

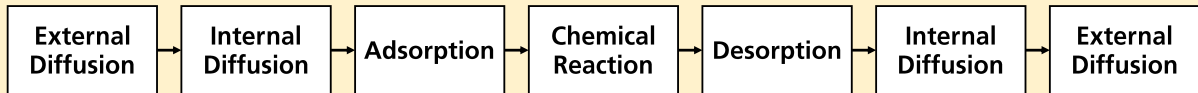
PART 3 & 4 Heterogeneous Reaction

In this PART we focus on the kinetics of heterogeneous reaction, especially on G/S and G/L reaction instead of performance equation. Except for chemical reaction, there are a lot of mass transfer steps in heterogeneous reaction, like diffusion, adsorption, etc. These steps are arranged in series, so the rate of these steps should be equal. If they are parallel, the total rate should be the sum of these rates. For the kinetics include mass transfer, we will attach something you should have learned in Transport Phenomena.

PART 3 Gas - Solid Reaction

Chap 18 Solid Catalyzed Reactions

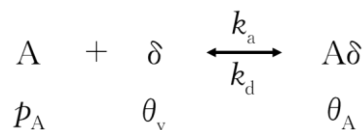
There are 7 steps in solid-catalyzed Reactions :



— The Intrinsic Rate ※

1. Adsorption — Langmuir isotherm equation (Actually you have learned in Physical Chemistry)

① Adsorption of single molecule



- δ The position on the surface that can adsorb A
- θ_A Fraction of position that have adsorbed A
- θ_v Fraction of empty position
- k_a Rate constant of adsorption
- k_d Rate constant of desorption
- K_A Eq constant of the process

When reaches equilibrium :

$$\theta_A = \frac{K_A p_A}{1 + K_A p_A}$$

How is That Done ?

- Adsorption Rate : $r_a = k_a p_A \theta_v$ Desorption Rate : $r_d = k_d \theta_A$ Notice $\theta_A + \theta_v = 1$
- When eq. $r_a = r_d$ so $k_a p_A \theta_v = k_d \theta_A$ make $K_A = k_a / k_d$

$$\text{Thus } \theta_v = \frac{\theta_A}{K_A p_A} = 1 - \theta_A \rightarrow \theta_A = \frac{K_A p_A}{1 + K_A p_A}$$

② Adsorption of two molecules



When reaches equilibrium :

$$\theta_A = \frac{K_A p_A}{1 + K_A p_A + K_B p_B} \quad \theta_B = \frac{K_B p_B}{1 + K_A p_A + K_B p_B}$$

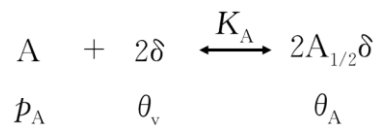
How is That Done ?

- When eq. $K_A = \frac{\theta_A}{p_A \theta_v}$ $K_B = \frac{\theta_B}{p_B \theta_v}$ with $\theta_A + \theta_B + \theta_v = 1$

$$\text{Thus } K_A p_A \theta_v + K_B p_B \theta_v + \theta_v = 1 \rightarrow \theta_v = \frac{1}{1 + K_A p_A + K_B p_B}$$

$$\text{Thus } \theta_A = \frac{K_A p_A}{1 + K_A p_A + K_B p_B} \quad \theta_B = \frac{K_B p_B}{1 + K_A p_A + K_B p_B}$$

③ Dissociative adsorption



When reaches equilibrium :

$$\theta_A = \frac{\sqrt{K_A p_A}}{1 + \sqrt{K_A p_A}}$$

How is That Done ?

- When eq. $K_A = \frac{\theta_A^2}{p_A \theta_v^2}$ with $\theta_A + \theta_v = 1$

$$\text{Thus } \frac{\theta_A}{\sqrt{K_A p_A}} + \theta_A = 1 \rightarrow \theta_A = \frac{\sqrt{K_A p_A}}{1 + \sqrt{K_A p_A}}$$

2. Rate Controlling Step

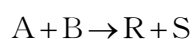
- The slowest step (whose resistance \gg others) determine the whole rate
At that time the other steps reach equilibrium.
- Mass transfer control: external and internal diffusion
Kinetic control: adsorption, surface reaction and desorption

3. Hyperbolic Reaction Rate

For gas-solid reaction, the rate is usually based on the weight per unit catalyst.

$$-r_A = \frac{1}{W} \frac{dN_A}{dt}$$

① surface reaction controls



$$r = (-r_A) = \frac{k_r K_A K_B p_A p_B}{(1 + K_A p_A + \dots + K_S p_S)^2}$$

If the adsorption of each component is very weak, the surface coverage is very low

$$r = k p_A p_B$$

How is That Done ?

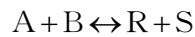
- Adsorption : $A + \sigma \leftrightarrow A\sigma$ $\therefore \theta_A = K_A p_A \theta_v$
 $B + \sigma \leftrightarrow B\sigma$ $\therefore \theta_B = K_B p_B \theta_v$
- Surface Reaction : $A\sigma + B\sigma \rightarrow R\sigma + S\sigma$ $\therefore r = (-r_A) = k_r \theta_A \theta_B$
- Desorption: $R\sigma \leftrightarrow R + \sigma$ $\therefore \theta_R = K_R p_R \theta_v$
 $S\sigma \leftrightarrow S + \sigma$ $\therefore \theta_S = K_S p_S \theta_v$

With $\theta_A + \theta_B + \theta_R + \theta_S + \theta_v = 1$

- Solve these equations: $\theta_A = \frac{K_A p_A}{1 + K_A p_A + \dots + K_S p_S}$ $\theta_B = \frac{K_B p_B}{1 + K_A p_A + \dots + K_S p_S}$

