Heterogeneous noncatalytic reactions

Reactions of fluid reactants

→ gas-liquid reaction

→ liquid-liquid reaction (immiscible)

<u>Reactions with solid state</u>

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

  $2\ ZnS + 3\ O_2 \rightarrow 2\ ZnO + 2\ SO_2$

- metals from the oxides

  $Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4\ H_2O$

  $Fe_3O_4 + 4CO \rightarrow 3Fe + 4\ CO_2$

- combustion of coal
- metal layer depositions
- hydrogen production

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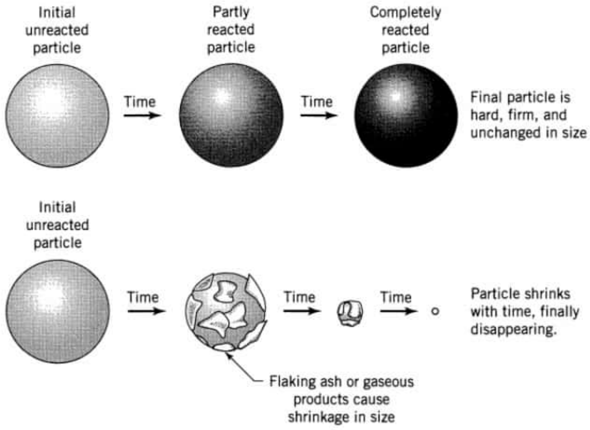
Heterogeneous noncatalytic reactions

Two diferent solid-fluid reactions:

1) <u>Particle size is not changing</u>

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) <u>Shrinking Core Model</u>
3) Grain Model

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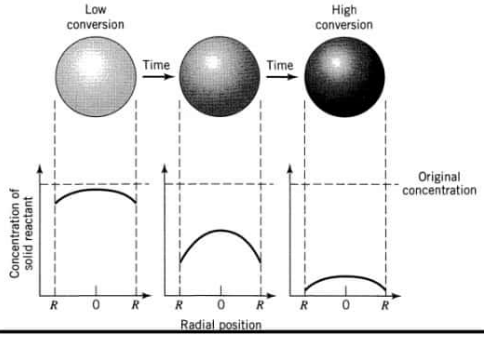
Progressive Conversion Model

- 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 - limitting 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 stechiometry
- distribustion of solid reactant in particles is homogeneous

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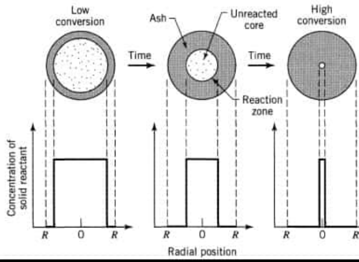
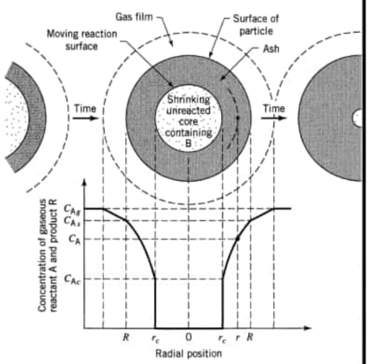
Shrinking Core Model (Unreacted Core Model)

- 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: Difussion 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: Difussion of fluid products thru the film surrounding solid particle to the bulk



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Shrinking Core Model

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

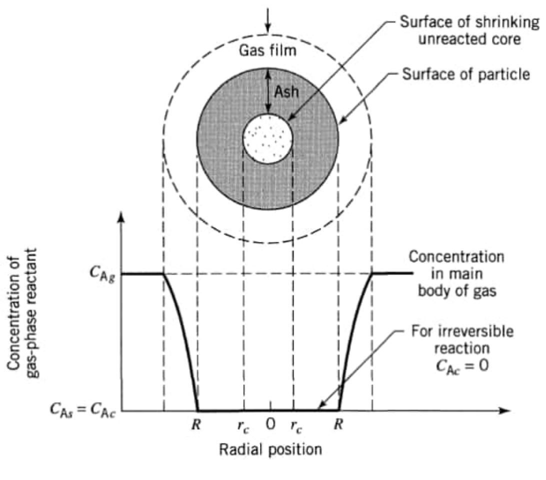
Limitting assuptions for further mathematical descriptions:

a) chemical reaction is elementar and one dirrection

b) partical has spherical shape

Shrinking Core Model

a) rate limitting step – film diffusion



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Shrinking Core Model

a) rate limitting step – film diffusion

$$-dn_A/dt = 4\pi R^2 k_{cA} c_A = konst. \rightarrow -4\pi \frac{\nu_A \rho_B}{\nu_B M_B} r_c^2 \frac{dr_c}{dt} = 4\pi R^2 k_{cA} c_A$$

$$dn_B = \frac{4\pi r_c^2 \rho_B}{M_B} dr_c$$

$$t = \frac{\nu_A \rho_B R}{3\nu_B k_{cA} c_A M_B}\left[1-\left(\frac{r_c}{R}\right)^3\right]$$

$$1 - X_B = \frac{V_c}{V_{total}} = \left(\frac{r_c}{R}\right)^3 \qquad \frac{t}{\tau_k} = 1-\left(\frac{r_c}{R}\right)^3$$

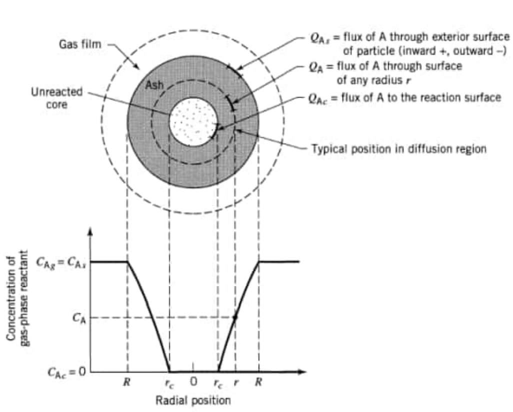
$$\tau_k = \frac{\nu_A \rho_B R}{3\nu_B k_{cA} c_A M_B} \quad [r_c/R=0]$$

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

k_{cA} mass transfer coefficient between fluid and particle
τ_k time for full conversion
r_c radius of unreactedcore / R radius of particle

Shrinking Core Model

b) rate limitting step – diffusion thru ash layer



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Shrinking Core Model

b) rate limitting step – diffusion thru ash layer

$$-\frac{dn_A}{dt} = J_{Ac} = J_{Ar} = J_{AR} \qquad -\frac{dn_A}{dt} = 4\pi r_c^2 j_{Ac} = 4\pi r^2 j_{Ar} = 4\pi R^2 j_{As}$$

$$-\frac{dn_A}{dt} = 4\pi r^2 D_{A,ef}\frac{dc_A}{dr} = konst.$$

$$-\frac{dn_A}{dt}.\int_R^{r_c}\frac{dr}{r^2} = 4\pi D_{A,ef}\int_{c_A=c_{As}}^{c_{Ac}=0} dc_A \qquad -\frac{dn_A}{dt}\left(\frac{1}{r_c}-\frac{1}{R}\right) = 4\pi D_{A,ef}c_{As}$$

$D_{A,ef}$ effective difusion coefficient of the fluid reactant in the inert layer

Shrinking Core Model

b) rate limitting step – diffusion thru ash layer

$$-\frac{4\pi v_A \rho_B r_c^2}{v_B M_B}.\frac{dr_c}{dt}\left(\frac{1}{r_c}-\frac{1}{R}\right) = 4\pi D_{A,ef}c_{As}$$

$$t = \frac{v_A \rho_B R^2}{6 v_B M_B D_{A,ef} c_{As}}\left[1-3\left(\frac{r_c}{R}\right)^2 + 2\left(\frac{r_c}{R}\right)^3\right]$$

Time of reaction (r_c=0)

$$\tau_k = \frac{v_A \rho_B R^2}{6 v_B M_B D_{A,ef} c_{As}}$$

$$\frac{t}{\tau_k} = 1-3\left(\frac{r_c}{R}\right)^2 + 2\left(\frac{r_c}{R}\right)^3 = 1-3(1-X_B)^{2/3} + 2(1-X_B)$$

