

化學 및 冶金工程에서 流固體間에 일어나는 非觸媒的
反應의 速度論 : I. 單一非孔質固體의 反應

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Kinetics of Non-Catalytic Fluid-Solid Reactions in Chemical
and Extractive Metallurgical Processes: Part I.
Reaction of a Single Nonporous Particle

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요 약

이 總說의 目的은 流體와 固體間의 非觸媒的 反應速度論을 檢査함에 있다. 數年前까지만 하여도 工業的으로 매우 重要한 이런 種類의 反應에 對한 理論은 未開拓된 狀態에 있었던바 지난 몇年사이에 여러面으로 이 分野에 注視 할만한 進展이 있었다. 이 總說의 第一部에서는 單一非孔質固體의 反應을 要約하고 第二部에서는 單一多孔質固體의 反應을 檢討하려고 한다. 그리고 氣體를 媒介로하여 일어나는 二固體間의 反應이 第三部に 記述되겠으며 끝으로 工業的으로 重要한 多粉體系의 工程을 第四部에서 取扱하고자한다.

Abstract

Recent developments in the theory of the kinetics of non-catalytic fluid-solid reactions are reviewed. Until recently, the treatments of this important group of reactions have been in an embryonic stage. In the last few years, however, significant progresses have been made in various aspects of fluid-solid reactions. In Part I, the reaction of an initially nonporous solid will be reviewed. Part II will discuss the reaction of an initially porous solid, and the reactions between two solids proceeding through gaseous intermediates will be described in Part III. Finally, the treatment of industrially important multiparticle systems will be presented in Part IV.

Fluid-solid reactions occupy an important position in materials processing technology, encompassing such diverse processes as the combustion and gasification of solid fuels, the gaseous reduction of metal oxides, the roasting of sulfide minerals, the leaching of metal values from ores, and the calcination of limestone, to name but a few examples. Furthermore, certain industrially important reactions between two solids frequently proceed through gaseous intermediates. Such systems can be analyzed by considering the overall reaction as a pair of coupled gas-solid reactions as will be discussed in part III of this review.

Although most fluid-solid reactions involve a rather complex set of reaction steps and may require individual treatments, there are certain aspects of the overall reactions that are common to a wide range of systems. Such aspects are amenable to systematic generalization.

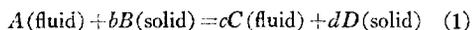
In this review we shall examine these aspects and their application to a number of reaction systems. In analyzing fluid-solid reactions, one must recognize the basic difference between a homogeneous and a heterogeneous reaction. In the latter, two or more phases are involved, and hence the reaction almost always occurs at an interface. It becomes readily apparent that mass and heat must be transported to and from this reaction interface. It follows that the analysis of a fluid-solid reaction must start from the consideration of the structure of the solid before, during, and after the reaction, namely one must ask the following questions before deciding on the method of attack:

1. Is the solid initially porous or nonporous?
2. Does the reaction form solid products, or leave solid ash behind?
3. Does the solid product or ash form a coherent layer, or peel off continuously?

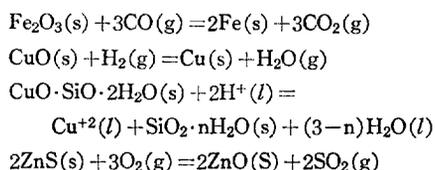
These questions must be borne in mind as we proceed with our discussions.

1.1 Elementary steps of fluid-solid reactions

Let us consider a fluid-solid reaction of the following type:



Examples of reactions of this type include:



The overall reaction process may involve the following individual steps, as sketched in Fig. 1.

- (1) Mass transfer of reactants and products between the bulk of the fluid and the external surface of the solid particle.
- (2) Diffusion of reactants and products within the pores of the solid.
- (3) Chemical reaction between the reactants in the fluid and in the solid.

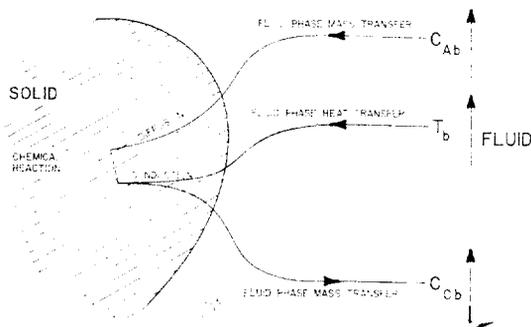


Fig. 1. Schematic diagram of the overall reaction process.

Only recently it has been recognized that the rate-controlling step can change depending upon reaction conditions, and thus rate information obtained under a given set of conditions may not be applicable under another set of conditions. Furthermore, frequently there may not be a single rate-controlling step because several steps may have more or less equal effects on determining the overall rate. The relative importance of these steps could also change in the course of reaction. Therefore, understanding how the individual reaction steps interact with each other is important in determining not only the rate-controlling step under given reaction conditions but also whether more than a single step must be considered in expressing the overall rate.

In addition to the above steps involving the chemical change of species, there are two other processes that may have significant influences on the overall rate: heat

transfer and changes in the structure of the solid during reaction. Many fluid–solid reactions either generate or consume heat. The heat of reaction must be transferred from the surrounding to where the reaction takes place, or vice versa. Heat transfer involves (1) convection and/or radiation between the surroundings and the solid surface, and (2) conduction within the solid. The chemical reaction and heat may cause sintering or other changes in the pore structure, which in turn could have significant effects on the overall reaction rate.

Since these elementary steps occur in many other types of reaction systems and thus not unique to fluid–solid reactions, we will not discuss these further and the reader is referred to other sources for detailed discussions. (For external mass transfer, see Refs. 1–7; for estimation methods of diffusivity and viscosity, Refs. 1 and 8; for diffusion through porous media, Refs. 3, 5, 9–11; for intrinsic kinetics on solid surfaces, Refs. 5, 12–14; for external heat transfer, Refs. 1 and 5; for conduction of heat in porous solids, Refs. 3, 15 and 16. These references are by no means exhaustive; they are meant to be some representative examples only.)

