

# EFFECT OF ADSORPTIVE GASEOUS REACTANT ON NON-ISOTHERMAL BEHAVIOR FOR GAS-SOLID REACTIONS

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**Abstract**—The effect of adsorptive species on non-isothermal gas-solid reactions is studied on the basis of Langmuir-Hinshelwood kinetics. The concept of an effectiveness factor provides good information to ascertain the effect of adsorptive species and the transition of the rate controlling regime, in connection with the parameters generally used in the analysis of non-isothermal behavior.

For highly exothermic reactions, the effectiveness factor-Thiele modulus curves with multiple solutions are presented with respect to the modified adsorption equilibrium constant. The variations of the rate-controlling regime by the effect of adsorptive species are also discussed.

## INTRODUCTION

When a gas reacts with a porous solid reactant, its behavior may deviate appreciably from the intrinsic chemical behavior of the reaction because of the mass and heat transfer resistance within the particles [1]. Under this situation, the effect of transport resistance has been explained by the concept of an effectiveness factor as in the case of catalytic reactions [2,3]. The effectiveness factors for gas-solid reactions have been studied experimentally [4] and theoretically [5] in recent years for the purpose of simulating fixed bed performance for highly exothermic reactions.

Analysis of non-isothermal effectiveness factors should be usually considered based on the three mutual rate-controlling steps of adsorption, chemical reaction and intraparticle diffusion. Although extensive studies have been carried out in the chemical reaction and intraparticle diffusion controlling regimes, there are few papers which deal with the effect of adsorptive species on the non-catalytic gas-solid reactions [6].

Langmuir-Hinshelwood (L-H) kinetics have usually been adopted for the explanation of adsorptive effects of gaseous reactants for catalytic reactions [7,8].

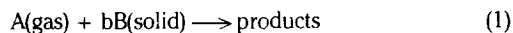
Dudukovic et al. [6] proposed a new zone model for zeroth-order reaction with respect to gaseous reactant with strongly adsorptive species and obtained analytical solutions for conversion and effectiveness factors. However, this does not have general applicability for gas-solid reactions with intermediate adsorptive species. Park [9] studied the effect of adsorptive species on the

reaction rate for isothermal gas-solid reactions by using the L-H kinetics which represented the fractional order of reaction rate from 0 to 1 with respect to gaseous reactant. Park et al. [10] also applied the L-H type kinetics to the reaction of reduced iron with water-vapor.

The purpose of the present study is to attempt a case study analysis of the characteristics of non-isothermal effectiveness factors using L-H single site kinetics and to ascertain the rate-controlling shifts according to the adsorptivity of gaseous species, particularly, in the multiple steady state region of relatively low Thiele modulus.

## THEORETICAL

A non-catalytic gas-solid reaction may be represented by the following equation:



To investigate the effect of adsorptive species on the reaction rate, the rate equation can be given as:

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt} = -\frac{1}{bV} \frac{dN_B}{dt} = \frac{kC_A C_B}{1 + K_A C_A} \quad (2)$$

where  $k$  is the reaction rate constant and  $K_A$  is the adsorption equilibrium constant of species  $A$ .

The rate equation (2) has the two limiting cases. The first case of  $K_A \rightarrow 0$  leads to the first-order reaction and the second case of  $K_A \rightarrow \infty$  leads to the zeroth-order reaction with respect to the gaseous reactant concentration. Therefore, Eq. (2) represents the fractional order reaction with respect to the adsorptive gaseous reactant.

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The non-catalytic gas-solid reaction becomes inherently transient since the solid reactant is consumed gradually and physical properties change progressively. In dealing with this transient system, there are two representative models, a shrinking core model (SCM) and a volume reaction model (VRM). It has been shown that the latter is more practical in describing the reaction behavior in the wide range of rate controlling regimes in a porous particle [5].

