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Materials & Molecular Research Division

THE THERMODYNAMICS AND KINETICS OF THE REACTION:
 $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$

Gary F. Knutsen
 (Ph.D. thesis)

September 1980

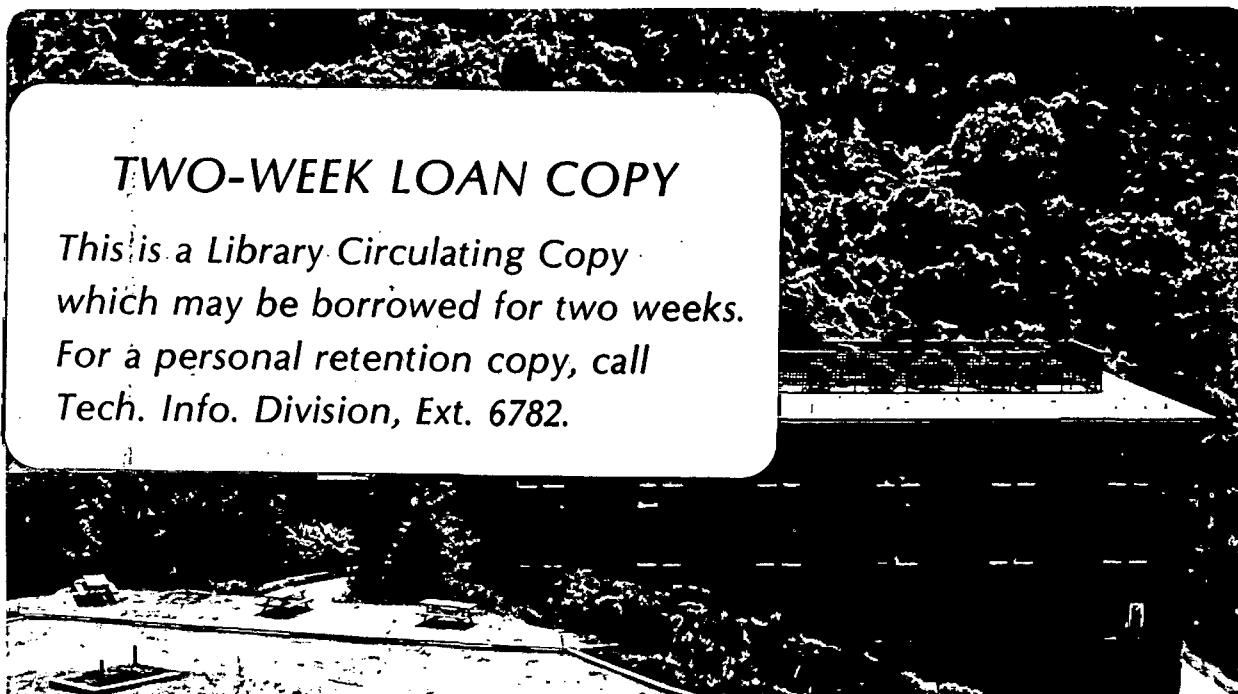
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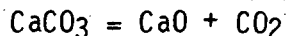
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THE THERMODYNAMICS AND KINETICS OF THE REACTION:
 $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$

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THE THERMODYNAMICS AND KINETICS OF THE REACTION:



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ABSTRACT

Reaction hot pressing of CaCO_3 powder samples at 900°C gave CaO bodies of 84 percent theoretical density compared to 50 percent theoretical density for CaO powders hot pressed at 900°C . CO_2 from the CaCO_3 decomposition was shown to catalyze the densification of CaO . Sintering results in the hot press could not be interpreted quantitatively because CO_2 pressures were unknown and probably varied from run to run.

To obtain more quantitative measures of the effect of CO_2 pressure on the surface area of CaO from calcite decomposition and to investigate the possibility of catalyzing the decomposition reaction, the CO_2 pressures from CaCO_3 were measured by the Knudsen effusion and Langmuir techniques in the temperature range $600\text{--}700^\circ\text{C}$ with and without possible catalysts for decomposition and CaO sintering. It was shown that, without a catalyst, CO_2 pressures only about 80 percent of the equilibrium pressures were obtained with a very small (0.23 mm diameter) orifice. The CaO produced when this orifice was used looked unchanged in SEM pictures from that produced at lower CO_2 pressures, but because of

reduced internal particle porosity the CaO had a $30 \text{ m}^2/\text{g}$ surface area compared to $90 \text{ m}^2/\text{g}$ surface area, which was obtained at low CO_2 pressures.

Additions of C, Na_2CO_3 , or Fe_2O_3 caused no significant changes in decomposition rates, but additions of NaCl, Na_2CO_3 or LiCl increased the rates by factors of 1.5 or more. When 10-weight percent LiCl was added to the CaCO_3 , equilibrium CO_2 pressures could be obtained in Knudsen cells with the 0.23 mm orifice. The CaO produced with LiCl present showed a considerable change in morphology from that of the CaO obtained from the vacuum decomposition of CaCO_3 . The CaO surface area after LiCl was vaporized by continued heating in vacuum was $<1 \text{ m}^2/\text{gram}$. LiCl additions caused decomposition rates to increase by about a factor of 2 and caused essentially the same morphological changes and surface area reductions in CaO if decomposition was carried out under Langmuir conditions, for which CO_2 pressures were only about 3×10^{-3} times those produced in effusion cells. The influence of LiCl on decomposition rates is probably not through reducing the free energy of activation of the process, but through prevention of formation of an effusion barrier of finely porous CaO. Probably, the LiCl catalyzed CaO crystal growth by forming a LiCl-CaO eutectic in which small CaO crystals dissolve and from which large CaO crystals precipitate.

CaCO_3 powder was studied under controlled static CO_2 pressure conditions and the equilibrium CO_2 pressures were determined. The pressures measured were 40 percent below the reported equilibrium CO_2 values.²⁹

CaO powders with external surface areas of $\sim 1 \text{ m}^2/\text{g}$ and internal surfaces of $\sim 90 \text{ m}^2/\text{g}$ were shown to react with CO_2 at $600\text{--}700^\circ\text{C}$ at a rate that is independent of time until 70 percent of theoretical recarbonation was achieved, regardless of the temperature of reaction. Rates then decreased sharply, probably because CaCO_3 blocked entrances to the internal pores of the CaO powder particles. For the time-independent reaction, the activation enthalpy at constant CO_2 activity is calculated to be 56.9 KJ/mole . The x-ray diffraction pattern showed the product to be crystalline CaCO_3 . The surface area was less than $1 \text{ m}^2/\text{g}$.

GENERAL INTRODUCTION

Glasson¹ and Ewing et al.² have studied the effect of CO_2 pressure on the surface area of CaO particles near 700°C . Their studies indicated that if CaCO_3 is decomposed under conditions that keep the CO_2 pressure close to the equilibrium decomposition pressure, the surface area of the CaO produced is much lower than that produced by decomposition in vacuum. Thus, CO_2 causes what can be interpreted as significant sintering at temperatures far lower than half the melting point, which is about 2600°C .

These results suggested the possibility that CaO , and perhaps other refractory oxides as well, might be densified at markedly lower temperatures than has been thought possible. Accordingly, we attempted the reactive hot pressing of CaCO_3 that is reported in the next section.

The hot pressing results were promising, but variations in scanning electron micrograph (SEM) pictures, and sample densities in successive runs showed that controlled experiments in known CO_2 pressures near the decomposition pressure were needed to clarify the influence of CO_2 pressure on CaO densification. Two other considerations made such studies desirable. First, while many studies of decomposition kinetics for CaCO_3 have been made,^{3,4,5,6,7,8} we find only one previously published direct determination of equilibrium CO_2 decomposition pressures.⁹ Second, a comparison of measured free surface decomposition rates to equilibrium decomposition data³ shows that the decomposition reaction is highly irreversible. A highly

reversible reaction can in principle be catalyzed. We know of no previous attempt to catalyze the decomposition of a carbonate; success might make it possible to produce CaO from CaCO_3 with less energy expenditure than now required.

Searcy and Beruto⁴ developed a general theory for decomposition reactions that anticipated a possibly large increase in the surface area as the reaction proceeds. In this theory, solid AB decomposes into a porous solid A, plus a gas, B. The model is schematically illustrated in Fig. 1, where volume elements of A and pores replace solid AB.

When CaCO_3 particles decompose, the external dimensions remain almost constant during the decomposition² so that the approximate porosity can be calculated from the relative molar volumes of CaCO_3 and CaO. These calculations show that the CaO produced from CaCO_3 decomposition should have a porosity of approximately 55 percent. The CaO is produced, as needles of approximately 10 nm diameter,⁸ and the surface area is high.²

Another feature of this theory is that it incorporates the possibility of the formation of a metastable solid phase. A metastable CaO phase was assumed to be a possible product of calcite decomposition.⁶

If CaO is metastable because it is produced in a form of high surface area and/or of amorphous crystal structure, a decrease in the CO_2 equilibrium decomposition pressure should be the result.¹⁰

Therefore, the equilibrium decomposition CO_2 pressures of CaCO_3 in Knudsen cells were measured with and without materials that might catalyze the decomposition of CaCO_3 , and the results were correlated with measurements of the CaO surface area and crystallinity. These measurements are reported in the second section of this thesis.

A third section of the thesis describes the measurement of equilibrium CO_2 pressures by a static method. These data provide a second test of the equilibrium decomposition pressures. Because Beruto et al.¹² found the interesting result that water vapor reacts with a linear rather than a parabolic rate law with porous CaO particles, we also used the apparatus that was built for static measurements of the equilibrium CO_2 pressures to determine the rate of CO_2 reaction with porous CaO particles as a function of time and temperature at CO_2 pressures just above the equilibrium decomposition pressures.

REACTIVE HOT PRESSING

Introduction

Various studies^{1,6,11,13} have shown that when calcite is decomposed in air, dry nitrogen, or carbon dioxide, in the temperature range from 650°C to 1100°C , the product is composed of CaO particles that have rounded surfaces and neck areas. These particle forms indicate that considerable sintering has occurred.

Glasson¹ concluded that CO_2 catalyzes the sintering of CaO , and Ewing, Beruto, and Searcy² have found supporting results.

Chaklader^{14,15} and Wheat¹⁶ have shown that the application of pressure during the decomposition of carbonates can produce considerable interparticle bonding. Therefore, it was of interest to hot press calcite powder in hopes of producing a dense CaO at temperatures well below the temperature at which one would expect sintering in CaO.

Hedvall¹⁷ has shown that there may be an increased reactivity during a phase transformation or during decomposition. Thus, by hot pressing CaCO_3 as it decomposes, it may be possible to produce a CaO more dense than could be produced by hot pressing CaO in a CO_2 atmosphere. One experiment was designed to test whether or not CaO densification in CO_2 could result when the CaO is not simultaneously produced by CaCO_3 decomposition.

Experimental

In order to hot press CaCO_3 , a special graphite die was fabricated with a central core composed of boron nitride (Fig. 2). Boron nitride spacers were also made to fit tightly inside the die cavity. The boron nitride was used to insure that there would be no reaction of the CaCO_3 or CaO with the graphite die.

The spacers also maintained the CO_2 pressure within the die close to the equilibrium decomposition pressure, thus making the interior of the die analogous to an effusion cell. The temperature could be measured both with an optical pyrometer and with a thermocouple.

The die was charged with 2.5 grams of CaCO_3 and loaded into the hot pressing apparatus, which was attached to a 15 cm silicone oil diffusion pump and a liquid nitrogen cold trap capable of pumping the system to 1.0×10^{-6} torr.

The heating elements were made of molybdenum, and there were four molybdenum heat shields around the die to insure that the sample was evenly heated and to minimize heat loss. A pressure of $3.51 \times 10^6 \text{ Kg/m}^2$ was applied while the sample was still at room temperature and maintained until the sample was completely decomposed. The samples were hot pressed at about 900°C in vacuum, and complete decomposition of the sample was measured by means of a displacement gauge.

At the end of the run, the pressure was released and the sample was annealed at 900°C for one hour. The samples were subsequently weighed and the density determined with a high-pressure mercury porisimeter. X-ray diffraction was also used to insure that the CaCO_3 was completely decomposed to CaO .

Results and Discussion

There were variations from run to run in the density of the CaO obtained from the decomposition of CaCO_3 under pressure; however, all samples showed that considerable sintering had taken place. Figures 3 and 4 show CaO particles with rounded surfaces and neck areas that were typical of the microstructures obtained.

The density measurements with a mercury porisimeter showed that calcium oxides with densities as high as 84 percent of the theoretical density could be achieved. In contrast, the highest density that could be obtained by hot pressing porous CaO at 900°C was 50 percent of theoretical density (Fig. 5).

In order to determine if the high densification of CaO generated from CaCO_3 was a unique consequence of the Hedvall effect, which is a high reactivity that accompanies the decomposition of CaCO_3 , or if the densification can be achieved by exposing high surface area CaO to CO_2 pressures only a little below the equilibrium decomposition pressure, a layer of porous CaO was placed on top of a layer of CaCO_3 and the sample was then hot pressed.

Figure 6 shows that the CO_2 from the decomposing CaCO_3 had caused some interparticle sintering in the porous CaO that had an initial surface area of about $90 \text{ m}^2/\text{gram}$. Evidently sintering of high surface area CaO is somewhat enhanced by CO_2 , but because the CO_2 pressures were unknown in the hot pressing experiments and may have varied from run to run, the results are only suggestive.

In another experiment, 10-weight percent LiCl was added to CaCO_3 and hot pressed at 900°C in vacuum. The resultant CaO exhibited considerable sintering (Fig. 7). The resultant density, 74 percent of theoretical, was less than the 84 percent obtained in the best sample, in which only CaCO_3 was used, but again, because of uncertainties of how much the CO_2 pressures varied from run to run, a quantitative conclusion could not be drawn.

The hot-pressing data show that (a) CO_2 does cause some sintering of CaO even when it is not a direct product of CaCO_3 decomposition, and (b) LiCl may promote densification. But CO_2 pressures are unknown and might well have varied from run to run because of variations in the rate of CO_2 leakage from the die chamber. It was evident that more controlled experiments were needed to further investigate these questions.

EFFUSION AND LANGMUIR STUDIES

Introduction

Measurements by Beruto and Searcy³ for CaCO_3 decomposition show that the ratio of the free surface decomposition rate to the maximum possible rate, which can be calculated by substituting from the equilibrium pressure into the Hertz-Knudsen-Langmuir equation,^{18,19} is 10^{-5} . In contrast, for most congruent vaporization reactions this ratio is 10^{-2} to 1 times the maximum rate. The high degree of irreversibility for CaCO_3 decomposition implies that it may be difficult to achieve equilibrium decomposition pressures for the reaction by measurements with effusion cells.

According to the Whitman-Motzfelt analysis, to approach equilibrium in a Knudsen cell requires that the orifice area a , times the Clausing factor C ,^{20,21} be of the same magnitude or smaller than RA_e , where A_e is the effective area of the sample and R is the ratio of flux from a free surface to the flux from an equilibrium source. A_e is an

ill-defined quantity, which has a minimum value equal to the cross-sectional area A_c of the effusion cell and a maximum value given by the total surface area of the solid reactant particles. For reasons that are not understood,¹²² A_e appears in decomposition reactions to be approximated by A_c . When R is only 10^{-5} , as it is for CaCO_3 decomposition, it is difficult to construct effusion cells for which $RA_c < aC$ without making the orifice so small that leakage causes significant errors in measured fluxes.

Furthermore, for at least two decomposition reactions—the decomposition of Mg(OH)_2 ²³ and of dolomite $\text{MgCa(CO}_3)_2$ ²⁴—the Whitman-Motzfelt extrapolation of fluxes measured from crucibles of different orifice areas to zero orifice area yields apparent equilibrium pressures that are several orders of magnitude below the true equilibrium pressure that can be measured by static techniques or calculated from thermodynamic data for the reactants and products of reaction. It is important to determine whether the method fails for CaCO_3 as well; low apparent equilibrium pressures may reflect production of metastable solid products.

It will also be of interest to see if the decomposition reaction can be catalyzed. In principle, a suitable catalyst could increase the rate of CO_2 escape from the free surface of CaCO_3 by a factor of $1/R = 10^5$.

Until the study of Beruto and Searcy,³ the possibility that a carbonate decomposition could be catalyzed had not apparently been

recognized, and no attempt to increase a carbonate decomposition rate had been attempted. Schoonmacher²⁵ has shown that GaN decomposition is catalyzed by liquid gallium. In light of the demonstration by Brewer and Kane²⁶ that a liquid catalyzes P_4 sublimation and of Schoonmacher's results for GaN decomposition, it seemed probable that something that forms a liquid at the temperature of study may catalyze $CaCO_3$ decomposition. The effects of several possible catalysts for $CaCO_3$ decomposition were, therefore, tested.

Experimental

The thermogravimetric device used for the effusion and Langmuir studies is shown in Fig. 8. A platinum basket was hung from a Cahn RG recording microbalance in a platinum resistance furnace. The vacuum was maintained below 1.3×10^{-4} Pa by a 15 cm silicone oil diffusion pump and a liquid nitrogen cold trap.

The temperature was measured with a Pt-Pt/10 percent Rh thermocouple, and was controlled to $\pm 2^\circ C$ of the desired temperature by a proportional band control unit. The temperature of the sample was recorded by a digital thermocouple display unit. The sample weight losses were continuously measured on a strip chart recorder with a sensitivity of either 100 mg or 10 mg full scale.

The sample temperature was carefully calibrated by determining the well-known vapor pressure of NaCl in effusion cells using the Knudsen effusion technique. The vapor pressure was within 3 percent of the JANAF²⁶ table values (Fig. 9).

Baker analytical reagent CaCO_3 , low in alkali, powder of about 2 to 5 μm average dimensions was used for all experiments. The powder had a specific surface area of $\sim 0.6 \text{ m}^2/\text{gram}$. For catalytic experiments Mallinckrodt analytical reagent LiCl , NaCl , Fe_2O_3 , and Na_2CO_3 powders were used. The spectrographic analysis of the LiCl and NaCl are given in Fig. 10.

Surface Area Determination

Surface areas were determined by the BET method.²⁸ The Quantosorb BET apparatus, which was used to measure the surface areas, has been described in other papers.²

X-Ray Analysis

The powder samples were packed in an aluminum holder and irradiated in a Picker x-ray diffractometer using $\text{CuK}\alpha$ radiation. The samples were analyzed directly after removal from the thermobalance in order to minimize any hydration of the CaO , Fig. 11 gives the d-spacings measured for CaO and CaCO_3 .

