

化學 및 冶金工程에서 流固體間에 일어나는 非觸媒的
反應의 速度論 : III. 氣狀의 媒介體를 通하여
進行되는 固體間的 反應*

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Kinetics of Non-Catalytic Fluid-Solid Reactions in Chemical
and Extractive Metallurgical Processes : Part III
Reactions Between Solids Proceeding Through
Gaseous Intermediates*

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요 약

固體사이에서 일어나는 反應中에는 氣狀 媒介體의 存在로 因하여 그 反應速度가 매우 촉진되는 境遇가 많다. 近來에 이런 反應의 一種으로 分類 될 수 있는 工程이 상당수 工業化된 바 있다. 重要한 例의 하나로는 炭素나 石炭을 利用한 鐵鑛石의 “直接”還元을 들 수 있는데 이 工程은 在來式 熔鑛爐 工程의 대체 方法으로 注目을 받고 있다. 여러 種類의 카바이드 製造도 또한 例라 할 수 있다. 이런 種類의 反應은 그 數學的 處理가 容易치 않은 바 最近에 發表된 理論을 여기에 소개한다. 다음 第四部에서는 工業的으로 重要한 多粉體系의 反應을 檢討하고자 한다.

Abstract

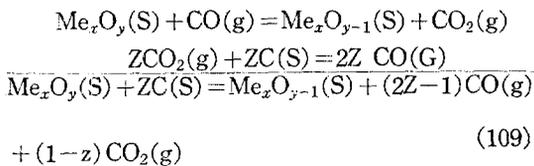
The reactions between solids the rates of which are greatly enhanced by gaseous intermediates are described in this article. In recent years many important industrial processes have been developed and may be classified as one of the reactions of this type. Notable examples include the “direct”

* Part II: Hwahak Konghak, 14(1976), 65.

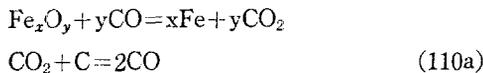
reduction of iron ores by carbon or coal as an alternative to the conventional blast furnace process. The formations of carbides are further examples. Recent developments on the mathematical analysis of this type of a system are discussed. In Part IV the treatment of multiparticle systems encountered in industrially important processes will be presented.

A number of reactions between solids are of considerable importance in pyrometallurgical processes. Some of these reactions are true solid-solid reactions which take place in the solid state between two species in contact with each other. Many other important reactions, however, occur through gaseous intermediates. These latter reactions may be considered as coupled gas-solid reactions, and can thus be analyzed in light of the mathematical analyses developed in the previous parts of this review.

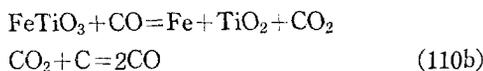
It is generally recognized that the carbothermic reduction of most metal oxides occurs through the gaseous intermediates of CO and CO₂. The reaction mechanism is:



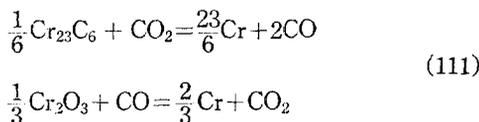
Some examples of this type of reactions are:
Reduction of iron oxides [58, 59]



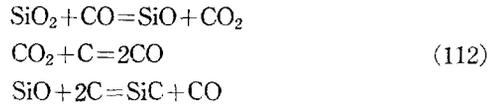
Reaction between ilmenite and carbon [60];



Reaction between chromium oxide and chromium carbide [61];

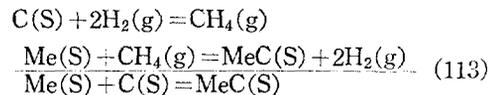


Recent evidence [63] has shown that the formation of silicon carbide proceeds according to the following reaction steps:



In this system CO₂, CO and SiO are the gaseous intermediates.

In all these reactions, there is a net generation of gaseous species CO and CO₂ resulting in a bulk flow of the gas mixture from the reaction zone. There are other group of reactions between solids proceeding without a net generation of gases. The preparation of metal carbides from metals and carbon is an example:



In this case there is no net consumption or generation of the gaseous intermediates and the gaseous species do not appear in the overall stoichiometry. The gaseous species simply act as carriers of the solid reactant (carbon). In this respect, the mechanism for this type of reactions might be termed "catalysis by gases."

