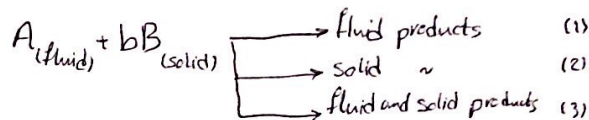


① Fluid-Particle Relations

- In type 2 and 3, the fluid product is a solid or non-flaking ash in which case the size of particles remain unchanged.

- In type 1 particles shrink in size.



- Eq. type 2, 3
 - Roasting (oxidation) of Sulfide ores to metal oxides.
 - $2ZnS_{(s)} + 3O_{2(g)} \rightarrow 2ZnO_{(s)} + 2SO_{2(g)}$
 - $4FeSO_{4(s)} + 11O_{2(g)} \rightarrow 2Fe_2O_{3(s)} + 8SO_{2(g)}$
 - Rxn of metal oxides in reducing atmospheres to give metals
 - $Fe_2O_{3(s)} + 4H_{2(g)} \rightarrow 3Fe_{(s)} + 4H_2O_{(g)}$
 - Nitrogenation of Calcium Carbide to produce Cyanamid
 - $CaC_{2(s)} + N_{2(g)} \rightarrow CaCN_{2(s)} + C_{(amorphous)}$
 - Protective surface treatment of metals.

- Eq. type 1
 - Rxn of Carbonaceous material such as coal, wood, etc.
 - $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$
 - Rxn with steam
 - $C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)}$
 - Carbon disulfide
 - $C_{(s)} + 2S_{(g)} \rightarrow CS_{2(g)}$
 - Sodium cyanide
 - $NaNH_2_{(l)} + C_{(s)} \rightarrow NaCN_{(l)} + H_{2(g)}$
 - Sodium thiosulfate
 - $NaSO_3_{(solution)} + S_{(s)} \rightarrow Na_2S_2O_3_{(solution)}$

①.1 Development of Rate expressions for fluid-solid rxns

- modification of kinetic expression resulting from mass transfer between phases.

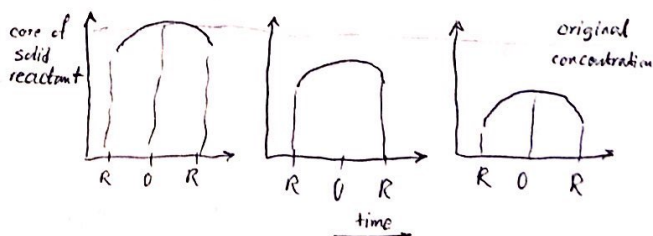
①.1.1 Selection of a model

- Once a model is chosen the rate form associated with that model evolves and vice versa. Its predictive ability depends on how well it corresponds to the actual process.

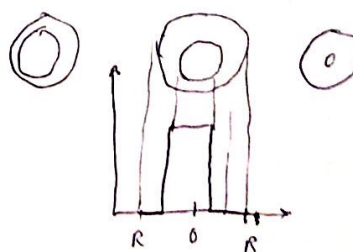
- Two models for non-catalytic rxn of particles with surrounding fluid

- Progressive-Conversion model
- Unreacted core model

- Progressive-Conversion model
 - gas enters throughout all particle and reacts with solid at all times at different rate.
 - solid reactant is converted continuously and progressively.
 - Symmetry on solid concentration



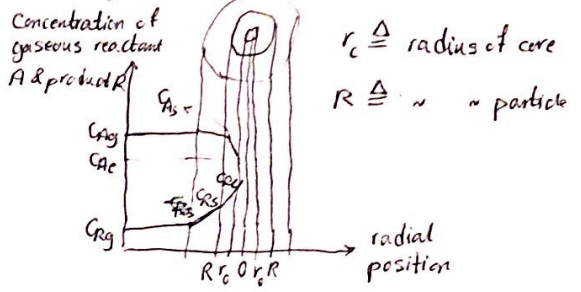
- Unreacted Core model
 - rxn occurs at the outer surface first
 - the zone of rxn then moves into solid
 - leaves behind converted material and inert solid ash.
 - unreacted core material shrinking in size.
 - with time
 - ash layer expands
 - core shrinks



1.1.2 Unreacted Core model for spherical particles of unchanging size



- The model is based on the following steps:
 - 1 → Diffusion of reactant A through the film surrounding the solid particle.
 - 2 → Diffusion through the ash layer to the surface of unreacted core
 - 3 → Rxn of A with the solid.
 - 4 → Diffusion of gaseous products through the ash layer to the external surface.
 - 5 → Diffusion of products through the film to bulk fluid.

