

# A MATHEMATICAL MODEL FOR COUPLED GAS-SOLID REACTIONS IN A REACTING GAS ATMOSPHERE

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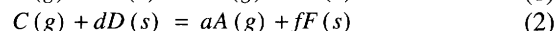
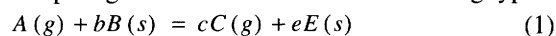
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**Key Words:** Mathematical Model, Gas-Solid Reaction, Coupled Gas-Solid Reaction, Carbothermic Reduction

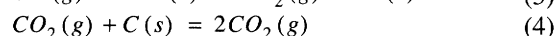
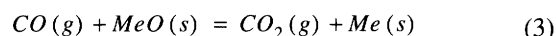
A mathematical model has been proposed for describing the coupled gas-solid reactions in a reacting gas atmosphere. Effects of the following five parameters on the conversions of solids B and D have been examined: reaction/diffusion ratio, Sherwood number, reactivity ratio, factors of catalytic activity and reactant amount ratio. The conversion of solid B was found to be able to be increased by reducing the pellet size, increasing the relative initial amount of solid D to solid B, or increasing the velocity of bulk gas.

## Introduction

Coupled gas-solid reactions of the following type



are normally found in the carbothermic reduction of metal oxide:



Most investigations (experimental and theoretical) of this kind of coupled gas-solid reactions have utilized an inert gas atmosphere<sup>5, 10-13, 14, 16</sup>. Only a few reports have been found that involve reactant gases A or C<sup>1, 7, 16</sup>. The behavior of coupled gas-solid reactions in a reacting gas atmosphere is different from that in an inert gas atmosphere. In the latter case the reactant gases A and C required in reactions (1) and (2) are originated from solids B and D, while in the former case, besides from solids B and D, reactant gases A and C may be diffused into or out of the solid matrix. The model of Tseng and Lin<sup>16</sup> has been adopted with the boundary conditions altered here for explaining this more complex system. The effects of reaction/diffusion ratio, mass transfer, reactivity ratio, factor of catalytic activity and reactant amount ratio on the conversions of solids B and D are studied in this investigation.

## 1. Formulation

A slab-like pellet made up of uniformly mixed solid grains consisting of species B and D are considered here. Solids B and D react with gases A and C according to reactions (1) and (2). Gases A and C are assumed to be present in the bulk gas.

The following assumptions are made:

(1) The system is isothermal and isobaric;

(2) It can be considered as a one-dimensional system;

(3) The pellet structure does not change during reactions;

(4) Pseudo-steady state assumption is applicable;

(5) First-order expression is employed for reaction (1);

(6) Rate expression of Langmuir-Hinshelwood type and first-order with respect to concentration of catalyst E is employed for a solid E catalyzed gas-solid reaction (2);

(7) Gas diffusion in the pore is in the Knudsen diffusion region.

Pseudo-steady state has proved to be a good assumption for gas-solid reaction<sup>2, 3</sup>. Assumption (6) is arbitrarily made due to a lack of experimental data. The model is only valid in the case where pore diameter is much smaller than a mean free path of diffusing gas, because only Knudsen diffusion is considered.

Within the framework of the above assumptions the problem may be stated by combining equations for the conservation of the gases with a mass balance for the solids. The results are expressed as

$$-\left(\frac{D_{eKA}}{RT}\right) \frac{\partial^2 P_A}{\partial Z^2} = -\alpha_B S_B \left(\frac{C_B}{C_{Bo}}\right)^m k_1 P_A + a \alpha_D S_D \left(\frac{C_D}{C_{Do}}\right)^{m'} \frac{(k_2 + k_{21} C_E) P_C}{1 + k_{22} P_A + k_{23} P_C} \quad (5)$$

$$-\left(\frac{D_{eKC}}{RT}\right) \frac{\partial^2 P_C}{\partial Z^2} = c \alpha_B S_B \left(\frac{C_B}{C_{Bo}}\right)^m k_1 P_A - \alpha_D S_D \left(\frac{C_D}{C_{Do}}\right)^{m'} \frac{(k_2 + k_{21} C_E) P_C}{1 + k_{22} P_A + k_{23} P_C} \quad (6)$$

where

$$\varepsilon + \alpha_B + \alpha_D = 1 \quad (7)$$

The meanings of all symbols can be found in Nomenclature.  $D_{eKA}$  and  $D_{eKC}$  are effective Knudsen diffusivities in which porosity and tortuosity have been

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taken into account. The values of  $m$  and  $m'$  depend on the structure of the solid. If solid pellet is made of spherical grains,  $m = m' = 2/3$ . For long cylinders,  $m = m' = 1/2$  and for flat plate,  $m = m' = 0$ . The magnitude of  $k_{21}$  indicates the significance of the catalytic effect of solid E on reaction (2).  $k_{21}$  is null if solid E is not a catalyst.

