Module 2 :

"Diffusive" heat and mass transfer

Lecture 17:

Gas Absorption with Chemical Reaction

1. Gas Absorption with Rapid Chemical Reaction (Moving Boundary Problem)

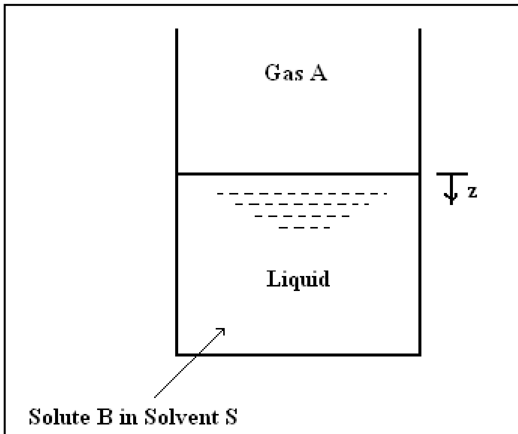

Fig.17.1. Gas absorption in solvent B

Consider the case of a Gas A in contact with a liquid in a container. The liquid contains solute B dissolved in solvent S. The system is illustrated in Fig. 17.1 and the coordinate system z has its origin at the gas-liquid interface. We make the following assumptions for this system:

1. Quiescent liquid (no convective currents)

2. Instantaneous reaction $A+B \rightarrow AB$

3. Dilute solution

Find concentration profiles of A and B in liquid

Beacuase reaction is instantaneous, concentration of and A and B is zero at the reaction plane. A and B cannot coexist. The applicable equation is

$$\frac{\partial c_i}{\partial t}+\left(\underline{U}\bullet\nabla c_i\right)=D\nabla^2 c_i+R_i \tag{17.1}$$

Here $\underline{U}=0$ and $R_A=0$

Therefore

$$\left.\begin{aligned} \frac{\partial c_A}{\partial t} &= D_{As}\frac{\partial^2 c_A}{\partial z^2} \qquad 0<z \le z'(t) \\ \frac{\partial c_B}{\partial t} &= D_{Bs}\frac{\partial^2 c_B}{\partial z^2} \qquad z'(t) \le z < \infty \end{aligned}\right\} \tag{17.2}$$

For eqn. (17.2), no source term in mass balance has been considered and the reaction takes place only at z=z' (t).

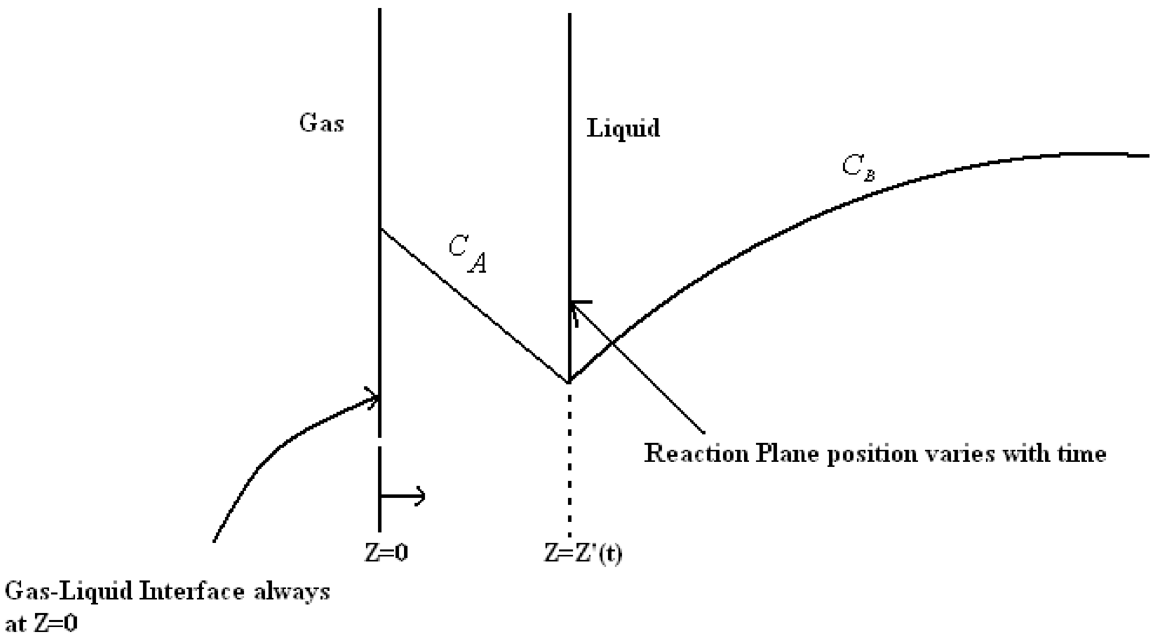

Fig.17.5. Concept of moving reaction plane with time

The initial and boundary conditions are as follows:

I.C.: At $t=0 \Rightarrow C_B = C_{B0}$

B.C.: At $z=0 \Rightarrow C_A = C_{A0}$ (saturation concentration)

