

① Fluid-Fluid Rxns

- rate expression → mass transfer and chemical rxn terms are involved with the overall rate expression
- equilibrium solubility → limit the movement of materials from phase to phase
- contacting schemes → Semi-batch, counter-current for gas-liquid  
batch contacting, mixer-settlers for liquid-liquid

1.1 The Rate Equation

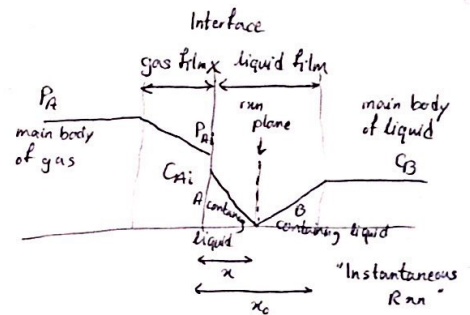
- Nomenclature → A. reactant in the gas phase - Soluble in liquid  
B. ~ ~ ~ liquid ~ - does not enter gas

- same procedure with two liquid phases

- A must enter and move into liquid phase and rxn occurs in the liquid phase
- Resistances → mass transfer to bring reactants together  
chemical rxn rate

- Different kinetic regimes for mass transfer and rxn. In terms of two film theory of Lewis and Whitman

1.1.1 Case A - Instantaneous Rxn with respect to mass transfer



$A + bB \rightarrow \text{products}$

$C_{A,i}$  and  $P_{A,i}$  are related by equilibrium constant. e.g. Henry's law for solubility of gases in liquids

The movement of material within the film is visualized to occur by diffusion alone

$$-r_A'' = \frac{-r_B''}{b} = \frac{-1}{S} \frac{dN_A}{dt}$$

$$D_A \frac{(C_{A1} - C_{A2})}{x_c} = k_A (C_{A1} - C_{A2})$$

$$= k_{Ag} (P_A - P_{A,i})$$

$$= D_{AL} \frac{(C_{A,i} - 0)}{x} = k_{AL} (C_{A,i} - 0) \frac{x_0}{x}$$

$$-r_B'' = k_{BL} (C_B - 0) \frac{x_0}{x_0 - x} \Rightarrow -r_A'' = k_{Ag} (P_A - P_{A,i}) = k_{AL} (C_{A,i} - 0) \frac{x_0}{x} = \frac{k_{BL}}{b} (C_B - 0) \frac{x_0}{x_0 - x}$$

Henry's law for interface concentration:  $P_{A,i} = H_A C_{A,i} \Leftrightarrow -r_A'' = k_{Ag} (P_A - H_A C_{A,i}) = k_{AL} C_{A,i} \frac{x_0}{x} = \frac{k_{BL}}{b} C_B \frac{x_0}{x_0 - x}$  "we need to eliminate  $x, x_0, C_{A,i}, P_{A,i}$ "

2<sup>nd</sup> equity of  $\oplus \Rightarrow \frac{k_{BL} C_B}{b k_{AL} C_{A,i}} = \frac{x_0 - x}{x} = \frac{x_0}{x} - 1 \Rightarrow \frac{x_0}{x} = 1 + \frac{k_{BL} C_B}{b k_{AL} C_{A,i}}$

1<sup>st</sup> equity of  $\oplus \Rightarrow k_{Ag} (P_A - H_A C_{A,i}) = k_{AL} C_{A,i} \frac{x_0}{x} = k_{AL} C_{A,i} \left[ 1 + \frac{k_{BL} C_B}{b k_{AL} C_{A,i}} \right] \Rightarrow k_{Ag} P_A - k_{Ag} H_A C_{A,i} = k_{AL} C_{A,i} + \frac{k_{BL} C_B}{b}$

$$\Rightarrow C_{A,i} = \frac{k_{Ag} P_A - \frac{k_{BL} C_B}{b}}{k_{AL} + k_{Ag} H_A}$$

