

Lecture 7Heterogeneous SystemsGas - Solid Noncatalytic Reactions

This includes a variety of reactions of solid particles with fluids such as:

A. Pyrolysis or thermal decomposition



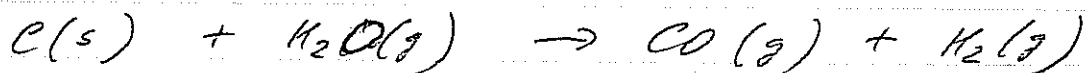
Solid \rightarrow fluid

B. Pyrolysis or thermal decomposition (calcination)



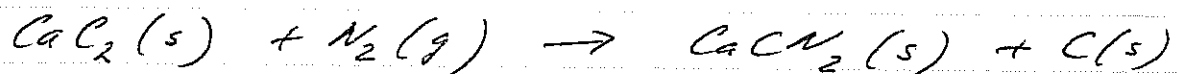
Solid \rightarrow Solid + gas

C. Gasification



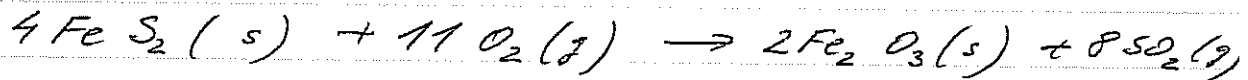
Solid + gas \rightarrow Fluids

D. Nitrogenation



Solid + gas \rightarrow Solids

E. Oxidation



Solid + gas \rightarrow Solid + gas

In order to design reactors for the above types of gas-solid reactions it is important to have:

- models of the phenomena on particle scale
- models for flow patterns on the reactor scale.

We will examine here particle scale phenomena only.

On the particle scale all of the above processes can be classified into two groups according to solid porosity.

I. Solid reactant is porous ($\epsilon_p > 0.1$).

II. Solid reactant is nonporous ($\epsilon_p < 0.1$).

The general reaction stoichiometry can be described by:



and the additional classification can be made:

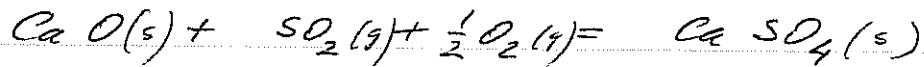
A. Pellet size changes little or not at all with reaction ($b \neq 0, \rho \neq 0$)

B. Pellet size changes dramatically with reaction

1) pellet decreases in size ($s = 0$)

2) pellet grows in size ($b = 0$)

For example



fits in category IA.



fits in category IB1



fits in category IIB1

Case A

Factors affecting the rate of solid conversion:

- mass transfer through boundary layer
- diffusion through solid reactant and/or product
- surface reaction rate: order, type
- heat transfer through boundary layer
- heat transfer through the pellet and heat of reaction
- change of solid structure and morphology during reaction and its effect on transport parameters and

4

Consider isothermal ($T = \text{const}$) in two hours first, for simplicity.

Two basic approaches in developing ~~the~~ a model for reaction of the whole pellet

1. Consider the pellet to be a single, homogeneous entity. This leads to various forms of diffusion with simultaneous reaction models and shrinking core models

2. Consider the pellet to be composed of many individual grains. The rate per unit volume of the pellet is now expressed as the rate per grain times the number of grains per unit volume of the pellet. This leads to structural models.

For the reaction



The model equations are:

$$\epsilon_p \frac{\partial C_A}{\partial t} = D_e \nabla^2 C_A - (-R_A) \quad (1)$$

$$\frac{\partial C_B}{\partial t} = -\left(\frac{b}{a}\right)(-R_A) \quad (2)$$

$$-R_A = a R(C_A, C_B) \quad (3)$$

$$t=0 \quad ; \quad C_A = 0 \quad ; \quad C_B = C_{B0} \quad (4)$$

on pellet exterior surface S_{ex} : $D_e \frac{\partial C_A}{\partial r} \Big|_{S_{ex}} = k_m (C_{A0} - C_{A_{se}})$

on line of symmetry C : $\frac{\partial C_A}{\partial r} = 0 \quad (5)$

$\epsilon_p \left(\frac{\text{m}^3 \text{ voids}}{\text{m}^3 \text{ pellet}} \right)$ - pellet porosity