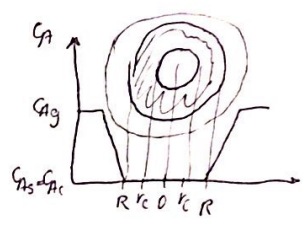


- depending on the rxn, steps 4 and 5 may be absent
- one of the steps may be considered as the "rate controlling step"
- let's consider the case where steps 4 and 5 are absent and when steps 1, 2, or 3 can be the rate controlling step

(irreversible rxn)
(no gas phase product)

A) Diffusion through gas film controls

- A diffusion through the ash layer and its rxn with B at the core is fast
- for irreversible rxn: $C_{As} = C_{Ac} = 0$
- the rxn rate is governed by the rate of diffusion of A through the gas film



- for unchanging size of particle

It is convenient to express the rate of rxn based on the exterior surface of the particle, S_{ex}

for a single particle: $S_{ex} = 4\pi R^2$

for the stoichiometry: $A + bB \rightarrow$ solid products, $-r_A = \frac{1}{b} \frac{dN_B}{dt} = \frac{dN_A}{dt}$

$$\frac{-1}{S_{ex}} \frac{dN_B}{dt} = \frac{-1}{4\pi R^2} \frac{dN_B}{dt} = \frac{-b}{4\pi R^2} \frac{dN_A}{dt} \quad (I)$$

On the other hand, the rate of disappearance of A is governed by mass transfer from bulk fluid to particle surface by diffusion through the gas film. Hence,

$$-r_A'' = \frac{-1}{S_{ex}} \frac{dN_A}{dt} = k_g(C_{Ag} - C_{As}) \quad [kg, m, s]$$

for $C_{As} = 0$ we have: $-r_A'' = k_g C_{Ag} \quad (II)$

$-r_A'' = \frac{-r_B''}{b} \Rightarrow -r_B'' = \frac{-1}{S_{ex}} \frac{dN_B}{dt} = b(-r_A'') = bk_g C_{Ag} \quad (III)$

$(I), (II), (III) \Rightarrow \frac{-1}{4\pi R^2} \frac{dN_B}{dt} = bk_g C_{Ag} \quad (IV)$

$N_B = \rho_B V$ $\rho_B \triangleq$ molar density of B, $V \triangleq$ volume of a particle

for a constant ρ_B , the disappearance of B is related to a decrease in the volume of unreacted core or a decrease in r_c , the radius of unreacted core:

$$-\frac{dN_B}{dt} = -\rho_B \frac{dV}{dt} = -\rho_B \frac{d}{dt} \left(\frac{4}{3} \pi r_c^3 \right) = -4\pi \rho_B r_c^2 \frac{dr_c}{dt} \quad (V)$$

$(IV), (V) \Rightarrow \frac{-1}{4\pi R^2} \frac{dN_B}{dt} = \frac{\rho_B r_c^2}{R^2} \frac{dr_c}{dt} = bk_g C_{Ag} \quad (VI)$

$$\int_{C_{Ag}}^{0} \frac{-\rho_B}{R^2} r_c^2 dr_c = bk_g C_{Ag} \int_0^t dt \Rightarrow t = \frac{\rho_B R}{3bk_g C_{Ag}} \left[1 - \left(\frac{r_c}{R} \right)^3 \right]$$

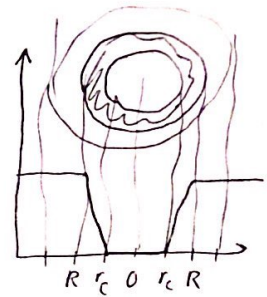
Some definitions and parameters

- $\tau \triangleq$ time for complete conversion $= \frac{\rho_B R}{3bk_g C_{Ag}}$
- $\frac{t}{\tau} \triangleq$ fractional time for complete conversion $= 1 - \left(\frac{r_c}{R} \right)^3$
- $X_B \triangleq$ volume of unreacted core $= \frac{\frac{4}{3} \pi r_c^3}{\frac{4}{3} \pi R^3} = \left(\frac{r_c}{R} \right)^3$