The reaction rate constant,  $k$ , may be represented by an exponential function of  $T$  for nonisothermal reactions:

$$k = A \exp(-E/RT) \quad (3)$$

Introducing the temperature of the bulk stream,  $T_0$ , and the corresponding reaction rate constant,  $k_0 = A \exp(-E/RT_0)$ , yields

$$k = k_0 \exp \left\{ \frac{E}{RT_0} \frac{\Delta T}{T_0} \frac{1}{(1 + \Delta T/T_0)} \right\} \quad (4)$$

where  $\Delta T = T - T_0$ .

Some workers [2, 11, 12] have pointed out that the reaction rate constant can be represented in terms of one variable,  $C_A$ , by using a relationship between the temperature and the reactant concentration at any point within the particle:

$$\Delta T = \frac{C_{A0} (-\Delta H_r) D_e}{k_h} (1 - C_A/C_{A0}) \quad (5)$$

Under assumptions such as the pseudosteady state approximation for both mass and heat transfer in the particle, negligible gas film resistance and temperature independent physical properties of solid, the differential material balance with respect to the gas and solid reactants in a spherical porous particle is given in dimensionless form by:

$$\frac{1}{\lambda^2} \frac{\partial}{\partial \lambda} \left( \lambda^2 \frac{\partial y}{\partial \lambda} \right) + \phi^2 \frac{\partial z}{\partial \theta} = 0 \quad (6)$$

$$-\frac{\partial z}{\partial \theta} = \frac{yz}{1 + Ky} \exp \left\{ \frac{\gamma \beta (1-y)}{1 + \beta (1-y)} \right\} \quad (7)$$

The initial and boundary conditions are

$$z = 1 \text{ and } y = 0 \text{ at } \theta = 0 \quad (8)$$

$$\frac{\partial y}{\partial \lambda} = 0 \text{ at } \lambda = 0 \quad (9)$$

$$y = 1 \text{ at } \lambda = 1 \quad (10)$$

$\phi$  is the Thiele modulus,  $\gamma$  is the sensitivity of the reaction rate to temperature,  $\beta$  is the maximum temperature variation within a particle and  $K$  is the modified adsorption equilibrium constant defined as:

$$\phi = R \sqrt{\frac{k_0 C_{B0}}{D_e}} \quad (11)$$

$$\gamma = \frac{E}{RT_0} \quad (12)$$

$$\beta = \frac{C_{A0} (-\Delta H_r) D_e}{k_h T_0} = \left( \frac{\Delta T}{T_0} \right)_{\max} \quad (13)$$

$$K = K_A C_{A0} \quad (14)$$

The dimensionless variables in Eqs. (6) and (7) are defined as:

$$y = \frac{C_A}{C_{A0}}, \quad z = \frac{C_B}{C_{B0}}, \quad \lambda = \frac{r}{R} \text{ and } \theta = bk_0 C_{A0} t \quad (15)$$

To represent the effect of diffusion resistance and heat of reaction in gas-solid reactions, the concept of an effectiveness factor can be used as in catalytic reactions. The effectiveness factor is usually defined as:

$$\eta = \frac{\text{actual reaction rate}}{\text{reaction rate obtained at bulk conditions}} \quad (16)$$

In terms of the associated symbols,  $\eta$  becomes

$$\eta = \frac{(1+K)}{1-X_B} \left( \frac{dX_B}{d\theta} \right) \quad (17)$$

The overall conversion of solid reactant,  $X_B$ , is the particle-volume average value and is calculated as:

$$X_B = 1 - 3 \int_0^1 \lambda^2 z \, d\lambda \quad (18)$$

However, since  $\eta$  as defined in Eq. (17) cannot be appropriately used to explain the relative effect of adsorptive species, a new modified effectiveness factor should be defined based on the reaction rate at bulk conditions without thermal and adsorption effects as follows:

$$\eta^* = \frac{\eta}{1+K} \quad (19)$$

$\eta^*$  stands for the effectiveness factor which represents the relative effect of adsorptive species on reaction rate.

