



# Advance Chemical Reaction Engineering

## Multiphase Reacting Systems: Gas-Liquid Systems

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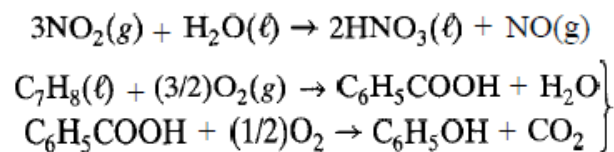


# Introduction

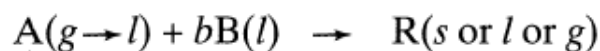
- In a number of important industrial processes, it is necessary to carry out a reaction between a gas and a liquid to make a particular product,
- Gas-liquid reacting systems may be considered from one of two points of view, depending on the purpose of the reaction as:
  - Separation process: the reaction is used for the removal of an undesirable substance from a gas stream (gas absorption with Reaction)

**removal of H<sub>2</sub>S or CO,**

- Reaction process: the reaction is used to yield a desirable product



Or generally,



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# Introduction

The following factors will determine how we approach this process

➤ ***The Overall Rate Expression:***

- Materials in the two separate phases must contact each other before reaction can occur,
- Both the mass transfer and the chemical rates will enter the overall rate expression

➤ ***Equilibrium Solubility:***

- The solubility of the reacting components will limit their movement from phase to phase.
- This will influence the form of the rate equation since it will determine whether the reaction takes place in one or both phases

➤ ***The Contacting Scheme:***

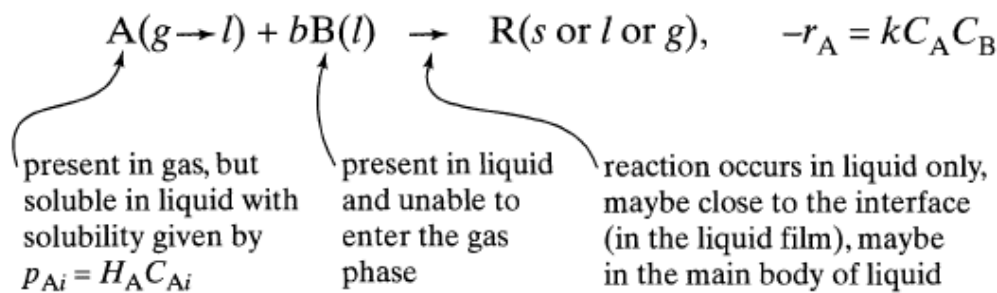
- In gas-liquid systems semibatch and countercurrent contacting schemes predominate.
- In liquid-liquid systems mixed flow (mixer settlers) and batch contacting are used in addition to counter and concurrent contacting.

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# The Rate Equation

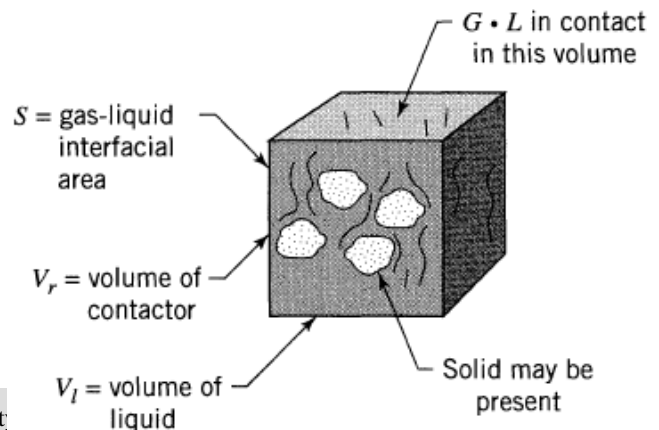
➤ For a second-order reaction



Define

$$f_l = \frac{V_l}{V_r}, \quad f_g = \frac{V_g}{V_r}, \quad \epsilon = f_l + f_g$$

$$a_l = \frac{S}{V_l}, \quad a = \frac{S}{V_r}$$



# The Rate Equation

## Two-Film Mass-Transfer Model for Gas-Liquid Systems

➤ In the two-film model, the following assumptions are made

- i. The two-film model is a steady-state model; that is, the concentration profiles are established instantaneously and remain unchanged.
- ii. The steady-state transport of A through the stagnant gas film is by molecular diffusion, characterized by the molecular diffusivity  $D_{Ag}$ .
- iii. The rate of transport, normalized to refer to unit area of interface, is given by Fick's law, in the integrated form

$$N_A = D_{Ag}(p_A - p_{Ai})/RT\delta_g = k_{Ag}(p_A - p_{Ai})$$

$\frac{\text{mol}}{\text{m}^2 \cdot \text{Pa} \cdot \text{s}}$   
 ↓

where  $N_A$  is the molar flux of A,  $\text{mol m}^{-2} \text{s}^{-1}$ ,



# The Rate Equation

$k_{Ag}$  is the gas-film mass transfer coefficient

$$k_{Ag} = D_{Ag}/RT\delta_g$$

- iv. The transport of A through the liquid film is by molecular diffusion, characterized by  $D_{AL}$  and the flux (at steady-state)

$$N_A = D_{AL}(c_{Ai} - c_A)/\delta_\ell$$

$$= k_{AL}(C_{Ai} - C_A)$$

$\frac{\text{m}^3 \text{ liquid}}{\text{m}^2 \text{ surface} \cdot \text{s}}$

where the liquid-film mass transfer coefficient is  $k_{AL} = D_{AL}/\delta_\ell$



