Mass Transfer Operations I
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Module - 1
Diffusion Mass Transfer
Lecture - 8
Multi component Diffusion and Diffusivity in Solids

Welcome to the eighth lecture of module one which is diffusion mass transfer. In this lecture, we will discuss the multicomponent diffusions and diffusivity in solids and its application.

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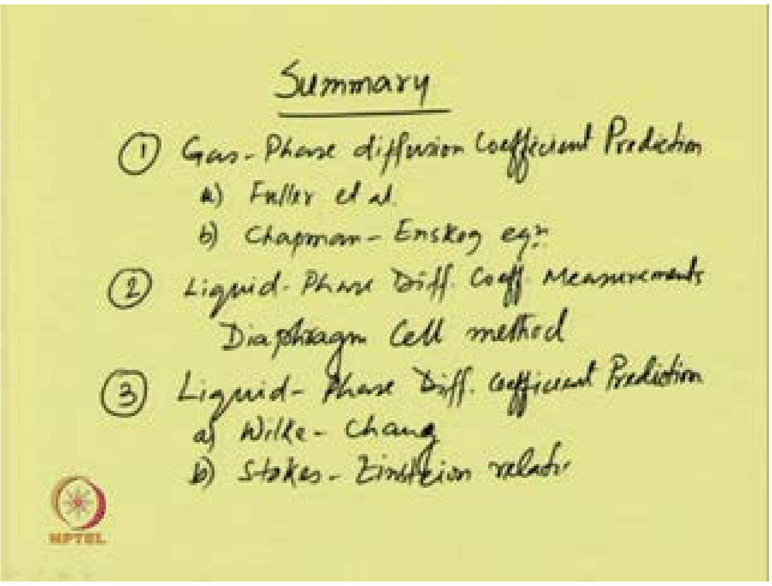

Summary

① Gas-Phase diffusion Coefficient Prediction
  a) Fuller et al.
  b) Chapman-Enskog eqn
② Liquid-Phase Diff. Coeff Measurements
  Diaphragm Cell method
③ Liquid-Phase Diff. coefficient Prediction
  a) Wilke-Chang
  b) Stokes-Einstein relatn

So, before going to this lecture, we will have a brief summary on our previous discussion where we have discussed on the diffusivity measurements and prediction. And in our previous class, we have considered gas phase diffusion coefficient prediction, gas phase diffusion coefficient prediction and mainly we have discussed two empirical correlations which is fuller et al equations. And secondly, we have considered Chapman and Enskog equation, Chapman and Enskog equation. These are the predictable method for gas phase diffusion coefficient prediction. And secondly, we have considered the liquid phase diffusion coefficient measurements. Liquid phase diffusion coefficient measurements, mainly we have considered a very simple method of diaphragm cell - diaphragm cell method. And the third thing, we have considered liquid phase diffusion coefficient prediction, coefficient prediction. Here we have considered two unknown correlations Wilke and Chang, and the other one is Stokes-Einstein relation.

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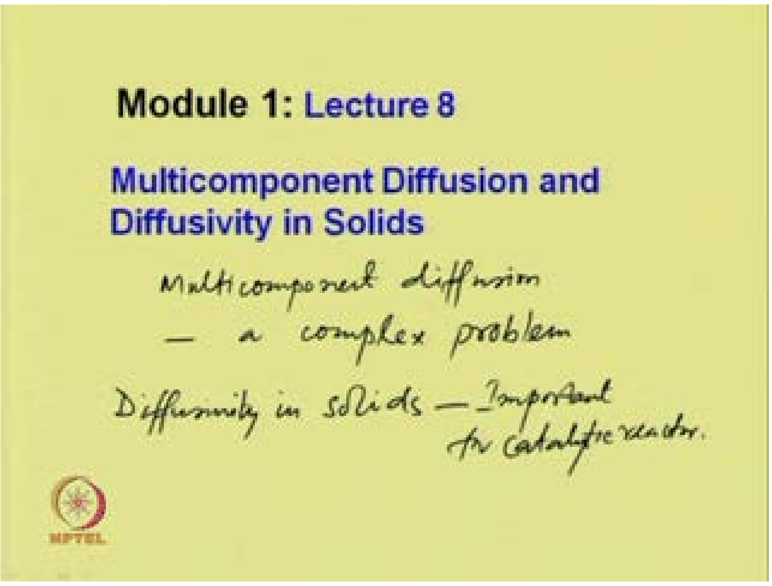

Module 1: Lecture 8

Multicomponent Diffusion and Diffusivity in Solids

Multicomponent diffusion
— a complex problem

Diffusivity in solids — Important for catalytic reactor.

Now, in this lecture we will discuss multi component diffusion and diffusivity in solids as we know for multi-component diffusion the system or the diffusivity for different components will effects on the other components. So, it is a bit complex problems to analyze multi component diffusion complex problem and diffusivity in solids is important particularly for catalytic reactors. So, there are some other examples we will consider later when we will discuss the diffusivity in solids.

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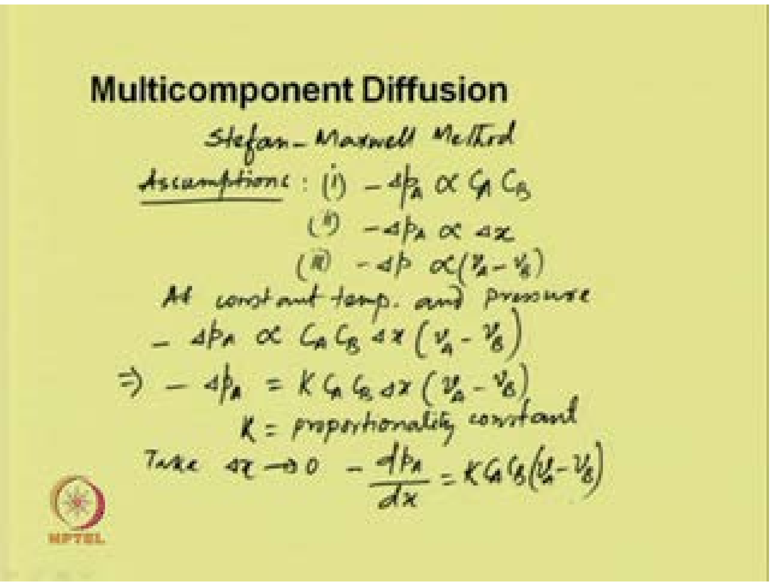

