Mass Transfer Operations - I
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Diffusion Mass Transfer - II
Lecture – 08
Multicomponent diffusion and diffusivity in solids

Welcome to the 8th lecture of module 1 of mass transfer operation. In this module we are discussing Diffusion Mass Transfer. Before going to this lecture let us have recap on our previous lecture.

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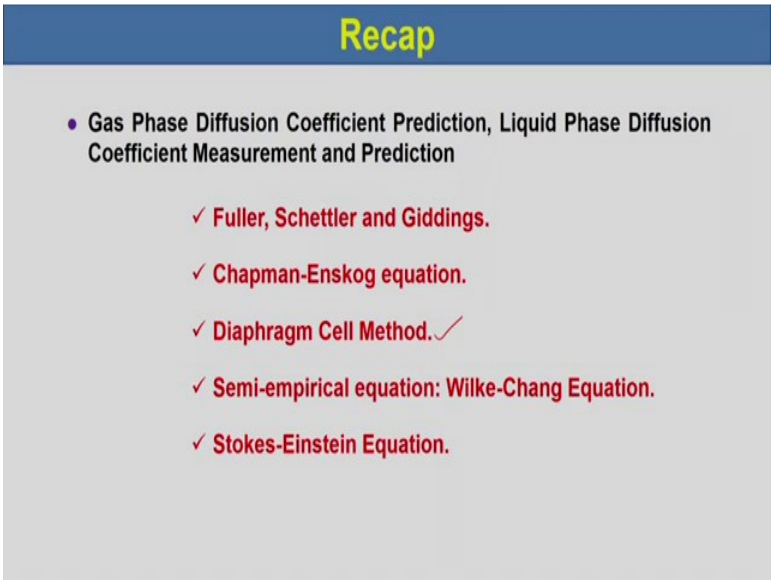

Recap

- Gas Phase Diffusion Coefficient Prediction, Liquid Phase Diffusion Coefficient Measurement and Prediction
  - ✓ Fuller, Schettler and Giddings.
  - ✓ Chapman-Enskog equation.
  - ✓ Diaphragm Cell Method.
  - ✓ Semi-empirical equation: Wilke-Chang Equation.
  - ✓ Stokes-Einstein Equation.

On our previous lecture we have discussed mainly gas phase diffusion coefficient prediction, liquid phase diffusion coefficient measurement and its prediction. So, for gas phase diffusion coefficient prediction we have used fuller equations and also Chapman equations. Then for the liquid phase diffusion coefficient measurements we have considered two method, one is the diaphragm cell method and the second one we have considered the semi empirical equation which is Wilke-Chang equation.

Then we have finally, you Stokes Einstein equation for the determination of the diffusion coefficient in the liquid phase.

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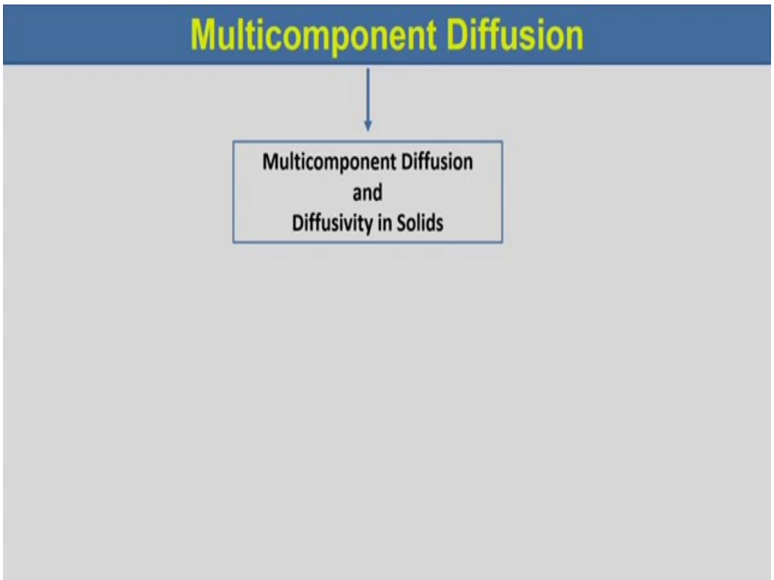

Multicomponent Diffusion

Multicomponent Diffusion
and
Diffusivity in Solids

In this lecture we will consider multi component diffusion and the diffusivity of the solid. So, first we will consider multi component diffusion and then we will consider diffusivity in solids.