In spite of the practical importance of the reactions between solids, there have been few mathematical descriptions developed for these systems which would provide suitable bases for prediction and interpretation of their behaviors. Until recently the majority of investigators reported the kinetic data as were obtained from experiments without appropriate reaction models. In more recent studies the possibility of applying the analysis of gas-solid reactions to solid-solid reactions has been recognized.

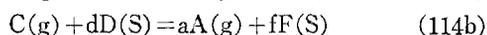
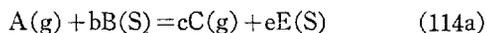
In early theoretical work the kinetics of solid-solid reactions were analyzed for specific conditions of one of the gas-solid reactions controlling the overall reaction. Thus, the rate of reaction

could be represented from the consideration of the rate of this single rate-controlling step. Under such conditions, the analysis of the reaction of nonporous solids presented in Part I would apply directly. The criterion for which reaction is rate-controlling under what conditions was not established. Rather, experimental observation was relied upon for the determination of such a controlling step.

The studies on the carbothermic reduction of hematite by Rao [59], on the reaction between ilmenite and solid carbon by El-Guindy and Davenport [60], and on the reaction between chromium oxide and chromium carbide by Maru et al. [61] make use of the assumption of such a single controlling reaction. These studies represent significant advances in presenting the rates of solid-solid reactions quantitatively. It would, however, be of interest to have a theoretical basis for establishing a criterion for the controlling reaction. This would be very important especially for reactions whose controlling step might change under different reaction conditions. A first step in this direction has been made by Sohn and Szekely [62] who considered reactions between solids proceeding through gaseous intermediates controlled by chemical kinetics.

3.1 Formulation of Model

A reaction between solids B and D which proceeds through the gaseous intermediates of A and C can in general be expressed as follows:



In order for this reaction to be self-sustaining without requiring external supply of gaseous species, the condition $a \times c \geq 1$ must be satisfied.

Let us consider a porous pellet made up of uniformly mixed grains of B and D as sketched in Fig. 13. Solids B and D may have different shapes and sizes. The particle size of either

solid is assumed to be uniform. We shall consider isothermal system, which reacts under a uniform concentration of gaseous species.

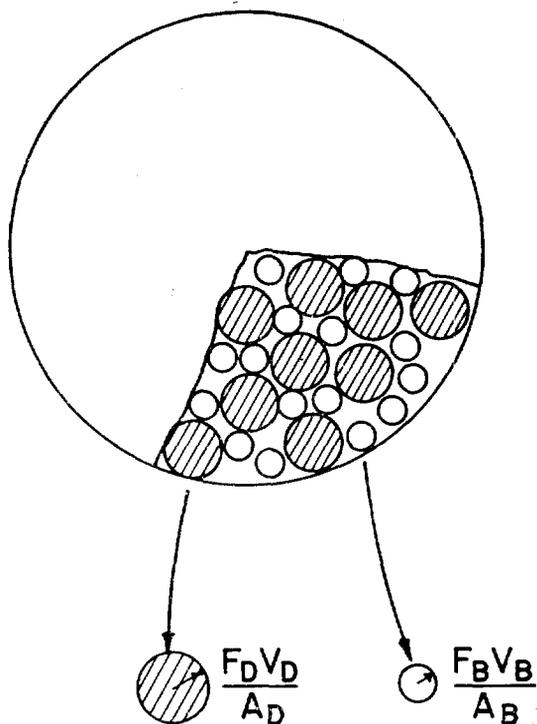


Fig. 13. Schematic representation of the system. [Adapted from H. Y. Sohn and J. Szekely, *Chem. Eng. Sci.*, 28, (1973), 1789.]

This latter condition will be valid when (1) the pore diffusion is fast and the external gas concentration is kept constant, and (2) the net generation of gaseous intermediate is sufficiently fast so as to prevent any ambient gas diffusing into the interior of the pellet [58]. The first case is rather trivial and the reaction of each solid depends on the given gas concentration. In the following we will discuss the case where the second condition is satisfied.

