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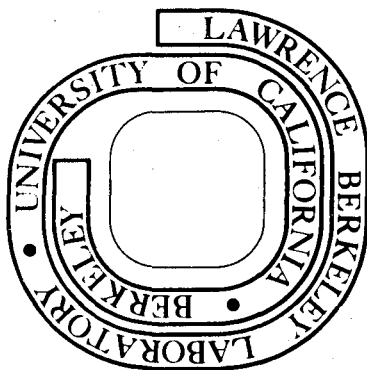
Sheldon Chil Pin Lim
(M. S. thesis)

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THE EFFECT OF A POROUS LAYER ON THE KINETICS
OF DECOMPOSITION OF CALCITE

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ABSTRACT

Weight loss and mass spectrometry measurements have been used to determine the effect of porous alumina barriers on the flux of CO_2 from calcite single crystals and powdered calcite. It is found that the porous alumina barriers reduce the CO_2 flux by less than an order of magnitude, which is in striking contrast to the reduction of a NaCl vapor flux by more than a factor of 100.

There are two possible explanations for the high flux of carbon dioxide. One possibility, that the irreversibility of the calcite decomposition is responsible for the high efficiency of transport of CO_2 through porous alumina, was eliminated by means of the calcite powder experiments which provided an equilibrium vapor source. It can then be concluded that the small effect of porous alumina on the CO_2 flux is due to rapid surface diffusion and that this is also the probable mechanism for the efficient CO_2 transport which has been measured through the CaO product layer in calcite decomposition.

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I. INTRODUCTION

Searcy and Beruto¹ have studied endothermic decomposition reactions of the type



which predict the effect of porous barriers on the gaseous product flux in vacuum when gas transport is by Knudsen flow. They argued that the reaction rate will decrease with increasing thickness of the solid reaction product layer except in the case of a highly irreversible chemical step at the reaction interface and/or in the case of highly efficient surface diffusion of B(g) through the porous product, A(s).

The rate of decomposition of calcite single crystals has been shown to be independent of the thickness of the porous calcium oxide product layer when that layer is as much as 1 mm thick.² The flux of carbon dioxide from a 10 $\bar{1}$ 1 crystal face of calcite is about 10⁻³ times the maximum possible flux, which can be calculated³ from the Hertz-Knudsen-Langmuir⁴ equation. The ratio of the diameter of the pores through the calcium oxide layer to the maximum calcium oxide layer thickness was also of the order of 10⁻³ or less. If the Searcy-Beruto equation¹ is correct, with these two quantities both of the same magnitude, a decrease in carbon dioxide flux from that observed with a negligible thickness of calcium oxide should have been observed unless surface diffusion is the principle mode of vapor transport.

The research described in this thesis was undertaken to obtain experimental evidence of whether or not surface diffusion is a more important mode of transport than Knudsen flow through the oxide pores during calcite decomposition.

Mohazzabi⁵ has observed that under conditions for Knudsen flow, porous alumina layers from 0.3 to 0.8 mm thick with pores about 10 microns diameter reduce the total flux of sodium chloride vapor from one to two orders of magnitude. The measured decreases in sodium chloride flux with increased thicknesses of the porous alumina layers are consistent with the interpretation that the sodium chloride passes through the alumina primarily by vapor phase transport. The sodium chloride vapor source has a negligible activation free energy barrier to vaporization or condensation of the sodium chloride vapor.^{3,6} If the flux of carbon dioxide generated by decomposition of calcite were to show a similar reduction when passed through a porous alumina barrier, it could be concluded that the decomposition of calcium carbonate to carbon dioxide and a metastable form of calcium oxide observed by Beruto and Searcy² is also reversible, not only with respect to the chemical steps, but also with respect to surface diffusion of carbon dioxide through the calcium oxide layer. Reasons for believing that this interpretation may be correct are presented in a recent paper.⁷

From the kinetic theory of gases⁸ the flux of gas flowing through a cylindrical tube is given by

$$J = \frac{2\pi r^3 (P_o - P_l)}{M \bar{u} l}$$

where J is the number of moles of gas flowing through per unit time, r is the radius of the tube, P_o and P_l are the pressures at the ends, M the molecular weight, l the length of the tube, and $\bar{u}$ is the mean velocity