Multicomponent Diffusion

Stefan-Maxwell Method

Assumptions: (i) $-\Delta p_A \propto C_A C_B$

(ii) $-\Delta p_A \propto \Delta x$

(iii) $-\Delta p \propto (v_A - v_B)$

At constant temp. and pressure

$-\Delta p_A \propto C_A C_B \Delta x (v_A - v_B)$

$\Rightarrow -\Delta p_A = K C_A C_B \Delta x (v_A - v_B)$

K = proportionality constant

Take $\Delta x \to 0$ $-\frac{dp_A}{dx} = K C_A C_B (v_A - v_B)$

Let us consider the multi-component diffusion all though it is a bit complex problem we can analyze these multi-component diffusions by using a Stefan max well method Stefan max well method first we will consider for binary system and then we will extend for the multicomponent systems for binary systems following are the assumptions the partial pressure difference minus delta p A is proportion alto molar concentration of species a and molar concentration of species B C A and C B and. Secondly, this delta p A is also proportional to the diffusion path length. So if we consider delta x is the diffusion path length. So, delta p A partial pressure difference would be is proportional to delta x and then third point is minus delta p A is proportional to the velocity difference between component A and B that is B A minus B B. So from this we can write at constant temperature and pressure we can write minus delta p A is proportional to C A C B delta x B A minus B B.

So, we can write minus delta p A is equal to K C A C B delta x into v A minus v B where K is the proportionality constant now if we take limit delta x tends to 0 we can write minus d p A d x will be equal to K C A C B v A minus v B.

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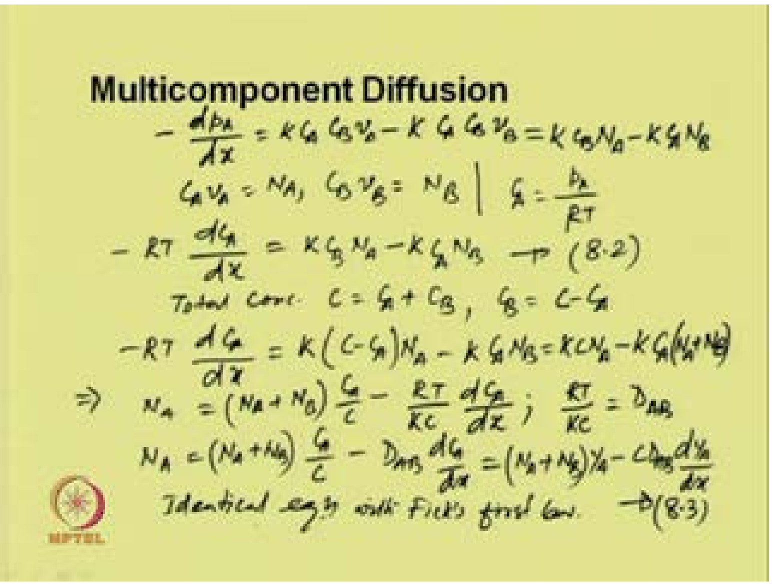

Multicomponent Diffusion

$$-\frac{dp_A}{dx} = K C_A C_B v_A - K C_A C_B v_B = K C_B N_A - K C_A N_B$$

$$C_A v_A = N_A,\quad C_B v_B = N_B \quad \Big| \quad C_A = \frac{p_A}{RT}$$

$$-RT\frac{dC_A}{dx} = K C_B N_A - K C_A N_B \rightarrow (8.2)$$

Total conc. $C = C_A + C_B,\ C_B = C - C_A$

$$-RT\frac{dC_A}{dx} = K(C - C_A)N_A - K C_A N_B = K C N_A - K C_A (N_A + N_B)$$

$$\Rightarrow N_A = (N_A + N_B)\frac{C_A}{C} - \frac{RT}{KC}\frac{dC_A}{dx};\quad \frac{RT}{KC} = D_{AB}$$

$$N_A = (N_A + N_B)\frac{C_A}{C} - D_{AB}\frac{dC_A}{dx} = (N_A + N_B)y_A - C D_{AB}\frac{dy_A}{dx}$$

Identical eqn with Fick's first law. $\rightarrow (8.3)$

So, we can write minus d p A d x will be equal to K C A C B v A minus K C A C B v B and we know that we can write C A v A is N A C b v b is n b. So, this equation will reduce to K C b N A minus K C A N B C A is equal to p A by RT then the above relations will be minus RT d C A d x is equal to K C b N A minus K C A N B if we give this is equation number 8.1.

So, we can write this is equation number eight point two now we know that the total concentration concentration C is equal to C A plus C B. So, we can write C B will be equal to C minus C A. So, if we substitute this in equation 8.2 it will be minus RT d C A d x is equal to K into C minus C A into N A minus K into C A N B. So, we can write this will be equal to K C N A minus K C A into N A plus N B from where we can write N A is equal to N A plus N B into C A by C minus RT by K C d C A d x now if we consider RT by K C is the d A b the diffusivity in that case this equation will reduce to N A is equal to N A plus N B C A by C minus d A B d C A dx. So, we can write this will be equal to N A plus N B y A minus C into d A b d y A d x this equation number 8.3.

So, this is the similar equation or identical equations with the identical equation with Fick's first law now if we consider multicomponent mixture then this equation equation 8.2 we can write multi component mixture mixture.