SEM Analysis

Samples of CaO were dispersed in CCl_4 as soon as they were removed from the furnace to avoid hydration and agglomeration. The CaO dispersion was dropped upon a holder using an eyedropper, and a layer of gold approximately 200 $\text{\AA}$ thick was deposited on the powder.

Effusion Cells

Equilibrium CO_2 pressures were determined for calcite in the temperature range 600°C to 700°C . Graphite effusion cells with tight-fitting lids having orifice diameters of 1.0 mm and 0.23 mm were used. The samples were held for at least 30 minutes at each temperature in order to insure that equilibrium had been achieved.

RESULTS

Effusion Studies on CaCO_3

All pressures reported were determined during the first 20 percent of the decomposition, because the rate of weight loss decreased during the course of an entire run. The measured pressures decreased approximately 50 percent during the time that the sample had progressed from 10 percent of theoretical decomposition to the time the decomposition was 80 percent complete.

With both orifices, the pressures determined were well below the equilibrium CO_2 vapor pressures calculated from the heats and entropies of formation given by Stearn and Weiss.²⁹ With the 1.0 mm orifice, pressures were 1.5 orders of magnitude lower than the accepted value, which is calculated from thermochemical data (Fig. 12). When the 0.23 mm diameter orifice was used, the CO_2 pressures increased but were still about a factor of 5 below the accepted values (Fig. 13). This orifice was quite small and effusion rates were so low that going to a smaller orifice was experimentally unrealistic. A Whitman-Motzfelt extrapolation

of the data (Fig. 3) shows that, even when the data is extrapolated to zero orifice area, the pressures are still a factor of 1.5 lower than the equilibrium CO_2 pressure calculated from thermochemical data.²⁹

The surface areas of the CaO powders that resulted from the CaCO_3 decomposition in cells with the two orifices were quite different. The CaO produced in the cell with a 1.0 mm diameter orifice at 700°C had surface areas of $\sim 90 \text{ m}^2/\text{gram}$, whereas the CaO from the cell with a 0.23 mm diameter orifice had a surface area of $\sim 30 \text{ m}^2/\text{gram}$.

Langmuir Decomposition

CO_2 fluxes from calcite powder in open crucibles were determined at 600°C . The flux-per-unit cross-sectional area of powder bed was $\sim 10^{-3}$ times the equilibrium flux. Again as in the equilibrium measurements the flux decreased with time, and measurements were only taken during the first 20 percent of the decomposition.

The flux-per-unit cross-sectional area of powder bed decreased with the amount of powder used, from $3.34 \times 10^{-7} \text{ moles/cm}^2 \text{ sec}$ with 0.1 grams of CaCO_3 to $2.46 \times 10^{-7} \text{ moles/cm}^2 \text{ sec}$ with 0.5 grams of CaCO_3 , but with 1.0 grams of CaCO_3 , the CO_2 flux increased to $4.59 \times 10^{-7} \text{ moles/cm}^2 \text{ sec}$. The flux thus is about $3 \pm 1 \times 10^{-7} \text{ moles/cm}^2 \text{ sec}$ independent of bed depth.

The surface area of the CaO obtained in Langmuir decompositions was $90 \text{ m}^2/\text{gram}$. The powder x-ray diffraction pattern (Fig. 15) shows a poorly crystalline CaO , which will be referred to as sr- CaO because it is similar to the reactive CaO given that designation by Searcy and Beruto.¹⁰

Catalysis of Calcite Decomposition

Failure to obtain equilibrium CO_2 pressures and fluxes in effusion cells with small orifices is consistent with the conclusion of Beruto and Searcy¹⁰ that the decomposition of calcite is highly irreversible.

The idea of catalyzing endothermic decomposition reactions has received almost no attention. As a practical matter, substances tested for catalysis of calcite decomposition were chosen which have equilibrium vapor pressures at least an order of magnitude below that of CO_2 in equilibrium with calcite, and have low vapor molecular weights. These characteristics were desired so that the catalyst would make only a negligible contribution to the mass of flux measured by the microbalance.

The addition of C, Na_2CO_3 , and Fe_2O_3 to CaCO_3 in cells with a 1.0 mm orifice diameter had no effect on the CaCO_3 decomposition rate. However, Li_2CO_3 and NaCl increased the CO_2 pressure by a factor of 1.5 over the uncatalyzed decomposition when a 1.0 mm orifice was used. LiCl turned out to be the best catalyst.

Figure 16 shows a plot of LiCl equilibrium pressure vs CO_2 equilibrium decomposition pressure over CaCO_3 . The LiCl pressure is almost two orders of magnitude lower than that for CO_2 , so that LiCl vaporization has a negligible effect over the mass flux if near-equilibrium CO_2 pressures are established. When 10-weight percent of LiCl was added to calcite in the 1.0 mm diameter effusion cells, the decomposition pressure of CO_2 was increased by a factor of 2 over the uncatalyzed pressure in effusion runs.

While the rate of the uncatalyzed reaction decreased throughout the run, the rate of effusion of CO_2 from the cell with LiCl present was constant from the start of the run until almost the end of the run. There was an abrupt change in the rate of effusion when the calcite was 90 percent decomposed and the rate then dropped to the equilibrium rate for LiCl effusion. Measurement of this LiCl sublimation rate gave an excellent in situ temperature calibration.

Figure 12 shows a plot of CO_2 vapor pressures for calcite and for calcite with 10-weight percent LiCl for the 1.00 mm diameter orifice. When 10-weight percent LiCl was added to CaCO_3 in the effusion cell with a 0.23 mm diameter, the CaCO_3 decomposition rate was increased over the catalyzed rate from the cell with the 1.00 mm orifice. The rate from the 0.23 mm orifice increased by a factor of 2 over the rate measured in the absence of LiCl. The apparent decomposition pressures were actually a little above the CO_2 pressures calculated from thermochemical data, as shown in Fig. 13. This difference may be a consequence of a small leak in the effusion cell.

The rate of effusion from the 0.23 mm diameter orifice, like the rate measured with the 1.0 mm orifice, was constant throughout 90 percent of the run, and changed abruptly to the subsequent equilibrium LiCl effusion rate when the calcite was completely decomposed:

The cells were heated after the calcite was completely decomposed until the LiCl had completely vaporized from the sample. Subsequent x-ray diffraction examination shows an extremely crystalline

CaO diffraction pattern (Fig. 17). No pattern of LiCl can be detected and the sample did not hydrate as readily as did the high surface area sr-CaO produced in a free-surface decomposition without a catalyst.

The surface area of the CaO produced in the runs with the LiCl present was determined to be $\sim 1.0 \text{ m}^2/\text{gram}$. This is in contrast to the $90 \text{ m}^2/\text{gram}$ for uncatalyzed CaO from the cells with 1.0 mm diameter orifices and the $30 \text{ m}^2/\text{gram}$ from cells with the 0.23 mm diameter orifice when no LiCl was added. The SEM micrographs show a glassy appearing CaO (Figs. 18 and 19), in contrast to the typical CaO from a cell with the 1.0 mm diameter orifice when LiCl was not used (Fig. 20).

A Langmuir experiment was carried out with 10-weight percent LiCl added to the calcite powder, and the CO_2 flux increased by a factor of 2 as it did in the effusion experiments. This catalyzed flux was still about a factor of 2×10^{-3} below the equilibrium flux. The flux measured with the catalyst present was essentially constant for 90 percent of the run, and the subsequent x-ray pattern and surface area was the same as those when the runs were completed with the catalyst in the effusion cells.

In order to find out if the reduction in the surface area of the CaO required the presence of CaCO_3 , 10-weight percent of LiCl was added to sr-CaO of $\sim 90 \text{ m}^2/\text{gram}$ surface area, and placed in an effusion cell with a 1.0 mm diameter orifice. The cell was heated to 700°C and all of the LiCl was vaporized at that temperature. The remaining CaO was then examined in the scanning electron microscope. Figure 21 shows that the

sr-CaO has undergone a change in morphology that must be a consequence of the reaction between sr-CaO and LiCl. The surface area of the CaO was also $\sim 1.0 \text{ m}^2/\text{gram}$.

Discussion

The CO_2 pressures measured by decomposing CaCO_3 in the absence of a catalyst in effusion cells lay below those reported by Stern and Weiss²⁹ (Figs. 12 and 13). There was an increase in the pressure when the 0.23 mm orifice was substituted for the 1.0 mm orifice, but the CO_2 pressure was still a factor of 3 below the equilibrium CO_2 decomposition pressure. This orifice area effect showed that the CaCO_3 was not decomposing at the equilibrium rate. The Whitman-Motzfelt extrapolation of the data (Fig. 14) to zero orifice area still did not yield equilibrium CO_2 pressures.

It is significant to note that the surface area of CaO obtained when the 0.23 mm orifice was used was one-third that obtained when the 1.00 mm orifice was used ($30 \text{ m}^2/\text{gram}$ vs $90 \text{ m}^2/\text{gram}$). The CO_2 pressure in the cell with the 0.23 mm orifice was four times greater than that in the cell with the 1.00 mm orifice. This fact reaffirms the findings of Glasston¹ and Ewing et al.² that CO_2 pressure affects the surface area of CaO obtained from the decomposition of CaCO_3 .

It is possible to calculate the surface free energies per mole associated with the $30 \text{ m}^2/\text{gram}$ and $90 \text{ m}^2/\text{gram}$ calcium oxides by the method of Giaque.²³ Assuming that the surface free energy of CaO is

equal to that for MgO , about 1200 erg/cm^2 , the metastability of the $90 \text{ m}^2/\text{gram}$ and $30 \text{ m}^2/\text{gram}$ samples are calculated to be $\gamma_m = 6.05 \text{ KJ/mole}$ and 2.01 KJ/mole , respectively. The drop in equilibrium CO_2 pressure that can be calculated from these metastabilities does not account for the low pressures measured in the effusion cells. The ratio between the pressure measured for the metastable equilibrium P_m and the pressure P for the decomposition to CaO of negligible surface area is given by $P_m/P = \exp(\gamma_m/RT)$. The calculated pressure ratios are 0.47 and 0.78 at 700°C , instead of ~ 0.1 and ~ 1.3 as observed. Furthermore, the Langmuir decomposition of calcite powder produced fluxes that were 10^{-3} times the equilibrium flux. The surface area of the sr-CaO obtained from the Langmuir decomposition was $\sim 90 \text{ m}^2/\text{gram}$, which was comparable to that of CaO produced in the cell with the 1.00 mm orifice.

The measurements of CaO produced in the free surface sublimation experiments confirmed Searcy and Beruto's¹¹ findings that when CaCO_3 is decomposed under conditions that make the pressure of CO_2 far below the equilibrium decomposition pressure, CaO of high surface area is obtained. The x-ray diffraction pattern of this material shows a CaO of fairly low crystallinity that can be attributed to the extremely small crystallites of CaO (Fig. 8).⁸

The Knudsen effusion data confirmed the expectation from the low fluxes obtained in free surface decomposition measurements that equilibrium could not be achieved in the absence of a catalyst without an

impractically small effusion orifice. Consequently, the concept of catalyzing the decomposition was pursued.

The addition of C, Fe_2O_3 , and Na_2CO_3 had no measurable effect on the decomposition rate of calcite. The addition of NaCl and Li_2CO_3 increased the decomposition rate by a factor of 1.5, but when 10-weight percent of LiCl was added to the CaCO_3 the measured CO_2 pressures were increased in the cells with both the 1.00 mm and 0.23 mm orifice by a factor of two over pressures measured in the uncatalyzed cell. This increase in pressure could not be attributed to the vapor pressure of LiCl; therefore the LiCl did in fact increase the rate of CaCO_3 decomposition.

Furthermore, in the presence of LiCl, the rate of CO_2 effusion did not decrease as the CaCO_3 decomposed, but instead was constant until the reaction was about 95 percent complete. Figures 22 and 23 show the rate of weight loss vs time for catalyzed and uncatalyzed Langmuir and Knudsen runs.

The CaO powder obtained from the catalyzed decomposition yielded an x-ray pattern of a highly crystalline CaO (Fig. 17). The SEM micrographs show the difference between CaO obtained from uncatalyzed CaCO_3 (Fig. 20), and the glasslike CaO obtained from the catalyzed CaCO_3 at 700°C (Figs. 18 and 19). It is evident from these pictures that LiCl promotes extensive sintering of CaO at temperatures as low as 700°C .

The sintered CaO particles must not adhere to the CaCO_3 because an adherent CaO layer would reduce the rate of decomposition. In fact, the catalysis of the decomposition of CaCO_3 may probably be a consequence of stripping of CaO from the CaCO_3 surface, thus increasing the effective area of decomposition by about a factor of two.

The use of LiF as a liquid phase in the sintering of MgO has been shown to be effective by several authors.^{30,31,32,33} Whelan³⁰ and Pask^{31,33} have shown that if LiF is added to MgO powders, a film covers the MgO particles in compacts that have been heated to a temperature below the melting point of LiF. They observed that a rapid densification of MgO resulted.

Although this film was presumed to be a liquid, neither its composition nor the reaction by which it forms has been identified. Given the fact that MgO is soluble in LiF, it follows that CaO may well be soluble in LiCl. Furthermore, there could possibly be a ternary eutectic reaction among $\text{CaO-CaCO}_3\text{-LiCl}$, which provides a liquid intermediate in the CaCO_3 decomposition.

MEASUREMENTS OF $\text{Sr-CaO} + \text{CO}_2$ REACTIONS

Introduction

When reactions of the type $\text{A(s)} + \text{B(g)} = \text{AB(s)}$ occur, there usually is an increase in the molar volume of the solid. Accordingly, a protective coating can be expected to form. If so, the rate of reaction will be limited by solid-state diffusion through the protective coating and a parabolic time dependence will be observed.

In the reaction $\text{CaO(s)} + \text{CO}_2\text{(g)} = \text{CaCO}_3\text{(s)}$, the molar volume of the solid increases by a factor of 2, and Cutler⁶ reports that the reaction shows the parabolic behavior expected when a protective coating forms.

In contrast, Beruto, Searcy, Barco, and Bellari¹² find that the reaction of water vapor with porous sr-CaO particles has a constant reaction rate until the reaction is 80 percent complete. It is of interest to see if the reaction of CO_2 with porous sr-CaO shows a parabolic time dependence like that shown by CO_2 with nonporous CaO powders, or linear like that shown by H_2O vapor with porous sr-CaO.

In addition to measuring the rate of $\text{CaO} + \text{CO}_2$ reaction at several temperatures, the apparatus was also used to determine the equilibrium CaCO_3 decomposition pressure by a null point method. These pressures are then compared to pressures measured by a tensivolometric technique,⁷ to the effusion pressures reported in a previous section of this thesis, and to pressures calculated from thermochemical data.²⁹

Experimental

A specially designed thermogravimetric apparatus, which was built for use in this study, is shown in Fig. 24. The microbalance is a Cahn model R-1000. It was mounted on a 1-1/2-inch thick plate of aluminum and supported on four air-filled shock absorbers in order to damp vibrations. A flexible stainless steel hose was used between the sytem and the pump in order to reduce any extraneous vibrations. With

this vibration isolation system, the balance could be used at a sensitivity of 1.0 mg full scale.

A tube furnace wound with Kanthal wire was used to heat the sample. The temperature was measured with a chromel alumel thermocouple interfaced with a digital readout device. The sample was suspended from a 1.0 mm diameter quartz hangdown rod. Sample weight gains and losses were measured continuously on a strip chart recorder with a sensitivity of 10 mg full scale. The sample temperature was calibrated by comparing the vapor pressure of LiCl measured by the Knudsen effusion technique to the vapor pressure reported in the JANAF²⁴ thermochemical tables (Fig. 25).

This system was specifically designed for use with CO₂ atmospheres at controlled pressures. Two electronic capacitive manometers with ranges of 1.33×10^{-1} Pa to 1.33×10^5 Pa were used to measure the backpressure of CO₂ in the system. A description of how the manometers work is given by Shukla.⁷

The manometers were mounted in parallel with a Granville Phillips automatic pressure controller that controlled pressure to ± 13 Pa. The pressure could also be continuously monitored along with weight gain or loss on a dual-channel strip-chart recorder.

RESULTS

Equilibrium CO₂ Pressure Determination

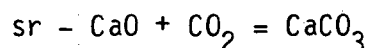
When CaCO₃ is decomposed in vacuum at 600°C, porous CaO particles are produced that have the same external dimensions as those of

the original CaCO_3 particles but that have surface areas of $90 \text{ m}^2/\text{grams}$. It has been speculated that this high surface area could make the thermodynamic activity of the porous high surface area CaO (sr- CaO) significantly higher than that of CaO of low-surface area.¹⁰ In the apparatus described in Fig. 24, it is possible to decompose CaCO_3 in vacuum and then adjust the CO_2 pressure in the system to any desired value. By determining the point at which there is no weight gain or weight loss for a particular temperature, the equilibrium CO_2 decomposition pressure for the porous CaO powder can be determined for comparison with decomposition pressures when the surface area of the CaO powder is low.

Initially, 0.7 grams of CaCO_3 were decomposed in vacuum at 600°C . The system was then adjusted to the desired temperature, and CO_2 gas was introduced into the system. The CO_2 pressure was increased in 13.3 Pa increments until a constant weight gain was observed. The CO_2 pressure was then lowered until there was no weight gain or loss by the sample. The pressure that produced no weight change was assumed to be the CO_2 vapor pressure in equilibrium with the CaO powder. The pressure could be precisely determined because if the pressure was increased or decreased by 13.3 Pa there was a measurable weight gain or weight loss in the sample. The CO_2 pressures in equilibrium with porous CaO at five different temperatures are shown in Fig. 26.

Reaction of CO₂ with Porous CaO Powder

After equilibrium CO₂ pressures were determined, the CaO powders were reacted with CO₂ at 1.4 times the experimentally determined CO₂ equilibrium pressure. The rate of the reaction corresponding to the equation:



is given in Fig. 27 for 600°, 650°, and 700°C. The reaction was linear until the sample reached 65 to 75 percent of theoretical recarbonation, regardless of the temperature of reaction. For the linear portion of the reaction, the activation enthalpy of constant CO₂ activity is calculated to be 56.9 KJ/mole. The results are compared in Fig. 28 with the data obtained by Beruto and Searcy for the decomposition of single crystal CaCO₃.

The x-ray diffraction pattern of the recarbonated product was that of crystalline CaCO₃ with no evidence of CaO being present (Fig. 29). The surface area of the CaCO₃ product was determined to be 1.0 m²/gram. The scanning electron micrograph (Figs. 30 and 31) show the rumpled surface obtained in the 700°C, which was characteristic of the samples from all the temperatures studied.