1.2 Introduction to the reaction of a single nonporous particle

The subsequent discussion in this Part I concerns the reaction of a single solid particle which is initially nonporous. If the reactant solid is initially nonporous, the reaction occurs at a sharp interface between the fluid and solid phases.

If no solid product is formed, as in the gasification or dissolution, or the solid product is removed from the surface as it is formed, the solid reactant will always be in contact with the bulk fluid and the size of the particle will diminish as the reaction progresses. If, on the other hand, a coherent layer of solid product is formed around the reactant solid, the reaction will occur at the interface between the unreacted and the completely-reacted zones. If the solid product is porous, the fluid reactant can reach the reaction interface by diffusing through the pores of the product

solid. If the product is nonporous, either the fluid species must diffuse into the solid by solid–state diffusion, or a constituent species of the solid reactant must diffuse to the surface to react with fluid reactants. The overall size of the solid will depend on whether the solid product has a greater or smaller volume than the reactant solid.

In the reaction of a nonporous solid and a fluid, the chemical reaction and mass transport are connected in series, making the analysis much easier than in the case of a porous solid.

In certain fluid–solid reactions, nucleation presents an important step. The growth of nuclei is a rather complex phenomenon. As the solid size becomes larger or the reaction temperature is raised, the time within which nucleation is important becomes a small portion of the total reaction time and thus nucleation becomes less important. We shall confine our discussion here to reactions occurring at a sharp boundary which advances in parallel to the external surface of the solid.

1.3 Reactions in which no solid product layer is Formed

Examples of such reactions are the dissolution of metal in acids, the formation of nickel carbonyl, the chlorination of metals, the roasting of cinnabar (HgS), the combustion of relatively pure carbon, among other. This type of a reaction may in general be described by the following scheme:

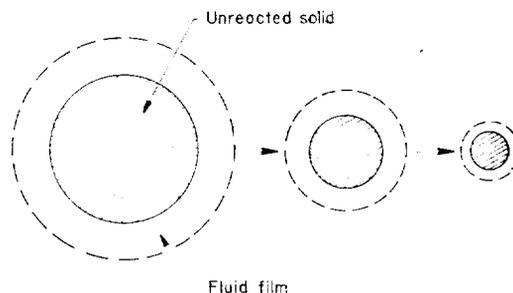
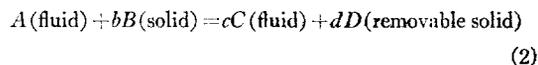


Fig. 2. Schematic diagram of a shrinking particle while reacting with the surrounding fluid.

where b , c , and d are stoichiometric coefficients.

Let us consider a spherical particle of a nonporous solid reacting with a fluid without forming a solid product, as illustrated in *Fig. 2*. The rate of consumption of the fluid species A at the solid surface by reaction is given as follows:

$$n_A = k \cdot f(C_{A_s}) \quad (3)$$

Where n_A is the rate per unit surface area, k is the reaction-rate constant, and f designates the dependence of the rate on concentration. Neglecting accumulation in the boundary layer surrounding the solid, the rate of chemical reaction must equal the rate at which fluid species are transferred between the surface and the bulk fluid. As discussed earlier, the rate of external mass transport is described by

$$n_A = k_m(C_{Ab} - C_{A_s}) \quad (4)$$

Thus, equating Eqs. (3) and (4), we obtain

$$k \cdot f(C_{A_s}) = k_m(C_{Ab} - C_{A_s}) \quad (5)$$

The overall rate can be determined by solving this equation for the unknown C_{A_s} , and substituting it back into either Eq. (3) or (4). Before obtaining the general solution including the effects of both chemical kinetics and external mass transfer, it is instructive to examine asymptotic cases first.

When $k \ll k_m$, Eq. (5) yields $C_{A_s} \approx C_{Ab}$. This is the case where external mass transfer offers little resistance, and thus chemical reaction controls the overall rate of reaction. The rate is then given by

$$n_A = k \cdot f(C_{Ab}) \quad (6)$$

On the other hand, when $k \gg k_m$, $f(C_{A_s})$ tends to zero which occurs when the concentration of A approaches its equilibrium concentration under the conditions prevailing at the surface of the solid, $C_{A_s}^*$. Thus, in this case chemical reaction offers little resistance and external mass transfer controls the overall rate. Substituting $C_{A_s}^*$ for C_{A_s} into Eq. (4), we obtain

$$n_A = k_m(C_{Ab} - C_{A_s}^*) \quad (7)$$

In the intermediate regime where both chemical kinetics and mass transfer offer significant resistances, the analysis will be illustrated with a first-order irreversible reaction. (The case of first-order, reversible reaction is described elsewhere⁵). Thus, we have

$$n_A = k C_{A_s} \quad (8)$$

$$\text{and } C_{A_s}^* = 0 \quad (9)$$

Solving Eqs. (4) and (8) simultaneously to eliminate C_{A_s} , we obtain

$$n_A = \frac{C_{Ab}}{\frac{1}{k} + \frac{1}{k_m}} \quad (10)$$

Equation (10) indicates the familiar result for first-order processes coupled in series that the resistances are additive. It is also noted that Eq. (10) reduces to either Eq. (7) or (8) under appropriate conditions.