$D_e \left(\frac{\text{m}^2}{\text{s}} \right)$ - effective diffusivity for reactant A

$C_A \left(\frac{\text{kmol}}{\text{m}^3 \text{ voids}} \right)$ - concentration of A

$C_B \left(\frac{\text{kmol}}{\text{m}^3 \text{ pellet}} \right)$ - concentration of B

$t \text{ (s)}$ - time

$k_m \left(\frac{\text{m}}{\text{s}} \right)$ - mass transfer coefficient for A

$n \text{ (m)}$ - normal direction to the surface

$C_{Ab} \left(\frac{\text{kmol}}{\text{m}^3} \right)$ - concentration in bulk of fluid

∇^2 - Laplace's operator

Considering the pellet to be a single, homogeneous entity leads to reaction rates of the form:

i) $R = k C_A^m C_B^p$

ii) $R = \frac{k C_B^p C_A}{(1 + K C_A)^2}$

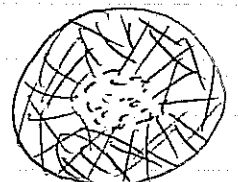
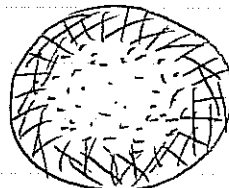
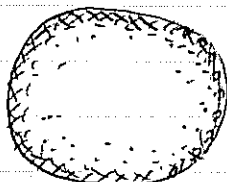
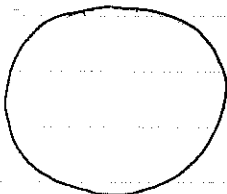
The reaction of the pellet can be qualitatively depicted as:

$t = 0$

$t = t_1$

$t = t_2 > t_1$

$t = t_3 > t_2$



The width of the effective reaction zone depends on the relative magnitude of the rates of diffusion $D_e \frac{dC_A}{dr}$ and reaction $(-R_A)$.

$$\frac{L^2}{D_e} = \tau_d \text{ - characteristic diffusion time (diffusional resistance)}$$

$$\frac{1}{k C_{A0}^{m-1} C_{B0}^p} = \tau_R \text{ - characteristic reaction time (reaction resistance)}$$

Recall the definition of a modulus (in catalytic heterogeneous reactions)

$$\phi^2 = \frac{\tau_d}{\tau_R} = \frac{k C_{A0}^{m-1} C_{B0}^p L^2}{D_e}$$

$\phi^2 < 1$ ($\tau_R > \tau_d$) - reaction takes place almost uniformly throughout the pellet since the diffusion resistance is small compared to the reaction resistance. In the limit $\phi \rightarrow 0$ at a given time every point in the pellet reacts at the same rate.

$\phi^2 > 10$ ($\tau_R < \tau_d$) the reaction takes place in a narrow zone. The diffusion rate is now so slow that all the gas that reaches unreacted solid reacts before it has the chance to diffuse further. In the limit ($\phi \rightarrow \infty$ i.e. $\phi^2 > 400$) all the reactant gas reacts at the interface between unreacted and completely reacted solid and

The shrinking core model applies.

The shrinking core model is also always obtained when the original solid reactant is non porous.

The model can be described by the following equations:

$$D_{eS} \nabla^2 C_A = \tau_p \frac{\partial C_A}{\partial t} \approx 0 \quad (1)$$

on outer surface $D_{eS} \frac{\partial C_A}{\partial r} \Big|_{s_{ex}} = k_m (C_{A,b} - C_A|_{s_{ex}}) \quad (2)$

