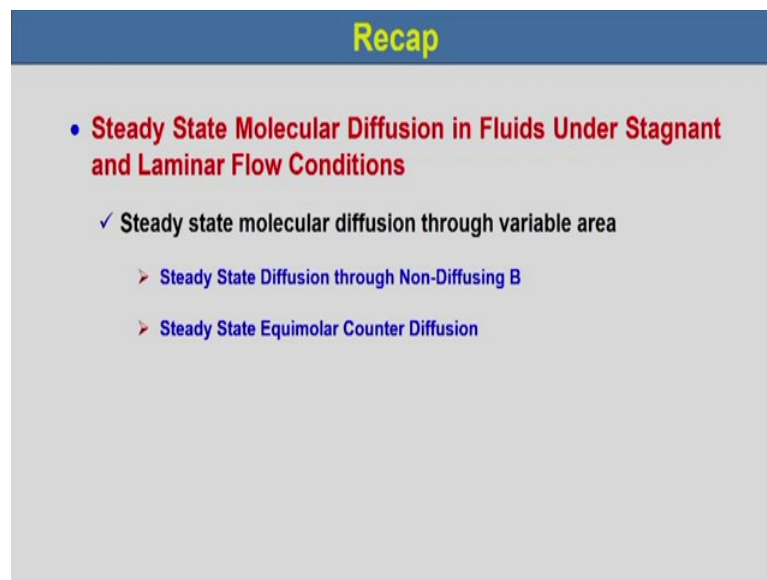**Mass Transfer Operations - I**
Prof. Bishnupada Mandal
Department of Chemical Engineering
Indian Institute of Technology, Guwahati

Diffusion Mass Transfer - II
Lecture – 06
Gas Phase Diffusion Coefficient Measurement

Welcome to the 6th lecture on Mass Transfer operation - I. In this module we are discussing Diffusion Mass Transfer. Before going to this lecture, let us have small recap on our previous lecture.

(Refer Slide Time: 00:43)

In our previous lecture we have started discussion on steady state molecular diffusion in fluid under stagnant and laminar flow conditions and we have considered steady state molecular diffusion through variable area.

Under the variable area we have considered two specific cases. One is steady state diffusion through non-diffusing B and the another case we have considered steady state equimolar counter diffusion.

(Refer Slide Time: 01:23)

Gas Phase Diffusion Coefficient Measurement

- The proportionality factor of Fick's law is called **diffusivity** or **diffusion coefficient (D_{AB})**. Diffusivity = (flux /concentration gradient) m²/s.

- Diffusivity is a function of the **temperature, pressure, nature** and **concentration** of other constituents.

- Diffusivity of gases decreases with increase in pressure $D_{AB} \propto 1/p$ for moderate ranges of pressures, up to 25 atm) because number of collisions between species is less at lower pressure.

- Diffusivity is hardly dependent on pressure in case of liquid.

In this lecture, we will discuss on the diffusion coefficient measurements. So, there are two different kind of diffusion coefficient. One is for the gas phase and another is for the liquid phase. So, we will discuss over here the gas phase diffusion coefficient measurements. The proportionality factor of Fick's law is called diffusivity or diffusion coefficient which we have discussed before while discussing the Fick's first law.

Then we can write diffusivity is equal to flux by concentration gradient. So, if we just incorporate the unit of flux and the concentration gradient, we will get unit of diffusivity which is metre square per second. Diffusivity as we know is a function of temperature pressure and nature of the component and the concentration of other constituents. So, diffusivity of gases decreases with increase in pressure. As we increase the pressure, the diffusivity decreases so, the relations between the diffusivity and the pressure is inversely proportional. So, D AB is proportional to 1 by p for moderate ranges of pressure that is up to 25 bar.

This is due to the fact that the number of collisions between species is less at lower pressure. Diffusivity is hardly dependent on pressure in case of liquid. So, if we take liquid and if we apply pressure, the diffusion coefficient remains independent. So, it does not change much appreciably. So, we considered the diffusivity is independent on pressure in case of the liquid.

(Refer Slide Time: 03:37)

Gas Phase Diffusion Coefficient Measurement

- The diffusivity increases with increase in temperature $D_{AB} \propto T^{1.5}$ because random thermal movement of molecules increases with increase in temperature.