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of the gas molecules, equal to

$$\left(\frac{8RT}{\pi M}\right)^{1/2}$$

For a gas flowing through a tube into vacuum, the flux equation becomes

$$J = \frac{2\pi r^3 P_o}{M \bar{u}} \quad (1)$$

Adzumi⁹ in his treatment of effusion through a porous solid, considered that the pores, each of which may vary in diameter along its length, are in parallel with one another. Also, a pore of varying diameter may be considered as several pores in series so that the r^3/ℓ factor in Eq. (1) is replaced by $\Sigma r^3/\ell$. Then, to sum over the pores in parallel, the expression

$$\Sigma \left(\frac{1}{\Sigma \ell / r^3} \right)$$

should be used. If one assumes that there are n pores of average radius $\bar{r}$, the summation becomes $n\bar{r}^3/\ell$ where ℓ is now the thickness of the porous solid. Substitution in Eq. (1) gives

$$J = \frac{2\pi n \bar{r}^3 P_o}{M \bar{u}} \quad (2)$$

Thus, in cases where the transport of a gas or vapor through a porous solid is via the vapor phase, the flux should be inversely proportional to the thickness of the porous barrier. In the present study.

the dependence of flux of CO_2 vapor from calcite decomposition on the thickness of a porous alumina layer was tested.

II. EXPERIMENTAL PROCEDURE

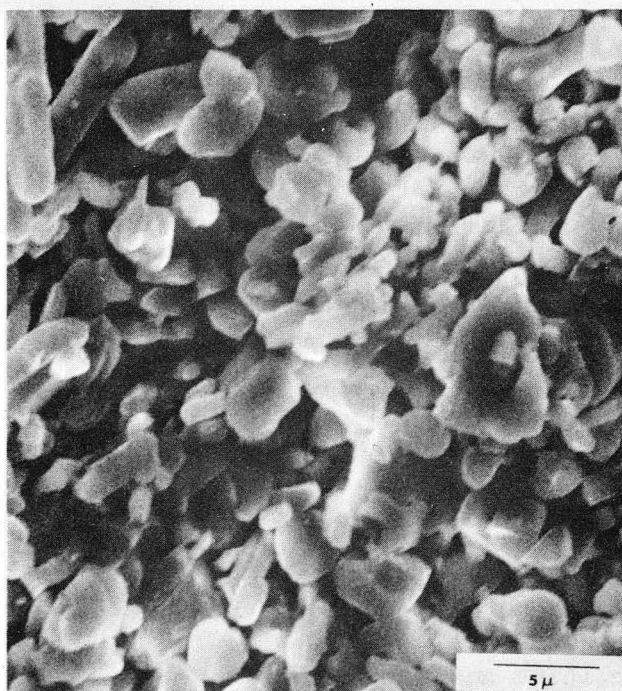
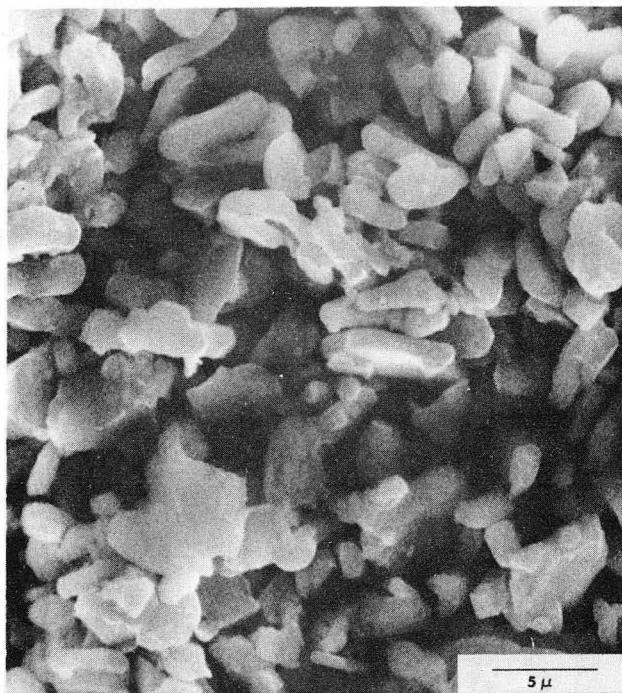
Calcite single crystals were cleaved on the $10\bar{1}1$ plane to obtain wafers 3 to 4 mm thick. These were then ground to discs of 1.106 cm diameter to fit inside a 1.107 cm diameter tantalum cell. Measurements were made on the same calcite crystal from which Beruto² had obtained his samples as well as on an additional crystal. Spectrographic analysis¹⁰ of Beruto's crystal (#1) and of the new crystal (#2) yielded:

	#1	#2
Mg	0.15%	0.004%
Al	-	.002
Cu	-	< .001
Sr	.025	< .003
Fe	-	.004
Mn	.02	-

Both crystals showed the proper lattice spacing and symmetry for calcite.¹¹

The density of the porous alumina used in these experiments was 54.1% of the theoretical value, and the pores, as observed through a scanning electron microscope, were estimated to range between 0.5 and 2 microns in diameter (Fig. 1a). Discs of 1.106 cm diameter and 0.305, 0.406, 0.704, 0.152, 0.650, and 0.605 mm thicknesses were used.

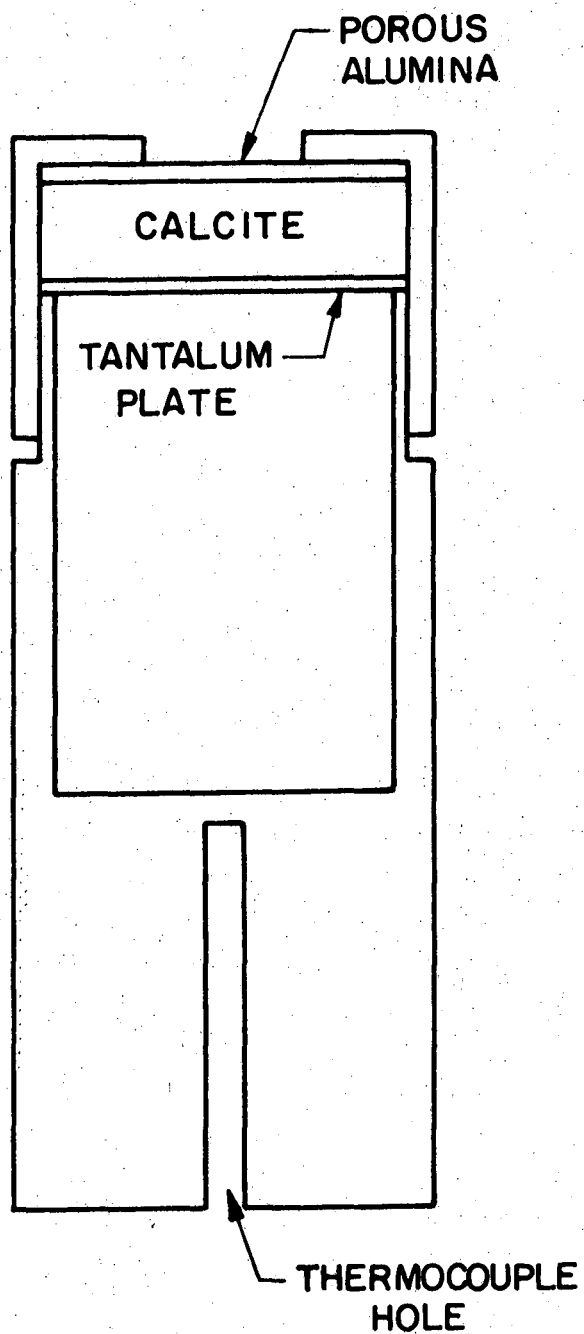
Both the calcite and alumina discs were mounted in a tantalum cell as shown in Fig. 2. The calcite disc rested on a 0.15 mm thick tantalum plate, and the alumina disc was held in contact with the calcite by means of the lid. A 4.76 mm diameter orifice in the lid allowed the vapor to effuse through the porous barrier.



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Figure 1. (a) Porous alumina photography by scanning electron microscope.
(b) Porous alumina after an experiment (photographs not of same area).

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Figure 2. Cell arrangement for calcite single crystal decomposition through porous alumina.