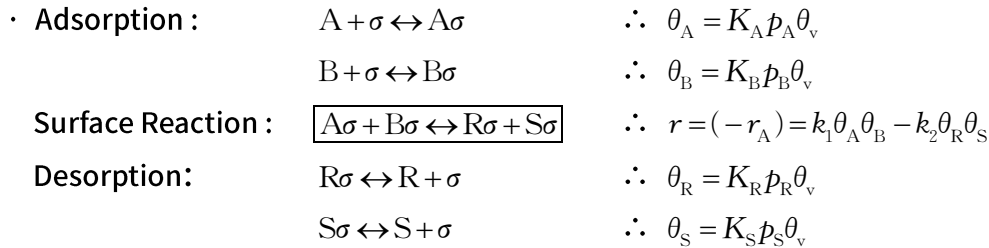
$$\text{Thus } r = (-r_A) = \frac{k_r K_A K_B p_A p_B}{(1 + K_A p_A + \dots + K_S p_S)^2} = \frac{k p_A p_B}{(1 + K_A p_A + \dots + K_S p_S)^2}$$

② reversible surface reaction controls



$$r = (-r_A) = \frac{k(p_A p_B - p_R p_S / K)}{(1 + K_A p_A + \dots + K_S p_S)^2}$$

How is That Done ?



With $\theta_A + \theta_B + \theta_R + \theta_S + \theta_v = 1$

• Solve these equations: $\theta_A = \frac{K_A p_A}{1 + K_A p_A + \dots + K_S p_S}$ $\theta_B = \frac{K_B p_B}{1 + K_A p_A + \dots + K_S p_S}$
 $\theta_R = \frac{K_R p_R}{1 + K_A p_A + \dots + K_S p_S}$ $\theta_S = \frac{K_S p_S}{1 + K_A p_A + \dots + K_S p_S}$

Thus $r = (-r_A) = \frac{k_1 K_A K_B p_A p_B}{(1 + K_A p_A + \dots + K_S p_S)^2} - \frac{k_2 K_R K_S p_R p_S}{(1 + K_A p_A + \dots + K_S p_S)^2}$
 $= \frac{k_1 K_A K_B p_A p_B - k_2 K_R K_S p_R p_S}{(1 + K_A p_A + \dots + K_S p_S)^2}$ make $k = k_1 K_A K_B$ and $K = \frac{k_1 K_A K_B}{k_2 K_R K_S}$
 $= \frac{k(p_A p_B - p_R p_S / K)}{(1 + K_A p_A + \dots + K_S p_S)^2}$

- Effect of inert molecule I that can be absorbed

$$r = (-r_A) = \frac{k(p_A p_B - p_R p_S / K)}{(1 + K_A p_A + \dots + K_S p_S + K_I p_I)^2}$$

- Effect of dissociation

If A is dissociated $r = (-r_A) = \frac{k(p_A p_B - p_R p_S / K)}{(1 + \sqrt{K_A p_A} + \dots + K_S p_S)^3}$

How is That Done ?

- When there is an inert molecule “I” that can be absorbed, just add



and modify $\theta_A + \theta_B + \theta_R + \theta_S + \theta_v = 1$ to $\theta_A + \theta_B + \theta_R + \theta_S + \theta_I + \theta_v = 1$

- When A is dissociated, just modify related formula to



and $2A_{1/2}\sigma + B\sigma \leftrightarrow R\sigma + S\sigma + \sigma$ $\therefore r = (-r_A) = k_1 \theta_A^2 \theta_B - k_2 \theta_R \theta_S \theta_v$

③ Controlling step is the reaction between adsorbed A and gas B

Now the rate is $r = (-r_A) = \frac{k_r K_A p_A p_B}{1 + K_A p_A}$

How is That Done ?

- We delete $B + \sigma \leftrightarrow B\sigma$, $R\sigma \leftrightarrow R + \sigma$, $S\sigma \leftrightarrow S + \sigma$

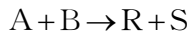
and modify $A\sigma + B\sigma \leftrightarrow R\sigma + S\sigma$ to $A\sigma + B \rightarrow R + S + \sigma$

- Adsorption : $A + \sigma \leftrightarrow A\sigma$ $\therefore \theta_A = K_A p_A \theta_v$

Surface Reaction : $A\sigma + B \rightarrow R + S + \sigma$ $\therefore r = (-r_A) = k_1 \theta_A p_B$

With $\theta_A + \theta_v = 1$ Now you can solve the equation yourself

④ Adsorption Controls — Controlling step is the adsorption of A



$$r = \frac{k_1(p_A - p_R p_S / K p_B)}{1 + K_{rs} p_R p_S / p_B + K_B p_B + K_R p_R + K_S p_S}$$

How is That Done ?

- Adsorption : $A + \sigma \leftrightarrow A\sigma$ $\therefore r = r_a - r_d = k_1 \theta_v p_A - k_2 \theta_A$

$$B + \sigma \leftrightarrow B\sigma \quad \therefore \theta_B = K_B p_B \theta_v$$

Surface Reaction : $A\sigma + B\sigma \leftrightarrow R\sigma + S\sigma$ $\therefore K_r = \theta_R \theta_S / \theta_A \theta_B$

Desorption: $R\sigma \leftrightarrow R + \sigma$ $\therefore \theta_R = K_R p_R \theta_v$

$$S\sigma \leftrightarrow S + \sigma \quad \therefore \theta_S = K_S p_S \theta_v$$

With $\theta_A + \theta_B + \theta_R + \theta_S + \theta_v = 1$

- Thus $\theta_A = \frac{\theta_R \theta_S}{K_r \theta_B} = \frac{K_R p_R \theta_v K_S p_S \theta_v}{K_r K_B p_B \theta_v} = K_{rs} \frac{p_R p_S}{p_B} \theta_v$ ($\frac{K_R K_S}{K_r K_B} = K_{rs}$)

$$\rightarrow K_{rs} p_R p_S \theta_v / p_B + K_B p_B \theta_v + K_R p_R \theta_v + K_S p_S \theta_v + \theta_v = 1$$

$$\rightarrow \theta_v = \frac{1}{1 + K_{rs} p_R p_S / p_B + K_B p_B + K_R p_R + K_S p_S}$$

- Thus $r = \frac{k_1 p_A - k_2 K_{rs} p_R p_S / p_B}{1 + K_{rs} p_R p_S / p_B + K_B p_B + K_R p_R + K_S p_S} = \frac{k_1(p_A - p_R p_S / p_B K)}{1 + K_{rs} p_R p_S / p_B + K_B p_B + K_R p_R + K_S p_S}$

⑤ desorption controls

$A \rightarrow R$ but desorption of R controls

$$r = \frac{k(p_A - p_R / K)}{1 + p_A K_A + K_r K_A p_A}$$

How is That Done ?