Discussion

Figure 32 compares the equilibrium decomposition pressures obtained by the different methods in this thesis to the pressures calculated from thermochemical data, and measured by Shukla⁷ by a static method. The back reaction of high-surface area CaO with CO₂ yielded measured equilibrium CO₂ pressures that were 40 percent below the equilibrium values calculated from thermochemical data,²⁹ and 20 percent below values measured directly by the static technique. The decrease of 40 percent would be consistent with a 2 KJ/mole metastability in the porous CaO, and the decrease of 20 percent would be consistent with a 1.0 KJ/mole metastability. The calculated metastability for a surface area of 90 m²/gram with a surface energy of 1200 erg/cm² is 6.05 KJ/mole.

It is interesting to note that all the pressures were below the calculated equilibrium values except the runs in cells with the 0.23 mm orifice with 10-weight percent LiCl. Those catalyzed pressures may be greater than the accepted value because of a slight leak in the effusion cell. The static method of this work yielded pressures close to those found by Shukla's tensivolumetric method and within experimental error were probably the same.

The rates of reaction of CO₂ with the porous CaO powder are shown in Fig. 26 for 600°, 650°, and 700°C. The reaction rate was linear until the sample reached ~70 percent of theoretical recarbonation, regardless of the temperature of reaction. The initial linear reaction

rate implies that the rate limiting process until the reaction is more than 65 percent complete is a surface step rather than diffusion through the CaCO_3 product layer. It is not surprising that the rate limiting process during the initial phase of reaction is different from that found by Oakeson and Cutler⁶ because, until the pores are blocked, solid-state diffusion distances in the porous powders are low. The fact that the surface area measured for samples that were 70 percent reconverted to CaCO_3 is only $\sim 1.0 \text{ m}^2/\text{gram}$, about the area expected for nonporous powders, implies that the decrease in rate in the later stages of reaction is a consequence of blockage of pores well before the reaction is complete.

GENERAL CONCLUSIONS

Hot-pressing experiments with CaCO_3 and CaO suggested that CO_2 promotes significant sintering of CaO at 800°C . The Knudsen and Langmuir studies show that sintering of CaO is indeed catalyzed by CO_2 , but at 700°C pressures must be within about 20 percent of the equilibrium CaCO_3 decomposition pressure to reduce surface areas at 700°C from $90 \text{ m}^2/\text{gram}$ to $30 \text{ m}^2/\text{gram}$.

LiCl additions, however, increase the CaCO_3 decomposition rates and markedly reduce the surface area of the product CaO . At 700°C the CaO surface area is reduced to $\sim 1 \text{ m}^2/\text{gram}$ by either decomposing CaCO_3 in the presence of LiCl or by heating high surface area CaO with LiCl . This suggests that hot pressing of CaO with LiCl which is later

vaporized may be a practical means of making high-density CaO at relatively low temperatures.

The equilibrium CO_2 pressure for CaCO_3 decomposition, measured by a null-point method in this study, agrees to within 10 percent of values measured by a static method by Shukla.⁷ Within estimated experimental errors there is no clear effect of surface area on decomposition pressure.

Reaction of porous CaO with CO_2 in the range of 600° to 700°C is time independent until the reaction is 70 percent complete. Beruto et al.¹² found similar results for reaction of porous CaO with water vapor. Rates of both reactions fall off sharply, probably because pores are blocked by the reaction product.

It seems evident that if high surface area particles of larger relative pore volumes can be produced, then a fast linear rate may extend until reaction is 100 percent complete. This possibility should be investigated because effective removal of gases such as sulfur oxides by metal oxides like CaO is of great importance in the development of industrial processes that do not seriously contribute to environmental pollution.

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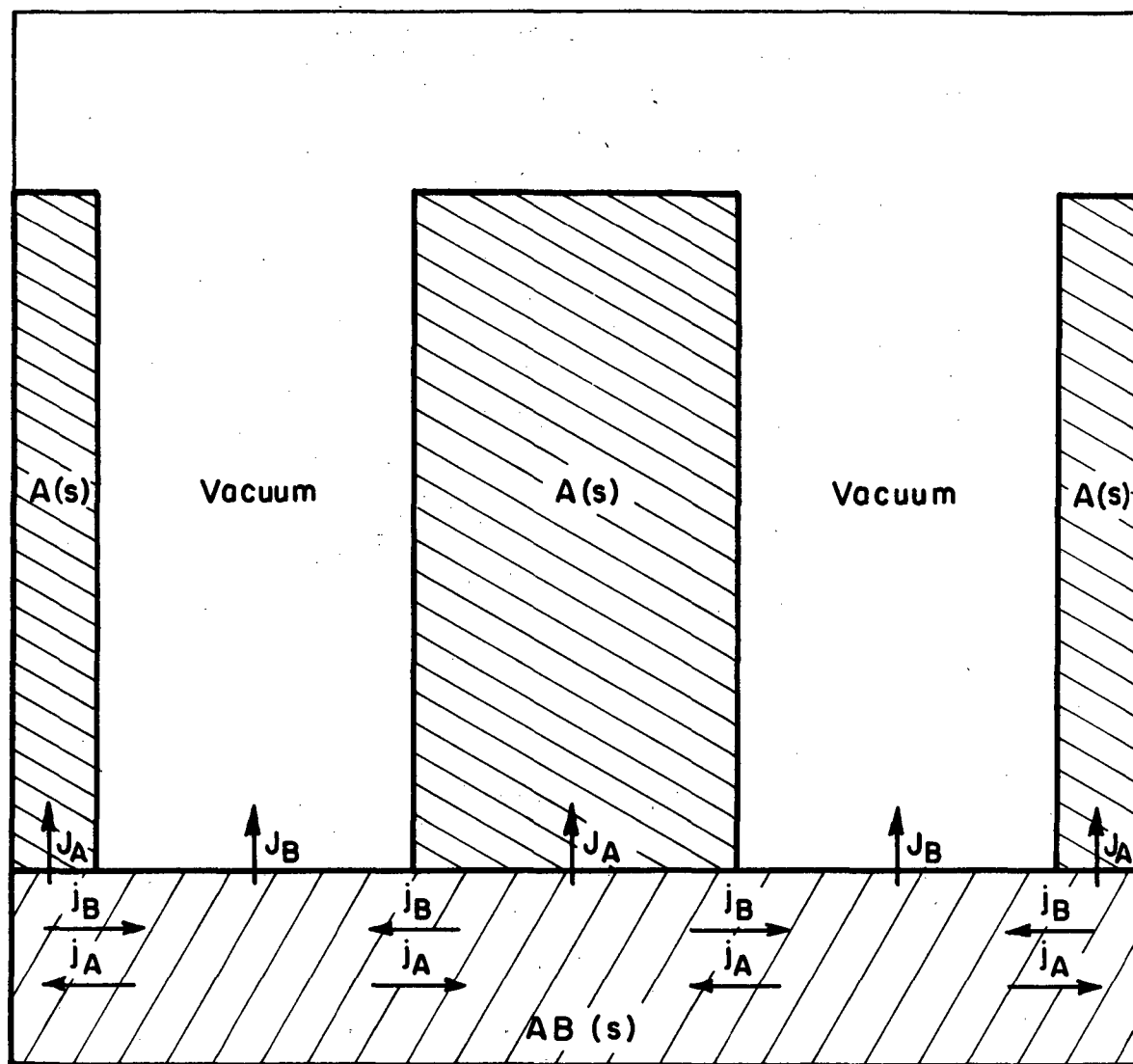
FIGURE CAPTIONS

- Figure 1. Schematic drawing of cross-section for the reaction
 $AB(s) = A(s) + B(g)$.
- Figure 2. Schematic drawing of hot press die.
- Figure 3. CaO product from reactive hot pressed $CaCO_3$.
- Figure 4. CaO product from reactive hot pressed $CaCO_3$, dense section.
- Figure 5. Hot pressed sr-CaO.
- Figure 6. Hot pressed layer of $CaCO_3$ /sr-CaO.
- Figure 7. Hot pressed $CaCO_3$ produced with 10-weight percent LiCl.
- Figure 8. Experimental apparatus for decomposing $CaCO_3$ in vacuum.
- Figure 9. NaCl temperature calibration.
- Figure 10. Spectrographic analysis of reagents.
- Figure 11. X-ray d-spacings table.
- Figure 12. CO_2 pressures for uncatalyzed and catalyzed $CaCO_3$ in 1.00 mm diameter effusion cells.
- Figure 14. Whitman-Motzfelt extrapolation of CO_2 vapor pressures.
- Figure 15. X-ray pattern of CaO from decomposition of $CaCO_3$ at $700^\circ C$ in vacuum.
- Figure 16. Equilibrium pressures for $CaCO_3$ decomposition and LiCl vaporization from thermochemical data.
- Figure 17. X-ray pattern for CaO from catalyzed decomposition of $CaCO_3$ at $700^\circ C$.

- Figure 18. CaO from catalyzed LiCl decomposition of CaCO_3 in cell with 0.23 mm diameter orifice.
- Figure 19. CaO from catalyzed decomposition of CaCO_3 in cell with 1.0 mm orifice.
- Figure 20. sr-CaO from decomposition of CaCO_3 in vacuum at 700°C .
- Figure 21. CaO from sr-CaO + 10-weight percent LiCl.
- Figure 22. Rate of decomposition of CaCO_3 in effusion cells for catalyzed and uncatalyzed runs at 700°C .
- Figure 23. Rate of decomposition of CaCO_3 in Langmuir cells for catalyzed and uncatalyzed runs at 600°C .
- Figure 24. Experimental apparatus for decomposition of CaCO_3 in a controlled CO_2 atmosphere.
- Figure 25. LiCl temperature calibration.
- Figure 26. Equilibrium CO_2 pressures determined from recarbonation reaction.
- Figure 27. Rates of the recarbonation reaction.
- Figure 28. Enthalpy of activation for the recarbonation reaction, lower curved. Enthalpy of activation for decomposition reaction, upper curve.
- Figure 29. X-ray pattern that results from the reaction
 $\text{sr} - \text{CaO} + \text{CO}_2 = \text{CaCO}_3$ at 700°C and
 $P_{\text{CO}_2} = 3.5 \times 10^3 \text{ Pa}$.
- Figure 30. CaCO_3 from recarbonation reaction.

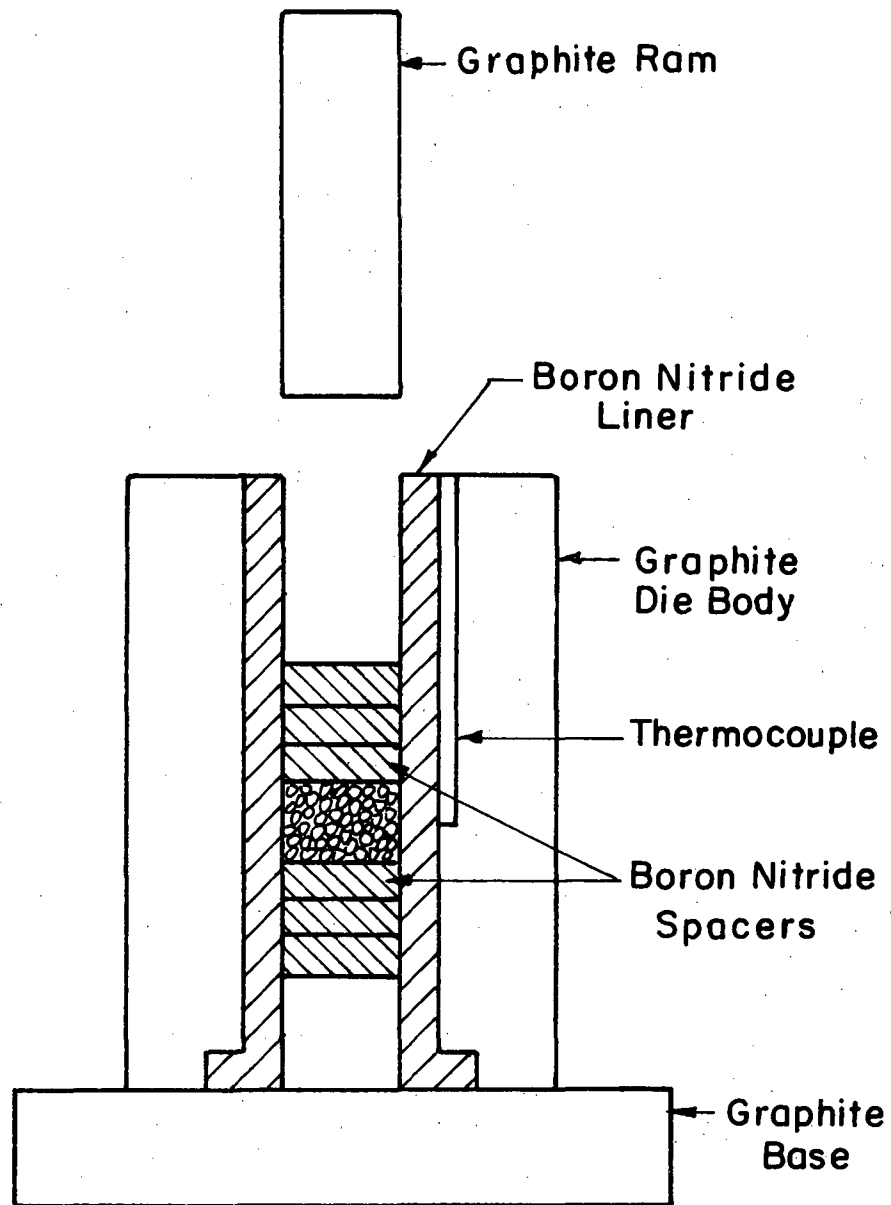
Figure 31. CaCO_3 from recarbonation reaction.

Figure 32. Comparison of the decomposition pressures obtained by various methods.



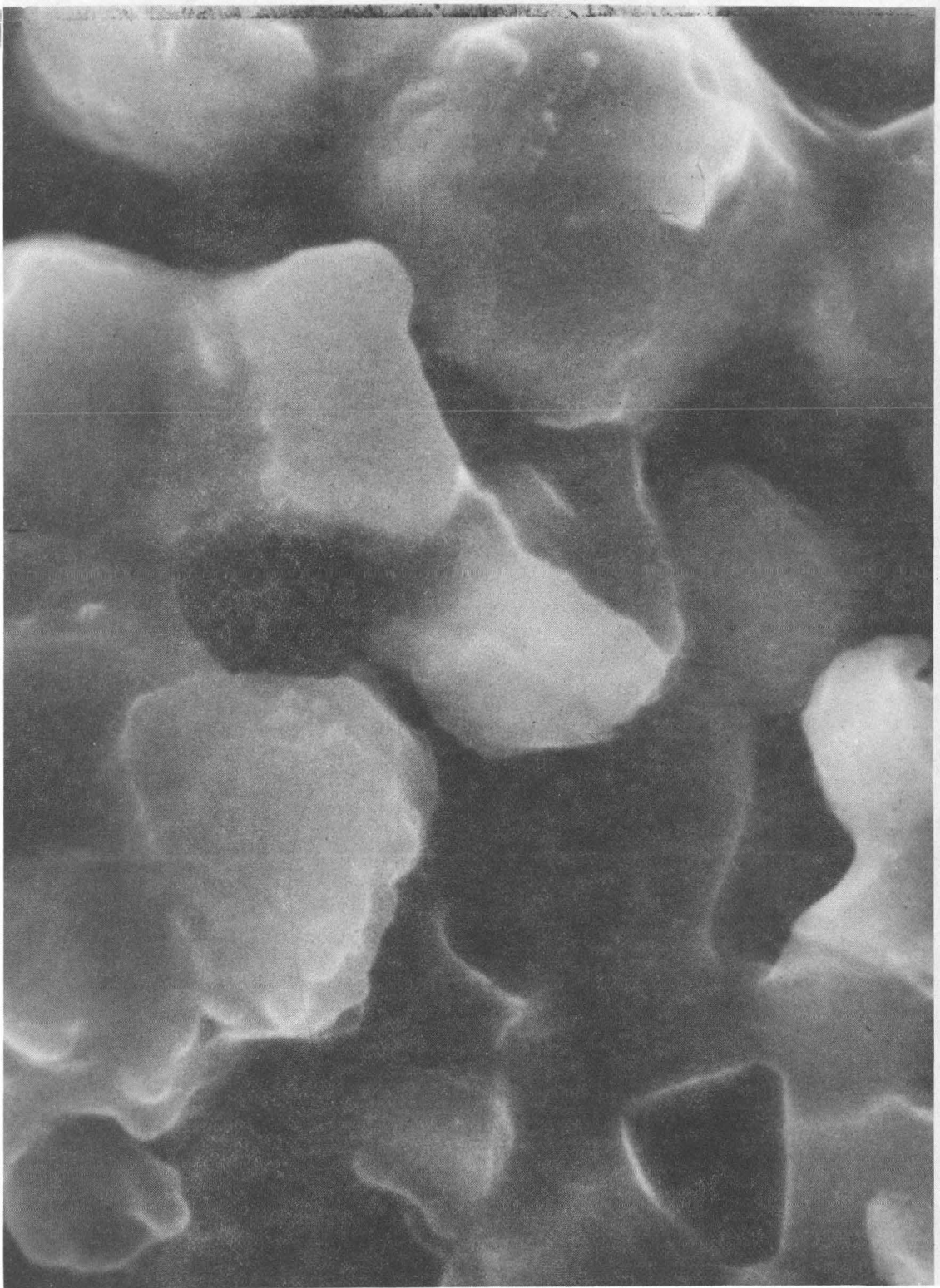
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Fig. 1



