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

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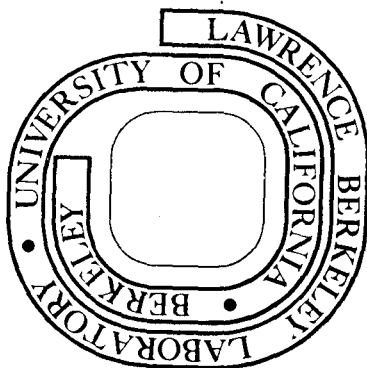
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ABSTRACT

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 ($CaCO_3$)
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
30μ thick layer, probably a metastable form of calcium oxide, separating
the calcite from the growing layer of oriented stable calcium oxide. The
30μ 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 decompo-
sition rate in vacuum to the maximum rate, which can be calculated from
the Hertz-Knudsen-Langmuir equation, is shown   to be a useful para-
meter in correlating and predicting decomposition reaction rates.

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The Knudsen effusion[1] and torsion-effusion[2] methods are used for thermodynamic studies of both congruent and incongruent vaporization. The related Langmuir[3] and torsion-Langmuir[4] 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 vaporization[5-9] 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) equation[3] 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 reactions[11] and for con-

gruent 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 devia-

tion 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 signifi-

cantly from those reported in the many previous investigations of cal-

cite 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 re-

action 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 Searcy[15] 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

cm^2 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 $CaCO_3$

because the flux of carbon dioxide produced by the decomposition reaction

$CaCO_3(s) = CaO(s) + CO_2(g)$ proved to be considerably lower than the maxi-

mum possible flux calculated by means of the H-K-L equation. In con-

sequence, 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 pro-

vided a 6 cm zone in which the temperature was constant within ±1°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 decompo-

sition 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 sig-

nificant 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 $903°K - 1010°K$.

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 cool-

ing 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 un-

reacted 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 predominent 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 20µ 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 analysis[22] 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 investigators[23] 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 CO_2 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 vapori-

zation 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

Johnson[40] 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 pro-

gramed 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 acti-

vation 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 vacuua 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]

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

where P_{eq} is the equilibrium carbon dioxide pressure, M is the molecular weight, R is the gas constant, and ΔG_d^o 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 con-

sequent 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 decompo-

sition 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 meta-

stable 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.

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

REFERENCES

1. K. D. Carlson in The Characterization of High Temperature Vapors,
    ed. J. L. Margrave (Wiley, New York, 1967) Chap. 5.

2. R. D. Freeman, ibid., Chap. 7.

3. I. Langmuir, J. Am. Chem. Soc. 1913, 35, 931.

4. R. C. Paule and J. L. Margrave in The Characterization of High
    Temperature Vapors, ed. J. L. Margrave (Wiley, New York, 1967)
    Chap. 6.

5. J. P. Hirth and G. M. Pound, Condensation and Evaporation-Nucleation
    and Growth Process, (Pergamon, Oxford, 1963).

6. A. W. Searcy, Chemical and Mechanical Behavior of Inorganic
    Materials, ed. A. W. Searcy, D. V. Ragone, U. Colombo (Wiley-
    Interscience, New York, 1970) Chap. 6.

7. G. A. Somorjai and J. E. Lester in Progress in Solid State Chemistry
    1968, 4, 1.

8. G. M. Rosenblatt in Heterogeneous Kinetics at Elevated Temperature,
    eds. G. R. Belton and W. L. Worrell (Plenum, New York, 1970).

