Mass Transfer Operations I

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Module - 1
Diffusion Mass Transfer
Lecture - 6
Diffusion coefficient: Measurement and Prediction
(Part 1)

Welcome to the sixth lecture of module 1 on diffusion mass transfer. In this lecture, we will discuss on the diffusion coefficient measurements and its prediction. So before going to this lecture, we will just have a recap on our previous lecture.

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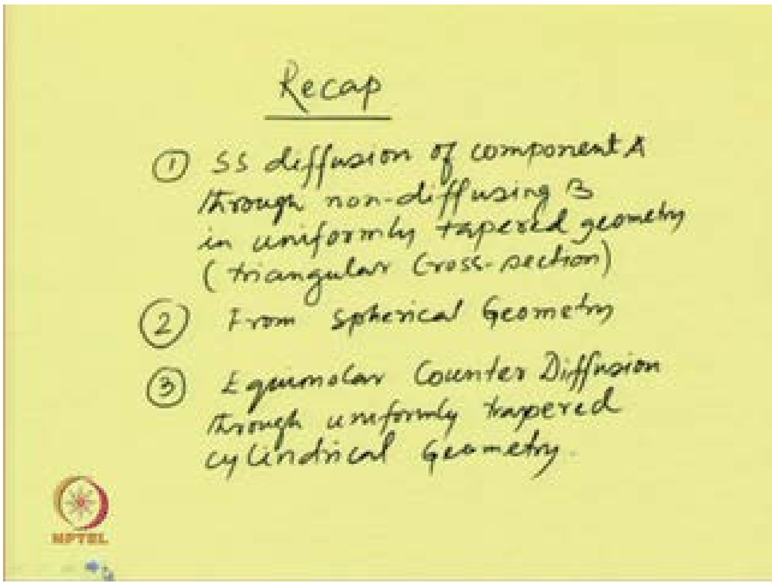

Recap

① SS diffusion of component A through non-diffusing B in uniformly tapered geometry (triangular cross-section)

② From spherical Geometry

③ Equimolar Counter Diffusion through uniformly tapered cylindrical geometry.

In our previous lecture, we have discussed steady state molecular diffusion of a component through variable cross-sectional area or non-uniform geometries. So in this case, we have considered three cases. In first case, we have considered steady state diffusion of component A through non-diffusing B in a uniformly tapered tapered geometry - triangular cross-sectional area. And in the second case, we have considered steady state diffusion of component A through non-diffusing B from spherical geometry, from spherical geometry, and the third case we have considered uniformly tapered cylindrical geometry and equimolar counter diffusion equimolar counter diffusion through uniformly tapered cylindrical geometry.

So today, we will discuss diffusion coefficient measurements and prediction. As we have already said when we discussed the Fick's first law, we have seen that the proportionality constant for that Fick's first law equation is the diffusion coefficient.

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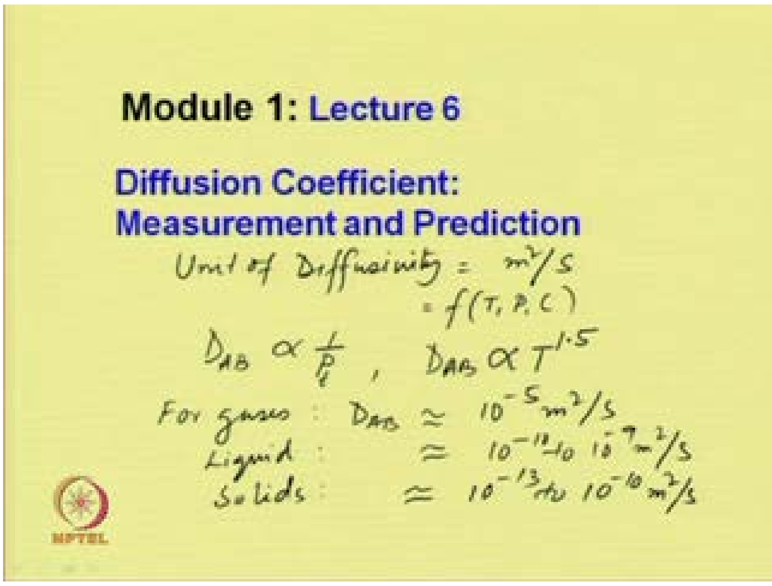

Module 1: Lecture 6

Diffusion Coefficient: Measurement and Prediction

Unit of Diffusivity $= m^2/s$

$= f(T, P, C)$

$D_{AB} \propto \frac{1}{P_t}$, $D_{AB} \propto T^{1.5}$

For gases : $D_{AB} \simeq 10^{-5}\ m^2/s$

Liquid : $\simeq 10^{-10}$ to $10^{-9}\ m^2/s$

Solids : $\simeq 10^{-13}$ to $10^{-10}\ m^2/s$

So the diffusion coefficient we can define from the Fick's first law. The flux divided by the concentration gradient and unit of diffusivity is meter square per second; that is length square per time, and it is a function of temperature, pressure, and concentration. For gases, the diffusivity increases with inversely with the pressure; that is D of A into B is inversely proportional to pressure of the system P t say total pressure and with temperature, it is directly proportional; in general, T to the power 1.5. But for liquid, the pressure dependence on diffusivity is negligible and diffusion co-efficient. for gases varies in the range of 10 to the power For gases, the diffusivity values varies in the range of 10 to the power minus 5 meter square per second; into liquid, liquid it is around 10 to the power minus 10 to 10 to the power minus 9 meter square per second; and in case of solids, that is diffusivity of a particular gaseous components into the solids is approximately in the range of 10 to the power minus 13 to 10 to the power minus 10 meter square per second.