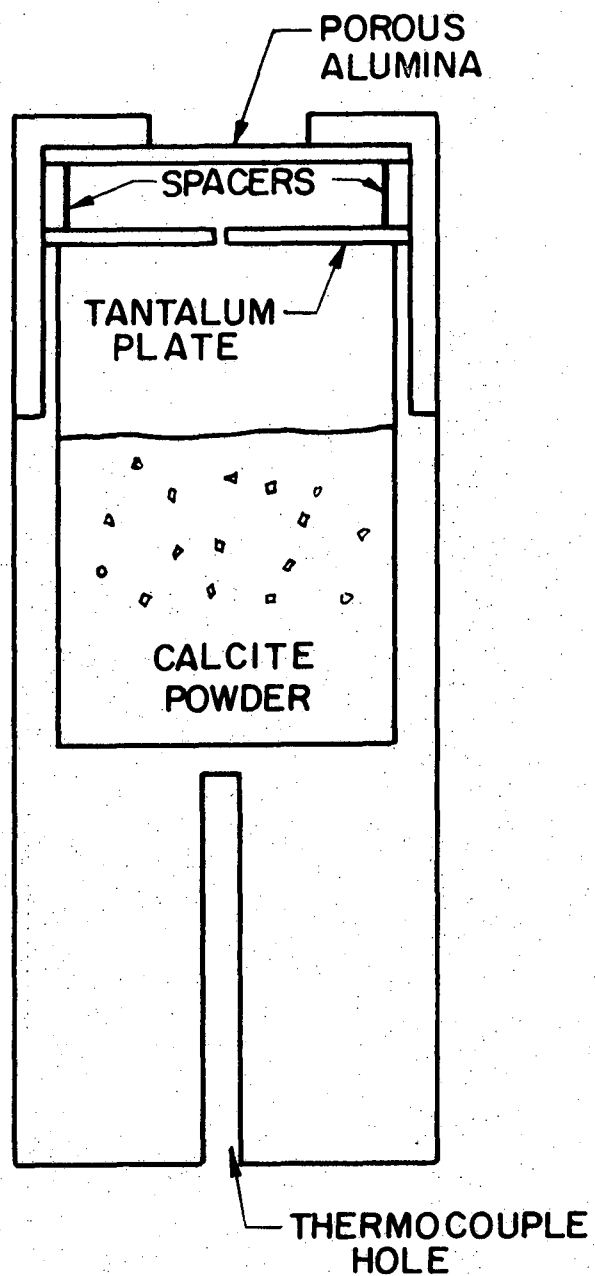
Because it was found that decomposition occurred over the entire top surface of the calcite crystal when the alumina discs were used, spacers were put between the calcite and the lid in the Langmuir experiments to allow decomposition over the entire top surface also. The spacers, which were small fragments taken from a previously used alumina disc of .305 mm thickness, covered no more than 1% of the calcite surface.

The effect of the porous alumina on the equilibrium vapor pressure was studied by grinding pieces of single crystal calcite into powder which was placed in the same cell as that used for the single crystal experiments. The 0.307 and 0.201 mm thick porous alumina discs used were placed over a 0.3 mm tantalum plate with a 0.15 mm diameter orifice and was separated from it by two spacers, 0.1 mm thick, 2 mm high, and 3 mm in length, spot welded to the tantalum plate as shown in Fig. 3. Measurements were made at $665 \pm 2^\circ\text{C}$ and $523 \pm 2^\circ\text{C}$.

The arrangement for the sodium chloride vaporization experiments through the porous alumina was the same as for the single crystal calcite decomposition except that the sample, consisting of 0.2 to 0.3 gm of reagent grade NaCl powder was sandwiched between the tantalum and alumina discs. Because the vaporization coefficient of NaCl is unity, the layer of powder acts as an equilibrium source of NaCl vapor.⁶

The cell was heated in an Atlas CH4 mass spectrometer by radiation from a 0.254 mm diameter tungsten wire. Temperatures were measured with a chromel-alumel thermocouple inserted into the bottom of the cell. This was checked against a Pt-Pt 10% Rh thermocouple inserted through a porous alumina disc at the top of the cell where the calcite or sodium

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Figure 3. Cell arrangement for calcite powder decomposition.

chloride sample would be located normally. For the calibration the alumina was supported by three pieces of calcite about 3 mm thick to provide approximately the same conditions as those of the experiments.

