Fluid-fluid Reaction: Kinetics and Reactor Design

# Case A: Instantaneous Reaction with respect to Mass Transfer, low C_B

- The reaction is <u>extremely fast</u> and an element of <u>liquid can either contain A or B</u> but not both

- The <u>reaction occurs</u> at a <u>plane between A containing and B containing liquid</u>

- Since reactants must diffuse to this reaction plane, the <u>diffusion of A and B will determine the rate</u>, so that a change in <u>p_A</u> or <u>C_B</u> will move the plane one way or the other

- At steady state, the flowrate of B towards the reaction zone will be b times the flow rate of A towards the reaction zone

- Thus, $$-r_A'' = \frac{-r_B''}{b} = k_{Ag}(p_A - p_{Ai})$$
$$= k_{AL}(C_{Ai} - 0)\frac{x_0}{x} = \frac{k_{BL}}{b}(C_B - 0)\frac{x_0}{x_0 - x}$$

  $(-r_A'')$ is based on interfacial area

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- k_{Ag} and k_{AL}, k_{BL} are gas and liquid mass transfer coefficients

- Liquid side coefficients are for straight mass transfer and are based on flow through the entire film of thickness x_0

- At the interface, $p_{Ai} = H_A C_{Ai}$
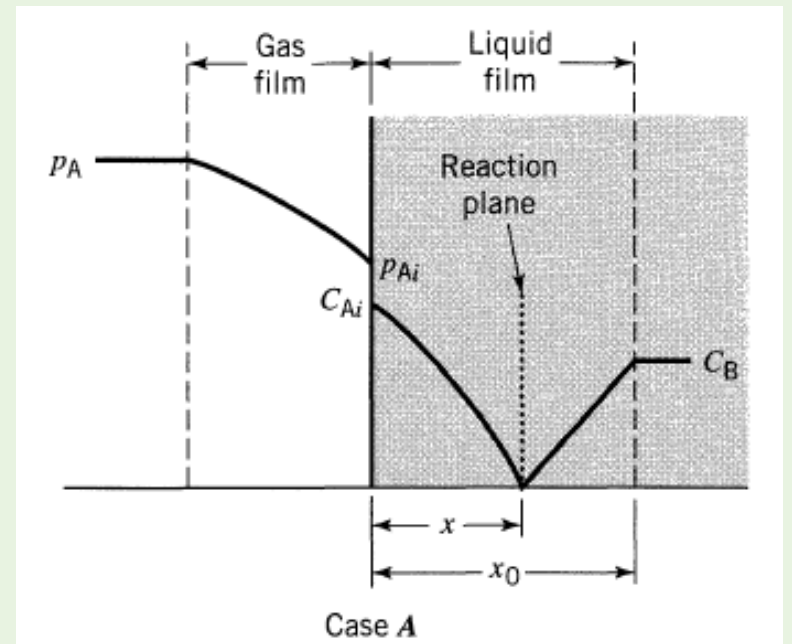
- If the movement of the material within the film is visualized to occur by diffusion alone,

$$\frac{k_{AL}}{k_{BL}} = \frac{D_{AL}/x_o}{D_{BL}/x_o} = \frac{D_{AL}}{D_{BL}}$$

- Eliminating x, x_0, p_{Ai} and C_{Ai} within the previous three equations we get,

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

for $$k_{Ag}p_A > \frac{k_{BL}C_B}{b}$$

Special case: For <u>negligence gas phase resistance </u>(in case pure A is used in gas phase, $p_A = p_{Ai}$), $k_{Ag} \rightarrow \infty$, the above equation is,

$$-r_A'' = k_{AL}C_{Ai}\left(1 + \frac{D_{BL}}{D_{AL}}\frac{C_B}{bC_{Ai}}\right)$$

Here, we define a new term called the **enhancement factor**

Enhancement factor indicates how the mass transfer rate is enhanced by means of chemical reaction