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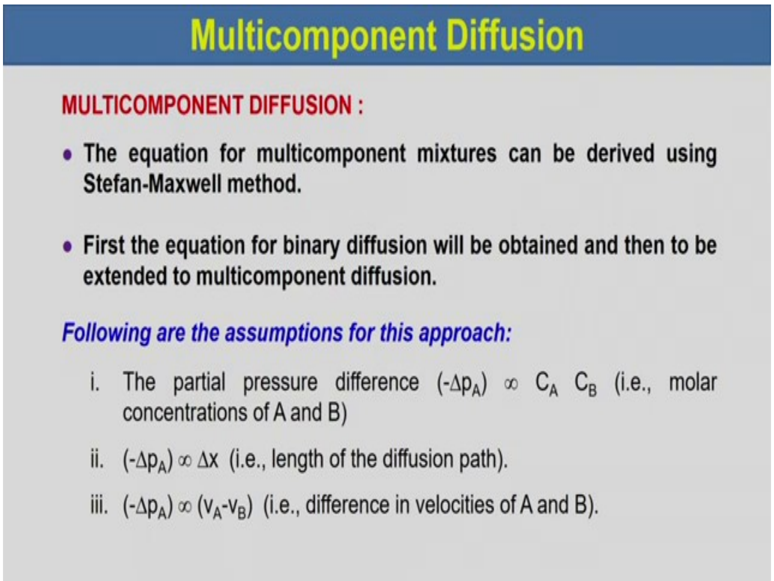

Multicomponent Diffusion

MULTICOMPONENT DIFFUSION :

- **The equation for multicomponent mixtures can be derived using Stefan-Maxwell method.**
- **First the equation for binary diffusion will be obtained and then to be extended to multicomponent diffusion.**

Following are the assumptions for this approach:

i. The partial pressure difference $(-\Delta p_A) \infty C_A C_B$ (i.e., molar concentrations of A and B)

ii. $(-\Delta p_A) \infty \Delta x$ (i.e., length of the diffusion path).

iii. $(-\Delta p_A) \infty (v_A - v_B)$ (i.e., difference in velocities of A and B).

Multi component diffusion: in this case the equation for multi component mixture can be derived using Stefan Maxwell method. First the equation for binary diffusion will be obtained and then to be extended to the multi component diffusion.

Now, while deriving the equation for the binary diffusion coefficient and then to the multi component systems are the following assumptions would be taken, the first one is the partial pressure difference that is delta P A is proportional to the C A and C B, C A and C B are the molar concentration of A and B. So, delta P A partial pressure difference is proportional to the concentration C A into C B. Second one is the partial pressure difference is proportional to the length of the diffusion path which is delta x. And the third one is the partial pressure difference is proportional to the difference in the diffusion velocities of A and B which is v A minus v B.

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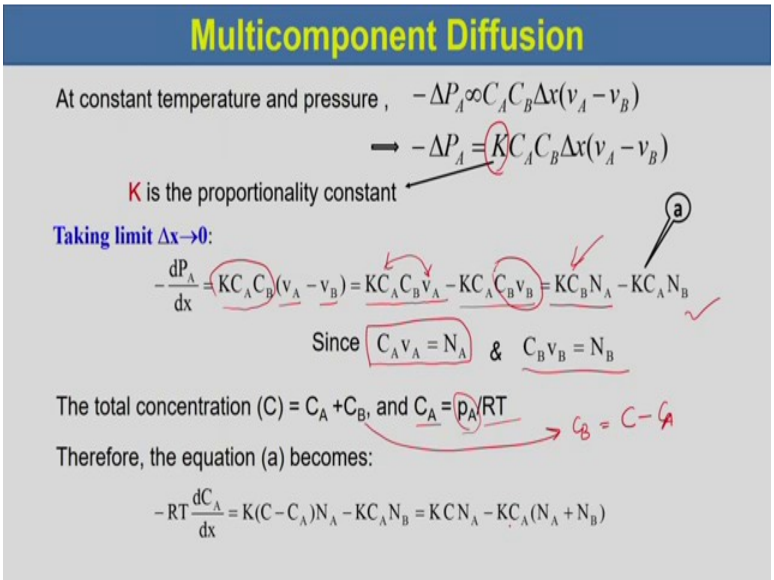

