UIT-RGPV (Autonomous) Bhopal
Department of Petrochemical Engineering

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Semester: VII
Subject code – PC 702 **Subject: Transport Phenomena**

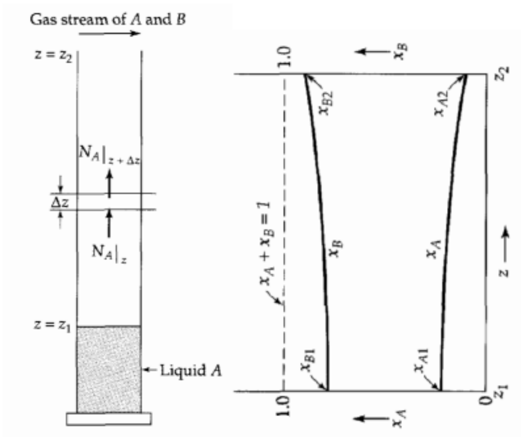
Unit: -V
Lecture no.27

Mass transfer

1. **Derive the expression which shows the rate of mass transfer is related to characteristic concentration deriving force for diffusion through a stagnant gas film.**

Diffusion Through a Stagnant Gas Film

Problem: Consider the schematic shown below. Note that B is immiscible with A, so while B can be present in the system at steady state, there is no net flux of B down or out, just across such that $N_{B.z} = 0$. For the full description of the problem, see Section 18.2 of BSL.



1. We write the mass balance in the z direction as

$$N_{A,z} = -c\mathscr{D}_{AB}\frac{dx_A}{dz} + x_A N_{A,z}$$

2. Solving for $N_{A,z}$ yields

$$N_{A,z} = \frac{-c\mathscr{D}_{AB}}{1 - x_A}\frac{dx_A}{dz}$$

3. A steady-state mass balance can be written as

$$SN_{A,z}|_z - SN_{A,z}|_{z+\Delta z} = 0$$

where S is a cross-sectional area

4. Dividing by $S\Delta z$ and letting $\Delta z \to 0$ yields

$$\frac{-dN_{Az}}{dz} = 0$$

5. This can therefore be written as

$$\frac{d}{dz}\left(\frac{c\mathscr{D}_{AB}}{1-x_A}\frac{dx_A}{dz}\right) = 0$$

   (a) For an ideal gas mixture, c is constant for a constant T and P. Also, for gases, $\mathscr{D}_{AB}$ is usually independent of the composition such that

$$\frac{d}{dz}\left(\frac{1}{1-x_A}\frac{dx_A}{dz}\right) = 0$$

   which can be integrated to yield[6]

$$-\ln(1-x_A) = C_1 z + C_2$$

6. Although this is not obvious, we can let $C_1 = -\ln K_1$ and $C_2 = -\ln K_2$ such that[7]

$$1 - x_A = K_1^z K_2$$

7. The boundary conditions are: $x_A(z_1) = x_{A1}$ and $x_A(z_2) = x_{A2}$

8. Applying the boundary conditions yields $1 - x_{A1} = K_1^{z_1}K_2$ and $1 - x_{A2} = K_1^{z_2}K_2$, which can be combined to yield

$$\frac{1-x_{A2}}{1-x_{A1}} = K_1^{z_2-z_1}$$

   (a) A little algebraic manipulation yields

$$K_1 = \left(\frac{1-x_{A2}}{1-x_{A1}}\right)^{1/(z_2-z_1)}$$

   (b) We need an expression for K_2, so

$$1 - x_{A1} = \left(\frac{1-x_{A2}}{1-x_{A1}}\right)^{z_1/(z_2-z_1)} K_2 \to K_2 = (1-x_{A1})\left(\frac{1-x_{A2}}{1-x_{A1}}\right)^{-z_1/(z_2-z_1)}$$

9. Plugging in the results for K_1 and K_2 yields

$$1 - x_A = \left(\frac{1-x_{A2}}{1-x_{A1}}\right)^{z/(z_2-z_1)}(1-x_{A1})\left(\frac{1-x_{A2}}{1-x_{A1}}\right)^{-z_1/(z_2-z_1)}$$

which can be rearranged to

$$\frac{1-x_A}{1-x_{A1}} = \left(\frac{1-x_{A2}}{1-x_{A1}}\right)^{(z-z_1)/(z_2-z_1)}$$

10. To obtain the profile for x_B, recognize that $x_A + x_B \equiv 1$

[6]Note that a useful integral for these types of problems is $\int \frac{1}{ax+b}\,dx = \frac{1}{a}\ln|ax+b|$

[7]Generally speaking, for an equation of the form $a\ln(1+bx_A) = C_1 z + C_2$, you want to make $C_1 = a\ln K_1$ and $C_2 = a\ln K_2$. From this, the final equation will be of the form $1 + bx_A = K_1^{\frac{z}{a}} K_2$.