Solutions of Eqs. (6) and (7) with their initial and boundary conditions cannot be obtained analytically because the equations are not linear. The numerical method of a finite difference scheme was, therefore, used. To evaluate the multiple solutions in the unstable range of  $\phi$ , Eqs. (6) and (7) were transformed from a two-point boundary value problem to an initial value problem. The procedures used in this study are those developed by Weisz et al. [12]. Numerical integration of the transformed initial value problem was performed on a computer using the 4th-order Runge-Kutta formula assuming the initial value of gaseous concentration in the center of particles

## RESULTS AND DISCUSSIONS

### III.1. General feature of non-isothermal behavior

It has been shown by many workers [5,13] that the non-catalytic gas-solid reactions can be treated by methods similar to those used in catalytic reactions. Figure 1 shows the effectiveness factors with the conversion of solid reactant and the modified adsorption

equilibrium constant for  $\gamma = 20$  and  $\beta = 0.5$ . Since the range of  $\gamma$  is 0 to 30 and that of  $\beta$  is 0 to 1 in practical reaction systems, the mean value among these ranges was selected to illustrate the general feature of non-isothermal characteristics. The results of  $K=0$  in Table I and figures represent the behavior of the first-order reaction with respect to the gaseous reactant as the limiting case of  $K \rightarrow 0$  which has been analyzed in the literature [5].

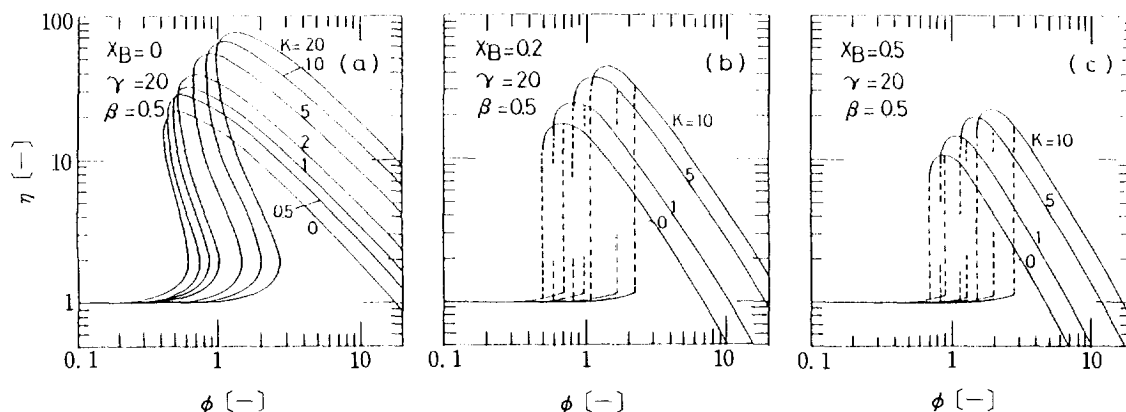


Fig. 1. Variation of effectiveness factor  $\eta$  with Thiele modulus  $\phi$  and modified adsorption equilibrium constant  $K$  during the reaction for  $\gamma=20$  and  $\beta=0.5$ : (a),  $X_B=0$ ; (b),  $X_B=0.2$ ; (c),  $X_B=0.5$ .

For the case of exothermic reactions, it is seen that  $\eta$  can become larger than unity for large enough values for  $\gamma\beta > 5$  and specific values of  $\phi$  [12]. This occurs as a result of the increase in the internal effective rate constant over the value of  $k_0$  by the intraparticle temperature rise.

The initial effectiveness factor at  $X_B=0$  shown in Fig. 1 (a) corresponds to that for a solid-catalyzed reactions as obtained by Weisz et al. [12]. As the conversion level increases, the effectiveness factor decreases for specific values of  $\phi$ . This can be explained by the solid reactant depletion during the reaction. Kimura et al. [5] reported similar results about the effectiveness factors for irreversible first-order reactions with respect to  $\gamma$  and  $\beta$  by adopting a VRM. The critical difference between the gas-solid and catalyzed reactions is that, for gas-solid reactions the solid phase participates as a reactant itself and the concentration of solid reactant diminishes progressively during the reaction. Thus, the effectiveness factor varies with the conversion of solid reactant.