The maximum rate of physical mass transfer $= k_{AL} C_{Ai}$

$$\text{Enhancement factor } (E) = \frac{\text{Rate of absorption of } A \text{ with reaction}}{\text{Rate of absorption of } A \text{ with straight mass transfer}}$$
$$\text{in liquid film}$$

$$-r_A'' = k_{AL} C_{Ai} E_i$$

where $E_i = 1 + \dfrac{D_{BL}}{D_{AL}} \dfrac{C_B}{b C_{Ai}}$

E_i is the *enhancement factor for infinitely fast reaction*

The value of E is always $>$ or equal to 1

Case B: Instantaneous Reaction with high C_B

- If the concentration of B is high, i.e., if $\boxed{k_{Ag}p_A \leq \dfrac{k_{BL}C_B}{b}}$, the reaction zone moves to and stays at the interface $(x = 0)$ rather than remain in the liquid film

- Here the resistance of the gas phase controls, and the rate is not affected by any further increase in the concentration of B

$$\boxed{-r_A'' = -\frac{1}{S}\frac{dN_A}{dt} = k_{Ag}p_A}$$
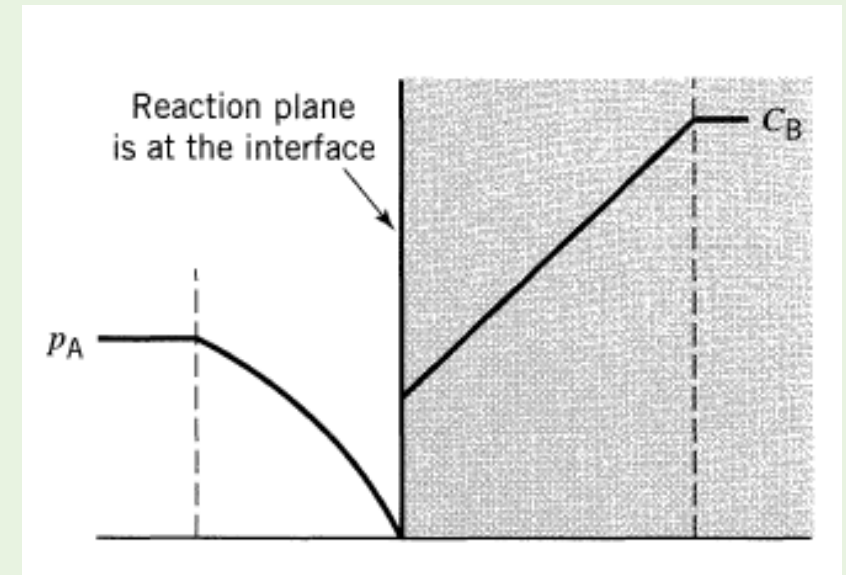
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- Before studying the other case (Case C to H) it is important to define a general rate equation which is applicable for reactions of different rates

- The general rate expression showing the influence of both mass transfer and reaction rate is given as

$$\boxed{-r_A''' = \frac{p_A}{\dfrac{1}{ak_{Ag}} + \dfrac{H_A}{k_{AL}aE} + \dfrac{H_A}{kC_Bf_L}}}$$

where E is the liquid film enhancement factor

- **Enhancement factor (E) tells us how the chemical reaction has a positive influence on the absorption of gas**

- E is dependent on two quantities:

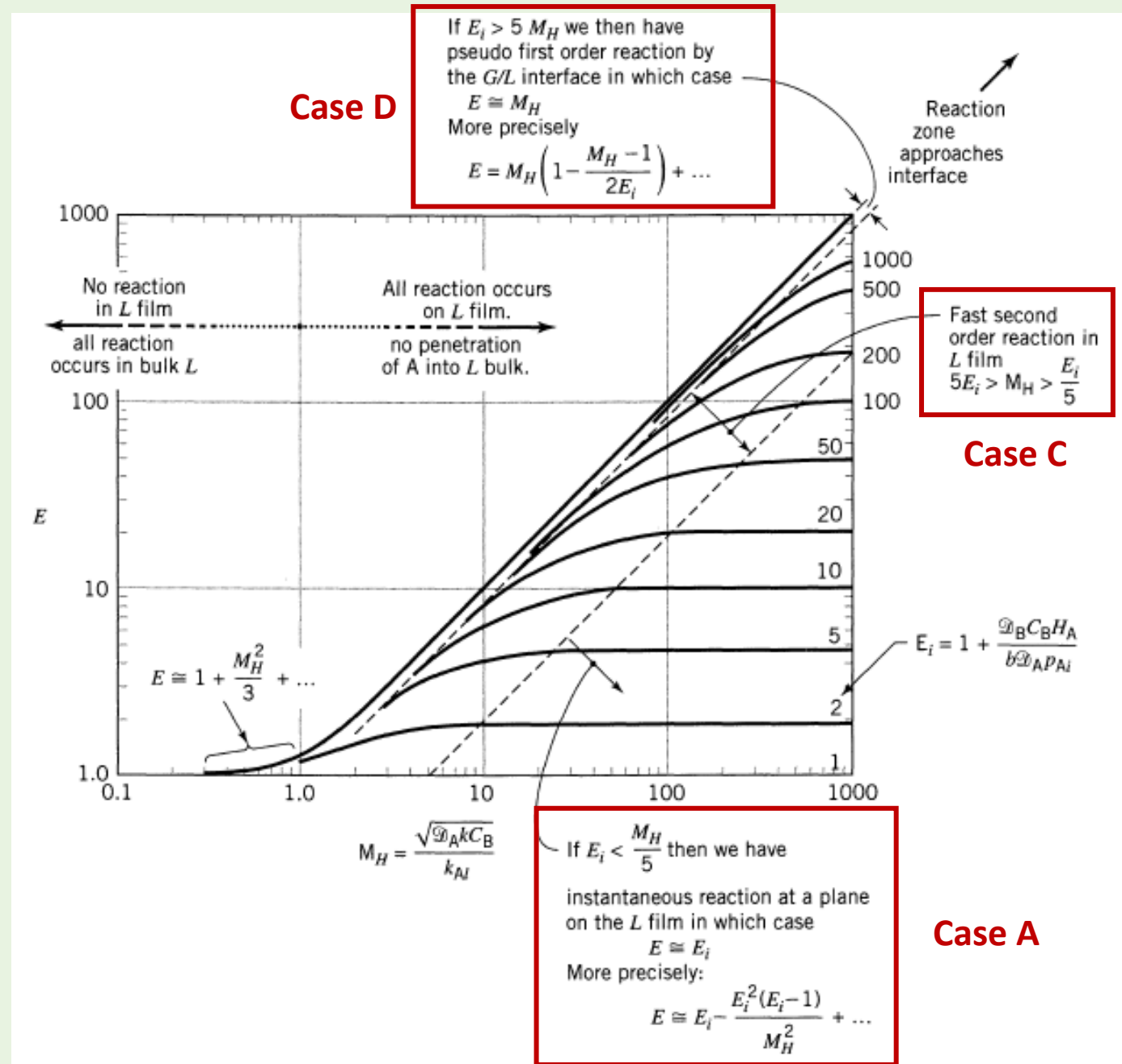 - E_i (enhancement factor for infinitely fast rxn)
  - M_H^2 (Hatta number)

- $$M_H^2 = \frac{maximum\ possible\ conversion\ in\ the\ film}{maximum\ diffusional\ transport\ through\ the\ film}$$

$$M_H^2 = \frac{kC_{Ai}C_B x_o}{\frac{D_{AL}}{x_o} \cdot C_{Ai}} = \frac{kC_B D_{AL}}{k_{AL}^2}$$

$$\because k_{AL} = \frac{D_{AL}}{x_o}$$

$$M_H = x_o \sqrt{\frac{kC_B}{D_{AL}}}$$

(similar to Thiele modulus defined for gas – solid catalytic reactions)

Case D — If $E_i > 5\ M_H$ we then have pseudo first order reaction by the G/L interface in which case $E \cong M_H$ More precisely $E = M_H\left(1 - \frac{M_H - 1}{2E_i}\right) + \dots$

Reaction zone approaches interface

No reaction in L film — all reaction occurs in bulk L

All reaction occurs on L film. no penetration of A into L bulk.