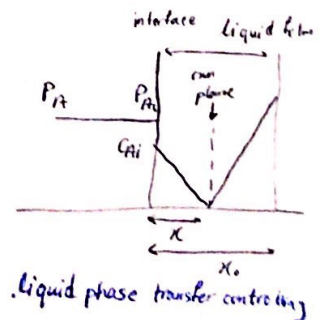
$-r_A'' = \frac{1}{S} \frac{dN_A}{dt} = k_{Ag} (P_A - H_A C_{A,i}) = k_{Ag} P_A - k_{Ag} H_A \left( \frac{k_{Ag} P_A - \frac{k_{BL} C_B}{b}}{k_{AL} + k_{Ag} H_A} \right) = \frac{k_{Ag} k_{AL} P_A + k_{Ag} H_A k_{BL} C_B / b}{k_{AL} + k_{Ag} H_A}$

$$\Rightarrow -r_A'' = \frac{\frac{P_A}{H_A} + \frac{k_{BL} C_B}{k_{AL} b}}{\frac{1}{k_{Ag} H_A} + \frac{1}{k_{AL}}} \quad \frac{k_{BL}}{k_{AL}} = \frac{D_{BL}}{D_{AL}} \quad -r_A'' = \frac{\frac{D_{BL} C_B}{D_{AL} b} + \frac{P_A}{H_A}}{\frac{1}{H_A k_{Ag}} + \frac{1}{k_{AL}}}$$

1.1.2 Case A - special case - Negligible gas phase resistance

- $-r_A'' = k_{AL} C_{A,i} \left( 1 + \frac{D_{BL} C_B}{P_A b k_{AL}} \right)$  - if we were dealing with absorption of A into liquid, the rate of mass transfer would be:  $-r_A'' = k_{AL} C_{A,i}$
- $\frac{x_0}{x} = E \triangleq \frac{\text{rate of with rxn}}{\text{rate for mass transfer alone}}$

- Application → Addition of a reagent to enhance gas absorption  
in the absence of rxn, absorption of A into liquid would be through a film of thickness  $x_0$ , enhanced gradient with instantaneous rxn

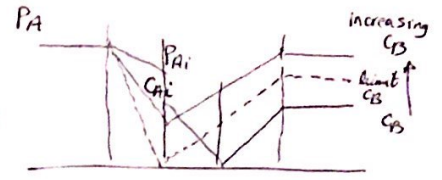


**1.1.3 Case B - Special case of high  $C_B$**

- In the treatment of the general case, we obtained the following relationship:
- we can see that the limiting value for  $C_{Ai}$  is zero when
- when  $C_B$  becomes high, we can have the situation where
- In which case, the rxn plane moves to the gas-liquid interface and  $C_{Ai} = 0$ ,  $\frac{x}{x_0 - x} = \frac{b k_{A2} C_{Ai}}{k_{B2} C_B}$  ( $C_{Ai} = 0$ )

$$C_{Ai} = \frac{k_{Ag} P_A - k_{B2} C_B / b}{k_{A2} + k_{Ag} H_A}$$

$$k_{Ag} P_A = \frac{k_{B2} C_B}{b} \rightarrow k_{Ag} P_A < \frac{k_{B2} C_B}{b}$$

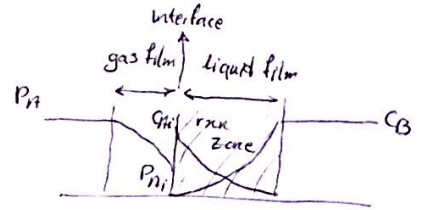


- The governing rate expression for the case where  $C_{Ai} = 0$  ( $C_B$  is very high):  $-r_A'' = \frac{-1}{S} \frac{dN_A}{dt} = k_{Ag} P_A$  (gas phase transfer controlling)
- The transition between liquid and gas phase control occurs when  $k_{Ag} P_A < \frac{k_{B2} C_B}{b}$
- Order of magnitude calculation:  $D_L \approx 10^{-5} \text{ cm}^2/\text{s}$ ,  $D_G \approx 10^{-1} \text{ cm}^2/\text{s}$ ,  $x_0 \approx 10^{-2} \text{ cm}$ ,  $k_g = \frac{D_G}{x_0} \approx 10$ ,  $k_L = \frac{D_L}{x_0} \approx 10^{-3} \text{ cm/s}$

$$\frac{P_A}{RT} = C_{Ai} < \frac{k_{B2} C_B}{k_{Ag} b} \Rightarrow \frac{P_A}{RT} < 10^{-4} \frac{C_B}{b} \Rightarrow \text{Criteria for establishing gas phase control}$$