# The Rate Equation

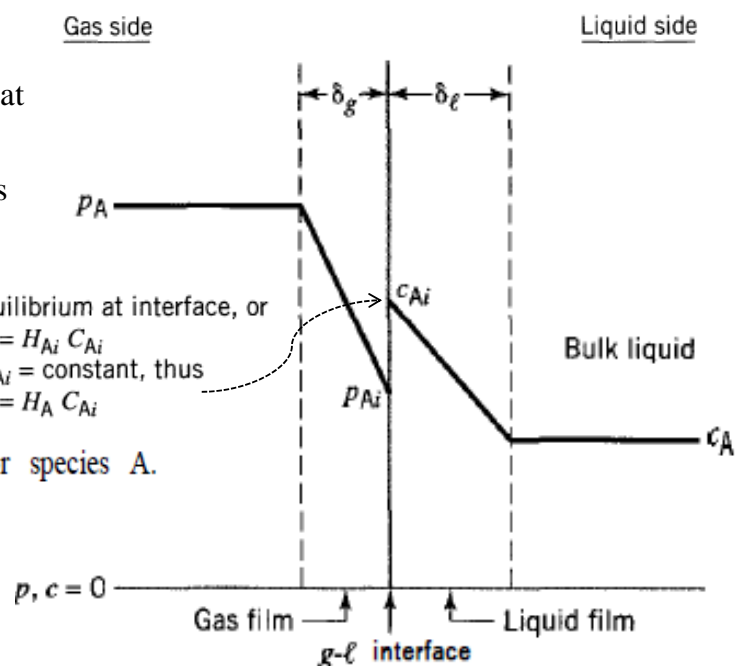
- v. There is equilibrium at the interface, which is another way of assuming that there is no resistance to mass transfer at the interface. The equilibrium relation may be expressed by means of Henry's law:

$$p_{Ai} = H_A c_{Ai}$$

Assume equilibrium at interface, or  
 $p_{Ai} = H_{Ai} C_{Ai}$   
 and take  $H_{Ai} = \text{constant}$ , thus  
 $p_{Ai} = H_A C_{Ai}$

where  $H_A$  is the Henry's law constant for species A.

- Gaseous A is soluble in the liquid but that B does not enter the gas. Thus A must enter and move into the liquid phase before it can react, and reaction occurs in this phase alone.



# The Rate Equation

By eliminating interface conditions  $p_{Ai}$  and  $C_{Ai}$   $p_{Ai} = H_A c_{Ai}$

$$\begin{aligned} N_A &= k_{Ag} (p_A - H_A c_{Ai}) \\ &= k_{Al} (C_{Ai} - C_A) \end{aligned}$$

$$\rightarrow N_A = \frac{1}{\frac{1}{k_{Ag}} + \frac{H_A}{k_{Al}}} (p_A - H_A C_A)$$

$\frac{\text{Pa} \cdot \text{m}^3 \text{ liquid}}{\text{mol}}$

And 
$$\frac{1}{K_{Ag}} = \frac{1}{k_{Ag}} + \frac{H_A}{k_{Al}}$$

Similarly, 
$$\frac{1}{K_{Al}} = \frac{1}{H_A k_{Ag}} + \frac{1}{k_{Al}}$$



# The Rate Equation

- Since B does not enter the gas phase, the reaction between A and B then takes place at some “location” within the liquid phase: the liquid film and the bulk liquid,
- The location and size of the reaction zone depends on the rate of mass transfer of species A, on the rate of reaction and the concentration of B in the liquid phase.

## Classification in Terms of Location of Chemical Reaction

- i. Reaction in bulk liquid only;
- ii. Reaction in liquid film only;
- iii. Reaction in both liquid film and bulk liquid.



# The Rate Equation

- There are three rate processes involve in this case
  - i. Mass transfer of A through gas film
  - ii. Mass transfer of A through liquid film
  - iii. Reaction of A and B in bulk liquid

At steady state

$$N_A = -r_A$$

Solve for  $C_A$  ➔

$$c_A = \frac{p_A}{k'_A c_B \left( \frac{1}{k_{Ag}} + \frac{H_A}{k_{Al}} \right) + H_A}$$

$$\text{➔ } (-r_A) = \frac{p_A}{\underbrace{\frac{1}{k_{Ag}}}_{\text{gas film resistance}} + \underbrace{\frac{H_A}{k_{Al}}}_{\text{liquid film resistance}} + \underbrace{\frac{H_A}{k'_A c_B}}_{\text{liquid bulk resistance}}}$$

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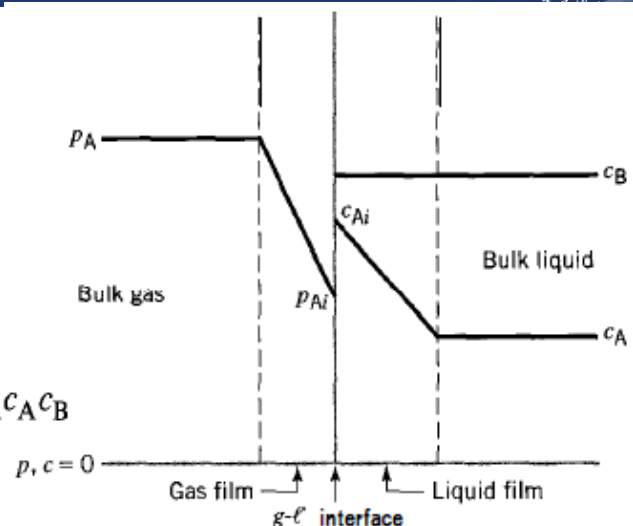
# Reaction in Bulk Liquid

