

# **Fluid-fluid Reaction: Kinetics and Reactor Design**

Book: *Chemical Reaction Engineering*, O. Levenspiel, (Chapter 23 and 24), 3<sup>rd</sup> Edition, Wiley and Sons

Heterogeneous fluid-fluid reactions take place for three main reasons:

(1) Product of reaction is the desired material

There are a whole lot of liquid-liquid and gas-liquid reactions

- Nitration of organics with  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  to form nitro-glycerine (liquid-liquid)
- Chlorination of benzene to form chlorobenzenes (gas-liquid)
- Reaction of ammonia and sodium to form sodium amide (gas-liquid)
- Air oxidation of aldehyde to acids (gas-liquid)
- Oxidation of cyclohexane to adipic acid (gas-liquid)

(2) Removal of unwanted components (gas purification processes)

Absorption of a solute gas by water may be accelerated by adding a suitable material to water which will react with the solute being absorbed

- $\text{CO}_2$  removal from synthesis gas by aqueous solution of hot potassium carbonate, ethanol amines
- Removal of  $\text{H}_2\text{S}$  by ethanol amines or  $\text{NaOH}$

(1) Vastly improved product distribution for homogeneous multiple reactions than is possible by using single phase alone

- $A \rightarrow R_{desired} \rightarrow S \quad \Rightarrow$  a solvent can be used to selectively remove  $R$  from the medium

Certain features of such fluid-fluid reactions are:

(1) Materials in the **two separate phases must contact each other before reaction can occur**

Therefore, both the *mass transfer* and *chemical rates* enter the overall rate expression

(2) The **solubility of the reacting components will limit their movement from phase to phase**

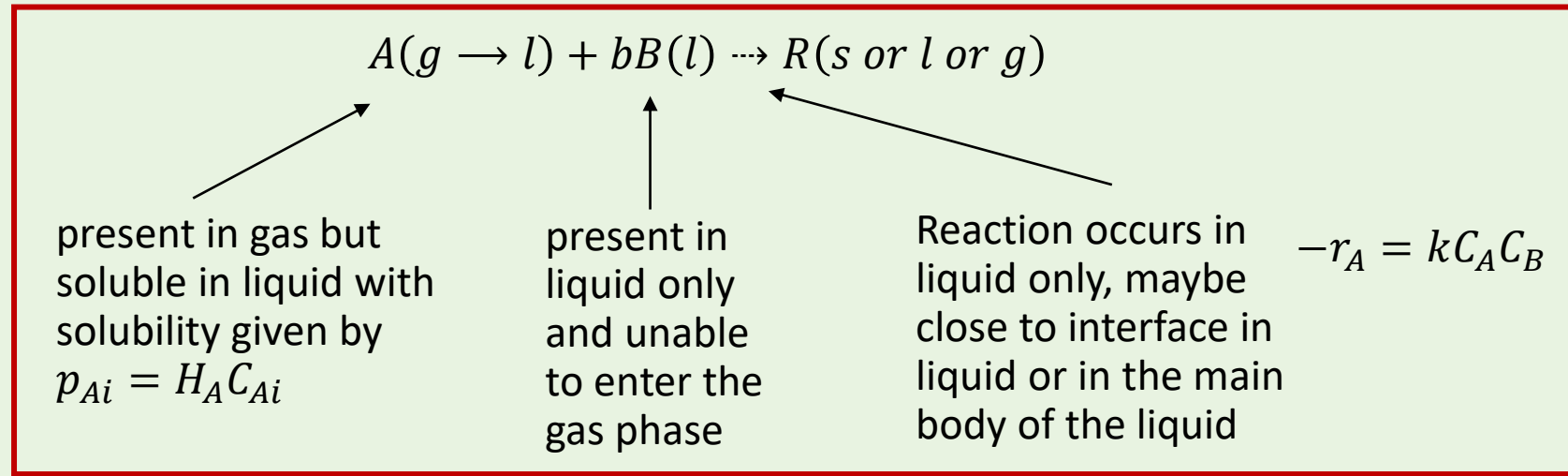
This factor influences the form of the rate equations as it determines whether the reaction takes place in one or both phases

(3) The **contacting patterns for gas-liquid systems** are dominated by (1) semi-batch and (2) counter-current contacting schemes

In liquid-liquid systems, mixed flow and batch contacting are used along with counter and co-current contacting

# The Rate Equation

- Here we shall talk of Gas -Liquid systems, but all the discussions are applicable for Liquid-Liquid systems too
- A *second-order reaction* is considered for studying the gas-liquid reaction



Assumption:

- Gaseous  $A$  is soluble in liquid  $B$  but  $B$  is not volatile and will never enter the gas
- $A$  must enter and move into the liquid phase before it can react and reaction occurs in this phase alone
- Overall rate expression for the reaction will account for mass transfer resistance and the resistance of the chemical reaction step