In all calcite runs, the temperature variation was less than $\pm 3^\circ\text{C}$ and in the early runs, remained at $665^\circ\text{C} \pm 2^\circ\text{C}$ during most of the experiment. Temperature fluctuations were more severe during the later calcite and sodium chloride runs, but the temperature always remained in the range $662^\circ\text{--}668^\circ\text{C}$ for calcite and 711° to 717°C for sodium chloride and was stable at the midpoints for a large portion of the time.

Fluxes of CO_2 and NaCl were calculated from the weight changes and the known periods of heating as well as from mass spectrometric measurements. The relative amount of CO_2 effused was determined by monitoring the mass 45 peak which corresponds to $\text{C}^{13}\text{O}^{16}\text{O}^{16}$ and $\text{C}^{12}\text{O}^{16}\text{O}^{17}$. The mass 44 peak was too intense to be used since it saturated the electron multiplier. Effusion of sodium chloride vapor was measured by monitoring masses 23 (Na^+), 58 (NaCl^+), and 81 (Na_2Cl^+).

Background pressures ranged from 2.4×10^{-7} to 2.9×10^{-7} torr, as measured by an ion gauge, before each run following an overnight bake-out. The runs varied in duration from 43 to 196 minutes after the desired temperature was reached. Measurements of the mass intensities were made at approximately 5 minute intervals for calcite decomposition and at 10-15 minute intervals for sodium chloride vaporization. Inspection of the cell and sample after the runs showed that there was no apparent reaction between the tantalum cell, the porous alumina, and the calcite or sodium chloride.

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A shutterable intensity at the mass 45 peak was detected upon heating in the absence of a calcite sample, but this peak, which averaged 0.047V was negligible compared with the lowest intensities measured (about 2.5V).