In order to obtain the overall conversion vs. time, the rate of disappearance of A, n_A , must be equated with the rate of consumption of the solid B. From the stoichiometry of the reaction (2), we have

$$n_A = -\frac{\rho_B}{b} \frac{dr_c}{dt} \quad (11)$$

where ρ_B is the molar concentration of solid B and r_c is the radius of the solid at any time. Therefore, from Eqs. (10) and (11), we get

$$\frac{dr_c}{dt} = -\frac{bC_{Ab}/\rho_B}{\frac{1}{k} + \frac{1}{k_m}} \quad (12)$$

All parameters except k_m on the right-hand side of Eq. (12) are independent of r_c . If k_m could be considered to be independent of r_c , integration of Eq. (12) would be straightforward. In reality, however, k_m will vary with r_c .

Given such a relationship one can perform the integration to obtain r_c and hence the conversion as a function of time. An example of the procedure can be found elsewhere⁵. The general procedure can be illustrated as follows: Rearranging Eq. (12) and integrating,

$$t = \frac{\rho_B}{bC_{Ab}} \left[\frac{r_0 - r_c}{k} + \int_{r_c}^{r_0} \frac{dr_c}{k_m(r_c)} \right] \quad (13)$$

which gives the relationship between r_c and time. Conversion X is related to r_c by the following:

$$X = 1 - \left(\frac{r_c}{r_0} \right)^3 \quad (14)$$

where r_0 is the original radius of the solid. Equation (13) also shows that the time necessary to attain a certain r_c (and hence a certain conversion) is the sum of the time to attain the same r_c in the absence of mass-transfer resistance and the time to reach the same r_c under mass transfer control. This important result applies to any reaction system made up of first-order rate

processes coupled in series.

When the reaction accompanies a significant enthalpy change, considerations must be given to the transfer of heat as well as of mass. The complete equations involving heat conduction inside the solid as well as external heat transfer would be rather difficult to solve.

The formulation of the problem is in many ways similar to that in the case of a fluid-solid reaction forming a solid product. The effect of heat of reaction is much more pronounced in the latter case. Therefore, the detailed discussion of nonisothermal effect will be postponed until later when the system of shrinking unreacted core is described. Interested readers may consult other articles dealing with this subject.^{17,18)}

1.4 Reactions in which a product layer is formed

This type of a reaction is frequently encountered in chemical and extractive metallurgical processes, some typical examples being the combustion of ashy coals, the production of lime, the leaching of minerals from ores, the reduction of metal oxides, the oxidation of metals, and the roasting of sulfide ores. This group of reactions may in general be described by the following:

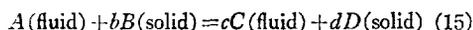


Figure 3 illustrates how the reaction progresses in this type of systems.

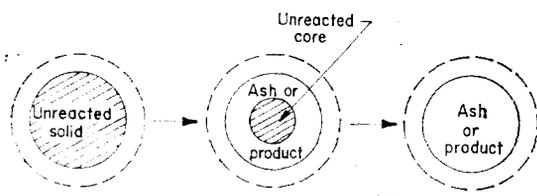


Fig. 3. Schematic diagram of a shrinking unreacted-core system.

The overall process can be divided into three steps: external mass transfer, diffusion through the product layer, and the chemical reaction at the interface between the unreacted and completely reacted zones. In the following we will formulate equations including all

these steps and show conditions under which one of the steps may become the controlling step. The criteria for these asymptotic regimes will also be developed. The analysis will be made for an isothermal system on a first-order, irreversible reaction occurring in an initially nonporous spherical particle. Generalization for non-first order or reversible reactions and other geometries can be found elsewhere.^{5,19)}

1.4.1 Mathematical formulation

At steady state the interfacial chemical reaction and mass transfer processes must occur at the same rate. Thus, in terms of species *A* the following three rates are equal:

Interfacial chemical reaction:

$$-N_A = 4\pi r_c^2 k C_{Ac} \quad (16)$$

Diffusion through the product layer:

$$-N_A = 4\pi r^2 D_e \frac{dC_A}{dr} \quad (17)$$

External mass transport:

$$-N_A = 4\pi r_p^2 k_m (C_{Ab} - C_{Ai}) \quad (18)$$

In the above, $-N_A$ is the total rate of transport of *A* into the sphere, r_c is the radius of the unreacted core,

C_{Ac} is the concentration of *A* at r_c

D_e is the effective diffusivity of *A* in the product layer, and

r_p is the radius of the sphere at any time.

The solution is obtained by applying the pseudo-steady-state approximation, that is, the movement of r_c is much slower compared with the time scale for establishing the concentration profile of *A*. Thus, as far as the diffusing of *A* is concerned, the position of r_c appears to be stationary and N_A is independent of position. Then, Eq. (17) can be integrated for constant N_A with Eqs. (16) and (18) as boundary conditions to give the concentration profile as a function of r_c . From the concentration profile thus obtained, N_A may be calculated using any of Eqs. (16)–(18). As before, the consumption of *A* can be related to that of solid *B* through the following relationship:

$$N_A = \frac{4\pi r_c^2 \rho_B}{b} \frac{dr_c}{dt} \quad (19)$$

If the volume of solid product is different from the

volume of initial solid reactant, r_p will change as reaction progresses. In many fluid-solid reactions the change is negligible. Therefore, we will discuss the case of constant r_p . The system with variable r_p will be discussed later.

The procedure for solving Eqs. (16)–(18) together with Eq. (19) is straightforward and may be found elsewhere.^{5,20} For constant r_p , the result can be expressed in terms of r_c as follows:

$$\frac{bkC_{Ab}}{\rho_B r_p} t = 1 - \frac{r_c}{r_p} + \frac{kr_p}{6D_e} \left\{ 1 - 3 \left(\frac{r_c}{r_p} \right)^2 + 2 \left(\frac{r_c}{r_p} \right)^3 + \frac{2D_e}{k_m r_p} \left[1 - \left(\frac{r_c}{r_p} \right)^3 \right] \right\} \quad (20)$$

It should be noted that, in the presence of an inert solid mixed with solid B, ρ_B represents only the number of moles of species B per unit volume of the entire solid mixture.