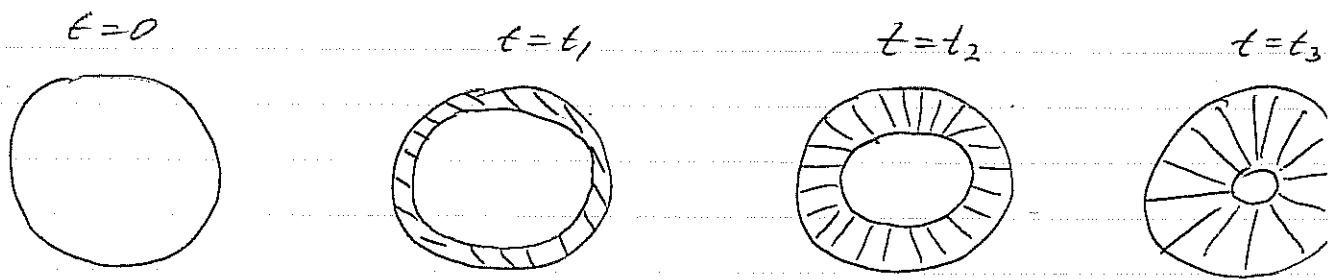
at the interface between unreacted and reacted solid S_c $D_{eS} \frac{\partial C_A}{\partial r} \Big|_{s_c} = k f(C_{A,c}) \quad (3)$

$$-C_{B0} \frac{dV_B}{dt} = \left(\frac{b}{a}\right) k f(C_{A,c}) S_c \quad (4)$$

- $t = 0$ $V_B = V_{p0}$
- $D_{eS} \left(\frac{m^2}{s}\right)$ - effective diffusivity through solid product S
- $S_c (m^2)$ - surface of the interface separating completely reacted and unreacted solid
- $V_B (m^3)$ - volume of the shrinking core of unreacted reactant.
- $k f(C_A) = (-R_A)$ rate of reaction of A

The time derivative in eq (1) can be set to zero due to PSSA assumption.

Reaction progresses as follows:



For a spherical pellet with shrinking core model equations are (1st order reaction)

$$\frac{d}{dr} \left(r^2 \frac{dC_A}{dr} \right) = 0 \quad (1)$$

$$r = R \quad D_{es} \left. \frac{dC_A}{dr} \right|_R = k_m (C_{A0} - C_A|_R) \quad (2)$$

$$r = r_c \quad D_{es} \left. \frac{dC_A}{dr} \right|_{r_c} = k C_{Ac} \quad (3)$$

$$-C_{B0} \frac{d}{dt} \left(\frac{4}{3} \pi r_c^3 \right) = \frac{b}{a} 4\pi r_c^2 k C_{Ac} \quad (4)$$

$$t = 0 \quad r_c = R$$

First solving (1) to (3) we get

$$C_{Ac} = \frac{C_{A0}}{1 + \frac{k r_c^2}{k_m R^2} + \frac{k r_c}{D_{es}} + \frac{k r_c^2}{R D_{es}}}$$

Substituting into (4) and integrating yields:

$$t = \frac{C_{B0}}{\left(\frac{b}{a}\right) k C_{A0}} \left\{ \frac{1}{3} \left[\frac{1}{k_m R^2} - \frac{1}{D_{es} R} \right] \left(1 - \frac{r_c^3}{R^3} \right) + \frac{1}{2 D_{es} R} \left(1 - \frac{r_c^2}{R^2} \right) + \frac{1}{k R^2} \left(1 - \frac{r_c}{R} \right) \right\}$$

Define solid conversion, x_B .

$$x_B = \frac{N_{B0} - N_B}{N_{B0}} = 1 - \frac{r_c^3}{R^3}$$

$$t = \frac{C_{B0} R}{\left(\frac{b}{a}\right) C_{Ab}} \left\{ \frac{1}{3k_m} x_B + \frac{R}{6D_{es}} \left[1 + 2(1-x_B) - 3(1-x_B)^{2/3} \right] + \frac{1}{k} \left[1 - (1-x_B)^{1/3} \right] \right\}$$

The rate of change of conversion is:

$$\frac{dx_B}{dt} = \frac{3 \left(\frac{b}{a} \right) C_{Ab} R}{\frac{1}{k_m} + \frac{R}{D_{es}} \left[(1-x_B)^{-1/3} - 1 \right] + \frac{1}{k} (1-x_B)^{-2/3}}$$

$$a) \quad \frac{1}{3k_m} \gg \frac{R}{6D_{es}} \quad ; \quad \frac{1}{3k_m} \gg \frac{1}{k}$$