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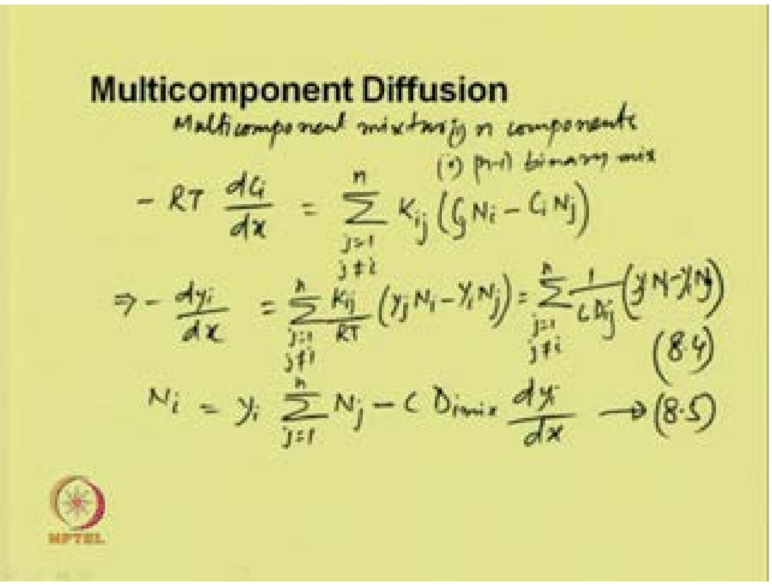

Multicomponent Diffusion

Multicomponent mixture of n components

(2) (n-1) binary mix

$$-RT\frac{dC_i}{dx} = \sum_{\substack{j=1\\j\neq i}}^{n} K_{ij}\left(C_j N_i - C_i N_j\right)$$

$$\Rightarrow -\frac{dy_i}{dx} = \sum_{\substack{j=1\\j\neq i}}^{n} \frac{K_{ij}}{RT}\left(y_j N_i - y_i N_j\right) = \sum_{\substack{j=1\\j\neq i}}^{n} \frac{1}{CD_{ij}}\left(y_j N_i - y_i N_j\right) \quad (8.4)$$

$$N_i = y_i \sum_{j=1}^{n} N_j - C D_{i\,mix}\frac{dy_i}{dx} \rightarrow (8.5)$$

So, n components and. Secondly, N minus one binary mixture. So, from contribution from all these binary pairs will have to taken in the account. So, this equation eight point two for this multi component mixture we can write as minus RT d C i d x will be equal to summation over j is equal to one to n j not equal to i K i j C j N i minus C i N j . So, now, divides both sides by C N R T. So, from where we can write minus d y i d x would be equal to summation over j is equal to one to N j not equal to i K i j divided by RT y j N i minus y i N j which is equal to we can write summation over j is equal to one j not equal to i to N 1 by C d i j from the definition of diffusivity we can substitute y j N i minus y i N j. So, this is equation number 8.4.

Now, this equation 8.3 this equation which we have obtained this we can apply for multicomponent mixture and we can write n i is equal to y i summation over j equal to one to N N j minus C d i mix d y i d x this is equation number 8.5 now if we compare these 28.4 and 8.5 then we can obtain this d i mix the mixture diffusivity.

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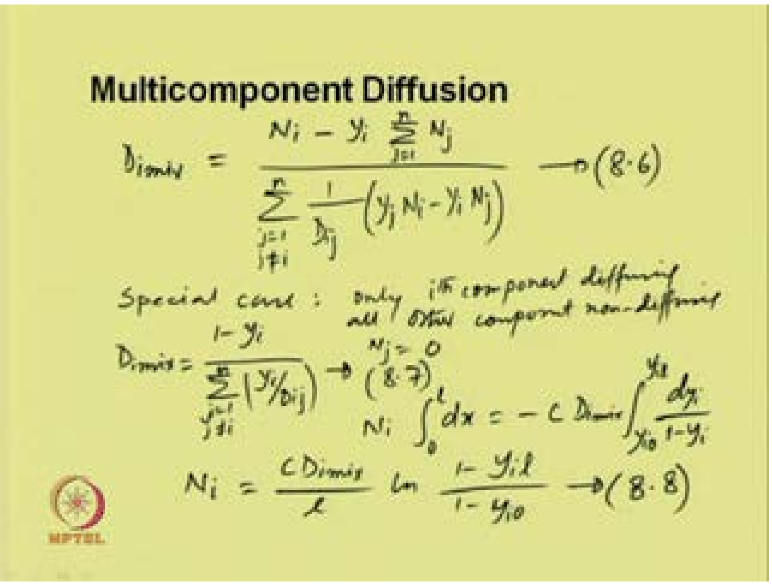

Multicomponent Diffusion

$$D_{i\,mix} = \frac{N_i - y_i \sum_{j=1}^{n} N_j}{\sum_{j=1,\, j\neq i}^{n} \frac{1}{D_{ij}}\left(y_j N_i - y_i N_j\right)} \longrightarrow (8.6)$$

Special case : only i^{th} component diffusing
all other component non-diffusing

$N_j = 0$

$$D_{i\,mix} = \frac{1 - y_i}{\sum_{j=1,\, j\neq i}^{n} \left(y_j / D_{ij}\right)} \rightarrow (8.7)$$

$$N_i \int_0^l dx = -C\, D_{i\,mix} \int_{y_{i0}}^{y_{il}} \frac{dy_i}{1-y_i}$$

$$N_i = \frac{C\, D_{i\,mix}}{l} \ln \frac{1 - y_{il}}{1 - y_{i0}} \longrightarrow (8.8)$$

So, the mixture diffusivity d i mix we can write N i minus y i ith components summation over j is equal to one to N N j divided by summation over j is equal to one to N j naught equal to i 1 by d i j binary diffusivity into y j N i minus y i N j. So, this is 8.6. So, this is the mixture diffusivity now if we considered a special case only i-th component diffusing all other component non diffusing.

So, n j will be zero. So, we can write for this special case d i mix will be equal to one minus y i divided by summation over j equal to 1 j naught equal to i to N y i divided by d i j. So, this is equation number 8.7 now if we take this equation number 8.5 and the diffusion path length is l then we can integrate this equation. So, we will have n i integral 0 to l d x will be equal to minus C d i mix integral y i 0 to y i l d y i divided by 1 minus y i. So, from this we can obtain N i is equal to C d i mix by l l n 1 minus y i l divided by 1 minus y i 0 this is equation 8.8.