$z = z'(t) \Rightarrow C_A = 0$

$z = z'(t) \Rightarrow C_B = 0$

$z = z'(t) \Rightarrow -D_{As}\frac{\partial C_A}{\partial t} = D_{Bs}\frac{\partial C_B}{\partial t}$

The last B.C. is the result of the 1:1 stoichiometry of the reaction. Applying the same method as described in semi-infinite slab and defining the dimensionless parameters as

$$\eta = \frac{z}{\sqrt{4D_{As}\ t}};\ C_A = \phi_1(\eta) \text{ and } C_B = \phi_2(\eta)$$

So after transforming, we get

$$\frac{\partial C_A}{\partial t} = -\frac{1}{2}\frac{\eta}{t}\phi_1' \text{ and}$$
$$\frac{\partial^2 C_A}{\partial z^2} = \frac{1}{4D_{As}t}\phi_1''$$

After substituting and rearranging, we get

$$\phi_1'' + 2\eta\phi_1' = 0 \tag{17.3}$$

Substituting ψ for ϕ' equation (17.12.) becomes

$$\frac{d\psi}{d\eta} + 2\eta\psi = 0 \tag{17.4}$$

Integrating and back substituting for ψ we get

$$\frac{C_A}{C_{A0}} = a_1 + a_2 \int_0^{\eta} e^{-\xi^2} d\xi$$
$$= a_1 + a_2 erf\left(\eta\right) \qquad (17.5)$$
$$= a_1 + a_2 erf\left(\frac{z}{\sqrt{4D_{As}t}}\right)$$

Similarly for component B

$$\frac{C_B}{C_{B0}} = b_1 + b_2 \int_0^{\eta} e^{-\xi^2} d\xi$$
$$= b_1 + b_2 erf\left(\frac{z}{\sqrt{4D_{Bs}t}}\right) \qquad (17.6)$$

The location of the reaction plane is found by setting C_A (or C_B) =0

Equation (17.5) yields $z' = \lambda\sqrt{4D_{As}t}$ where λ is a constant.

There are five constants to be determined: a_1, b_1, a_2, b_2, and λ. Use the five initial and boundary conditions given at the top to get

$$1 - erf\sqrt{\frac{a}{D_{Bs}}} = \frac{C_{B0}}{C_{A0}}\sqrt{\frac{D_{Bs}}{D_{As}}} erf\sqrt{\frac{a}{D_{As}}} \exp\left(\frac{a}{D_{As}} - \frac{a}{D_{Bs}}\right)$$

Thus, we get

$$a = \lambda^2 \sqrt{D_{As}}$$
$$a_1 = 1$$
$$a_2 = -\left(erf\sqrt{\frac{a}{D_{As}}}\right)^{-1} \qquad (17.7)$$
$$b_1 = 1 - \left(1 - erf\sqrt{\frac{a}{D_{Bs}}}\right)^{-1}$$
$$b_2 = \left(1 - erf\sqrt{\frac{a}{D_{Bs}}}\right)^{-1}$$

The net rate of mass transfer at the interface is

$$N_A\Big|_{z=0} = -D_{As}\frac{\partial C_A}{\partial z}\Big|_{z=0} \tag{17.8}$$

Substituting a_1 and a_2 in eqn. (17.5) and evaluating for C_A and integrating, we get

$$N_A\Big|_{z=0} = \frac{C_{A0}}{erf\sqrt{a/D_{As}}}\sqrt{\frac{D_{As}}{\pi t}} \tag{17.9}$$

