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Microstructure, kinetic, structure, thermodynamic analysis for calcite decomposition: free-surface and powder bed experiments

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Abstract

This paper describes studies of incongruent vaporization reactions that were carried out in Berkeley and Genoa from 1970 to about 1987, but that have not previously been described in terms of the overall research objectives and the extent to which those objectives were achieved. When the research was initiated, it was already known that for metals and some simple salts the rates of vaporization in vacuum are predictable as functions of temperature if the thermodynamic properties of the solid and vapors were known. That simple behavior was not shown by the few congruent decomposition reactions that had been quantitatively studied. Our review focuses on calcite decomposition because it illustrates the daunting array of variables—heat transfer, CO_2 pressure, crystal structure and crystal orientation, particle size, particle shape, particle-pore distribution, surface energy of the CaO reaction product, and interface strain—all of which could influence the reaction kinetics. In the body of the paper we review the theoretical bases of our kinetic evaluations and experimental studies for single crystals and powder beds. As a major conclusion we identify an easily achievable range of experimental conditions within which investigators in different laboratories have obtained concordant measurements of calcite decomposition rates. This is an important result because a prominent international committee concluded a decade ago that goal had not yet been achieved.

Another important conclusion is that the rate limiting step of calcite decomposition probably occurs in a CO_2-depleted surface layer or layers of calcite. At high relative pressures of CO_2 the process is kinetically reversible, but at low relative pressures, it is highly irreversible. We think the latter rate is determined by a strain-induced collapse of CO_2-deficient calcite at its interface with crystalline CaO rods with simultaneous expulsion of CO_2 gas. Such a mechanism seems not to have been suggested before, but it probably accounts for some of the exothermic events observed during heating of solids that decompose incongruently. The role of particle size on such a mechanism has been investigated and discussed.

Keywords: Vaporization; Incongruent; CO_2

1. Introduction

The class of endothermic decomposition reactions that is described by the general equation:

$$AB(s) = A(s) + B(g) \qquad (1)$$
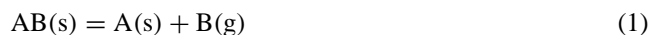
is of particular interest in ceramic technology because this class includes reactions which are used in the production or purification of a variety of important ceramics such as CaO, MgO, Al_2O_3 and ZrO_2.

As has been pointed out by the participants of the Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry, there is a need for a standard process in decomposition kinetic studies that yields data that can be duplicated by different investigators in different laboratories. When the Committee met in 1995, its members were disappointed because evidence collected in several laboratories, failed in establishing the suitability of $Li_2SO_4 \cdot H_2O$ [1]. It is evident that all experimental and materials properties that determine decomposition rates need to be identified and controlled.

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The long term goal of our research was to identify the rate limiting step of calcite decomposition under a variety of controlled experimental conditions. As shown at the end of Section 2, this process led to the demonstration that nearly the same temperature-dependent steady state decomposition rate of calcite was obtained in several different laboratories using three strikingly different experimental designs.

Extending the points of view reported, for instance, by Schamalzried [2] and Bamford and Tipper [3], we agree that kinetic, thermodynamic, morphological, and structural information alone cannot provide a positive demonstration of the reaction mechanism that controls the rate determining step of decomposition reactions. To obtain a good insight into a reaction mechanism, one needs to compare reliable kinetic, thermodynamic, morphological, and structural data on the same system decomposed under the same experimental conditions. This approach in which Microstructure, Kinetics, Structure, and Thermodynamics are interrelated, here will be named, for the sake of simplicity, MKST analysis We and our colleagues in Berkeley and Genoa began the studies on calcite reviewed here over 30 years ago. We expected that quantitative evaluations of the temperature dependence of isothermal decomposition rates could give insights into reactions described by Eq. (1), like insights already established as valuable for simple vaporization of metals and salts described by

$$M(s) = M(v) \tag{2}$$

and for congruent decomposition to two or more product gases [4]. That expectation was based on *two* important facts that should apply to reaction 1, even though one of its products is a solid.

The first is the fact exploited by Langmuir in relating the kinetics of metal vaporization to equilibrium thermodynamic properties [5]. He correctly deduced that every molecule of a metal vapor that strikes the parent metal surface will condense, and consequently, the flux leaving a metal by reaction (2) in vacuum is exactly the same as that which passes in each direction through an imaginary "surface" in the equilibrium vapor. Subsequently, studies of the kinetics of simple vaporization and congruent vaporization of solids (see, for instance [4,6,7]) have been analyzed in terms of their possible deviations from the Hertz–Knudsen–Langmuir (H–K–L) equation:

$$J = \alpha_c (2\pi mkT)^{-1/2} p_e \tag{3}$$

Here α_c is a coefficient that accounts for the fact that sometimes only a fraction of the molecules that strike the M surface reach equilibrium [4], m the mass of the vaporizing species, k the Boltzmann constant, T the absolute temperature of vaporization and p_e the equilibrium pressure of M(s) at the selected isothermal temperature.

At equilibrium, J must equal J_e, the flux that escapes from the solid into the vapor. If α_c is less than 1, it must be balanced at equilibrium by an equal term $\alpha_v = \alpha_c$.

The second fact is that the temperature dependence of the H–K–L equation defines the maximum possible value of the activation entropy of the reaction. This datum is most easily seen for simple vaporization. When $\alpha_v = \alpha_c = 1$, the slowest step of vaporization is the escape of molecules from the bulk solid to the vapor. The enthalpy of activation for this process is just the enthalpy of vaporization and the entropy of activation is the entropy increase when the vapor is formed from the bulk solid at its equilibrium vapor pressure p_e. When $\alpha_v = \alpha_c < 1$, the enthalpy of activation can be either higher or lower than the equilibrium value for a surface process [4]. But for particles large enough to make their surface energy per mole negligible, the laws of thermodynamics limit the escape flux to that in the equilibrium vapor at every temperature, and the actual entropy of activation can not exceed the entropy of vaporization.