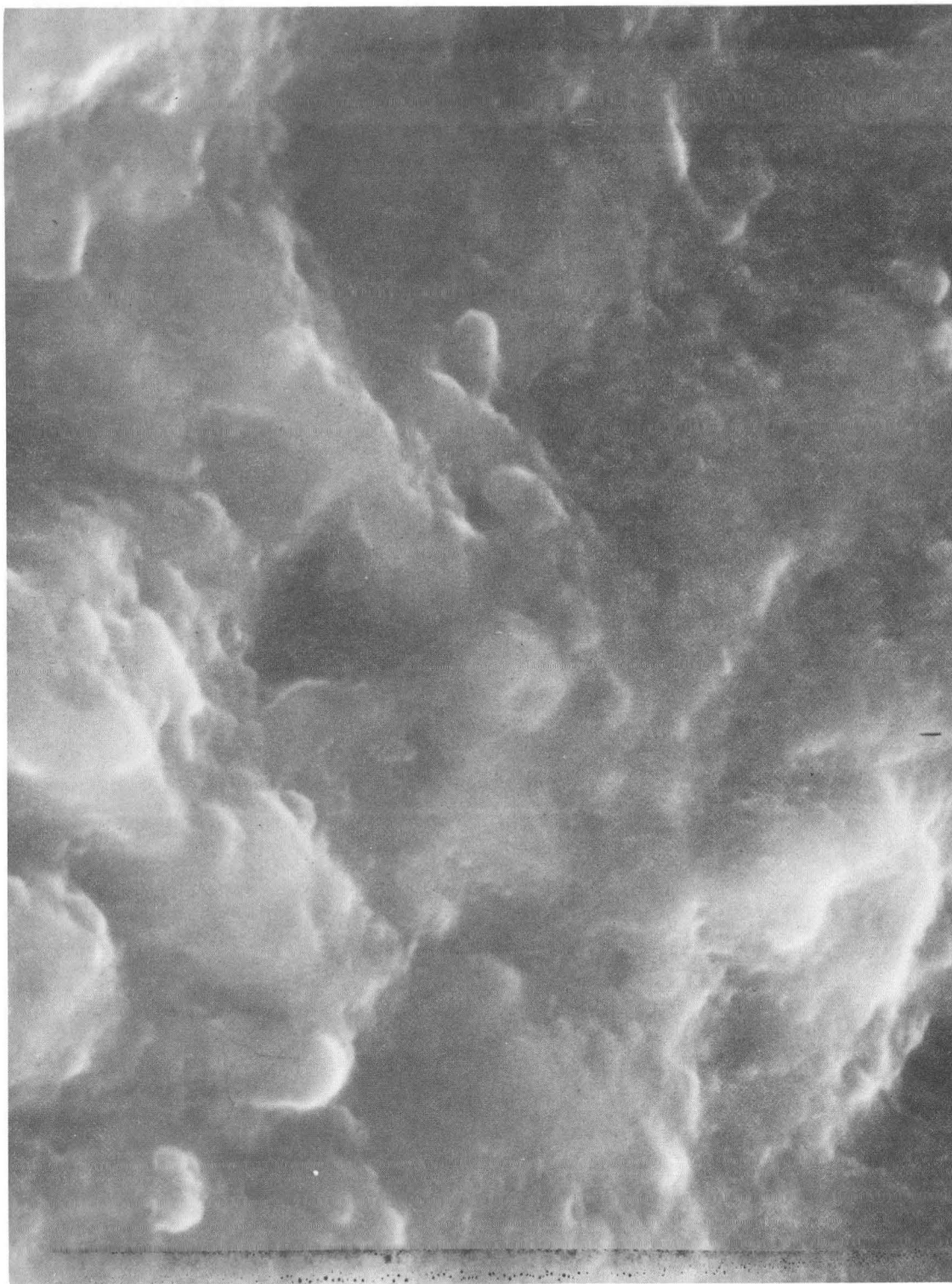
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Fig. 2



XBB 770-12357

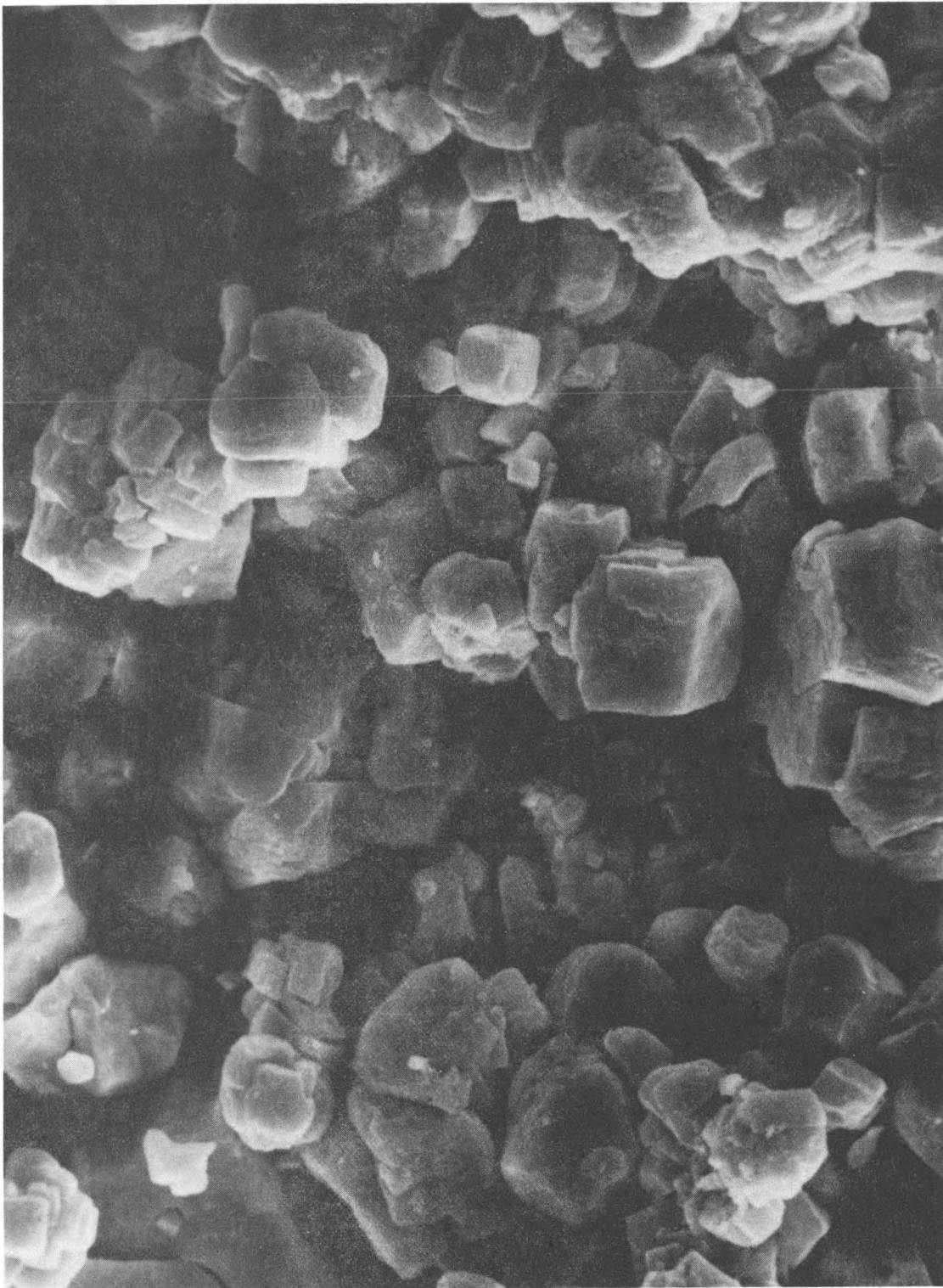
Fig. 3



4 μm

XBB 770-12353

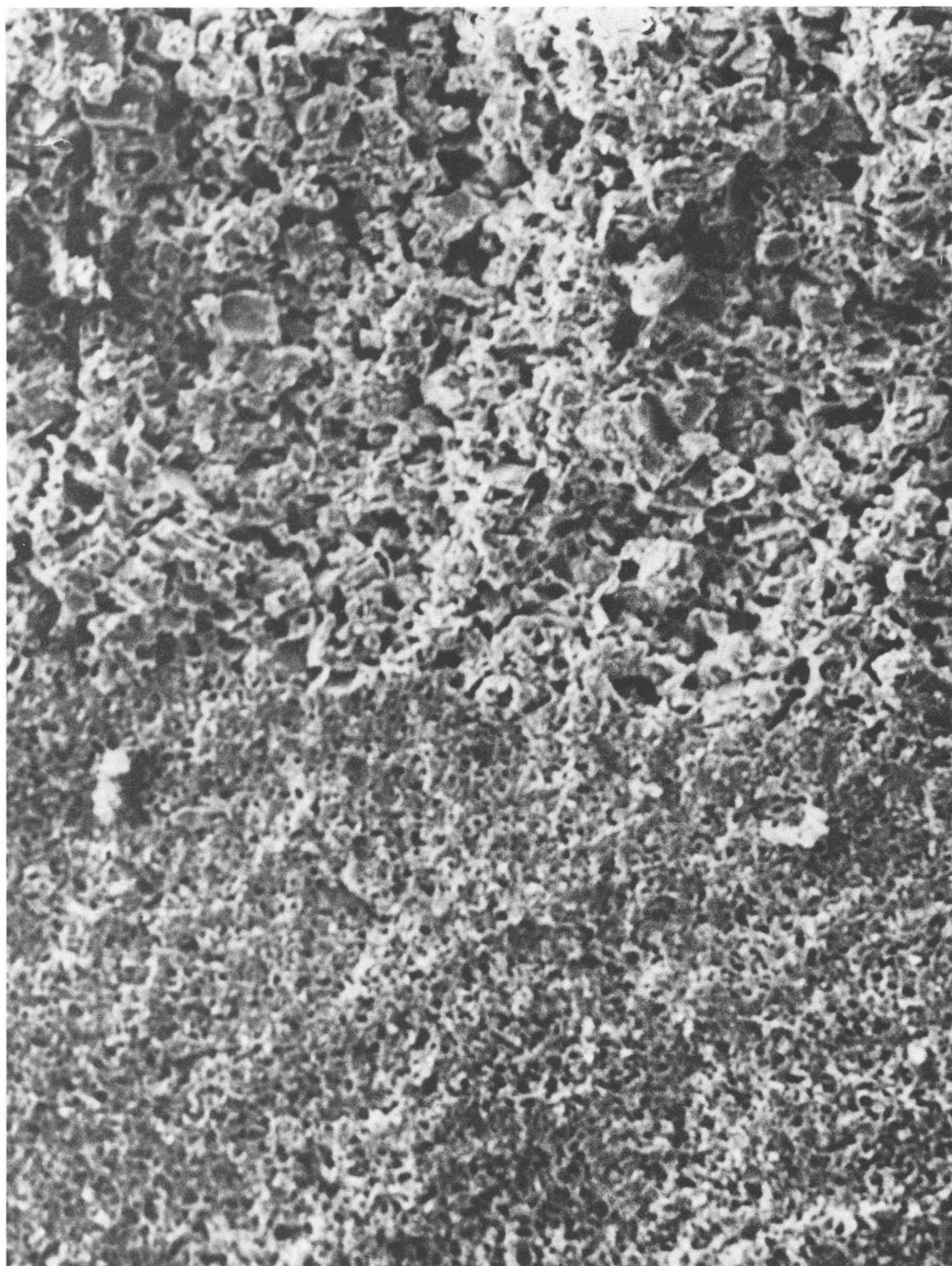
Fig. 4



6 μm

XBB 781-317

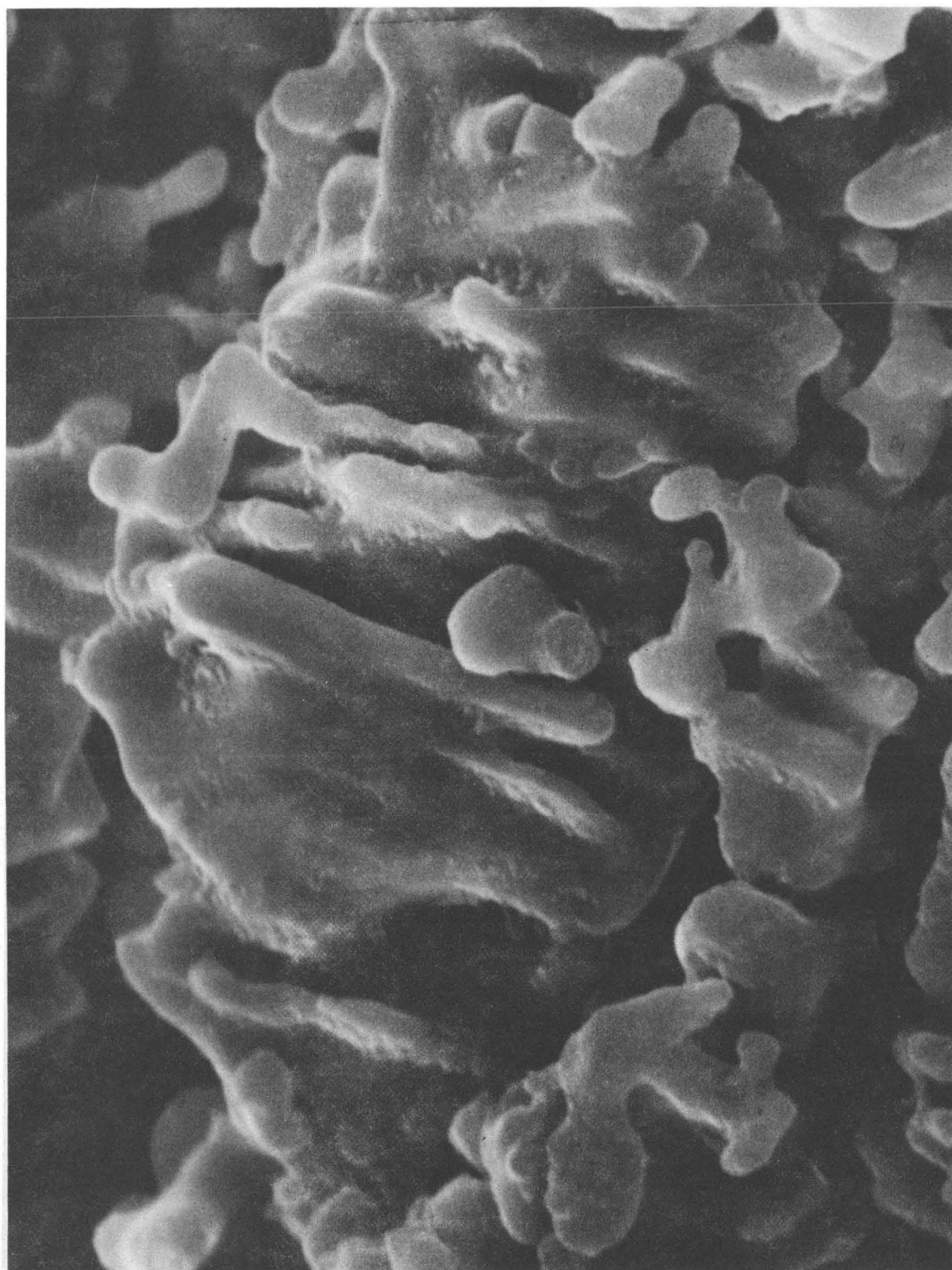
Fig. 5



XBB 784-4856

10 μ m

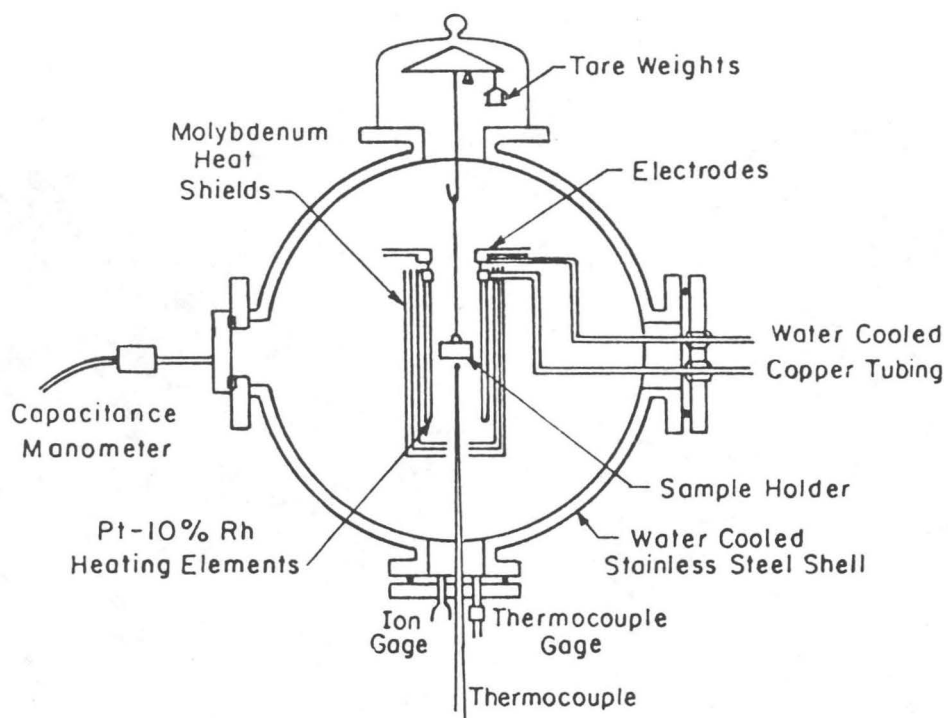
Fig. 6



3 μm

XBB 803-2533

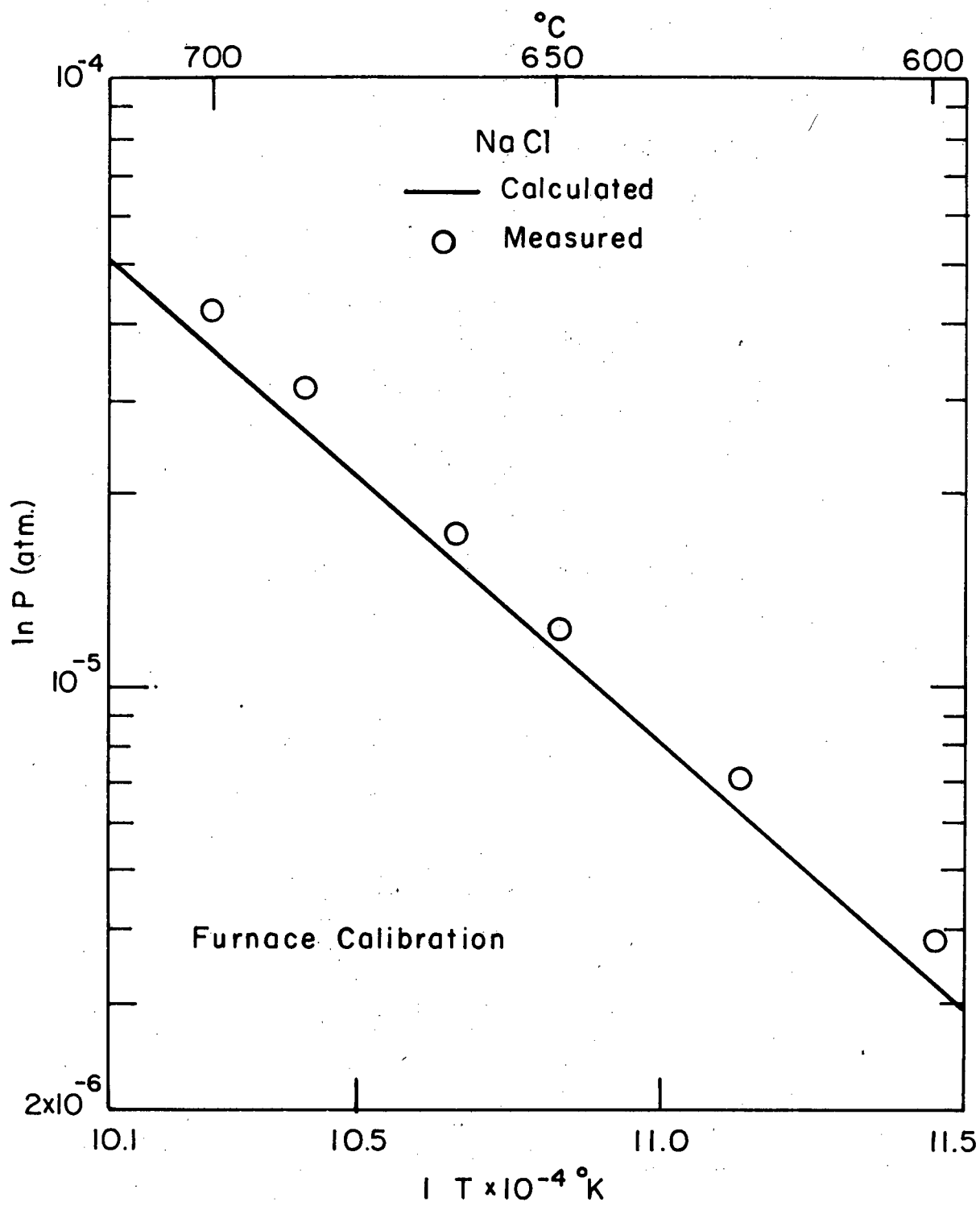
Fig. 7



XBL 784-4857

Experimental apparatus for decomposing CaCO_3

Fig. 8



XBL 80I-4511

Fig. 9

Baker Calcium Carbonate, Low in Alkalies

Cl	0.001 percent
F	0.001
So ₄	0.005
Ba	0.002
Heavy metals	0.0005
Fe	<0.0005
Mg	<0.01
K	0.008
Na	0.007
Sr	0.01