- If  $V_r$  = volume of contactor with gas, liquid and solid,  $V_l$  = volume of liquid and  $S$  = gas-liquid interfacial area

Liquid holdup:  $f_l = \frac{V_l}{V_r}$  ;

Gas holdup:  $f_g = \frac{V_g}{V_r}$

Interfacial area per unit volume of tower,  $a_l = \frac{S}{V_l}$  and  $a = \frac{S}{V_r}$

Rate of reaction  $-r_A''' = -\frac{1}{V_r} \frac{dN_A}{dt}$   $-r_{Al} = -\frac{1}{V_l} \frac{dN_A}{dt}$   $-r_A'' = -\frac{1}{S} \frac{dN_A}{dt}$

$\therefore r_A''' \cdot V_r = r_{Al} \cdot V_l = r_A'' \cdot S$

$\therefore r_A''' = r_{Al} \cdot f_l = r_A'' \cdot a$

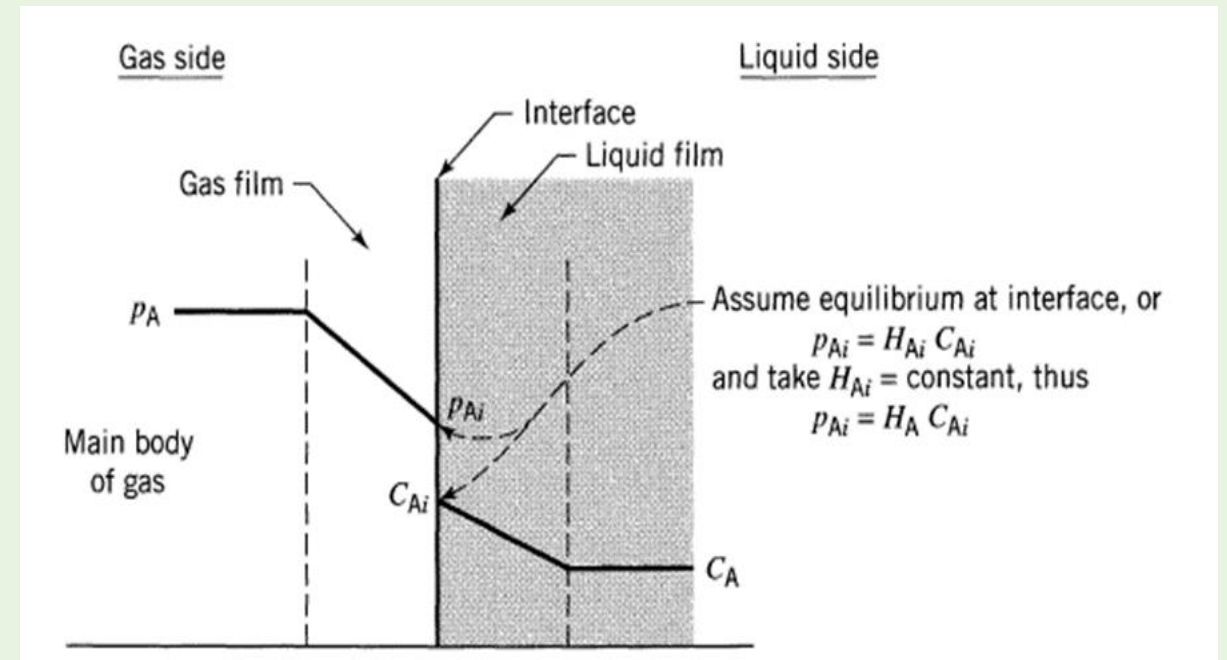
- Since reactant  $A$  moves from gas to liquid for the reaction to occur, diffusional resistances enter the rate
- The system is analysed in terms of the **two-film theory**
- Other theories such as *surface renewal theory* or *penetration theory* may also be used. They give essentially the same results but uses more complicated mathematics (though these represent more real situations)

# Two Film Theory

- This theory assumes that all the resistances to mass transfer is located in the thin film surrounding the interface
- Here there are two films – gas film and liquid film around the interface and these two resistances are in series
- On both sides of the film (in the bulk) there is an uniformity of concentration
- At the interface, the partial pressure of gas is  $p_{Ai}$  and there exists an equilibrium between the gas and the liquid concentration

$$p_{Ai} = H_A C_{Ai}$$

- Film theory assumes that the profiles are established instantaneously
- Interface has no capacity to store mass so steady state is instantaneously reached – this is a steady state model



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# Rate equation for Straight Mass Transfer (Absorption) of A