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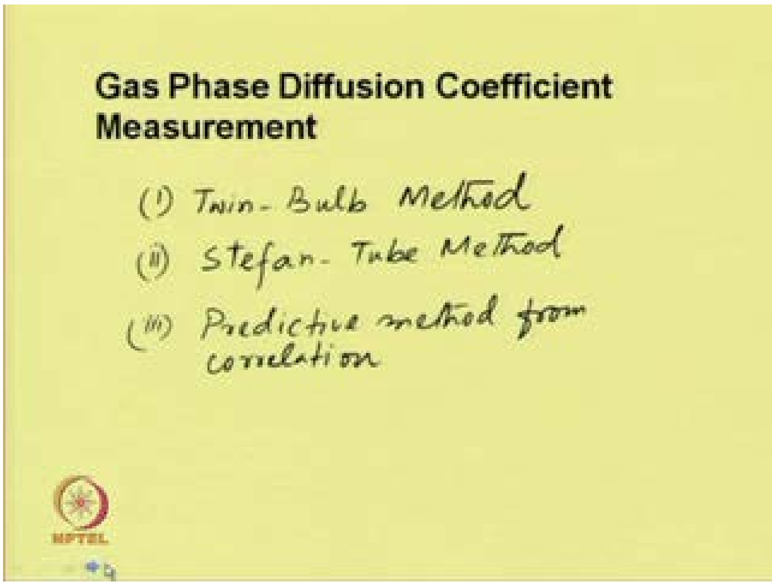

Gas Phase Diffusion Coefficient Measurement

(i) Twin-Bulb Method
(ii) Stefan-Tube Method
(iii) Predictive method from correlation

So today, first we will consider that diffusion coefficient measurement for the gas phase. So, the liquid phase diffusion coefficient measurements we will come later. There are several methods available for the diffusion coefficient measurements for the gas phase. Out of the available methods in the two simple methods we will consider for this lecture. One is very simple method is Twin-Bulb method; and second one is Stefan tube method, and there are some empirical correlations available by which we can also predict the diffusion coefficients; and third one, we will discuss for the gas phase diffusion coefficient prediction is the predictive method from correlation.

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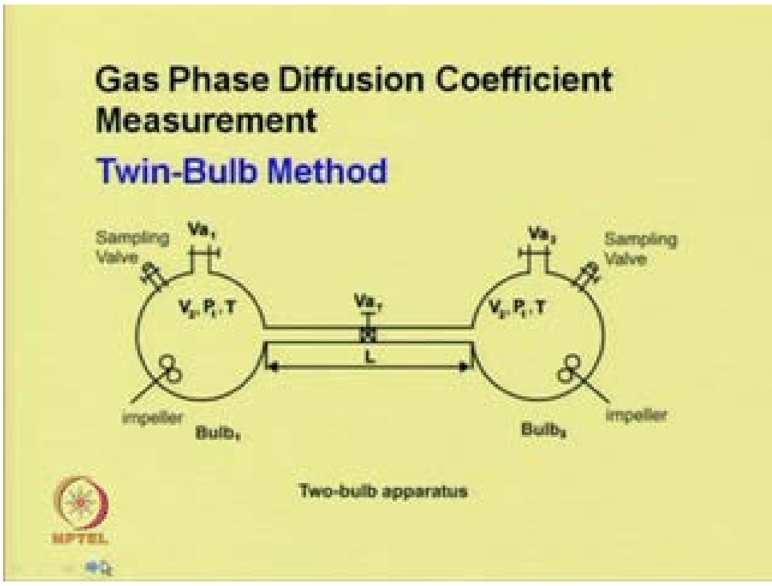

Gas Phase Diffusion Coefficient Measurement

Twin-Bulb Method

Two-bulb apparatus

So, let us consider the first gas phase diffusivity measurement method; that is Twin-Bulb method. In this method, the two large volume bulbs are connected with a capillary tube or narrow tube, and the volume of one bulb is b 1 and volume of other bulb b 2, and they are kept at constant pressure and temperature say P t and T both the bulb, and then there are three valves; valve 1 for bulb 1, valve 2 for bulb 2, and there is a valve and in the capillary tube at the middle. So initially all this three valves are open, and then this system is evacuated and then the three valves Va 1, Va 2, and Va t. These are closed. Then the valve 1, Va 1 is open and filled with a pure component A and then the valve a 1 is closed. The valve a 2 is opened and then pure B is filled through Va 2 and then Va 2 is closed. The whole system remains at a constant temperature and pressure. Then the valve Va t is opened for a period of time say T and then Va t is closed, and the sampling through the sampling valve from both the bulb was taken out and analyzed for their composition.

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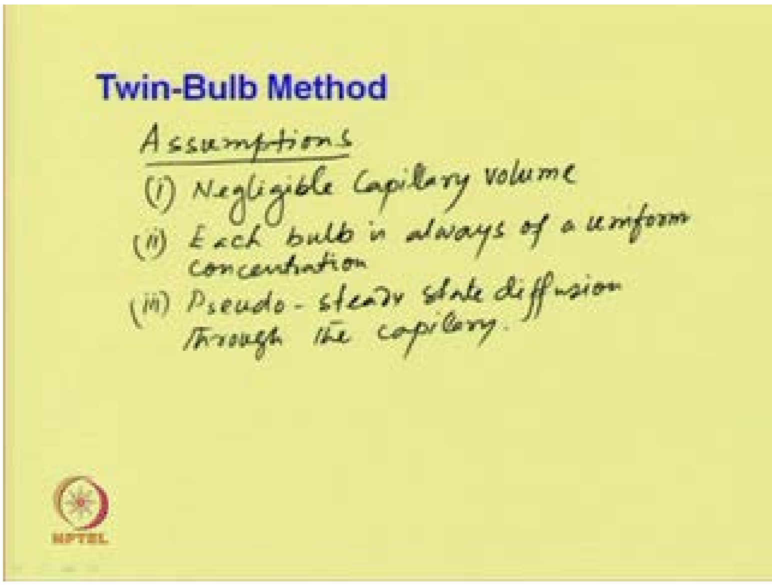

Twin-Bulb Method

Assumptions

(i) Negligible Capillary volume

(ii) Each bulb is always of a uniform concentration

(iii) Pseudo-steady state diffusion through the capillary.