Thus, for studies of vaporization, the H–K–L equation, besides its simplicity, has great advantages [4,8]:

- It predicts the maximum possible vaporization rate from only the equilibrium pressure p_e.
- It predicts that desorption is the rate limiting process of the vaporization kinetics when the *experimentally measured* apparent activation entropy ΔS^* is very close (within 5%) to the standard entropy of the equilibrium reaction.
- Because chemically related compounds are likely to decompose by similar mechanisms, the probable rates of decomposition of members of a chemical family can be estimated from measurement of α_c for the solid selected as a prototype of this class. As illustrated for a number of oxide, carbide, and nitride vaporization processes, the changes in equilibrium entropy can be very nearly the same for members of a class of similar reactions [9].

It would be very nice if the application of a modified H–K–L equation to the rates of endothermic decomposition reactions would yield the same results. Unfortunately this field is more complex than decompositions that yield only gases because desorption and surface steps of the gaseous decomposition product:

$$B(a, s) = B(g) \tag{4}$$

are not the only possible rate limiting steps. Fortunately, when kinetic studies in vacuum are coordinated with studies of the solid product crystal structure, particle shape, particle size, and product porosity, insights into those other possible slow steps can be obtained.

In vacuum and for a medium–low decomposition temperature range, many decomposition reactions occur without changing the external shape of the initial reactant particles. These are the so-called pseudomorphous reactions see, e.g. [10]. Since the molar volume of AB(s) is larger than that of A(s), the conservation of the external reactant particle shape and volume has important consequences. The first is that the solid product is a three-dimensional array of A(s) crystallites with high specific surface areas and of

pores. Because the mobility of A(s) in the reaction zone is much less than that of B(g), a second consequence is that A(s) may form with crystallographic orientations related to that of the parent solids (topotactic reactions) see, e.g. [11], Bonding across A(s)–AB interfaces might prevent the local rearrangements necessary to produce the atomic packing and interatomic distances characteristic of the A(s) equilibrium phase.

Both features are important in producing new active ceramic oxides from endothermic decomposition reactions in vacuum and/or in low partial pressure regimes of B(g) from some parent inorganic salts [12–14]. The technological importance of this fact is evident nowadays where part of the scientific community is strongly involved in the formation and characterization of nanostructures. Thus a generalization about the kinetics of endothermic decomposition in vacuum would be very important and strategic for the production of active oxides.

Unfortunately, generalizations about either the kinetics of vacuum decomposition reactions or about the spatial relationships between the parent and daughter solid phases are difficult to make [15]. For this reason, it is important to identify classes of decomposition reactions and try to anticipate the extent to which the behavior shown by some selected salt of the class may or may not be typical.

2. The kinetics of vacuum decomposition of large calcite single crystals in vacuum

Our initial study of calcite decomposition kinetics [16] used cleavage plane of natural 1 mm calcite single crystal, 0.75 mm cross-section in a Langmuir cell and isothermally decomposed it in the temperature range 934–1013 K in vacuum at 10^{-3} Pa. Linear steady-state isothermal kinetics were observed until approximately 80% of the calcite had decomposed. A plot of $\ln J_{CO_2}$ versus $1/T$ gives the activation enthalpies and entropies [17]. A finding of the initial study of decomposition in vacuum was that the activation enthalpy is higher than the enthalpy of the equilibrium reaction and the activation entropy is lower than the entropy change in the equilibrium reaction. Later studies show that the reaction is highly irreversible over a long CO_2 pressure range, but becomes reversible near the equilibrium decomposition pressure.

The equations that we use in evaluating the equilibrium reaction:

$$CaCO_3(s) = CaO(s) + CO_2(g) \tag{5}$$
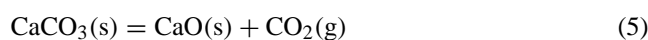
takes into account that the produced CaO may not be in its standard state because it has a high surface energy, crystallites with internal strains, and/or because it has a metastable crystal structure.

The CO_2 flux leaving the reacting surface under a steady state condition, neglecting the possible influence of the porous CaO barrier [18,19], is

$$J_{CO_2} = \left[\frac{P_{CO_2,d}}{(2\pi MRT)^{1/2}} \right] \left[\frac{1}{a_{CaO}} \right] \tag{6}$$

where P_{CO_2} is the CO_2 decomposition pressure at the interface reaction zone at constant temperature. The H–K–L equation has been restated in terms of M, the molecular weight of the $CO_2(g)$ and R the gas constant to yield the flux density in moles of gas per unit area of solid [4]. Then the thermodynamic activity of the produced oxide a_{CaO}, is

$$a_{CaO} = \exp\left[\frac{\Delta G_{CaO}}{RT} \right] \tag{7}$$

where ΔG_{CaO} is the positive free energy of formation of the solid reaction product from CaO in its standard state.

When equilibrium is reached between CO_2 and the solid phases at the surface, but the CaO for any reason is less stable than bulk calcite, Eq. (6) becomes:

$$J_{CO_2} = \left[\frac{P^*_{CO_2,d,eq}}{(2\pi MRT)^{1/2}} \right] \left[\frac{1}{a_{CaO^*}} \right] \tag{8}$$

where $P^*_{CO_2,d,eq}$ is the pressure of CO_2 at equilibrium with the formed calcium oxide, CaO*, and with $CaCO_3$; while a_{CaO^*} is the thermodynamic activity of the solid product.

When the calcium oxide is produced in its standard state, then the H–K–L equation:

$$J_{CO_2,MAX} = \frac{P_{CO_2,eq}}{(2\pi MRT)^{1/2}} \tag{9}$$

is recovered. Thus the H–K–L equation predicts the *maximum calcite decomposition rate* when CO_2 is at equilibrium with the calcite and with the standard CaO at its interface with the calcite. This equation is entirely predictable from the thermodynamics of the equilibrium decomposition reaction, and it is useful to take it as a *reference state*. The apparent activation entropy predicted through (9) equals to that of the equilibrium decomposition reaction.