Case C — Fast second order reaction in L film $5E_i > M_H > \frac{E_i}{5}$

$E \cong 1 + \frac{M_H^2}{3} + \dots$

$E_i = 1 + \frac{\mathcal{D}_B C_B H_A}{b \mathcal{D}_A p_{Ai}}$

$M_H = \frac{\sqrt{\mathcal{D}_A k C_B}}{k_{Al}}$

Case A — If $E_i < \frac{M_H}{5}$ then we have instantaneous reaction at a plane on the L film in which case $E \cong E_i$ More precisely: $E \cong E_i - \frac{E_i^2(E_i - 1)}{M_H^2} + \dots$

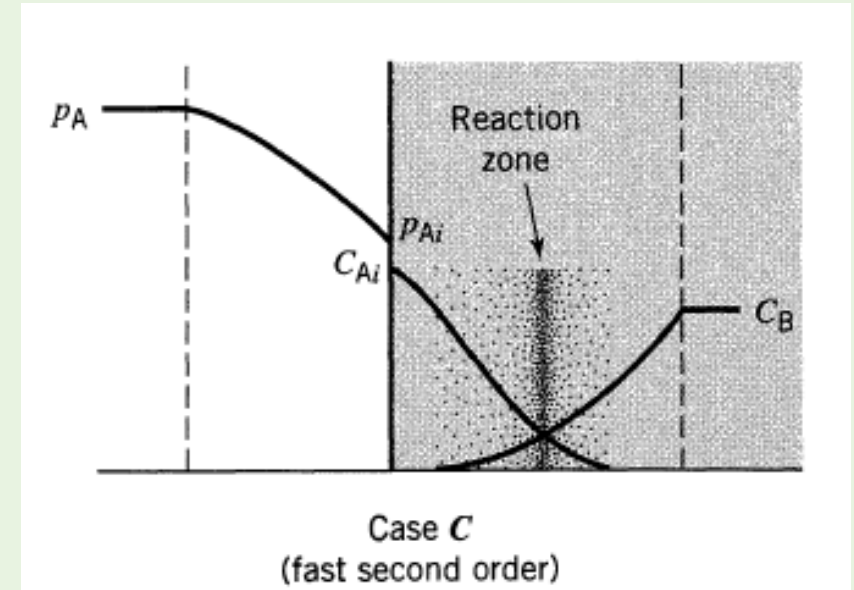*Chemical Reaction Engineering*, O. Levenspiel

Case C: Fast reaction, low C_B

- The plane of reaction as seen in Case A now spreads into a zone of reaction in which A and B are both present

- The <u>reaction is fast enough so that the reaction zone remains totally within the liquid film</u>

- <u>No A enters the main body of the liquid to react there</u>

- As the reaction rate is high, the resistance due to reaction is negligible

$$-r_A''' = \frac{p_A}{\dfrac{1}{ak_{Ag}} + \dfrac{H_A}{k_{AL}aE}}$$

- For the fast, second order reaction in film

$$5E_i > M_H > \frac{E_i}{5}$$

Case C
(fast second order)

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Case D: Fast reaction, high C$_B$, pseudo first order with respect to A

- When the <u>concentration of B is high, its concentration does not drop appreciably within the film and can be taken to be constant</u>

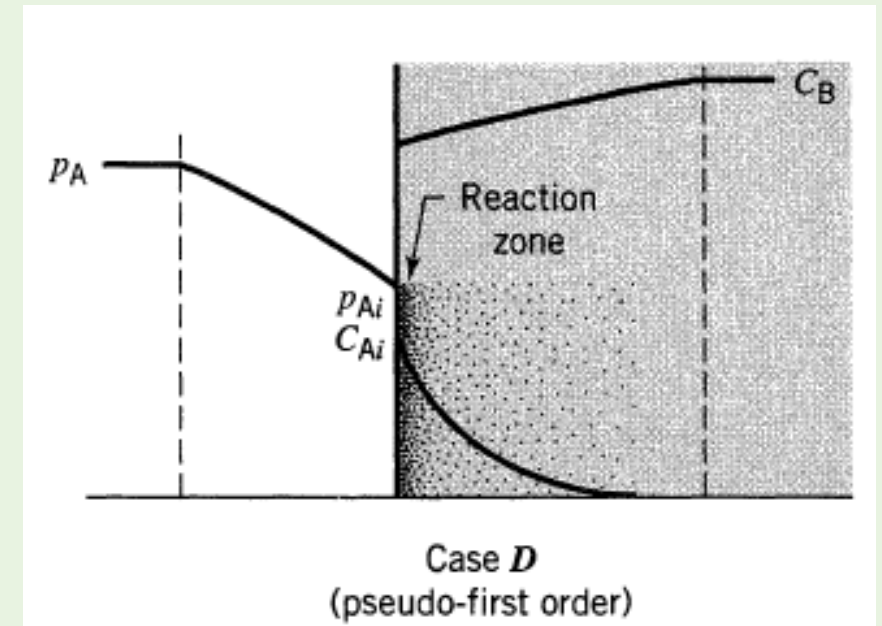- The <u>second order reaction then reduces to a pseudo first order</u> expression