## Relatively Slow Reaction

- If chemical reaction occurs only in the bulk liquid, but resistance to mass transfer of A through gas and liquid films is not negligible

For a 2<sup>nd</sup> order reaction,

$$N_A = (-r_A) = (-r_A)_{int}/a_i = (k_A/a_i)c_A c_B = k'_A c_A c_B$$



where, for consistency with the units of  $(-r_A)$  used above, the interfacial area  $a_i$  (e.g.,  $\text{m}^2$  (interfacial area)  $\text{m}^{-3}$  (liquid)) is introduced to relate  $(-r_A)$  to  $(-r_A)_{int}$  (in  $\text{mol m}^{-3}$  (liquid)  $\text{s}^{-1}$ ).

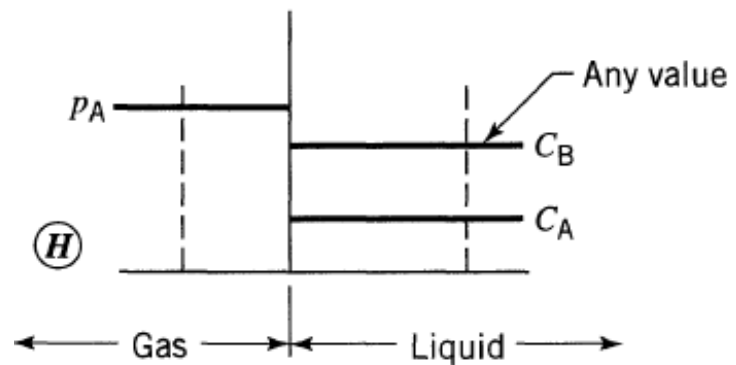
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# Reaction in Bulk Liquid: Relatively Slow Reaction

- **If all mass transfer resistance is negligible**, the situation is the same as that for a homogeneous liquid-phase reaction,

$$(-r_A)_{int} = k_A c_A c_B$$



Slow reaction, no mass transfer resistance

If the liquid-phase reaction is pseudo-first-order with respect to A ( $c_B$  constant and  $\gg c_A$ ),

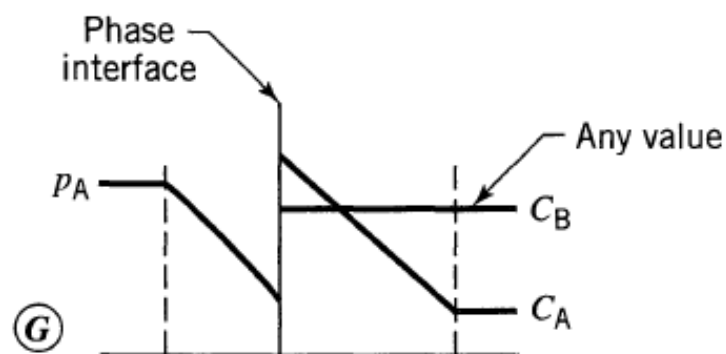
$$(-r_A) = (-r_A)_{int}/a_i = (k'_A c_B) c_A = k''_A c_A$$

where  $k''_A = k'_A c_B = k_A c_B / a_i$ .

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# Reaction in Bulk Liquid



Slow reaction in main body but with film resistance

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# Reaction in Liquid Film

## Instantaneous reaction

- If the rate of reaction between A and B is so high as to result in instantaneous reaction,
- A and B cannot coexist anywhere in the liquid phase.
- Reaction occurs at some point in the liquid film
- The location of which is determined by the relative concentrations and diffusivities of A and B.
- The three diffusion steps can be treated as series processes

$$N_A = k_{Ag} (p_A - p_{Ai}) \quad \text{A in gas film}$$

$$N_A = \frac{D_{A\ell}}{\delta} (c_{Ai} - 0) = \frac{\delta_\ell}{\delta} k_{A\ell} c_{Ai} \quad \text{A in liquid film}$$

$$N_B = \frac{D_{B\ell}}{\delta_\ell - \delta} (c_B - 0) = \frac{\delta_\ell}{\delta_\ell - \delta} k_{B\ell} c_B \quad \text{B in liquid film}$$

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# Reaction in Liquid Film :Instantaneous reaction

The rates  $N_A$  and  $N_B$  are related through stoichiometry

$$N_B = bN_A$$

and the concentrations  $p_{Ai}$  and  $c_{Ai}$  are related by Henry's law:

$$p_{Ai} = H_A c_{Ai}$$

- The liquid-phase diffusivities and mass-transfer coefficients are related, as

$$k_{A\ell}/k_{B\ell} = D_{A\ell}/D_{B\ell}$$

elimination of  $p_{Ai}$ ,  $c_{Ai}$ ,  $N_B$ ,  $k_{B\ell}$  and  $\delta_\ell/\delta$