The following expression has been derived to systematically describe the conversion-vs.-time relationship for, an isothermal first-order reaction of a nonporous solid with a fluid in which the solid may be an infinite slab, an infinite cylinder, or a sphere⁵:

$$t^* = g_{F_p}(X) + \sigma_s^2 \left[P_{F_p}(X) + \frac{2X}{Sh^*} \right] \quad (21)$$

where

$$t^* \equiv \frac{bkC_{Ab}}{\rho_B} \left(\frac{A_p}{F_p V_p} \right) t \quad (22)$$

$$\sigma_s^2 \equiv \frac{k}{2D_e} \left(\frac{V_p}{A_p} \right) \quad (23)$$

$$Sh^* \equiv Sh \left(\frac{D_M}{D_e} \right) = \frac{k_m}{D_e} \left(\frac{F_p V_p}{A_p} \right); \text{ modified} \quad (24)$$

Sherwood number (24)

and A_p and V_p are the external surface area and the volume of the particle, respectively, and F_p is the particle shape factor which takes the value of 1, 2, or 3 for an infinite slab, an infinite cylinder, or a sphere, respectively. We note that $\left(\frac{F_p V_p}{A_p} \right)$ is the half thickness of an infinite slab, and the radius of an infinite cylinder or a sphere.

Other quantities in Eq. (21) are defined as follows:

$$g_{F_p}(X) \equiv 1 - (1-X)^{1/F_p} \quad (25)$$

$$P_{F_p}(X) \equiv X^2 \quad \text{for } F_p=1$$

$$\equiv X + (1-X) \ln(1-X) \quad \text{for } F_p=2 \quad (26)$$

$$\equiv 1 - 3(1-X)^{2/3} + 2(1-X) \quad \text{for } F_p=3$$

and we also used the relationship that

$$X = 1 - \left(\frac{r_c}{r_p} \right)^{F_p} = 1 - \left(\frac{A_p r_c}{F_p V_p} \right)^{F_p} \quad (27)$$

1.4.2 The case of changing particle size

The case in which particle size changes during the reaction may be solved⁵ by using the following relationship in integrating Eq. (17):

$$(r_p)^{F_p} \text{ at any time} = Z(r_p)^{F_p} \text{ original} + (1-Z)(r_c)^{F_p} \quad (28)$$

where Z is the volume of the product solid formed from a unit volume of the reactant solid. If we neglect the change of k_m with particle size, the solution is of the same form as Eq. (21) except that the following definition of $P_{F_p}(X)$ should be used:

$$P_{F_p}(X) \equiv ZX^2 \quad \text{for } F_p=1$$

$$\equiv \frac{[Z + (1-Z)(1-X)] \ln[Z + (1-Z)(1-X)]}{Z-1} + (1-X) \ln(1-X) \quad \text{for } F_p=2 \quad (29)$$

$$\equiv 3 \left\{ \frac{Z - [Z + (1-Z)(1-X)]^{2/3}}{Z-1} - (1-X)^{2/3} \right\}$$

for $F_p=3$

We note that, as Z approaches unity, Eqs. (29) reduce to Eqs. (26).

1.4.3 Additivity of reaction times

It is seen in Eq. (21) that the time required to attain a certain conversion is the sum of the times to reach the same conversion under the control of the three separate steps, the first term being that of chemical reaction, the second that of product-layer diffusion, and the third that of external mass transport. This is analogous to the result obtained for reactions in which no solid product layer is formed, given by Eq. (13).

1.4.4 The importance of σ_s^2

It is noted that σ_s^2 provides the numerical criteria for establishing the respective regimes of chemical reaction and diffusion controls. For porous solids, Sh^* is usually quite large due to the fact that D_e is about an order of magnitude smaller than the molecular diffusivity. Thus,

external mass transport plays only a secondary role to the diffusion through the product layer. Therefore, we will examine the effect of the shrinking-core reaction modulus, σ_s^2 , for $Sh^* = \infty$. Figure 4 shows the conversion function *vs.* time for various σ_s^2 . When σ_s^2 is larger than 10, the system is controlled by the diffusion through the product layer. When σ_s^2 approaches ∞ , Eq. (21) can be rearranged to give

$$t^* \equiv \frac{2bF_p D_c C_{Ab}}{\rho_B} \left(\frac{A_p}{F_p V_p} \right)^2 t = g_{F_p}(X) + \frac{2X}{Sh^*} \quad (30)$$

Thus, we have established important criteria in terms of σ_s^2 as follows:

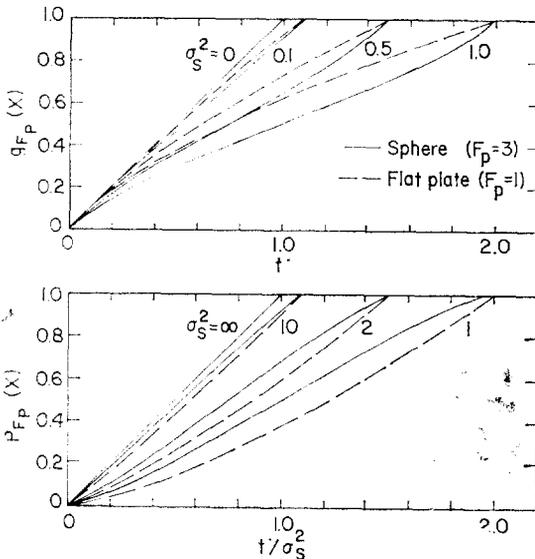


Fig. 4. Effect of σ_s^2 on conversion *vs.* time relationship for the reaction of a nonporous solid with a fluid (Adapted from J. Szekely, J. W. Evans, and H. Y. Sohn, "Gas-Solid Reactions," Academic Press, in press).

