Applied chemical processes

Heterogeneous noncatalytic reactions

Heterogeneous noncatalytic reactions
Reactions of fluid reactants
→ gas-liquid reaction
→ liquid-liquid reaction (immiscible)

Reactions with solid state
gas or liquid became to contact with solid substance and react with it and form product
aA (g or l) + bB (s) → fluid (g or l) products
→ solid products
→ fluid and solid products

Heterogeneous noncatalytic reactions
High industrial importance
• roasting of sulfidic ores
  2 ZnS + 3 O₂ → 2 ZnO + 2 SO₂
• metals from the oxides
  Fe₃O₄ + 4H₂ → 3Fe + 4 H₂O
  Fe₃O₄ + 4CO → 3Fe + 4 CO₂
• combustion of coal
• metal layer depositions
• hydrogen production
Heterogeneous noncatalytic reactions

Two different solid-fluid reactions:
1) Particle size is not changing
2) Particle size is changing during reaction

Heterogeneous noncatalytic reactions

- description by simple, ideal models
- express the reaction rate dependence, time of reaction
  \[ A_{(g,l)} + B_{(s)} \rightarrow P_{(g,l,s)} \]

1) Progressive Conversion Model
2) Shrinking Core Model
3) Grain Model

Progressive Conversion Model

- reactant enters and reacts with the particle at all times
- different rates at different locations within the particle
- solid reactant is converted continuously and progressively throughout the particle
Progressive Conversion Model - limiting assumptions

- solid particles are monodisperse and spherical
- pseudostationary state
- 1st order chemical reaction (fluid reactant), rate is not dependent on concentration of solid reactant
- effective diffusion coefficients and coefficients of mass transfer are not changing during reaction
- thickness of reactive zone is constant
- excess of fluid phase over stoichiometry
- distribution of solid reactant in particles is homogeneous

Shrinking Core Model (Unreacted Core Model)

- reaction proceeds at a narrow interface which moves into the solid particle
- reactant is completely converted as the reaction interface passes
- at any time there exists an unreacted core of material which shrinks in size during reaction

Shrinking Core Model

1. step: Diffusion of fluid A thru the diffusion film surrounding solid particle to its surface
2. step: Penetration and diffusion of fluid A thru the ash layer to the surface of unreacted core
3. step: Chemical reaction of fluid A with solid reactant B
4. step: Diffusion of fluid products thru the ash to the surface of solid
5. step: Diffusion of fluid products thru the film surrounding solid particle to the bulk
Shrinking Core Model

- All steps have to be in consequence to proceed overall process
- Slowest step is rate-limiting
  a) diffusion thru the film
  b) diffusion thru internal layer
  c) chemical reaction

Limiting assumptions for further mathematical descriptions:
- a) chemical reaction is elementar and one direction
- b) partical has spherical shape

\[ \frac{d n_R}{dt} = 4 \pi R^2 k_c \frac{c_A}{M_p} = \text{konst.} \]
\[ \frac{d n_s}{dt} = 4 \pi \rho \frac{\rho_s}{M_p} \frac{dx}{dR} = 4 \pi R^2 k_c \frac{c_A}{M_p} \]
\[ 1 - X_A = \frac{V_A}{V_{total}} = \left( \frac{r}{R} \right)^3 \]
\[ t = \frac{V_s \rho_s R}{3 \pi k_c \frac{c_A}{M_p}} \]
\[ \tau_3 = \frac{V_s \rho_s R}{3 \pi k_c c_A M_p} \]
\[ t_{R=0} \]

\( k_c \): mass transfer coefficient between fluid and particle
\( \tau_3 \): time for full conversion
\( r \): radius of unreacted core
\( R \): radius of particle
Shrinking Core Model
b) rate limiting step – diffusion thru ash layer

\[
\frac{dn}{dt} = J_c = \frac{dn}{dt} = \frac{4\pi D_c}{v_c M_k} \left( \frac{1}{r} - \frac{1}{R} \right) = 4\pi D_c c_a
\]

\[
t = \frac{v_c D_c R^2}{6v_c M_k D_{eff} c_a} \left[ 1 - \left( \frac{r_e}{R} \right)^2 + 2 \left( \frac{r_e}{R} \right) \right]
\]

\[
\tau_a = \frac{v_c D_c R^2}{6v_c M_k D_{eff} c_a}
\]