Experimental data evaluated by means of Eq. (6) will give the maximum possible entropy of activation of the decomposition process. The entropy calculated from the temperature dependence of the decomposition rate can only be as high as the entropy of the equilibrium reaction if desorption limits the rate. If the two values *are equal* the entropy of activation is set at its maximum value, if the entropy of activation *is less* than the equilibrium one then the desorption of the gaseous product *cannot* be the rate determining step. We calculate the activation entropy from the temperature dependence of the vaporizing flux, obtaining a value of $100\,J\,mol^{-1}\,K^{-1}$. Comparison with the entropy of the equilibrium reaction calculated from standard tables, $151.5\,J\,mol^{-1}\,K^{-1}$, shows that the activation entropy is lower than the entropy of the precisely known equilibrium decomposition process.

In searching the literature of the period since our studies of decomposition reactions were completed, we found that L'vov et al. see, for instance [20,21] dismissed our evaluations of calcite decomposition rates as unsatisfactory [16] on both theoretical and experimental grounds.

The theoretical grounds reflect a marked difference in research philosophy. They assume that "all decomposition reactions proceed in accordance with the equilibrium laws (but with the formation of primary gaseous products which may differ of those at equilibrium) [20]." For example, to fit the rate of calcite decomposition to their model, they assume that the rate limiting step is the reaction $CaCO_3(s) = CaO(g) + CO_2(g)$ with the simultaneous recondensation of low-volatility CaO (g) molecules on the calcite [21]. We think that theoretical models should be based as closely as possible on experimental data, and this review describes experiments that strengthen our conviction that vaporization is seldom the rate limiting step of decomposition reactions.

The experimental reason advanced in criticism of our theoretical evaluations is that we failed in our initial study of calcite decomposition to correct for self cooling of the calcite surface by molecules vaporizing in vacuum. Our critics calculated, for example, that when our furnace temperature was 1000 K, the surface temperature of the calcite was only 920 K. The 80 K self cooling, however, is not actually measured. They calculate the large degree of cooling by first assuming that ΔS^* of the experimental plot $R \ln P = E/T + \Delta S^*$, should be replaced with ΔS^0, the equilibrium entropy of the assumed total vaporization reaction. They then assert that the discrepancy thus introduced is due to surface cooling by the vaporization flux. In justification of that conclusion, they calculate a consistent temperature reduction from their estimate of heat transfer through crucible and sample to the calcite surface.

There is strong experimental evidence that their very low calculated surface temperature cannot be correct. For congruent decomposition reactions, a difference in surface and furnace temperatures would be revealed by a difference between the *directly* measured recoil pressure of molecules leaving the surface in vacuum (torsion-Langmuir method) and the pressure *calculated* from the weight loss by means of the H–K–L equation. The first measurement is a datum that does not employ any assumption on possible differences between surface and furnace temperature, while the second one is, in principle, affected by this assumption. Fig. 1, reproduced from a Mar and Searcy study [22], demonstrated experimentally that, for congruent decomposition of GaN to Ga and $1/2N_2$, the pressures directly measured *exactly superimposed* on pressures calculated at several temperatures from the weight loss by means of the H–K–L equation. Thus the surface temperature must be the same to within a few degree as the furnace temperature.

Evidence that self cooling of calcite in vacuum is not an impediment to reliable measurement of decomposition fluxes, was collected by Powell and Searcy [23] at a time when there was concern among chemical engineers that heat transport always limited decomposition rates. Fig. 2 is an update of their plot. Pressures measured by Beruto and Searcy [16] and Powell and Searcy in vacuum, by Hyatt et al. in flowing nitrogen [25], and by Borgwardt [24] with particles of ~1 μm cross-section, a fluidized bed reactor in nitrogen, helium, and argon gases, all agree to within 10% in flux over a range of four orders of magnitude in the rate.

We should emphasize that the most difficult and most time consuming experimental barrier to reducing systematic error at high temperatures is that of calibrating the temperature at a vaporizing surface against that of a thermocouple or other temperature measuring device. It is particularly difficult to do so in an experiment that depends on collecting data during sample heating or cooling.
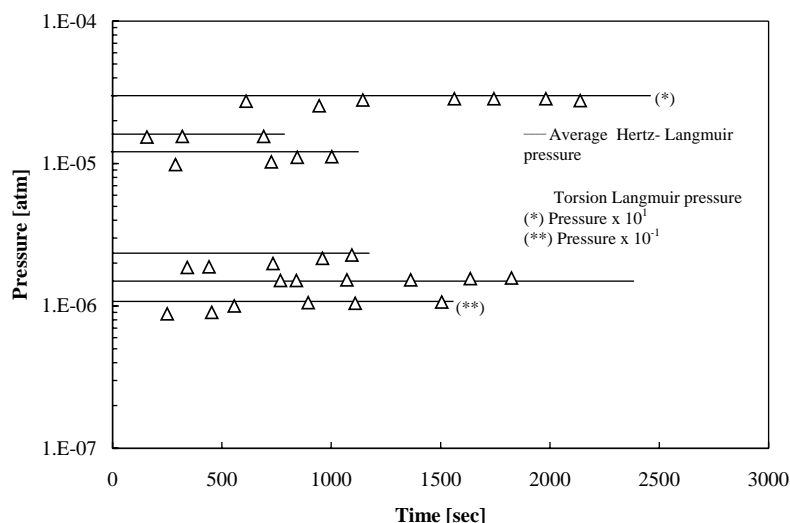

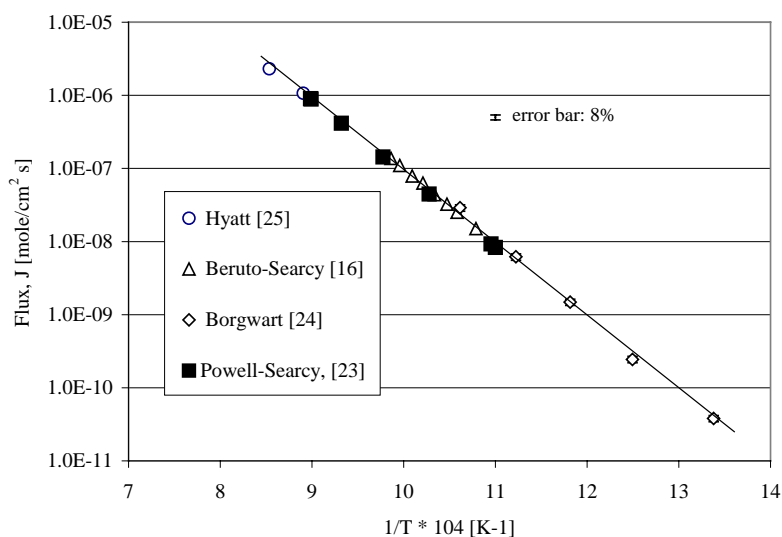Fig. 1. Comparison of average Hertz–Langmuir pressures with torsion-Langmuir pressures from [22].