There is no non-isothermal effect for  $\phi < 0.1$  where  $\eta$  is close to unity, attained in the regime of chemical reaction control. However, when  $\phi$  lies roughly between 0.1 and 3, there exist multiple steady state solutions for highly exothermic reactions. The physical situation leading to multiple solutions can be understood by the interrelationship between the rate of heat generation

by reaction and the rate of heat removal by conduction [1].

The metastable solution which lies between two stable solutions shifts to any stable solution immediately after the start of the reaction depending on the operating conditions. The upper stable solution provides the rate in the diffusion controlling regime whereas the lower stable one provides the rate in the chemical reaction controlling regime. The rough ranges of  $\phi$  which show multiple solutions are summarized in Table 1 with  $\gamma$ ,  $\beta$  and  $K$  for  $X_B=0$ .

When  $\beta < 0.1$ , there are no multiple solutions in the ranges of  $\gamma$  used in this study whereas when  $\beta = 0.3$ , multiple solutions exist in narrow ranges of  $\phi$ . However, if  $\beta > 0.5$ , the multiplicities exist explicitly in the whole range of  $\gamma$  from 10 to 30. These results yield the general conclusion that multiple solution can exist when a highly exothermic reaction occurs in a porous solid and catalyst with low heat conductivity.

When the conversion of solid reactant is not zero, the multiple solutions cannot be obtained by the method mentioned in previous section. The dashed lines in Figs. 1 (b) and (c) represent the approximate regions of multiple solutions.

### III.2. Effect of adsorptive species

There are some studies [9,14] which deal with the ef-

**Table 1.** The range of Thiele modulus having multiple solutions for  $\eta$  according to parameters  $\gamma$  and  $\beta$  with  $X_B = 0$ .

$\gamma = 10$		K	0	0.5	1	2	5	10	20
$\beta$	0.3	—	—	—	—	—	—	—	—
	0.5	—	—	—	—	—	2.2	3.8 —3.95	4.7 —5.0
	0.8	—	0.9	0.94—1.02	1.06—1.24	1.40—1.70	1.75—2.30	2.3 —3.2	
$\gamma = 20$		K	0	0.5	1	2	5	10	20
$\beta$	0.3	—	0.97—1.03	1.05—1.40	1.15—1.40	1.50—1.92	1.80—2.6	2.40—3.6	
	0.5	0.41—0.64	0.45—0.75	0.49—0.87	0.53—1.05	0.66—1.50	0.81—2.01	1.0 —2.7	
	0.8	0.16—0.49	0.17—0.6	0.18—0.7	0.2 —0.83	0.24—1.15	0.3 —1.6	0.38—2.2	
$\gamma = 30$		K	0	0.5	1	2	5	10	20
$\beta$	0.1	—	—	—	—	—	—	—	—
	0.3	0.42—0.67	0.45—0.78	0.48—0.9	0.53—1.10	0.64—1.53	0.80—2.1	1.0 —2.9	
	0.5	0.12—0.5	0.12—0.6	0.13—0.7	0.15—0.84	0.17—1.2	0.21—1.6	0.27—2.3	

fectiveness factors by L-H kinetics in isothermal reaction systems. However, the effect of adsorptive species for non-isothermal reactions has not been studied extensively up to the present.

Figure 1 (a) shows that the  $\eta$ - $\phi$  curves tend to have multiple solutions and shift to the right with increasing  $K$ . This means that the effect of the adsorptive species causes the chemical reaction controlling regime to be wider up to high values of  $\phi$ .

The modified effectiveness factor defined in Eq. (19) at bulk conditions becomes as follows:

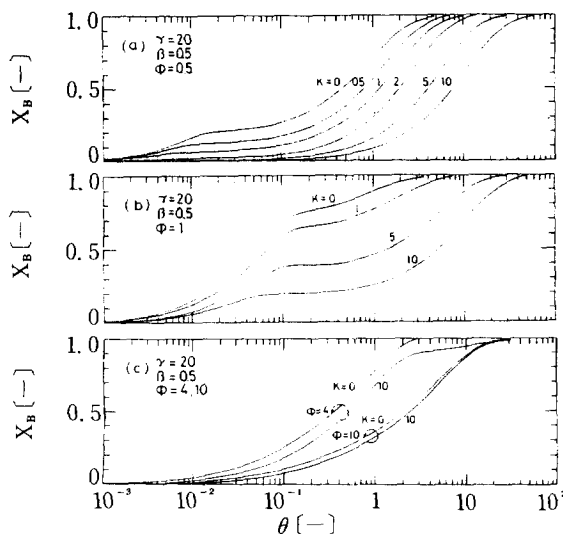
$$\eta^* = \frac{1}{1+K} \quad (20)$$

The reaction rate for gas-solid reaction decreases inversely with  $1+K$ . Thus, although the effectiveness factors defined by Eq. (17) are represented as high values in Fig. 1, the real rate of reaction is reduced greatly by the restricting effect of adsorption on reaction rate.

Shah et al. [7] have encountered multiple steady state solutions while computing non-isothermal effectiveness factors using generalized L-H kinetics and indicated the non-existence of multiple steady states for a complete formulation of the L-H rate expression. Furthermore, the parameter  $\gamma$  involving the activation energy was not used for the reason that there is no single activation energy which controls the rate of reaction. They used values of  $\beta$  between 0 and 0.3 assuming these as practical values. Table 1 shows there are no multiple solutions for  $\beta < 0.3$  except for large values of  $\gamma$  and  $K$ . This gives results similar to those obtained by Shah et al.

Figures 2 (a), (b) and (c) show the  $X_B$ - $\theta$  curves.

For  $\phi = 0.5$ , there exists a flat portion on these curves at any conversion level when  $K < 2$ . For  $\phi = 1$ , the flatness



**Fig. 2.** Extent of over-all conversion  $X_B$  varying with dimensionless time  $\theta$  and  $K$  for  $\gamma = 20$  and  $\beta = 0.5$ : (a),  $\phi = 0.5$ ; (b),  $\phi = 1$ ; (c),  $\phi = 4, 10$ .

exists explicitly for all values of  $K$  encountered. In Fig. 2 (c), however, which corresponds to  $\phi = 4$  and 10, the  $X_B$ - $\theta$  curves become similar to the case of isothermal reaction. The effect of adsorptive species for  $\phi = 1.0$  is greater than those for  $\phi = 0.5$  and 4. When  $\phi = 10$ , the variations of  $K$  negligibly affect the  $X_B$ - $\theta$  curves. As  $\phi$  becomes about 10, the reaction proceeds completely in the diffusion controlling regime without the transition of rate controlling regime.

### III-3. Transition of rate controlling regime

The existence of multiple solutions in the  $\eta$ - $\phi$  curves

is related to the transition of the rate-controlling regime depending on the operating reaction conditions. This

phenomenon can be observed more explicitly in Fig. 3. Figure 3 shows the effectiveness factor for any  $\phi$  in terms