$$N_A\Big|_{z=0} \sim t^{-1/2}$$

The average rate up to time *t* is

$$N_{A,avg} = \frac{1}{t}\int_0^t N_A dt$$

$$=2\frac{C_{A0}}{erf\sqrt{a/D_{As}}}\sqrt{\frac{DAs}{\pi t}}$$

$$=2\,\mathrm{N_A}\Big|_{z=0}$$

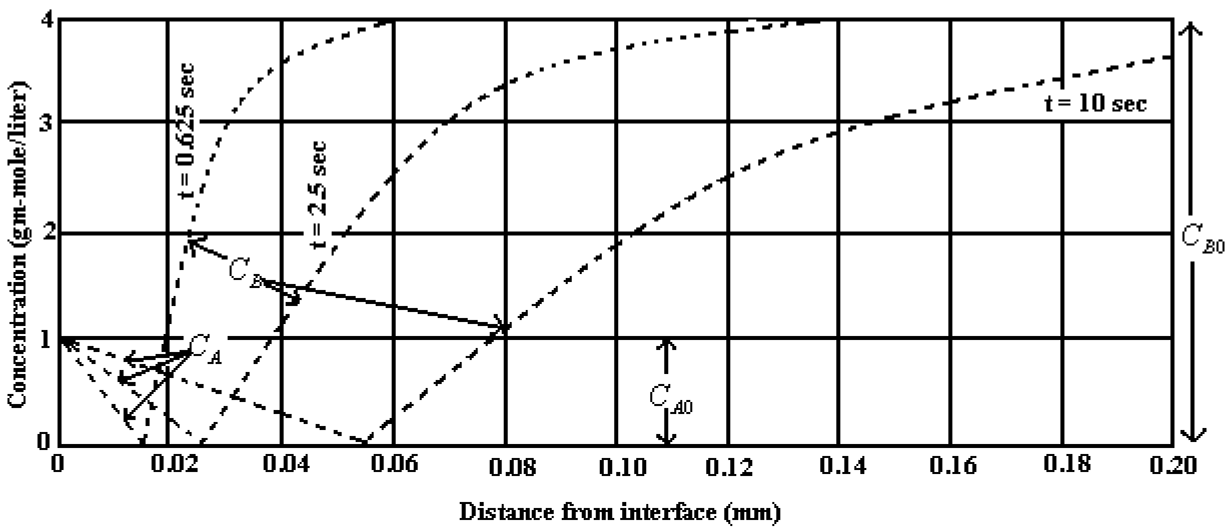

Fig.17.6. Gas absorption with rapid chemical reaction. Concentration profiles according to eqns. (17.5) and (17.6).

2. Absorption with Chemical Reactions in a Semi-Infinite Medium: Reaction of finite speed

Here same situation is assumed as considered in the case of gas absorption with rapid chemical reaction with moving boundary. Here we are assuming that the reaction is not instantaneous and reaction happens throughout the domain of interest.

So the governing equation is

$$\frac{\partial C_A}{\partial t} = D_{As}\frac{\partial^2 C_A}{\partial x^2} - k_1'''C_A \tag{17.10}$$

Eqn. (17.10) containing rate of reaction assumes excess quantity of B or that solvent is B.

The initial and boundary conditions are

$$\begin{aligned}
&\text{I.C.} \quad t=0 \quad \Rightarrow \quad C_A=0\\
&\text{B.Cs.} \quad x=0 \quad \Rightarrow \quad C_A=C_{A0} \ \text{(at saturation)}\\
&\qquad\quad x\to\infty \quad \Rightarrow \quad C_A=0
\end{aligned}$$

Equation (17.10) can be solved using Laplace Transform and the solution is given as

$$\begin{aligned}\frac{C_A}{C_{A0}} &= \frac{1}{2}\exp\left(-x\sqrt{\frac{k_1'''}{D_{As}}}\right)erfc\left(\frac{x}{\sqrt{4D_{As}t}} - \sqrt{k_1'''t}\right)\\
&+\frac{1}{2}\exp\left(x\sqrt{\frac{k_1'''}{D_{As}}}\right)erfc\left(\frac{x}{\sqrt{4D_{As}t}} + \sqrt{k_1'''t}\right)\end{aligned} \tag{17.11}$$

The molar flux of A at x=0 is

$$NA\big|_{x=0} = C_{A0}\sqrt{D_{As}k_1'''}\left(erf\sqrt{k_1'''t} + \frac{\exp(-k_1'''t)}{\sqrt{\pi k_1'''t}}\right) \tag{17.12}$$

The total moles of A absorbed from time t=0 to t=t_0 is given by

$$\mu_A = C_{A0}\sqrt{D_{As}t_0}\left[\left(\sqrt{k_1'''t_0} + \frac{1}{2\sqrt{k_1'''t}}\right)erf\sqrt{k_1'''t_0} + \frac{1}{\sqrt{\pi}}\exp(-k_1'''t_0)\right] \tag{17.13}$$

For large values of k_1''' to (>5), μ_A becomes

$$\mu_A = C_{A0}\sqrt{D_{As}k_1'''}\left(t_0 + \frac{1}{2k_1'''}\right) \tag{17.14}$$

Considering the more general situation, let us take the example of following non-instantaneous reaction

$$A + zB \xrightarrow{k_2} yP$$

$$\frac{\partial C_A}{\partial t} = D_{As}\frac{\partial^2 C_A}{\partial x^2} - k_2 C_A C_B$$

with following I.C and B.Cs

$$\begin{cases} t=0 & \Rightarrow \ \mathrm{C_A=0} \ \ \forall \ \mathrm{x>0} \\ x=0 & \Rightarrow \ \mathrm{C_A=C_{A0}} \ \ \forall \ \mathrm{t} \\ x\to\infty & \Rightarrow \ \mathrm{C_B=C_{B0}} \ \ \forall \ \mathrm{x>0} \end{cases}$$

$$\frac{\partial C_B}{\partial t} = D_{Bs}\frac{\partial^2 C_B}{\partial x^2} - zk_2 C_A C_B$$

with following I.C and B.Cs

$$\begin{cases} t=0 & \Rightarrow \ \mathrm{C_B=C_{B0}} \ \ \forall \ \mathrm{x>0} \\ x=0 & \Rightarrow \dfrac{\partial C_B}{\partial x}=0 \ \ \forall \ \mathrm{t>0} \\ x\to\infty & \Rightarrow C_B = C_{B0} \ \ \forall \ \mathrm{t>0} \end{cases}$$

The equations can be solved by procedure described above.