Fig. 2. Flux densities measured for decomposition of calcite: black squares Powell and Searcy [23]; circles Hyatt et al. (flowing N_2) [25]; diamonds Borgwardt (in differential reactor, in He, N_2, Ar, particles size 1 μm) [24]; triangles Beruto and Searcy [16].

3. MKST analysis of decomposition kinetics of single crystals in vacuum

One reason that calcite decomposition rates in vacuum are low could be that the CaO produced is thermodynamically unstable relative to normal bulk CaO. The influence of an unstable solid on the maximum possible flux of CO_2 can be predicted by the ratio between the experimental flux (J_{CO_2}) with the maximum possible given by the H–K–L equation ($J_{CO_2,MAX}$). This ratio is

$$\frac{J_{CO_2}}{J_{CO_2,MAX}} = \frac{a_{CO_2}}{a_{CaO}} \qquad (10)$$

where the activity of CO_2 is set equal to the ratio $P_{CO_2}/P_{CO_2,MAX}$ [18] When the decomposing surface is acting as equilibrium source of CO_2 and when CaO is obtained in its standard form, the CO_2 thermodynamic activity is equal to 1. When the decomposing surface is not an equilibrium source for the CO_2 molecules, this parameter is always less than 1 independently of the nature of the CaO produced. Thus the CO_2 thermodynamic activity, defined as in [18], can be taken as a parameter related to the thermally activated CO_2 surface steps, just as is the vaporization coefficient α_v of CO_2 from the $CaCO_3$ decomposing surface. Therefore, Eq. (10) becomes:

$$\frac{J_{CO_2}}{J_{CO_2,MAX}} = \frac{\alpha_{v,CO_2}}{a_{CaO}} \qquad (11)$$

The ratio between the experimental flux J_{CO_2} with the maximum predicted by the H–K–L equation ($J_{CO_2,MAX}$) is the decomposition coefficient α_d [16]; thus the meaning of this coefficient is:

$$\alpha_d = \frac{\alpha_{v,CO_2}}{a_{CaO}} \qquad (12)$$

In other words, the decomposition coefficient depends on a combination of vaporization and solid state steps. The ratio of the fluxes is experimentally measurable from kinetic experiments and from thermodynamic equilibrium data of the decomposition reaction. When α_d is less than one, the observation might be explained in term of non-equilibrium vaporization steps, or by the formation of a non-standard solid product, or by both processes.

If one can measure the thermodynamic activity of the CaO *independently* from the kinetic data, then Eq. (11) and/or Eq. (12) can give information on α_{v,CO_2}, i.e. on the irreversible and/or reversible character of the vaporization process that reduces the decomposition rate.

In the following we show how this approach can be developed from microstructure and structural data analysis on the solid product obtained from the same calcite decomposition.

Micrographic examination of the CaO obtained in Ref. [16] showed an approximately 30 μm thick CaO layer near the free-decomposing surface, which had a different texture from the outer layer. It was thought that the inner layer might be a metastable form of CaO. But Towe [27] showed, by TEM and XRD analysis, that even from the early stage of the calcite single crystal decomposition, the solid decomposition product is CaO with the peaks corresponding to the normal NaCl-type crystallographic structure. Fenwick [28] did the same kind of analysis on the same kind of calcite that was used in the kinetic studies and he agrees with Towe's results. He was able to characterize the CaO as rods of 10 nm cross-section. The rods are usually 300–700 nm long, and form two layers with different microstructures. Near the reacting surface, in the inner layer (10–50 μm thick), the rods are typically separated from their neighbors by pores, while rods of the outer layer are typically collapsed into bundles of ~1 μm cross-section separated by ~1 μm pores. These

data indicate that the open microstructure of the inner un-bundled rods is mechanically unstable and that strains can be engendered in it, but do not support the existence of a CaO phase of other than the normal NaCl crystal structure. These experimental results imply a correction in all the previous publications, including ours [16,18], where it is quoted that the vacuum decomposition of large calcite single crystals proceed through the formation of a metastable phase of CaO.

Powell and Searcy [29] made surface area measurements of the CaO formed by complete isothermal decomposition of calcite single crystals in vacuum. They showed that the CaO surface area ranges from $127 \pm 10\,\mathrm{m^2/g}$ at 923 K to $60 \pm 20\,\mathrm{m^2/g}$ at 1173 K. Surface areas are not significantly reduced by annealing the CaO rods at 1173 K in vacuum. Beruto et al. [30], confirmed these measurements and proved that at 923 K the surface area of the CaO rods is independent of the time required for the vacuum decomposition reaction. For our CaO the surface energy is unknown, but presumably would be comparable with that of MgO (1.2–1.5 J/cm^2 [31]). If so for a CaO of N_2-accessible surface area of about $100\,\mathrm{m^2/g}$, it is possible to estimate a surface free energy contribution of about 5 kJ/mol. If this is the only source of extra-free energy over the free energy of the standard calcium oxide, the ratio $\Delta G_{CaO}/RT$ at 1000 K is 0.63 and the calcium oxide activity is 1.9.

In vacuum, calcite decomposition is pseudomorphous. As is true for many topotactic reactions see for instance [32,33], the CaO crystallites may be strained because the mobility of the CaO species at the reaction interface is low. If an amount equal to 5 kJ/mol is assumed to arise from strain, the calcium oxide activity rises from 1.9 to 3.5 at 1000 K.