Time of reaction 

\[
\frac{L}{\tau_a} = 1 - \left( \frac{r_e}{R} \right)^2 + 2 \left( \frac{r_e}{R} \right) = 1 - 3 \left( 1 - X_a \right)^2 / 2 + 2(1 - X_a)
\]
Shrinking Core Model

c) rate limiting step – chemical reaction

\[ -\frac{ds}{dt} = -\frac{v_m}{v_s} \frac{du}{dt} = 4m^2 \frac{dC}{dt} \]
\[ \frac{v}{v_s} \frac{dC}{dt} = kC \]

\[ t = \frac{v_s \rho_d R}{v_d M_d k c_d} (R - r_c) \]

Time of reaction \( (r = 0) \)

\[ \tau_c = \frac{v_s \rho_d R}{v_d M_d k c_d} \]

\[ \tau_a = 1 - \frac{r_c}{R} = 1 - (1 - X_a)^{\frac{3}{5}} \]

Shrinking Core Model

c) rate limiting step – chemical reaction

Progress of reaction of a single spherical particle with surrounding fluid measured in terms of time for complete conversion.
Areas where Shrinking core model is not apliccable

Shrinking core model is bestsimple representation for the majority of gas-solid reactions except:

- slow gas-solid reaction with porous material – catalyst poisoning
  - Continuous reaction model
- „The second exception occurs when solid is converted by the action of heat, and without needing contact with gas. Baking bread, boiling missionaries, and roasting puppies are mouthwatering examples of such reactions.” Levenspiel O., Chemical reaction engineering 3rd ed., ISBN 0-471-25424-X
  - Continuous reaction model

Grain Model

- solid spherical partial with some porosity, which is formed by lot of nonporous-spherical grains with same diameter
- very good description of the real systems
Grain Model

Limiting assumptions

• solid reactant is in form of spherical particle, diameter of particle is not changing during reaction
• spherical particles are formed of grains and is not changing size during reaction
• particle is porous, but grains of reactant are not, porous is only product
• product is not resistant for fluid flow
• first order reaction according to fluid phase
• pseudostationary state
• temperature gradient in the grain is changing, but temperature gradient in the particle is negligible
• temperature conductivity of the grain is not dependent at the extend of the reaction

Heterogeneous noncatalytic reactions

Reactor design

Calculation of solid-fluid phase reactors is determined by:

• Reaction kinetics of the particles
• Size distribution of the solid phase
• Pattern of solid and fluid flows inside the reactor

The kinetics is often unknown – experimental and experience is required

Heterogeneous noncatalytic reactions

Reactor design

Patterns of the reactant flows:

Solid and fluid, both as piston flow.

Concentration of the reactant is changing

Commonly nonisothermal reactions

a) counter-current flow
b) cross-flow
c) co-current flow
d) combinations
Heterogeneous noncatalytic reactions
reactor design

Ideal mixing of the solid reactant
Fluidised bed – best example
The flow is at this cases hard to describe
Usually transision between ideal mixing and piston flow
Isothermal conditions are common for this types of reactions

Heterogeneous noncatalytic reactions
reactor design

Semicontinual operations
Ionex column, close to the piston flow

Batch operations
Dissolving

Example:
Inflow consist of
30 % particles of diameter 50 \( \mu \)m
40 % particles of diameter 100 \( \mu \)m
30 % particles of diameter 200 \( \mu \)m
is continuously supply to the roasting grit. Gas reactant is cross-flowing through the solid reactant. Necessary times for the conversion of the fractions are:

- 50 \( \mu \)m: 5 min
- 100 \( \mu \)m: 10 min
- 200 \( \mu \)m: 20 min

Determine the conversion of solid substances if the reaction time is 8 minutes. Assume that reaction rate is the time determine step.