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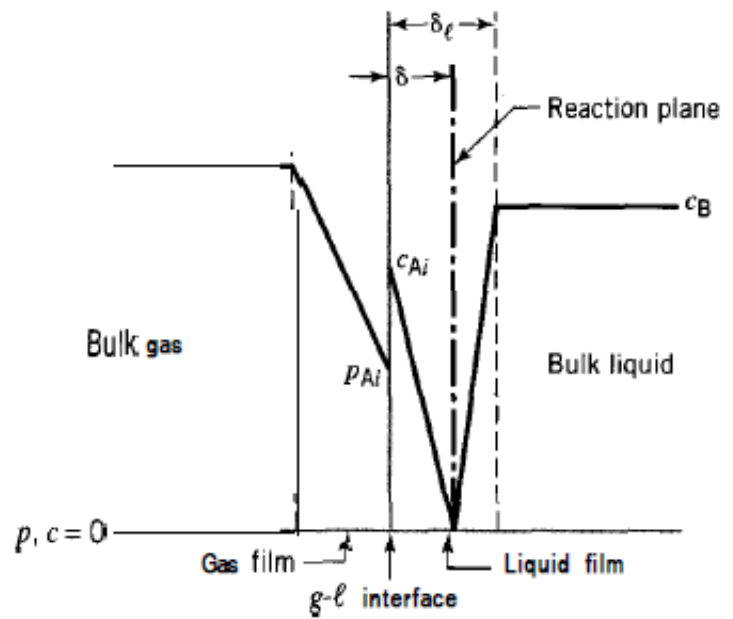




# Reaction in Liquid Film : Instantaneous reaction



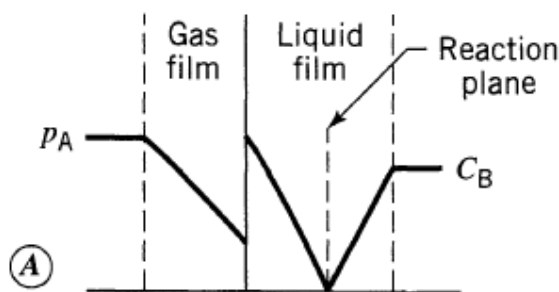
$$N_A \equiv (-r_A) = \frac{p_A + \frac{D_{B\ell} H_A}{D_{A\ell} b} c_B}{\frac{1}{k_{Ag}} + \frac{H_A}{k_{A\ell}}}$$



# Reaction in Liquid Film : Instantaneous reaction

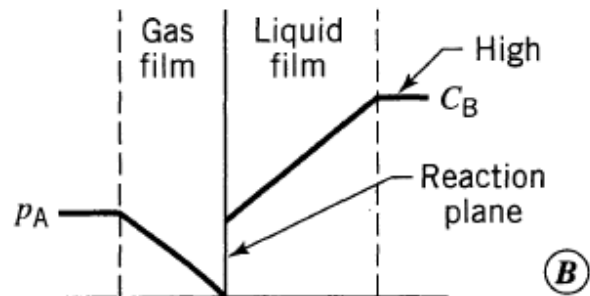
$$\text{or } (-r_A) = K_{Ag} \left( p_A + \frac{D_{B\ell} H_A}{D_{A\ell} b} c_B \right) = K_{A\ell} \left( \frac{p_A}{H_A} + \frac{D_{B\ell}}{D_{A\ell} b} c_B \right)$$

If=



Instantaneous reaction with low  $C_B$

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



Instantaneous reaction with high  $\bar{C}_B$

$$\left( k_{Ag} p_A \leq \frac{k_{Bl} C_B}{b} \right) \text{ gas-film control,}$$

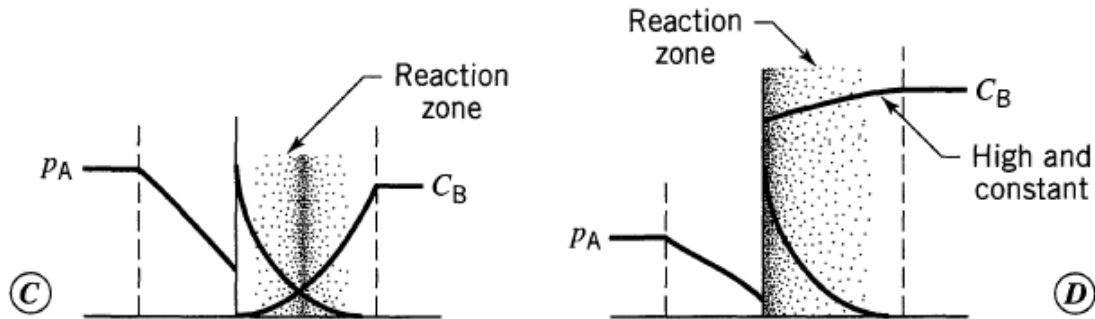
$\delta$  decreasing as  $c_B$  increases.



# Reaction in Liquid Film

## Relatively Fast Reaction

- If chemical reaction is sufficiently fast, even though not instantaneous, it is possible for it to occur entirely within the liquid-film, but not at a point or plane.



Fast reaction in liquid film, with low  $C_B$

Fast reaction in liquid film, with high  $C_B$

- This case is considered as a special case of reaction in both bulk liquid and liquid film



# Reaction in Liquid Film: Enhancement Factor

- For reaction occurring only in the liquid film, whether instantaneous or fast, the rate law may be put in an alternative form by means of a factor that measures the enhancement of the rate relative to the rate of physical absorption of A in the liquid without reaction.
- Reaction occurring only in the liquid film is characterized by  $c_A \rightarrow 0$  somewhere in the liquid film,
- The enhancement factor  $E$  is defined by

$$\left( \begin{array}{c} \text{Liquid film} \\ \text{enhancement} \\ \text{factor} \end{array} \right), E = \left( \frac{\text{rate of take up of A} \\ \text{when reaction occurs}}{\text{rate of take up of A for} \\ \text{straight mass transfer}} \right)_{\text{same } C_{Ai}, C_A, C_{Bi}, C_B \\ \text{in the two cases}}$$

$$E = \frac{\text{rate of reaction or flux of A}}{\text{maximum rate of mass transfer of A through the liquid film}} \\ = \frac{(-r_A)/k_{Af}(c_{Ai} - c_A)}{k_{Af}c_{Ai}} = \frac{(-r_A)}{k_{Af}c_{Ai}}$$