The ratio between the experimental flux J_{CO_2} and the maximum flux predicted by the H–K–L equation ($J_{CO_2,MAX}$) is measured to be 10^{-5} at 973 K [16]. Consequently, equilibrium within the calcite [18] would require that:

$$\alpha_{CO_2} = a_{CaO} \times 10^{-5} \tag{13}$$

But at 1000 K the a_{CaO} does not exceed a few units, thus it can be concluded that the rate limiting step of decomposition of large calcite single crystal in vacuum is a highly irreversible surface or interfacial step. The apparent entropy calculated from the temperature dependence of the CO_2 activity eliminates desorption as rate limiting.

We undertook a number of experiments directed toward identifying how the solid product grew during decomposition and how that might or might not influence the decomposition rate. Studies by Ewing et al. [34] showed that when the CO_2 pressure was about 10^{-5} the sintering effect of the CO_2 on the CaO is negligible in the time of the decomposition reaction. Beruto et al. [35] suggested that to catalyze the oxide sintering a gas must chemically adsorb first and then diffuse into some layers of oxide to change the concentration of the diffusing species. CO_2 must be strongly bonded to the surface of the CaO rods as shown for CaO of lower specific surface [36], but the size of CO_2 (as carbonate ions) probably precludes significant solubility at low partial pressures.

Molecules of CO_2, before escaping from the reaction surface to the space surrounding the sample, must diffuse through the small pores between CaO rods. In the Knudsen regime this flux might become the rate limiting step when the barrier reaches a critical thickness [4,6] But the following analysis and experiments show that this possibility can be ruled out.

The probability that a vapor molecule entering one side of a porous barrier will emerge at the opposite side instead of being returned to the source is:

$$\Gamma = \frac{\beta}{\lambda} \tag{14}$$

where β is a constant with the units of a length and a magnitude of the order of the average pore cross-section and λ is the barrier thickness. If a vapor molecule that has returned to the source side has a probability α_C of undergoing back reaction, the fraction of vapor molecules Λ_1 that escape from the parent solid and also escape from the barrier is:

$$\Lambda_1 = \frac{\Gamma}{\Gamma + \alpha_C} \tag{15}$$

thus in order to obtain Λ_1 almost equal to 1, the requirement is:

$$\Gamma \gg \alpha_C \tag{16}$$

Roberts et al. [26] measured the value of β from experiments of transmission of CO_2 and He through aggregates formed by fully decomposing calcite slices in the same temperature and vacuum conditions. Most calcite samples were 0.5 mm thick, but some were 1 mm thick [16]. Thus Γ ranges between 5×10^{-4} and 10^{-3}. We do not known the activated complex for the effusion process from the reactive surface. But it must be one in which the CO_2 is strongly bonded to the CaO surface, as indicated by the high enthalpy and relatively low entropy calculated for the transition state. The CO_2 molecules that effuse into the CaO pores at constant temperature should be in a nearly equilibrium thermal state. When one of these molecule hits the reactive surface, its probability α_C of reacting to form the activated complex, if the nature of activate complex remains almost unchanged, should be equal to α_V. This statement, which is a consequence [37] of the microscopic reversibility principle [38] of elementary steps of a chemical reaction, applied to steady-state conditions, allows us to write:

$$\alpha_C \approx \alpha_V \tag{17}$$

Being α_V at least a factor 10 lower than Γ, Eq. (16) is satisfied and the CaO barrier produced by single crystal decomposition has a negligible effect on the escape flux.

4. MKST analysis of endothermic decomposition of calcite in particle beds heated in vacuum

To determine the inter-related influences of particle size, particle packing, and other parameters on the decomposition of calcite powders in vacuum we used experimental apparatus and materials described elsewhere [39].

In order to be consistent with the previous MKST analysis the weight loss measurements *must* be expressed in terms of molecular fluxes instead of the usual kinetic plot of α versus time [3,40]. To do so let us use a steady state approximation, which is often experimentally justified because the observed rates were nearly independent of time up to 50% of reaction.

Then the total number N of CO_2 molecules which are in the vapor phase in the cell will be constant with time. This leads to the mass balance:

$$(J_1 - J_2)\Omega_S = J_b\Omega_C \tag{18}$$

where J_1 is the flux density of CO_2 molecules provided by the calcite interfaces to the vapor, J_2 the flux density of CO_2 molecules that strike the reaction interface Ω_S and that can overcome any free energy barrier that inhibits calcite reformation, J_b the flux density that escapes from the cell into vacuum, and Ω_C the cross-section of the cell through which that flux escapes. In vacuum and in the molecular flux regime, the flux densities can be expressed by the H–K–L equations [4,5], as follows:

- $J_1 = (2\pi MRT)^{-1/2} P^0 \exp(-(G^* - G_c)/RT)$
- $J_2 = (2\pi MRT)^{-1/2} P_b \exp(-(G^* - G_b)/RT)$
- $J_b = C(2\pi MRT)^{-1/2} P_b$

where M is the molecular weight of CO_2, G^* the apparent free energy of activation of the decomposition reaction, G_c the free energy content of the calcite, G_b the sum of the free energy content of the solid product and of CO_2 at its standard pressure, P^0 the standard pressure, P_b the CO_2 pressure in the powder bed and C the transmission probability for the CO_2 to escape through the channels formed by the cell walls above the powder bed surface.

The free flux equations can be combined with the mass balance to yield:

$$J_b = \frac{[C\Omega_S P^0 \exp[-(G^* - G_c)]/RT}{(2\pi MRT)^{-1/2}[\Omega_S \exp[-(G^* - G_b)]/RT + C\Omega_C]} \tag{19}$$

Eq. (19) can be discussed under the boundary conditions:

- $\Omega_S \exp[-(G^* - G_b)/RT] \ll C\Omega_C$.

then the flux density is

$$J_b = \frac{\Omega_S[P^0 \exp[-(G^* - G_c)]/RT]}{\Omega_C(2\pi MRT)^{-1/2}} \tag{20}$$

and when the inequality is reversed, the flux density is

$$J_b = \frac{CP^0 \exp[-(G^* - G_c)]/RT}{(2\pi MRT)^{-1/2}} \tag{21}$$

It is important to note from these equations that, at constant temperature, in one case the flux density from the crucible is dependent upon the surface area of the decomposing particles, while in the second case it is not.