The mass balances on solids B and D yield

$$\frac{\partial C_B}{\partial t} = -b\alpha_B S_B \left( \frac{C_B}{C_{Bo}} \right)^m k_1 P_A \quad (8)$$

$$\frac{\partial C_D}{\partial t} = -d\alpha_D S_D \left( \frac{C_D}{C_{Do}} \right)^{m'} \frac{(k_2 + k_{21} + C_E) P_C}{1 + k_{22} P_A + k_{23} P_C} \quad (9)$$

For solid E we have

$$C_E = -\left(\frac{e}{b}\right) (C_B - C_{Bo}) \quad (10)$$

Initial solid concentrations of B and D are  $C_{Bo}$  and  $C_{Do}$ , respectively.

$$\text{at } t = 0, \quad C_B = C_{Bo} \text{ and } C_D = C_{Do} \quad (11) \quad (12)$$

The boundary conditions at the center of the pellet can be written, due to symmetry, as

$$\text{at } t = 0, \quad \frac{\partial P_A}{\partial Z} = 0 \quad \text{and} \quad \frac{\partial P_C}{\partial Z} = 0 \quad (13) \quad (14)$$

At the surface of the pellet, the fluxes of gases transferred through the boundary layer are equal to the fluxes diffused through the pellet. Thus, we have

$$\text{at } Z = L, \quad -D_{eKA} \frac{\partial P_A}{\partial Z} = k_m (P_A - P_{Ab}) \quad (15)$$

$$\text{at } Z = L, \quad -D_{eKC} \frac{\partial P_C}{\partial Z} = k_m (P_C - P_{Cb}) \quad (16)$$

To facilitate the analysis, Eqs. (5)-(16) are transformed into dimensionless forms, and they can be found in Reference 15. The definitions of dimensionless quantities are listed in **Table 1** and the physical meanings of the parameters,  $\sigma^2$ ,  $\beta$ ,  $\gamma$  and  $I_1$  are explained as follows.  $\sigma^2$  is a capability ratio of the first reaction to diffusion of gas A.  $\beta$  is a reactivity ratio of the second reaction to the first one.  $\gamma$  is a measure of the initial amount of solid D to that of solid B.  $I_1$  indicates how important is the catalytic effect of the solid E on reaction (2).

The conversions of the solid reactants,  $X_B$  and  $X_D$ , may then be calculated by using the following expressions:

$$X_B = \int_0^1 (1 - \xi_B) d\eta \quad (17)$$

$$X_D = \int_0^1 (1 - \xi_D) d\eta \quad (18)$$

## 2. Solution Method

Governing equations, initial conditions and boundary conditions were solved numerically. Boundary-value problems were solved by a DTPTB subprogram of shooting method<sup>8</sup>, and the initial-value problems by RKF45 program<sup>6</sup>. The conversions of solid reactants B and D,  $X_B$  and  $X_D$  at each stage were deter-

**Table 1.** Definitions of dimensionless quantities

|                                  |   |
|----------------------------------|---|
| gas concentrations               | $\Psi_A = \frac{P_A}{P_t}, \Psi_C = \frac{P_C}{P_t}$                            |
| gas concentrations in bulk phase | $\Psi_{Ab} = \frac{P_{Ab}}{P_t}, \Psi_{Cb} = \frac{P_{Cb}}{P_t}$                |
| coordinate                       | $\eta = z/L$  |
| time                             | $t^* = (b\alpha_B S_B P_t k_1 / C_{Bo}) t$                                      |
| solid concentrations             | $\xi_B = C_B / C_{Bo}, \xi_D = C_D / C_{Do}, \xi_E = C_E / C_{Eo}$              |
| reaction/diffusion ratio         | $\sigma^2 = L^2 R T k_1 \alpha_B S_B / D_{eKA}$                                 |
| reactivity ratio                 | $\beta = (d/b) (\alpha_D / \alpha_B) (S_D / S_B) (C_{Bo} / C_{Do}) (k_2 / k_1)$ |
| reactant amount ratio            | $\gamma = (b/d) (C_{Do} / C_{Bo})$  |
| factor of catalytic activity     | $I_1 = (k_{21} / k_2) C_{Bo}$   |
| reaction rate constants          | $I_2 = k_{22} P_t, I_3 = k_{33} P_t$  |
| Sherwood number                  | $N_{sh} = \frac{h_m L}{D_{eKA}}$  |

mined on the basis of Eqs. (17) and (18) by employing Simpson's rule.