So the assumptions over here, we have taken the negligible capillary volume. The second one is each bulb is always of a uniform concentration, and then pseudo-steady state diffusion through the capillary, through the capillary. This means that at any instant, the diffusion through the connecting tube occurs at steady state. As soon as the concentration between these two bulbs changed a little, a new steady state condition is maintained. So at any instant steady state condition is maintained, and the volume in this case we have considered of this copular volume is negligible, and there is suitable arrangement to keep this is bulb concentration at all the times at uniform concentration.

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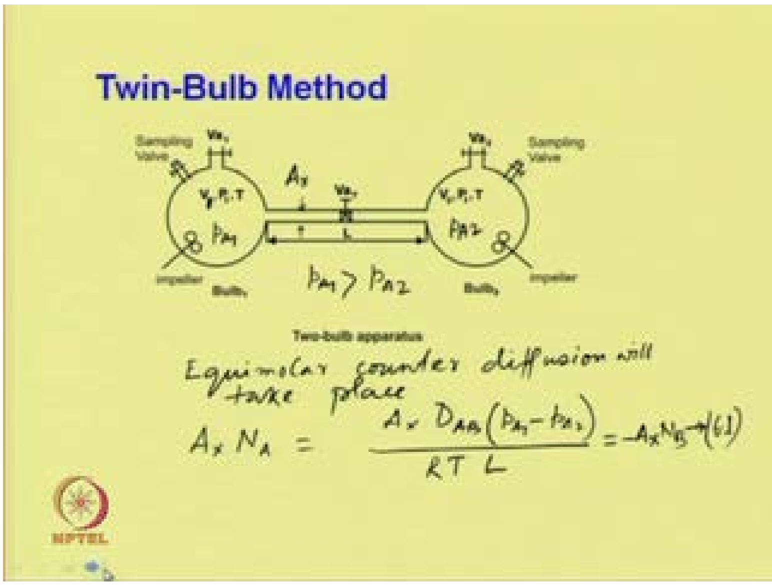

Twin-Bulb Method

Two-bulb apparatus

Equimolar counter diffusion will take place

$$A_x N_A = \frac{A_x D_{AB} (p_{A1} - p_{A2})}{RT\ L} = -A_x N_B \rightarrow (6.1)$$

Let us consider the cross sectional area of this tube is A x and the length which is given is l, and volume B 1 and B 2, and the partial pressure for bulb 1 is P A 1 for component A and for component A in bulb 2 is P A 2, and P A 1 is greater than P A 2, and the total pressure remains constant. Since the total pressure remains constant, equimolar counter diffusion will take place; equimolar counter diffusion will occur and will take place. So, at steady state transport of A from bulb 1 to bulb 2 we can write as A x into flux of A is equal to A x diffusion coefficient AB into the partial pressure difference (P A 1 minus P A 2) divided by RT L, which will be equal to minus A x N B. So, this is equation number 6.1.

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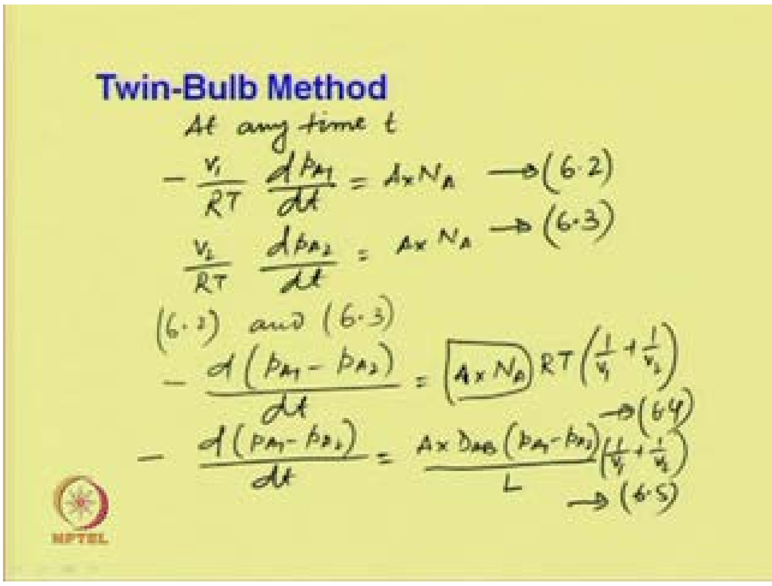

Twin-Bulb Method

At any time t

$$-\frac{V_1}{RT}\frac{dp_{A1}}{dt} = A\times N_A \rightarrow (6.2)$$

$$\frac{V_2}{RT}\frac{dp_{A2}}{dt} = A\times N_A \rightarrow (6.3)$$

(6.2) and (6.3)

$$-\frac{d(p_{A1}-p_{A2})}{dt} = \boxed{A\times N_A}\, RT\left(\frac{1}{V_1}+\frac{1}{V_2}\right) \rightarrow (6.4)$$

$$-\frac{d(p_{A1}-p_{A2})}{dt} = \frac{A\times D_{AB}(p_{A1}-p_{A2})}{L}\left(\frac{1}{V_1}+\frac{1}{V_2}\right) \rightarrow (6.5)$$

Now at any times if we assume the gas is ideal gas; in that case, we can write at any time t minus v 1 by RT d P A 1 dt will be is equal to A x N A is 6.2 and v 2 by RT d P A 2 dt will be A x N A. The negative sign in the equation 6.2 indicates that the partial pressure is decreasing with with time, whereas in bulb 2 the partial pressure of component 1 is increasing in bulb 2. The partial pressure of A in bulb 1 is decreasing with time, whereas the some component is increasing with time in bulb 2 because of deputation from higher partial pressure to the lower partial pressure. If we sum this two equations 6.2 and 6.3, we will have minus d (p A 1 minus p A 2) dt will be equal to A x N A RT (1 by v 1 plus 1 by v 2); this is equation number 6.4. Now if we substitute these relations A x N A in place of this term, so we will have minus d (p A 1 minus p A 2) dt will be equal to A x D AB (p A 1 minus p A 2) divided by l into (1 by v 1 plus 1 by v 2). So, this is equation number 6.5.