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

B Diffusion through ash layer controls

- note that in the case of gas film controlling the diffusion path was constant.
- In the case of diffusion through ash layer as the controlling step, the thickness of the ash layer increases with time; thus decreasing the rate of diffusion. (i.e. the rxn rate decreases with time)
- Hence, we carry the analysis in two parts
 - to obtain the rate at any time in terms of r_c
 - then integrate between 0 and R
 (Similar to Quasi-Steady-State approximation)



At any time $\rightarrow -\frac{dN_A}{dt} = 4\pi R^2 Q_{A_s} = 4\pi r_c^2 Q_{A_c} = 4\pi r^2 Q_A = cte$

\rightarrow flux of A at any radius r , $Q_A = D_e \frac{dC_A}{dr}$ Fick's law
 \rightarrow through rxn surface \rightarrow effective diffusivity
 \rightarrow exterior \rightarrow

$\rightarrow -\frac{dN_A}{dt} = 4\pi r^2 D_e \frac{dC_A}{dr} = cte$

$\Rightarrow \int -\frac{dN_A}{dt} \int_R^{r_c} \frac{dr}{r^2} = 4\pi D_e \int_{C_{Ag}}^0 dC_A \Rightarrow -\frac{dN_A}{dt} \left(\frac{1}{r_c} - \frac{1}{R} \right) = 4\pi D_e C_{Ag}$ (i)

Recall that: $-\frac{dN_B}{dt} = -4\pi \rho_B r_c^2 \frac{dr_c}{dt} = -b \frac{dN_A}{dt}$ (ii)

(i), (ii) $\Rightarrow -\frac{4\pi \rho_B r_c^2}{b} \frac{dr_c}{dt} \left(\frac{1}{r_c} - \frac{1}{R} \right) = 4\pi D_e C_{Ag}$

$\Rightarrow -\rho_B \int_R^{r_c} \left(\frac{1}{r_c} - \frac{1}{R} \right) r_c^2 dr_c = b D_e C_{Ag} \int_0^t dt$

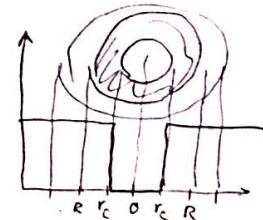
Thus $\rightarrow t = \frac{\rho_B R^2}{6b D_e C_{Ag}} \left[1 - 3\left(\frac{r_c}{R}\right)^2 + 2\left(\frac{r_c}{R}\right)^3 \right]$

$\tau \triangleq$ time for complete rxn $= \frac{\rho_B R^2}{6b D_e C_{Ag}}$, $1 - X_B = \frac{(r_c)^3}{R^3}$

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

C Chemical Rxn Controls

Concentration of A at the rxn surface (external surface of unreacted core) is the same as that on catalyst surface and bulk fluid phase ($C_{Ag} = C_{As} = C_{Ac}$)



$\rightarrow -r_A = k_s C_{As}$, rxn rate per unit surface area of unreacted core is given by: $\frac{-1}{4\pi r_c^2} \frac{dN_B}{dt} = \frac{-b}{4\pi r_c^2} \frac{dN_A}{dt} = b k_s C_{Ag}$ (a)

furthermore recall that: $-\frac{dN_B}{dt} = -4\pi \rho_B r_c^2 \frac{dr_c}{dt}$ (b)

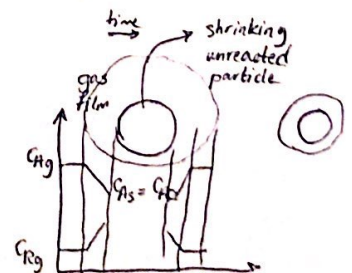
(a), (b) $\Rightarrow -\rho_B \frac{dr_c}{dt} = b k_s C_{Ag} \Rightarrow -\rho_B \int_R^{r_c} dr_c = b k_s C_{Ag} \int_0^t dt$

$\Rightarrow t = \frac{\rho_B}{b k_s C_{Ag}} (R - r_c)$

$\tau \triangleq$ time for complete conversion $= \frac{\rho_B R}{b k_s C_{Ag}}$, $\frac{t}{\tau} = 1 - \frac{r_c}{R} = 1 - (1 - X_B)^{1/3}$

1.7.2 Unreacting Core Model for Shrinking spherical particles

- This is the situation where no ash layer is formed, as in the case of burning of pure carbon in O_2 .
- The particle shrinks during rxn, finally disappearing
- what occurs
 - Diffusion of A from bulk fluid phase through the gas film to particle surface.
 - Surface rxn between reactant A and solid.
 - Diffusion of products from the surface through the gas film, back to the bulk fluid phase
- any of the above processes can be the rate controlling step.