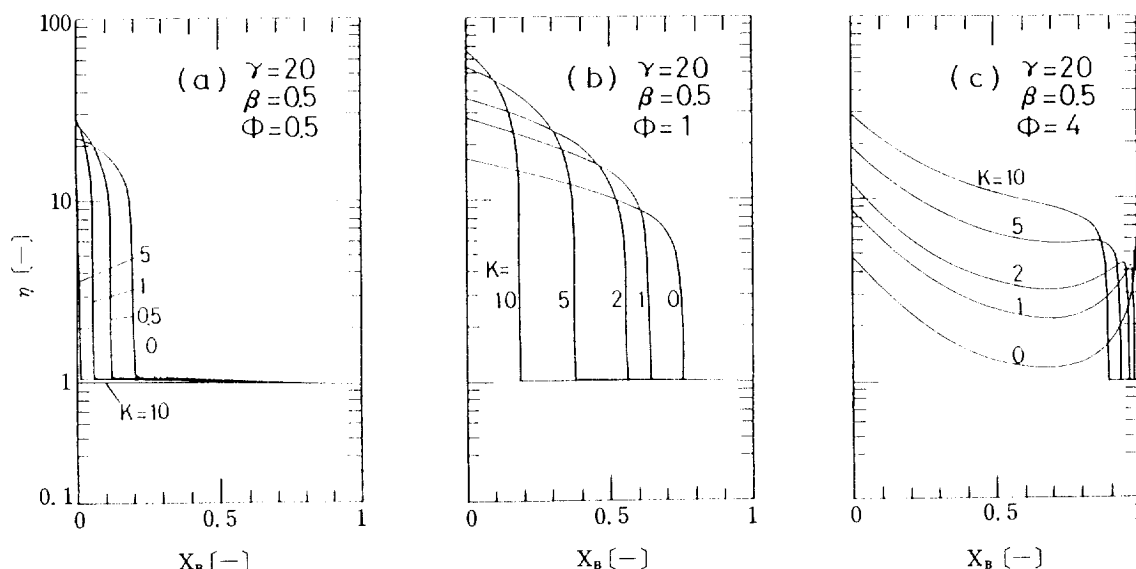


Fig. 3. Variation of effectiveness factor with conversion and modified adsorption equilibrium constant for  $\gamma = 20$  and  $\beta = 0.5$ : (a),  $\phi = 0.5$ ; (b),  $\phi = 1$ ; (c),  $\phi = 4$ .

of  $X_B$ . The reaction proceeds with a high value of  $\eta$  due to intraparticle temperature rise in the diffusion controlling regime at low conversion and shifts gradually to that in chemical reaction controlling regime with  $\eta$  close to unity. In the early stage of reaction, the reaction occurs in diffusion controlling regime up to some conversion level and after the sudden transition of the rate controlling regime, then the reaction proceeds slowly to the chemical reaction controlling regime to form the sigmoid type  $X_B - \theta$  curves shown in Fig. 2. This sudden transition from the diffusion to chemical reaction controlling regimes may be caused by a decrease of reaction rate due to solid reactant depletion and thermal effect. The sharply decreasing point appeared at lower conversion levels as  $K$  increased.

Figure 3 (b) which corresponds to  $\phi = 1.0$  shows clearly the occurrence of transition and in Fig. 3 (c) for  $\phi = 4.0$ , this transition disappears except for high values of  $K$ :  $\eta - X_B$  curves for low  $K$  become those predicted by SCM. The transition point shown in Fig. 3 moves forward to the end of the reaction as  $\phi$  increases. Figures 2 and 3 show that the flatness of the  $X_B - \theta$  curves is formed at the conversion levels where the transition occurs. The flatness of the  $X_B - \theta$  curves may be explained by a shift of the rate controlling regime. The transition from the diffusion control regime to chemical reaction control regime of this kind has been observed in the case of combustion of coke or charcoal in practical situations

[15]. This sudden shift cannot be predicted by the non-isothermal shrinking core model [16].

#### III-4. Intraparticle reactant concentration

The profile of gaseous reactant and solid reactant concentration within the particle can provide more valuable information to identify the phenomena occurring in the particle. Figures 4 (a)-(c) show the variation of local solid reactant concentrations for each case of  $\phi$  and  $K$  for  $\gamma = 20$  and  $\beta = 0.5$ . When  $\phi = 0.5$ , there is no diffusional limitation, the reaction proceeds uniformly within particles for high  $K$ . In the case of low  $K$ , the reaction occurs more rapidly at certain radial positions inside the particle than at the outer surface of the particles due to the non-isothermal effect. These phenomena are observed at high conversion levels for  $\phi = 1.0$  in Fig. 4 (b). When  $\phi = 4.0$ , however, a sharp reaction boundary regardless of the value of  $K$  is formed and an unreacted zone near the particle surface remains as shown in Fig. 4 (c). This indicates that the reaction proceeds practically at the unreacted core even for a relatively small value of  $\phi$  of about 4.

In high values of  $\phi$ , there is no big difference between VRM and SCM in representing the reaction behavior for highly exothermic reactions.