**Table 2.** Values of stoichiometric number and pertinent parameters

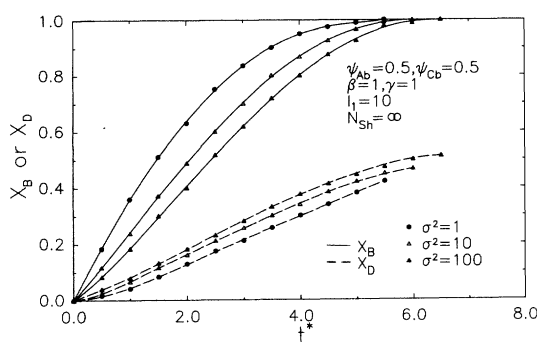
| stoichiometric number or parameter | a | b | c | d | e | f | $I_2$ | $I_3$ | $m$ | $m'$ | $M_A$ | $M_C$ |
|------------------------------------|---|---|---|---|---|---|-------|-------|-----|------|-------|-------|
| value                              | 2 | 1 | 1 | 1 | 1 | 0 | 83.5  | 2.42  | 2/3 | 2/3  | 28    | 44    |

## 3. Results and Discussion

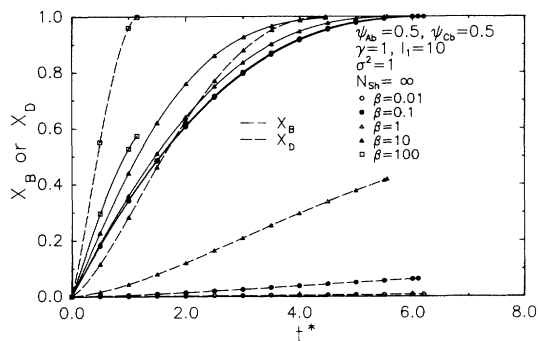
The values of stoichiometric numbers and pertinent parameters employed for calculation are listed in **Table 2**. The stoichiometric numbers corresponded to the carbothermic reduction of FeO or NiO. Solid grains B and D are assumed to be spherical.  $m = m' = 2/3$  was then taken for the calculation. The values of  $I_2$  and  $I_3$  were calculated according to the rate equation of the Boudard reaction at 1000°C by Wu<sup>17</sup>. Molecular weights of carbon monoxide and carbon dioxide were assigned to  $M_A$  and  $M_C$  respectively.

### 3.1 Conversion curves of different reaction/diffusion ratios $\sigma^2$ and different values of Sherwood number, $N_{sh}$

Conversion curves of solids B and D with different



**Fig. 1** Plot of conversion  $X_B$  and  $X_D$  against reaction time. The effect of  $\sigma^2$ .



**Fig. 2** Plot of conversions  $X_B$  and  $X_D$  against reaction time. The effect of  $\beta$ .

reaction/diffusion ratios  $\sigma^2$  are depicted in **Fig. 1**. It is observed that increasing the value of  $\sigma^2$  renders a low conversion of solid B and a high conversion of solid D. The effect of decreasing  $N_{sh}$  is similar to that of increasing  $\sigma^2$ , and the results are not shown here. Increasing the value of  $\sigma^2$  and decreasing the value of  $N_{sh}$  respectively reduce the diffusion resistance in the pellet and the mass transfer resistance in the gas film. Concentration of gas A in the pellet is reduced and that of gas C is increased such that conversion of B is reduced and conversion of D is enhanced.

### 3.2 Conversion curves of different reactivity ratios, $\beta$

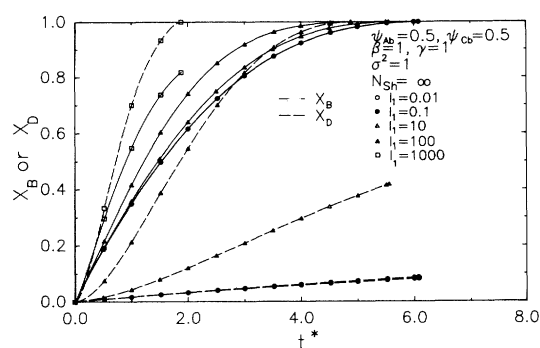
Larger value of  $\beta$  means a higher rate of the second reaction in comparison with that of the first one. A fast second reaction produces more gas A, which in consequence accelerates the first reaction. Both reactions are then accelerated. The computed conversion curves (**Fig. 2**) confirm this viewpoint.

### 3.3 Conversion curves of different factors of catalytic activity, $I_1$

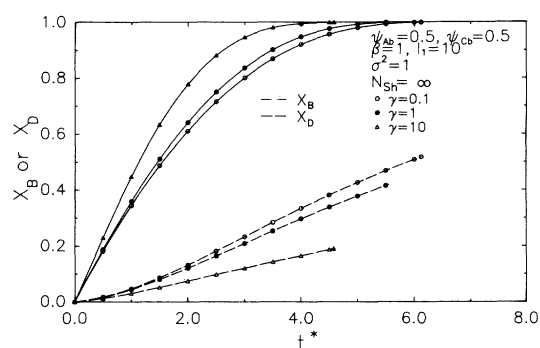
In the carbothermic reduction of nickel oxide, the nickel produced in reaction (3) is usually a good catalyst for the Boudard reaction, reaction (4)<sup>9</sup>. Therefore, the catalytic effect is considered in this model.