Multicomponent Diffusion

At constant temperature 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 is the proportionality constant

Taking limit $\Delta x \to 0$:

$$-\frac{dP_A}{dx} = KC_AC_B(v_A - v_B) = KC_AC_Bv_A - KC_AC_Bv_B = KC_BN_A - KC_AN_B \quad (a)$$

Since $\boxed{C_Av_A = N_A}$ & $C_Bv_B = N_B$

The total concentration (C) = $C_A + C_B$, and $C_A = p_A/RT$ $\rightarrow C_B = C - C_A$

Therefore, the equation (a) becomes:

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

So, from this assumption we can write at constant temperature and pressure minus delta P A is proportional to C A into C B into delta x into v A minus v B. Now if we equate these two with a proportionality constant K we can write minus delta P A would be equal to K into C A into C B into delta x into v A minus v B, here this K is the proportionality constant. Now if we take limit delta x tends to 0 we can write minus d P A d x would be equal to K into C A C B into v A minus v B. Now if you just multiply K C A C B with v A and with v B we can write K C A C B into v A minus K into C A into C B into v B.

Now, as we know C A into v A is N A. So, we can substitute C A and v A this two terms with N A. So, we can write K C B N A and similarly C B into v B is N B. So, in this case if we substitute C B v B with N B we will have minus K C A N B. So, this is equation 1. Now we know the total concentration C would be equal to C A plus C B for two component system and if we consider ideal gas we can write C A would be equal to P A by R T, that is partial pressure of component A divided by R is the universal gas constant into the temperature T.

Therefore the equation a becomes this equation, we can write minus R T d C A d x would be equal to K into C minus C A into N A. So, we have substituted over here this C B from here we can write C minus C A. So, which is substituted over in this equation A. So, we will have K into C minus C A into N A minus K C A N B; now if you multiply we can write K c N A minus K C A into N A plus N B.

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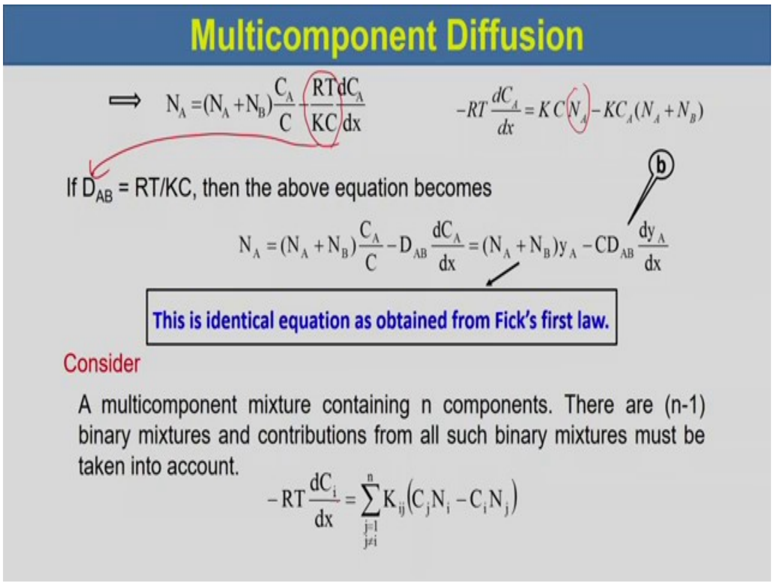

Multicomponent Diffusion

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

$$-RT\frac{dC_A}{dx} = KCN_A - KC_A(N_A + N_B)$$

If $D_{AB} = RT/KC$, then the above equation becomes

ⓑ

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

This is identical equation as obtained from Fick's first law.

Consider

A multicomponent mixture containing n components. There are (n-1) binary mixtures and contributions from all such binary mixtures must be taken into account.

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

So, from this now if we rearrange we can write flux N A this one would be equal to N A plus N B into C A by C minus R T by K C into d C A d x. Now if we consider D AB would be equal to R T by K C then this equation we can write. So, this part is D AB. So, then we can write N A would be equal to N A plus N B, C A by C minus D AB D C A D x which would be equal to N A plus N B C A by C each.