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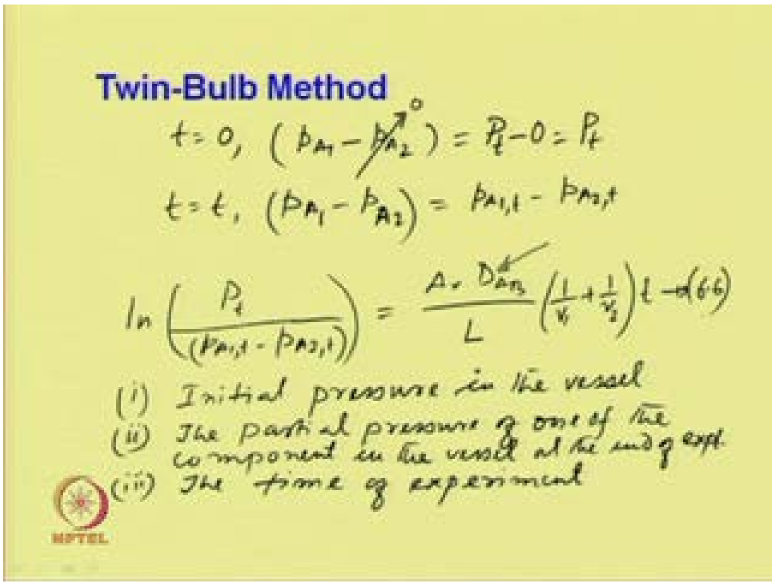

Twin-Bulb Method

$t = 0,\ (p_{A1} - \cancel{p_{A2}}^{\,0}) = P_t - 0 = P_t$

$t = t,\ (p_{A1} - p_{A2}) = p_{A1,t} - p_{A2,t}$

$$\ln\left(\frac{P_t}{(p_{A1,t} - p_{A2,t})}\right) = \frac{A \cdot D_{AB}}{L}\left(\frac{1}{V_1} + \frac{1}{V_2}\right)t \quad \text{--- (6.6)}$$

(i) Initial pressure in the vessel
(ii) The partial pressure of one of the component in the vessel at the end of expt.
(iii) The time of experiment

Now if use the following conditions at t is equal to 0 (p A 1 minus p A 2). So, initially this partial pressure in bulb 2 of component A is 0. So, this will be equal to P t the total pressure; partial pressure will be equal the total pressure minus 0. So, is equal to P t and at t is equal to t, (p A 1 minus p A 2) would be equal to p A 1 t minus p A 2 t.

So with these conditions if we integrate this equation 6.5, so we will have the relation l n P t by (p A 1 t minus p A 2 t)will be equal to A x D B by L (1 by v 1 plus 1 by v 2) into t; so equation number 6.6. So from these equations, we can determine the diffusion coefficient of component A. So in this case, the parameters we need to measure is initial pressure in the vessel; second, the partial pressure of one of the component the partial pressure of one of the component in the vessel at the end of experiment; and the third thing, the time of experiment. With these parameters, we can be able to find out the mutual diffusivities from equation 6.6.

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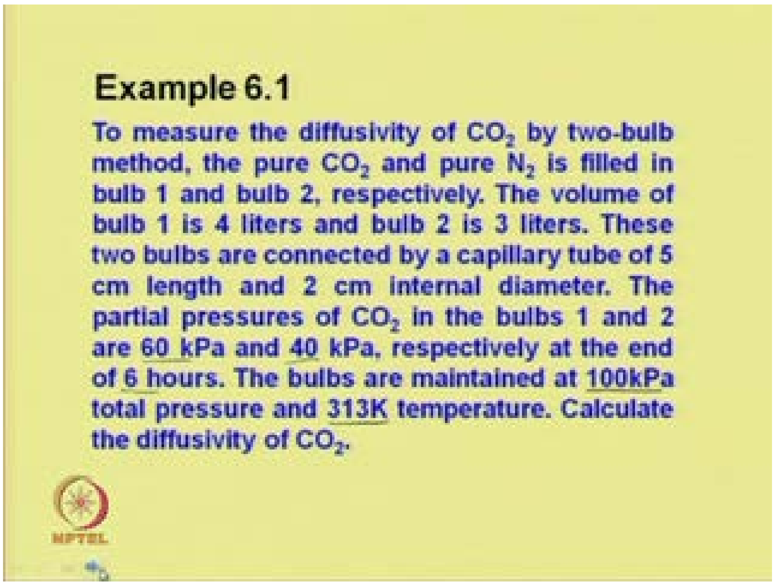

Example 6.1

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.

Let us consider a simple example to major the diffusivities from this experiments. To measure the diffusivity of CO 2 by two-bulb method, the pure CO 2 and nitrogen 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 centimeter length, 2 centimeter internal diameter. The partial pressure of CO 2 in the bulbs 1 and 2 are 60 kilo Pascal and 40 kilo Pascal, respectively at the end of 6 hours. The bulbs are maintained at 100 kilo Pascal pressure and 313 Kelvin temperature. Calculate the diffusivity of CO 2.

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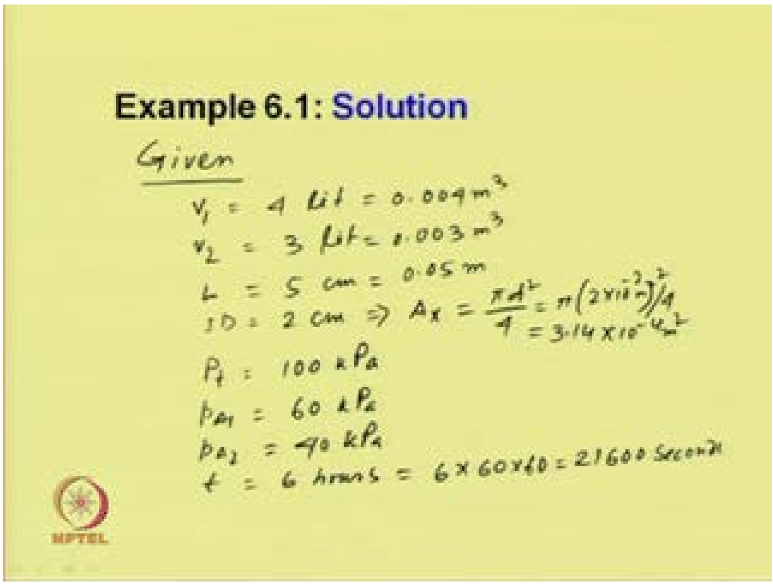