- The diffusivity is generally higer for gases (in the range of 0.5×10^{-5} to 1.0×10^{-5} m²/s) than liquids (in the range of 10^{-10} to 10^{-9} m²/s).

- The diffusivity value of the gases into solids are in the range of 10^{-13} to 10^{-10} m²/s.

- The diffusivity of permanent gases is in the order of 10^{-10} m²/s for polymer.

The diffusivity and the temperature relation, the diffusivity increases with increase in temperature and that is directly proportional with the temperature and it is D AB is proportional to T to the power 1.5. This is because of the fact that the random thermal movement of the molecules increases with increase in temperature. The diffusivity is generally higher for the gaseous components that is for gaseous component, the diffusivity is in the range of 0. 5 into 10 to the power minus 5 to 1.0 into 10 to the power minus 5 meter square per second and which is much higher of than the diffusivity of the liquids and the diffusivity of the liquids is in the range of 10 to the power minus 10 to 10 to the power minus 9 meter square per second.

The diffusivity value of the gases into solids are in the range of 10 to the power minus 13 to 10 to the power minus 10 metre square per second and the diffusivity of permanent gases is in the order of 10 to the power minus 10 metre square per second for the polymers. So, this gives a picture on the diffusion coefficient for different situations.

(Refer Slide Time: 05:13)

There are several methods of experimental determination of gas phase diffusion coefficient. One of them is the Twin bulb method and the other method is very well known method as Stefan tube method.

These both the methods generally we practiced in our undergraduate lab. Let us consider Twin bulb method.
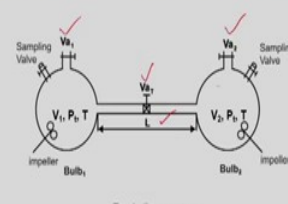
(Refer Slide Time: 05:40)

So, basically we have two bulbs which are connected by a narrow or capillary tube. This is the capillary tube you can see over here capillary tube and these are connected with

you know two bulbs. All the valves you can see there are 3 valves that is Va 1 which is over here Va 1 then Va 2 and Va T. Va T is connected in middle of the tube which is connected the two bulbs all are initially kept closed.

Now, Va 1 is open and then, bulb 1 is filled with pure A at a total pressure of Pt. So, the pressure for bulb 1 is maintained at P t total pressure and that is when the other two valves that is Va T and VA 2 are closed. So, Va 1 is open and it is filled with a component A pure component A to the bulb 1. The samples from the individual chambers are then collected and analysed their composition.

(Refer Slide Time: 07:04)

The valve Va 2 is opened and then bulb 2 is filled with pure B at the same pressure P t. So, this is the similar phenomena. Similar process is followed as in case of bulb 1.

So, bulb 2 is again filled and with pure B and then, the valve is closed and all the compositions are measured. Now, the valve Va T is opened and diffusion proceed for some period of time say at time T, then the valve is closed. The sample from the individual chambers are then collected and analysed their composition. So, the assumptions over here we have taken that negligible capillary volume that is the volume of the tube connected the two bulb are very less compared to the volume of each bulb.
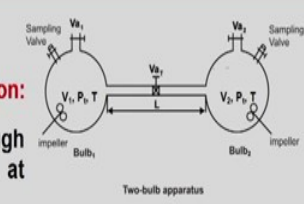
The second assumption is each bulb which always of a uniform concentration and third assumption is that pseudo steady state diffusion through the capillary. What is pseudo steady state diffusion?

(Refer Slide Time: 08:29)

The pseudo steady state approximation is that at any instant the diffusion through the connecting tube occurs at steady state. So, if we look into the overall process and the time of diffusion, the concentration will slowly change as the time passed, but at any instant the diffusion through the connecting tube should occur at steady state. That means at any instant the concentration will be uniform each in each case. As the concentration in the bulbs change a little a new steady state of diffusion is attained simultaneously. This assumption would be valid or correct if the time scale for change of concentration in the bulbs is considerably larger than the time scale for attainment of the steady state of diffusion through the connecting tube.