No concentration of A divided by the total concentration. So, it is the mole fraction of component A. So, we can write N A plus N B into Y A minus C into D AB d y A d x. So, this is identical equation as obtained from Fick's first law. Now if we consider a multi component mixture containing n components. If there are n components then there would be n minus 1 binary mixture and contribution from all such binary mixture must be taken into account. So, you can write minus R T d C i d x would be equal to summation over j is equal to 1 j not equal to i to n K i j into C j into N i minus C i into N j, this is for multi component system.

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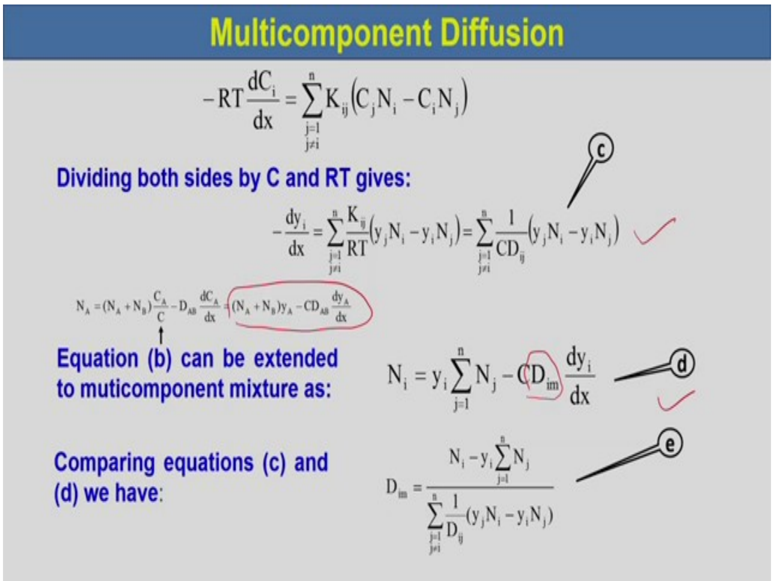

Multicomponent Diffusion

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

Dividing both sides by C and RT gives:

$$-\frac{dy_i}{dx}=\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{K_{ij}}{RT}\left(y_jN_i-y_iN_j\right)=\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{1}{CD_{ij}}\left(y_jN_i-y_iN_j\right)$$

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

Equation (b) can be extended to muticomponent mixture as:

$$N_i=y_i\sum_{j=1}^{n}N_j-CD_{im}\frac{dy_i}{dx}$$

Comparing equations (c) and (d) we have:

$$D_{im}=\frac{N_i-y_i\sum_{j=1}^{n}N_j}{\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{1}{D_{ij}}\left(y_jN_i-y_iN_j\right)}$$

Now, if we divide this equation both sides by C and RT, it gives minus d y i by d x would be equal to summation over j is equal to 1 j not equal to i to n K i j by R T into y j into N i minus i y into N j and we can write this as summation over j is equal to 1, j not equal to i to n 1 by CD i j into y j N i minus y i N j. So, the K i j by R T we can write 1 by CD i j. So, this is equation C, now equation B which you have derived before this one N A would be N A plus N B into y A minus C into DAB into d y A d x can be extended to multi component mixture as.

Now, N i would be equal to y i summation over j is equal to 1 to N into N j minus CD i mix. So, this is the diffusivity of the mixture into d y i by d x. If there are two components we have two flux N A plus N B similarly. So, N j represents the flux of different components. Now comparing equation c and d these two equation if we compare. So, we can write D i m would be equal to N i minus y i summation over j is equal to 1 to n divided by summation over j is equal to 1, j not equal to i to n 1 by Di j into y j N i minus y i N j.

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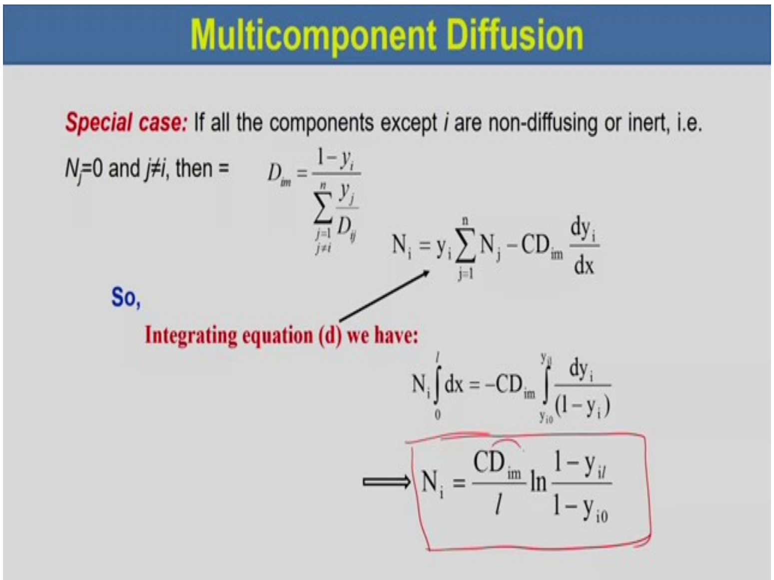