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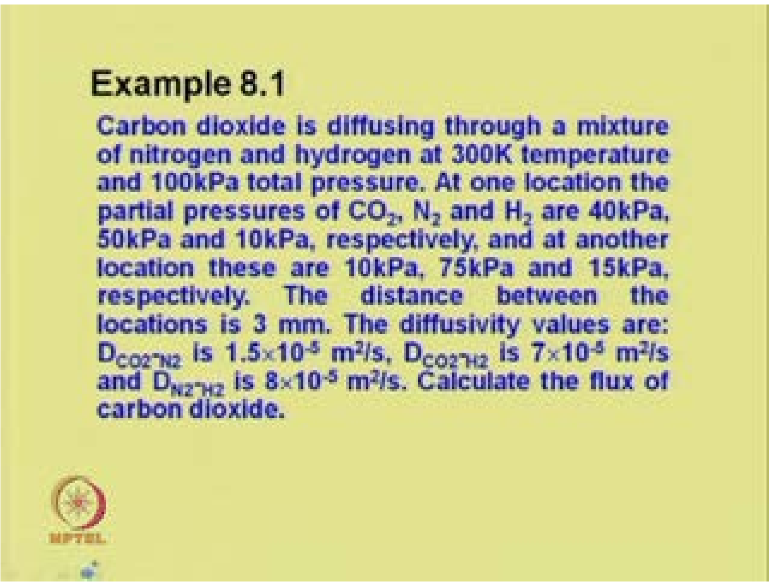

Example 8.1

Carbon dioxide is diffusing through a mixture of nitrogen and hydrogen at 300K temperature and 100kPa total pressure. At one location the partial pressures of CO_2, N_2 and H_2 are 40kPa, 50kPa and 10kPa, respectively, and at another location these are 10kPa, 75kPa and 15kPa, respectively. The distance between the locations is 3 mm. The diffusivity values are: D_{CO2-N2} is 1.5×10^{-5} m²/s, D_{CO2-H2} is 7×10^{-5} m²/s and D_{N2-H2} is 8×10^{-5} m²/s. Calculate the flux of carbon dioxide.

Now let us consider a simple example carbon dioxide is diffusing through a mixture of nitrogen and hydrogen at three hundred kelvin temperature and hundred kilo pascal total pressure at one location the partial pressure of CO2 nitrogen hydrogen are 40 kilopascal 50 kilopascal and ten kilopascal respectively and at another locations these components C02 is 10 kilopascal nitrogen is 75 kilopascal and hydrogen is 15 kilopascal.

The distance between these 3 locations is 3 millimeter the diffusivity values are given this Co2 nitrogen is 1.5 into 10 raise to minus 5 meter square per second this C02 hydrogen is 7 into 10 to the power minus 5 meter square per second and d n 2 hydrogen is 8 into 10 to the power minus 5 meter square per second at the respective temperature and pressure calculate the flux of carbon dioxide.

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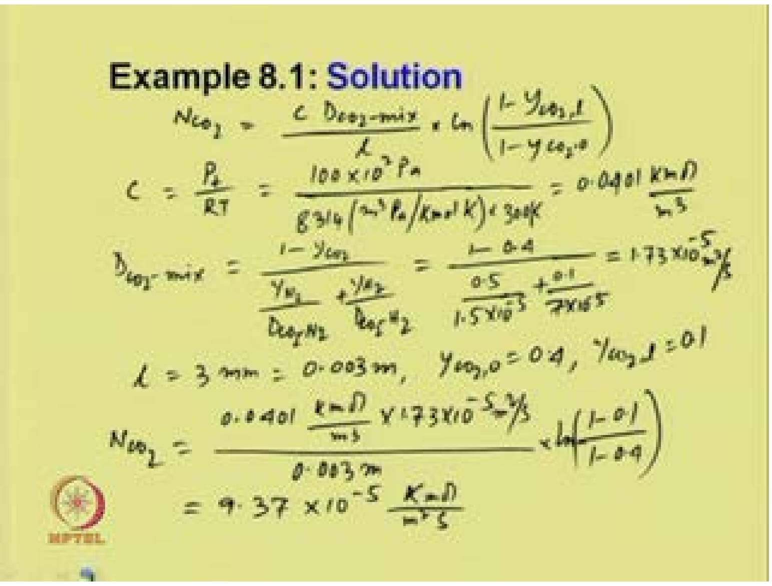

Example 8.1: Solution

$$N_{CO_2} = \frac{c\, D_{CO_2\text{-mix}}}{l} \times \ln\left(\frac{1-y_{CO_2,l}}{1-y_{CO_2,0}}\right)$$

$$c = \frac{P_t}{RT} = \frac{100\times10^{3}\,Pa}{8314\,(m^3 Pa/Kmol\,K)\times 300K} = 0.0401\,\frac{Kmol}{m^3}$$

$$D_{CO_2\text{-mix}} = \frac{1-y_{CO_2}}{\frac{y_{N_2}}{D_{CO_2\text{-}N_2}}+\frac{y_{H_2}}{D_{CO_2\text{-}H_2}}} = \frac{1-0.4}{\frac{0.5}{1.5\times10^{-5}}+\frac{0.1}{7\times10^{-5}}} = 1.73\times10^{-5}\,m^2/s$$

$$l = 3\,mm = 0.003\,m,\quad y_{CO_2,0} = 0.4,\quad y_{CO_2,l} = 0.1$$

$$N_{CO_2} = \frac{0.0401\,\frac{Kmol}{m^3}\times1.73\times10^{-5}\,m^2/s}{0.003\,m}\times\ln\left(\frac{1-0.1}{1-0.4}\right)$$

$$= 9.37\times10^{-5}\,\frac{Kmol}{m^2 s}$$

Now we know N CO2 we have to calculate C D CO2 mix divided by l into l N 1 minus y CO2 l by 1 minus y CO2 0 so C is equal to p T by R T. So, p is 100 kilopascal into 10 to power 2 Pascal and RT is given R is 8314 meter cube Pascal per K mol Kelvin and into 300 Kelvin temperature.