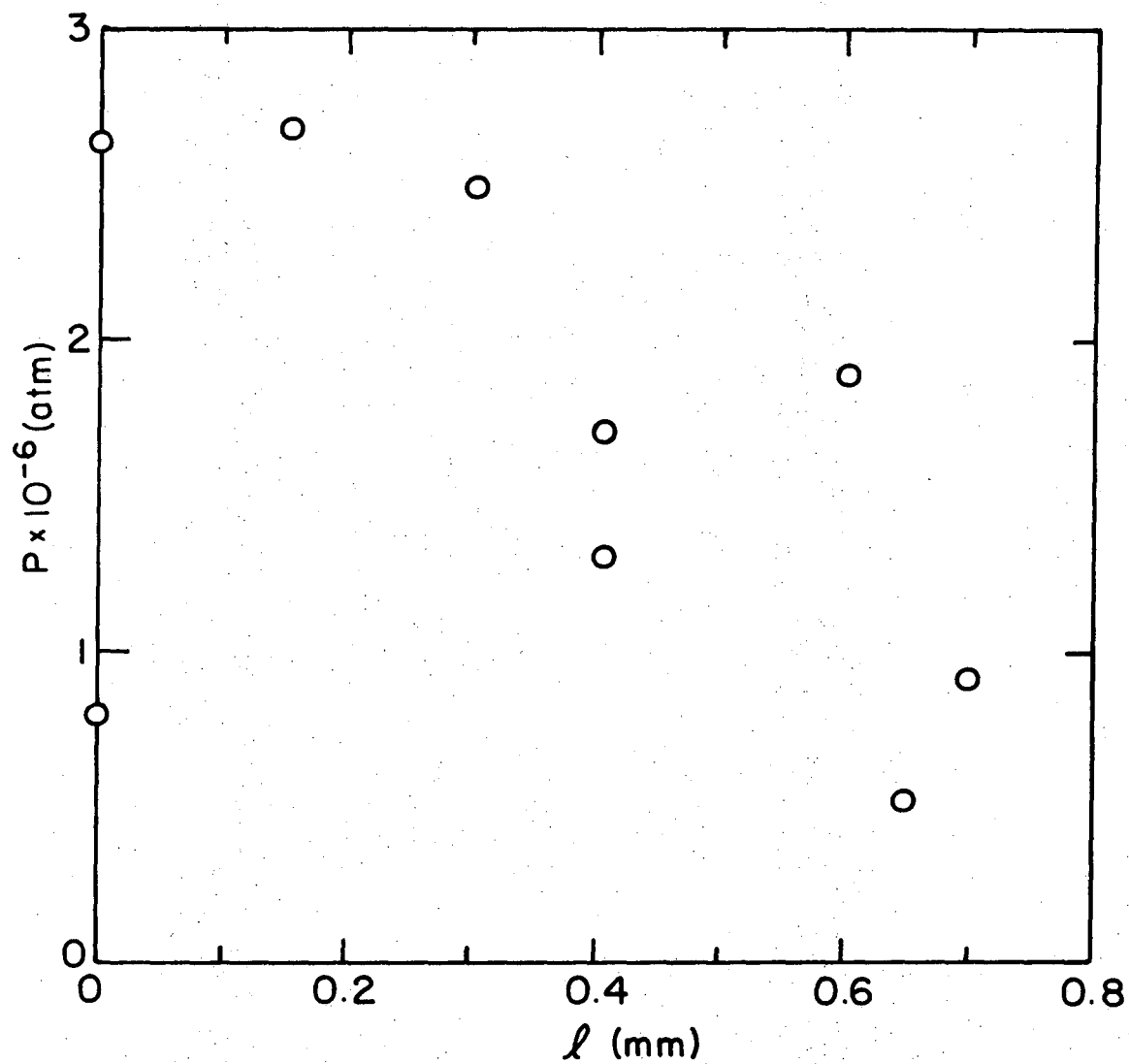
III. RESULTS

The apparent measured pressures of CO_2 vapor through the porous alumina discs, based on weighings of the samples made in air, are plotted versus the thickness of the porous layer in Fig. 4. Unfortunately, because of rapid absorption of water and carbon dioxide vapor by the CaO product, the data show considerable scatter, despite transfer of the cell into a closed weighing jar containing CaSO_4 and NaOH pellets immediately after removal from the vacuum system. Nevertheless, the data indicate that the interposition of the porous alumina discs reduced the CO_2 pressure from calcite single crystals by less than one order of magnitude, even for the thickest disc.

Similar reductions from the equilibrium pressure¹² were obtained in the runs made on calcite powder. Mass spectrometric intensities for the equilibrium run at 665°C decreased with time. This decrease probably was due to a decrease of surface area available for decomposition as the small grains of calcite underwent decomposition. The run at 523°C showed no such decrease with time, probably because the lower equilibrium vapor pressure made the changes in effective areas of reaction smaller.

Because the equilibrium vapor pressure at 665°C is 1.66×10^{-2} atm¹², the mean free path between vapor phase collisions was approximately 6×10^{-2} mm and the transport of CO_2 through the 0.15 mm diameter orifice was by hydrodynamic flow rather than by Knudsen flow. Carlson had reported that the transition from molecular to hydrodynamic flow for mercury vapor in Knudsen cells occurs when the ratio of the mean free path and the orifice diameter becomes about unity.^{13,14} Hence, the equation

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Figure 4. Apparent pressures of CO_2 with different porous alumina thicknesses.

$$P = \frac{1}{A} \frac{dm}{dt} \left(\frac{eRT}{M} \right)^{1/2}$$

which Carlson¹³ derived for hydrodynamic isothermal effusion was used to calculate the pressure. Here P is the pressure, A the orifice area, R the gas constant, e is the base number of natural logarithms, T the temperature and M the molecular weight of the effusing gas.

At 523°C, the equilibrium pressure, 3.71×10^{-4} atm,¹² is low enough that the conditions for Knudsen flow are met. Hence, the usual equation derived by Hertz¹⁵

$$P = \frac{1}{AC} \frac{dm}{dt} \left(\frac{2\pi RT}{M} \right)^{1/2} \quad (3)$$

with C, the Clausing correction factor for non-ideal orifices and equal to 0.5136^{16} for this experiment, was used. The results are given in Table I.

Table I

Temperature	Porous layer thickness	Equilibrium pressure	Measured apparent pressure
665°C	0.310 mm	1.66×10^{-2} atm	8.85×10^{-3} atm
523°C	0.300 mm	3.71×10^{-4} atm	3.27×10^{-4} atm

The reduction in the carbon dioxide pressure caused by the porous disc is less than a factor of 2 in both runs.