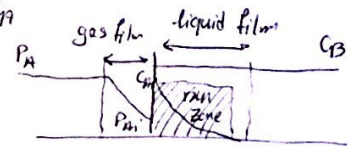
**1.1.4 Cases C & D - Fast rxn, 2<sup>nd</sup> order rxn**

- Case C: the rxn is not instantaneous, however it is fast enough to be carried out in the liquid film
- In this case we have a rxn zone
- $-r_A'' = \frac{-1}{V_L} \frac{dN_A}{dt} = k_{CA} C_B$ ,  $-r_A'' = k_{Ag} (P_A - P_{Ai}) = k_{AL} C_{Ai} E$  (Enhancement factor  $E$ )
- Eliminating  $C_{Ai}$ ,  $P_{Ai}$ :  $-r_A'' = \frac{1}{\frac{1}{k_{Ag}} + \frac{H_A}{k_{AL} E}} P_A$



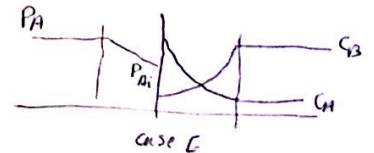
a precise analytical expression for  $E$  has not been obtained. only approximate solution is available.

- Case D:  $C_B$  is high enough to have a pseudo-first order rate constant:  $(-r_A) = k_{CB} C_B$
- In this case, there is analytical solution for  $E$ :  $E = \frac{\sqrt{P_{Ai} k_1}}{k_{AL}}$
- with the following rate expression:  $-r_A'' = \frac{1}{\frac{1}{k_{Ag}} + \frac{H_A}{\sqrt{P_{Ai} k_1} k_{AL}}} P_A$



**1.1.5 Cases E & F - Intermediate rates**

- Case E: the rxn occurs in the film and main liquid film body
- complex rate expressions: analytical rate expression not available, some approximate solutions available.
- Case F: similar to case E, except  $C_B$  is very high and constant

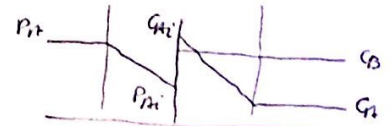


**1.1.6 Case G - slow rxn**

- Gas and liquid film and the main body of liquid act as resistances in series.

$$\frac{-1}{S} \frac{dN_A}{dt} = k_{Ag} (P_A - P_{Ai}) = k_{AL} (C_{Ai} - C_A)$$

$$\frac{-1}{V_L} \frac{dN_A}{dt} = k_{CA} C_B \Rightarrow \frac{-1}{S} \frac{dN_A}{dt} = \frac{k}{a_i} C_A C_B, \text{ where } a_i = \frac{A}{V_L} S = \frac{\text{interfacial surface}}{\text{volume of liquid}}$$



- considering Henry's law.  $P_{Ai} = H_A C_{Ai}$ , we have:  $k_{Ag} (P_A - H_A C_{Ai}) = k_{AL} (C_{Ai} - C_A) = \frac{k}{a_i} C_A C_B$

- 2<sup>nd</sup> equty  $\Rightarrow C_A = \frac{k_{AL} a_i}{k_{AL} a_i + k_{CB}} C_{Ai}$  first equty  $\Rightarrow C_{Ai} = \frac{k_{Ag} P_A}{k_{Ag} H_A + k_{AL} - \frac{k_{AL}^2 a_i}{k_{AL} a_i + k_{CB}}}$

$$\Rightarrow -r_A'' = \frac{k_{Ag} P_A k_{AL} k_{CB}}{k_{Ag} H_A k_{AL} a_i + k_{Ag} H_A k_{CB} + k_{AL} k_{CB}}$$

$$\Rightarrow -r_A'' = \frac{-1}{S} \frac{dN_A}{dt} = \frac{1}{\frac{H_A a_i}{k_{CB}} + \frac{H_A}{k_{AL}} + \frac{1}{k_{Ag}}} P_A$$

**1.1.3 Case B - Special case of high  $C_B$**

- In the treatment of the general case, we obtained the following relationship:

- we can see that the limiting value for  $C_{Ai}$  is zero when

$$C_{Ai} = \frac{k_{Ag} P_A - k_{BL} C_B / b}{k_{AL} + k_{Ag} H_A}$$

- when  $C_B$  becomes high, we can have the situation where

$$k_{Ag} P_A = \frac{k_{BL} C_B}{b} \rightarrow k_{Ag} P_A < \frac{k_{BL} C_B}{b}$$

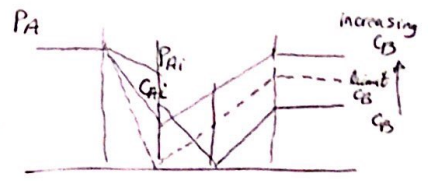
- In which case, the rxn plane moves to the gas-liquid interface and  $C_{Ai} = 0$ ,  $\frac{x}{x_0 - x} = \frac{b k_{AL} C_{Ai}}{k_{BL} C_B}$  ( $C_{Ai} = 0$ )

- The governing rate expression for the case where  $C_{Ai} = 0$  ( $C_B$  is very high):  $-r_A'' = \frac{-1}{S} \frac{dN_A}{dt} = k_{Ag} P_A$

gas phase transfer controlling

- The transition between liquid and gas phase control occurs when  $k_{Ag} P_A < \frac{k_{BL} C_B}{b}$

- Order of magnitude calculation  $D_L \approx 10^{-5} \text{ cm}^2/\text{s}$ ,  $D_g \approx 10^{-1} \text{ cm}^2/\text{s}$ ,  $x_0 \approx 10^{-2} \text{ cm}$ ,  $k_g = \frac{D_g}{x_0} \approx 10$ ,  $k_L = \frac{D_L}{x_0} \approx 10^{-3} \text{ cm/s}$

$$\frac{P_A}{RT} = C_{Ag} < \frac{k_{BL} C_B}{k_{Ag} b} \Rightarrow \frac{P_A}{RT} < 10^{-4} \frac{C_B}{b} \Rightarrow \text{criteria for establishing gas phase control}$$


**1.1.4 Cases C & D - Fast rxn, 2<sup>nd</sup> order rxn**

- Case C  $\rightarrow$  the rxn is not instantaneous, however it is fast enough to be carried out in the liquid film

$\rightarrow$  in this case we have a rxn zone

Enhancement factor  $E$

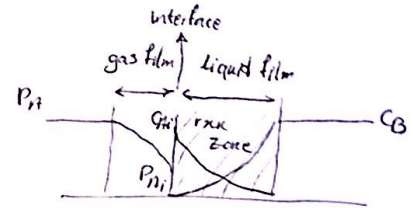
$$-r_A'' = \frac{-1}{V_L} \frac{dN_A}{dt} = k_{CA} C_B, \quad -r_A'' = k_{Ag} (P_A - P_{Ai}) = k_{AL} C_{Ai} E$$

Eliminating  $C_{Ai}$ ,  $P_{Ai}$ :

$$-r_A'' = \frac{1}{\frac{1}{k_{Ag}} + \frac{k_{CA}}{k_{AL} E}} P_A$$

gas film  $\rightarrow$   $\leftarrow$  liquid film

a precise analytical expression for  $E$  has not been obtained. only approximate solution is available.

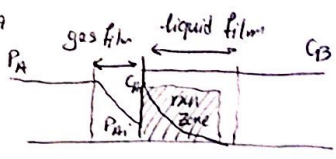


- Case D  $\rightarrow$   $C_B$  is high enough to have a pseudo-first order rate constant:  $(-r_A) = \frac{k_{CA} C_B}{k_C} C_A$

$\rightarrow$  In this case, there is analytical solution for  $E$ :  $E = \sqrt{\frac{D_{AL} k_1}{k_{AL} k_C}}$

$\rightarrow$  with the following rate expression:

$$-r_A'' = \frac{1}{\frac{1}{k_{Ag}} + \frac{H_A}{k_{Ag} \sqrt{D_{AL} k_1 / k_{AL} k_C}}} P_A$$



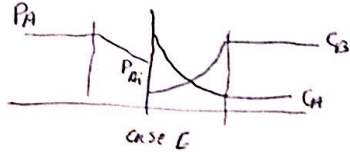
**1.1.5 Cases E & F - Intermediate rates**

- Case E  $\rightarrow$  the rxn occurs in the film and main liquid film body

$\rightarrow$  complex rate expressions  $\rightarrow$  analytical rate expression not available

$\rightarrow$  some approximate solutions available.