The transition of the rate controlling regime is clearly demonstrated by the variation of profile of gaseous reactant in the particle [5]. Figure 5 shows that the concen-

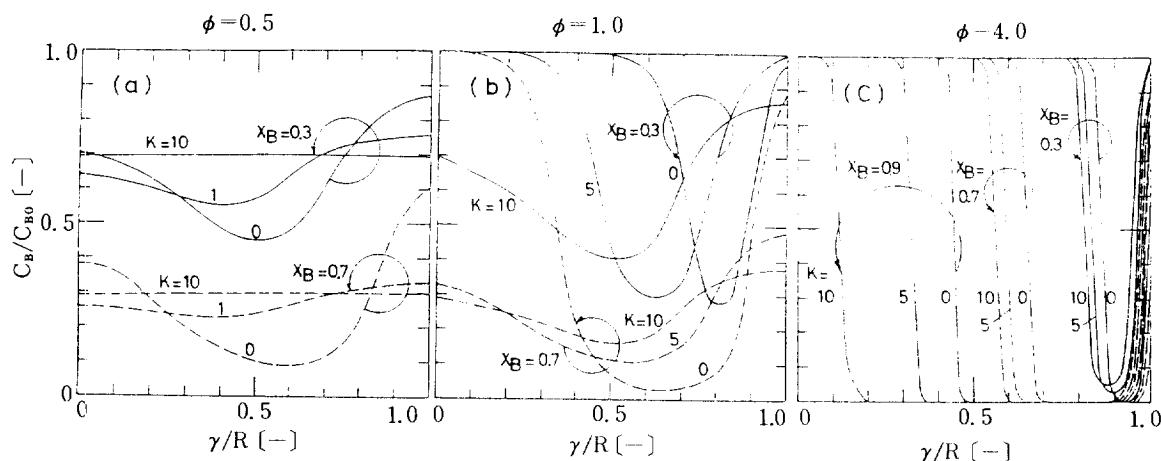


Fig. 4. Profile of solid reactant concentration varying with  $K$  and  $\phi$  in a particle for  $\gamma=20$  and  $\beta=0.5$ : (a),  $X_B=0.3$  and  $0.7$ ; (b),  $X_B=0.3$  and  $0.7$ ; (c),  $X_B=0.3$ ,  $0.7$  and  $0.9$ .

tration profiles become suddenly flat when the conversion reaches about 0.6. This means that the diffusion-limited concentration profile changes to the chemical

controlled profile because the reaction rate is reduced suddenly to the value corresponding to the chemical reaction controlling regime.

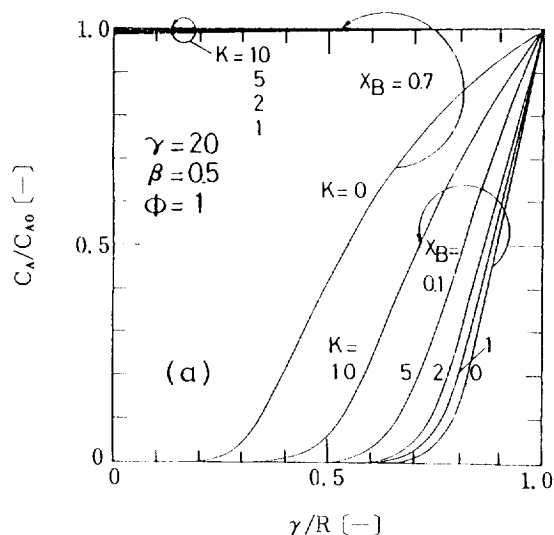
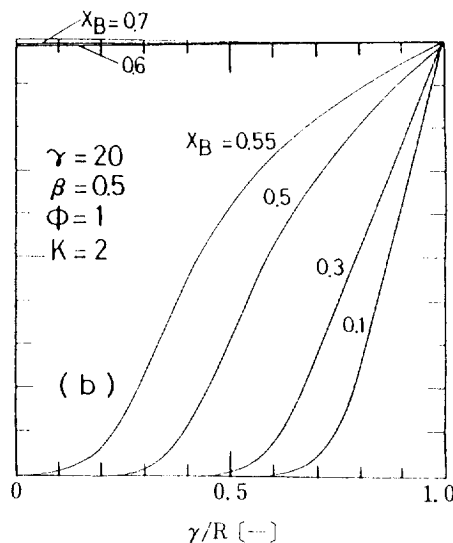


Fig. 5. (a) Profile of gaseous reactant concentration in a particle showing transition of rate controlling regime varying with  $K$  at  $X_B=0.1$  and  $0.7$ :  $\gamma=20$ ,  $\beta=0.5$  and  $\phi=1$ .



