

2-2.1.1 Decomposition

The most widely studied systems are CaCO_3 , MgCO_3 , and $\text{Mg}(\text{OH})_2$. We will focus on the basic thermodynamics, reaction kinetics and mechanism, and process parameters pertinent to the production of powders. Considering the thermodynamics, for the decomposition of CaCO_3 defined by Eq. (2.1), the standard heat (enthalpy) of reaction at 298K, ΔH_R° , is 44.3 kcal/ mol. The reaction is strongly *endothermic* (i.e., ΔH_R° is positive), which is typical for most decomposition reactions. This means that heat must be supplied to the reactant to sustain the decomposition. The Gibbs free energy change associated with any reaction is given by:

$$K = \frac{a_{\text{CaO}} a_{\text{CO}_2}}{a_{\text{CaCO}_3}} = P_{\text{CO}_2} \quad (2-3)$$

Where ΔG_R° is the free-energy change for the reaction when the reactants are in their standard state, R is the gas constant, T is the absolute temperature, and K is the equilibrium constant for the reaction. For the reaction defined by Eq. (2.1),

$$\Delta G_R = \Delta G_R^\circ + RT \ln K \quad (2-4)$$

Where a_{CaO} and a_{CaCO_3} are the activities of the pure solids CaO and CaCO_3 , respectively, taken to be unity, and a_{CO_2} is the activity of CO_2 , taken to be the partial pressure of the gas. At equilibrium, $\Delta G_R = 0$, and combining Eqs. (2.3) and (2.4), we get

$$\Delta G_R^\circ = -RT \ln P_{\text{CO}_2} \quad (2-5)$$

Kinetic investigations of decomposition reactions can provide information about the reaction mechanisms and the influence of process variables such as temperature, particle size, mass of reactant, and the ambient atmosphere. They are conducted isothermally or at a fixed heating rate. In isothermal studies, the maintenance of a constant temperature represents an ideal that cannot be achieved in practice, since a finite time is required to heat the sample to the required temperature. However, isothermal decomposition kinetics is easier to analyze. The progress of the reaction is commonly measured by the weight loss and the data are plotted as the fraction of the reactant decomposed α versus time t with α defined as:

$$\alpha = \frac{\Delta W}{\Delta W_{\max}} \quad (2-6)$$

Where ΔW and ΔW_{\max} are the weight loss at time t and the maximum weight loss according to the decomposition reaction, respectively. There is no general theory of decomposition reactions. However, a generalized α versus time curve similar to that shown in Fig. 2.1 is often observed. The stage A is an initial reaction, sometimes associated with the decomposition of impurities or unstable superficial material. B is an induction period that is usually regarded as terminated by the development of stable nuclei, while C is the acceleratory period of growth of such nuclei, perhaps accompanied by further nucleation, which extends to the maximum rate of reaction at D. Thereafter, the continued expansion of nuclei is no longer possible due to impingement and the consumption of the reactant, and this leads to a decay period, E, that continues until the completion of the reaction F. In practice, one or more of these features (except D) may be absent or negligible.

The molar volume of the solid product is commonly smaller than that for the reactant, so that very often, the product forms a porous layer around the nonporous core of reactant (Fig. 2.2). Like most solid-state reactions, the reaction is *heterogeneous* in that it occurs at a sharply defined interface. The kinetics may be controlled by any one of three processes: (1) the reaction at the interface between the reactant and the solid product, (2) heat transfer to the reaction surface, or (3) gas diffusion or permeation from the reaction surface through the porous product layer. As seen from Table 2.2, several expressions have been developed to analyze the reaction kinetics. It is generally assumed that the interface moves inward at a constant rate, so that for a spherical reactant of initial radius r_0 , the radius of the unreacted core at time t is given by

$$r = r_0 - Kt \quad (2-7)$$

Where K is a constant. When the reaction at the interface is rate controlling, the different expressions reflect the different assumptions on the nucleation and

growth of stable particles of the product from the reactant (*nucleation* equations in Table 2.2). If the nucleation step is fast, the equations depend only on the geometry of the model (*geometrical models*). The geometry for powder decomposition is complex.