The rates at which reactions proceed, in terms of the generation of gaseous intermediates, are given as follows:

$$\frac{dn_A}{dt} = -v_1 + av_2 \quad (115a)$$

$$\frac{dnc}{dt} = cv_1 - v_2 \quad (115b)$$

where v_1 and v_2 are the net forward rates of reactions (114a) and (114b), respectively, per unit volume of the pellet.

If we assume that each grain reacts according to the shrinking-unreacted-core scheme, the reaction rates of the solids may be expressed as

$$-\rho_B \frac{dr_B}{dt} = bk_1 C_A \quad (116a)$$

$$-\rho_D \frac{dr_D}{dt} = dk_2 C_C \quad (116b)$$

Here we assumed that the reactions are irreversible and of first order. It is possible to incorporate other rate expressions [62]. We can also express v_1 and v_2 as follows:

$$v_1 = \alpha_B \left(\frac{A_B}{V_B} \right) \left(\frac{A_B r_B}{F_B V_B} \right)^{F_B-1} k_1 C_A \quad (117a)$$

$$v_2 = \alpha_D \left(\frac{A_D}{V_D} \right) \left(\frac{A_D r_D}{F_D V_D} \right)^{F_D-1} k_2 C_C \quad (117a)$$

where α_B and α_D are volumes occupied by solids B and D , respectively, per unit volume of the pellet. These expressions are analogous to Eq. (86) in Part II.

If the total pressure of the system is maintained constant, the following relationships hold:

$$\frac{dn_A}{dt} = \frac{C_A}{V_p} \frac{dV}{dt} \quad (118a)$$

$$\frac{dn_C}{dt} = \frac{C_C}{V_p} \frac{dV}{dt} \quad (118b)$$

where dV/dt is the rate of generation of the gas mixture and V_p is the volume of the pellet. We have made a pseudo-steady-state assumption that the gas-phase concentrations at any time are at the steady-state values corresponding to the amounts and sizes of the solids at that timenamely, $CdV/dt \gg VdC/dt$.

We also have the condition that

$$C_A + C_C = C_T \quad (119)$$

Equations (115)-(119) may be solved for C_A and C_C . Using these values, the rates of reaction of the solids may then be obtained from Eqs. (116a and b). It would be worthwhile to determine the criteria for the regimes where one of the pair of gas-solid reactions controls the over-all

rate. The derivation is facilitated if we rearrange the governing equations in the following dimensionless forms:

$$\psi_A (\psi_C + c\psi_A) = \gamma \beta \left(\frac{F_D \xi_D^{F_D-1}}{F_B \xi_B^{F_B-1}} \right) \psi_C (\psi_A + a\psi_C) \quad (120)$$

which is obtained by combining Eqs. (115), (117) and (118).

$$\frac{d\xi_B}{dt^*} = -\psi_A \quad (121a)$$

$$\frac{d\xi_D}{dt^*} = -\beta(1-\psi_A) \quad (121b)$$

and

$$\psi_A + \psi_C = 1 \quad (122)$$

where

$$\psi_A \equiv \frac{C_A}{C_T}, \quad \psi_C \equiv \frac{C_C}{C_T} \quad (123)$$

$$\xi_B = \frac{A_B r_B}{F_B V_B}, \quad \xi_D = \frac{A_D r_D}{F_D V_D} \quad (124)$$

$$\gamma \equiv \left(\frac{b}{d} \right) \left(\frac{\alpha_D}{\alpha_B} \right) \left(\frac{\rho_D}{\rho_B} \right) \quad (125)$$

$$\beta \equiv \left(\frac{d}{b} \right) \left(\frac{\rho_B}{\rho_D} \right) \left(\frac{F_R V_B / A_B}{F_D V_D / A_D} \right) \left(\frac{k_2}{k_1} \right) \quad (126)$$

$$t^* \equiv \frac{bk_1 C_T}{\rho_B} \left(\frac{A_B}{F_B V_B} \right) t \quad (127)$$

The conversion of the solid reactants may then be calculated as follows:

$$X_B = 1 - \xi_B^{F_B} \quad (128a)$$

$$X_D = 1 - \xi_D^{F_D} \quad (128b)$$

It is noted that the conversion and the rate of reaction are related to time (t^*) through two parameters, γ and β . The parameter γ represents the relative molar quantities of the two solids, and β corresponds to the ratio of reactivities of the two solids. As will be seen subsequently, the quantities γ and β allow us to define asymptotic regimes and hence the rate-controlling step.