$$-r_A''' = \frac{p_A}{\dfrac{1}{ak_{Ag}} + \dfrac{H_A}{k_{AL}aE}}$$

Replacing the value of E we have,

$$\boxed{-r_A''' = \frac{p_A}{\dfrac{1}{k_{Ag}a} + \dfrac{H_A}{a\sqrt{D_{AL}kC_B}}}}$$

If $E_i > 5M_H$, then there is a pseudo first order reaction

and $E \cong M_H$

Case **D**
(pseudo-first order)

$$E \cong M_H = \sqrt{\frac{kC_B D_{AL}}{k_{AL}^2}}$$

$$\therefore \quad \frac{H_A}{k_{AL}aE} = \frac{H_A}{k_{AL}a\sqrt{\dfrac{kC_B D_{AL}}{k_{AL}^2}}}$$

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Case E and F: Intermediate reaction rate with respect to mass transfer

- Here the reaction is slow enough for some A to diffuse through the film into the main body of the fluid

- Consequently, <u>A reacts both within the film and in the main body of the fluid</u>

Case E   Case F

- In these cases, <u>the general rate expression showing all the three resistances are used</u>
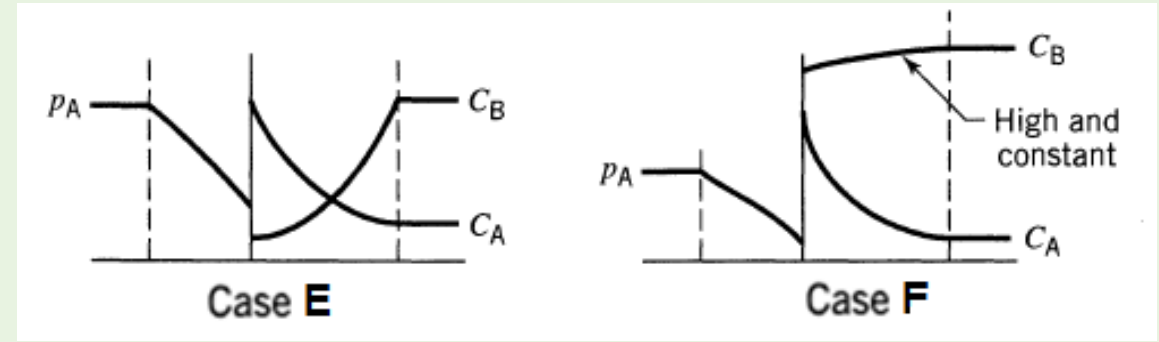
Case G: Slow reaction rate with respect to mass transfer

- For this case, <u>all reactions occur in the main body of the liquid</u> but the <u>film still provides a resistance to the transfer of A into the main body of the fluid</u>
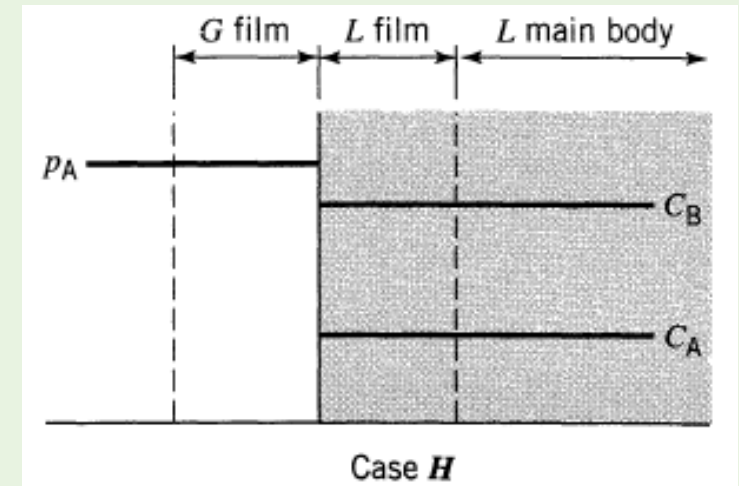
$$-r_A''' = \frac{p_A}{\dfrac{1}{k_{Ag}a} + \dfrac{H_A}{k_{AL}a} + \dfrac{H_A}{kC_B f_L}}$$