A Chemical Rxn controls

- The behavior is identical to that of particles of unchanging size.

B Gas film diffusion controls

film resistance depends on

- relative velocity between particles and fluid
- particle size
- fluid properties

In the case where gas film diffusion controls, $C_{As} = C_{Ac} = 0$

we also have $-\frac{1}{4\pi R^2} \frac{dN_B}{dt} = bk_g C_{Ag}$ (I), $-\frac{dN_B}{dt} = -4\pi \rho_B R^2 \frac{dR}{dt}$ (II)

(I), (II) $\Rightarrow -\rho_B \frac{dR}{dt} = bk_g C_{Ag}$

Relationship for k_g as a function of particle size: $\frac{k_g d_p}{D} = 2 + 0.6 Sc^{1/3} Re^{1/2} = 2 + 0.6 \left(\frac{\mu}{\rho D}\right)^{1/3} \left(\frac{\rho u d_p}{\mu}\right)^{1/2}$

for small particles or low velocities: $\frac{k_g d_p}{D} = 2 \Rightarrow k_g \propto \frac{1}{d_p} \rightarrow$ Stokes regime

for large u or large d_p : $\frac{k_g d_p}{D} \propto \left(\frac{\rho u d_p}{\mu}\right)^{1/2} \Rightarrow k_g \propto \left(\frac{u}{d_p}\right)^{1/2}$

Stokes regime for small particles: $k_g = \frac{2D}{d_p} = \frac{D}{R} \Rightarrow -\rho_B \frac{dR}{dt} = \frac{bD}{R} C_{Ag}$

$$\int_{R_0}^R R dR = \frac{b C_{Ag} D}{\rho_B} \int_0^t dt \Rightarrow t = \frac{\rho_B R_0^2}{2b C_{Ag} D} \left[1 - \left(\frac{R}{R_0}\right)^2\right]$$

$$\tau = \frac{\rho_B R_c^2}{2b C_{Ag} D}, \quad \frac{t}{\tau} = 1 - \left(\frac{R}{R_c}\right)^2 = 1 - (1 - x_B)^{2/3}$$

1.2 Combination of Resistances

- Approach I

Resistances act in series and are all linear in concentration
Hence, time to reach any stage of conversion is the sum of times needed if each resistance acted alone

$$t_{total} = t_{film\ alone} + t_{ash\ alone} + t_{rxn\ alone}$$

$$\tau_{total} = \tau_{film\ alone} + \tau_{ash\ alone} + \tau_{rxn\ alone}$$

- Approach II

Individual resistances can be combined to give an overall resistance.
consider the unreacted model for particles of unchanging size (spheres):

$$\frac{-1}{S_{ex}} \frac{dN_A}{dt} = k_g (C_{Ag} - C_{As}) = \frac{4\pi D_c (C_{As} - C_{Ac})}{4\pi R^2 (1/r_c - 1/R)} \Rightarrow \frac{-1}{4\pi R^2} \frac{dN_A}{dt} = k_g (C_{Ag} - C_{As}) = \frac{D_c r_c}{R(R-r_c)} (C_{As} - C_{Ac}) = \underbrace{\left(\frac{r_c}{R}\right)^2}_{k_1} k_s C_{Ac}$$