- Adsorption : $A + \sigma \leftrightarrow A\sigma$ $\therefore \theta_A = K_A p_A \theta_v$

Surface Reaction : $A\sigma \leftrightarrow R\sigma$ $\therefore K_r = \theta_R / \theta_A$

Desorption: $R\sigma \leftrightarrow R + \sigma$ $\therefore r = k_1 \theta_R - k_2 p_R \theta_v$

With $\theta_A + \theta_R + \theta_v = 1$

- Thus $\theta_R = K_r \theta_A = K_r K_A p_A \theta_v$

$$\rightarrow K_A p_A \theta_v + K_{rs} p_A \theta_v + \theta_v = 1 \rightarrow \theta_v = \frac{1}{1 + K_A p_A + K_A K_r p_R}$$

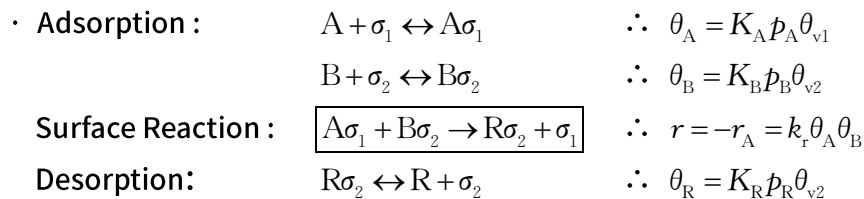
- Thus $r = \frac{k_1 K_r K_A p_A - k_2 p_R}{1 + K_A p_A + K_A K_r p_R} = \frac{k(p_A - p_R / K)}{1 + K_A p_A + K_A K_r p_R}$

⑥ double active centers

$A + B \rightarrow R$ BUT active center 1 adsorb A while a.c. 2 adsorb B & R

$$r = \frac{k p_A p_B}{(1 + K_A p_A)(1 + K_B p_B + K_R p_R)}$$

How is That Done ?



With $\theta_A + \theta_{v1} = 1$ and $\theta_B + \theta_R + \theta_{v2} = 1$

• Solve these equations: $\theta_A = \frac{K_A p_A}{1 + K_A p_A}$ $\theta_B = \frac{K_B p_B}{1 + K_B p_B + K_R p_R}$ $\theta_R = \frac{K_R p_R}{1 + K_B p_B + K_R p_R}$

Thus $r = (-r_A) = \frac{k_r K_A K_B p_A p_B}{(1 + K_A p_A)(1 + K_B p_B + K_R p_R)} = \frac{k p_A p_B}{(1 + K_A p_A)(1 + K_B p_B + K_R p_R)}$

Summary

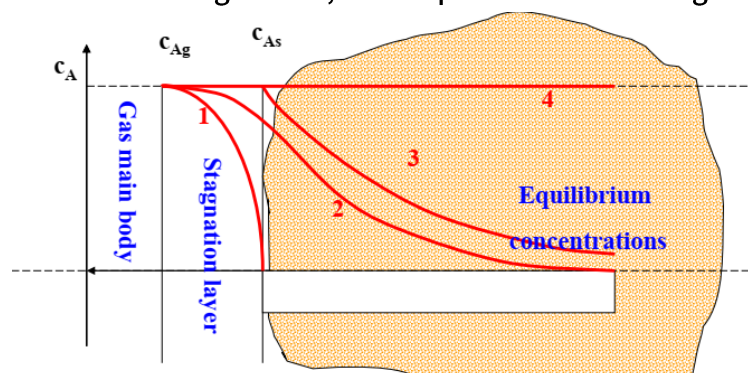
You need to focus on how the factors ABOVE affect the rate equation based on basic one.

And you are required to have ability in writing the equation based on given mechanism as well as writing the possible mechanism for given rate equation.

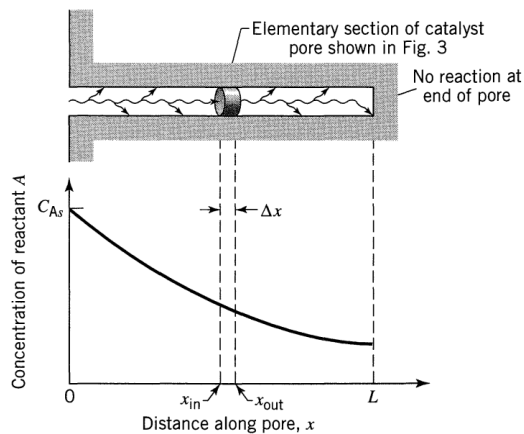
Internal Diffusion Control

1. Gradient of Concentration Shows the Controlling Step

- External Diffusion : molecules A move between gas bulk to entrance of solid pore
 - Internal Diffusion : molecules A move between from entrance of solid pore to internal surface
 - Along the path the C_A decreases to give driving force
- The larger C_A gradient means larger resistance, so that it may become the control step
- So if the concentration have no gradient, this step are not controlling step



2. Single Cylindrical Pore & First order Reaction



Condition:

Reaction Rate Constant k

Diffusion Coefficient D

Concentration at Entrance C_{As}

Total Pore Length L

① Solution :

$$\frac{C_A}{C_{As}} = \frac{\cosh m(L-x)}{\cosh mL} \quad \text{where } m = \sqrt{\frac{k}{D}}$$

Review of Mathematics

$$\cosh x = \frac{e^x + e^{-x}}{2} \quad \sinh x = \frac{e^x - e^{-x}}{2}$$

How is That Done ?

