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THE KINETICS OF DECOMPOSITION IN POWDER BEDS: THEORY AND EXPERIMENT

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Abstract. The usual analysis of kinetics of decomposition reactions in terms of fraction of sample decomposed vs time, $f(t)$ vs $t$, data are shown to be misleading when applied to calcite powder decomposition. Such an analysis erroneously fits these small particle data to an irreversible reaction model. Expressions are derived to describe flux densities from powder beds when either a slow chemical step or escape of gas from the bed into vacuum is rate limiting. Small beds of calcite crystals of greater than 0.5 mm particle cross sections show behavior predicted for irreversible decomposition; similar beds of 20 μm or smaller particles establish a metastable equilibrium in the bed. This metastable equilibrium may be between calcite and a transient CaO-CaCO$_3$ intermediate phase.

Dissociation
Kinetics
Thermodynamics
Vaporization
In their recent comprehensive review of reactions in the solid state, Bamford and Tipper (1) comment, "The purpose of many kinetic studies is to obtain information concerning the reaction mechanism, through comparisons of a series of measured \((\alpha, \text{time})\) values [where \(\alpha\) is the fraction of the maximum weight loss for the reaction in time \(t\)] and the theoretical functions which have been derived from models based on the geometry of interface initiation and advance and/or diffusion process occurring in the solid. The problem may be regarded as the identification of the functional relationship between \(\alpha\) and time, \(f(\alpha) = kt\), where \(k\) is the conventional rate coefficient. Most methods of analysis proceed by determining which rate equation . . . provides the most accurate fit to the experimental \([\alpha \text{ versus } t]\) data."

They go on to comment, "Kinetic evidence alone cannot be regarded as a positive demonstration of the operation of a particular mechanism," and recommend that interpretations of weight loss vs time data always be based on additional information such as microscopic observations.

We completely concur in this view of the importance of obtaining morphological and structural information, but we wish to call attention to a more serious limitation of analyses of decomposition reaction data in terms of \(f(\alpha) = kt\) plots. An underlying assumption of each of the nondiffusional rate equations listed in Bamford and Tipper's review is that the back reaction can be neglected. But it has recently been shown that powder beds of \(\text{CaCO}_3\) (2) and \(\text{MgSO}_4\) (3) when heated in open crucibles in vacuum yield weight changes that are
independent of powder bed depth, and therefore of calcite powder surface area. It will be shown in the section on Theory that the surface area independence implies that the decomposition rate is limited not by an irreversible chemical step of the reaction, but by escape of gas from the powder bed. For calcite the escape fluxes correspond to apparent equilibrium pressures only about a factor of 30 greater than the pressures which would yield the CO$_2$ fluxes measured from calcite single crystals during their irreversible decomposition in vacuum and only $\sqrt{3} \times 10^{-4}$ times the equilibrium CO$_2$ pressure if CaO is formed in its standard state (4,5,6).

This paper presents a theoretical framework for evaluating the relationship between irreversible decomposition of large crystals and the apparent approach to equilibrium in powder beds, and presents what is apparently the first detailed investigation of the influences of particle size, bed depth, and packing density on the kinetics of a decomposition reaction in an open crucible.

Gallagher and Johnson (7) reported the effects of sample size and heating rate on the kinetics of CaCO$_3$ decomposition, but under conditions which they concluded made heat transfer the rate limiting process. The most pertinent multiparticle and powder studies for calcite are those of Britton et al. (8). They concluded from their experiments on calcite decomposition in vacuum with three pieces weighing together 0.5 g and with the same weight of powders of -10 +12 mesh that the reaction proceeds at an interface which advances from the outside of each lump, or perhaps of the whole sample for a finely divided material, toward the interior at a constant linear
velocity. From an estimate of the surface areas, they calculated that their three lumps of calcite decomposed at a rate $\approx 1/132$ times the rate expected from the Polanyi-Wigner equation and termed this "normal" behavior. In their analysis of calcite powder decomposition, they followed the usual practice of reporting and analyzing data in terms of the fraction of sample decomposed $\alpha$ as a function of time.