On combining Eqs. (120) and (122), we get

$$\psi_A = \frac{v - \sqrt{v^2 - 4uw}}{2u} \quad (129)$$

where

$$u \equiv (a-1)\gamma\beta \frac{F_D \xi_D^{F_D-1}}{F_B \xi_B^{F_B-1}} - (c-1) \quad (130)$$

$$v \equiv (2a-1)\gamma\beta \frac{F_D \xi_D^{F_D-1}}{F_B \xi_B^{F_B-1}} + 1 \quad (131)$$

$$w \equiv a\gamma\beta \frac{F_D \xi_D^{F_D-1}}{F_B \xi_B^{F_B-1}} \quad (132)$$

We can now obtain the relationship between ξ_B and ξ_D , and t^* by substituting Eq. (129) into Eqs. (121a and b) and integrating with the following initial conditions:

$$\text{at } t^*=0, \xi_B=\xi_D=1 \quad (133)$$

3.2 Results

In general the integration of Eqs. (121a and b) must be done numerically. For the case of $F_B=F_D=1$, analytical solution is possible because u , v and w , hence ϕ_A become constant. We shall discuss only the latter case here. For the cases of other values of F_B and F_D , the reader is referred to the original paper [62].

When $F_B=F_D=1$, that is, the surface areas within the grains available for reaction do not change with conversion (zero-order reaction with respect to the solid), Eq. (129) gives

$$\phi_A = \frac{(2a-1)\gamma\beta + 1 - \sqrt{\gamma^2\beta^2 + 2(2ac-1)\gamma\beta + 1}}{2[(a-1)\gamma\beta - C + 1]} \quad (134)$$

This expression reduces to $\phi_A = \frac{\gamma\beta}{1+\gamma\beta}$ when $a=c=1$, which can also be obtained directly from Eq. (120).

Asymptotic behavior

When $\gamma\beta$ approaches zero, reaction (114b) is much slower than reaction (114a) and hence controls the overall rate. The gaseous intermediates consist mainly of C and the concentration of gas A will be small. [In the case of reversible reactions, the gaseous intermediates will correspond to the equilibrium gas mixture for reaction (114a)]. This expected behavior is readily demonstrated by the asymptotic behavior of the solution.

When $\gamma\beta \rightarrow 0$, Eq. (134) reduces to

$$\phi_A \cong a\gamma\beta \quad (135)$$

Equations (121a and b) become

$$\frac{d\xi_B}{dt^*} = -a\gamma\beta \quad (136a)$$

$$\frac{d\xi_D}{dt^*} = \beta \quad (136b)$$

Integration of these equations gives

$$\xi_B = 1 - a\gamma\beta t^* \quad (137a)$$

$$\xi_D = 1 + \beta t^* \quad (137b)$$

The latter asymptote corresponds to the reaction of flat nonporous particles of solid D in a constant gas composition... pure C in the present case and the equilibrium mixture for reaction (114a) for reversible reaction. The reaction of B is then determined from the following stoichiometric relationship obtained from Eqs. (137a and b):

$$X_B = a\gamma X_D \quad (138)$$

As shown above, the attainment of this asymptotic regime is characterized by the numerical value of $\gamma\beta$. It will be shown subsequently that $\gamma\beta < 10^{-2}$ adequately defines the $\gamma\beta \rightarrow 0$ the kinetics of reaction of D is independent of γ or the kinetics of reaction of B . It then follows that the intrinsic kinetics of reaction of D can be obtained from the conversion data obtained under the conditions of $\gamma\beta \rightarrow 0$, where the gas composition corresponds to that of the equilibrium mixture for reaction (114a).