(b) Profile of gaseous reactant concentration in a particle showing transition of rate controlling regime for  $K=2$ :  $\gamma=20$ ,  $\beta=0.5$  and  $\phi=1$ .

### CONCLUDING REMARKS

The concept of an effectiveness factor was used along with Langmuir-Hinshelwood kinetics to study the effect of adsorptive species on the reaction rate of non-isothermal gas-solid reactions.

As the effect of adsorptive species becomes larger, the real reaction rate decreases due to the restricting effect of adsorption on the reaction and the chemical reaction controlling regime where non-isothermal effect is not important shifts to high values of the Thiele modulus. At high values of  $K$ , the effectiveness factor

Thiele modulus curve tends to become sigmoid showing the reaction system to be unstable.

The transition from diffusion to chemical reaction controlling regime occurs at certain  $X_B$  values depending upon the value of  $K$  when  $\phi$  is in the range of 0.1-3. As  $K$  increases, the transition moves toward low conversion levels. When  $\phi$  reaches high values as large as 4, the effect of adsorptive species as well as the non-isothermal effect is not of prime importance in the range of parameters encountered in this study and the reaction behavior predicted by a VRM becomes identical with that predicted by a SCM for highly exothermic reactions.

### NOMENCLATURE

A	: gaseous reactant	(-)
A	: frequency factor for rate constant	( $m^3/mol \cdot s$ )
B	: solid reactant	(-)
b	: stoichiometric coefficient in Eq. (1)	(-)
$C_A$	: local gaseous reactant concentration	( $mol/m^3$ )
$C_{A0}$	: value of $C_A$ under bulk conditions	( $mol/m^3$ )
$C_B$	: concentration of solid reactant in particle	( $mol/m^3$ )
$C_{B0}$	: initial value of $C_B$	( $mol/m^3$ )
$D_e$	: effective diffusion coefficient	( $m^2/s$ )
E	: apparent activation energy	( $J/mol \cdot K$ )
$-\Delta H_r$	: heat of reaction	( $J/mol \cdot K$ )
K	: modified adsorption equilibrium constant, $K_A C_{A0}$	(-)
$K_A$	: adsorption equilibrium constant	( $m^3/mol$ )
k	: reaction rate constant	( $m^3/mol \cdot s$ )
$k_h$	: effective thermal conductivity of solid	( $J/m \cdot s \cdot K$ )
$k_0$	: reaction rate constant at $T_0$	( $m^3/mol \cdot s$ )
$N_A$	: moles of A	(mol)
$N_B$	: moles of B	(mol)
R	: ideal gas constant	( $J/mol \cdot K$ )
R	: particle radius	(m)
r	: radial distance from center of particle	(m)
$-r_A$	: reaction rate per unit particle volume	( $mol/m^3 \cdot s$ )
T	: local temperature in particle	(K)
$T_0$	: temperature of bulk stream	(K)
t	: reaction time	(s)
V	: particle volume	( $m^3$ )
$X_B$	: extent of overall conversion	(-)
y	: dimensionless gaseous concentration, $C_A/C_{A0}$	(-)

z : dimensionless solid concentration,  $C_B/C_{B0}$  (-)

### Greeks

$\beta$	: parameter defined by Eq. (13)	(-)
$\eta$	: effectiveness factor defined by Eq. (17)	(-)
$\eta^*$	: modified effectiveness factor defined by Eq. (19)	(-)
$\phi$	: Thiele modulus defined by Eq. (11)	(-)
$\gamma$	: parameter defined by Eq. (12)	(-)
$\lambda$	: dimensionless radial distance, $r/R$	(-)
$\theta$	: dimensionless time, $bk_0 C_{A0} t$	(-)

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