Module 9: Mass Transfer

Lecture 39: Analysis of Mass Diffusion

The Lecture Contains:

- **Equimolar Counter Diffusion**
- **Evaporation of a Column**
- **Mass Diffusion with Homogeneous Chemical Reaction**

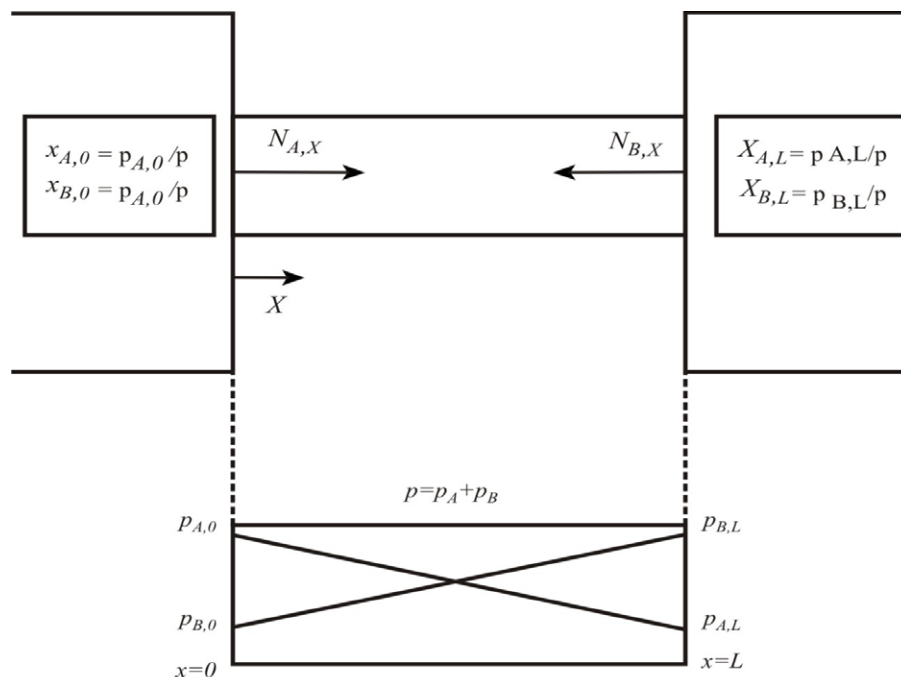◀▌▌ Previous   Next ▌▌▶

Equiimolar Counter Diffusion :

Figure 9.8

A channel connecting two large reservoirs contains an isothermal perfect gas mixture of species **A and B**. The species concentrations are maintained constant in each of the reservoirs, such that $x_{A,0} > x_{A,L}$ and $x_{B,0} < x_{B,L}$, while the total pressure $p = p_A + p_B$ is uniform throughout. The species concentration gradients cause diffusion of A molecules in the direction of increasing x and the diffusion of B molecules in the opposite direction. However, under steady state conditions, it is also necessary for the diffusion of the species to occur at equal and opposite rates.

◀‖ Previous   Next ‖▶

Total molar flux will be zero relative to the stationary coordinates. **This requirement is expressed as**

$$N''_{A,x} + N''_{B,x} = 0 \qquad \textbf{(9.49)}$$

and is necessiated by the fact that with **p and T are constant**, the total molar concentration **C** must also be constant throughout the system. This condition may only be maintained if the molar fluxes **A** to the right is balanced by the molar flux **B** to the left, in which case the process is referred to as equimolar counter diffusion. From $[N'' = N''_A + N''_B = CV^* = C_A V_A + C_B V_B]$. It is evident that the mixture molar average velocity V^*_x must be zero. The mixture is therfore stationary and from $[N''_A = -CD_{AB}\nabla x_A + x_A(N''_A + N''_B)]$ we get.

$$N''_{A,x} = -CD_{AB}\frac{dx_A}{dx} \qquad \textbf{(9.50)}$$

similarly,

$$N''_{B,x} = -CD_{AB}\frac{dx_B}{dx} \qquad \textbf{(9.51)}$$

We know $D_{AB} = D_{BA}$ from this and **(9.49)** it is also evident

$$\frac{dx_A}{dx} = -\frac{dx_B}{dx} \qquad \textbf{(9.52)}$$

◀❙❙❙ Previous   Next ❙❙❙▶

Since the mole fraction of either species may be expressed as a ratio of the species partial pressure to the total pressure, that is, $x_i = (p_i/p)$, we can write.

$$\frac{dp_A}{dx} = -\frac{dp_B}{dx}$$

(9.53)

Since we are dealing with one-dimensional, steady-state conditions involving no homogeneous chemical reactions, the species diffusion rate are independent of x. Assuming D_{AB} to be constant and recalling that **C** is independent of **x, equation (9.50)** may be expressed as.

$$N_{A,x} \int_0^L \frac{dx}{A} = -CD_{AB} \int_{x_{A,0}}^{x_{A,L}} dx_A$$

(9.54)

Assuming the channel **cross sectional area A**, to be constant, we then obtain for the species **A molar** diffusion rate

$$N_{A,x} = CD_{AB}\, A\frac{x_{A,0} - x_{A,L}}{L} = D_{AB}\, A\frac{C_{A,0} - C_{A,L}}{L}$$

(9.55)

Alternatively substituting from the equation of state

(9.56)

$$p_A = C_A\, \Re\, T$$

$$N_{A,x} = \frac{D_{AB}A}{\Re\, T}\, \frac{p_{A,0} - p_{A,L}}{L}$$

(9.57)

Similar results may be obtained for species B. Species mole fraction gradients and therefore the species pressure gradients are linear and of opposite sign.