Flow mass transfer controls the rate

$$t = \frac{C_{B0} R}{3 \left(\frac{b}{a} \right) C_{Ab} k_m} x_B$$

$$b) \quad \frac{R}{6D_{es}} \gg \frac{1}{3k_m} \quad ; \quad \frac{R}{6D_{es}} \gg \frac{1}{k}$$

Product layer diffusion controls the rate

$$t = \frac{C_{B0} R^2}{6 \left(\frac{b}{a} \right) C_{Ab} D_{es}} \left[1 + 2(1-x_B) - 3(1-x_B)^{2/3} \right]$$

$$c) \quad \frac{1}{k} \gg \frac{R}{6D_{es}} \quad ; \quad \frac{1}{k} \gg \frac{1}{k_m}$$

$$t = \frac{C_{B0} R}{\left(\frac{b}{a} \right) C_{Ab} k} \left[1 - (1-x_B)^{1/3} \right]$$

Reaction (surface) rate controls the overall rate.

In the shrinking core model we have 3 resistances in series: film mass transfer, solid layer diffusion, surface reaction.

The time, t_0 , required to reach some fixed conversion X_B depends on the particle radius, R_i , as:

$$\left(\frac{t_2}{t_1}\right) = \left(\frac{R_2}{R_1}\right)^{1.5 \text{ to } 2} \quad \text{— film mass transfer controls}$$

$$\left(\frac{t_2}{t_1}\right) = \left(\frac{R_2}{R_1}\right) \quad \text{— surface reaction controls}$$

$$\left(\frac{t_2}{t_1}\right) = \left(\frac{R_2}{R_1}\right)^2 \quad \text{— product layer diffusion controls}$$

Structural models

Replace equation (3) case 4 with

$$-R_A = \frac{(1-\epsilon_p) C_{A0} k_p}{\frac{R_p}{D_{eg}} \left[(1-x_g)^{-1/3} - 1 \right] + \frac{1}{k} (1-x_g)^{-2/3}}$$

and substitute into eq (1).

Replace eq (2) with

$$\frac{dx_g}{dt} = \frac{3 \left(\frac{b}{a}\right) \frac{C_A}{C_{B0} R_g}}{\frac{R_g}{D_{eg}} \left[(1-x_g)^{-1/3} - 1 \right] + \frac{1}{k} (1-x_g)^{-2/3}}$$

where:

$D_{eg} \left(\frac{m^2}{s} \right)$ - diffusivity through the product layer on the grain

$R_g (m)$ - grain radius

x_g - grain conversion

For details see J. Szekely et al. "Gas-Solid Reactions", Academic Press, 1977.

Case II B 1

- Gasification

- Reactions of nonporous solid particles with no solid product formation

isothermal conditions $T_s = T_b = \text{const}$

Consider the reaction stoichiometry:



Surface reaction rate is that of a reversible reaction

$$r_s = k \left[C_{As}^m - \frac{C_{Gs}^n}{K} \right] \quad \left(\frac{\text{kmol}}{m^2 \cdot s} \right)$$

$k \left(\frac{m}{s} \left(\frac{\text{kmol}}{m^3} \right)^{1-n} \right)$ - surface reaction rate constant

$C_{As}, C_{Gs} \left(\frac{\text{kmol}}{m^3} \right)$ - surface concentrations of reactant gas A & product gas G.

m, n - reaction order of forward and reverse reaction

K - equilibrium constant (in approximate concentration units)

The original volume of the solid reactant is V_0 (m^3) at molar density of C_{B0} ($\frac{\text{mol}}{\text{m}^3}$). The volume of the solid is V_c (m^3) at reaction time t (s). At the same time the external geometric surface area of the solid is S_c (m^2).