• Modeling

<p>Disappearance of A on surface by reaction = $\left(\frac{\text{rate of disappearance}}{\text{unit surface}} \right) (\text{surface})$ $= \left(-\frac{1}{S} \frac{dN_A}{dt} \right) (\text{surface}) = k''C_A (2\pi r \Delta x)$</p>	<p>Reaction : $-r_A'' = -\frac{1}{S} \frac{dN_A}{dt} = k''C_A$</p> <p>while $S = 2\pi r \Delta x$</p> <p>Output : $\pi r^2 D \frac{dC_A}{dx} \Big _{x+\Delta x}$</p> <p>Input : $\pi r^2 D \frac{dC_A}{dx} \Big _x$</p>
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Material Balance : $\text{output} - \text{input} + \text{reaction} = 0$

$$\text{Then } -\pi r^2 D \frac{dC_A}{dx} \Big|_{x+\Delta x} + \pi r^2 D \frac{dC_A}{dx} \Big|_x + k''C_A \cdot 2\pi r \Delta x = 0 \rightarrow \frac{\frac{dC_A}{dx} \Big|_x - \frac{dC_A}{dx} \Big|_{x+\Delta x}}{\Delta x} + \frac{2k''}{Dr} C_A = 0$$

$$\therefore \lim_{\Delta x \rightarrow 0} \frac{f(x+\Delta x) - f(x)}{\Delta x} = \frac{df}{dx} \quad \therefore \frac{d^2 C_A}{dx^2} + \frac{2k''}{Dr} C_A = 0 \quad \text{when } \Delta x \rightarrow 0$$

For definition of reaction rates $k = k''(V/S) = 2k''/r$ so $\frac{d^2 C_A}{dx^2} + \frac{k}{D} C_A = 0$

It is an ODE we have learned. Just make $m = \sqrt{\frac{k}{D}}$ and solve it :

• Solving

The solution is $C_A = c_1 e^{mx} + c_2 e^{-mx}$ where c_1 & c_2 are arbitrary constants

Now we look the boundary condition to determine these two constants

① At $x=0$, $C_A = C_{As}$

② At $x=L$, $\frac{dC_A}{dx} = 0$ for there is no mass transfer at $x=L$

So $c_1 + c_2 = C_{As}$ & $mc_1 e^{mL} - mc_2 e^{-mL} = 0 \Rightarrow c_1 e^{2mL} = c_2$

We can solve that $c_1 = \frac{C_{As} e^{-mL}}{e^{mL} + e^{-mL}}$ $c_2 = \frac{C_{As} e^{mL}}{e^{mL} + e^{-mL}}$

So $C_A = C_{As} \frac{e^{m(L-x)} + e^{-m(L-x)}}{e^{mL} + e^{-mL}}$ which can be written as $\frac{C_A}{C_{As}} = \frac{\cosh m(L-x)}{\cosh mL}$

② Analysis of the Result

• **Thiele modulus** $M_T = mL$

• **Effectiveness Factor** $\epsilon = \frac{\bar{r}_A(\text{with diffusion})}{r_A(\text{without diffusion})}$ for first-order $\epsilon = \frac{\bar{C}_A}{C_{As}} = \frac{\tanh mL}{mL}$

To understand : diffusion make $C_A < C_{As}$ thus slow down the reaction

For $M_T < 0.4$, $\epsilon \approx 1$; For $M_T > 4$, $\epsilon = 1/M_T$

2. General case for M_T and ϵ

① Affect by shape of particles


• L' s character size

$$L' \begin{cases} = \left(\frac{\text{volume of particle}}{\text{exterior surface available for reactant penetration}} \right), \text{ any particle shape} \\ = \frac{\text{thickness}}{2}, \text{ for flat plates} \\ = \frac{R}{2}, \text{ for cylinders} \\ = \frac{R}{3}, \text{ for spheres} \end{cases}$$

• $\epsilon - M_T$ relationship varies according to particle shape

$$\left. \begin{array}{l} A \rightarrow R \\ -r_A''' = k''' C_A \epsilon \end{array} \right\} \dots \text{where } \epsilon \begin{cases} = \frac{1}{M_T} \cdot \tanh M_T \\ = \frac{1}{M_T} \cdot \frac{I_1(2M_T)}{I_0(2M_T)} \\ = \frac{1}{M_T} \cdot \left(\frac{1}{\tanh 3M_T} - \frac{1}{3M_T} \right) \end{cases}$$

Bessel function

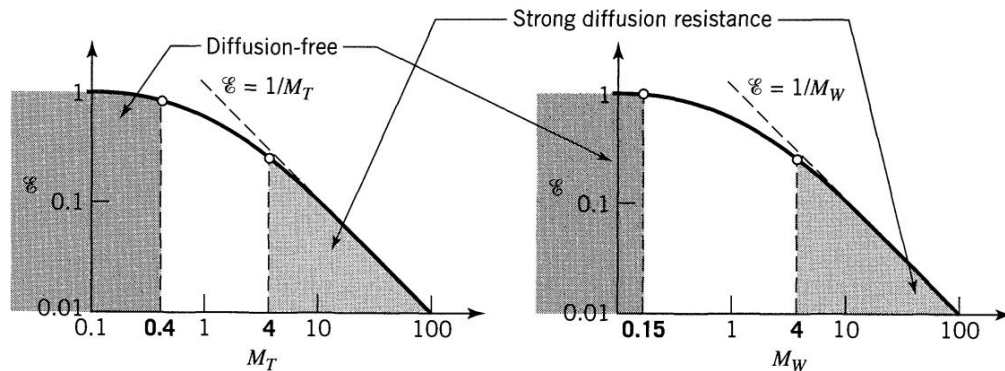


mol/m³ cat · s

② Finding pore resistance effects from experiment

$$\boxed{M_w = M_T^2 \epsilon} \quad \text{when } M_T < 0.4 \text{ or } M_w < 0.15 \text{ diffusion free regime}$$

$$\text{when } M_T > 4 \text{ or } M_w > 4 \text{ diffusion free regime}$$



- Particles of different sizes play a role only in strong diffusion regime
- The larger the size, the lower the ϵ