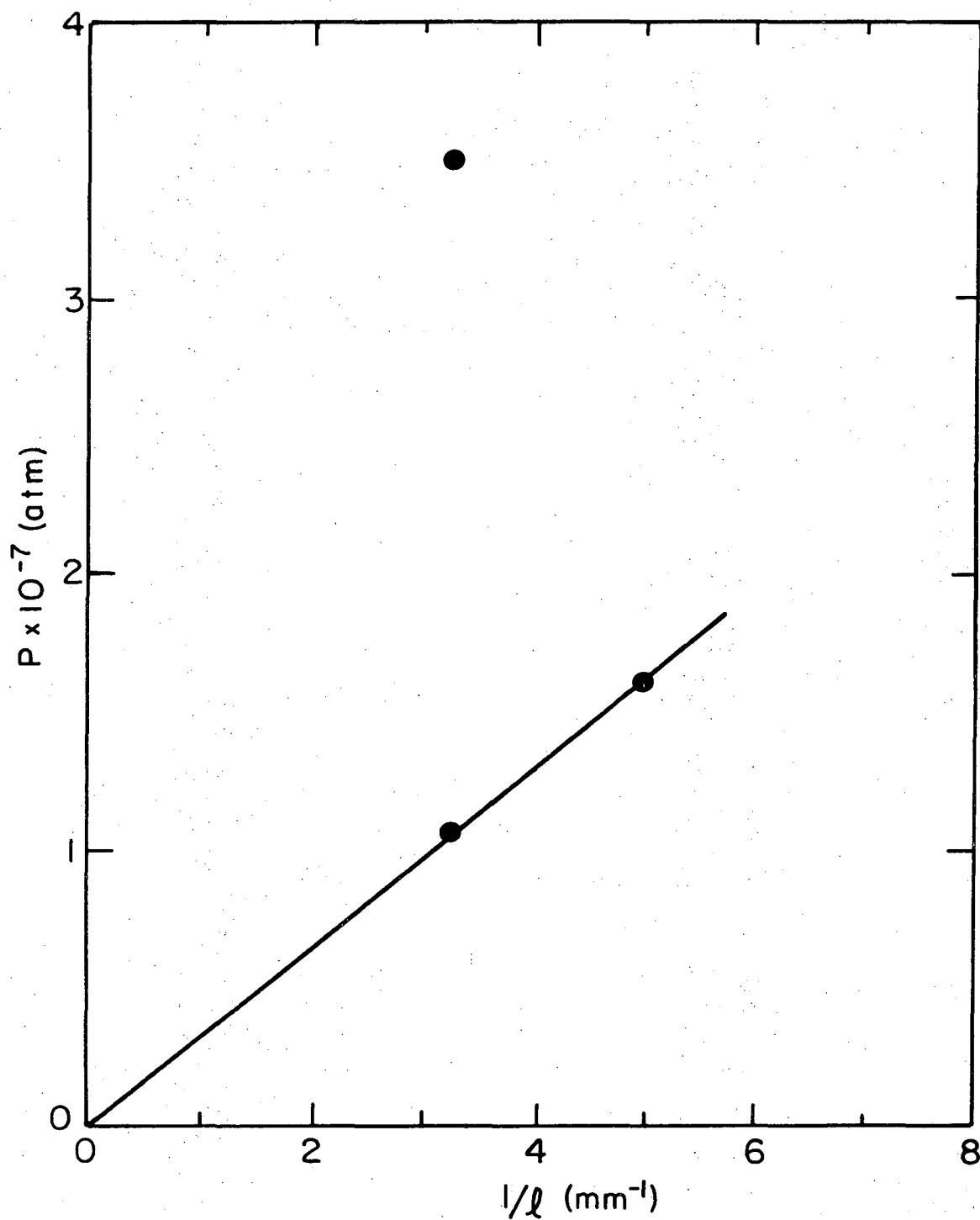
The results of the sodium chloride experiments (Table II) are in striking contrast with the results for calcite.

Table II

Temperature	Porous layer thickness	Equilibrium pressure ¹⁵	Measured apparent pressure
714°C	0.307 mm	5.94×10^{-5} atm	3.49×10^{-7} atm
714°C	0.201 mm	5.94×10^{-5} atm	1.60×10^{-7} atm
714°C	0.307 mm	5.94×10^{-5} atm	1.07×10^{-7} atm

The alumina discs reduced sodium chloride pressures by more than two orders of magnitude for these runs. The lesser reduction of one is felt to be due to significant leakage of vapor from the sides of the cell. These reductions are somewhat greater than those found by Mohazzabi because the alumina discs had smaller pores than those used in his experiments.