Rate of transfer of A from gas to liquid is given by,

For gas film

$$-r_A'' = k_{Ag}(p_A - p_{Ai})$$

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

$k_{Ag}$  is in mol/m<sup>2</sup>.Pa.s

$k_{Ag}a$  is in mol/m<sup>3</sup> contactor. Pa.s

For liquid film

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

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

$k_{AL}$  is in m<sup>3</sup> liquid /m<sup>2</sup> surface.s

$k_{AL}a$  is in m<sup>3</sup> liquid /m<sup>3</sup> contactor.s

The equations for gas and liquid films are combined and the unknown  $p_{Ai}$  and  $C_{Ai}$  terms are eliminated,

$$k_{Ag}a(p_A - p_{Ai}) = k_{AL}a(C_{Ai} - C_A)$$

Replacing the value of  $p_{Ai}$  using  $p_{Ai} = H_A C_{Ai}$  we get,  $k_{Ag}a(p_A - H_A C_{Ai}) = k_{AL}a(C_{Ai} - C_A)$

$$k_{Ag}p_A - k_{Ag}H_A C_{Ai} = k_{AL}C_{Ai} - k_{AL}C_A$$

$$k_{Ag}p_A + k_{AL}C_A = k_{AL}C_{Ai} + k_{Ag}H_A C_{Ai} = C_{Ai}(k_{AL} + k_{Ag}H_A) \Rightarrow C_{Ai} = \frac{k_{Ag}p_A + k_{AL}C_A}{k_{AL} + k_{Ag}H_A}$$

Now putting the value of  $C_{Ai}$  in the equation,  $-r_A''' = k_{Ag}a(p_A - p_{Ai}) = k_{Ag}a(p_A - H_A C_{Ai})$

$$-r_A''' = k_{Ag}a \left( p_A - H_A \frac{k_{Ag}p_A + k_{AL}C_A}{k_{AL} + k_{Ag}H_A} \right) = k_{Ag}a \left( \frac{p_A k_{AL} + p_A k_{Ag}H_A - H_A k_{Ag}p_A - H_A k_{AL}C_A}{k_{AL} + k_{Ag}H_A} \right) = k_{Ag}a \left( \frac{p_A k_{AL} - H_A k_{AL}C_A}{k_{AL} + k_{Ag}H_A} \right)$$

$$-r_A''' = k_{AL}k_{Ag}a \left( \frac{p_A - H_A C_A}{k_{AL} + k_{Ag}H_A} \right) \Rightarrow -r_A''' = \frac{p_A - H_A C_A}{\frac{1}{k_{Ag}a} + \frac{H_A}{k_{AL}a}}$$

# Rate equation for Mass Transfer and Reaction

- In general if we consider a situation where reaction occurs in a 'slow pace', such that all the reaction is in the bulk liquid
- In the film, there is only diffusion as the rate of reaction is very slow – mass is transferred through film and then reacts in the bulk

• Gas side

$$k_{Ag}a(p_A - p_{Ai}) = k_{AL}a(C_{Ai} - C_A)$$

• Liquid side (Bulk liquid)

$$k_{AL}a(C_{Ai} - C_A) = kC_A C_B f_L$$

• Also,  $p_{Ai} = H_A C_{Ai}$

The equations for gas and liquid side are combined and the unknown  $p_{Ai}$  and  $C_{Ai}$  terms are eliminated

Now,

$$k_{Ag}a(p_A - p_{Ai}) = k_{AL}a(C_{Ai} - C_A)$$

$$k_{Ag}a(p_A - H_A C_{Ai}) = k_{AL}a(C_{Ai} - C_A)$$

$$k_{Ag}p_A - k_{Ag}H_A C_{Ai} = k_{AL}C_{Ai} - k_{AL}C_A$$

$$k_{Ag}p_A + k_{AL}C_A = k_{AL}C_{Ai} + k_{Ag}H_A C_{Ai} = C_{Ai}(k_{AL} + k_{Ag}H_A)$$

$$C_{Ai} = \frac{k_{Ag}p_A + k_{AL}C_A}{k_{AL} + k_{Ag}H_A}$$



Now putting the value of  $C_{Ai}$  in the equation for the liquid side,

$$-r_A''' = k_{AL}a(C_{Ai} - C_A) = kC_A C_B f_L$$

$$k_{AL}a \left( \frac{k_{Ag}p_A + k_{AL}C_A}{k_{AL} + k_{Ag}H_A} - C_A \right) = kC_A C_B f_L$$

$$k_{AL}a \left( \frac{k_{Ag}p_A + k_{AL}C_A - C_A k_{AL} - C_A k_{Ag}H_A}{k_{AL} + k_{Ag}H_A} \right) = kC_A C_B f_L$$

$$k_{AL}ak_{Ag}p_A - k_{AL}aC_A k_{Ag}H_A = kC_A C_B f_L k_{AL} + kC_A C_B f_L k_{Ag}H_A$$

$$C_A = \frac{k_{AL}ak_{Ag}p_A}{kC_B f_L k_{AL} + kC_B f_L k_{Ag}H_A + k_{AL}ak_{Ag}H_A}$$