# Reaction in Liquid Film: Enhancement Factor

since  $c_A = 0$  for maximum rate of mass transfer.

$$\rightarrow (-r_A) = k_{A\ell} E c_{Ai}$$

Eliminating the interfacial concentration  $c_{Ai}$

$$\rightarrow (-r_A) = \frac{p_A}{\frac{1}{k_{Ag}} + \frac{H_A}{k_{A\ell} E}}$$

➤ For Instantaneous reaction this is equivalent to

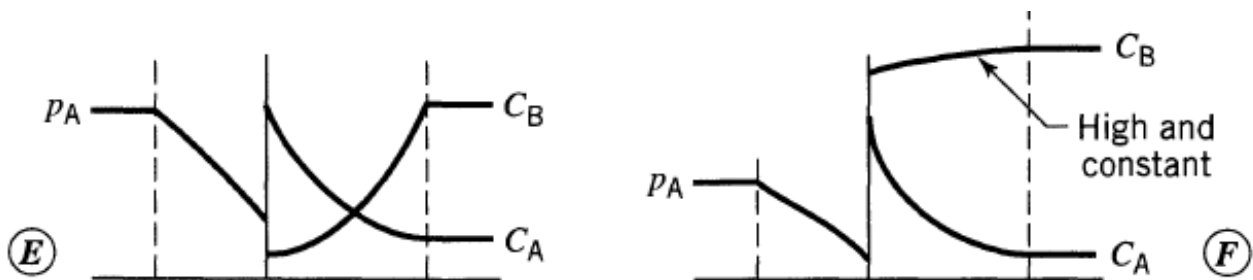
$$N_A \equiv (-r_A) = \frac{p_A + \frac{D_{B\ell} H_A}{D_{A\ell} b} c_B}{\frac{1}{k_{Ag}} + \frac{H_A}{k_{A\ell}}}$$

➤ An expression for  $E$  can be obtained from these two equations

$$E_i = \frac{1 + \frac{D_{B\ell} H_A c_B}{D_{A\ell} b p_A}}{1 - \frac{k_{B\ell} c_B}{k_{Ag} b p_A}}$$



# Reaction in Liquid Film and Bulk Liquid



**Intermediate rate with reaction in the film and in the main body of the liquid**

- The reaction occurs in the bulk liquid (in which there is no flux) as well as in the liquid film.
- The flux of A into the liquid film at the gas-liquid interface,  $N_A(z=0)$ , is not the same as the flux of A from the liquid film to the bulk liquid,  $N_A(z=1)$ , where  $z$  is the relative distance into the film from the interface;
- The two fluxes differ because of the loss of A by reaction in the liquid film.



# Reaction in Liquid Film and Bulk Liquid

- At steady state, the difference between the diffusion fluxes into and out of the differential element  $dx$  for a unit interfacial area is equal to the amount consumed in the element

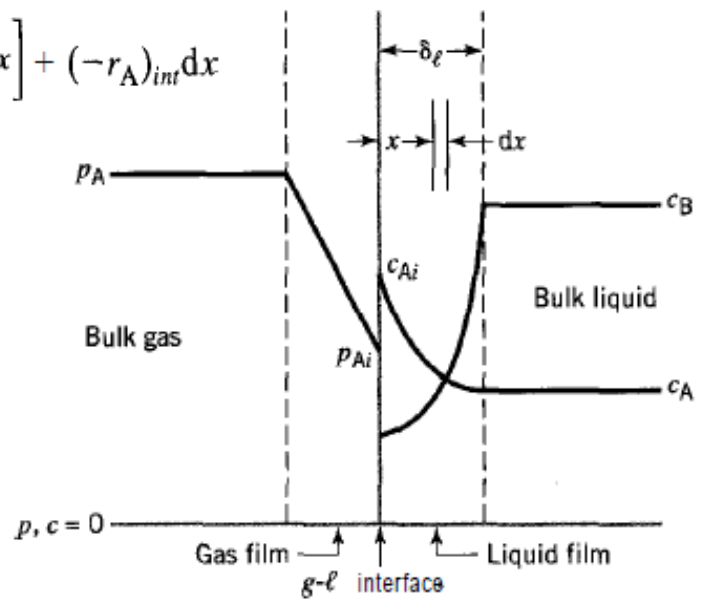
$$-D_{A\ell} \frac{dc_A}{dx} = -D_{A\ell} \left[ \frac{dc_A}{dx} + \frac{d}{dx} \left( \frac{dc_A}{dx} \right) dx \right] + (-r_A)_{int} dx$$

$$\rightarrow D_{A\ell} \frac{d^2 c_A}{dx^2} - (-r_A)_{int} = 0$$

For B, similarly,

$$D_{B\ell} \frac{d^2 c_B}{dx^2} - (-r_B)_{int} = 0$$

But  $(-r_B)_{int} = b(-r_A)_{int}$



# Reaction in Liquid Film and Bulk Liquid

- The boundary conditions for the two simultaneous second-order ordinary differential equations

$$\text{at } x = 0, \quad c_A = c_{Ai}$$

$$\frac{dc_B}{dx} = 0 \quad (\text{consistent with no transport of B through the interface, since B is nonvolatile})$$