(Refer Slide Time: 09:32)

So, now let us consider A x is the inner cross sectional area of this tube.
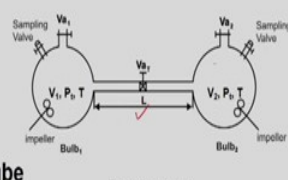
So, tube has the inner cross sectional area A x and the length of the tube capillary tube is L which is given over here, then volume of two bulbs, the left bulb is v 1 and right bulb is v 2, p A1 and p A2 are the partial pressures of component A in bulb 1 and bulb 2 respectively. That means, the partial pressure of component A in the bulb 1 is p A1 which is higher than the partial pressure of component A in bulb 2.

So, the diffusion will occur for component A from bulb 1 to bulb 2. If the total pressure in the bulbs remains constant and equal equimolar counter diffusion will occur.

At steady state the transport of A from bulb 1 to bulb 2 can be written as follows. A x is the area cross sectional area of the tube into flux molar flux of component A N A would be equal to A x D AB p A1 minus p A2 divided by RT into L which is equal to minus A x into N B. Since, this is equimolar counter diffusion, the N A would be equal to minus N B because the component of B is diffusing to the opposite direction.

If the partial pressure of A in bulb 1 and partial pressure of A in bulb 2 at any time for ideal gases, we can write minus v 1 by RT into dp A1 by dt would be equal to A x into N A. Let us call this equation a. Similarly for bulb 2 we can write v 2 that is the volume of bulb 2 divided by RT into dp A 2 by dt which would be equal to A x N A.

(Refer Slide Time: 12:15)

So, now from these two equations we can write minus d (p A1 minus p A2) divided by dt would be equal to A x N A RT into 1 by v1 plus 1 by v2. So, from these equations if we rearrange, it would be equal to minus dp A1 minus p A2 divided by dt would be equal to A x D AB p A1 minus p A2 by L into 1 by v 1 plus 1 by v 2. Let us call this equation c.

The negative sign over here is incorporated because the p A1 that is partial pressure of component one decreases with time while p A2 increases with time and hence, there is this negative sign in this equation.

(Refer Slide Time: 13:22)

Now, use the following conditions that is at t is equal to 0 p A1 minus p A2 would be Pt minus 0 which is equal to Pt when time is 0. The second boundary condition is that when t is equal to t p A1 minus p A2 would be equal to p A1 at t minus p A2 at t. Now, equation c which is over here written over here is minus dp A1 minus p A2 by dt is equal to A x D AB p A1 minus p A2 by L into 1 by v 1 plus 1 by v 2. We will obtain after the integration is L n PT by p A1 t minus p A2 t would be equal to Ax D AB by L into 1 by v 1 plus 1 by v t into t.

(Refer Slide Time: 14:26)
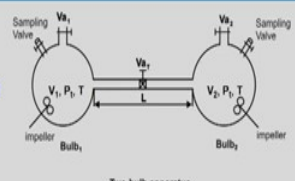
The parameters to be measured from the experiments from here is initial pressure in the vessels which is required, then we need to measure the partial pressure of one of the component in the vessel at the end of the experiments the time of experiments to be recorded and then, the mutual diffusion coefficient can be calculated directly from the equation c because the cross sectional area is known to us. Diffusion coefficient if we wanted to calculate, we need to know the partial pressure of any one component at the end of the operations and volume for both the bulbs. The volumes are known and the length of the tube are known and the time of operation if we can note, then we can calculate from this equation.

Example 6.1

To measure the diffusivity of CO_2 by two-bulb method, the pure CO_2 and pure N_2 is filled in bulb 1 and bulb 2, respectively. The volume of bulb 1 is 4 liters and bulb 2 is 3 liters. These two bulbs are connected by a capillary tube of 5 cm length and 2 cm internal diameter. The partial pressures of CO_2 in the bulbs 1 and 2 are 60 kPa and 40 kPa, respectively at the end of 6 hours. The bulbs are maintained at 100kPa total pressure and 313K temperature. Calculate the diffusivity of CO_2.

Now, let us consider an example to measure the diffusivity of component that is carbon dioxide by two bulb two bulb method. The pure carbon dioxide and pure nitrogen is filled in bulb 1 and bulb 2 respectively. The volume of bulb 1 is 4 litres and bulb 2 is 3 litres. These two bulbs are connected by a capillary tube of 5 centimetre length and 2 centimetre internal diameter. The partial pressure of carbon dioxide is given in case of bulb 1 and bulb 2 are 60 kilo Pascal and 40 kilo Pascal respectively at the end of 6 hours. So, time of operation over here is 6 hours.