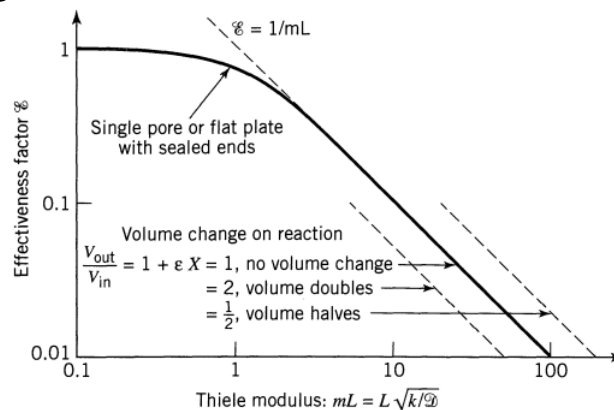
3. Extension

- ① Mixture of particles of various shapes and sizes

$$\bar{\epsilon} = \epsilon_1 f'_1 + \epsilon_2 f'_2 + \dots$$

f'_1, f'_2 are the volume fractions of particles of sizes 1,2,... in the mixture

- ② Molar Volume Change



- ③ Reaction Order Shift

In regime of strong pore resistance an order - n reaction behaves like an order- $\frac{n+1}{2}$ reaction

- ④ Activation Energy

$$E_{\text{obs}} = \frac{E_{\text{true}} + E_{\text{diff}}}{2}$$

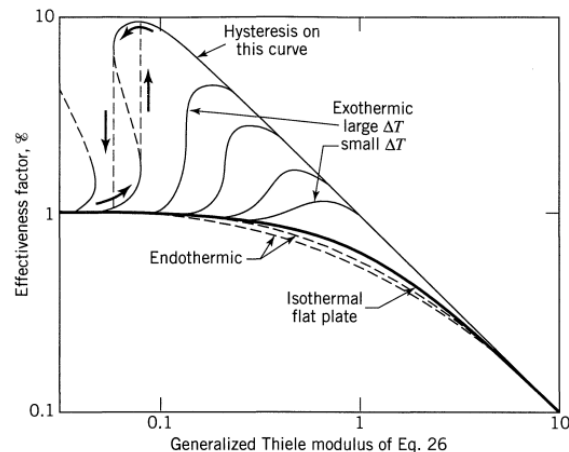
4. Heat Effects

- ① Film

By heat balance :
$$\begin{cases} Q_{\text{generated}} = V_{\text{pellet}} (-r''_{A,\text{obs}}) (-\Delta H_r) \\ Q_{\text{removed}} = hS_{\text{pellet}} (T_g - T_s) \end{cases} \Rightarrow \Delta T_{\text{film}} = T_g - T_s = \frac{L(-r''_{A,\text{obs}})(-\Delta H_r)}{h}$$

- ② Within Particle

By conservation : $-k_{\text{eff}} \frac{dT}{dx} = D_e \frac{dC_A}{dx} (-\Delta H_r) \rightarrow \Delta T_{\text{particle}} = T_{\text{center}} - T_s = \frac{D_e (C_{A,s} - C_{A,\text{center}}) (-\Delta H_r)}{k_{\text{eff}}}$



External Diffusion

To see whether film mass transfer resistance is important :

Compare $k_{\text{obs}}''' V_p$ vs $k_g S_{\text{ex}}$

- $k_{\text{obs}}''' V_p \sim k_g S_{\text{ex}}$ film resistance affects the rate
- $k_{\text{obs}}''' V_p \ll k_g S_{\text{ex}}$ negligible film resistance
- $k_{\text{obs}}''' V_p \gg k_g S_{\text{ex}}$ film resistance controlling

Exclude external diffusion : Increase gas flow and eliminate external diffusion

Exclude internal diffusion : Reduce particle diameter and eliminate internal diffusion

Chap 19 & 20 G/S Reactors

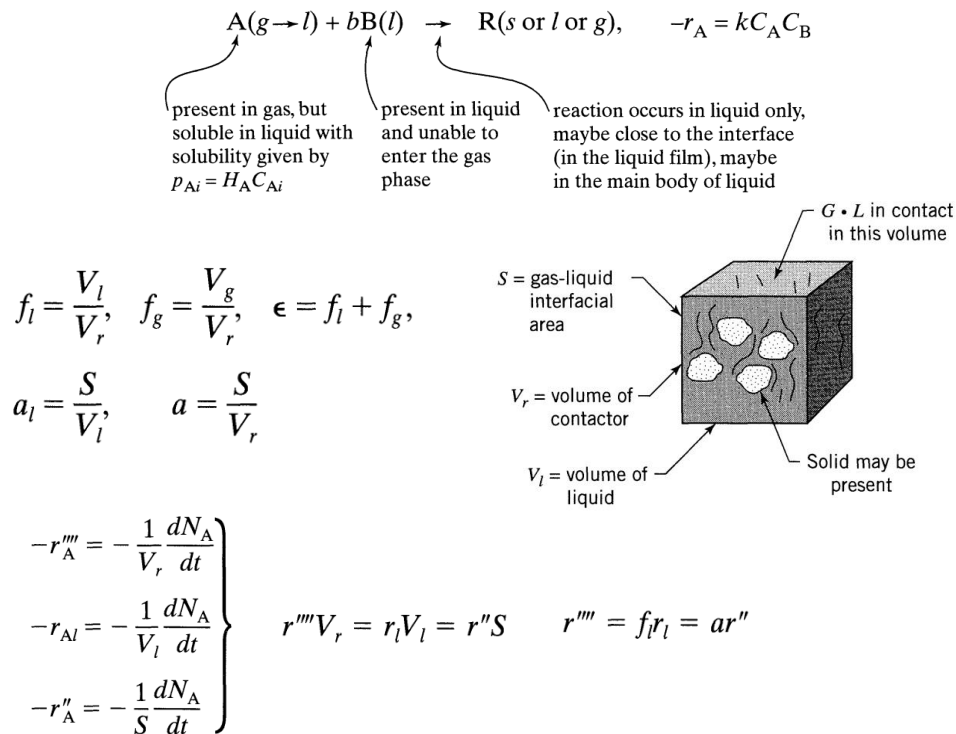
Packed/ Fixed bed reactor	Fluidized bed reactor
<ul style="list-style-type: none"> • Catalyst does not wear out easily • Plug flow of fluid • Low catalyst dosage and small reactor volume • Controllable temperature distribution beneficial to selectivity and conversion. 	<ul style="list-style-type: none"> • High heat transfer efficiency uniform temperature in bed maintained • Free transport of solid particles rapid deactivation and regeneration • Small particle size to eliminate internal diffusion
<ul style="list-style-type: none"> • Poor heat transfer • Production stopped to replace catalyst 	<ul style="list-style-type: none"> • Gas flow is in the bubble state • Mixed flow of particle backmixing of particle low conversion and partial backmixing of gas • Wear and take out of particles loss of catalyst