On the liquid side of the film where  $x = \delta$ ,

$$\text{at } x = \delta_\ell, \quad c_A = c_A(\text{in bulk liquid}) \equiv c_{Ab}$$

$$c_B = c_B(\text{in bulk liquid}) \equiv c_{Bb}$$

**Numerical solution may be required**

- For irreversible 1<sup>st</sup> order reaction in A or pseudo first order reaction

$$(-r_A)_{int} = k_A c_A \quad \text{or} \quad (-r_A)_{int} = k_A''' c_A \quad \text{where } k_A''' = k_A c_B,$$

$$\rightarrow D_{A\ell} \frac{d^2 c_A}{dx^2} - k_A c_A = 0$$



## Reaction in Liquid Film and Bulk Liquid

$$\rightarrow c_A/c_{Ai} = \frac{c_{Ab}/c_{Ai} \sinh(Ha z) + \sinh[Ha(1 - z)]}{\sinh(Ha)}$$

Where  $z = x/\delta_\ell$

$$Ha = \delta_\ell(k_A/D_{A\ell})^{1/2} = (D_{A\ell}k_A)^{1/2}/k_{A\ell} \quad (n = 1)$$

And the Hatta number, Ha, is a dimensionless group

$$Ha \equiv \delta_\ell * \sqrt{\frac{k}{D_{1,l}}} = \frac{\delta_\ell}{D_{1,l}} * \sqrt{k * D_{1,l}} = \frac{1}{k_{1,l}} * \underbrace{\sqrt{k * D_{1,l}}}_{\text{can be estimated}}$$

$$Ha^2 = \left( \begin{array}{l} \text{maximum possible conversion in the} \\ \text{film compared with maximum transport} \\ \text{through the film} \end{array} \right)$$



## Reaction in Liquid Film and Bulk Liquid

the steady-state rate of transfer or flux of A into the liquid film,  $N_A(x = 0)$ ,

$$\begin{aligned} N_A(x = 0) &= -D_{A\ell} \left( \frac{dc_A}{dx} \right)_{x=0} \\ &= \frac{Ha}{\tanh(Ha)} \left[ 1 - \frac{c_{Ab}}{c_{A\ell} \cosh(Ha)} \right] k_{A\ell} c_{Ai} \end{aligned}$$

Since  $N_A \equiv N_A(x = 0) = k_{Ag}(p_A - p_{Ai})$   
 $c_{Ai} = p_{Ai}/H_A$

$$N_A(x = 0) = \frac{p_A - \frac{H_A c_{Ab}}{\cosh(Ha)}}{\frac{1}{k_{Ag}} + \frac{H_A \tanh(Ha)}{k_{A\ell} H_A}}$$



# Reaction in Liquid Film and Bulk Liquid

- The flux or rate of transfer of A from the liquid film to the bulk liquid, we evaluate the rate of diffusion at  $x = \delta_\ell$ .

$$N_A(x = \delta_\ell) = \frac{k_{A\ell}Ha}{\tanh(Ha)} \left[ \frac{c_{Ai}}{\cosh(Ha)} - c_{Ab} \right]$$

eliminate  $c_{Ai}$  and take gas-film resistance into account,

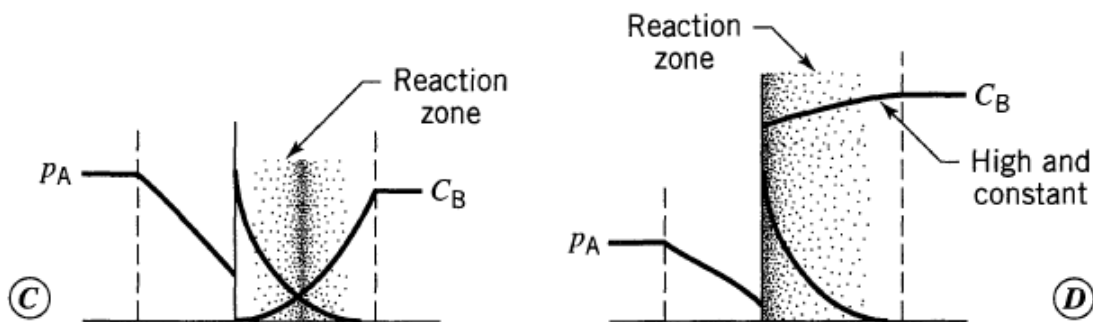
$$N_A(x = \delta_\ell) = \frac{k_{A\ell}Ha}{\tanh(Ha)} \left\{ \frac{\frac{k_{Ag} \tanh(Ha)}{k_{A\ell}Ha} p_A + \frac{c_{Ab}}{\cosh(Ha)}}{\cosh(Ha) \left[ 1 + \frac{k_{Ag} H_A \tanh(Ha)}{k_{A\ell}Ha} \right]} - c_{Ab} \right\}$$