The bulb are maintained at 100 kilo Pascal total pressure and 313 Kelvin temperature. Now, calculate the diffusivity of carbon dioxide.

(Refer Slide Time: 16:22)

Exemple: Solution 6.1

To measure the diffusivity of CO_2 by two-bulb method, the pure CO_2 and pure N_2 is filled in bulb 1 and bulb 2, respectively. The volume of bulb 1 is 4 liters and bulb 2 is 3 liters. These two bulbs are connected by a capillary tube of 5 cm length and 2 cm internal diameter. The partial pressures of CO_2 in the bulbs 1 and 2 are 60 kPa and 40 kPa, respectively at the end of 6 hours. The bulbs are maintained at 100kPa total pressure and 313K temperature. Calculate the diffusivity of CO_2.

We know that:

$$\ln \frac{P_t}{(p_{A1,t} - p_{A2,t})} = \frac{A_x D_{AB}}{L} \left(\frac{1}{v_1} + \frac{1}{v_2} \right) t \quad Or, \quad D_{AB} = \frac{L v_1 v_2}{A_x t (v_2 + v_1)} \ln \frac{P_t}{(p_{A1,t} - p_{A2,t})}$$

Given:

$L = 5 \text{ cm} = 0.05 \text{ m}$ $v_1 = 4 \text{ lit} = 0.004 \text{ m}^3$ $v_2 = 3 \text{ lit} = 0.003 \text{ m}^3$

$A_x = \pi d^2/4 = \pi (2 \times 10^{-2} \text{ m})^2/4 = 3.14 \times 10^{-4} \text{ m}^2$

$P_t = 100 \text{kPa}$ $p_{A1} = 60 \text{kPa}$ $p_{A2} = 40 \text{kPa}$

$t = 6 \text{ hours} = 360 \times 60 \text{ seconds} = 21600 \text{ seconds}$

$$D_{AB} = \frac{0.05 \text{m} \times 0.004 \text{ m}^3 \times 0.003 \text{ m}^3}{3.14 \times 10^{-4} \text{ m}^2 \times 21600 \text{ s} \times (0.003 \text{ m}^3 + 0.004 \text{ m}^3)} \ln \frac{100 \text{kPa}}{(60 \text{kPa} - 40 \text{kPa})} = 2 \times 10^{-5} \text{ m}^2/\text{s}$$

So, the parameters which are given we know the fundamental equations to calculate the mutual diffusion coefficients that is ln P t by p A1 t minus p A2 t would be equal to Ax D AB by L into 1 by v 1 plus 1 by v 2 into t. So, we can rearrange this relation as D AB would be equal to L into v 1 v 2 divided by A x t v 2 plus v 1 into ln pt by p A1 at t minus p A2 at t.

The given data the length is 5 centimetre which is equal to 0.05 metre, v 1 is also given that is 4 litre that is we can just convert unit to the metre cube s i unit 0.004 metre cube. The volume of bulb 2 that is v 2 is 3 litre which is equal to 0.003 metre cube. Cross sectional area of the tube is given as pi d square by 4 here D is 2 centimetre, internal diameter is given. So, pi into 2 into 10 to the power minus 2 metre whole square divided by 4 which is equal to 3.14 into 10 to the power minus 4 metre square. The total pressure is given 100 kilo Pascal and the partial pressure of two bulbs are given at the end of the operation. Partial pressure of bulb 1 for component A is 60 kilo Pascal p A1 and partial pressure of component A in bulb 2 is 40 kilo Pascal. Total time of operation is 6 hours we can convert this 360 into 60 seconds so, total 21600 seconds.

Now, if we just substitute all these parameters into the equations which we have derived, D AB would be equal to 0.05 into 0.004 metre cube into 0.003 metre cube divided by 3.14 into 10 to the power minus 4 metre square into 21600 seconds multiplied by 0.003 metre cube plus 0.004 metre cube l n total pressure is the 100 kilo Pascal divided by 60

kilo Pascal minus 40 kilo Pascal. So, if we just calculate it would be equal to 2 into 10 to the power minus 5 metre square per second.