When $\sigma_s^2 \leq 0.1$, chemical reaction controls and when $\sigma_s^2 \geq 10$, diffusion through product layer and external mass transfer controls the over-all rate. The criteria are general in that its numerical values for defining the asymptotic regimes are the same for all three geometries considered.

We can determine k and D_c from experimental data obtained in the chemical-reaction-controlled and diffusion-controlled regimes, respectively.

1.4.5 Comments regarding the shape factor F_p

An advantage of Eq. (21) and the definitions of dimensionless quantities using F_p , A_p , and V_p (for example using $F_p V_p / A_p$) rather than a characteristic dimension such as radius) is that the equation can be expected to hold approximately valid for geometries other than the three basic ones used in obtaining the result, provided that A_p and V_p are known and F_p can be estimated suitably. For examples, Eq. (21) is expected to be valid for a cube or a cylinder whose diameter is equal to its length if $F_p=3$ is used. A cylinder whose length is finite but greater than its diameter will have an F_p between 2 and 3. For a particle which has dimensions that are 'more or less' equal in these directions, F_p may be assumed to be 3. A particle with two more or less equal dimensions but a long third dimension can be assumed to have F_p equal to 2.

1.4.6 Further remarks

It is seen in Fig. 4 that the relationships between $g_{F_p}(X)$ and time is approximately linear for σ_s^2 as large as 0.5 where significant diffusional resistances are present. This shows that one cannot assume chemical reaction control based only on the linear relationship between $g_{F_p}(X)$ and time. Such mistakes have often been made in the past. On the other hand, $P_{F_p}(X)$ *vs.* t^*/σ_s^2 is seen to be approximately linear for σ_s^2 as small as unity where chemical reaction and diffusion are of equal importance. Again, the existence of a linear relationship between $P_{F_p}(X)$ and time does not guarantee the control by product-layer diffusion. A more reliable method would be to vary the particle size and test if the reaction time is proportional to the size of the particle or its square. Remarks may be made at this point regarding the Jander equation²¹⁾ which has been used to describe a diffusion-controlled gas-solid reaction in a spherical solid.^{22,23)}

$$[1 - (1 - X)^{1/3}]^2 = \frac{2bD_c C_{Ab}}{\rho_B F_p^2} t \quad (31)$$

This equation was obtained assuming that the product layer around the spherical particle is flat. It has been

shown⁵⁾ that, when the conversion is less than about 40%, this equation shows a reasonable agreement with the exact solution of Eq. (30) with $Sh^* = \infty$. As conversion increases, the assumption of flat product layer becomes inapplicable and the Jander equation becomes grossly erroneous. In fact, as can be seen by comparing Eqs. (30) and (31), the Jander equation does not even give the correct time for complete conversion. Furthermore, Carter²⁴⁾ has shown, using the data on the oxidation of nickel particles, that the Jander equation becomes clearly inapplicable at conversions higher than 60%. Thus, the exact relationship given by Eq. (30) should be used instead of the Jander equation.

1.5 Nonisothermal reactions in shrinking-unreacted-core systems

When the reaction involves a substantial enthalpy change, temperature gradients will develop within the particle. The reaction rate may be significantly influenced by this temperature difference. With an exothermic reaction, the increased temperature in the solid will enhance the reaction rate. The rate, however, will not increase indefinitely because, when the chemical reaction rate is very fast, diffusion through the product layer will control the overall rate. The rate of diffusion is relatively insensitive to further increases in temperature. Another interesting aspect of exothermic gas-solid reactions is the possible existence of multiple steady states and thermal instabilities.

1.5.1 Mathematical formulation

For a nonisothermal reaction system, energy balance is needed in addition to mass balance over the solid particle. To facilitate mathematics, we will develop the equations for a first-order, irreversible reaction. We will also assume that the effective diffusivity, the thermal conductivity and total concentration are constant within the temperature ranges. The energy balance equations are analogous to mass balance equations given by Eqs. (16)–(18). We will develop the equations for solids with small heat capacities. Then, the energy equations in a spherical shrinking-core system are given

as follows: At reaction interface:

$$Q = 4\pi r_c^2 k(T_c) C_{Ac} (-\Delta H) \quad (32)$$

where T_c is the temperature at the reaction interface.

Conduction through the product layer:

$$Q = 4\pi r^2 \lambda_e \frac{dT}{dr} \quad (33)$$

where λ_e is the effective thermal conductivity of product layer. External heat transfer:

$$Q = 4\pi r_p^2 h(T_s - T_b) \quad (34)$$

where T_s and T_b are the external surface and the bulk temperatures, respectively.

The solution can be obtained by determining C_{Ac} and T_c from Eqs. (16)–(18) and (32)–(34), with k in Eq. (32) evaluated at T_c . In keeping with our assumptions, D_e , λ_e , k_m , and h are kept constant. Equations (32)–(34) are solved using a pseudo-steady state assumption, that is, at any time Q is constant at any r . The results are as follows⁵⁾:

$$\frac{C_{Ac}}{C_{Ab}} - 1 - [\sigma_s(T_b)]^2 \left\{ \frac{1/Sh^* + P'_{Fp}(X)}{g'_{Fp}(X)} \right\} \exp \left[\gamma \left(1 - \frac{T_b}{T_c} \right) \right] = 0 \quad (35)$$

and

$$\frac{T_c}{T_b} - 1 - \beta [\sigma_s(T_b)]^2 \frac{C_{Ac}}{C_{Ab}} \left\{ \frac{1/Num^* + P'_{Fp}(X)}{g'_{Fp}(X)} \right\} \exp \left[\gamma \left(1 - \frac{T_b}{T_c} \right) \right] = 0 \quad (36)$$

where

$$\gamma \equiv E/R_g T_b \quad (37)$$

$$\beta \equiv \frac{(-\Delta H) D_e C_{Ab}}{\lambda_e T_b} \quad (38)$$

$$Num^* \equiv \frac{h}{\lambda_e} \left(\frac{F_p V_p}{A_p} \right) \quad (39)$$

and $g'_{Fp}(X)$ and $P'_{Fp}(X)$ represent the derivatives with respect to X of $g_{Fp}(X)$ and $P_{Fp}(X)$, respectively. C_{Ac} and T_c can now be determined for each conversion X by solving Eqs. (35) and (36) simultaneously. The conversion -vs.-time relationship is obtained by substituting C_{Ac} and T_c into Eq. (16), and combining it with Eq. (19) together with Eq. (27).