In the Discussion section of the present paper, we use our own data to demonstrate that this widely used kind of analysis can yield highly misleading results. An important objective of the paper is to persuade the reader that an essential component of a decomposition reaction should be to establish whether or not back reaction is significant; with this done, the data should be analyzed in terms of appropriate molecular fluxes, not in terms of $\alpha$.

**THEORY**

Darroudi and Searcy have shown that in the low CO$_2$ pressure range of the present study, the slowest chemical step of single crystal calcite decomposition is probably a step for the CO$_2$ as distinct from the CaO component of the reaction (6). At least until decomposition approaches completion, the calcite powder decomposition data obtained in the present study are not consistent with predicted behavior (9) when effusion of CO$_2$ through pores is rate limiting. Accordingly (10), it will be assumed in developing an equation for analyzing the present powder data that the rate limiting step of decomposition may either be a chemical step of escape of CO$_2$ from the calcite surface or escape of the CO$_2$ from the powder bed. Because the
observed rates are nearly independent of time, the steady state approximation can be used. To do so, the rate of change of the number of CO$_2$ molecules, $n$, in the vapor phase in the cell with time is set equal to zero,

$$\frac{\partial n}{\partial t} = (j_{sf} - j_{sr})A_s - j_b A_c = 0$$  \hspace{1cm} (1)

where $j_{sf}$ is the flux density of CO$_2$ molecules provided by the calcite to the vapor, $j_{sr}$ is the flux density of CO$_2$ molecules from the vapor that strikes the calcite surface $A_s$ and traverses any free energy barrier that inhibits reformation of calcite, $j_b$ is the flux density of CO$_2$ that escapes from the cell into vacuum, and $A_c$ is the cross section of the cell through which that flux escapes.

Using the arguments described elsewhere (9,10,11), these flux densities can be written as $j_{sf} = (2 \pi MRT)^{-\frac{1}{2}} P_o \exp[-(G^*-G_s)/RT]$, $j_{sr} = (2 \pi MRT)^{-\frac{1}{2}} P_b \exp[-(G^*-G_b)/RT]$, and $j_b = CP_b (2 \pi MRT)^{-\frac{1}{2}}$, where $M$ is the molecular weight of CO$_2$, $G^*$ is the free energy of activation for decomposition, $G_s$ is the free energy of the calcite, $G_b$ is the sum of the free energy contents of the solid product and of the CO$_2$ at its standard pressure, $P_o$ is the standard pressure, $P_b$ is the CO$_2$ pressure in the powder bed, and $C$ is the transmission probability for the channel formed by the cell walls above the powder bed surface.

The three flux equations and Eq. (1) can be combined to yield
\[ j_b = \frac{C A_s P_0 \exp[-(G^*-G_s)/RT]}{(2 \pi MRT)^{\frac{1}{2}} \{A_s \exp[-(G^*-G_b)/RT] + C A_c\}} \]  \hspace{1cm} (2)

When \( A_s \exp[-(G^*-G_b)/RT] \ll C A_c \), Eq. (2) gives for the \( \text{CO}_2 \) flux density from the cell

\[ j_b = \frac{A_s P_0 \exp[-(G^*-G_s)/RT]}{A_c (2 \pi MRT)^{\frac{1}{2}}} \]  \hspace{1cm} (3)

and when the inequality is reversed, the flux density is

\[ j_b = \frac{C P_0 \exp[-(G_b-G_s)/RT]}{(2 \pi MRT)^{\frac{1}{2}}} \]  \hspace{1cm} (4)

Equation (3) thus predicts that the flux density (and total flux) from the cell will increase in direct proportion to the sample surface area when that area is relatively small. But for powders \( A_s \) may be large enough to make Eq. (4) apply (except when exhaustion of sample reduces \( A_s \) toward zero), and the flux density or total flux from the cell no longer depends on \( A_s \).