Multicomponent Diffusion

Special case: If all the components except *i* are non-diffusing or inert, i.e.

N_j=0 and *j*≠*i*, then = $D_{im} = \frac{1-y_i}{\sum\limits_{\substack{j=1 \\ j\neq i}}^{n} \frac{y_j}{D_{ij}}}$

$$N_i = y_i\sum_{j=1}^{n} N_j - CD_{im}\frac{dy_i}{dx}$$

So,

Integrating equation (d) we have:

$$N_i\int_0^l dx = -CD_{im}\int_{y_{i0}}^{y_{il}} \frac{dy_i}{(1-y_i)}$$

$$\Longrightarrow \boxed{N_i = \frac{CD_{im}}{l}\ln\frac{1-y_{il}}{1-y_{i0}}}$$

Now, if we considered a special case, if all the components except i are non-diffusing or inert. So, only i is diffusing species or other components are non diffusing or inert that is N j would be equal to 0 and j not equal to i, then D i m would be equal to 1 minus y i divided by summation over j is equal to 1 j not equal to i to n y j by D i j. So, integrating equation d we have this is equation d N i is equal to y i summation over j is equal to 1 to n N j minus C D i m d y i by d x.

So, integrating this equation we have N i integral 0 to l d x would be equal to minus CD i m integral y i 0to y i l d y i divided by 1 minus y i. So, if we integrate we will get N i would be equal to CD i m by l ln 1 minus y i l divided by 1 minus y i i 0. So, this is the equation of the flux for know multi component systems having the know diffusivity of the mixture taken into consideration to calculate the flux.

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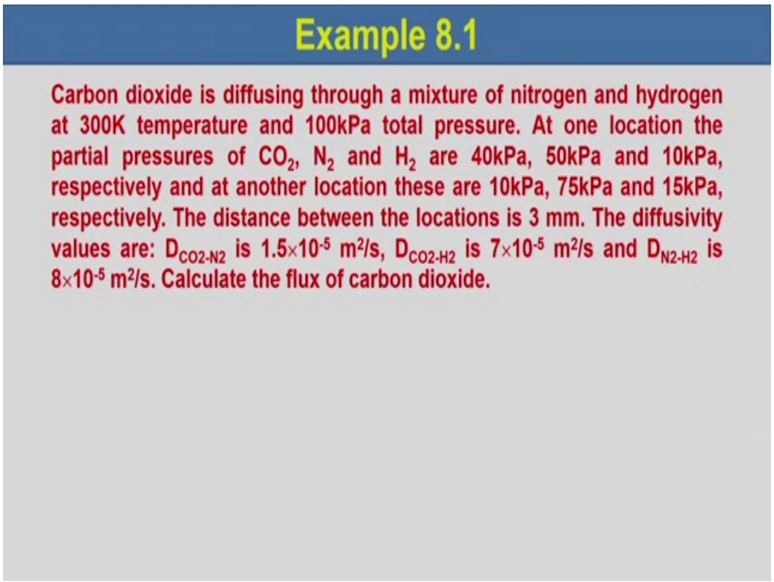

Example 8.1

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: $D_{CO2\text{-}N2}$ is 1.5×10^{-5} m^2/s, $D_{CO2\text{-}H2}$ is 7×10^{-5} m^2/s and $D_{N2\text{-}H2}$ is 8×10^{-5} m^2/s. Calculate the flux of carbon dioxide.

Now, let us consider one example. Carbon dioxide is diffusion through a mixture of nitrogen and hydrogen at 300 Kelvin temperature and 100 kilo Pascal total pressure. Now at one location the partial pressure of carbon dioxide nitrogen and hydrogen are 40 kilo Pascal, 50 kilo Pascal and 10 kilo Pascal respectively and at another location these are 10 kilo Pascal, 75 kilo Pascal and 15 kilo Pascal respectively. The distance between the two location is 3 millimeter. The diffusivity values are given D CO 2 N 2 is 1.5 into 10 to the power minus 5 meter square per second D CO 2 hydrogen is 7 into 10 to the power minus 5 meter square per second and D nitrogen hydrogen is 8 into 10 to the power minus 5 meter square per second.