So, it is point naught 4 naught 1 K mol per meter cube now this CO2 mix since only component CO2 is diffusing and all other component are stagnant. So, we consider this ci mix this equation will be valid one minus y CO 2 by y N 2 by d CO2 N2 plus y H 2 by DCO2 H 2. So, which will be equal to 1 minus 0.4 divided by at location 1 divided by 0.5 for nitrogen divided by 1.5 into 10 to the power minus 5 plus 0.1 divided by 7 into 10 to the power minus 5. So, this is 1.73 into 10 to the power minus 5 meter square per second l is given which is three millimeter is equal to point naught naught 0.3 meter and y CO2 naught is 0.4 and y CO2 l is 0.1. So, the flux NCO2 we can calculate point naught four naught one K mol per meter cube into 1.73 into 10 to the power minus 5 meter square per second divided by point naught naught 0.3 meter into l n 1 minus 0.1 divided by 1 minus 0.4.

So, this will give around 9.37 into 10 to the power minus 5 K mol per meter square second. So, now, we will consider diffusivity in solids the diffusivity in solids is relatively less compared to the other two phases like diffusivity in gases and in liquids from liquids it will around 1000 times less and from compared to gases it is around 10,000 times less.

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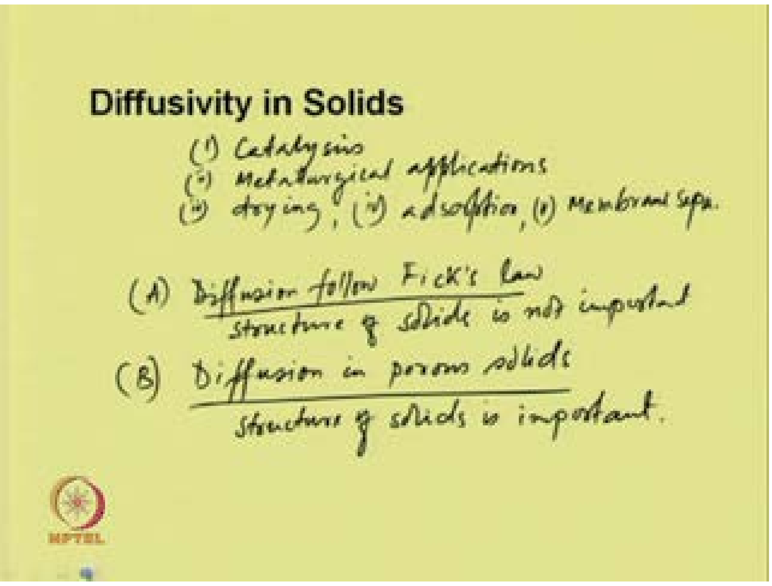

Diffusivity in Solids

(i) Catalysis
(ii) Metallurgical applications
(iii) drying, (iv) adsorption, (v) Membrane sepa.

(A) Diffusion follow Fick's law
structure of solids is not important

(B) Diffusion in porous solids
structure of solids is important.

And diffusivity values is important for catalysis catalysis and it also important for metallurgical application drying adsorption and also membrane separation membrane separation. So, as we have seen the diffusivity simple in the case of gases and liquids it is not as simple as in case of the solids the diffusion in solids we can broadly classify into two different categories one is diffusion follow Fick’s law in this case the structure of the solid is not important of solids is not important and the second case is diffusion in porous solids diffusion in porous solids where structure solids is important.

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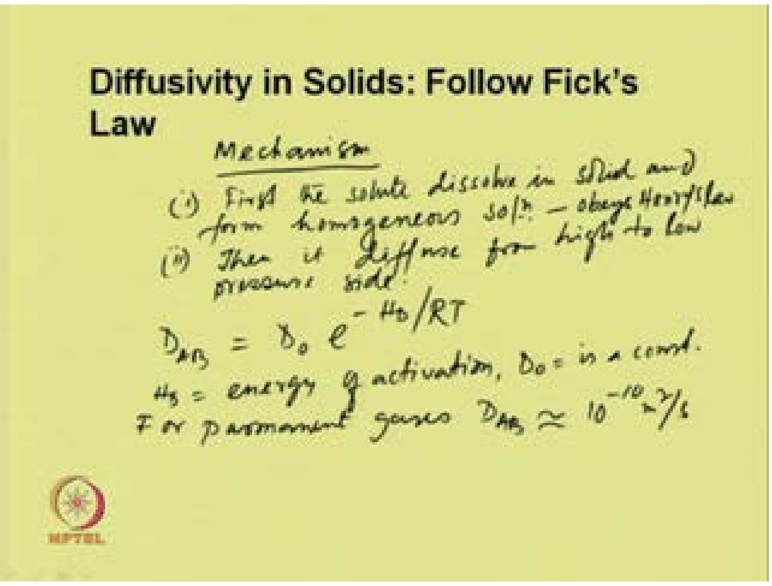

Diffusivity in Solids: Follow Fick's Law

Mechanism

(i) First the solute dissolve in solid and form homogeneous sol^n – obeys Henry's law

(ii) Then it diffuse from high to low pressure side.

$$D_{AB} = D_0 e^{-H_D/RT}$$

H_D = energy of activation, D_0 = is a const.

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

So, first let us consider the diffusion follow Fick's law in this case the phenomena is like this the components first dissolved in the solids and then it diffuse. So, the mechanism in this case is first the solute dissolves in solids and form homogeneous solution and then it diffuse from high to low pressure side and also when it dissolves from the solution it obeys henry's law.

The diffusivity can be expressed by Arrhenius relation type in case of polymers and other solids where it founds the homogeneous solutions particularly in polymers d A B we can define denote e to the power minus s D by RT where S D is the energy of activation activation and d naught is a constant and particularly for permanent gases the diffusivity values is approximately ten to the power minus ten meter square per second.