9. G. A. Somorjai, Advances in High Temperature Chemistry, ed. L.
    Eyring (Academic Press, New York 1969).

10. Chemistry of the Solid State, ed. W. E. Garner (Butterworths,
    London, 1955).

11. D. A. Young, Decomposition of Solids (Pergamon, New York, 1966).

12. R. J. Galluzzo and A. W. Searcy, High Temp. Sci. 1971, 3, 491.

13. A. W. Searcy and D. Beruto, submitted for publication.

14. K. H. Stern and L. W. Weise, High Temperature Properties and Decom-
    position of Inorganic Salts, Part 2: Carbonates (Nat. Bur. Standard,
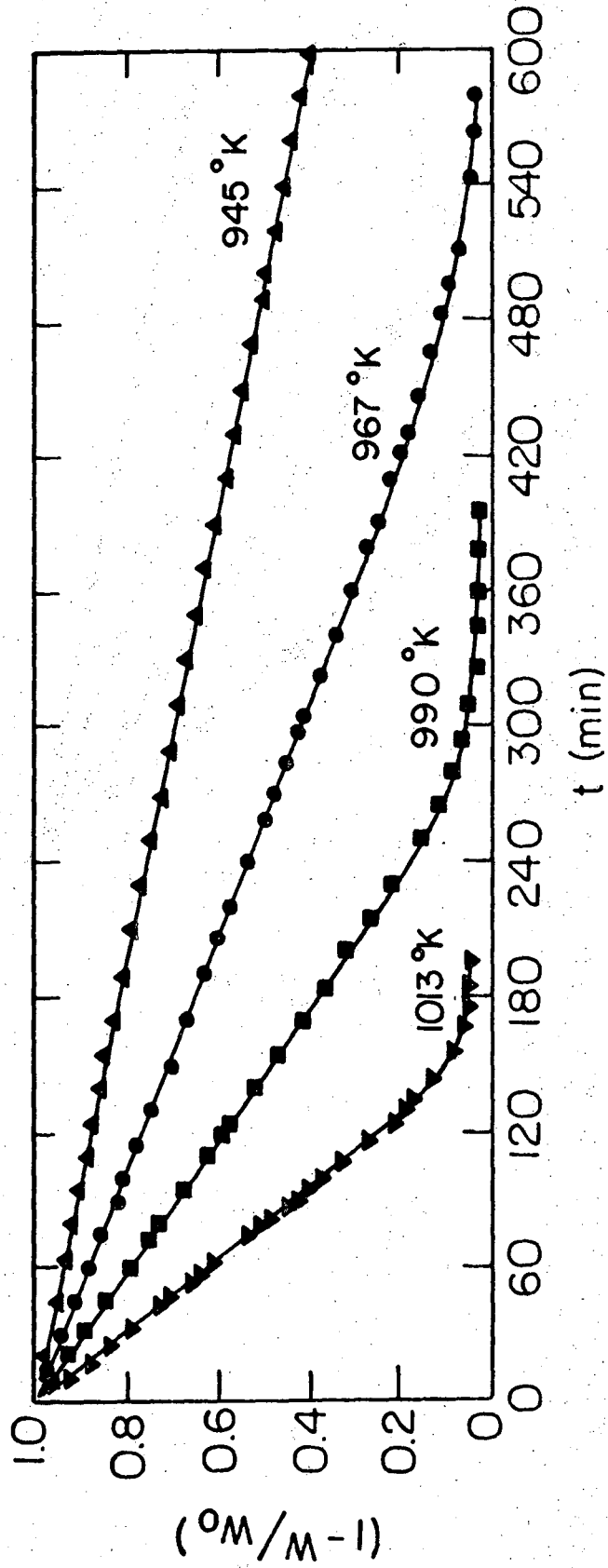   NSRDS-NB530, Nov. 1969).

15. R. B. Leonard and A. W. Searcy, J. Appl. Phys. 1971, $\underline{42}$, 4047.

16. D. A. Schulz and A. W. Searcy, J. Chem. Phys. 1962, $\underline{36}$, 3099.

17. A. W. Searcy, A. Büchler and D. Beruto, High Temp. Sci., 1974, $\underline{6}$.

18. R. Hultgren, R. S. Orr, P. D. Anderson and K. K. Kelly, Selected Values of Thermodynamic Properties of Metals and Alloys (Wiley, New York, 1963).