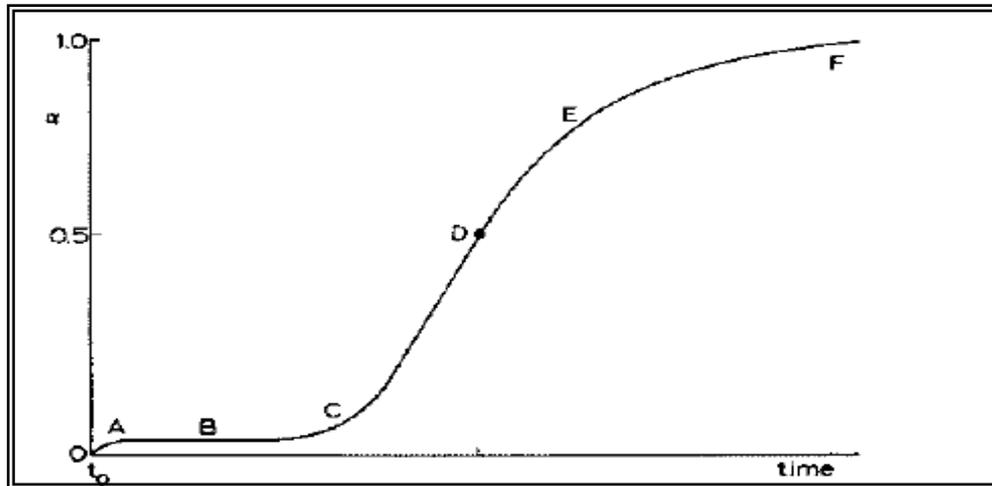


FIGURE 2.1 Generalized α versus time plot summarizing characteristic kinetic behavior observed for isothermal decomposition of solids. A represents the weight loss divided by the maximum weight loss.

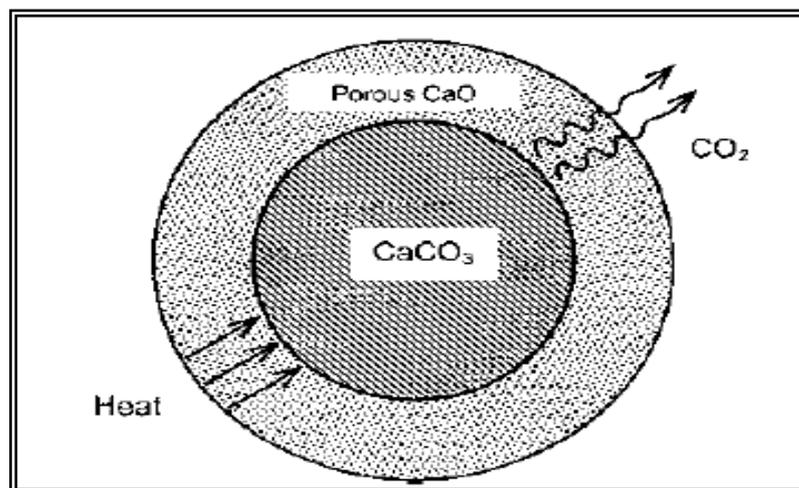


FIGURE 2.2 Schematic of the decomposition of calcium carbonate.

TABLE 2.2 Rate Equations for the Analysis of Kinetic Data in Decomposition Reactions

Equation ^a		Number
Nucleation		
Power law	$\alpha^{1/n} = Kt$	(1)
Exponential law	$\ln \alpha = Kt$	(2)
Avrami-Erofe'ev	$[-\ln(1 - \alpha)]^{1/2} = Kt$	(3)
	$[-\ln(1 - \alpha)]^{1/3} = Kt$	(4)
	$[-\ln(1 - \alpha)]^{1/4} = Kt$	(5)
Prout-Tompkins	$\ln \frac{\alpha}{1 - \alpha} = Kt$	(6)
Geometrical Models		
Contracting thickness	$\alpha = Kt$	(7)
Contracting area	$1 - (1 - \alpha)^{1/2} = Kt$	(8)
Contracting volume	$1 - (1 - \alpha)^{1/3} = Kt$	(9)
Diffusion		
One-dimensional	$\alpha^2 = Kt$	(10)
Two-dimensional	$(1 - \alpha) \ln(1 - \alpha) + \alpha = Kt$	(11)
Three-dimensional	$[1 - (1 - \alpha)^{1/3}]^2 = Kt$	(12)
Ginstling-Brounshtein	$(1 - \frac{2\alpha}{3}) - (1 - \alpha)^{2/3} = Kt$	(13)
Reaction Order		
First order	$-\ln(1 - \alpha) = Kt$	(14)
Second order	$(1 - \alpha)^{-1} = Kt$	(15)
Third order	$(1 - \alpha)^{-2} = Kt$	(16)

^aThe reaction rate constants K are different in each expression, and the times t are assumed to have been corrected for any induction period t_0 .