◀⫿⫿ Previous   Next ⫿⫿▶
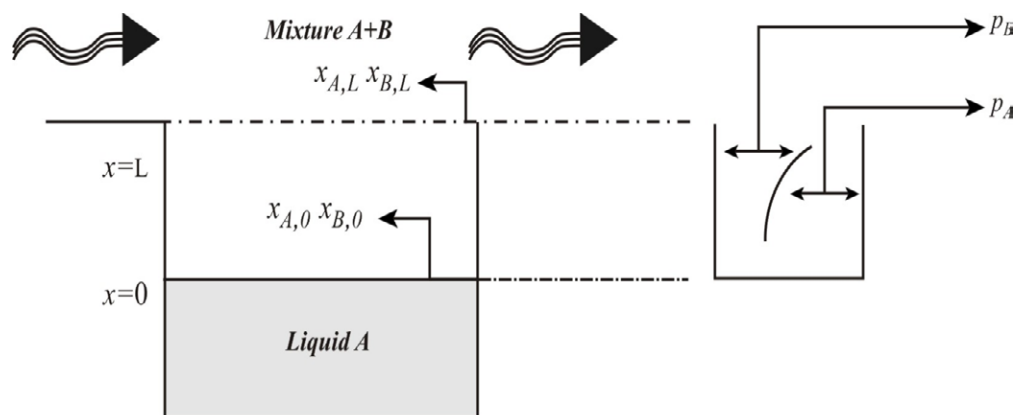
Evaporation of a Column:-

Figure 9.9: Evaporation of liquid A into a binary gas

Consider diffusion of a binary gas mixture. Fixed species concentrations $x_{A,L}$ and $x_{B,L}$ are maintanied at the top of a beaker containing a liquid layer of species A and the system is at constant pressure and temperature. Since equilibrium exists between the vapour and liquid phases at the interface, the vapour concentration is determined from the saturated vapour properties. Assuming the $x_{A,0} > x_{A,L}$, species A evaporates from the liquid interface and is transferred upwards by diffusion. Moreover, for steady state one dimensional conditions with no chemical reactions, the absolute molar flux of A must be constant throughout the column. Hence,.

$$\frac{dN''_{A,x}}{dx} = 0 \qquad\qquad \textbf{(9.58)}$$

◆ Since p and T are constant $\rightarrow C = C_A + C_B$

◆ In which case $x_A + x_B = 1$ throughout the column

◆ $x_{A,0} > x_{A,L} \rightarrow$ we conclude $\rightarrow x_{B,L} > x_{B,0}$.

◆ The species B must diffuse from the **top of the column to the liquid interface**

◀▌▌Previous   Next ▌▌▶

If B is insoluble in liquid A, steady state conditions can only be maintained if the downward diffusion of **B** is balanced by an upward bulk motion. This is equivalent to absolute flux of species $B = 0$ $\left(N''_{B,x} = 0\right)$. So we are not dealing with a stationary medium and hence $\left[N''_A = -CD_{AB}\nabla x_A\right]$ does not apply.

Now an appropriate expression for $N''_{A,x}$ may be obtained by substituting the requirement

$N''_{A,x} = 0$ $into$ $\left[N''_A = -CD_{AB}\nabla x_A + x_A(N''_A + N''_B)\right]$

$$N''_{A,x} = -CD_{AB}\frac{dx_A}{dx} + x_A N''_{A,x} \qquad (9.59)$$

From equation $\left[N'' = N''_A + N''_B = CV^* = C_A V_A + C_B V_B\right]$

$$N''_{A,x} = -CD_{AB}\frac{dx_A}{dx} + C_A V^*_x \qquad (9.60)$$

We can see that the diffusion transport is enhanced by the bulk motion

Rearranging (9.59) we get

$$N''_{A,x} = -\frac{CD_{AB}}{1 - x_A}\left[\frac{dx_A}{dx}\right] \qquad (9.61)$$

◀‖Previous   Next‖▶

For constant p and T, C and D_{AB} are constants. **Substituting (9.61) in (9.58)**

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

Integrating we have

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

Applying the conditions $x_A(0) = x_{A,0}$, $x_A(L) = x_{A,L}$ the concentration distribution becomes.

$$\frac{1-x_A}{1-x_{A,0}} = \left(\frac{1-x_{A,L}}{1-x_{A,0}}\right)^{x/L} \qquad \textbf{(9.62)}$$