1.5.2 Multiple steady states and thermal instability

These phenomena occur due to the fact that for an exothermic reaction Eqs. (35) and (36) may have

more than one solution at a fixed conversion. This can be best explained by comparing the rates of heat generation at and conduction away from the reaction interface when the interface is at a given r_c .

Thus, from Eq. (32),

$$Q_{\text{generation}} = 4\pi r_c^2 k(T_c) C_{Ac} (-JH) \quad (40)$$

and from Eqs. (33) and (34),

$$Q_{\text{conduction}} = \lambda_c (A_p/V_p) (T_c - T_b) \left[\frac{g'_{FB}(X)}{1/Nu^* + P'_{r,c}(X)/2} \right] \quad (41)$$

In deriving Eq. (41), we again made use of Eq. (27). The heat generation is typically an S-shaped function of T_c : At a low T_c the reaction is chemically controlled and the reaction rate increases exponentially with T_c . As T_c increases, chemical kinetics becomes fast and the overall reaction is controlled by the product-layer diffusion which increases very slowly with temperature. The conduction term given by Eq. (41) is essentially a straight line with respect to T_c . Thus, there exist the possibility of three solutions for T_c and hence C_{Ac} , as shown in Fig. 5. Of the three solutions, the middle solution is unstable and cannot exist in reality. The upper solution is usually controlled by diffusion, whereas the lower solution is controlled by chemical reaction due to the low temperature and hence slow reaction rate.

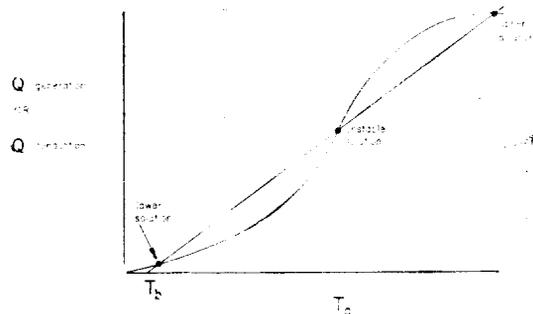


Fig. 5. Schematic diagram of the possible existence of multiple steady state.

Figure 5 represents the possible relative positions of $Q_{\text{generation}}$ and $Q_{\text{conduction}}$ at a certain r_c . During the reaction, r_c Change with time and the position of these curves will also change. These changes may occur such that no sudden change in T_c is experienced. But

under conditions depicted in Fig. 6, a sudden transition from the lower to the upper operating condition will occur, resulting in a thermal instability. In this system, the bulk gas is maintained at temperature T_b . The reaction starts at the external surface of the solid where heat transfer is rapid and hence the reaction temperature is not much higher than T_b , as shown by point A. At this low temperature, chemical reaction is likely to control the overall rate. As reaction progresses into the interior of the particle, heat transfer becomes slower and point B is reached followed by a rapid transition to point B'. Thus, the system is "ignited" to the upper reaction regime, and will be in general operated at a state represented by point C. As the reaction progresses further (or in a system starting at point C), the system may go through point D at which a sudden jump to point D' occurs causing an "extinction" of the reaction.

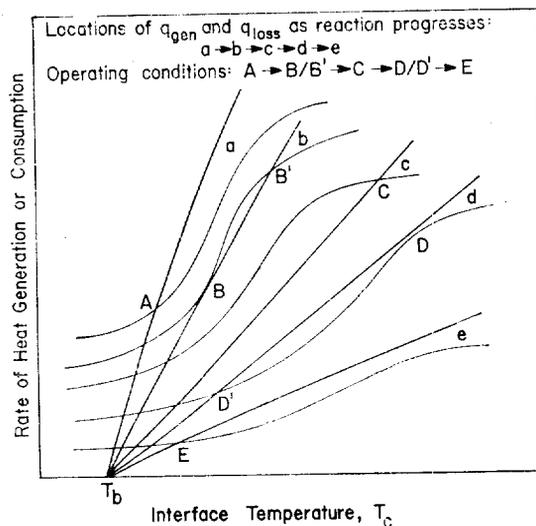


Fig. 6. Thermal balance at the reaction interface (Adapted from J. Szekeley, J. W. Evans, and H. Y. Sohn, "Gas-Solid Reactions", Academic Press, in press).

Criteria have been developed for the possibility of a thermal instability in gas-solid reactions^{20, 25, 26}. In these studies the heat capacity of the solid is assumed to be negligible. Wen and Wang²⁷ have discussed the

effect of solid heat capacity in a nonisothermal gas-solid reaction.