Now, putting the value of in the rate expression,  $-r_A''' = kC_A C_B f_L$

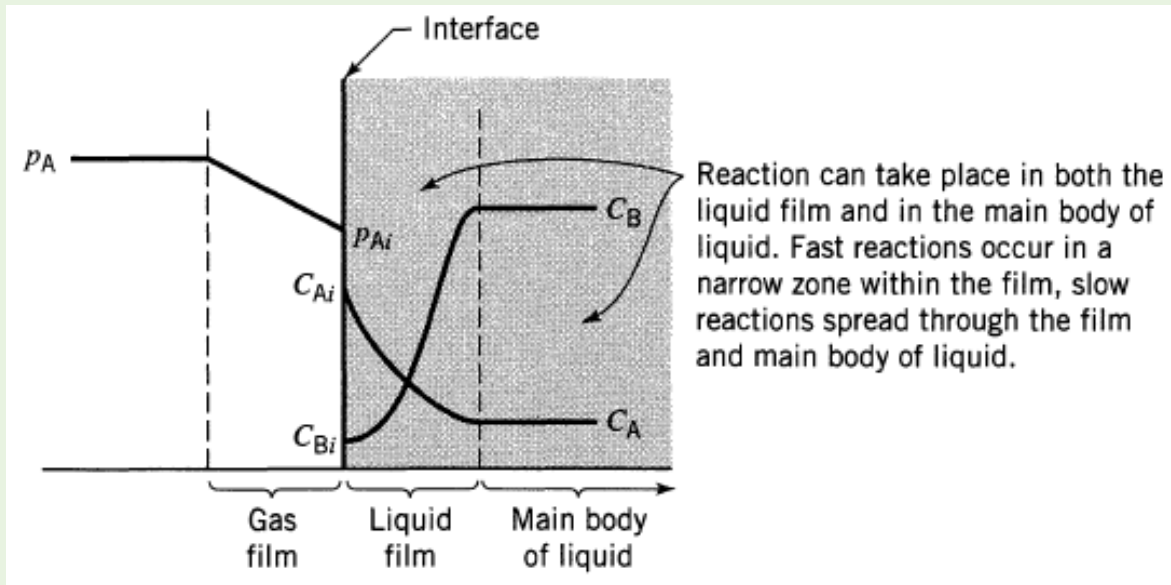
$$-r_A''' = \frac{kC_B f_L k_{AL}ak_{Ag}p_A}{kC_B f_L k_{AL} + kC_B f_L k_{Ag}H_A + k_{AL}ak_{Ag}H_A}$$

$$-r_A''' = \frac{p_A}{\frac{1}{ak_{Ag}} + \frac{H_A}{k_{AL}a} + \frac{H_A}{kC_B f_L}}$$

$k_{Ag}$  is in  $\text{m}^3 \text{ liq} / \text{mol.h}$   
 $C_A, C_B$  is in  $\text{mol} / \text{m}^3 \text{ liq}$   
 $f_L$  is in  $\text{m}^3 \text{ liq} / \text{m}^3 \text{ contactor}$

- Now, if the real value of mass transfer coefficient ( $k_L, k_g$ ) and diffusivity ( $D$ ) of different materials found in various industrial reactions and reaction rate constant for such reactions are compared, it is found that there is not much variation in the values of  $k_g, k_L$  and  $D$
- Mass transfer coefficients range from 0.5 to 1.5 m<sup>3</sup>/m<sup>2</sup>.h and diffusivities are in the order of 10<sup>-5</sup> m<sup>3</sup>/m.h
- On the other hand, reaction rate constants vary between 10<sup>-4</sup> to 10<sup>5</sup> in the temperature range of 20-100°C for different components
- Thus, it is seen that the ***behaviour of the different gas-liquid systems vary according to the speed of the reaction – instantaneous, moderate and slow***
- Reactions can occur in both the liquid film and in the main body of the liquid
- Fast reactions occur in the narrow zone within the film, slow reactions spread through the film and the main body of the fluid

In studying the different situations there are **eight** possible cases –



*Chemical Reaction Engineering, O. Levenspiel*

- Case A** – Instantaneous reaction with low  $C_B$
- Case B** – Instantaneous reaction with high  $C_B$
- Case C** – Fast reaction in liquid film with low  $C_B$
- Case D** – Fast reaction in liquid film with high  $C_B$
- Case E** – Intermediate reaction rate with reaction in film and bulk with low  $C_B$
- Case F** – Intermediate reaction rate with reaction in film and bulk with high  $C_B$
- Case G** – Slow reaction in main body with film resistance
- Case H** – Slow reaction, no mass transfer resistance