EXPERIMENTAL

A natural calcite single crystal was cut, ground, and sieved to make samples of 74-90 \( \mu \text{m} \), 0.5-0.6 mm, 1.0-1.4 mm, and 4 mm average particle cross section. Samples of particles 5-10 \( \mu \text{m} \) and 10-20 \( \mu \text{m} \) in cross section were obtained from Baker analytical reagent \( \text{CaCO}_3 \), low in alkali, using an ultrasonic fine sieve. For powder of about 3 \( \mu \text{m} \) particle size, Mallinckrodt analytical reagent \( \text{CaCO}_3 \) was used. Calcite particles from these different sources are observed in
scanning electron micrograph (SEM) pictures to have rhombohedral shapes. These observation imply the particles to be individual crystallites. Spectrographic analyses showed the highest concentration of impurity in the 3 \( \mu \text{m} \) powder to be 0.5\% K. Impurities in the coarser samples were present at concentrations of 0.01\% or less. Surface areas of the calcite powders measured by the BET method were all less than 1 m\(^2\)/g; this result implies negligible internal particle porosities.

For runs in which equilibrium was approached, the net rate of decomposition would be reduced by CO\(_2\) molecules that returned to the sample after striking the cell walls above the powder bed. Alumina sample cells of 9.8 mm inner diameter and various heights between 10.5 mm to 24.4 mm were used so that sample heights could be changed with the distance between the top of a sample and the top of its cell held at 1 cm.

The sample cell was fitted into a platinum basket which was suspended from a 1.0 mm diameter quartz rod in an alumina tube. The rod was connected to a Cahn 1000 recording microbalance that measured the continuous weight change at a full-scale sensitivity of 1.0 mg during thermogravimetric reactions.

The sample was hung in a 15 cm long uniform temperature zone. The temperature was measured with a chromel alumel thermocouple which was placed near the sample cell and connected to a digital readout device. Sample weight changes were measured continuously on a strip chart recorder at a scale of 10 mg or 100 mg full scale. A silicone oil diffusion pump maintained the pressure at \( 10^{-3} \) to \( 10^{-4} \) torr during
the decomposition. The temperature was increased to 400°C slowly, and to 610°C or 670°C at a rate of about 20°C/min. This rate of temperature increase limited the decomposition to less than 5% before the desired temperature was reached. When a desired fraction of decomposition was achieved, the furnace power was turned off.

When the sample was near room temperature, the vacuum system was closed and dry N₂ was introduced to fill the apparatus to atmospheric pressure. CaO reacts rapidly with atmospheric moisture and CO₂; therefore, the sample was quickly removed, and either transferred as rapidly as possible to the appropriate apparatus for other experiments such as BET surface area measurements, XRD, and SEM observation, or was stored in a small sealed bottle in a desiccator dried by anhydrous CaSO₄.

RESULTS AND DISCUSSION

It is well established that calcite crystals decompose along an advancing interface (4-6,8). The expected f(α) vs t equation, therefore, for an irreversible reaction (in the absence of product sintering) is (1)

\[ 1 - (1-\alpha)^{1/3} = kt, \]  

which can conveniently be compared to experimental data on a logarithmic plot. Figure 1 shows that a good fit to Eq. (5) can be obtained from our calcite powder data at 670°C over the range \( \alpha = 0.05 \) to \( \alpha = 0.9 \). At this temperature, measurements at smaller values
of \( \alpha \) are impracticable because of the short times involved compared to the time necessary to reach temperature. From lower temperature studies, we know that a fit to the same curve could be expected for small values of \( \alpha \). Thus, the powder data are seemingly consistent with predictions of the irreversible model, Eq. (5).

But if decomposition is irreversible, the analysis of the present study shows that Eq. (3) becomes the appropriate expression for the flux density; at constant temperatures Eq. (3) takes the simple form

\[
j_b = q A_s
\]  

(6)

where \( q \) is a constant at constant temperature.