$$E \approx 1$$

Case G

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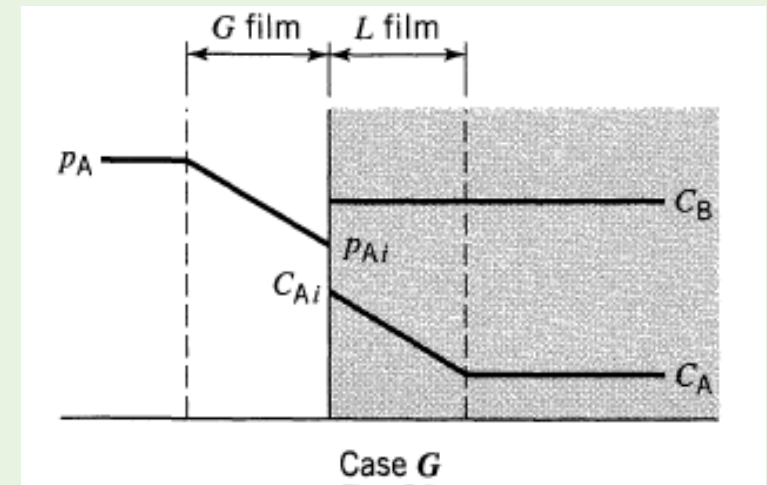
Case H: Infinitely slow reaction

- Here the <u>mass transfer resistance is negligible</u>

- The composition of A and B are uniform in the liquid and rate is determined by kinetics alone

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

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Role of Hatta Number, M_H

$$M_H = x_o \sqrt{\frac{kC_B}{D_{AL}}} = \frac{\sqrt{kC_B D_{AL}}}{k_{AL}}$$

- If $M_H \gg 1$, **all reaction occurs in the film** (high reaction rate) and **"surface area" is the rate controlling factor**

- If $M_H \ll 1$, **no reaction occurs in the film,** and **"bulk volume" becomes the controlling factor**

- If $M_H > 2$, **reaction** occurs in the **film** (Case A, B, C, D)

- If $0.02 < M_H < 2$, **intermediate case** (Case E, F, G)

- If $M_H < 0.02$, infinitely slow reaction, **reaction** in **bulk** (Case H)

- If M_H **is large**, a **contacting device which develops or creates a large interfacial area is used**

- If M_H **is very small**, a **large volume of liquid is required**

- **Agitation helps to create large interfacial area** and is of use if M_H is large and is ineffective for small M_H

- For **fast reaction, large** M_H - **spray or plate columns**

- For **slow reaction, small** M_H - **bubble columns**

Kinetic regime from solubility data

- For reactions occurring in the film, the phase distribution coefficient H_A can suggest whether gas phase resistance is important or not

- For straight mass transfer, $$-r_A'' = -\frac{1}{S}\frac{dN_A}{dt} = \frac{\Delta p_A}{\frac{1}{k_{Ag}} + \frac{H_A}{k_{AL}}}$$

H_A values (Pa m³/mol)						
	N_2	H_2	O_2	CO	CO_2	NH_3
20°C	1.45×10^5	1.23×10^5	0.74×10^5	0.96×10^5	2600	0.020
60°C	2.16×10^5	1.34×10^5	1.13×10^5	1.48×10^5	6300	0.096

Gases are more soluble at lower temperature

- For slightly soluble gases, H_A is large and the liquid film resistance term is large – the opposite is true for highly soluble gases

- Liquid film resistance controls for slightly soluble gases while gas film resistance controls for highly soluble gases

- Since a highly soluble gas is easy to absorb and has its main resistances in the gas phase, it is not necessary to add a liquid phase reactant to promote absorption

- For a sparingly soluble gas which is difficult to absorb and has its main resistance in the liquid phase, a reaction in the liquid phase would be highly beneficial