Fig. 3 is a log–log plot of the flux density from the crucible at 943 K as a function of particle size for a sample of 179 ± 2 mg weight. Each point of the plot is the average of 2–4 measurements, and the error bars indicate average deviations from the mean. It can be observed that the kinetics of decomposition of small calcite particles show the behavior predicted by Eq. (21), while the rate of large calcite obey Eq. (20).

The quantity:

$$J^* = \frac{J_b\Omega_C}{\Omega_S} \tag{22}$$

is the flux density from the decomposing $CaCO_3$ particles, being J_b the experimental flux density. During the first 50% of the decomposition for the three sets of large particles J^* ranges from $(5.7 \pm 0.7) \times 10^{-8}$ to $(4.8 \pm 0.9) \times 10^{-8}$ mol/cm^2 s. Flux densities measured in three studies of calcite single crystal decomposition in vacuum at the same temperature amounted to 6.5×10^{-8}, 2.2×10^{-8} and 1.3×10^{-8} [16,23,41]. Therefore the kinetic data measured in free-surface calcite decomposition predicts the kinetics of decomposition of coarsely ground calcite particles in open crucible. Consequently, the highly irreversible surface step that control the free-surface calcite decomposition, is still the rate limiting step for the decomposition of large calcite particles in open crucible and in vacuum.

But the values of J^* for the decomposition of small calcite particles are fairly independent from their surface area (1250–750 cm^2). The average value is $(1.5 \pm 0.2) \times 10^{-9}$ mol/cm^2 s at 943 K, much lower than the flux densities measured in the calcite single crystal decomposition studies. On this ground it is possible to state that the kinetic rate of decomposition of calcite single crystal in vacuum does not predict that of small calcite particles in open crucibles and in vacuum.

Fig. 4 shows that the time required to completely decompose calcite particles of 1.0–1.4 mm cross-section is independent of the height h to which particles are loaded in the crucible in the range $h = 0.5$ mm to at least $h = 1.5$ mm. This result is expected when back reaction is negligible and *each particle decomposes independently* of the others. But the time required for decomposition of ~3 μm particles is a linear function of sample height, as when the bed acts as an equilibrium source of the product vapor. For the 3 μm particles an increase in the number of particles does not change the flux from the bed, but simply reduces the net flux from each of the particles present. The reduction of the net flux from each particle is the kind of behavior that is predicted when CO_2 back reactions become important in approaching the equilibrium decomposition conditions. But the apparent equilibrium pressure, derived from these fluxes, is several orders of magnitude less than that for decomposition to bulk
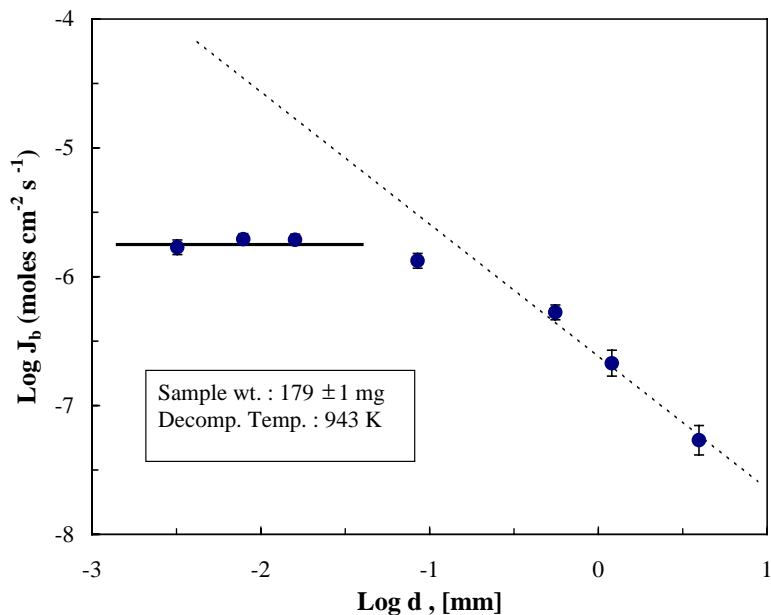
Fig. 3. Flux density of CO_2 from a crucible with samples of the same weight but different average particle sizes.

CaO. Identifying the reaction responsible became a focus of subsequent studies.

Ewing et al. [34] and Beruto et al. [42] proved that CO_2 catalyzed the sintering of CaO. If an equilibrium CO_2 pressure is established in the bed, the CaO surface decreases with the exposure time of CaO to CO_2 in the bed. In fact for the decomposition of the small particles in an open crucible the total time of decomposition is proportional to the sample height (see Fig. 4). Beruto et al. [30] investigated the pore structure of the CaO produced from the decomposition of

large and of fine calcite particles under similar experimental conditions. By means of mercury porosimetry measurements and N_2 adsorption at 78 K, they showed that a duplex pore structure is formed in the CaO produced from large calcite particles. The CaO surface area was $116 \pm 4\,m^2/g$ and independent of the extent of reaction. The volume occupied by the CaO aggregates is almost equal (98%) to that of the original calcite crystal. The 54% total porosity includes 42% pores of about 5 nm cross-section and 12% pores of about $10\,\mu m$ cross-section. We think that the duplex pore