Now, calculate the flux of carbon dioxide. Since this is an example of multi component systems. So, we have to use equation for to calculate the mixture diffusivity and then we can calculate the flux.

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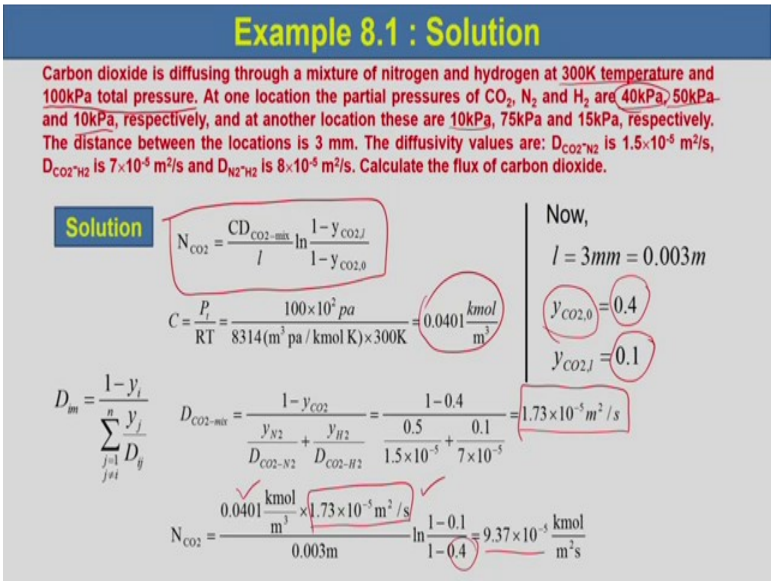

Example 8.1 : Solution

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.

Solution

$$N_{CO2} = \frac{CD_{CO2-mix}}{l}\ln\frac{1-y_{CO2,l}}{1-y_{CO2,0}}$$

$$C = \frac{P_t}{RT} = \frac{100\times10^2\ pa}{8314(m^3\ pa/kmol\ K)\times300K} = 0.0401\frac{kmol}{m^3}$$

Now,

$$l = 3mm = 0.003m$$

$$y_{CO2,0} = 0.4$$

$$y_{CO2,l} = 0.1$$

$$D_{im} = \frac{1-y_i}{\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{y_j}{D_{ij}}}$$

$$D_{CO2-mix} = \frac{1-y_{CO2}}{\frac{y_{N2}}{D_{CO2-N2}}+\frac{y_{H2}}{D_{CO2-H2}}} = \frac{1-0.4}{\frac{0.5}{1.5\times10^{-5}}+\frac{0.1}{7\times10^{-5}}} = 1.73\times10^{-5}m^2/s$$

$$N_{CO2} = \frac{0.0401\frac{kmol}{m^3}\times1.73\times10^{-5}m^2/s}{0.003m}\ln\frac{1-0.1}{1-0.4} = 9.37\times10^{-5}\frac{kmol}{m^2s}$$

So, the flux equation which we have derived is for carbon dioxide over here is N CO 2 would be equal to C into DCO 2 mixture divided by l into l n 1 minus Y CO 2 at l divided by one minus Y CO 2 at 0. Now, if we consider ideal gas then C would be equal to P t by R T the system is at atmospheric pressure 100 kilo Pascal.

So, P t is 100 into 10 to the power 2 Pascal divided by R is 8314 meter cube Pascal per kilo mole Kelvin into T is 300 Kelvin which is given. So, we can calculate concentration C would be equal to 0.0401 kilo mole per metre cube. Now we know the mixture diffusivity equation which is equal to 1 minus y i divided by summation over j is equal to 1 j not equal to i y i divided by D i j. So, we can calculate D CO 2 mixture would be equal to 1 minus y CO 2 divided by y j would be the other two components that is y N2 divided by D CO 2 N 2 plus y H 2 divided by D CO 2 H 2 which is equal to 1 minus 0.4 divided by 0.5 by 1.5 into 10 to the power minus 5 plus 0.1 divided by 7 into 10 to the power minus 5.