Since $(1-x_A) = x_B$ we also obtain

$$\frac{x_B}{x_{B,0}} = \left(\frac{x_{B,L}}{x_{B,0}}\right)^{x/L} \qquad \textbf{(9.63)}$$

To determine the evaporation rate of species A, **equation (9.62)** is first used to evaluate the concentration gradient $\dfrac{\partial x_A}{\partial x}$ Substituting the result in **(9.61)** we get

$$N''_{A,x} = \frac{C D_{AB}}{L} \ln\left(\frac{1 - x_{A,L}}{1 - x_{A,0}}\right)$$

(9.64)

Mass Diffusion with Homogeneous Chemical Reaction

We start with the following arguments :

1) Heat diffusion is influenced by **internal heat sources.**

2) Mass diffusion is influenced by **homogeneous chemical reactions**

3) We restrict our attentions to stationary media, in which case the mass average velocity and the molar average velocities are not present.

The absolute mass flux and molar flux are **(with respect to species A)**

$$n_A'' = -\rho D_{AB} \nabla m_A \quad and \quad N_A'' = -C D_{AB} \nabla x_A$$

From the diffusion equation

$$\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} + \frac{\dot{N}_A}{D_{AB}} = \frac{1}{D_{AB}} \frac{\partial C_A}{\partial t}$$

◀▌▌ Previous   Next ▌▌▶

we get

$$D_{AB}\frac{\partial^2 C_A}{\partial x^2} + \dot{N}_A = 0 \qquad\qquad \textbf{(9.65)}$$

If there is no homogeneous chemical reactions involving species A, the volumetric species production rate $\mathbf{N_A}$ is zero. When reactions do occur, they are often of the form .

Zero order reaction : $\dot{N}_A = k_0$ (constant rate)
First order reaction : $\dot{N}_A = k_1 C_A$ (rate proportional to local concentration)

The units of k_0 and k_1 are $kmol/s.m^3$ and s^1 respectively . If $\mathbf{N_A}$ is positive , the reaction results in the generation of species A; if it is negative it results in the consumption of A. In many applications, the species of interest is being converted to another form through a first order chemical reaction and **equation (9.65) become**S**:**

$$D_{AB}\frac{d^2 C_A}{dx^2} - k_1 C_A = 0 \qquad\qquad \textbf{(9.66)}$$

This linear homogeneous differential equation has the general solution

$$C_A(x) = C_1 e^{mx} + C_2 e^{-mx} \qquad \textbf{(9.67)}$$

where $m = [k_1/D_{AB}]^{1/2}$ and the constants C_1 and C_2 depend on the prescribed boundary conditions.

Gas **A is soluble in liquid B**, where it is transferred by diffusion and experiences a first order chemcial reaction. The solution is dilute, and the concentration of A in the liquid at the interface is known as $C_{A,0}$ **If the bottom of the container is impermeable to A, the boundary conditions are:**
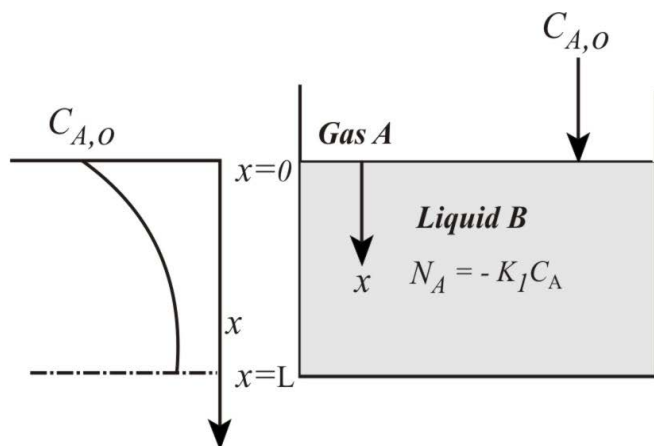

Figure 9.10: Diffusion and homogenous reaction of gas A in liquid B

◀‖Previous   Next‖▶

$$C_A(0) = C_{A,0} \quad and \quad \frac{dC_A}{dx}\Big|_{x=L} = 0$$

Using these boundary conditions in **equation (9.67),** it may be shown

$$C_A(x) = C_{A,0}(\cosh mx - \tanh mL \; \sinh mx) \qquad \textbf{(9.68)}$$

Quantities of special interest are:

(i) concentration of A at the bottom and
(ii) the flux of A across gas liquid interface

Applying (9.68) at $x = L$, we obtain

$$C_A(L) = C_{A,0}\frac{(\cosh^2 mL - \cosh^2 mL)}{\cosh mL} = \frac{C_{A,0}}{\cosh mL} \qquad \textbf{(9.69)}$$

Moreover,

$$N''_{A,x}(0) = -D_{AB}\frac{dC_A}{dx}\Big|_{x=0}$$
$$= -D_{AB}C_{A,0}m[\sinh mx - \tanh mL \cosh mx]\|_{x=0}$$

or

$$N''_{A,x}(0) = D_{AB}C_{A,0} \, m\tan h \, mL \qquad \textbf{(9.70)}$$

◀▮▮ Previous   Next ▮▮▶