Example 6.1: Solution

Given

$V_1 = 4 \text{ lit} = 0.004 \text{ m}^3$

$V_2 = 3 \text{ lit} = 0.003 \text{ m}^3$

$L = 5 \text{ cm} = 0.05 \text{ m}$

$ID = 2 \text{ cm} \Rightarrow A_x = \frac{\pi d^2}{4} = \pi(2\times10^{-2} \text{ m})^2/4 = 3.14\times10^{-4} \text{ m}^2$

$P_t = 100 \text{ kPa}$

$p_{A_1} = 60 \text{ kPa}$

$p_{A_2} = 40 \text{ kPa}$

$t = 6 \text{ hours} = 6\times60\times60 = 21600 \text{ seconds}$

Let us write down the parameters which are given. The volume of the two bulbs, 1 bulb v A 1 is v 1 is 4 liter; v 2 is 3 liter, and length of the capillarity tube is given which is 5 centimeter, and the ID internal diameter of the tube; ID is 2 centimeter, length is 5 centimeter. Total pressure P t is 100 kilo Pascal. Partial pressure one is 60 kilo Pascal; p A 2 is 40 kilo Pascal, and time t is 6 hours. So, these are the parameters which are given.

So now, L the volume which is given is we can write it is 0.004 meter cube, and this is 0.003 meter cube, and this length is 0.05 meter, and then from this we can calculate cross-sectional area, which is pi d square by 4 which will be equal to pi (2 into the 10 to the power minus 2 meter) whole square by 4; and it will be 3.14 into 10 to the power minus 4 meter square. So this is the cross sectional area, and time we can convert into seconds. So, it will be 6 into 60 into 60; so it will be 21600 seconds.

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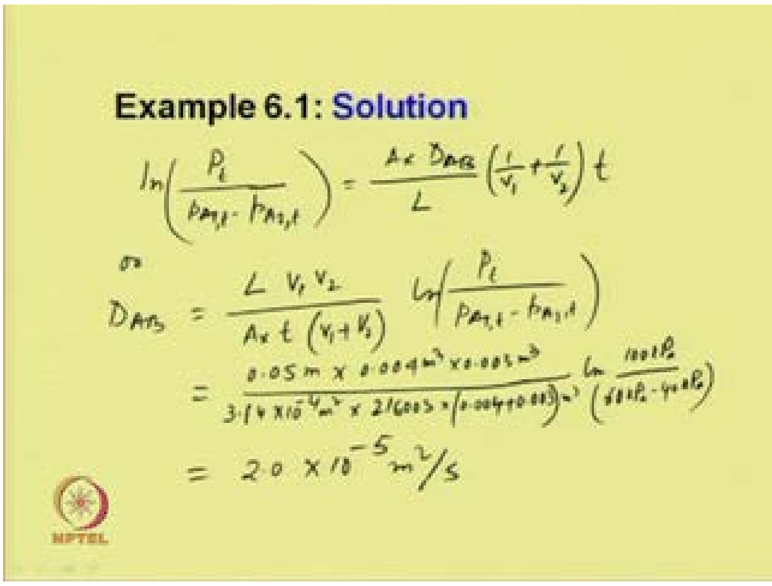

Example 6.1: Solution

$$\ln\left(\frac{P_t}{p_{A1,t} - p_{A2,t}}\right) = \frac{A_x D_{AB}}{L}\left(\frac{1}{V_1} + \frac{1}{V_2}\right) t$$

or

$$D_{AB} = \frac{L\, V_1 V_2}{A_x\, t\, (V_1 + V_2)} \ln\left(\frac{P_t}{p_{A1,t} - p_{A2,t}}\right)$$

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

$$= 2.0 \times 10^{-5}\,\text{m}^2/\text{s}$$

If we replace in the governing equations, which is ln (P t by p A 1 t minus p A 2 t) is equal to A x D AB by L into (1 by v 1 plus 1 by v 2) into t, or we can write D A B will be equal to L v 1 v 2 by A x t (v 1 plus v 2) ln (P t by p A 1 t minus p A 2 t). If we substitute these values, so D AB will be 0.05 meter into 0.004 meter cube into 0.003 meter cube divided by 3.14 (14) into 10 to the power minus 4 meter square into 21600 second into the sum of volumes (0.004 plus 0.003) meter cube ln 100 kilo Pascal divided by (60 kilo Pascal minus 40 kilo Pascal). So, this will be 2.0 into 10 to the power minus 5 meter square per second.

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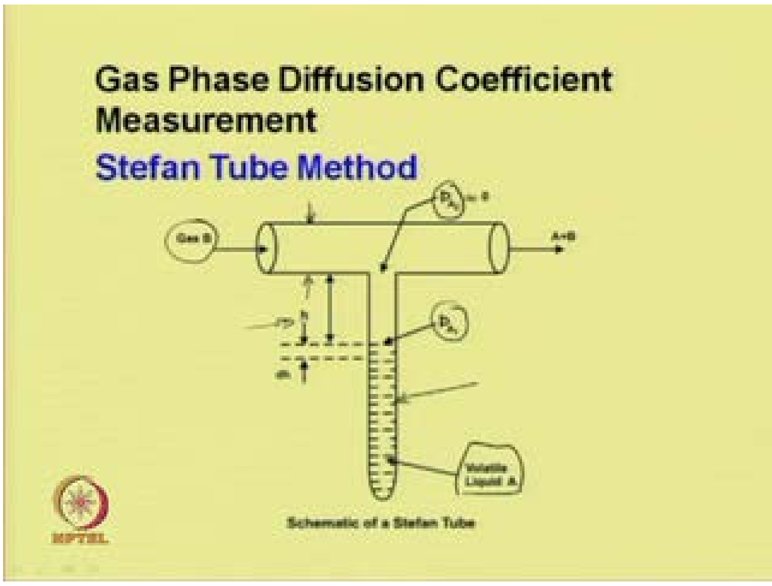