# Reaction in Liquid Film and Bulk Liquid

## Fast first-order or pseudo- first order reaction in liquid film

- $C_A$  drops to zero in the liquid film, and reaction takes place only in the liquid film, since A does not reach the bulk liquid



$$\text{at } x = \delta_\ell, \quad c_{Ab} = 0;$$

$$c_A/c_{Ai} = \frac{\sinh[Ha(1-z)]}{\sinh(Ha)}$$

Where  $z = x/\delta_\ell$



## Fast first-order or pseudo- first order reaction in liquid film

$$N_A(x = 0) \equiv (-r_A) = \frac{Ha}{\tanh(Ha)} k_{A\ell} c_{Ai}$$

elimination of  $c_{Ai}$

$$(-r_A) = \frac{p_A}{\frac{1}{k_{Ag}} + \frac{H_A \tanh(Ha)}{k_{A\ell} Ha}}$$

➤ This is equivalent to

$$(-r_A) = \frac{p_A}{\frac{1}{k_{Ag}} + \frac{H_A}{k_{A\ell} E}}$$

➤ And in this case

$$E = Ha / \tanh(Ha)$$

Fast first-order or pseudo- first order reaction in liquid film



## Hatta Number

➤ The Hatta number  $Ha$ , as a dimensionless group, is a measure of the maximum rate of reaction in the liquid film to the maximum rate of transport of  $A$  through the liquid film, and as such is analogous to the Thiele modulus in catalytic reactions

$$Ha^2 = \frac{\text{maximum rate of reaction or flux in liquid film}}{\text{maximum rate of transport through liquid film}}$$

$$= \frac{v_f k_A c_{Ai}}{a_i k_{A\ell} c_{Ai}}$$

$a_i$  is the interfacial area, for example, in  $m^2 m^{-3}$  (liquid),

$v_f$  is the volume of the liquid film.

if  $Ha$  (strictly,  $Ha^2$ )  $\gg 1$ , reaction occurs in the liquid film only,

$Ha^2 \ll 1$ , reaction occurs in bulk liquid.



# Hatta Number

## Fast second-order reaction in Liquid film only

$$(-r_A)_{int} = k_A c_A c_B$$

An approximate solution  $E = \psi / \tanh \psi$

where 
$$\psi = \text{Ha} \left( \frac{E_i - E}{E_i - 1} \right)^{1/2}$$

$E_i$  is the enhancement factor for an instantaneous reaction

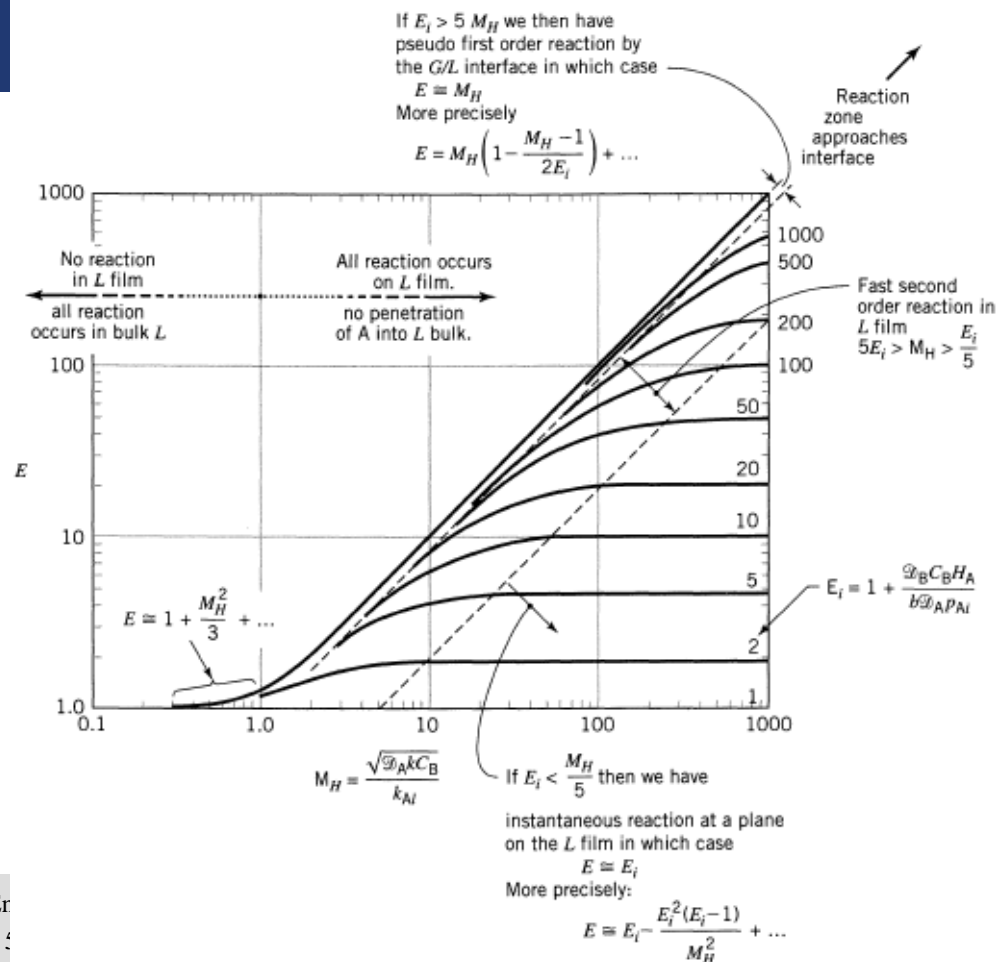
$$E_i = 1 + \frac{D_B \ell c_B}{D_A \ell b c_{A_i}} \quad \text{Instantaneous reaction}$$

OR 
$$E_i = 1 + \frac{D_B l H_A c_B}{D_A l b p_A}$$

And 
$$\text{Ha} = (k_A D_A \ell c_B)^{1/2} / k_{A\ell} \quad (n = 2)$$



# Hatta Number





## Hatta Number

For Fluid/Fluid - system there are three different patterns, that can be characterised through their size of the  $Ha$  - number.