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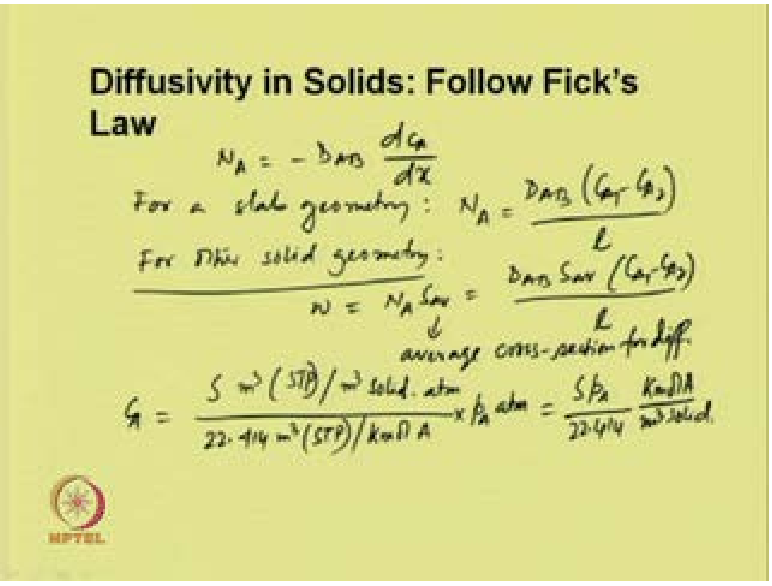

Diffusivity in Solids: Follow Fick's Law

$$N_A = -D_{AB}\frac{dc_A}{dx}$$

For a slab geometry: $N_A = \frac{D_{AB}(c_{A1}-c_{A2})}{l}$

For other solid geometry:

$$w = N_A S_{av} = \frac{D_{AB} S_{av}(c_{A1}-c_{A2})}{l}$$

$\downarrow$ average cross-section for diff.

$$c_A = \frac{S\ m^3(STP)/m^3\ solid.atm}{22.414\ m^3(STP)/kmol\ A} \times p_A\ atm = \frac{S p_A}{22.414}\ \frac{kmol\ A}{m^3\ solid}$$

Now if the diffusivity is independent of concentration and the bulk flow then steady state molar flux in the x directions we can derive by Fick's law N A will be minus d A B d C A d x where d A B is the diffusivity of component d A through the solids for a slag geometry we can write if we integrate the thickness of l of the slag.

So, it will be d A B C A 1 minus C A two divided by l where C A and C A 2 are the concentration at the two different locations for other solid geometry this we can write w will be N A s average which is equal to d A B s average C A 1 minus C A 2 by l s average is the average cross section for diffusion section for diffusion now diffusion co-efficient in the solids is not depend on the pressure on the surface of the solids which is outside on the surface of the solids for example,

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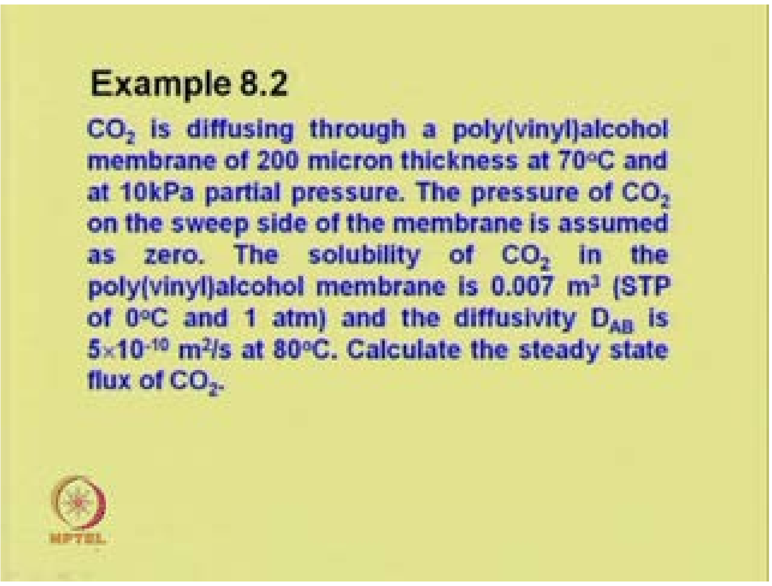

Example 8.2

CO_2 is diffusing through a poly(vinyl)alcohol membrane of 200 micron thickness at 70°C and at 10kPa partial pressure. The pressure of CO_2 on the sweep side of the membrane is assumed as zero. The solubility of CO_2 in the poly(vinyl)alcohol membrane is 0.007 m^3 (STP of 0°C and 1 atm) and the diffusivity D_{AB} is 5×10^{-10} m^2/s at 80°C. Calculate the steady state flux of CO_2.

If C O2 is diffusing through a rubber or any polymer materials the diffusivity or diffusion co-efficient would be independent on the partial pressure of CO2 on the surface, but the solubility of CO2 into the rubber or into the polymer will depend on the partial pressure of CO2 in the surface or it is directly proportional.

So, the solubility and the concentration we can directly relate with C A the concentration of the solute in the solids can be defined by solubility meter cube STP meter cube solid into atmosphere divided by twenty two point four one four meter cube STP per K mol a into partial pressure of a in atmosphere which will be SPA by 22.414 K mol a by meter cube solid now let us take an example the CO2 is diffusing through a polyvinyl alcohol membrane of 200 micron thickness at 70 degree centigrade and at 10 kilopascal partial pressure the pressure of CO2 on the sweep side of the membrane is assumed as 0 the solubility of CO2 in the polyvinyl alcohol is given and the diffusivity of d A bis also given at the temperature calculate the steady state flux.