For a sample of given mass, the value of \( A_s \) should change very little during the first 50% of decomposition, so the net flux per unit area of calcite surface, \( j_b A_c / A_s \) according to Eq. (3), should be the same during early stages of decomposition with samples of various known initial surface areas. The third column of Table 1 shows that the predicted constancy of flux densities is obtained for calcite particles of 0.5 mm cross section or greater, but not for the powders.

For the powders of the two smallest particle sizes, the flux density of \( \text{CO}_2 \) from the crucible is independent of total powder surface area, as predicted by Eq. (4). (See column 4 of the table.) This result implies that a near-equilibrium pressure is developed in the powder bed. Figure 2 shows that the flux density leaving a crucible from a constant weight of sample increases according to
Eq. (6) for large crystals, but becomes independent of surface area for fine powders.

Figure 3 shows additional evidence that a near-equilibrium pressure is reached in the powder beds. Within the scatter of the data, the flux densities of $CO_2$ leaving beds of these small cross-section calcite powders are independent of sample height and sample packing density, both of which change $A_s$. But if a reaction is near equilibrium at an advancing interface, the apparent rate constant in the decreasing volume model must decrease as reaction proceeds because the "constant" then is inversely proportional to the diffusion path length (9). Clearly, the apparent fit of the calcite weight-loss data to Eq. (5) that was found from Fig. 1 is fortuitous.

If an irreversible interfacial step is rate limiting, decomposition of each particle proceeds independently, and the interface must advance simultaneously into each separate particle. However, when the surface area is high enough, an equilibrium pressure is approached in an isothermal bed; then the particles at the exposed bed surface should decompose at a faster rate than those far from the surface. But if the temperature is lower at the bed surface through which the gas product flux escapes than at the bottom of the bed—as is likely to be the case for an endothermic process in vacuum—then distillation of product from bottom to top of the bed can eliminate or reverse this reaction gradient. Differences in our observations of the effect of extent of reaction on sample surface areas from these found by Ewing, Beruto, and Searcy (12) for calcite decomposed under
seemingly very similar conditions probably reflect this effect of a
temperature gradient.

Ewing et al. found, for a partially decomposed powder, that the
surface area of a sample taken from close to the bottom of the bed was
slightly higher than that of a sample taken from the top of the bed,
as expected if the bottom is hotter than the top. But we find for a
14.4 mm deep bed formed of 3 µm cross section calcite powder that when
the reaction was 40% complete the surface area from particles at the
top of the sample was 84 m²/g while that of powder at the bottom was
only 6.2 m²/g. For a sample of 10-20 µm cross section powder, when
reaction was 29% complete, the surface area of powder from the top was
45 m²/g and that of powder from the bottom was 1.3 m²/g. Our surface
areas must reflect preferential decomposition from the top of the bed,
as expected if an equilibrium process proceeds in an isothermal bed.
Ewing et al. found no change in specific surface areas of CaO as
decomposition of calcite powders proceeded in vacuum. But we find
that the final specific surface area of the CaO from calcite powders
(though not large crystals) decreases with bed depth (Fig. 4). CO₂
catalyzes CaO sintering (12). Because for these powders the total
time of decomposition is directly proportional to bed depth (Fig. 5),
the influence of bed depth on surface area can be attributed to
sintering that occurs during longer exposure to CO₂ at the pressure
characteristic of the powder beds. For the single crystals,
 decomposition times are independent of bed depth so that surface areas
are unaffected by bed depth. Because CO₂ pressures are lower for the
large crystals, sintering of the CaO is slight despite the longer times required for decomposition.

The origin of the apparent equilibrium established when CO₂ pressures are >3 orders of magnitude below the pressures characteristic of calcite decomposition to CaO is a major puzzle. The only product phase so far identified in calcite decomposition is normal CaO (13,14). But the near-equilibrium behavior of the powder bed implies that CO₂ is equilibrated with calcite and a metastable solid for which the CaO activity is 1/(3x10⁻⁴), where 3x10⁻⁴ is the ratio of the CO₂ pressure in the bed to the CO₂ pressure when calcite is equilibrated with CaO in its standard state. Dai (14) has reported transmission electron microscopy evidence that calcite may become highly deficient in its CO₂ content in small volume elements near its surface before the diffraction pattern of normal CaO suddenly appears.