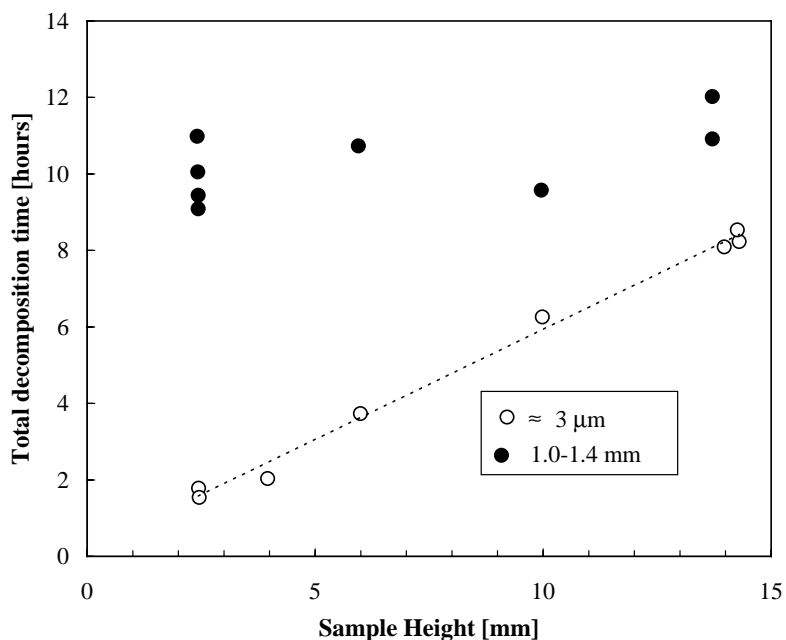Fig. 4. Dependence of calcite decomposition time on bed depth and particle size for about $3\,\mu m$ and 1.0–1.4 mm particles decomposed at 883 and at 943 K, respectively.

structure is formed by a diffusionless re-packing into bundles of initially relatively regularly spaced rod-shaped CaO crystallites. Such a diffusionless process would not obey the principle of microscopic reversibility.

No macropores have been observed in the more uniform mesoporous structure of 92 m^2/g CaO produced from decomposition of small calcite particles. The fact that a re-packing occurs in the oxide from large calcite particles is experimental evidence that suggests that size-dependent strains accumulate at the calcite–CaO rod interfaces. A state of stress corresponds to this state of strain. When the level of stress exceeds a critical value the mechanical stability of the CaO aggregate is broken. The formation of macropores would relieve the stresses. The CaO from small calcite particle decomposition evidently does not reach the critical level of stress.

5. Effects of calcite particle size and CO$_2$ pressure: irreversible, partially reversible, and reversible decomposition regimes

To clarify the nature of the reactants and products of the equilibrium described above, Darroudi and Searcy [41] measured rates of decomposition of calcite single crystals under CO$_2$ pressures in a range that extended from $10^{-5}P_{eq}$ to pressures higher than $10^{-1}P_{eq}$. They found that at 943 K the rates are essentially independent of CO$_2$ background pressures $<10^{-2}P_{eq}$, but decrease when the CO$_2$ pressure exceeds $10^{-1}P_{eq}$. Consequently, the apparent equilibrium pressure in the decomposition of large-single crystal calcite in vacuum can be set equal to $\approx 10^{-1}P_{eq}$. Since the kinetics of decomposition of large-single crystal in vacuum predicts the rate of decomposition of large calcite particles decomposing in an open crucible, this value can be considered also the equilibrium pressure of CO$_2$ in the beds of large calcite particles.

The ratio between the CO$_2$ vaporizing flux from the open crucible with small particles of calcite and the maximum H–K–L value is 4×10^{-4}. On account of Eq. (11), the equilibrium CO$_2$ pressure in the bed is

$$P_b = 4 \times 10^{-4}P_{eq} \qquad (23)$$

at 973 K if the activity of calcium oxide produced is equal to one. At 883 K this value is $2.2 \times 10^{-4}P_{eq}$. But

$$a_{CO_2}a_X = 1 \qquad (24)$$

Eq. (24) tells us that if a_{CO_2} is 10^{-4}, the activity of CaO must be 10^{+4} if CO$_2$ and CaO are in equilibrium with calcite. Accordingly, if the equilibrium is that described by Eq. (24), the extra free energy of formation of the unknown solid phase from the standard CaO must be +61 kJ/mol. For a CaO of about 90 m^2/g surface, which is produced from this decomposition, the actual extra free energy content is below 5 kJ/mol (see calculation in the above section). Thus, the maximum value for CaO activity that can be accounted for

by surface energy is about 2 for a reversible reaction [18]. The CaO crystallites do not have an high surface area, nor can they be sufficiently strained to account for such a high instability. Studies by Towes (27) and Fenwick (28) showed that no CaO metastable phase is present as a metastable product.

In seeking evidence that may reveal the nature of the mysterious equilibrium, Shukla [43] performed some very difficult, but enlightening, experiments. He used a sensitive pressure gauge to measure the CO$_2$ deficiency that could be produced in calcite as a function of temperature and CO$_2$ pressure. His apparatus was equipped with a quadrupole mass spectrometer to insure that water and other volatile impurities did not confuse the experiments. He found that he could reproduce equilibrium measurements by cycling up or down in CO$_2$ pressure, but only after his calcite particles desorbed irreversibly about 0.4 monolayers of CO$_2$. That observation implies almost half the CO$_3^{2-}$ ions of a surface monolayer are replaced by O^{2-} ions. When calcite particles are heated in vacuum, their surface layer(s) would lose still more CO$_2$ and become highly unstable.

Therefore, formation of CaO could start, not from the calcite surface, but from *a nonporous* Ca(O)$_{(1-x)}$(CO$_3$)$_x$ layer. If so, the reaction can be written as

$$CaCO_3(s) = Ca[(O)_{(1-x)}(CO_3)_x] + (1-x)CO_2 \qquad (25)$$
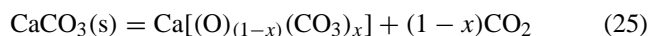
For this reaction, the gaseous CO$_2$ can be brought to equilibrium with the metastable CO$_2$-deficient calcite structure at a partial pressure much lower than $0.1P_{eq}$, as observed for the small particles of calcite in vacuum.

However, if Eq. (25) describes equilibrium decomposition of small calcite particles in open crucibles in vacuum, why should equilibrium not occur in the decomposition of large particles under the same conditions? In answer to this question we suggest that Eq. (25) describes equilibrium of CO$_2$ with a CO$_2$-deficient interface film that is maintained at constant thickness by stress-induced collapse of successive layers into the structure of normal CaO. In these circumstances, the CO$_2$ is in equilibrium with the CO$_2$-depleted surface layer(s) of calcite. But that layer undergoes a steady state, diffusionless retreat by collapsing into the ordered array of CaO rods and voids that are observed by SEM when larger crystals are decomposed.