19. The Microscopic Determination of the Non-opaque Minerals, second edition, Geological Survey Bulletin 848, p. 88.

20. P. Hart and A. W. Searcy, J. Phys. Chem. 1966, $\underline{70}$, 2763.

21. Inorganic Index to the Powder Diffraction File, J. C. P. D. S. 1970.

22. C. N. R. Rao, S. R. Yoganaraimhan and M. P. Lewis, Can. J. Chem. 1960, $\underline{38}$, 2359.

23. E. P. Hyatt, I. B. Cutler and M. E. Wadsworth, J. Am. Ceram.Soc., 1958, $\underline{41}$, 70.

24. I. Langmuir, J. Am. Chem. Soc., 1916, $\underline{38}$, 2263.

25. G. H. Whiting, W. E. S. Turner, J. Soc. Glass. Technol., 1930, $\underline{14}$, 409.

26. J. Zadwadzki and S. Bretsznajder, Z. Physik. Chem., 1933, $\underline{B22}$, 60.

27. J. Zadwadzki and S. Bretsznajder, Trans. Faraday Soc., 1938, $\underline{34}$, 951.

28. H. T. S. Britton, S. J. Gregg, G. W. Winsor, Trans. Faraday Soc., 1952, $\underline{48}$, 63.

29. A.W.D. Hills, Chem. Eng. Sci., 1968, $\underline{23}$, 297.

30. A.W.D. Hills, Heat and Mass Transfer in Process Metallurgy (Inst. of Min. and Met., London, 1967).

31. A. L. Draper and L. K. Sveum, Thermochim. Acta, 1970, $\underline{1}$, 345.

32. H. Kappel and G. F. Hüttig, Kolloid. Z., 1940, $\underline{91}$, 117.

33. T. R. Ingraham and P. Marier, Can. J. Chem. Eng., 1963, $\underline{41}$, 170.

34. P. Barret, R. Perret, and R. DeHartoulari, C. R. Acad. Sci. Paris 1959, $\underline{248}$, 2862.

35. C. Slonim, Z. Elektrochem., 1930, $\underline{36}$, 439.

36. J. H. Sharp, S. A. Wentworth, Anal. Chem. 1969, $\underline{41}$, 1614.

37. J. Splichal, St. Skramovsky, and J. Goll, Coll. Czech. Chem. Commun. 1937, $\underline{9}$, 302.

38. J. P. Auffredic and P. Vallet, C. R. Acad. Sci. Paris, 1970, $\underline{271c}$, 178.

39. J. P. Auffredic and P. Vallet, C. R. Acad. Sci, Paris, 1967, $\underline{265c}$, 329.

40. P. K. Gallagher and D. W. Johnson, Jr., Thermochim. Acta, 1973, $\underline{6}$, 67.

41. J. H. Sharp and S. A. Wentworth, Anal. Chem. 1969, $\underline{41}$, 2060.

42. R. D. Shannon, Trans. Far. Soc., 1964, $\underline{60}$, 1902.

43. E. Cremer and W. Nitsch, Z. Elektrochem., 1962, $\underline{66}$, 697.

44. A. W. Searcy in Progress in Inorganic Chemistry, ed. F. A. Cotton (Interscience, New York, 1962).

FIGURE CAPTIONS
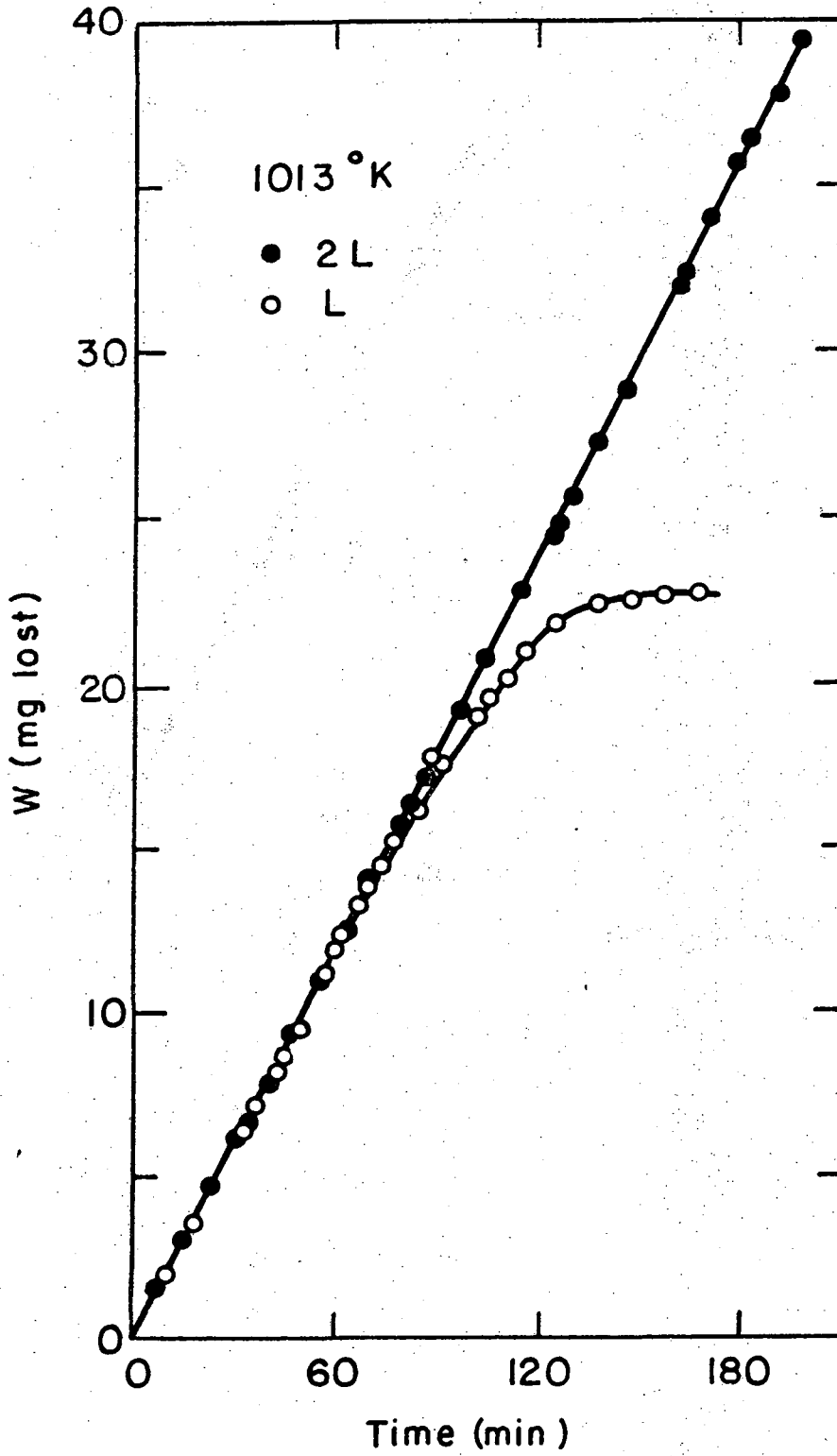
Fig. 1. Typical values of $1 - w/w_o$, where w_o is the initial CO_2 content and w is the weight of CO_2 lost plotted as functions of time at several temperatures.

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 valuum (lower curve) and of the maximum possible flux calculated from the equilibrium dissociation pressure by means of the Langmuir equation (upper curve).

Fig. 1

XBL7III-4785

Fig. 2

XBL7III-4787

XBL 7III-4786

Fig. 3