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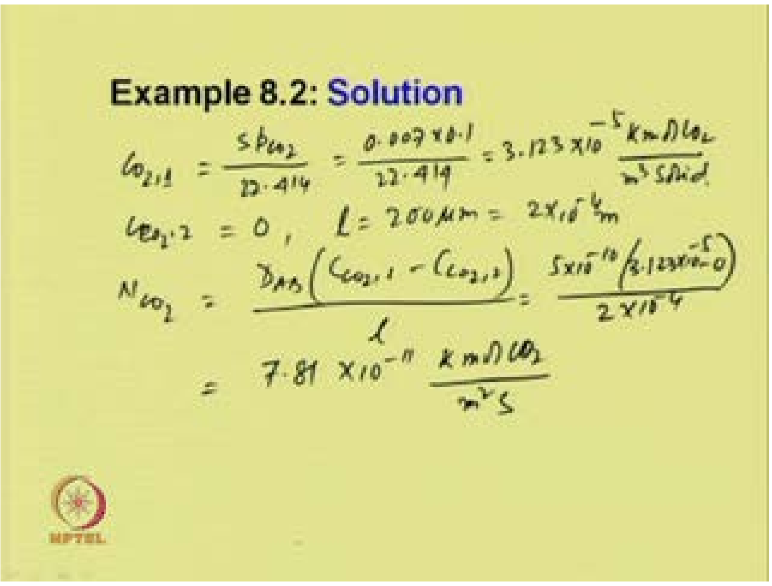

Example 8.2: Solution

$$C_{CO_2,1} = \frac{S p_{CO_2}}{22.414} = \frac{0.007 \times 0.1}{22.414} = 3.123 \times 10^{-5} \frac{\text{kmol CO}_2}{\text{m}^3 \text{ solid}}$$

$$C_{CO_2,2} = 0, \quad l = 200 \mu m = 2 \times 10^{-4} m$$

$$N_{CO_2} = \frac{D_{AB}\left(C_{CO_2,1} - C_{CO_2,2}\right)}{l} = \frac{5 \times 10^{-10}\left(3.123 \times 10^{-5} - 0\right)}{2 \times 10^{-4}}$$

$$= 7.81 \times 10^{-11} \frac{\text{kmol CO}_2}{m^2 s}$$

So, we can calculate CO2 at 1 in 1 side that is fit side will be s p CO2 by 22.414 is equal to point naught naught 7 into 0.1 by 22.414 is equal to 3.123 into 10 to the power minus 5 K mol CO2 per meter cube solid now CO2 at 2 that is on the sweep side is taken as 0 assumed as 0 and l is given as 200 micron which 2 into 10 to the power minus 4 meter. So, we can calculate flux NCO2 will be d A B CO21 C CO2 at 2 divided by l which is equal to 5 into 10 to the power minus 10 into 3.123 into 10 to the power minus 5 minus 0 divided by 2 into 10 to the power minus 4. So, it will be 7.81 into 10 to the power minus 11 K mol CO2 per meter square second.

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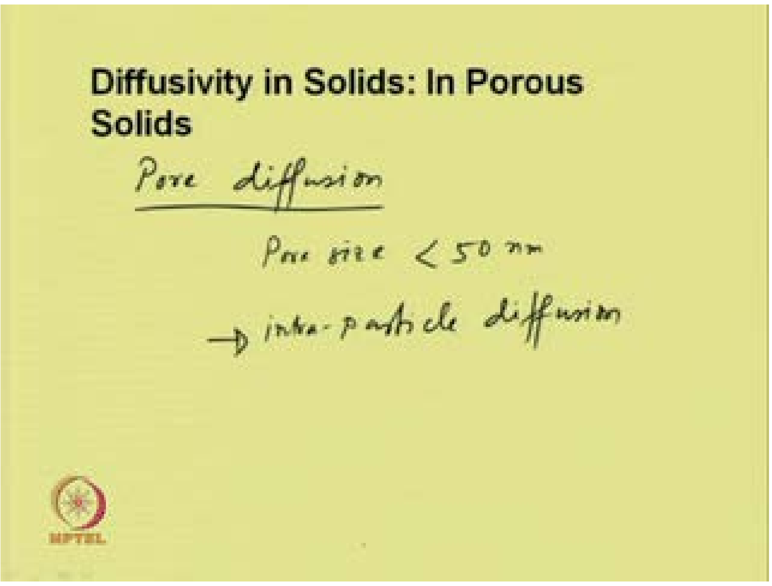

Diffusivity in Solids: In Porous Solids

Pore diffusion

Pore size < 50 nm

→ intra-particle diffusion

Now let us consider diffusion in porous solids if we consider porous solids then the structure of the pores is very important and this is particularly for catalytic reactor where we can have the diffusivity inside the pore or adsorbed surface on the catalyst.

So, if we considered pore diffusion then at low pressure the collisions of the gas molecules will be less and the mean free path of the travelling molecules will be higher. So, pore diffusion first we will consider pore diffusion. So, if the mean free path of the molecules at low pressure are higher then the diameter of the passage in that case there will be a collisions between the molecules and the pore wall and that will be very significant amount and the diffusion occurs due to these collisions is known as the Knudsen diffusion and this occurs when the pore size below 50 nano meter and very much important for intra particle diffusion.

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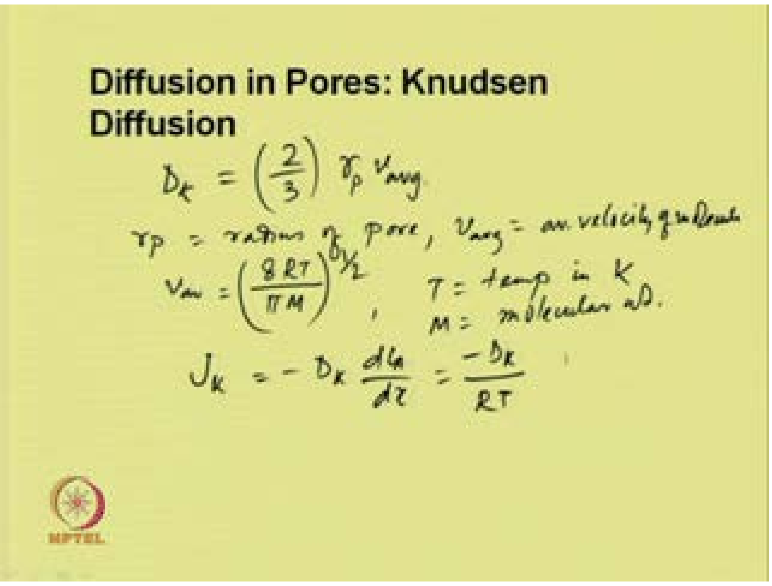

Diffusion in Pores: Knudsen Diffusion

$$D_K = \left(\frac{2}{3}\right) r_p v_{avg}$$

r_p = radius of pore, v_{avg} = av. velocity of molecule

$$v_{av} = \left(\frac{8RT}{\pi M}\right)^{1/2}, \quad T = \text{temp in K}, \quad M = \text{molecular wt.}$$

$$J_K = -D_K \frac{dC_A}{dx} = \frac{-D_K}{RT}$$

So, the simple equations can be derived for the Knudsen diffusivity as proposed based on the kinetic theory of gases is d K is equal to 2 by third r p into v average. So, r p is radius of pore and v average is the average velocity of the molecule velocity of molecule and this v average we can obtain from the kinetic theory of gases is 8 RT by pi m to the power half where T is the temperature in Kelvin and M is the molecular weight. Now, the Knudsen diffusivity can be obtained similar to the Fick’s law j K will be minus d K d C A d x is equal to minus d K by RT d p A d x.