$I_1$  appearing in governing equations is known to indicate the importance of a catalytic reaction in comparison with that of a noncatalytic reaction. In a system without catalytic reaction,  $I_1$  equals zero. For the other extreme, an uncatalyzed Boudard reaction can be neglected.

Also it should be mentioned here that the catalytic



**Fig. 3** Plot of conversions  $X_B$  and  $X_D$  against reaction time. The effect of  $I_1$ .



**Fig. 4** Plot of conversions  $X_B$  and  $X_D$  against reaction time. The effect of  $\gamma$ .

effect in the initial stage is not important since the value of  $\xi_E$  is small.

The effects of increasing the values of  $I_1$  and  $\beta$  for reaction (2) are similar. Their effects on solid conversions,  $X_B$  and  $X_D$ , are then similar, as shown in, **Figs. 2** and **3**.

### 3.4 Conversion curves of various reactant amount ratios, $\gamma$

$\gamma$ , defined in Table 1, is a measure of the initial amount of solid D to that of solid B. When the value of  $\gamma$  is large, more solid D and less solid B are in the pellet, resulting in more gas A and less gas C in pellet through reactions (1) and (2). More gas A and less solid B (as well as less gas C and more solid D) render reaction (1) fast and reaction (2) slow, as shown in **Fig. 4**. The explanation is probably that the effect of the concentration of reactant gas is more significant than that of the concentration of a reactant solid.

### 3.5 General discussion

From the above results it is found that if solid B is the desired product, one may decrease the value of  $\sigma^2$  or increase the value of any of the following:  $\beta$ ,  $I_1$ ,  $\gamma$  or  $N_{sh}$ . Referring to the definitions of these parameters, **Table 1**, it is found that the values of  $\beta$  and  $I_1$  are not easy to change for a specific system. However, decreasing the value of  $\sigma^2$  as well as increasing the values of  $\gamma$  and  $N_{sh}$  can be achieved by reducing the pellet size, increasing the relative initial amount of solid D to solid B, and increasing the velocity of bulk gas, respectively.

## Acknowledgement

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## Nomenclature

|                                    |  |   |
|------------------------------------|--|---|
| $C_B, C_D, C_E$                    | = Concentrations of solids B, D and E respectively   | [mol/m <sup>3</sup> ]   |
| $C_{Bo}, C_{Do}$                   | = Initial concentrations of solids B and D respectively  | [mol/m <sup>3</sup> ]   |
| $D_{eKA}, D_{eKC}$                 | = Effective Knudsen diffusivity  | [m <sup>2</sup> /s]   |
| $k_1, k_2, k_{21}, k_{22}, k_{23}$ | = Reaction rate constants  |   |
|                                    | $\left[ \frac{\text{mol}}{\text{m}^2 \cdot \text{s} \cdot P_a} \right], \left[ \frac{\text{mol}}{\text{m}^2 \cdot \text{s} \cdot P_a} \right], \left[ \frac{\text{m}}{\text{s} \cdot P_a} \right], [p_a^{-1}], [p_a^{-1}]$ |   |
| $k_m$                              | = Mass transfer coefficient  | [m/s]   |
| $L$                                | = Half-thickness of pellet   | [m]   |
| $m, m'$                            | = Reaction order   | [-]   |
| $M_A, M_C$                         | = Molecular weights of gases A and C respectively  | [kg/mol]  |
| $P_A, P_C$                         | = Partial pressures of A and C respectively  | [P <sub>a</sub> ]   |
| $P_{Ab}, P_{Cb}$                   | = Partial pressures of A and C in bulk gas respectively  | [P <sub>a</sub> ]   |
| $P_t$                              | = Total pressure   | [P <sub>a</sub> ]   |
| $R$                                | = Gas constant   | $\left[ \frac{P_a \cdot \text{m}^3}{\text{mol} \cdot \text{K}} \right]$ |
| $S_B, S_D$                         | = Surface areas per unit volume of solids B and D respectively   | [1/m]   |
| $t$                                | = Reaction time  | [s]   |
| $T$                                | = Absolute temperature   | [K]   |
| $X_B, X_D$                         | = Conversions of solids B and D defined in Eqs. (17) and (18) respectively   | [-]   |
| $Z$                                | = Coordinate   | [m]   |

|                      |  |     |
|----------------------|--|-----|
| $\alpha_B, \alpha_D$ | = Volume fractions occupied by solids B and D per unit volume of pellet respectively | [-] |
| $\epsilon$           | = Porosity   | [-] |

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