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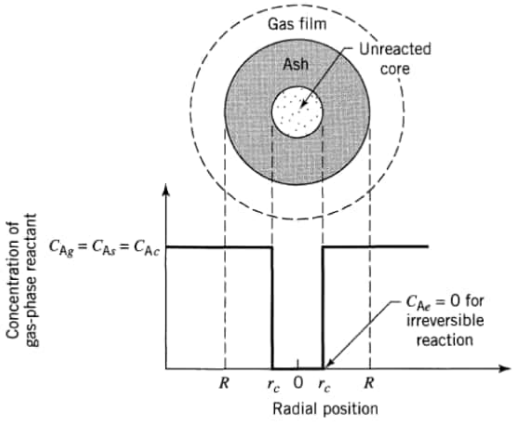
Shrinking Core Model

c) rate limitting step – chemical reaction



Shrinking Core Model

c) rate limitting step – chemical reaction

$$-\frac{dn_A}{dt} = -\frac{\nu_A dn_B}{\nu_B d\tau} = 4\pi r_c^2 k c_A \qquad \frac{\nu_A \rho_B}{\nu_B M_B} \cdot \frac{dr_c}{dt} = kc_A$$

$$t = \frac{\nu_A \rho_B}{\nu_B M_B k c_A}\left(R - r_c\right)$$

k first order rate constant of surface reaction

Time of reaction (r_c=0)

$$\tau_k = \frac{\nu_A \rho_B R}{\nu_B M_B k c_A}$$

$$\frac{t}{\tau_k} = 1 - \frac{r_c}{R} = 1 - (1 - X_B)^{1/3}$$

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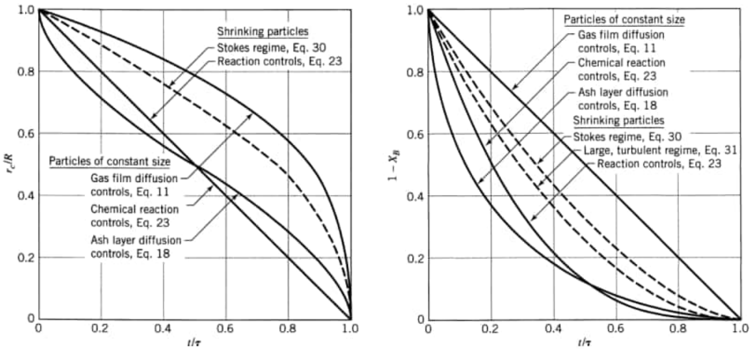
Shrinking Core Model

rate limitting steps - comparison

Progress of reaction of a single spherical particle with surrounding fluid measured in terms of time for complete conversion.

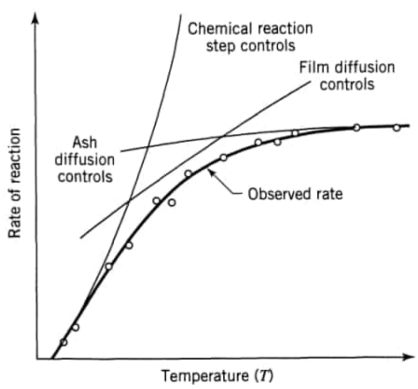


Shrinking Core Model

rate limitting steps - comparison

series relationship among the resistances to reaction:

observed rate is never higher than for any of the individual steps acting alon



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Areas where Shrinking core model is not apliccable

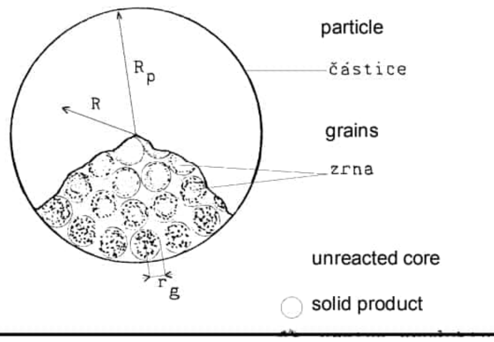
Shrinking core model is bestsimple representation for the majority of gas-solid reactions except:

- slow gas-solid reaction with <u>porous material</u> – 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 partical with some porosity, which is formed by lot of nonporous spherical grains with same diameter

very good description of the real systems



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