Mallinckrodt Lithium Chloride

Ca	0.01 percent
ClO ₃	0.001
Heavy metals	0.002
Fe	0.001
No ₃	0.001
K	0.01
Na	0.20
So ₄	0.01

Fig. 10

Calcite (CaCO_3) JCPDS* Number 5-0586

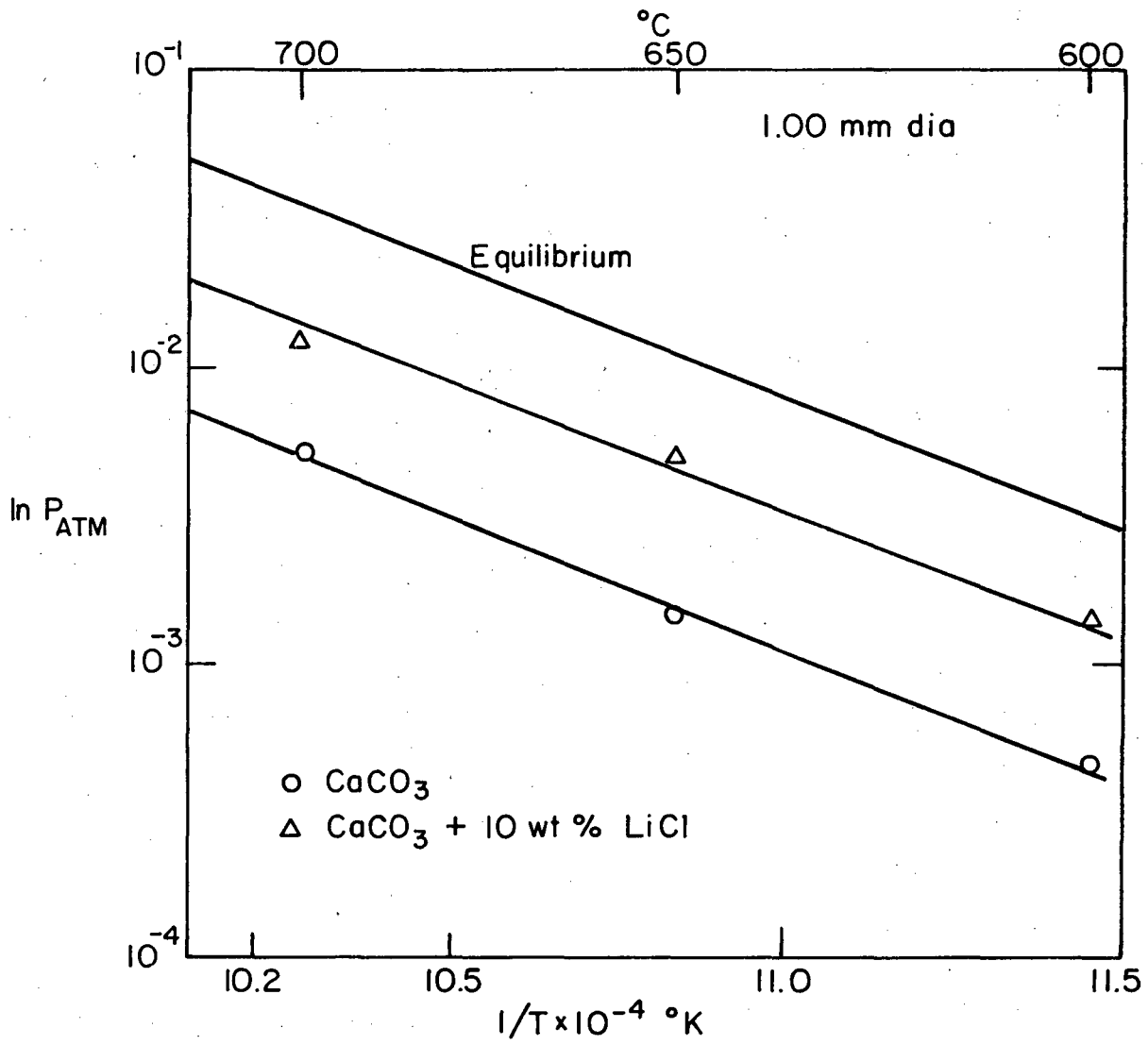
d	I/I ₁	2 θ
3.86	12	23.0
3.035	100	29.4
2.845	3	31.4
2.495	14	36.0
2.285	18	39.4
2.095	18	43.2
1.927	5	47.1
1.913	17	47.5
1.875	17	48.5
1.626	4	56.5
1.694	8	57.4

Calcium Oxide (CaO) JCPDS* Number 4-0777

d	I/I ₁	2 θ
2.778	34	32.2
2.405	100	37.4
1.701	45	53.9
1.451	10	64.1
1.390	5	67.3
1.203	4	79.6
1.1036	4	88.5
1.0755	9	91.5

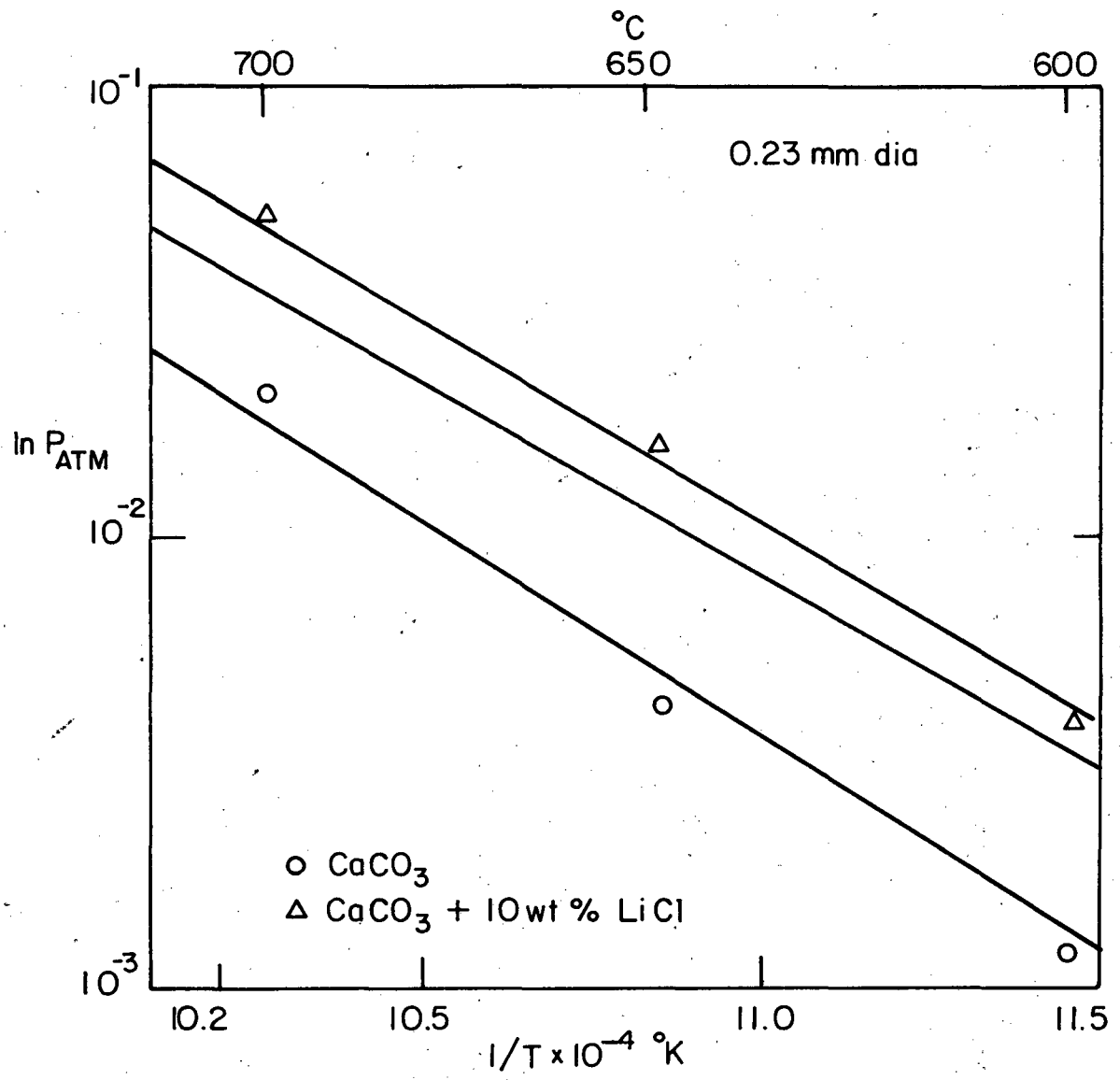
*Joint Committee on Powder Diffraction Standards