1. **slow reactions**,  $Ha < 0,3$   
mass transfer rate will not be increased through chemical reaction,  
i.e.  $E \approx 1$
2. **intermediate reaction rates**  $0,3 < Ha < 3$   
 $E > 1 \rightarrow$  chemical reaction leads to increase in the rate of mass transfer
3. **fast reaction**,  $Ha > 3$

$$E = Ha$$

- $\rightarrow$  reaction takes place only in the **boundary layer**.

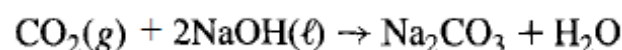
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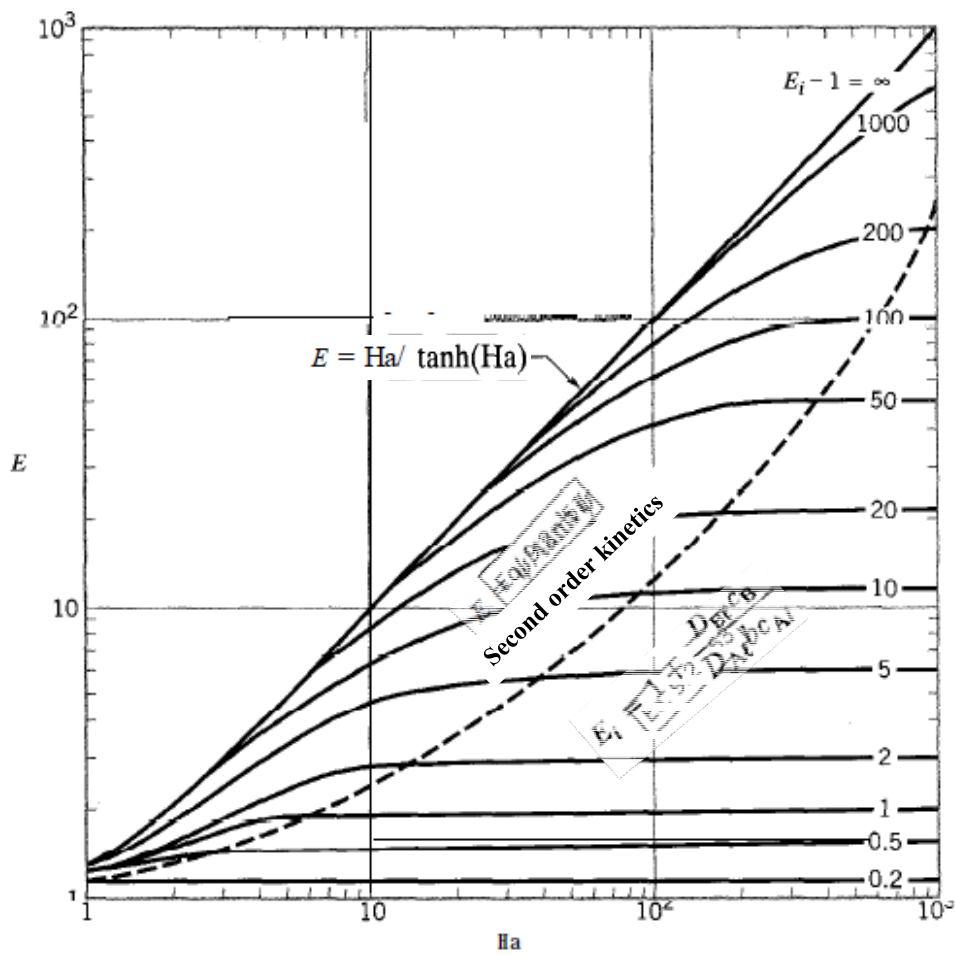


## Example

Suppose pure  $\text{CO}_2$  (A) at 1 bar is absorbed into an aqueous solution of  $\text{NaOH}$  (B) at  $20^\circ\text{C}$ . Based on the data given below and the two-film model, how should the rate of absorption be characterized (instantaneous, fast pseudo-first-order, fast second-order), if  $c_B =$  (a) 0.1 and (b) 6  $\text{mol L}^{-1}$ ?

Data (Danckwerts, 1970, p. 118, in part):  $k_A = 10,000 \text{ L mol}^{-1} \text{ s}^{-1}$ ;  $D_{A\ell} = 1.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ;  $k_{A\ell} = 0.04 \text{ cm s}^{-1}$ ;  $D_{B\ell} = 3.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ;  $H_A = 36 \text{ bar L mol}^{-1}$ .





## Example

- (a) Determine the rate of reaction for a particular gas-liquid reaction  $A(g) + 2B(l) \rightarrow$  products, which is pseudo-first-order with respect to A. The following data are available:

$$\begin{aligned}
 H_A &= 300 \text{ MPa L mol}^{-1} & k_A &= 450 \text{ m}^4 \text{ mol}^{-1} \text{ min}^{-1} \\
 D_{A\ell} &= 4.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} & k_{A\ell} &= 0.08 \text{ m s}^{-1} \\
 D_{B\ell} &= 1.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} & k_{Ag} &= 0.68 \text{ mol kPa}^{-1} \text{ m}^{-2} \text{ s}^{-1}
 \end{aligned}$$

The partial pressure of A is 250 kPa, and the concentration of B is 0.25 mol L<sup>-1</sup>.

- (b) If an enhancement factor can be used for this system, determine its value.  
 (c) If a Hatta number is appropriate for this system, determine its value.