11. Now, if the average concentration of B is desired,

$$\overline{x}_B = \frac{\int_{z_1}^{z_2} x_B\,dz}{\int_{z_1}^{z_2} dz}$$

so

$$\frac{\bar{x}_B}{x_{B1}} = \frac{\int_{z_1}^{z_2}\left(\frac{x_B}{x_{B1}}\right)\,dz}{\int_{z_1}^{z_2} dz}$$

12. Define the non-dimensional height variable $\xi = \frac{z - z_1}{z_2 - z_1}$, such that $dz = (z_2 - z_1)\,d\xi$ and

$$\frac{\overline{x}_B}{x_{B1}} = \frac{\int_0^1 \left(\frac{x_B}{x_{B1}}\right)^{\xi}\,d\xi}{\int_0^1 d\xi}$$

13. The integral table states that $\int a^x \, dx = \dfrac{a^x}{\ln x}$, so

$$\frac{\overline{x}_B}{x_{B1}} = \left. \frac{\left(\frac{x_{B2}}{x_{B1}}\right)^{\xi}}{\ln\left(\frac{x_{B2}}{x_{B1}}\right)} \right|_0^1$$

which yields

$$\overline{x}_B = \frac{x_{B2} - x_{B1}}{\ln\left(\frac{x_{B2}}{x_{B1}}\right)} \equiv (x_B)_{\ln}$$

14. The rate of evaporation is the rate of mass transfer at the liquid-gas interface and can be found by calculating $N_{A,z}$ at $z = z_1$. Therefore,

$$N_{A,z}|_{z_1} = -\frac{c\mathscr{D}_{AB}}{1 - x_{A1}} \left.\frac{dx_A}{dz}\right|_{z_1} = \frac{c\mathscr{D}_{AB}}{x_{B1}} \left.\frac{dx_B}{dz}\right|_{z_1}$$

(a) Implementing the dimensionless length,

$$\frac{c\mathscr{D}_{AB}}{x_{B1}} \left.\frac{dx_B}{d\xi}\right|_{\xi=0} \frac{d\xi}{dz} = \frac{c\mathscr{D}_{AB}}{z_2 - z_1} \left.\frac{d\left(x_B/x_{B1}\right)^{\xi}}{d\xi}\right|_{\xi=0}$$

15. The final expression is

$$N_{A,z}|_{z_1} = \frac{c\mathscr{D}_{AB}}{z_2 - z_1} \ln\left(\frac{x_{B2}}{x_{B1}}\right) = \frac{c\mathscr{D}_{AB}}{(z_2 - z_1)\,(x_B)_{\ln}} (x_{A1} - x_{A2})$$

(a) This expression can be used to find the diffusivity constant of an evaporating substance

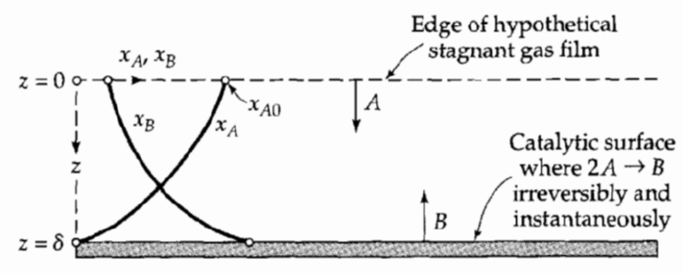
16. For diffusion with a moving interface, see Example 18.2-1 in BSL

2. Explain the diffusion with heterogeneous chemical reaction of dimerization.

1. Diffusion with a Heterogeneous Chemical Reaction (e.g. Gas Reacting on Solid Catalyst)

(a) Diffusion with an Instantaneous Heterogeneous Reaction

Problem: Consider the heterogeneous chemical reaction of $2A \rightarrow B$ shown in the diagram below. For the full problem statement,