When $\gamma\beta$ is large, reaction (114a) controls the overall rate. Mathematical development readily follows the procedure described for small $\gamma\beta$. Thus, when $\gamma\beta \rightarrow \infty$, Eq. (134) gives

$$1 - \phi_A = \phi_C = \frac{c}{\gamma\beta} \quad (139)$$

$$\frac{d\xi_B}{dt^*} = -1 \quad (140a)$$

$$\frac{d\xi_D}{dt^*} = -\frac{c}{\gamma} \quad (140b)$$

and

$$\xi_B = 1 - t^* \quad (141a)$$

$$\xi_D = 1 - \frac{c}{\gamma} t^* \quad (141b)$$

The relationship between X_B and X_D obtained

from Eqs. (141a and b) is

$$X_D = \frac{c}{\gamma} X_B \tag{142}$$

It is seen in this case of large $\gamma\beta$ that the kinetics of reaction of B is independent of γ or β . Thus, the intrinsic kinetics of the reaction of B can be obtained from the conversion data obtained under the condition of $\gamma\beta \rightarrow \infty$, where the gas composition is at the equilibrium concentration for reaction (114b). It will be shown below that the $\gamma\beta \rightarrow \infty$ asymptote is approached when $\gamma\beta > 10^2$.

For intermediate values of $\gamma\beta$, the composition of the gas is given by Eq. (134). The conversions of the solids are given by Eqs. (121a and b). One of more important reactions between two solids proceeding through gaseous intermediates is the carbothermic reduction of metal oxides described in Eqs. (109)-(111). For these reactions, $a=2$ and $c=1$. The solution to be presented below will be for these values of a and c .

Figure 14 shows the rates of reactions and the concentrations of the gaseous intermediates as functions of γ for various values of β . Since the rates are constant [see Eqs. (121) and (134)] until either one of the solids is completely reacted (when either B or D is all consumed the reaction stops), the behavior of a given system is represented by a point corresponding to given γ and β . When both F_B and F_D are not unity, the rate changes with conversion [62].

It was shown in Eqs. (136b) and (140a) that when $\gamma\beta \rightarrow 0$, $\frac{d\xi_D}{dt^*}$ is independent of γ . It is seen in Fig. 14 that these asymptotes are valid when $\gamma\beta < 10^{-2}$ and $\gamma\beta > 10^2$, respectively. These criteria have been shown to be valid also for other values of F_B and F_D [62].

The intersection of the curves for B and D for the same value of β provides the locus for the complete conversion of B and D simultaneously. It is of interest to note that the relative amount (γ) of B and D for simultaneous comp-

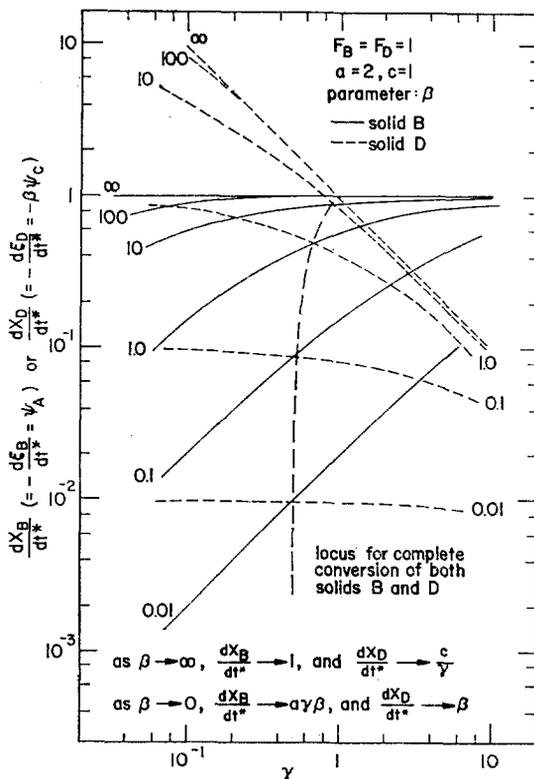


Fig. 14. Rate of reaction and concentration vs. γ for $F_B = F_D = 1$. [Adapted from H. Y. Sohn and J. Szekeley, *Chem. Eng. Sci.*, 28, (1973), 1789.]