In the present study, we found that the steady state decomposition of the fine powders held at 670°C was often interrupted by explosive ejection of powder from the crucible (Fig. 6). Sample ejection did not occur at 610°C.

It seems unlikely that sample ejection in vacuum from an apparently pore-free calcite is a consequence of escape of trapped gases. It may be that the high surface area calcite powders establish an equilibrium with an unstable CaCO₃-CaO phase; that phase may usually decompose exothermally but locally in volume elements of <<1 μm cross section, but with the reaction occasionally propagating through enough of the phase so that rapid evolution of the
$\text{CO}_2$ causes powder ejection. Further TEM studies are planned to test this hypothesis.

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REFERENCES

Table 1. Initial Fluxes of CO₂ at 670°C from 179±1 mg samples

<table>
<thead>
<tr>
<th>Particle size (µm)</th>
<th>Total suited CaCO₃ surface area (cm²)</th>
<th>Flux density from CaCO₃ surfaces (moles/cm²·sec)</th>
<th>Flux density from crucible (moles/cm²·sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-10</td>
<td>1250</td>
<td>(1.3±0.1)x10⁻⁹</td>
<td>(2.1±0.1)x10⁻⁶</td>
</tr>
<tr>
<td>10-20</td>
<td>750</td>
<td>(2.0±0.2)x10⁻⁹</td>
<td>(2.0±0.2)x10⁻⁶</td>
</tr>
<tr>
<td>74-90</td>
<td>900*</td>
<td>(1.2±0.2)x10⁻⁹</td>
<td>(1.4±0.2)x10⁻⁶</td>
</tr>
<tr>
<td>500-600</td>
<td>7.6</td>
<td>(5.7±0.7)x10⁻⁸</td>
<td>(5.7±0.7)x10⁻⁷</td>
</tr>
<tr>
<td>1000-1400</td>
<td>3.5</td>
<td>(4.8±0.9)x10⁻⁸</td>
<td>(2.3±0.5)x10⁻⁷</td>
</tr>
<tr>
<td>~4000</td>
<td>0.97</td>
<td>(5.2±1.1)x10⁻⁸</td>
<td>(5.9±1.6)x10⁻⁸</td>
</tr>
</tbody>
</table>

*Entries are averages of 2 to 4 measurements and average deviations.

*This BET measured surface area implies some aggregation of powders during sieving.
FIGURE CAPTIONS

Fig. 1. Misleading fit of the contracting sphere model to data measured for calcite powder decomposition in vacuum.

Fig. 2. Flux density of CO\textsubscript{2} from a crucible with samples of the same weight but different average particle sizes.

Fig. 3. Mass flux densities from a crucible plotted as functions of packing density for samples of various heights.

Fig. 4. Dependence of CaO surface area on bed depth and calcite particle size for \(\approx 3\) \(\mu\)m and 1.0-1.4 mm particles decomposed at 610°C and 670°C, respectively.

Fig. 5. Dependence of calcite decomposition time on bed depth and particle size for \(\approx 3\) \(\mu\)m and 1.0-1.4 mm particles decomposed at 610°C and 670°C, respectively.

Fig. 6. Sudden sample ejection during isothermal heating of \(\approx 3\) \(\mu\)m particle size powder in vacuum at 670°C.
Decomp. temp.: 670 °C
Particle size: 5-10 μm
CaCO₃ wt.: 177.5 mg

Figure 1
\[ \log j_b = \log (q \text{ As}) = \log q' - \log d \]

Sample wt.: 179 ± 1 mg
Decomp. temp.: 670°C

Figure 2
Figure 3
Figure 4
Figure 5
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