1. From the stoichiometry, we know that

$$N_{B,z} = -\frac{1}{2} N_{A,z}$$

2. We also know that

$$N_{A,z} = -c\mathscr{D}_{AB} + x_A \left(N_{A,z} - \frac{1}{2} N_{A,z} \right)$$

which simplifies to

$$N_{A,z} = -\frac{c\mathscr{D}_{AB}}{1 - \frac{1}{2}x_A} \frac{dx_A}{dz}$$

3. The shell mass balance states that

$$SN_{A,z}|_z - SN_{A,z}|_{z+\Delta z} = 0$$

which leads to

$$\frac{dN_{A,z}}{dz} = 0$$

4. This yields

$$\frac{d}{dz} \left(\frac{c\mathscr{D}_{AB}}{1 - \frac{1}{2}x_A} \frac{dx_A}{dz} \right) = 0$$

5. Integrating this yields

$$-2 \ln \left(1 - \frac{1}{2} x_A \right) = C_1 z + C_2$$

for constant $c\mathscr{D}_{AB}$

6. Substituting $C_1 = -2 \ln K_1$ and $C_2 = -2 \ln K_2$ yields

$$1 - \frac{x_A}{2} = K_1^z K_2$$

7. The boundary conditions are $x_A(0) = x_{A0}$ and $x_A(\delta) = 0$

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[8] For a reaction $aA \to bB$, $N_{B,z} = -\frac{b}{a} N_{A,z}$

8. Applying the boundary conditions yields

$$1 - \frac{1}{2} x_A = \left(1 - \frac{1}{2} x_{A0} \right)^{1 - z/\delta}$$

9. To get the molar flux, we need $\frac{dx_A}{dz}$. Since we want the molar flux at the film, and the film is at $z = 0$, we technically want $\left.\frac{dx_A}{dz}\right|_{z=0}$. The final result yields[9] so'

$$N_{A,z} = \frac{2c\mathscr{D}_{AB}}{\delta} \ln \left(\frac{1}{1 - \frac{1}{2} x_{A0}} \right)$$

(b) Diffusion with a Slow Heterogeneous Reaction

Problem: Attempt the previous problem with a slow reaction (i.e. not instantaneous). Assume that the rate A disappears at the catalyst surface is given as $N_{A,z} = k_1'' c_A = k_1'' c x_A$, in which k_1'' is a rate constant for the pseudo-first-order surface reaction. For the full problem statement,

1. The set-up is identical up until the boundary conditions at which point $x_A(\delta) = \dfrac{N_{A,z}}{k_1'' c}$ instead of $x_A(\delta) = 0$

2. Applying the boundary conditions yields

$$\left(1 - \frac{1}{2}x_A\right) = \left(1 - \frac{1}{2}\frac{N_{A,z}}{k_1'' c}\right)^{z/\delta} \left(1 - \frac{1}{2}x_{A0}\right)^{1-z/\delta}$$

3. Evaluating $\left.\dfrac{dx_A}{dz}\right|_{z=0}$ and solving for $N_{A,z}$ yields,

$$N_{A,z} = \frac{2c\mathscr{D}_{AB}}{\delta} \ln \left(\frac{1 - \frac{1}{2}\left(\frac{N_{A,z}}{k_1'' c}\right)}{1 - \frac{1}{2}x_{A0}} \right)$$

4. If k_1'' is large (note that this means the reaction is fast, but not so fast that it is instantaneous) then

$$N_{A,z} = \frac{2c\mathscr{D}_{AB}/\delta}{1 + \frac{\mathscr{D}_{AB}}{k_1''\delta}} \ln \left(\frac{1}{1 - \frac{1}{2}x_{A0}} \right)$$

which can be obtained by a Taylor expansion on the logarithm term and keeping just the first term such that $\ln(1+p) \approx p$ for small p

5. The Damkohler Number of the second order can be defined as

$$\mathrm{Da}^{\mathrm{II}} = \frac{k_1''\delta}{\mathscr{D}_{AB}}$$

   (a) In the limit of $\mathrm{Da}^{\mathrm{II}} \to \infty$, we obtain the expression for the instantaneous reaction

   (b) In words, the Damkohler number is the ratio of the chemical reaction rate compared to the diffusion rate (i.e. mass transfer)

   (c) A very fast reaction is governed by mass transfer, but a very slow reaction is governed by kinetics

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[9]The following is a helpful identity: $\dfrac{d}{dx}\left(a^{bx}\right) = ba^{bx}\ln(a)$