Gas Phase Diffusion Coefficient Measurement

Stefan Tube Method

Schematic of a Stefan Tube

So, let us consider another method for gas phase diffusion coefficient measurements; that is Stefan tube method. In this method a narrow tube, a narrow vertical tube which is connected with a horizontal tube of larger diameters. The diameter of this horizontal tube is much higher compared to the vertical tube, and in this vertical tube narrow tube, we used to take a volatile liquid A, and this volatile liquid at the top of the volatile surface which is say at time t, the height from the top is 8; height from the top of the vertical tube is 8 and the partial pressure at the surface is p A 1, which is the vapor pressure of the volatile liquids.

Here we have assumed the component B, which is flowing through the vertical tube is insoluble in the volatile liquids; that is component B is non-diffusing in to component A, and component A is diffusing through non-diffusing B, and the partial pressure at the top of the surface is considered p A 2 is always 0 because of the high flow rate of component B. The liquid level from the top will drop slowly, and always there is a pseudo-steady state condition is maintained; that means as soon as some liquid, a volatile liquid evaporates, and in every instance another steady state is reached and the pseudo-steady state condition is maintained. The liquid in the vertical tube usually maintain at constant temperature and the diffusion takes place.

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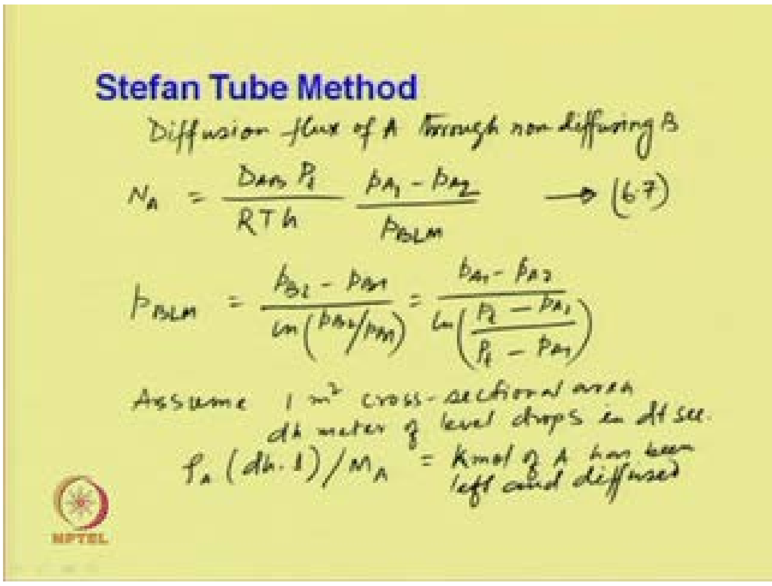

Stefan Tube Method

Diffusion flux of A through non-diffusing B

$$N_A = \frac{D_{AB} P_t}{RTh} \frac{p_{A1} - p_{A2}}{p_{BLM}} \rightarrow (6.7)$$

$$p_{BLM} = \frac{p_{B2} - p_{B1}}{\ln(p_{B2}/p_{B1})} = \frac{p_{A1} - p_{A2}}{\ln\left(\frac{P_t - p_{A2}}{P_t - p_{A1}}\right)}$$

Assume 1 m^2 cross-sectional area

dh meter of level drops in dt sec.

$\rho_A (dh \cdot 1)/M_A$ = Kmol of A has been left and diffused

At any time t, we can write steady state flux of A; diffusion flux of A through non-diffusing B can be written as N A, D AB P t by RTh p A 1 minus p A 2 by p BLM, where p BLM is the log mean pressure difference, which is p B 2 minus p B 1 divided by ln (p B 2 by p B 1), which is equal to p A 1 minus p A 2 by ln (P t minus p A 2 by P t minus p A 1). So, this is equation 6.7. Now if we assume you need cross-sectional area; that is 1 miter square cross-sectional area and dh meter of level level drops in dt second. In that case we can write the moles transfer rho A (dh into 1) divided by the M A. This will be the moles of A that has been transferred or diffused; Kmol of A has been left from the liquid and diffused.

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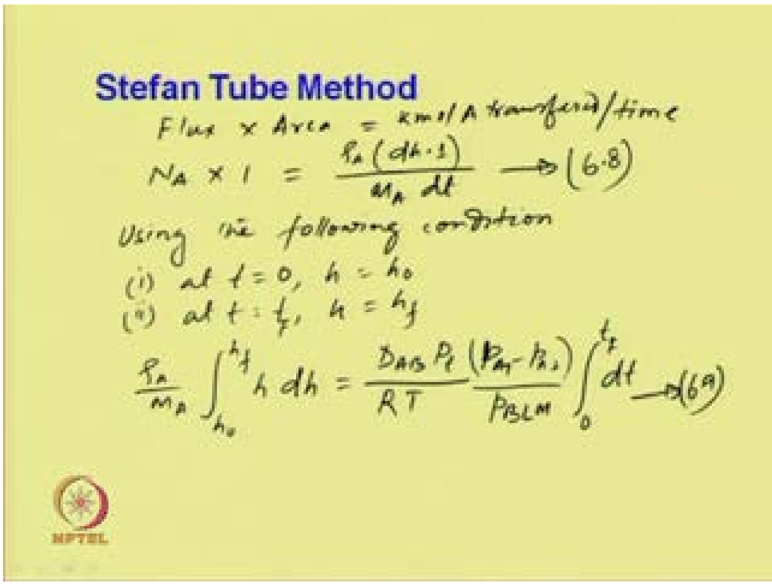