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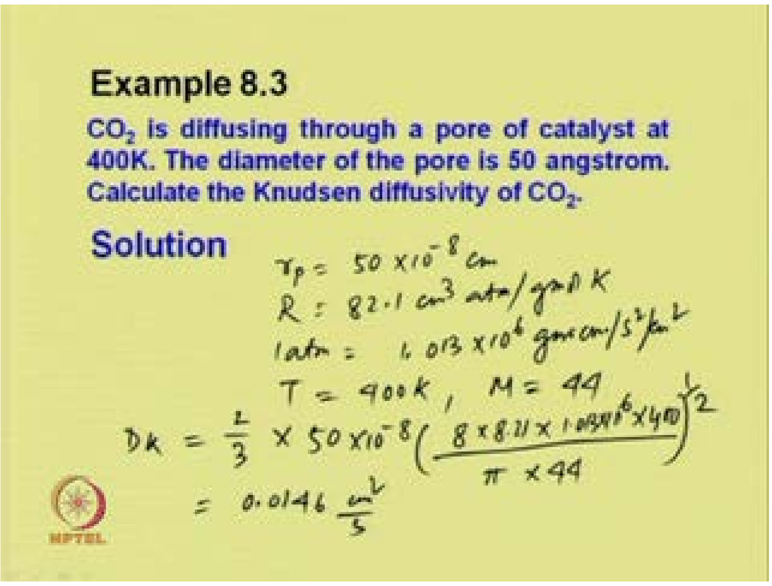

Example 8.3

CO_2 is diffusing through a pore of catalyst at 400K. The diameter of the pore is 50 angstrom. Calculate the Knudsen diffusivity of CO_2.

Solution

$r_p = 50 \times 10^{-8}$ cm

$R = 82.1$ cm^3 atm/gmol K

1 atm = 1.013×10^6 gm cm/s^2/cm^2

$T = 400$ K, $M = 44$

$$D_K = \frac{2}{3} \times 50 \times 10^{-8} \left(\frac{8 \times 8.21 \times 1.013 \times 10^6 \times 400}{\pi \times 44} \right)^{1/2}$$

$$= 0.0146 \ \frac{cm^2}{s}$$

Now let us take very simple examples CO2 is diffusing through a pore of catalyst at 400 kelvin the diameter of the pore is 50 angstrom calculate the Knudsen diffusivity of CO2 the given values are r p is 50 into 10 to the power of minus 8 centimeter r is equal to 82.1 centimeter cube atmosphere per gram mol Kelvin 1 atmosphere is equal to 1.0 naught 13 into 10 to the power 6 gram centimeter per second square per centimeter square and T is given 400 Kelvin and M is given which is 45. So, d K will be 2 by 3 into 50 into 10 raise to minus 8 multiplied by 8 into 8 point 2 1 into 1 point naught 1310 to the power 6 into 400 divided by pi into 45 to the power half. So, this will give you around point naught 146 centimeter square per second.

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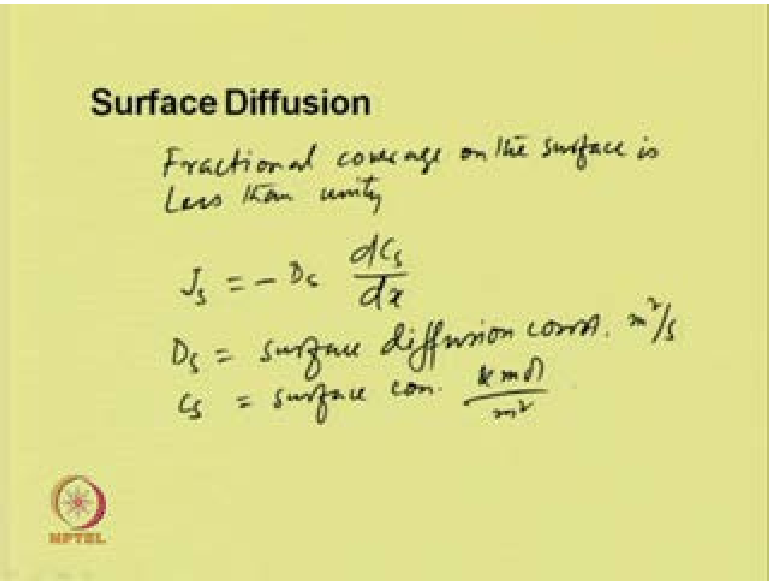

Surface Diffusion

Fractional coverage on the surface is less than unity

$$J_s = -D_s \frac{dC_s}{dx}$$

D_s = surface diffusion const. m^2/s

C_s = surface con. $\frac{kmol}{m^2}$

Now the surface diffusion this is particularly important when the adsorb molecules on the surface are diffuse due to the concentration gradient if the fractional coverage on the surface is less than unity in that case some molecules which have higher energy can jump to the vacant sides or empty sides and this mechanism is known as the hopping mechanism and the flux due to the surface diffusion can be represented by Fick’s law which is J S is equal to minus D S D C s D x where D s is surface diffusion constant in meter square per second and C S is the surface concentration in K mol per meter square this is end of lecture 8 of module one after this we will start with the lecture of module two that is on mass transfer coefficients.

Thank you.