PART 4 Gas - Liquid Reaction

Chap 23 Fluid-Fluid Reaction Kinetics — G/L Reactions

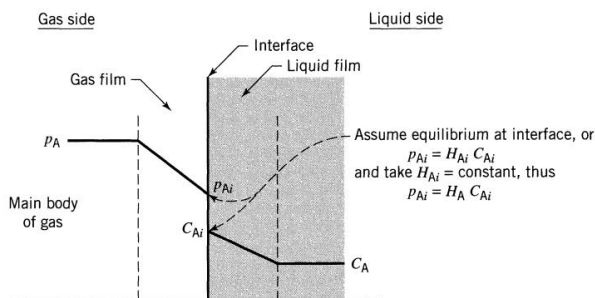
— G/L Reaction Schemes

Assumption : gaseous A is soluble in the liquid but B does not enter the gas.



二 The Rate Equation for Straight Mass Transfer of A

That is the double-film model which you have learned in Absorption :



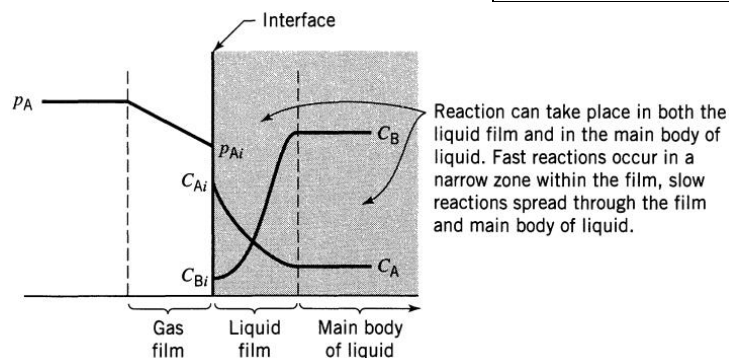
Gas Phase : $-r_A''' = k_{Ag} a (p_A - p_{Ai})$

G/L Interface : $p_{Ai} = H_A C_{Ai}$

Liquid Phase : $-r_A''' = k_{Al} a (C_{Ai} - C_A)$

Thus

$$-r_A''' = \frac{p_A - H_A C_A}{\frac{1}{k_{Ag} a} + \frac{H_A}{k_{Al} a}}$$



≡ Eight Cases for The Rate Equation

The general rate equation :

- Reactions may take place in liquid bulk or liquid film

In the bulk of liquid, there is no diffusion. A is consumed only by reaction

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt} = k C_A C_B$$

For $-r_A''' = -\frac{V_l}{V_r} r_A = -f_l r_A \rightarrow -r_A''' = k f_l \frac{C_A H_A}{H_A} C_B$ the resistance is $\frac{H_A}{k f_l C_B}$

Because of the reaction, diffusion in liquid film is enhanced, thus diminishes the resistance. Based on the resistance we introduce E to modify :

$$-r_A''' = \frac{p_A - H_A C_A}{\frac{1}{k_{Ag} a} + \frac{H_A}{k_{Al} a E}}$$

Combined with $-r_A''' = C_A H_A / \frac{H_A}{k f_l C_B}$, we finally get

$$-r_A''' = \frac{p_A}{\frac{1}{k_{Ag} a} + \frac{H_A}{k_{Al} a E} + \frac{H_A}{k f_l C_B}}$$

- Liquid Enhancement Factor**

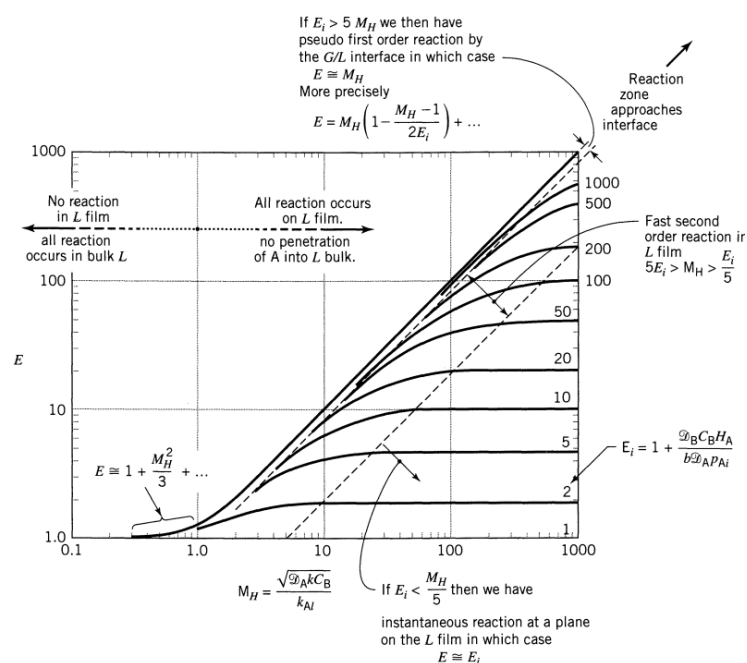
$$E = \left(\frac{\text{rate of take up of A when reaction occurs}}{\text{rate of take up of A for straight mass transfer}} \right)_{\text{same } C_{Ai}, C_A, C_{Bi}, C_B \text{ in the two phases}}$$