Stefan Tube Method

Flux × Area = Kmol A transferred/time

$$N_A \times 1 = \frac{\rho_A (dh \cdot 1)}{M_A \, dt} \longrightarrow (6.8)$$

Using the following condition

(i) at $t = 0$, $h = h_0$

(ii) at $t = t_f$, $h = h_f$

$$\frac{\rho_A}{M_A} \int_{h_0}^{h_f} h \, dh = \frac{D_{AB} P_t}{RT} \frac{(p_{A1} - p_{A2})}{p_{BLM}} \int_0^{t_f} dt \longrightarrow (6.9)$$

So, in this case we can write flux into area will be equal to Kmol A transferred per time. So, if you substitute flux is N A and considered unit cross-sectional area 1 will be equal to mole transfer rho A is density of component A into dh is the level in to the cross-sectional area divided by the molecular weight into dt. So this is the flux equation more balance equation, so 6.8. Now if we use the conditions, following condition and integrate the this equation. At the first conditions at t is equal to 0, h is equal to h 0; and the second conditions at t is equal to t, h is equal to h f; t is equal to t F, say. So with these conditions and if we integrate equation 6.8, we will have rho A by M A integral h 0 to h f h dh will be equal to D AB P t by RT (p A 1 minus p A 20 by P BLN integral 0 to t F dt. So, this is equation number 6.9.

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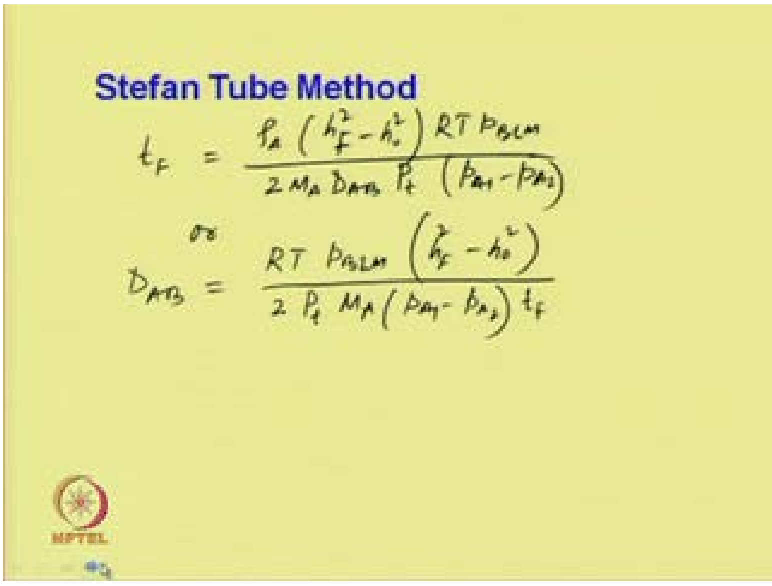

Stefan Tube Method

$$t_F = \frac{\rho_A \left(h_F^2 - h_0^2\right) RT\, p_{BLM}}{2 M_A D_{AB} P_t \left(p_{A1} - p_{A2}\right)}$$

or

$$D_{AB} = \frac{RT\, p_{BLM} \left(h_F^2 - h_0^2\right)}{2 P_t M_A \left(p_{A1} - p_{A2}\right) t_F}$$

So after integration, we will obtain t F will be rho A (h F square minus h 0 square) RT p BLM by twice M A D AB P t (p A 1 minus p A 2) or we can write D AB will be equal to RT p BLM (h F square minus h 0 square) divided by twice P t M A (p A 1 minus P A 2) into t F. So as we said, in this case we can consider p A 2 will be 0 all the times because there is a high flow rate of air through the or component B non-diffusing B through the horizontal tube, and the partial pressure p A 1 will be equal to the vapor pressure since it is a volatile liquid at that conditions.

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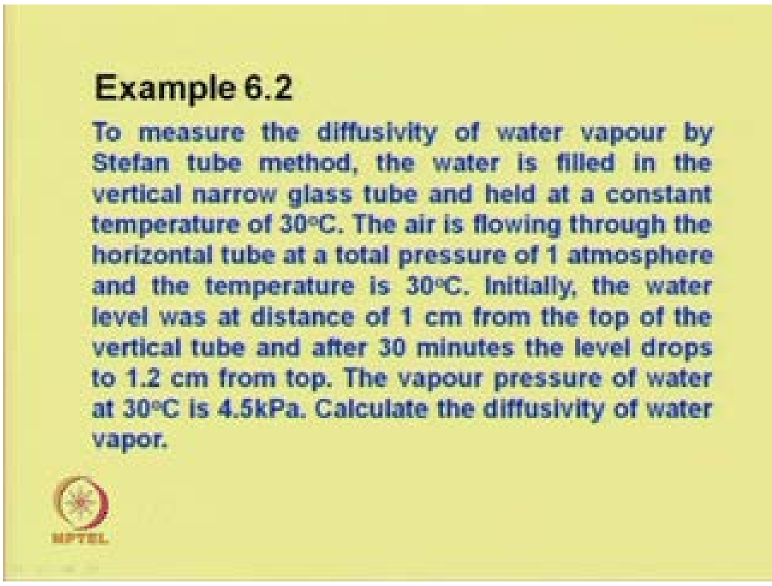

Example 6.2

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 horizontal 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.

So, let us consider a simple example to calculate the diffusivity using Stefan tube method. To measure the diffusivity of the water vapor by Stefan tube method, the water is filled in the vertical narrow glass tube and held at constant temperature of 30 degree centigrade. The air is flowing to the horizontal 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 centimeter from the top of the vertical tube and after 30 minutes the level drops to 1.2 centimeter from top. The vapor pressure of water at 30 degree centigrade is approximately 4.5 kilo Pascal. Calculate the diffusivity of water vapor.