The mass transfer through the boundary layer is given by

$$\dot{J}_A \left(\frac{\text{mol}}{\text{m}^2 \text{ s}} \right) = k_m (C_{Ab} - C_{As})$$

A mass balance on the solid particle gives:

$$- \frac{C_{B0}}{b} \frac{dV_c}{dt} = S_c k \left[C_{As}^m - \frac{C_{Gs}^m}{K} \right] =$$

$$= \frac{k_m}{a} [C_{Ab} - C_{As}] S_c$$

$$= \frac{k_m'}{g} [C_{Gs} - C_{Gb}] S_c$$

$$t=0 ; \quad V_c = V_0$$

Express V_c and S_c in terms of a shape factor and position coordinate R_c

For first order reaction $m = n = 1$

and equimolar counter diffusion $a = g$ and

$k_m = k_m'$ one gets (for a spherical

pellet) :

$$\frac{b k R (C_{A0} - \frac{C_{A0}}{K})}{C_{A0} R} t = \left(1 - \frac{r_c}{R}\right) + \frac{k R (1 + \frac{1}{K})}{k_{m0} / a} x$$

$$x \left[\frac{4}{3a'} \left(1 - \left(\frac{r_c}{R}\right)^{3/2}\right) - \frac{2}{a'^2} \left(1 - \frac{r_c}{R}\right) + \frac{4}{a'^3} \left(1 - \left(\frac{r_c}{R}\right)^{1/2}\right) - \frac{4}{a'^4} \ln \left(\frac{1+a'}{1+a'(\frac{r_c}{R})}\right) \right]$$

where:

$$a' = b' Sc^{1/3} Re_0^{1/2}$$

$$Sc = \frac{\nu}{D} = \frac{\mu}{\rho D}$$

$$Re_0 = \frac{2uPR}{\mu} = \frac{2uR}{\nu}$$

$$\frac{k_m r_c}{D} = 1 + b' Sc^{1/3} Re_0^{1/2} \left(\frac{r_c}{R}\right)^{1/2}$$

$$\frac{k_{m0} R}{D} = 1 + b' Sc^{1/3} Re_0^{1/2}$$

$R(r_0)$ - radius of original particle

$r_c(r_0)$ - radius of solid particle at reaction time t .

Conversion:

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

Damkohler number:

$$Da = \frac{k R (1 + \frac{1}{K})}{k_{m0} / a}$$

$Da < 1$ - chemical reaction controls the rate

$Da \gg 1$ - mass transfer controls the rate

When chemical reaction controls the rate ($Da < 1$)

$$\frac{b k (C_{A_0} - \frac{C_{B_0}}{K})}{C_{B_0} R} t = 1 - \left(\frac{r_c}{R}\right) = 1 - (1-X)^{1/3}$$

$$\left(\frac{t_2}{t_1}\right) = \left(\frac{R_2}{R_1}\right)$$

The ratio of times required to reach certain conversion directly proportional to the ratio of $\frac{R_2}{R_1}$ $\sqrt[3]{\text{initial solid radii}}$.

- Indicators for reaction control
- high activation energy
 - no effect of fluid velocity on rate of conversion

In this regime test for first order reaction behavior.

$$\frac{b k (C_{A_0}^m - \frac{C_{B_0}^m}{K})}{C_{B_0} R} t = 1 - (1-X)^{1/3}$$

When mass transfer controls the rate ($Da \gg 1$)

Laminar flow regime $b' = 0$

$$\frac{b k (C_{A_0} - \frac{C_{B_0}}{K}) k_m/a}{C_{B_0} R k R (1 + \frac{1}{K})} t = 1 - \left(\frac{r_c}{R}\right)^2 = 1 - (1-X)^{2/3}$$

$$\frac{(b/a) k_m (C_{A_0} - \frac{C_{B_0}}{K})}{C_{B_0} R^2 (1 + \frac{1}{K})} t = 1 - (1-X)^{2/3}$$

$$\left(\frac{t_2}{t_1}\right) = \left(\frac{R_2}{R_1}\right)^2$$

The ratio of times required to reach certain conversion is directly proportional to the square of ~~the~~ the ratio of initial solid radii.

For turbulent flow (large Re_0)

$$\left(\frac{t_2}{t_1}\right) = \left(\frac{R_2}{R_1}\right)^{3/2}$$

as evident from equation on top of page (13).

Nonisothermal Situations $T_s \neq T_b$

Most frequently the heat capacity of the particle is small and its conductivity is large compared to gas phase conductivity. The particle is then isothermal but a temperature difference may exist across the gas film. The temperature of the particle may vary in time as reaction progresses.