lete conversion, i.e. the 'stoichiometric' number of moles, vary with the relative kinetics (β). In the extreme regimes of $\gamma\beta \rightarrow 0$ and $\gamma\beta \rightarrow \infty$, the values of γ for the simultaneous complete conversion of both B and D may be obtained from Eqs. (138) and (142), respectively, to be:

$$\gamma = \frac{1}{a}, \text{ when } \gamma\beta \rightarrow 0 \tag{143a}$$

and

$$\gamma = c, \text{ when } \gamma\beta \rightarrow \infty \tag{143b}$$

These values can be seen in Fig. 14. [Note that $a=2$ and $c=1$ in this figure.] For intermediate values of $\gamma\beta$, the value of γ for the simultaneous complete conversion of B and D depends on the relative kinetics (β).

3.3 Discussion

A quantitative analysis has been described for the reactions between solids proceeding through gaseous intermediates when the effect of intra-pellet diffusion is negligible. The criteria for the negligible diffusional effects have been established elsewhere [62]. Many systems fall within this category.

There exist few systematic experimental data that may be compared with the model. The work of Otsuka and Kunii [58] and of Rao [59] on the reduction of hematite with carbon comes close to the analysis presented here. While there is qualitative agreement between these experimental results and the calculated results of the model, a quantitative comparison cannot be made because of the difficulties arising from the two-step reaction in the hematite-carbon system and the limited range of experimental parameters. Furthermore, the above analysis made use of a number of simplifying assumptions to facilitate the mathematical development. Although this was useful in expressing the underlying concept of the model, few systems can be expected to satisfy all the simplifying assumptions used above. For example the kinetics of the component gas-solid reactions used in Eqs. (116a and b) may be of different expressions such as the Langmuir-Hinshelwood type, or the reactions of solids B and D may be controlled by the intra-grain diffusion, i.e. diffusion of the gaseous reactant through the product layer around each grain. These cases can be treated by writing appropriate expressions for Eqs. (116) and (117).

It is noted that the analysis of a system with reversible, first order reactions follows directly, with minor adjustments, that for an irreversible reaction described in this section.

It is hoped that the model will not only aid the analysis of experimental results but also stimulate further research on this interesting area of solid-solid reaction systems.

Nomenclature

- a stoichiometric coefficient in reaction (114b)
- A_B, A_D surface area of a grain of solids B and D , respectively
- b number of moles of solid B reacted by one mole of fluid reactant A
- c stoichiometric coefficient in reaction (114a)
- C molar concentration of fluid species
- d stoichiometric coefficient in reaction (114b)
- F shape factor ($=1, 2$ and 3 for flat plates, long cylinders, and spheres, respectively)
- k reaction-rate constant
- r distance from the center of symmetry in a nonporous particle or a grain
- t time
- t^* dimensionless times defined by Eq. (127)
- V volume
- X fractional conversion of the solid

Greek symbols

- α fraction of volume of pellet occupied by reactant solid
- β relative reactivities of solids defined by Eq. (126)
- γ the relative molar quantities of solids defined by Eq. (125)
- ξ dimensionless position of the reaction front in the grain, defined by Eq. (124)
- ρ molar concentration of solid reactants
- ψ dimensionless concentration defined by Eq. (123)

Subscripts

- A gas A
 B solid B
 C gas C
 D solid D
p particle or pellet

References

References 1-31 are given in Part I and Refs. 32-57 are given in Part II of this review.

58. K. Otsuka and D. Kunii, *J. Chem. Eng. Jap.*, **2**(1), (1969), 46.
59. Y.K. Rao, *Met. Trans.*, **2**, (1971), 1439.
60. M.I. El-Guindy and W.G. Davenport *Met. Trans.*, **1**(1970), 1729.
61. Y. Maru, Y. Kuramasu, Y. Awakura, and Y. Kondo, *Met. Trans.*, **4**, (1973), 2591.
62. H.Y. Sohn and J. Szekely *Chem. Eng. Sci.*, **28**, (1973), 1789.
63. J.G. Lee, Carbide and Nitride Ceramics by Carbothermal Reduction of Silica, Ph.D. Dissertation, University of Utah, 1976.