Example

Gaseous A absorbs and reacts with B in liquid according to

$$A(g \rightarrow l) + B(l) \rightarrow R(l) \qquad\qquad -r_A = kC_AC_B$$
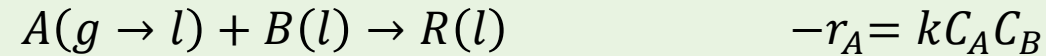
in a packed bed under conditions where

$k_{Ag}a$ = 0.1 mol/h.m² of reactor. Pa $\qquad\qquad$ a = 100 m²/m³ reactor

$k_{AL}a$ = 100 m³ liquid/m³ reactor. h $\qquad\qquad$ f_l = 0.01 m³ liquid/m³ reactor $\qquad\qquad$ $D_{AL} = D_{BL}$ = 10⁻⁶ m²/h

At a point in the reactor where p_A = 100 Pa and C_B = 100 mol/m³ liquid

(a) Calculate the rate of reaction in mol/h.m³ of reactor

(b) Location of the major resistance (gas film, liquid film, main body of liquid)

(c) Behaviour in liquid film (pseudo first order, instantaneous second order, physical transport)

For the following two cases – (i) k = 10 m³ liquid/mol. h $\qquad$ H_A = 10⁵ Pa.m³ liquid/mol

$\qquad\qquad\qquad\qquad\qquad$ (ii) k = 10⁶ m³ liquid/mol. h $\qquad$ H_A = 10⁴ Pa.m³ liquid/mol

(i) $\qquad M_H = \dfrac{\sqrt{kC_BD_{AL}}}{k_{AL}} = \dfrac{\sqrt{10 \times 100 \times 10^{-6}}}{100/100}$ = 3.16 x 10⁻² $\qquad\qquad \therefore E = 1$

(a) $-r_A''' = \dfrac{p_A}{\dfrac{1}{ak_{Ag}} + \dfrac{H_A}{k_{AL}aE} + \dfrac{H_A}{kC_Bf_L}} = \dfrac{100}{\dfrac{1}{0.1} + \dfrac{10^5}{100 \times 1} + \dfrac{10^5}{10 \times 100 \times 0.01}} = \dfrac{100}{10 + 1000 + 10000} = \dfrac{100}{11010}$ = 9.08 x 10⁻³ mol/h.m³.s

(b) Resistances: 91% in liquid body $\left(\frac{10000}{11010} \times 100 = 90.8\%\right)$

$\quad\quad\quad\quad\quad\quad\quad$ 9% in liquid film $\left(\frac{1000}{11010} \times 100 = 9.08\%\right)$

(c) Liquid film: physical transport

(ii) $\quad\quad M_H = \frac{\sqrt{kC_B D_{AL}}}{k_{AL}} = \frac{\sqrt{10^6 \times 100 \times 10^{-6}}}{100/100} = 10$

$$E_i = 1 + \frac{D_{BL}}{D_{AL}}\frac{C_B}{bC_{Ai}} = 1 + \frac{D_{BL}}{D_{AL}}\frac{C_B H_A}{bp_{Ai}} = 1 + \frac{10^{-6}}{10^{-6}}\frac{100 \times 10^4}{100} = 1 + 10^4 = 10001$$

$$\therefore \quad E_i > 5M_H, \text{and} \quad E \cong M_H$$

(a) $-r_A''' = \dfrac{p_A}{\frac{1}{ak_{Ag}} + \frac{H_A}{k_{AL}aE} + \frac{H_A}{kC_B f_L}} = \dfrac{100}{\frac{1}{0.1} + \frac{10^4}{100 \times 10} + \frac{10^4}{10^6 \times 100 \times 0.01}} = \dfrac{100}{10 + 10 + 0.01} = \dfrac{100}{20.01} = 4.9975 \text{ mol/h.m}^3.\text{s}$

(b) Resistances: 50% in gas film $\left(\frac{10}{20.01} \times 100 = 49.98\%\right)$

$\quad\quad\quad\quad\quad\quad\quad$ 50% in liquid film $\left(\frac{10}{20.01} \times 100 = 49.98\%\right)$

$\quad\quad\quad\quad$ Reaction zone: Gas-liquid interface (pseudo first order reaction)

(c) Liquid film: Reaction in liquid film