E is always ≥ 1 , dependent on two quantities :

- E_i = the enhancement factor for an infinitely fast reaction $= 1 + \frac{D_B C_B H_A}{b D_A p_{Ai}}$

- Hatta Modulus**

$$M_H^2 = \left(\frac{\text{maximum possible conversion in the film}}{\text{compared with maximum transport through the film}} \right)$$

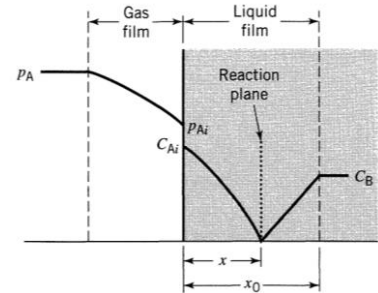


1. Case A : Instantaneous reaction with low C_B

- Instantaneous means A and B cannot coexist,
→ Reaction will occur at a plane between A-containing and B-containing liquid
- change in p_A or C_B will move the plane

for Case A: $\left(k_{Ag}p_A > \frac{k_{Bl}C_B}{b}\right)$

$$-r_A'' = -\frac{1}{S} \frac{dN_A}{dt} = \frac{\frac{D_{Bl}C_B}{D_{Al}b} + \frac{p_A}{H_A}}{\frac{1}{H_A k_{Ag}} + \frac{1}{k_{Al}}}$$



How is That Done ?

- For A and B only diffuse at liquid film except reaction plane x :

$$-r_A'' = -\frac{r_B''}{b} = \underbrace{k_{Ag}(p_A - p_{Ai})}_{\text{A in gas film}} = \underbrace{k_{Al}(C_{Ai} - 0)}_{\text{A in liquid film}} \frac{x_0}{x} = \underbrace{\frac{k_{Bl}}{b}(C_B - 0)}_{\text{B in liquid film}} \frac{x_0}{x_0 - x}$$

$$\cdot \quad p_{Ai} = H_A C_{Ai} \quad \text{and} \quad \frac{k_{Al}}{k_{Bl}} = \frac{D_{Al}/x_0}{D_{Bl}/x_0} \quad \text{so} \quad -r_A'' = \frac{p_A - p_{Ai}}{\frac{1}{k_{Ag}}} = \frac{p_{Ai}}{H_A \frac{x}{D_{Al}}} = \frac{\frac{D_{Bl}C_B}{b}}{x_0 - x}$$

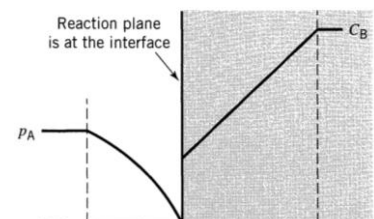
By elimination :

$$-r_A'' = \frac{p_A - p_{Ai}}{\frac{1}{k_{Ag}}} = \frac{p_{Ai}}{H_A \frac{x}{D_{Al}}} = \frac{\frac{D_{Bl}C_B}{D_{Al}b} H_A}{H_A \frac{1}{k_{Al}} - H_A \frac{x}{D_{Al}}} = \frac{p_A - p_{Ai} + p_{Ai} + \frac{D_{Bl}C_B}{D_{Al}b} H_A}{\frac{1}{k_{Ag}} + H_A \frac{x}{D_{Al}} + H_A \frac{1}{k_{Al}} - H_A \frac{x}{D_{Al}}} = \frac{\frac{p_A}{H_A} + \frac{D_{Bl}C_B}{D_{Al}b}}{\frac{1}{H_A k_{Ag}} + \frac{1}{k_{Al}}}$$

2. Case B : Instantaneous reaction with high C_B

for Case B: $\left(k_{Ag}p_A \leq \frac{k_{Bl}C_B}{b}\right)$

$$-r_A'' = -\frac{1}{S} \frac{dN_A}{dt} = k_{Ag}p_A$$

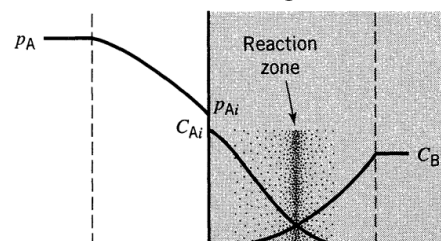


3. Case C : Fast reaction in liquid film, with low C_B

Now A and B can both present in the same zone, but the reaction is fast enough so no A in bulk.

$$-r_A''' = \frac{1}{\frac{1}{k_{Ag}a} + \frac{H_A}{k_{Al}aE}} p_A$$

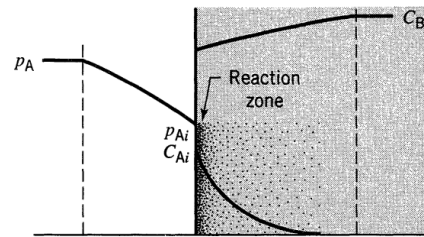
The third resistance term can be neglected



