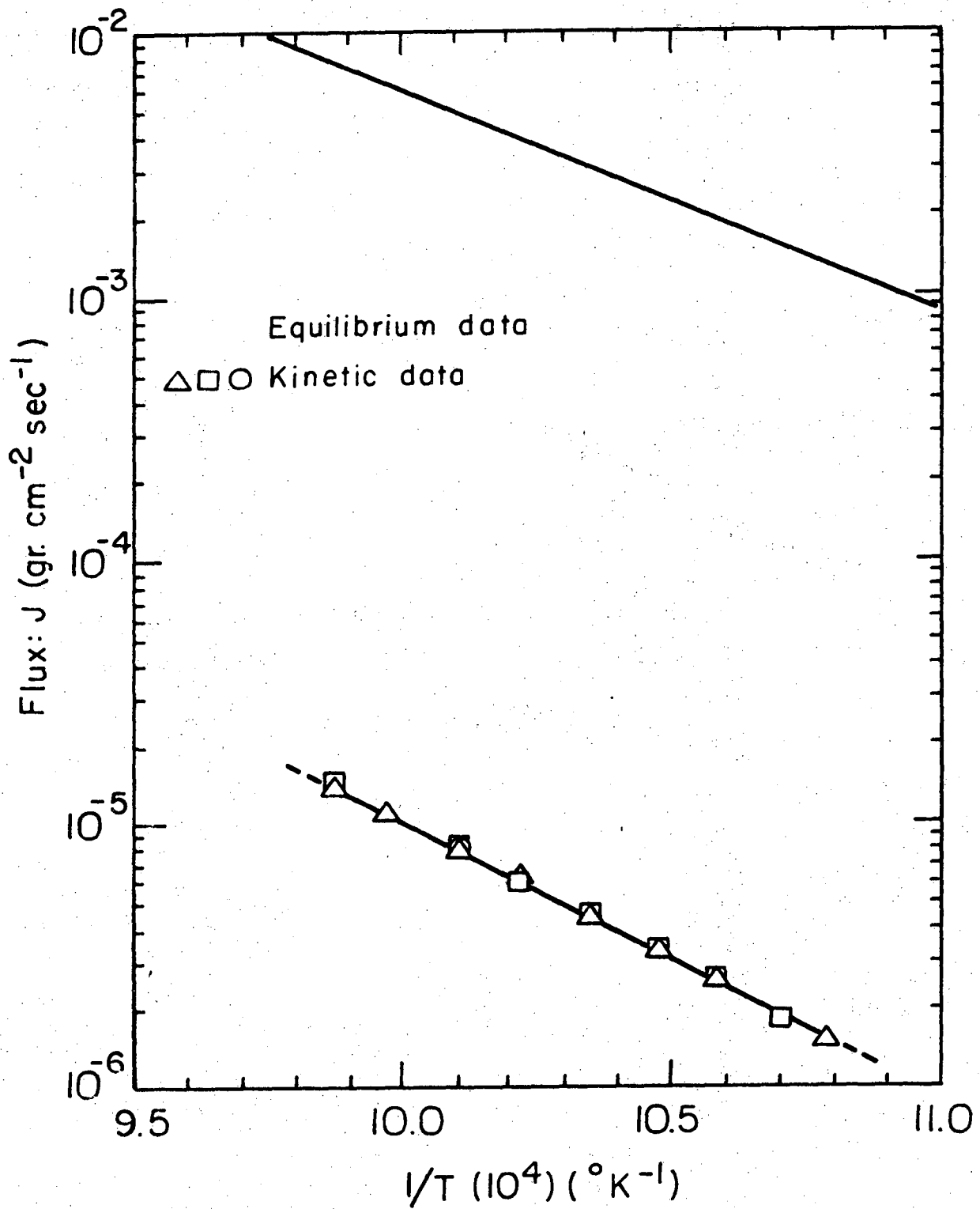
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Fig. 1



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Fig. 2



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Fig. 3

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