Fig. 11



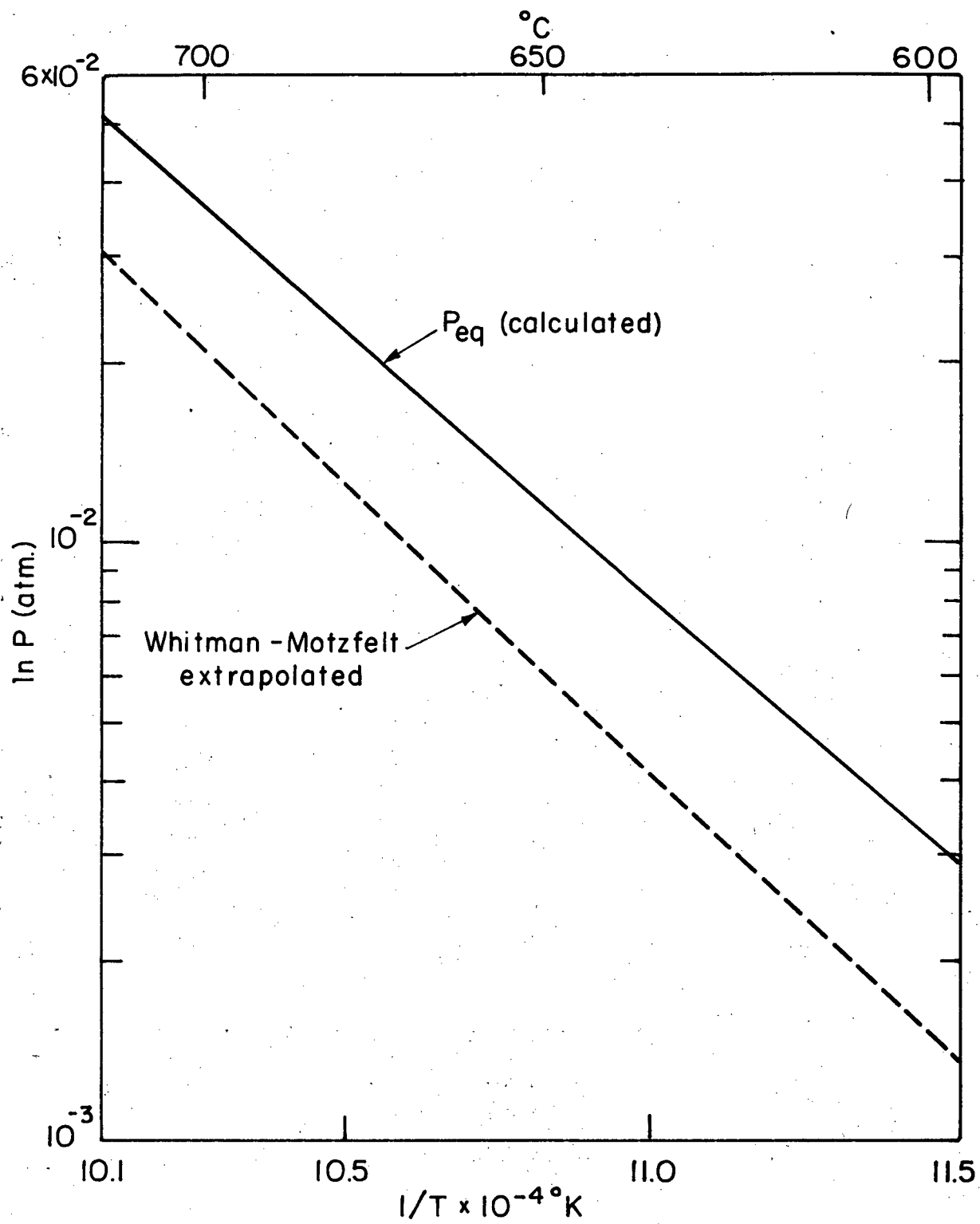
XBL799-7139

Fig. 12



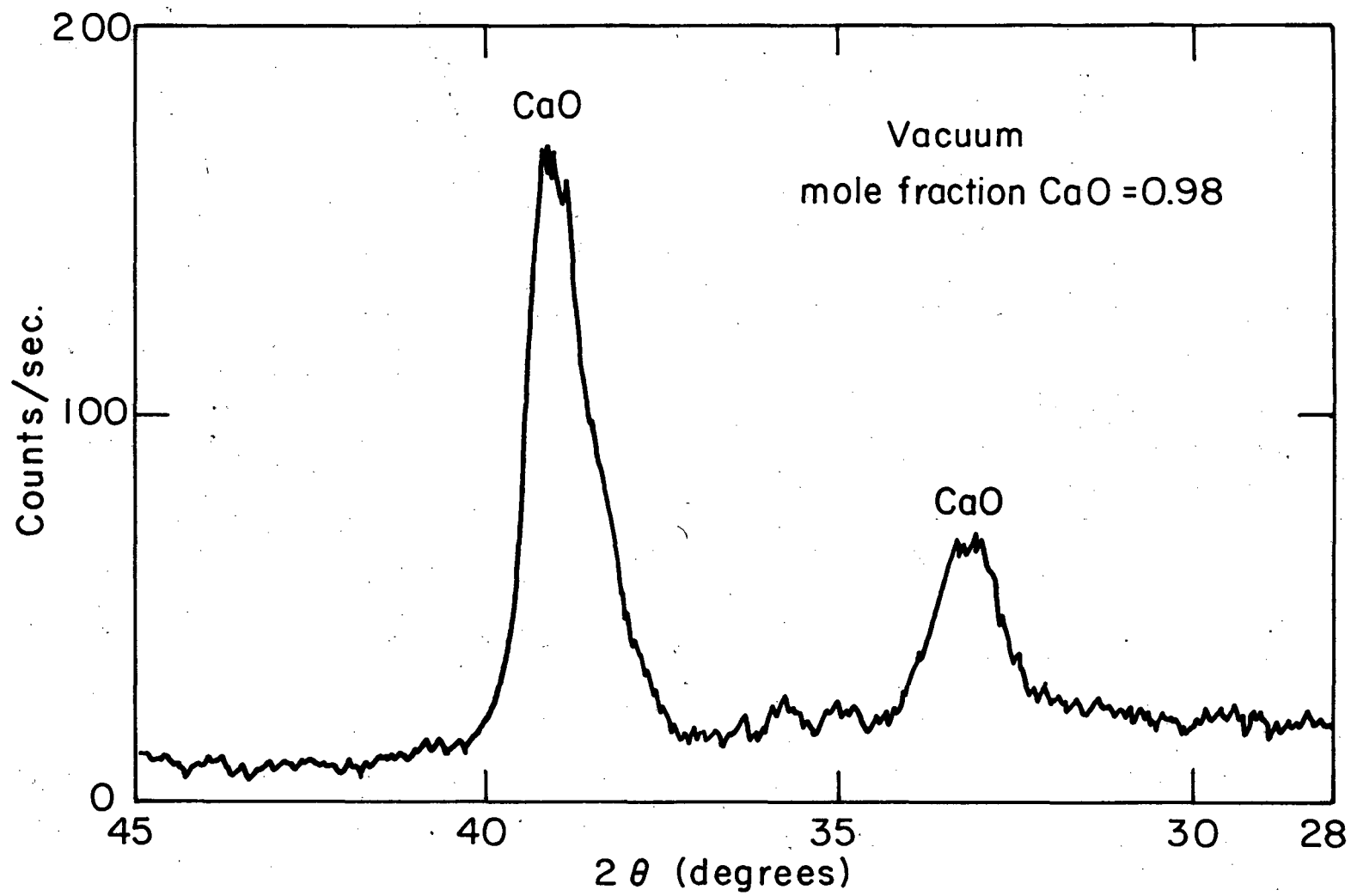
XBL 799-7141

Fig. 13



XBL 80I-4508

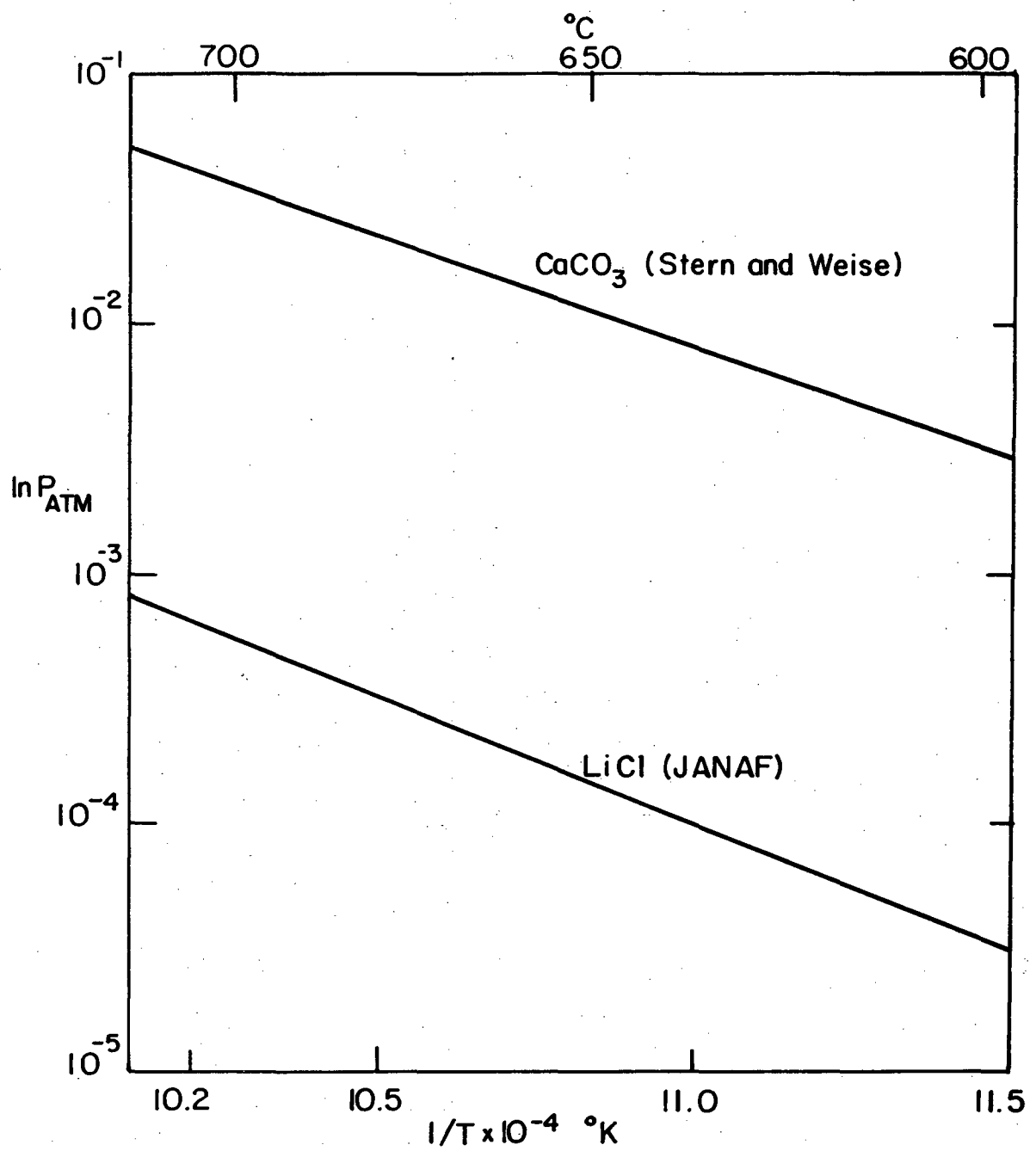
Fig. 14



51

XBL784-4842

Fig. 15



XBL 799-7140

Fig. 16

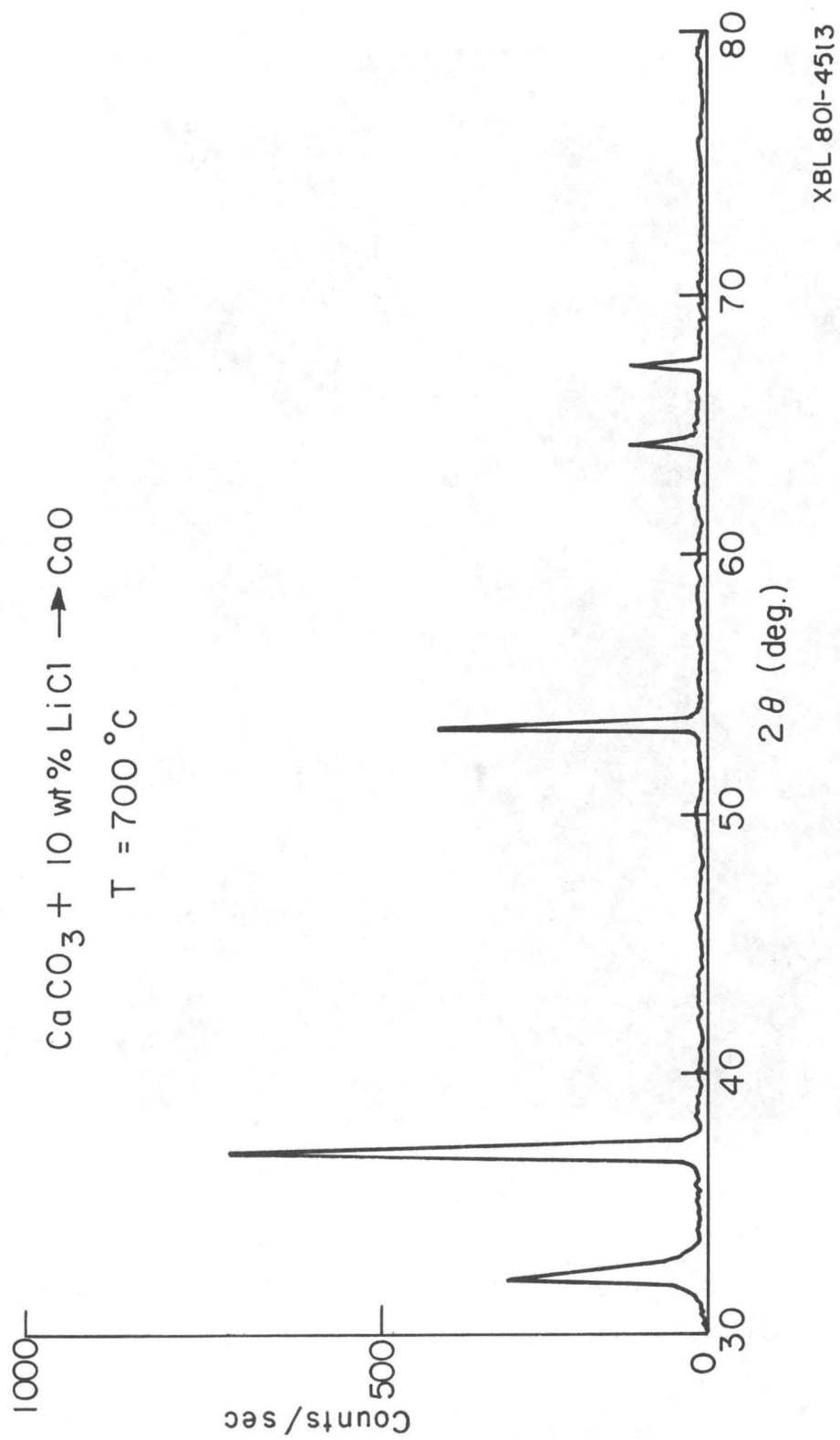
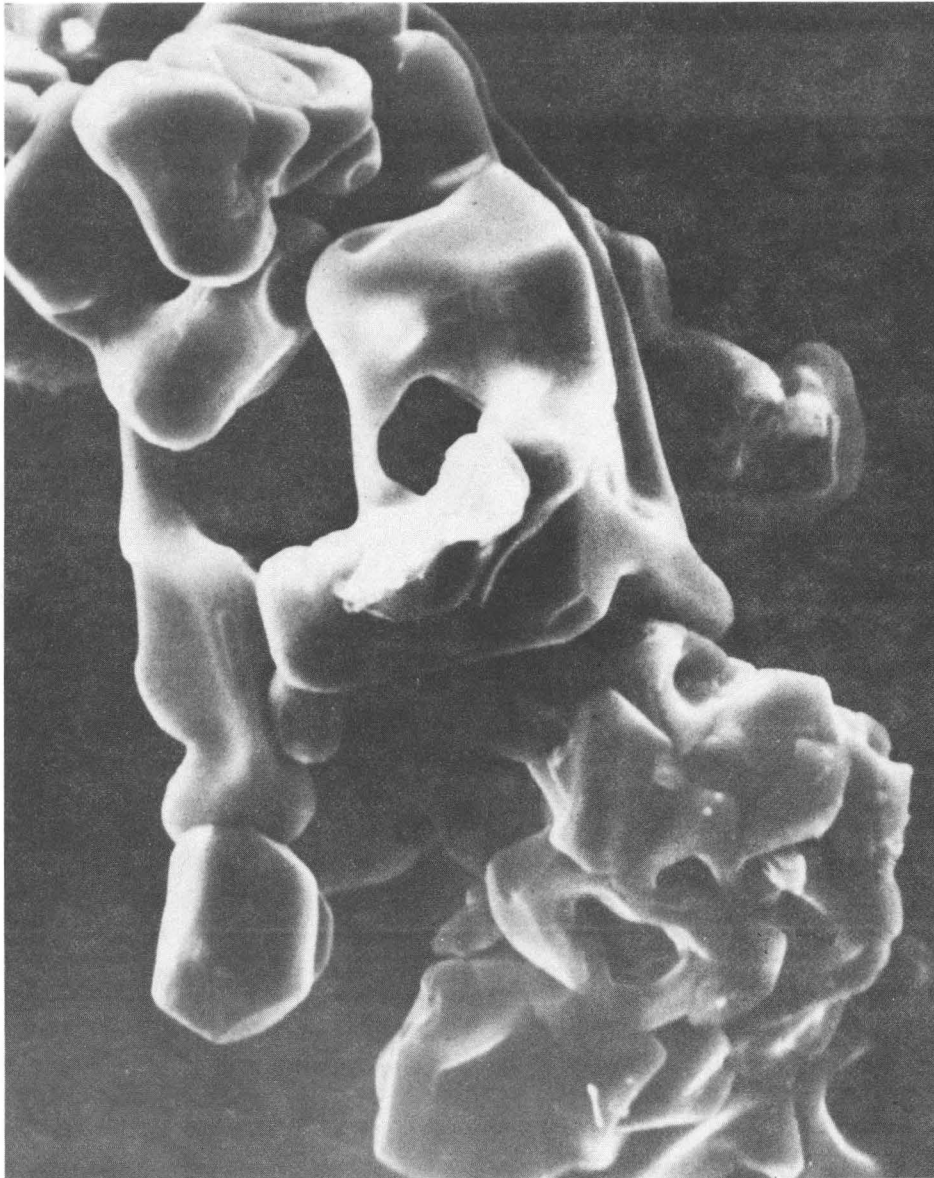