So, here in one location it is given as 40 percent or 40 kilo Pascal carbon dioxide. So, its mole fraction is 0.4 and for nitrogen it is 0.5 mole fraction and for hydrogen it is 0.1 mole fractions and then the diffusivity of CO 2 nitrogen is 1.5 into 10 to the power minus 5 meter square per second and diffusivity of CO 2 hydrogen is 7 into 10 to the power minus 5 meter square per second. So, if we substitute these values we will get DCO 2 mixture would be equal to 1.73 into 10 to the power minus 5 meter square per second.

Now length which is you know between the two location is 3 millimeter which is 0.003 meter and y CO 2 at 0 is 0.4, the mole fraction of CO 2 at location one is 0.4 and at location 2 is 0.1, which is know 10 kilo Pascal at other location for carbon dioxide.

So, with this if we substitute in this equation, we can get CH we have calculated which is 0.0401 kilo mole per meter cube into DCO 2 mixture which we have calculated 1.73 into 10 to the power minus 5 meter square per second. So, which is substituted here divided by the length which is 0.003 metre into l n 1 minus y CO 2 l which is 0.1 divided by 1 minus y CO 2 at 0 which is 0.4 which is substituted here. So, we can calculate the flux is 9.37 into 10 to the power minus 5 kilo mole per meter square second. So, this is how we can calculate the flux for a multi component system.

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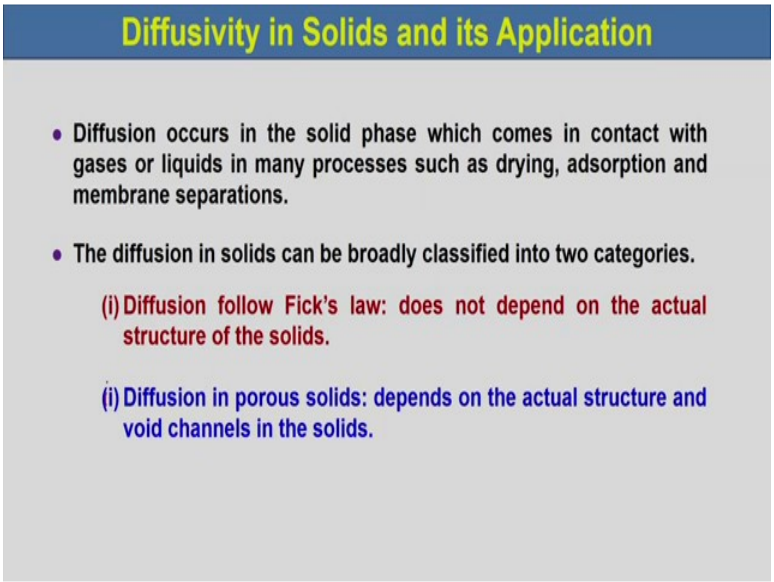

Diffusivity in Solids and its Application

- Diffusion occurs in the solid phase which comes in contact with gases or liquids in many processes such as drying, adsorption and membrane separations.
- The diffusion in solids can be broadly classified into two categories.
  (i) Diffusion follow Fick's law: does not depend on the actual structure of the solids.

  (i) Diffusion in porous solids: depends on the actual structure and void channels in the solids.

Now, we will discuss diffusivity in solids and its application. Diffusion occurs in solid phase which comes in contact with gases or liquids in many processes, such as you can see drying, adsorption and membrane separations. The diffusion in solids can be broadly classified into two major categories the first one is diffusion follow Fick's law, that is does not depend on the actual structure of the solid and the second one is diffusion in porous solids which depend on the actual structure and void channels in the solids.