- Case F  $\rightarrow$  similar case E, except  $C_B$  is very high and crushed



**1.1.6 Case G - slow rxn**

- Gas and liquid film and the main body of liquid act as resistances in series.

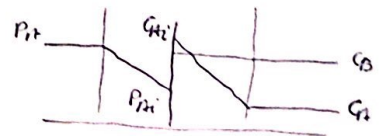
$$\frac{-1}{S} \frac{dN_A}{dt} = k_{Ag} (P_A - P_{Ai}) = k_{AL} (C_{Ai} - C_A)$$

$$\frac{-1}{V_L} \frac{dN_A}{dt} = k_{CA} C_B \iff \frac{-1}{S} \frac{dN_A}{dt} = \frac{k}{a_i} C_A C_B, \text{ where } a_i = \frac{A}{V_L} = \frac{\text{interfacial surface}}{\text{volume of liquid}}$$

- considering Henry's law:  $P_{Ai} = H_A C_{Ai}$ , we have:  $k_{Ag} (P_A - H_A C_{Ai}) = k_{AL} (C_{Ai} - C_A) = \frac{k}{a_i} C_A C_B$

- 2<sup>nd</sup> equity  $\Rightarrow C_A = \frac{k_{AL} a_i}{k_{AL} a_i + k_{CA} C_B} C_{Ai}$  first equity  $C_{Ai} = \frac{k_{Ag} P_A}{k_{Ag} H_A + k_{AL} - \frac{k_{AL}^2 a_i}{k_{CA} C_B + k_{AL}}}$

$$\Rightarrow -r_A'' = \frac{k_{Ag} P_A k_{AL} k_{CA} C_B}{k_{Ag} H_A k_{AL} a_i + k_{Ag} H_A k_{CA} C_B + k_{AL} k_{CA} C_B}$$



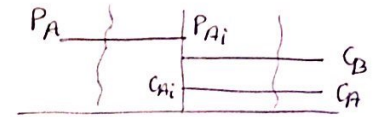
$$\Rightarrow -r_A'' = \frac{-1}{S} \frac{dN_A}{dt} = \frac{1}{\frac{H_A a_i}{k_{CA} C_B} + \frac{H_A}{k_{AL}} + \frac{1}{k_{Ag}}} P_A$$

### 1.1.7 Case H - Infinitely slow rxn

- concentration of A and B are uniform in the liquid and the rate is given by:

$$-r_{AL} = \frac{-1}{V_L} \frac{dN_A}{dt} = k C_A C_B$$

- The film offers no resistance, interfacial area does not enter into the rate expression.



### 1.1.8 film conversion Parameter, M

- neglect the gas phase resistance, and define M as:

$$M = \frac{\text{max possible conversion in the film}}{\text{max diffusion transport through film}} = \frac{k C_{A_i} C_B x_0}{\frac{D_{AL}}{x_0} \cdot C_{A_i}} = \frac{k C_B D_{AL}}{k_{AL}^2} \Rightarrow k_{AL} = \frac{D_{AL}}{x_0}$$

-  $M \gg 1$   $\left\{ \begin{array}{l} \rightarrow \text{rxn occurs in film} \\ \rightarrow \text{fast rxn} \\ \rightarrow \text{surface area controlling the rate} \end{array} \right.$

-  $M \ll 1$   $\left\{ \begin{array}{l} \rightarrow \text{No rxn in the film} \\ \rightarrow \text{bulk liquid becomes controlling rate factor} \end{array} \right.$

-  $M > 4$   $\left\{ \begin{array}{l} \rightarrow \text{cases A, B, C, D} \\ \rightarrow \text{instantaneous or fast rxn} \\ \rightarrow \text{rxn in film} \end{array} \right.$

-  $0.0009 < M < 4 \rightarrow$  Indicates cases E, F, G

-  $M < 0.0009 \rightarrow$  Infinitely slow rxn

- Large M  $\left\{ \begin{array}{l} \rightarrow \text{need a contacting device for large interfacial areas} \\ \rightarrow \text{energy for agitation to provide enhanced mass transfer} \end{array} \right.$

- Small M  $\rightarrow$  all we need is large volume of liquid

- Devices