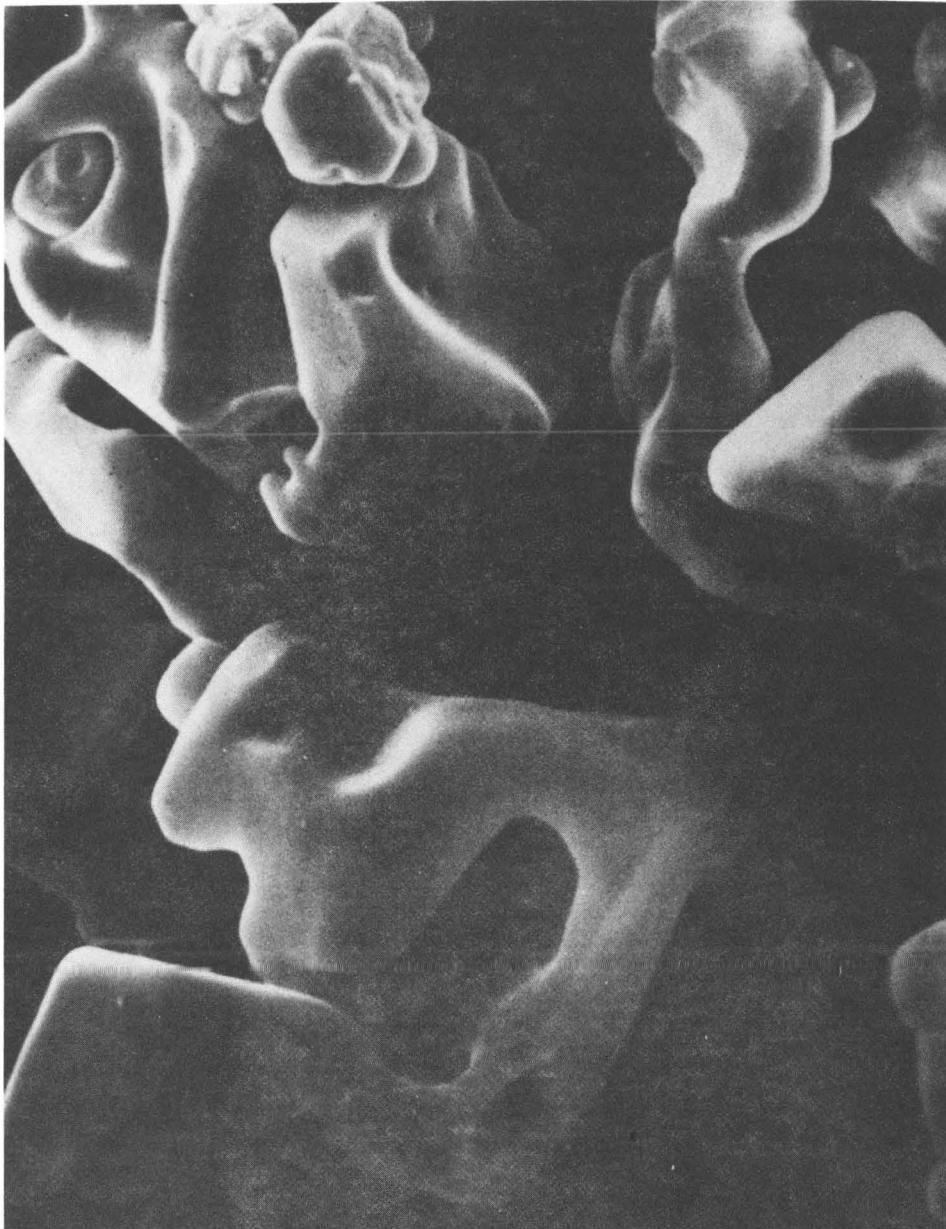
Fig. 17



5 μm

XBB 790-12872

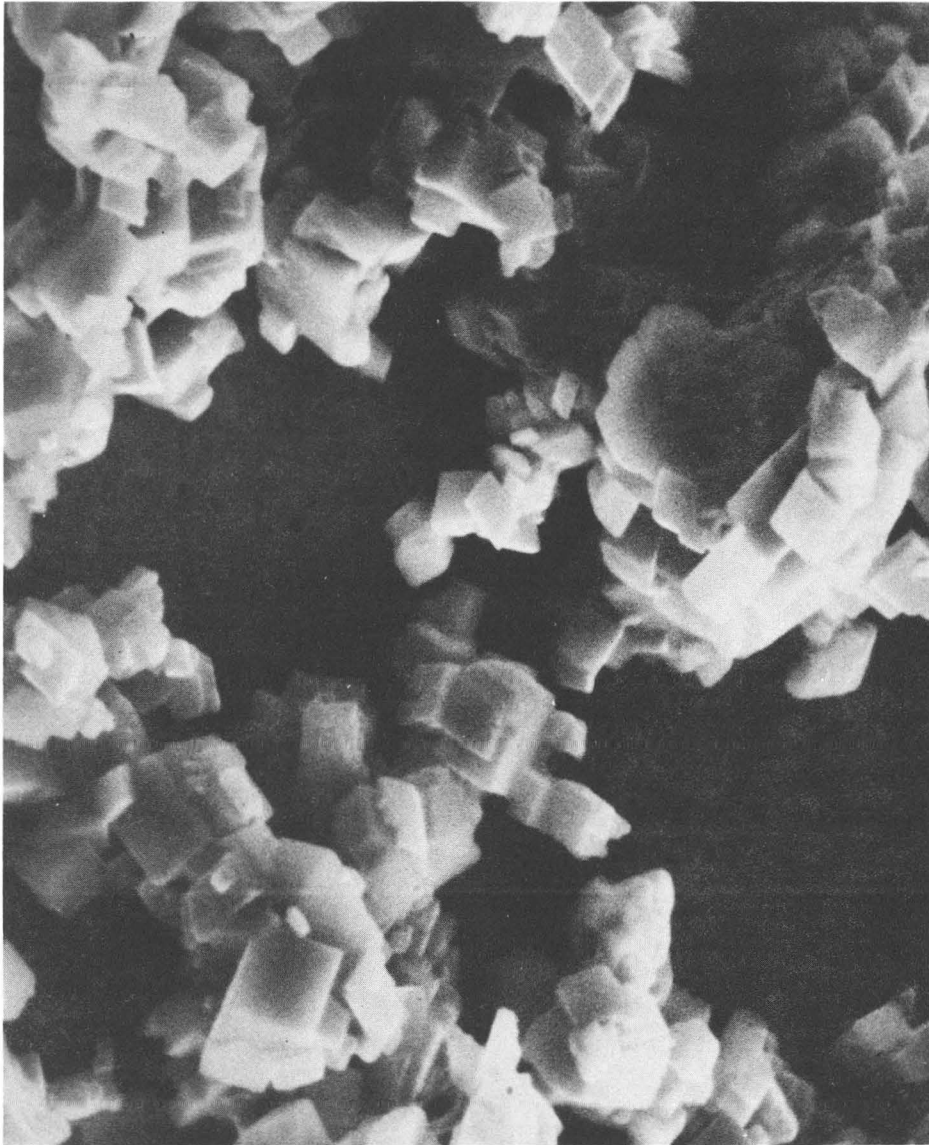
Fig. 18



5 μm

XBB 790-12874

Fig. 19



—
5 μ m

XBB 784-4505

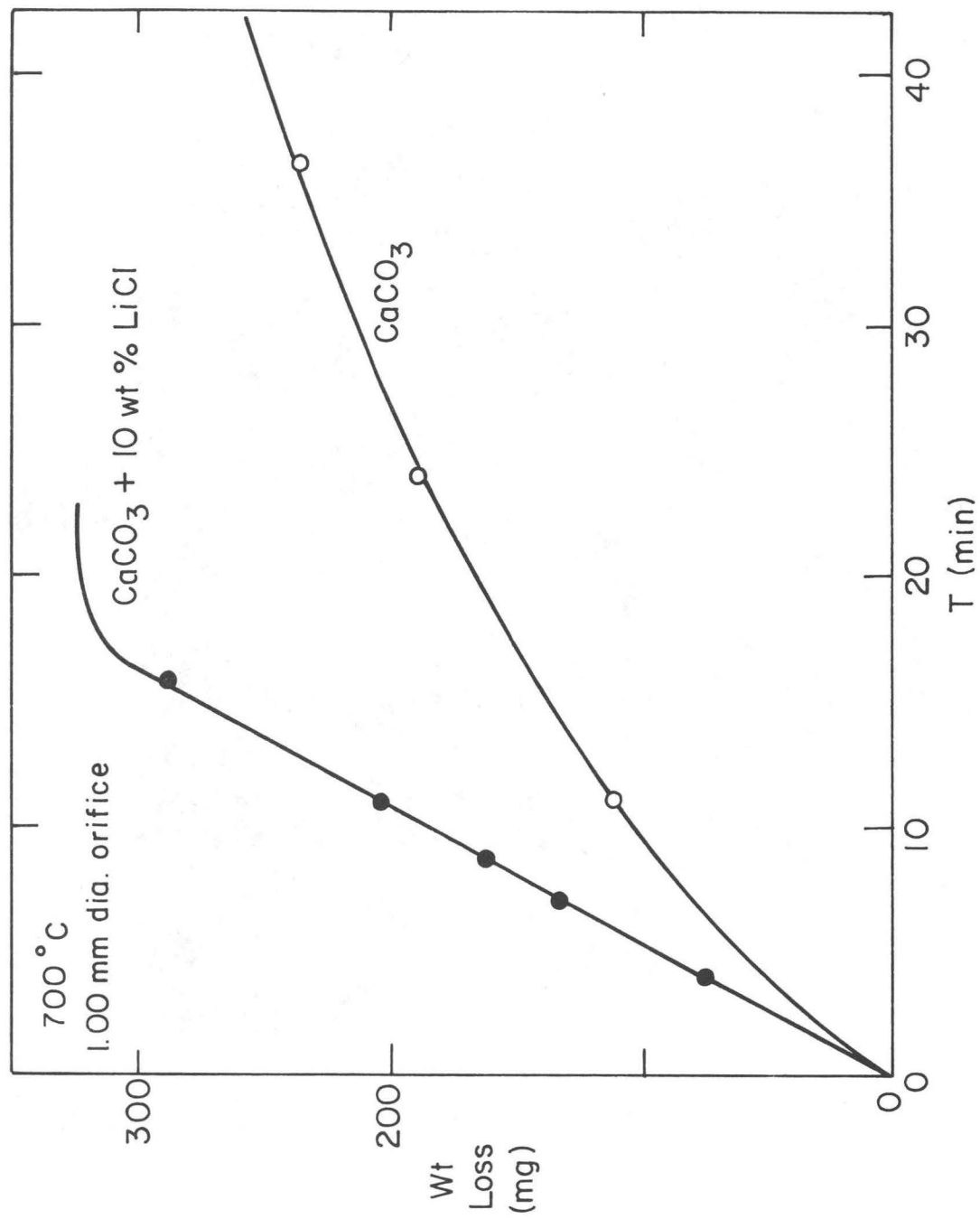
Fig. 20



2 μm

XBB 790-15763

Fig. 21



XBL 804 - 4998

Fig. 22

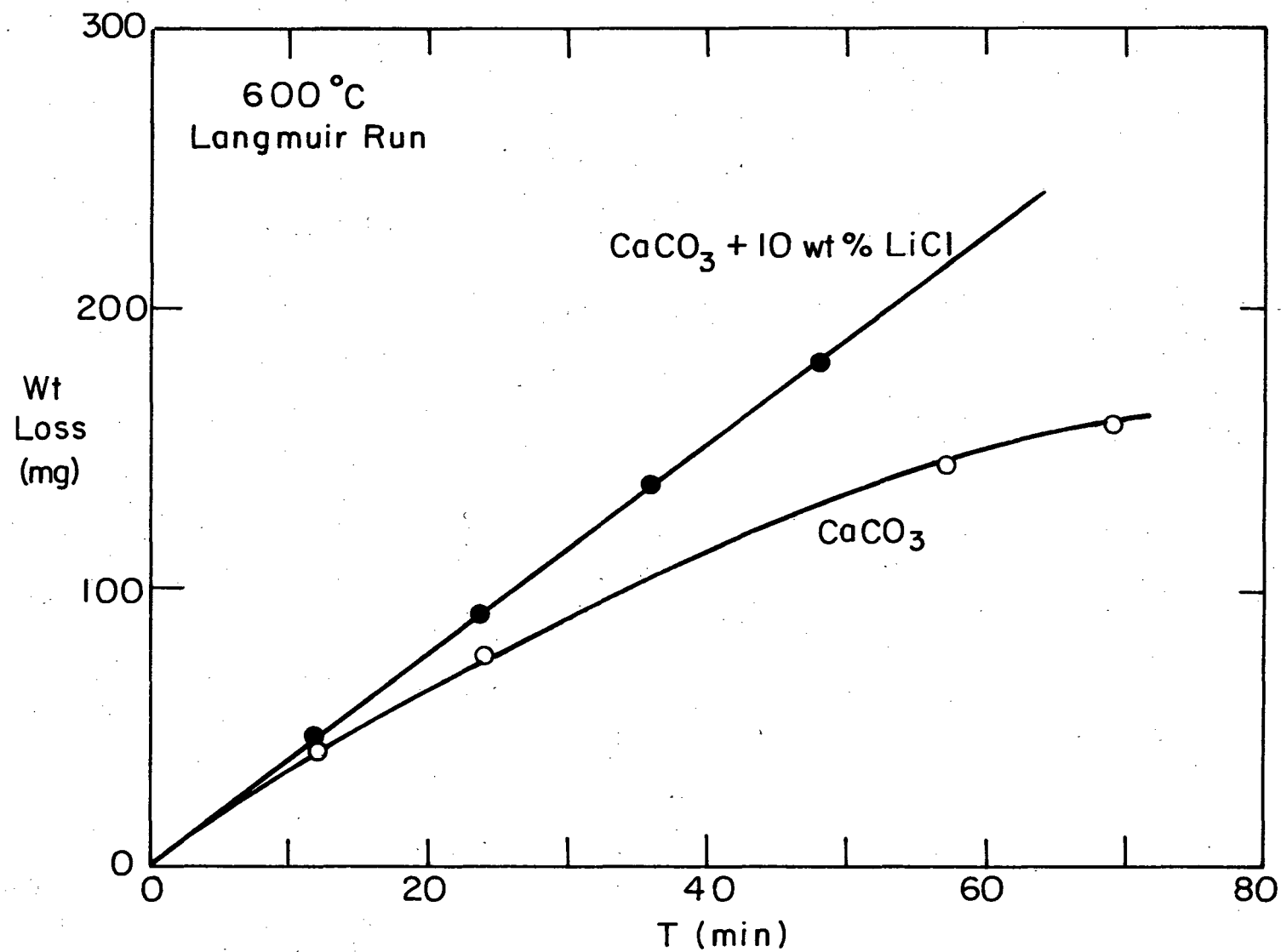
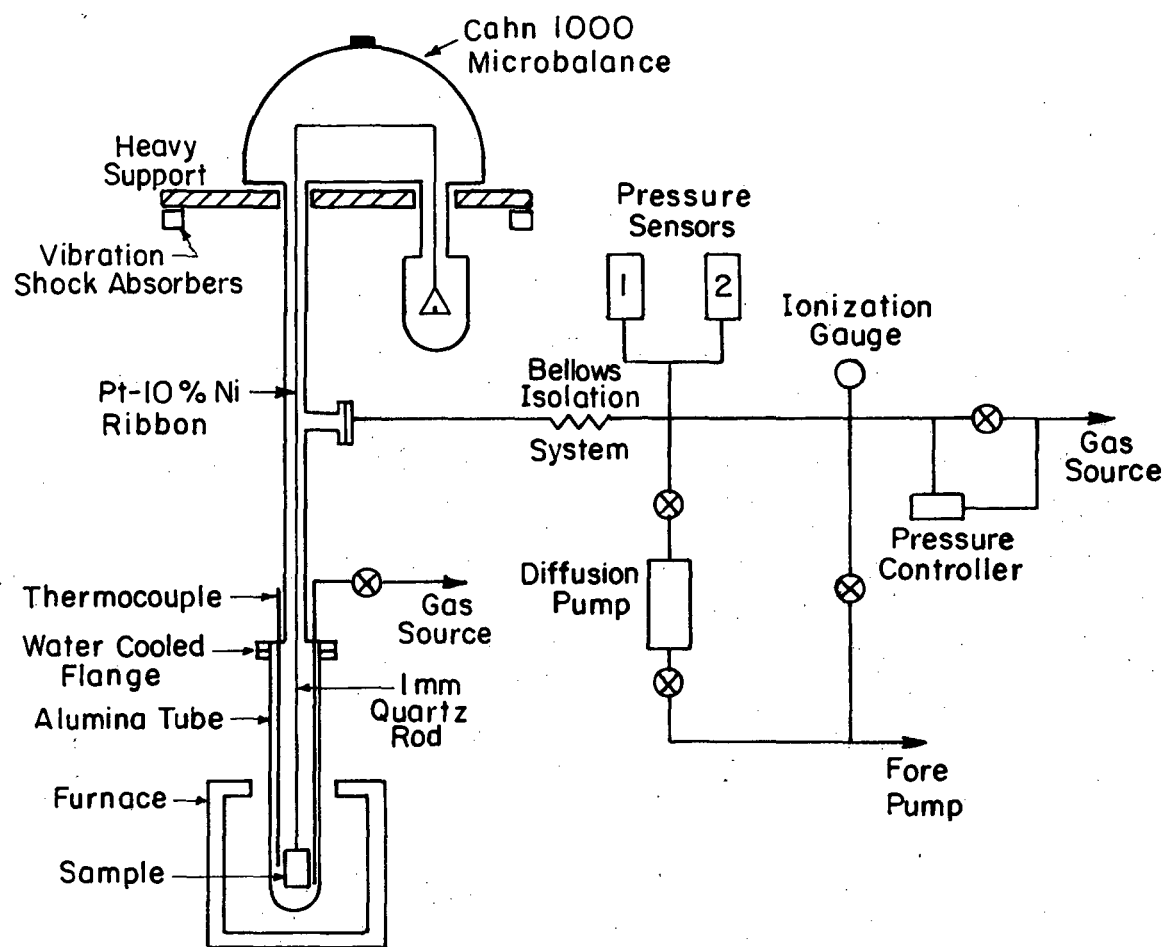