This model is consistent with observations and interpretations in an excellent review article by Lyakhov [44] and by a relevant observation made many years ago by Bernal [45] on topotactic reactions. Misfit in dimensions between a parent and daughter solid phase produces strains when interface diffusion is slow. Thus, at the interface between the CO$_2$-deficient calcite layer and calcite, strains accumulate, since the volume occupied by the CaO rods plus pores is nearly the same as that of calcite (30). A larger interface would accumulate more strain than a smaller interface. When strains exceed a critical level, fragmentation of the interface would occur. This has been well documented by a study of hydration of large non-porous calcium oxide
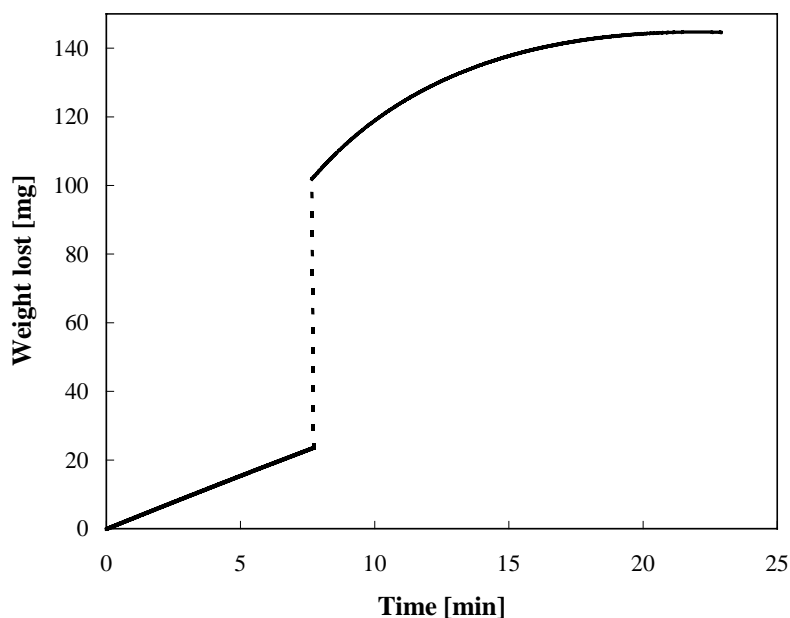
Fig. 5. Sudden sample ejection during isothermal heating of about 3 μm particle size powder in vacuum at 943 K.

surface and by small and porous calcium oxide particles with water vapor [46,47]. The nonporous particles undergo an interfacial hydration and suddenly develop a thin layer of hydroxide detached from the starting surface. The porous CaO can be hydrated completely without losing the external shape of CaO micrometric particles.

For the small calcite particles, the strain could increase as the CO_2 escaped from successive calcite surface layers until the stress reaches the ∼50 kJ/mol level needed to balance Eq. (25). Then the strained CO_2-deficient calcite layer(s) could relieve the stress by ejecting any remaining CO_2 as the CaO present in each layer collapses to add a layer of normal CaO to growing CaO rods. Fig. 5 shows that during the vacuum decomposition of calcite particles smaller than 50 μm, a sudden ejection of particles can occur. We think that this behavior, which could only be avoided by very slow heating to our run temperatures, is consistent with the formation of this mechanically unstable intermediate product. Indeed, the ejection cannot be a consequence of a sudden escape of gases trapped in pores, as had seemed possible. Shukla [43] looked for, but did not find, significant gas entrapment in calcite particles which were obtained from a variety of different sources. An exothermic decomposition like that of Eq. (25), could sometimes trigger auto-catalytic heating of surrounding particles to propagate the reaction throughout the bed and generate a sudden, but transient, increase of CO_2 pressure in the bed.

6. Major conclusions

- Calcite differs markedly from simple salts like sodium chloride in vaporizing incongruently, in vaporizing irre-

versibly, and in having an activation entropy that precludes desorption as the rate limiting step.
- The flux of CO_2 that desorbs from a calcite surface at 1000 K is ∼2×10^{-5} times the flux that would be measured in vacuum if the calcite acted like an unimpeded equilibrium vapor source.
- This high degree of irreversibility makes the reaction insensitive to background pressures of CO_2 as much as 1000 times the pressure from crystals or dispersed powders. For this reason, careful isothermal experimental measurements in vacuum agree with measurements in flowing inert gases. Consequently, the reaction is ideal for calibrating systems in different laboratories to eliminate systematic errors in measurements of temperature dependence and of weight loss or decomposition fluxes.
- The topotactic growth of initially ordered arrays of pores and single crystal rods of CaO inward from the original calcite surface, the kinetic data, and the sensitive CaO–CaCO_3–CO_2 thermodynamic study by Shukla (42) can all be explained by the assumption that the rate limiting step of thermal decomposition of calcite occurs in its surface and interface layers at any temperature, CO_2 pressure, calcite particle size, or sample size.
- At CO_2 pressures near the equilibrium decomposition pressure at 1000 K, CO_2 can be reversibly dissolved or evolved from the near-surface CO_2-depleted layers of the calcite. Then familiar kinetics of reversible chemical reactions apply, and the enthalpy of activation can be indistinguishable from the thermodynamic enthalpy as many investigators reported for systems that fostered near-equilibrium CO_2 pressures.
- At low CO_2 pressures, small calcite particles can decompose by a partial equilibrium process. The CO_2 is in

equilibrium with CO_2 in the calcite surface as CO_3 ions with CO_2 "vacant" sites occupied by oxide ions, but the calcite undergoes a steady state decomposition to CaO by a diffusionless separation into CaO and pores. In larger crystals and/or lower CO_2 pressures the decomposition becomes completely irreversible.

- The sudden ejection of powder shown by Fig. 5 during heating of pore-free calcite is evidence of an exothermic process that is triggered by neither a reduction in surface, nor crystal structure change, nor elimination of defects. It probably results from a reduction in interface strain that heats a powder bed and ejects a burst of CO_2 from the near-surface calcite.

Acknowledgements

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