(Refer Slide Time: 19:20)

Now, let us consider the other method which is Stefan tube method. Stefan Tube is consists of a vertical narrow glass. You can see the vertical narrow glass over here which is joint to a horizontal larger diameter tube to form a tee. So, you can see over here it looks like a t and then the vertical tube held at a constant temperature water bath. So, to maintain the temperature of this know the liquid which will be poured inside this tube, the bottom tube and that should be held in a water bath to measure the diffusion coefficient at a particular temperature.

Component B say air is pumped through the horizontal tube which is flowing that is gas B is flowing over here through this horizontal tube. The volatile component A is taken in the narrow vertical tube. So, the vertical tube is filled with the you know volatile component, so that it diffuses it vaporizers at a certain temperature or not very high temperature, at a certain low temperature and then, it diffused through the connecting tube t.
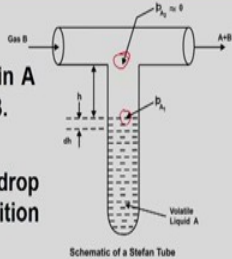
Evaporated A diffuses through B and reaches to the top of the vertical tube and then swept away by the following B. So, the gas which will diffuse to the horizontal tube, it will be swept away by the component B.

Component B is assumed to be insoluble in A and hence, considered to be non diffusing B. The liquid level in the vertical tube will drop very slowly and pseudo steady state condition can be assumed. Let at any time t, the partial pressure of component A at the h distance from the top of the vertical tube is p A1.

So, the partial pressure at the top of the tube over here is p A1 and that at the top it is at p A2. So, the partial pressure at this location is p A2 and the diffusion flux of a through non diffusing B, we can write the equations N A would be equal to D AB P t divided by RT into h p A1 minus p A2 ~~in~~ divided by p BLM. Let us call this equation a.

(Refer Slide Time: 22:16)

Now, p BLM as we have already discussed before that p BLM is the log mean partial pressure difference of component B which is p B2 minus p B1 divided by ln p B2 by p B1 which we can write p A1 minus p A2 divided by ln Pt minus p A2 divided by Pt minus pA1.
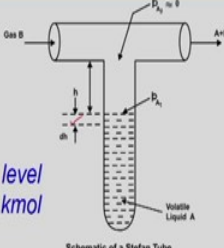
Now, assuming a cross sectional area of 1 metre square, the level drops d h metre in d t second. So, the level which will drop at a time of dt is known differential area which is shown over here is dh. We can then calculate rho a into dh into 1 divided by M A where rho A is the density of the component A and M A is the molecular weight of component A. This would be equal to the kilo mol of A that has been left and diffused. We can then write flux into area would be equal to kilo mol of a transferred per unit time. So, N A into area is 1 metre square would be equal to the kilo mol transferred rho A dh into 1 divided by M A divided by time is dt. So, this is equation b.

Now, the boundary conditions over here is at t is equal to 0, h is equal to h naught at t is equal to t F, h would be equal to h F.

(Refer Slide Time: 24:21)
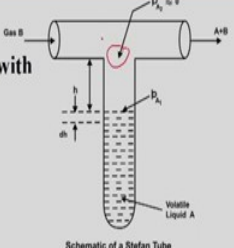
So, using this boundary condition if we integrate, so using this boundary condition and substituting the equation a in equation b and integrating with above boundary conditions, we can get rho A by M A integral h naught to h F hdh is equal to D AB Pt into p A1 minus p A2 divided by RT P BLM into integral 0 2 t F dt. So, from this we can get the final equations for after the integration t F would be equal to rho A h F square minus h naught square into RT p BLM divided by 2 M A D AB Pt into p A1 minus p A2.

So, from this we can rearrange this equation. We can write in terms of D AB would be equal to RT p BLM h F square minus h naught square divided by 2 Pt M A into partial pressure difference p A1 minus p A2 into t F. So, the partial pressure of A at liquid surface is p A1 which is equal to the vapour pressure at the same temperature and the partial pressure of A at the top of the vertical tube that is p A2. Over here A would be equal to 0. This is because of the fact that the gas B which is non diffusing is flowing with a high velocity and swept away all the components of a diffusive to the tube.