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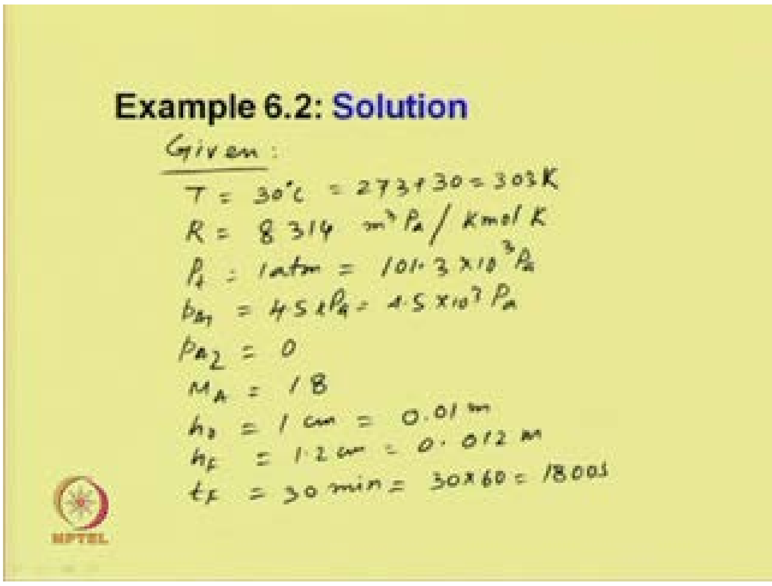

Example 6.2: Solution

Given :

$T = 30^\circ C = 273+30 = 303 K$

$R = 8314\ m^3 Pa / Kmol\ K$

$P_t : 1 atm = 101.3 \times 10^3 Pa$

$p_{A_1} = 4.5 kPa = 4.5 \times 10^3 Pa$

$p_{A_2} = 0$

$M_A = 18$

$h_0 = 1 cm = 0.01 m$

$h_F = 1.2 cm = 0.012 m$

$t_F = 30 min = 30 \times 60 = 1800 s$

Let us write down the parameters which are given in these examples. So given, T is 30 degree centigrade, which is 273 plus 30 is 303 Kelvin. R is known to us; 8314 meter cube Pascal Kmol Kelvin. P t total pressure is 1 atmosphere, which is equal to 101.3 into 10 to the power 3 Pascal. p A 1 is given 4.5 kilo Pascal, which is 4.5 into 10 to the power 3 Pascal. p A 2 which is equal to 0. Molecular weight of water is 18. h 0 is 1 centimeter, which is 0.01 meter. h F is 1.2 centimeter, which is 0.012 meter. t f is 30 minutes, which is 30 into 60; 1800 seconds.

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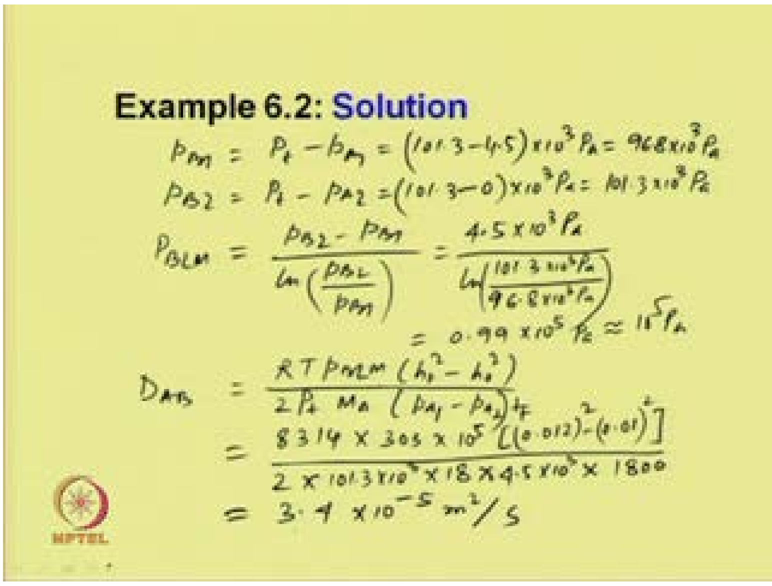

Example 6.2: Solution

$$p_{B1} = P_t - p_{A1} = (101.3 - 4.5) \times 10^3\ Pa = 96.8 \times 10^3\ Pa$$

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

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

$$= 0.99 \times 10^5\ Pa \approx 10^5\ Pa$$

$$D_{AB} = \frac{RT\,p_{BLM}\,(h_F^2 - h_0^2)}{2 P_t M_A (p_{A1} - p_{A2}) t_F}$$

$$= \frac{8314 \times 305 \times 10^5 \left[(0.012)^2 - (0.01)^2\right]}{2 \times 101.3 \times 10^3 \times 18 \times 4.5 \times 10^3 \times 1800}$$

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

Now calculate p B 1 is P t minus p A 1 is equal to (101.3 minus 4.5) into 10 to the power 3 Pascal, which is equal to 96.8 into 10 to the power 3 Pascal. p B 2 is P t minus p A 2 is equal to (101.3 minus 0) into 10 to the power 3 Pascal is equal to 101.3 into 10 to the power 3 Pascal. So, p BLM we can calculate is p B 2 minus p B 1 by ln (p B 2 by p B 1). Putting this value will be 4.5 into 10 to the power 3 Pascal divided by ln (101.3 into 10 to the power 3 Pascal divided by 96.8 into 10 to the power 3 Pascal). So, this will be equal to 0.99 into 10 to the power 5 Pascal, which we can write 10 to the power 5 Pascal.

Now if we substitute in this equation, D AB is equal to RT p BLM divided by twice P t M A (h F square minus h 0 square) divided by (p A 1 minus p A 2) into t F. So if you substitute these values, this will be 8314 into 303 into 10 to the power 5 into (0.012 square) minus (0.01 square) divided by 2 into 101.3 into 10 to the power 3 into 18 into the partial pressure difference which is 4.5 into 10 to the power 3 into the total times 1800 second. So, this will be around 3.4 into 10 to the power minus 5 meter square per second. This is the value of diffusion coefficient of water vapor by using the Stefan tube method.

So, this is end of lecture 6, and in the next lecture we will continue with the gas phase diffusion coefficient predictions by empirical methods, and then we will consider the experimental determination of the liquid phase diffusion coefficients.