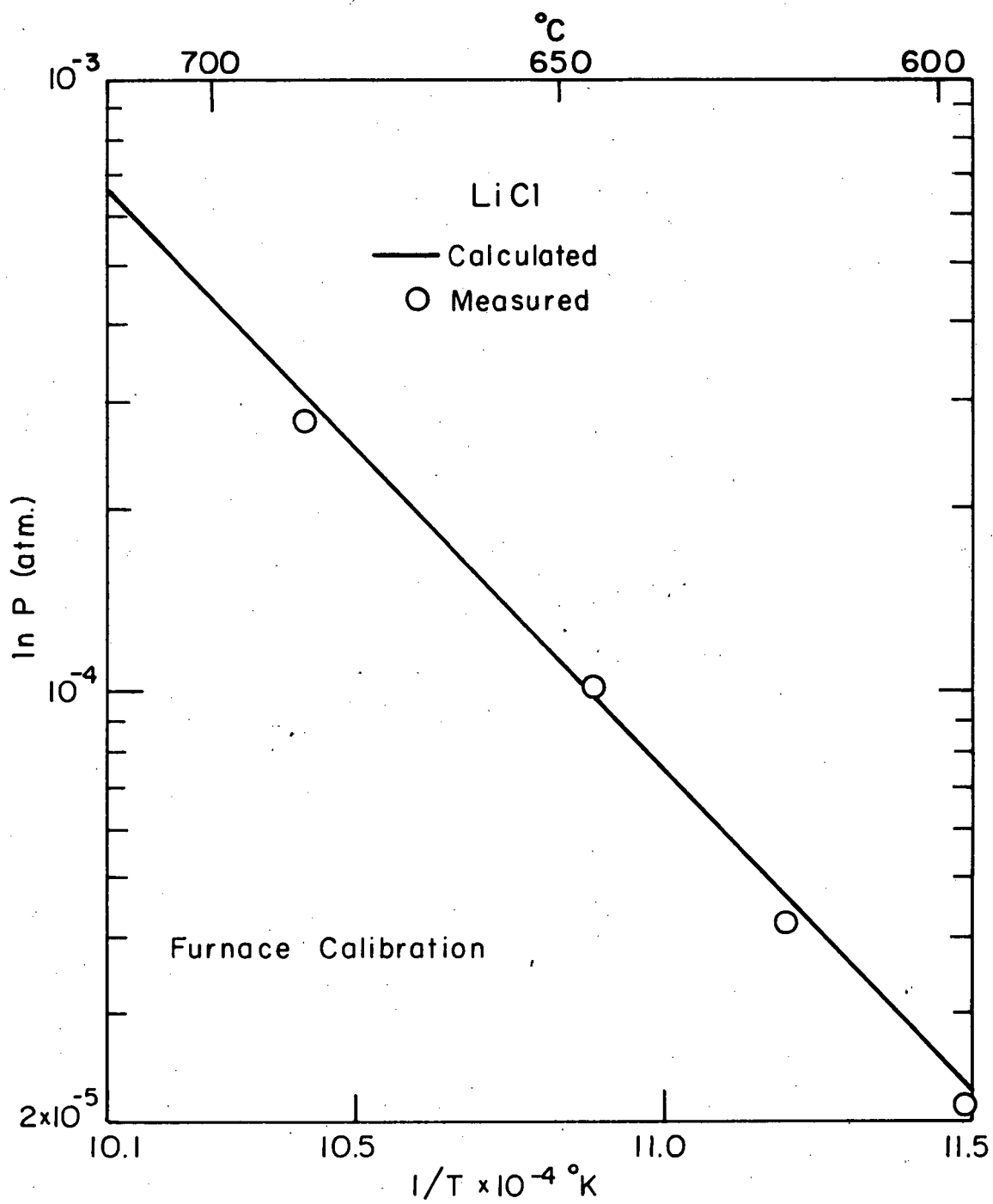
Fig. 23

XBL804-4996



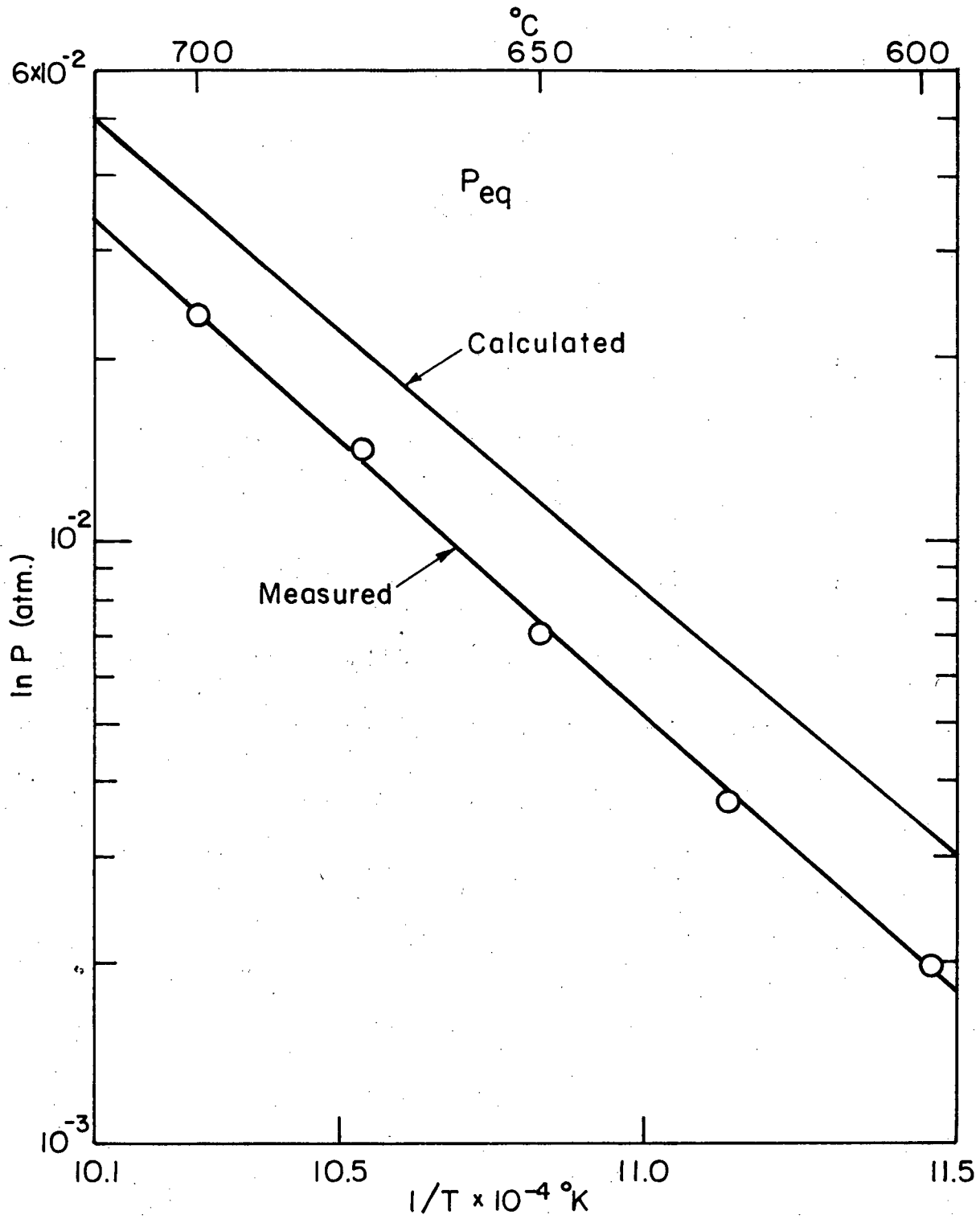
XBL 801-4515

Fig. 24



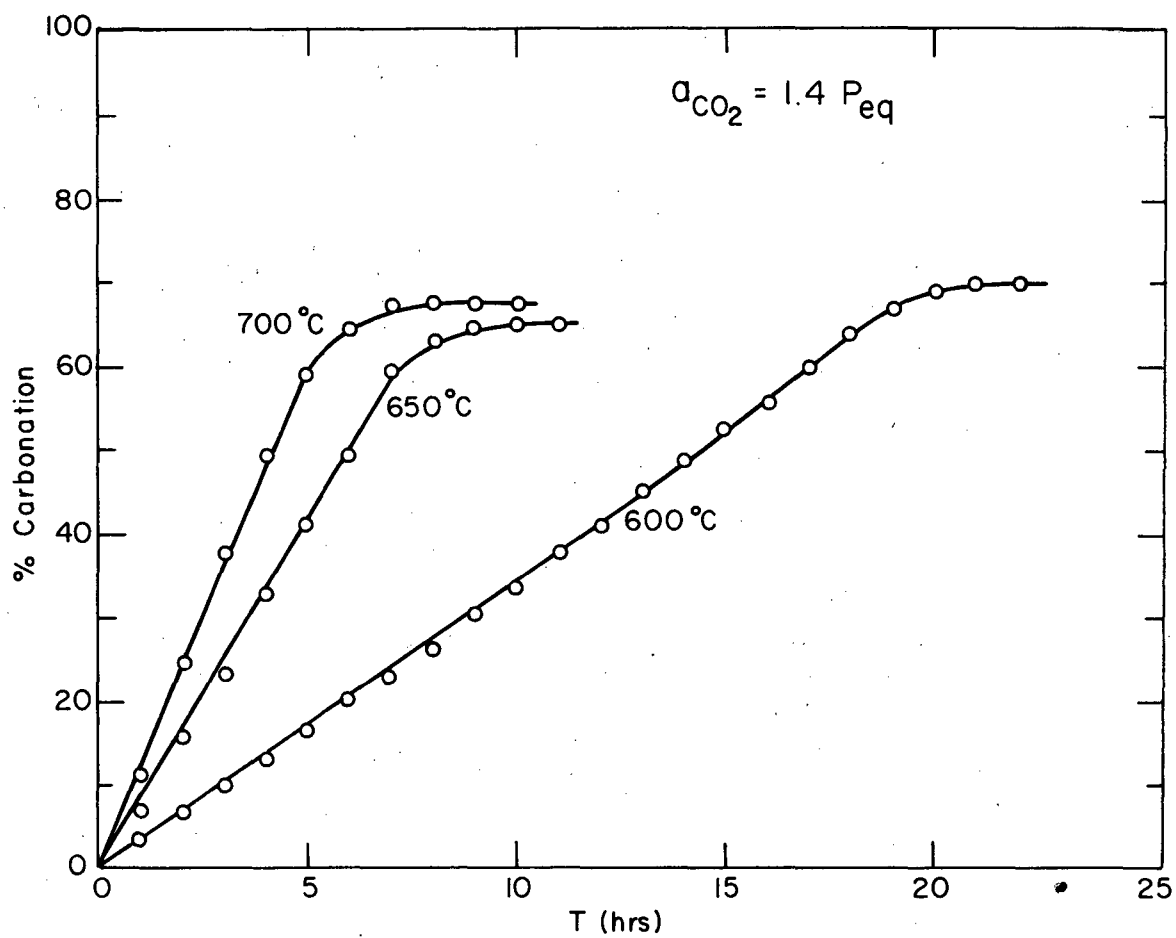
XBL 80I-4510

Fig. 25



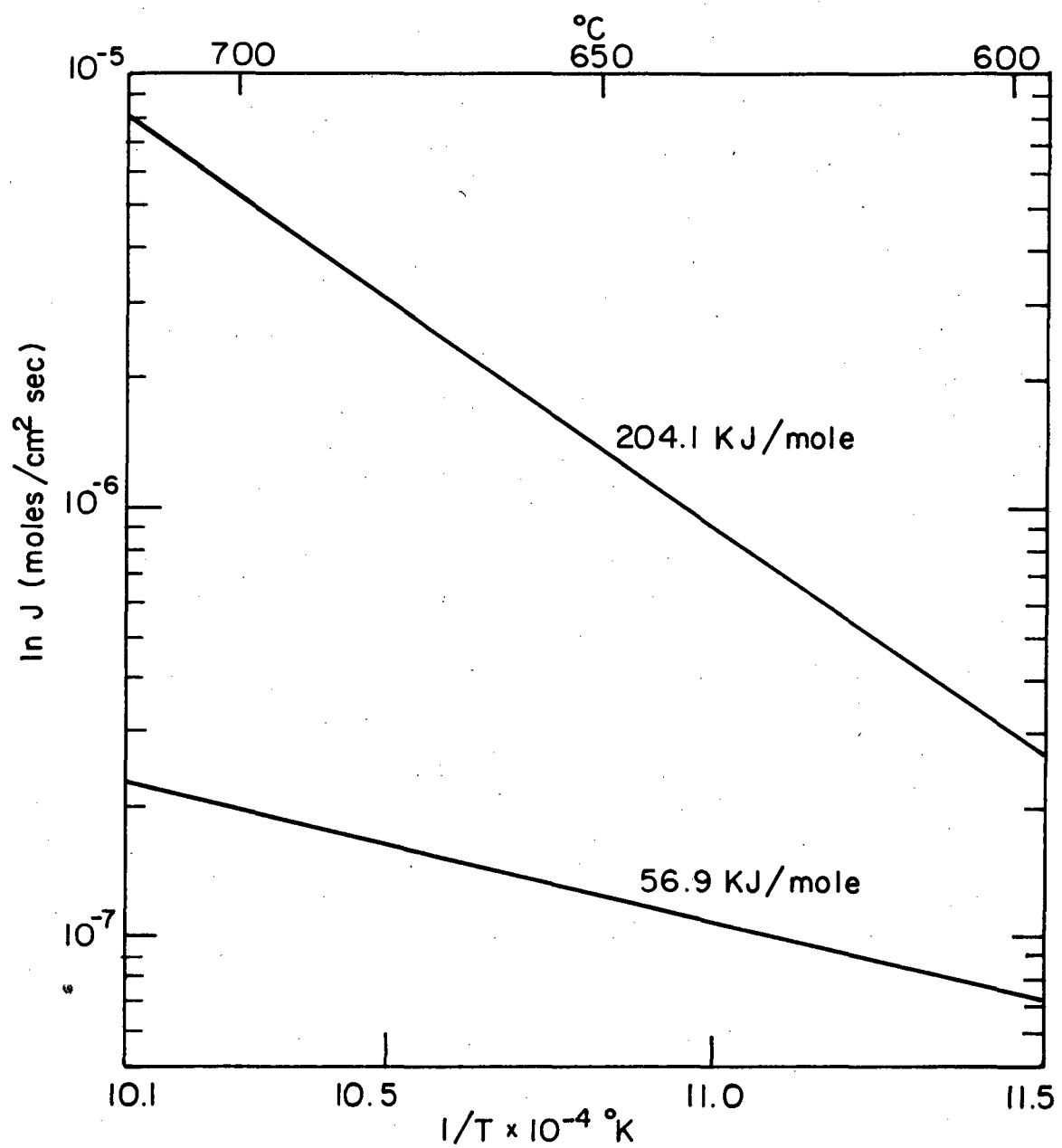
XBL 801-4507

Fig. 26



XBL79II-14560

Fig. 27



XBL 80I-4509

Fig. 28

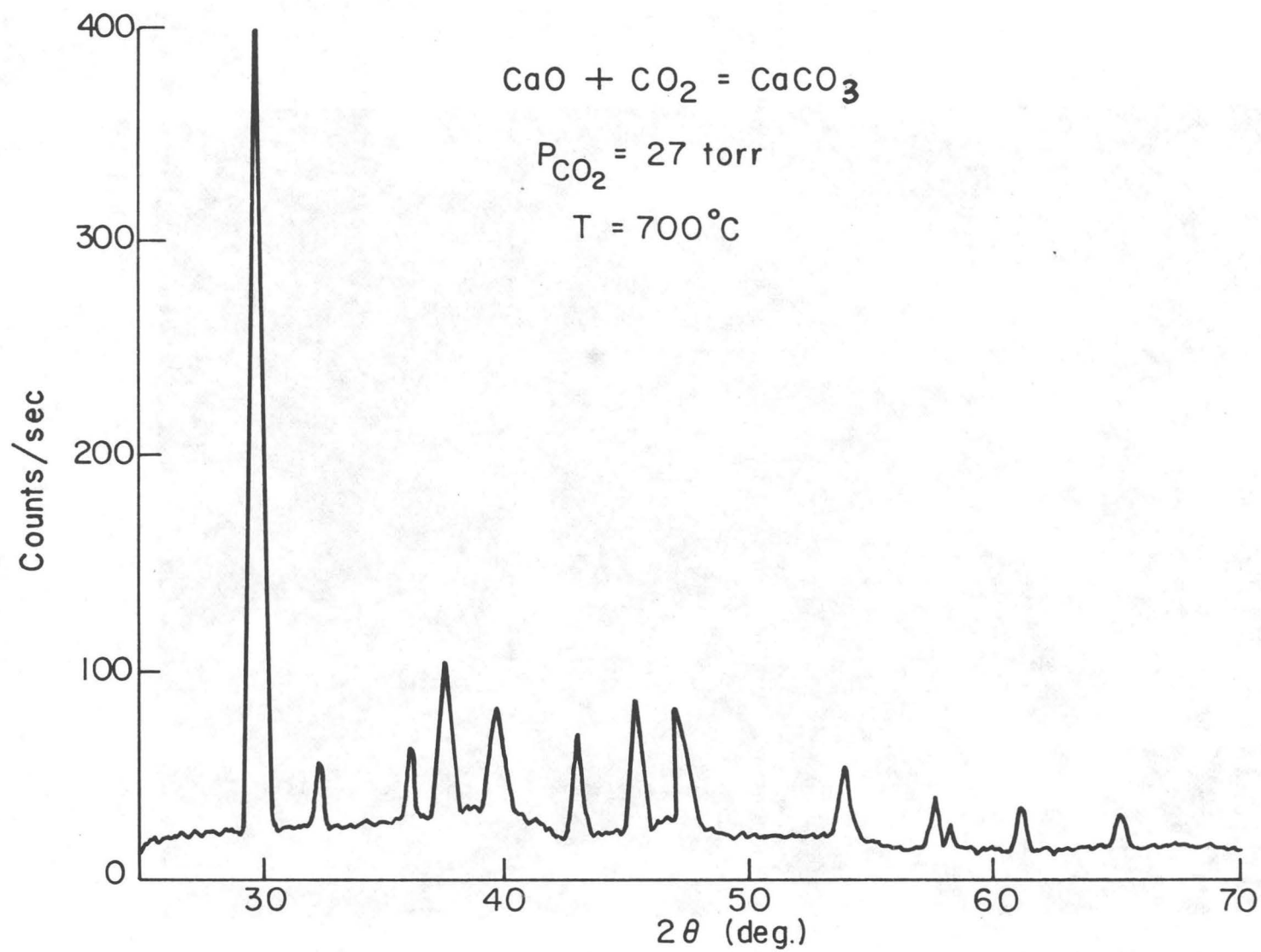
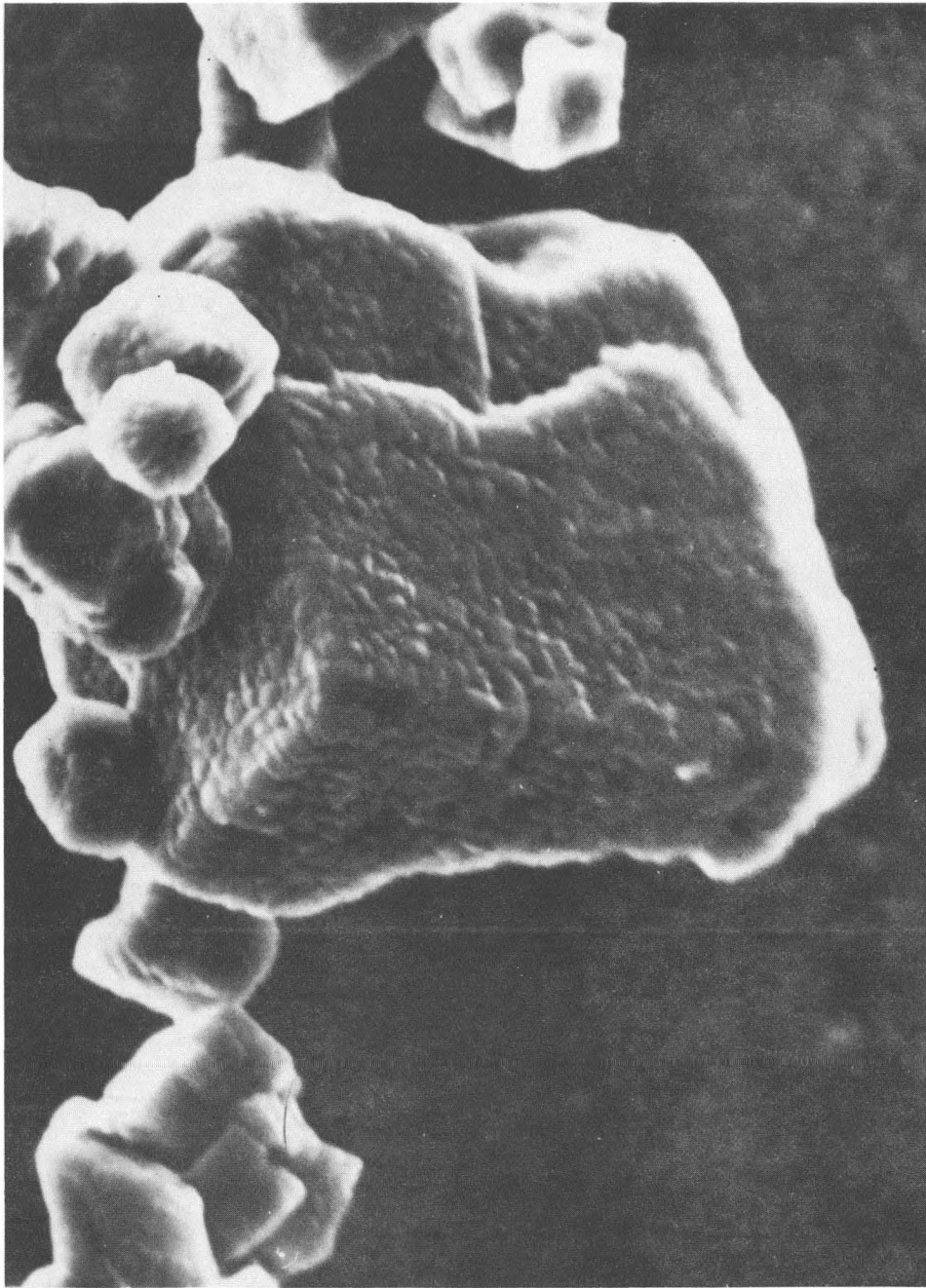


Fig. 29

XBL 80I-4514



5 μm

XBB 790-15764

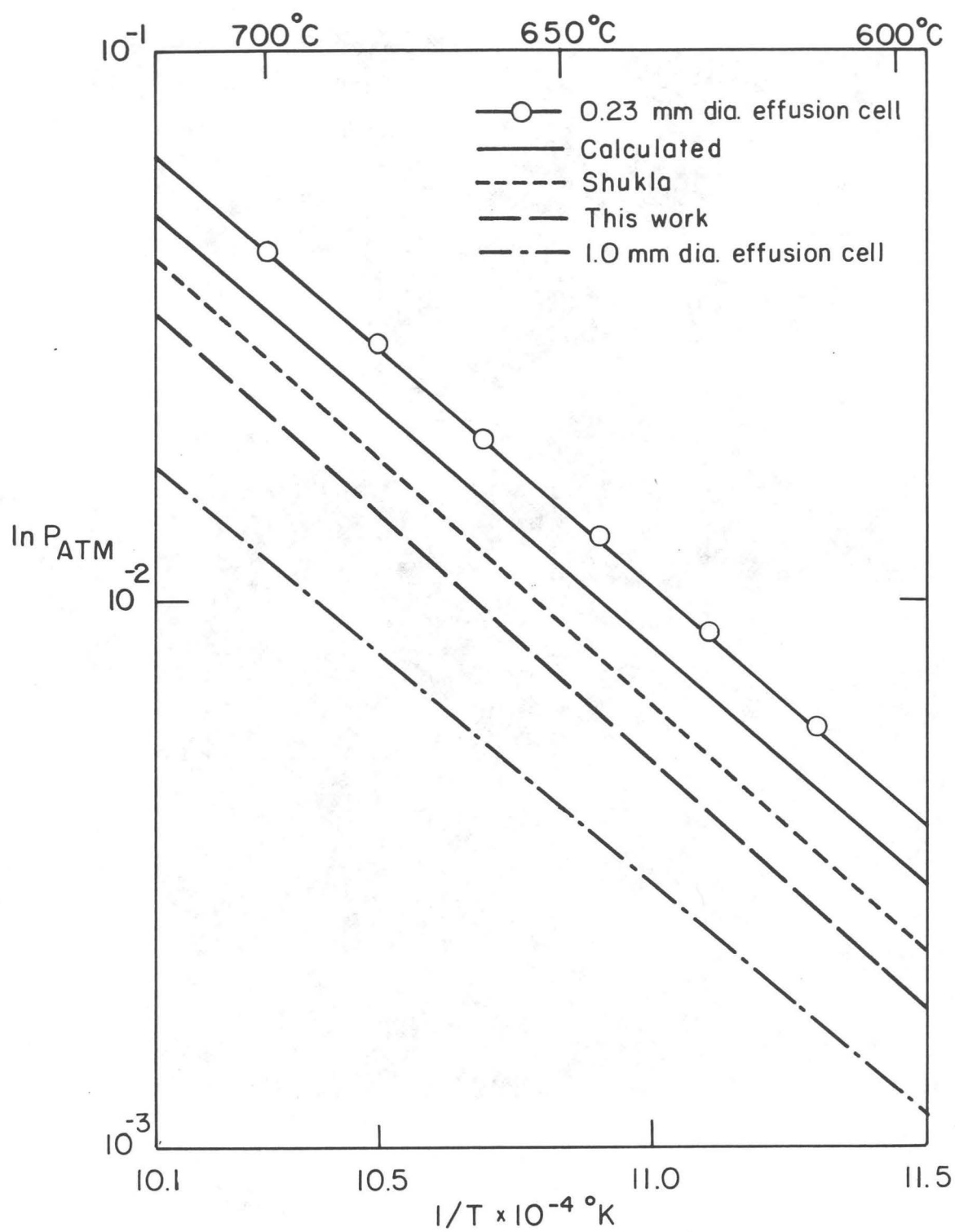
Fig. 30



2 μm

XBB 790-15765

Fig. 31



XBL 804 - 4997

Fig. 32

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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