So, the partial pressure of component A at point 2 are-at the top would be equal to 0.

Now, let us take an example. To measure the diffusivity of water vapour by Stefan tube method, the water is filled in the vertical narrow glass tube and held at a constant temperature of 30 degree centigrade. The air is flowing through the vertical tube at a total pressure of 1 atmosphere and the temperature is 30 degree centigrade. Initially the water level was at a distance of 1 centimetre from the top of the vertical tube and after 30 minutes the level drops to 1.2 centimetre from top. The vapour pressure of water at 30 degree centigrade is 4.5 kilo Pascal. Calculate the diffusivity of water vapour.

(Refer Slide Time: 27:28)

So, we know that D AB the diffusivity of component A and B would be equal to RT P BLM h F square minus h naught square divided by 2P t M A into p A1 minus p A2 into t F. The data which are given that is R is known to us are 8314 metre cube Pascal per kilo mol Kelvin, T is 30 degree centigrade which is 273 plus 30 would be 303 Kelvin.

Total pressure is 1 atmosphere which is equal to 101.3 into 10 to the power 3 Pascal partial pressure of component A at 1 that is p A1 at that is at the surface which is 4.5 kilopascal would be equal to 4.5 into 10 to the power 3 Pascal and partial pressure of A at 2 that is at the top would be equal to 0, molecular weight of water is 18 and then, the height is equal to 1 centimetre from the top that is 0.01 metre. And then, h f the final height after the diffusion takes place is 1.2 centimetre which is 0.012 metre, time of diffusion t f that is 30 minute which is equal to 30 into 60 is 1800 seconds. So, the p B1 we can calculate p B1 would be equal to Pt minus p A1 which is equal to 101.3 minus 4.5 into 10 to the power 3 which is equal to 96.8 into 10 to the power 3 Pascal.

(Refer Slide Time: 29:35)

Exemple: Solution 6.1

To measure the diffusivity of water vapour by Stefan tube method, the water is filled in the vertical narrow glass tube and held at a constant temperature of 30°C. The air is flowing through the vertical tube at a total pressure of 1 atmosphere and the temperature is 30°C. Initially, the water level was at distance of 1 cm from the top of the vertical tube and after 30 minutes the level drops to 1.2 cm from top. The vapour pressure of water at 30°C is 4.5kPa. Calculate the diffusivity of water vapor.

$$\therefore \quad p_{B2} = P_t - p_{A2} = (101.3 - 0) \times 10^3 = 101.3 \times 10^3 Pa$$

$$\therefore \quad p_{BLM} = \frac{p_{B2} - p_{B1}}{\ln\left(\frac{p_{B2}}{p_{B1}}\right)} = \frac{4.5 \times 10^3}{\ln\left(\frac{101.3}{96.8}\right)} = 10^5 \ Pa$$

$$So, \quad D_{AB} = \frac{8314 \times 303 \times 10^5 \times [(0.012)^2 - (0.01)^2]}{2 \times 101.3 \times 10^3 \times 18 \times 1800 \times 4.5 \times 10^3}$$

$$D_{AB} = \frac{2519142 \times 10^5 \times 0.00004}{2953908 \times 10^7}$$

$$D_{AB} = 3.4 \times 10^{-5} \ m^2/s$$

Now, p B2 in a similar way we can calculate Pt minus p A2 would be equal to 101.2 minus 0 because p A2 is 0 into 10 to the power 3 would be equal 101.3 into 10 to the power 3 Pascal. So, all the parameters we have calculated now we need to calculate p BLM.

If we substitute p B2 and p B1, then we can get p BLM which is equal to 10 to the power 5 Pascal. So, we can then calculate the diffusion coefficient of component A, that is

water into non diffusing B which is air flowing through the horizontal tube. So, if you just substitute, we will obtain D AB would be equal to 3.4 into 10 to the power 5 metre square per second.

So, in this case we should note that there should be a gap between the horizontal tube and the liquid field on the vertical tube, otherwise if the vertical tube is completely filled, then there will be a turbulence at the top surface and then, we cannot consider the case as a diffusion of component A through non diffusing B.

So, thank you very much to hearing this lecture. In the next lecture, we will discuss different methods, analytical or empirical relations to calculate the diffusion coefficient

Thank you.