In agreement with the results obtained by Mohazzabi,^{5,18} the mass spectrometric intensities showed that the sodium chloride monomer flux through the porous disc was more than 30 times as great as the dimer flux. Accordingly, the apparent pressure was calculated assuming the vapor to consist of monomeric species only. The apparent measured pressures are plotted against the reciprocal of the thickness of the porous layer in Fig. 5. In conformance to Eq. (2) and Mohazzabi's work, the plot is linear and passes through the origin by ignoring the run which had significant leakage.



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Figure 5. Apparent pressures of sodium chloride vapor with the inverse of porous alumina thickness.

IV. DISCUSSION

From the results obtained here, it is seen that the CO_2 vapor from the decomposition of calcite flows much more readily through a porous alumina disc than does NaCl vapor, which suggests that a different mechanism is involved in the two cases. That the presence of a porous layer has little effect on the decomposition rate of calcite is consistent with either of the two possibilities mentioned in the introduction, namely, that the desorption of CO_2 from the calcite surface is highly irreversible, or that transport of CO_2 through the porous layer is by means of rapid surface diffusion.

Searcy and Beruto¹ have shown that the flux leaving a pore may be related to the flux entering by

$$J = J_o \left[\frac{f}{f + (1-f)a_c} \right] \quad (4)$$

where J is the outlet flux, J_o the inlet flux, f is the transmission for the gas from a reversible source, and a_c is the condensation coefficient (a measure of the reversibility of the transfer processes at the gas source). The outlet flux, then, is equal to the inlet flux multiplied by the probability that a vapor molecule which enters the pore will leave the pore. For the case of $a_c \ll f$, which would be found for a highly irreversible source, Eq. (4) reduces to $J = J_o$ and a porous layer would have no effect on the flow. If surface diffusion is highly efficient f may remain essentially 1 even when the porous layer is thick. Then Eq. (4) again reduces to $J = J_o$ regardless of the value of a_c .

For Knudsen flow through pores from a reversible source, Eq. (4) reduces to

$$J = fJ_0 \quad (5)$$

where f is given by combining Eqs. (2) and (3) so that f has a linear dependence on the reciprocal of the thickness of the porous layer. The flow of sodium chloride vapor through the porous alumina used in this study is consistent with Eq. (5). The validity of Eq. (5) for sodium chloride vapor in alumina with 10μ pores has been shown in greater detail by Mohazzabi,⁵ who also measured the vaporization enthalpies and showed that their values are consistent with the mechanism of Knudsen flow.

The measurements made with single crystal calcite show that porous alumina had only slightly more effect on the decomposition rate than does the porous calcium oxide layer produced by calcite decomposition. This result was unexpected. Because only an upper limit could be set on the pore diameters in the calcium oxide layer,² the pores may be less than $100 \text{ \AA}$ in diameter so that the area of surface on which diffusion could occur is very high. But pores in the alumina discs had diameters of the order of 1μ so that Knudsen flow may be expected to dominate, which apparently is the case in the transport of sodium chloride vapor through these discs. Since the pressure is reduced by a factor of more than 100 in Knudsen flow, the slight reduction of the CO_2 pressure from calcite decomposition indicates that another mode of transport may be involved.

The most probable explanation of the small reduction of carbon dioxide fluxes by the alumina barriers was that surface diffusion of

carbon dioxide on oxide surfaces is more efficient than expected. However, it seemed desirable to prove that the efficiency of transport through the porous alumina was not a consequence of the irreversibility of the calcite decomposition reaction.

The experiments with powdered calcite heated in an effusion chamber below a porous disc provided this proof. Since the ratio of the effective area of the orifice of the effusion cell to sample surface area was less than 10^{-4} , it can be assumed^{19,20} that the equilibrium decomposition pressure was established inside the cell.

Since the measured pressure was reduced by less than a factor of 2 below the equilibrium pressure, it is shown that the alumina barriers used reduce a flux of equilibrium sodium chloride vapor about 100 times as effectively as for a flux of carbon dioxide from an equilibrium source. The fact that the porous layer has only a small effect on the carbon dioxide flux may be attributed to rapid surface diffusion. The fact that the growing porous calcium oxide product layer does not affect the flux or carbon dioxide vapor must almost certainly also be because surface diffusion is highly efficient.

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