1.5.3 Maximum temperature rise in diffusion-controlled gas-solid reactions

Excessive temperatures occurring in gas-solid reactions may cause severe structural changes such as serious sintering which may close pores, thus hindering further reaction. It is, therefore, of practical importance to be able to predict the magnitude of the maximum temperature that the solid may encounter in the course of reaction. A rigorous solution could be found from T_c obtained by solving Eqs. (35) and (36) for various conversion values. This procedure, however, is rather tedious. An alternative procedure is possible by recognizing that, if an appreciable temperature rise is attained within the solid, the reaction is likely to be controlled by diffusion in the product layer, as discussed earlier. Luss and Amundson²⁸⁾ obtained a numerical solution for the maximum temperature rise for diffusion-controlled gas-solid reactions occurring in a spherical particle. It is noted here that, if the reaction is controlled by diffusion the solution is identical whether the solid is initially nonporous or porous. Sohn²⁹⁾ has obtained an analytical solution which is exact for an infinite slab and is approximately correct for a particle of other geometries. He obtained, from the analytical solution, useful asymptotic solutions for the prediction of maximum temperature rise. Only the final solutions will be presented below. Interested readers are referred to the original article for detailed derivations. Sohn²⁹⁾ showed that the temperature rise in the solid when the reaction front is at a certain position is given by the following:

$$\theta = 2Ae^{-\alpha^2} [D(x) - D(\alpha)] \quad (42)$$

where

$$\theta \equiv \frac{h(T_s - T_b)}{b(-\Delta H)D_s C_{Ab}} \left(\frac{F_p V_p}{A_p} \right) \quad (43)$$

$$A \equiv \left(\frac{h}{\rho_s c_s} \right) \left(\frac{\rho_B F_p}{h D_s C_{Ab}} \right) \left(\frac{F_p V_p}{A_p} \right) \quad (44)$$

(Here, ρ_B is the molar concentration of only the reactant B in the solid which might contain other inert solids, and ρ_s is the density of the solid including the

inerts if any.)

$$x \equiv \frac{\sqrt{A}}{2} \left(\delta + \frac{1}{Sh^*} \right); \quad \delta \equiv 1 - \frac{r_c}{r_p} \quad (45)$$

$$\alpha \equiv \frac{1}{Sh^*} \frac{\sqrt{A}}{2} \quad (46)$$

and $D(x)$ is defined by the Dawson's integral

$$e^{-w^2} D(w) \equiv e^{-w^2} \int_0^w e^{t^2} dt \quad (47)$$

The value of which is tabulated in the literature^{29-31).}

The maximum temperature rise can be obtained from the maximum value of θ at a corresponding position r_c . However, the maximum temperature rise can be explicitly determined from the following asymptotic and approximate solutions of Eq. (42)²⁹⁾: For a large Sh^* (thus small α), Eq. (42) reduces to

$$\theta = \sqrt{2A} e^{-\alpha^2} D(\alpha) \quad (48)$$

From the maximum value of the Dawson's integral³⁰⁾, we get

$$\theta_{max, Sh^* \rightarrow \infty} = 0.765 \sqrt{A} \quad (49)$$

which occurs at

$$\delta = \frac{1.31}{\sqrt{A}} \quad (50)$$

This large Sh^* asymptote is recommended for $\alpha \leq 0.1$.³⁰⁾

For large values of α ($1 \leq \alpha$), the asymptotic solution is

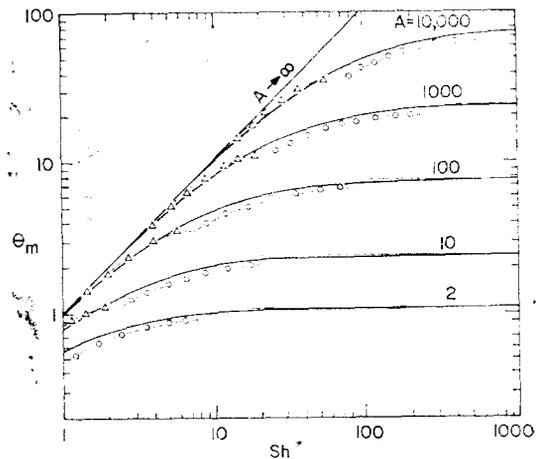


Fig. 7. Asymptotic and approximate analytical solutions for the maximum temperature rise. — Exact solution; --- Asymptotic solution ($\alpha \leq 0.1$); —O—O— Approximate solution ($0.1 < \alpha < 1$); —A—A— Approximate solution ($1 < \alpha$).

[Adapted from H. Y. Sohn, *AICHE J.*, 19 (1973), 191.]

$$\theta_{max, \alpha \rightarrow \infty} = Sh^* \left(\frac{1}{1 + 1/\alpha^2} \right) \quad (51)$$

For $0.1 < \alpha < 1$,

$$\theta_{max} = \sqrt{2A} \exp \left[- \left(\frac{\alpha + \alpha^{\sqrt{2}} + 2}{2} \right)^2 \right] \left[D \left(\frac{\alpha + \alpha^{\sqrt{2}} + 2}{2} \right) - D(\alpha) \right] \quad (52)$$

The asymptotic and approximate solutions are shown in Fig. 7. together with the exact solution obtained from Eq. (42).

1.6 Concluding remarks

The reaction of a nonporous solid with a fluid has been discussed and solutions to the governing equations have been derived. We have attempted a systematic generalization at the sacrifice of some less important details. As a result, we were able to establish an important criterion in σ_c^2 for determining the asymptotic regimes of chemical-reaction-controlled or diffusion-controlled reactions. Another consequence of this approach is the generalization for various geometries. Thus, the numerical values of σ_c^2 characterizing the asymptotic regimes are the same for all geometries.

The shrinking-unreacted-core model is attractive for its simplicity. But it should be noted that this is valid only for the reaction of a nonporous solid occurring at a well-defined sharp reaction interface. Various previous investigators have applied this model, mainly for its simplicity, to the reaction of a porous solid where chemical reaction occurs in a diffuse zone rather than at a sharp interface. This is permissible only for diffusion-controlled reactions for which mathematical expressions are identical. In general, the application of the shrinking-core model to the reaction of porous solids results in erroneous analyses of experimental data: incorrect dependence of the reaction rate on different reaction conditions (for example, activation energy) and various physical parameters (for example, the dependence of rate on particle size). The proper analysis of the reaction of porous solids with fluids will be discussed in Part II of this review.