4. Case D : Fast reaction in liquid film, with high C_B

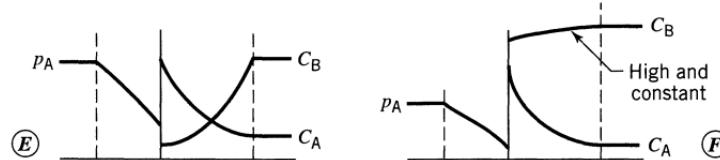
$$-r_A''' = \frac{1}{\frac{1}{k_{Ag}a} + \frac{H_A}{a\sqrt{D_A k C_B}}} p_A$$

E in the second term equals to M_H



5. Case E and F : Intermediate rate with reaction in the film and in the main body of the liquid

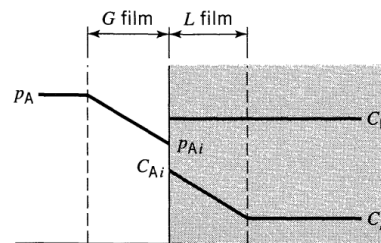
General Form including 3 resistances



7. Case G : Slow reaction in main body but with film resistance

$$-r_A''' = \frac{1}{\frac{1}{k_{Ag}a} + \frac{H_A}{k_{Al}a} + \frac{H_A}{k_{CB}f_l}} p_A$$

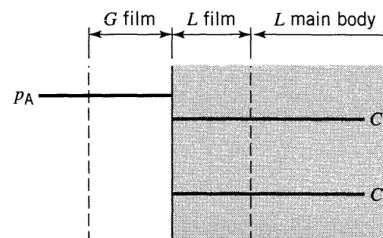
M_H is low then $E=1$



8. Case H : Slow reaction, no mass transfer resistance

$$-r_A''' = \frac{kf_l}{H_A} p_A C_B = kf_l C_A C_B$$

Only the third term remains



四 Review of the Role of Hatta Number

$$M_H^2 = \frac{k C_B D_{Al}}{k_{Al}^2}$$

- $M_H \gg 1$ Reaction in the film surface area controlling factor
 $M_H \ll 1$ No reaction in the film, and bulk volume becomes controlling factor
- More precisely : $M_H > 2$, reaction in the film Cases A, B, C, D
 $0.02 < M_H < 2$, intermediate Cases E, F, G
 $M_H < 0.02$, infinitely slow reaction of Case H

Clues to the Kinetic Regime from Solubility Data

- Slightly soluble gases, H_A large, liquid film resistance controls
- Highly soluble gases, H_A small, gas film resistance controls

Chap 24 G/L Reactors

— Choose Reactors for G/L Reaction

- M_H large \rightarrow reaction occurs close to interface
 - \rightarrow pick a contacting device which develops or creates large interfacial areas
 - Agitation is important
 - \rightarrow **spray or plate columns**
- M_H small \rightarrow reaction occurs in liquid bulk
 - \rightarrow all we need is a large volume of liquid
 - Agitation is of no benefit
 - \rightarrow **bubble contactors**

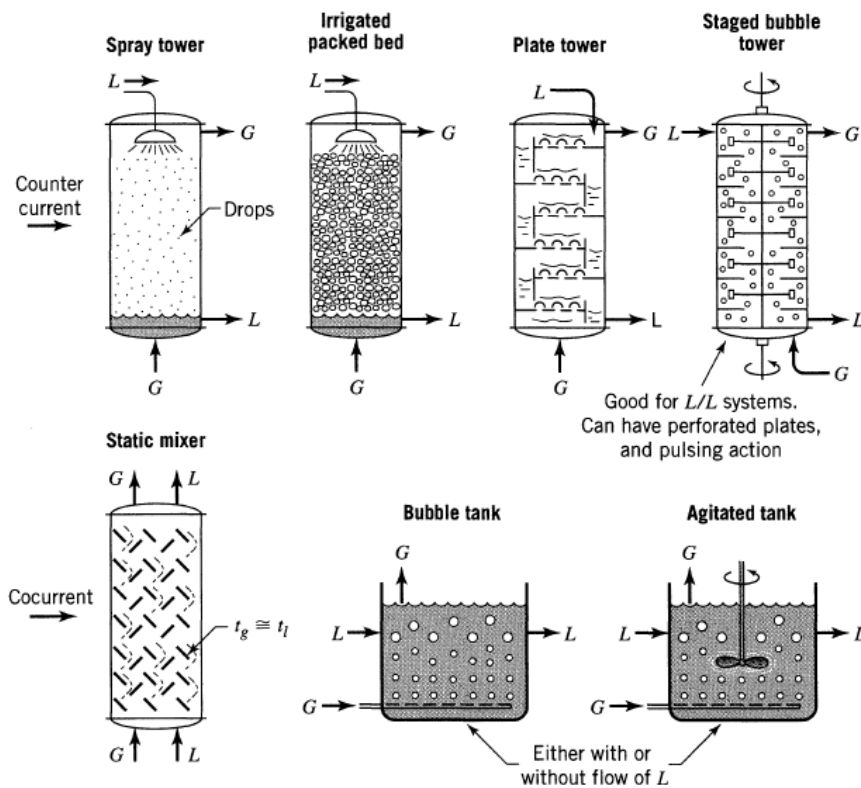


Table 24.1 Characteristics of G/L Contactors (from Kramers and Westerterp, 1961).

Flow Pattern	Contactors	a (m^2/m^3)	$f_i = \frac{V_i}{V}$ (-)	Capacity	Comments
Counter Current Flow	Spray tower	60	0.05	Low	Good for very soluble gases high k_g/k_l
	Packed bed	100	0.08	High	Good all rounder, but must have $F_l/F_g \approx 10$
	Plate tower	150	0.15	Medium-high	
	Staged bubble column	200	0.9	Low	Needs mechanical mixer or pulsing device. Good for slightly soluble gases and L_1/L_2 . Has low k_g/k_l .
Cocurrent flow	Static mixer	200	0.2–0.8	Very high	Very flexible, little reported data $i_g \approx i_l$.
Mixed flow of L	Bubble tank	20	0.98	Medium	Cheap to build
	Agitated tank	200	0.9	Medium	Cheap to build but needs a mechanical agitator