When large samples are used, the increasing thickness of the porous product layer may provide a barrier to the escape of the product gas. Kinetic equations for the decomposition of CaCO_3 controlled by the rate of removal of the product gas (CO_2) or the rate of heat transfer to the reaction interface have been developed by Hills. Table 2.2 includes equations for the reaction rate controlled by diffusion of the chemical components of the reactant. The kinetics of chemical reactions is frequently classified with respect to reaction order. Taking the simple case where a reactant A is decomposed:



The rate of the reaction can be written:

$$-\frac{dC}{dt} = KC^\beta \quad (2-9)$$

Where C is the concentration of the reactant A at time t , K is a reaction rate constant, and β is an exponent that defines the order of the reaction. The reaction is first order if $\beta = 1$, second order if $\beta = 2$, and so on. The kinetic equations for first-, second-, and third-order reactions are included in Table 2.2. When comparing experimental decomposition data with the theoretical equations, the

best fit to a particular equation is consistent with, but not proof of, the mechanism on which the equation is based. It is often found that the data can be fitted with equal accuracy by two or more rate equations based on different mechanisms. In seeking mechanistic information, the kinetic analysis should commonly be combined with other techniques such as structural observations by electron microscopy.

The observed rate of decomposition and the characteristics of the powder produced by the decomposition reaction depend on a number of material and processing factors, including the chemical nature of the reactants, the initial size and size distribution of the reactant particles, the atmospheric conditions, the temperature, and the time. Isothermal rate data measured at several different temperatures show that the rate of decomposition obeys the Arrhenius relation: the rate constant K in the kinetic equations is given by:

$$K = A \exp \frac{-Q}{RT} \quad (2-10)$$

Where A is a constant referred to as the *pre-exponential factor* or the *frequency factor*, Q is the activation energy, R is the gas constant, and T is the absolute temperature. Most reported activation energy values for CaCO_3 decompositions are close to the enthalpy of reaction. Equation (2.10) has been established for gas-phase processes by the collision theory of reaction rates. The reason why it should hold for decomposition reactions where a reactant is immobilized in the lattice of a solid phase has been the subject of some discussion.

Using the reaction described by Eq. (2.1) as an example, decomposition reactions are commonly carried out under conditions where the equilibrium is driven far to the right hand side. However, it is recognized that the decomposition kinetics of CaCO_3 will depend on the partial pressure of the CO_2 gas in the ambient atmosphere. High ambient CO_2 pressure drives the equilibrium to the left hand side. Studies of the effect of varying the ambient

CO₂ pressure on the decomposition kinetics of CaCO₃ show that the reaction rate decreases as the partial pressure of CO₂ increases.

In addition to the kinetics, the microstructure of the solid product particles is also dependent on the decomposition conditions. A feature of decomposition reactions is the ability to produce very fine particle size from a normally coarse reactant when the reaction is carried out under controlled conditions. In vacuum, the decomposition reaction is often *pseudomorphic* (i.e., the product particle often maintains the same size and shape as the reactant particle). Since its molar volume is lower than that of the reactant, the product particle contains internal pores. Often the product particle consists of an aggregate of fine particles and fine internal pores. In the decomposition of 1–10 μm CaCO₃ particles performed at ~923K, the specific surface area of the CaO product formed in vacuum is as high as ~100 m²/g with particle and pore sizes smaller than 10 nm. If the reaction is carried out in an ambient atmosphere rather than in a vacuum, then high surface area powders are not produced. In 1 atmosphere N₂, the surface area of the CaO particles is only 3–5 m²/g.

Sintering of fine CaO particles during decomposition is also catalyzed by increasing partial pressure of CO₂ in the ambient atmosphere. The atmospheric gas catalyzes the sintering of the fine particles, leading to larger particles and a reduction of the surface area. The sintering of fine MgO particles produced by decomposition of MgCO₃ or Mg(OH)₂ is catalyzed by water vapor in the atmosphere. High decomposition temperatures and long decomposition times promote sintering of the fine product particles, giving an agglomerated mass of low surface area powder. Although attempts are usually made to optimize the decomposition temperature and time schedule, agglomerates are invariably present so that a milling step is required to produce powders with controlled particle size characteristics.