Nomenclature

A	dimensionless quantity defined by Eq. (44), or area
A_s	external surface area of the pellet
b	number of moles of solid B reacted by one mole of fluid reactant A
C_s	specific heat of the particle including the inert solid, if any
C	molar concentration of fluid species
C^*	equilibrium molar concentration of fluid species
D_s	effective diffusivity in porous solid
F	shape factor (=1, 2 and 3 for flat plates, long cylinders, and spheres, respectively)
$g(x)$	conversion function defined by Eq. (25)
h	external heat transfer coefficient
$(-\Delta H)$	molar heat of reaction
k	reaction-rate constant
K_m	external mass transfer coefficient
Nu^*	the modified Nusselt number defined by Eq. (39)
$p(X)$	conversion function defined by Eq. (26)
r	distance from the center of symmetry in a nonporous particle
Sh, Sh^*	the Sherwood and the modified Sherwood numbers, respectively, defined in Eq. (24)
t	time
t^*, t^+	dimensionless times defined by Eqs. (22) and (30), respectively
T	temperature
V	volume
X	parameter defined by Eq. (45), or distance coordinate in Eq. (60)
X	fractional conversion of the solid
Z	volume of solid product formed from unit volume of initial solid

Greek symbols

α	dimensionless quantity defined by Eq. (46)
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β	dimensionless quantity defined by Eq. (38)
γ	dimensionless quantity defined by Eq. (37)
δ	dimensionless variable defined by Eq. (46)
θ	dimensionless temperature defined by Eq. (43)
λ_e	effective thermal conductivity of a porous solid
ρ	molar concentration of solid reactants
ρ_s	density of the particle including the inert solid, if any
σ_s	shrinking-core reaction modulus defined by Eq. (23)

Subscripts

A	fluid A
b	bulk property
B	solid B
c	value at reaction interface
o	original value
p	particle or pellet
s	value at external surface, or for entire solid including inert solid, if any

References

- R. B. Bird, W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena", Wiley, 1960.
- E. E. Petersen, "Chemical Reaction Analysis," Prentice-Hall, 1965.
- C. N. Satterfield, "Mass Transfer in Heterogeneous Catalysis," MIT Press, 1970.
- J. Szekeley and N. J. Themelis, "Rate Phenomena in Process Metallurgy," Wiley, 1971.
- J. Szekeley, J. W. Evans, and H. Y. Sohn, "Gas-Solid Reactions," Academic Press, to be published in 1976.
- V. G. Levich, "Physicochemical Hydrodynamics," Prentice-Hall, 1962.
- D. Kunii and O. Levenspiel, "Fluidization Engineering," Wiley, 1969.
- R. C. Reid and T. K. Sherwood, "Properties of Gases and Liquids," 2nd. ed., McGraw-Hill, 1966.
- J. M. Smith, "Chemical Engineering Kinetics," 2nd ed., McGraw-Hill, 1970.
- E. A. Mason and T. R. Marrero, *Adv. in Atomic and Molecular Physics*, **6** (1970), 155-232.
- T. R. Marrero and E. A. Mason, *J. Phys. Chem. Ref. Data*, **1** (1972), 1-118.
- J. M. Thomas and W. J. Thomas, "Introduction to the Principles of Heterogeneous Catalysis," Academic Press, 1967.
- O. A. Hougen and K. M. Watson, "Chemical Process Principles, Part 3 Kinetics and Catalysis," Wiley, 1947.
- K. J. Laidler, in "Catalysis", ed. by P. H. Emmett, Vol. 1, p. 75, 119, 195, Reinhold, 1954.
- J. Francl and W. D. Kingery, *J. Am. Ceram. Soc.*, **37** (1954), 99.
- A. V. Luikov, A. G. Shashkov, L. L. Vasillics, and Y. E. Fraimon, *Int. J. Heat Mass Trans.*, **11** (1968), 117.
- D. A. Frank-Kamenetskii, "Diffusion and Heat Transfer in Chemical Kinetics," 2nd ed., Plenum press, 1969.
- M. F. R. Mulcahy and I. W. Smith, *Rev. Pure and Appl. Chem.*, **19** (1969), 81.
- H. Y. Sohn and J. Szekeley, *Can. J. Chem. Eng.*, **50** (1972), 674.
- J. Shen and J. M. Smith, *Ind. Eng. Chem. Fundls.*, **4** (1965), 293.
- W. Jander, *Z. Anorg. Allgem. Chem.*, **163** (1927) 1.
- F. Habashi, "Extractive Metallurgy, Vol. 1 General Principles," Chap. 8, Gordon and Breach, 1969.
- P. P. Budnikov and A. M. Ginstling, "Principles of Solid State Chemistry, Reaction in Solids," trans. and ed. by K. Shaw, Chap. 5, McLaren and Sons (London), 1968.
- R. E. Carter, in "Ultrafine Particles," ed. by W. E. Kuhn, p. 491, Wiley, 1963; *J. Chem. Phys.*, **35** (1961), 1137.
- R. Aris, *Ind. Eng. Chem. Fundls.*, **6** (1967), 316.

26. G. S. G. Beveridge and P. J. Goldie, *Chem. Eng. Sci.*, **23** (1968), 913.
27. C. Y. Wen and S. C. Wang, *Ind. Eng. Chem.*, **62** (8) (1970), 30.
28. D. Luss and N. R. Amundson, *AIChE J.*, **15** (1969), 194.
29. H. Y. Sohn, *AIChE J.*, **19**, (1973), 191; **20** (1974), 416.
30. M. Abramowitz and I. A. Stegun, "Handbook of Mathematical Function," Dover Publications Inc., 1965.
31. J. B. Rosser, "Theory and Application of $\int_0^z e^{-x^2} dx$ and $\int_0^z e^{-p^2 y^2} dy \int_0^y e^{-x^2} dx$," Mapleton, House, 1948.

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