Now we need to eliminate intermediate concentrations C_{As} and C_{Ac}

$$k_g (C_{Ag} - C_{As}) = k_1 (C_{As} - C_{Ac}) = k_2 C_{Ac}$$

$$\Rightarrow k_1 C_{As} - k_1 C_{Ac} = k_2 C_{Ac} \Rightarrow C_{Ac} = \frac{k_1}{k_1 + k_2} C_{As}$$

$$\Rightarrow k_g C_{Ag} - k_g C_{As} = k_1 \left(C_{As} - \frac{k_1 C_{As}}{k_1 + k_2}\right) = \frac{k_1 k_2 C_{As}}{k_1 + k_2} \Rightarrow k_g C_{Ag} = k_g + \frac{k_1 k_2}{k_1 + k_2} C_{As} \Rightarrow C_{As} = \frac{k_g}{k_g + \frac{k_1 k_2}{k_1 + k_2}} C_{Ag}$$

$$\Rightarrow \frac{-1}{4\pi R^2} \frac{dN_A}{dt} = k_g (C_{Ag} - C_{As}) = k_g C_{Ag} \left(1 - \frac{k_g}{k_g + \frac{k_1 k_2}{k_1 + k_2}}\right) = \frac{1}{\frac{1}{k_g} + \frac{1}{k_1} + \frac{1}{k_2}} C_{Ag}$$

$$\Rightarrow \frac{-1}{4\pi R^2} \frac{dN_A}{dt} = \frac{C_{Ag}}{\frac{1}{k_g} + \frac{R(R-r_c)}{D_c r_c} + \frac{R^2}{r_c^2} k_s}$$

film
ash
rxn

on the other hand: $-\frac{dN_B}{dt} = -4\pi \rho_B R^2 \frac{dR}{dt}$

$$\Rightarrow -\frac{dR}{dt} = \frac{b C_{Ag} / \rho_B}{\frac{r_c^2}{R^2 k_g} + \frac{(R-r_c)r_c}{R D_c} + \frac{1}{k_s}}$$

which can be integrated to give variation of r_c with time

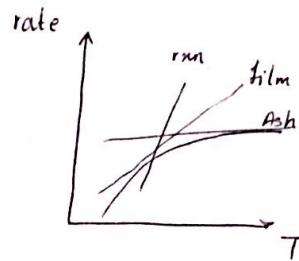
- for ash-free particles of the shrinking core model

$$\frac{-1}{S_{ex}} \frac{dN_A}{dt} = \frac{+1}{k_g + k_s} C_{Ag} \quad \left\{ \begin{array}{l} \frac{-1}{4\pi R^2} \frac{dN_B}{dt} = \frac{b C_{Ag}}{\frac{1}{k_g} + \frac{1}{k_s}} \\ -\frac{dN_B}{dt} = -4\pi \rho_B R^2 \frac{dR}{dt} \end{array} \right.$$

1.3 Determination of rate controlling step

Experiments to determine the RCS

- T \rightarrow rxn step more sensitive to T than physical transfer steps
- time \rightarrow $\frac{r_c}{R}$ or $1-X_B$ vs. t_T behavior is different for each case
- Particle Size
 - $\rightarrow t \propto R$: rxn
 - $\rightarrow t \propto R^{1.5-2}$: film
 - $\rightarrow t \propto R^2$: ash



- \rightarrow when hard ash forms, usually has greater resistance than gas film
- \rightarrow If the ash layer is flaky, then its resistance may be comparable to that of the film
- \rightarrow Ash resistance is independent of gas velocity

1.4 Application to design

- Important factors
 - \rightarrow Rxn kinetics for single particles
 - \rightarrow the size distribution of solids
 - \rightarrow flow pattern of solids and fluid in the reactor
- Sometimes, complexities arise
 - \rightarrow complex kinetics
 - \rightarrow ~~reduction~~ rxn products interfering (blanketing fluid phase)
 - \rightarrow T changes within the system.

1.5 Various types of contacting

- Gas and solids both in plug flow
 - \rightarrow composition of solid and fluid phase change during passage
 - \rightarrow usually non-isothermal
 - \rightarrow Counter current (blast furnace)
 - \rightarrow Cross flow (moving belt)
 - \rightarrow Cocurrent (driers for polymer and heat sensitive - rotary devices)
- Mixed Solid flow
 - \rightarrow fluidized bed
 - \rightarrow Intermediate gas flow
 - \rightarrow Isothermal due to high capacity of solids
- Semi-batch \rightarrow plug flow of fluid on a column of solids
- Analysis is greatly simplified if
 - \rightarrow Composition of fluid ~~is~~ assumed constant.
 - \rightarrow good assumption.
 - \rightarrow usually excess fluid, low fluid conversion and high degree of backmixing
 - \rightarrow for most fast rxns, kinetics do not come in the picture as the rates are controlled by physical transfer steps