It is easy to determine the film ΔT from experimental data:

$$\Delta T_{\text{film}} = T_s - T_b = \frac{(-\Delta H_r)(R_s)_{\text{observed}}}{h}$$

$R_s \left(\frac{\text{mol}}{\text{m}^2 \text{ s}} \right)$ - observed reaction rate

$h \left(\frac{\text{J}}{\text{m}^2 \text{ } ^\circ\text{C s}} \right)$ - heat transfer coefficient (from appropriate correlation)

$\Delta H_r \left(\frac{\text{J}}{\text{mol}} \right)$ - heat of reaction

Predicting "a priori" the ΔT_{lim} requires trial and error calculations since we must add to the equations on page 12 the following heat transfer equation

$$h(T_s - T_b) = k_o e^{-E/RT_s} \left(C_{A_s}^m - \frac{C_{G_s}^m}{k_o e^{-\Delta H_f/RT_s}} \right) (\Delta T)$$

and the equations on page (12) become:

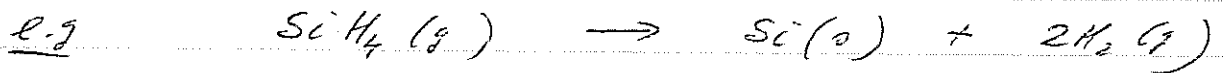
$$-\frac{C_{B_0}}{b} \frac{dV_c}{dt} = S_c k_o e^{-E/RT_s} \left(C_{A_s}^m - \frac{C_{G_s}^m}{k_o e^{-\Delta H_f/RT_s}} \right)$$

$$= \frac{k_m}{a} (C_{A_0} - C_{A_s}) S_c = \frac{k_m}{g} (C_{G_s} - C_{G_0})$$

$$t=0, \quad V_c = V_0$$

If the heat capacity of the solid is not negligible then an additional differential equation for temperature must be added.

Growth of Solid Particles



Nucleation & Coagulation Particles are formed by joint action of van der Waals and Brownian forces.

$$\frac{dR}{dt} \propto R^{-2}$$

growth rate inversely proportional to radius squared, directly proportional to concentration (supersaturation) and

a weak function of temperature. Rates very high.

Coalescence when the particles are of the size 0.1μ or more they are few and far apart from the standpoint of Brownian motion. Eddies bring them and fuse them together

$$\frac{dR}{dt} \propto R \quad \text{to} \quad \frac{dR}{dt} \propto R^{3/2}$$

For particles larger than 10μ the additional two processes become important.

Condensation (Film mass transfer)

$$\frac{dR}{dt} \propto \frac{1}{R} \quad \text{to} \quad \frac{dR}{dt} \propto \frac{1}{R^{1/2}}$$

Laminar flow

turbulent flow

Impaction

Here large particles ~~are~~ sweep up the finer particles. If one considers larger particles $> 10 \mu$ moving through a haze gas then their growth is:

$$\frac{dR}{dt} = k$$

Coagulation and ~~condensation~~ coalescence occur very rapidly on a time scale of less than one second. The mechanism that dominates for particles of longer residence time is either

condensation or impaction.

This suggests that growing solid particles are most likely to follow a linear or reciprocal growth rates i.e.

$$\frac{dR}{dt} = k \quad \text{or} \quad \frac{dR}{dt} = \frac{k'}{R}$$

Shrinkage of Solid Particles

As already discussed shrinkage of solid particles may obey one of the following laws

$$\frac{dR}{dt} = -k \quad \text{reaction control}$$

$$\frac{dR}{dt} = -\frac{k'}{R} \quad \begin{array}{l} \text{film diffusion control} \\ \text{small particles i.e.} \\ \text{small } Re_0 \end{array}$$

$$\frac{dR}{dt} = -\frac{k''}{R^{1/2}} \quad \begin{array}{l} \text{film diffusion control} \\ \text{large particles i.e.} \\ \text{large } Re_0 \end{array}$$

$$\frac{dR}{dt} = -k''' R \quad \text{empirical}$$