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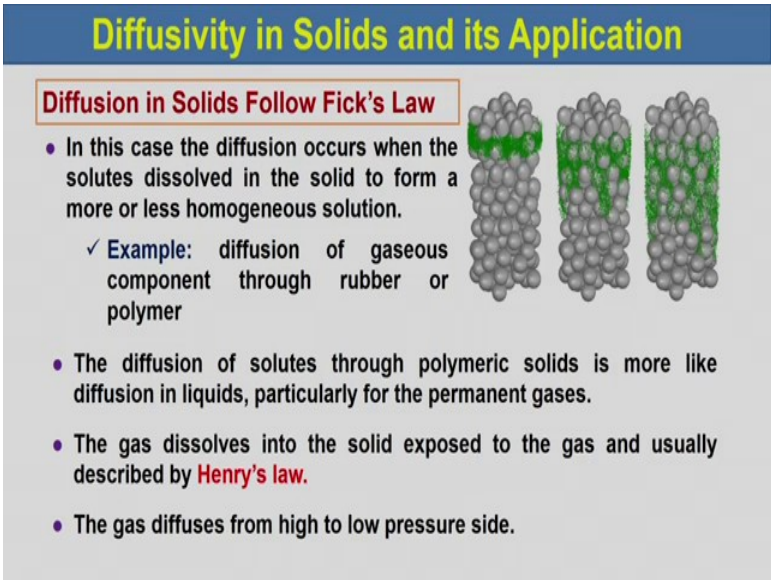

Diffusivity in Solids and its Application

Diffusion in Solids Follow Fick's Law

- In this case the diffusion occurs when the solutes dissolved in the solid to form a more or less homogeneous solution.
  - ✓ **Example:** diffusion of gaseous component through rubber or polymer
- The diffusion of solutes through polymeric solids is more like diffusion in liquids, particularly for the permanent gases.
- The gas dissolves into the solid exposed to the gas and usually described by **Henry's law.**
- The gas diffuses from high to low pressure side.

Now, diffusion in solids follow Fick's law the first one. Like if you see that in this case the diffusion occurs when the solutes dissolved in the solid to form a more or less homogenous solutions. For example, diffusion of gaseous component through rubber or polymer. So, it diffuses into the polymer and makes a almost a homogenous solution. The diffusion of solutes through polymeric solids is more like diffusion in liquids particularly for permanent gases. Gas dissolves into the solid exposed to the gas and usually described by Henry's law. So, in this case the gas which will diffuse to the solid materials forms the homogenous solutions and the solubility of the gases into the solid obeys Henry's law. The gas diffuses from high to low pressure side.

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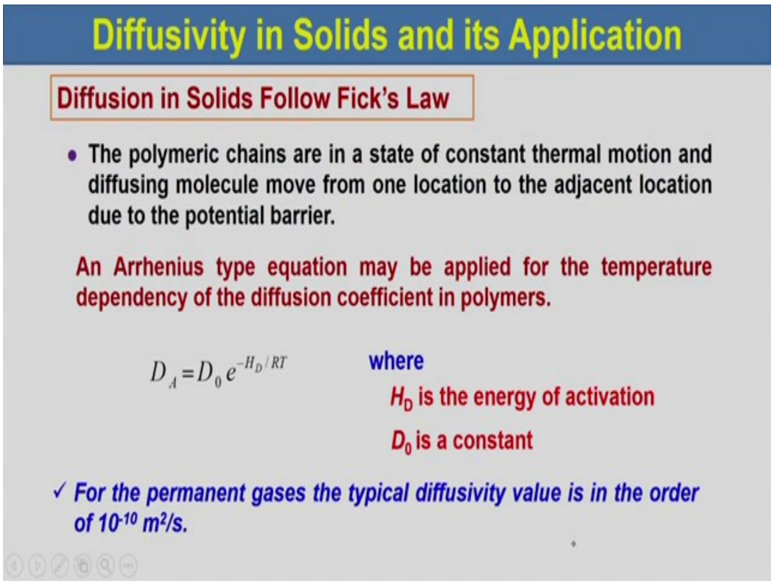

Diffusivity in Solids and its Application

Diffusion in Solids Follow Fick's Law

- The polymeric chains are in a state of constant thermal motion and diffusing molecule move from one location to the adjacent location due to the potential barrier.

An Arrhenius type equation may be applied for the temperature dependency of the diffusion coefficient in polymers.

$$D_A = D_0 e^{-H_D/RT}$$

where

H_D is the energy of activation

D_0 is a constant

✓ *For the permanent gases the typical diffusivity value is in the order of 10^{-10} m²/s.*

The polymeric chains are in a state of constant thermal motion and diffusing molecule move from one location to the adjacent location due to the potential barrier. An Arrhenius type equation may be applied for the temperature dependency of the diffusion coefficient in polymers. So, this is the relation of diffusion coefficient which is a Arrhenius type of relation, where we can write D A would be equal to D naught e to the power minus H D by R T. Here H D is the energy of activation, D naught is a constant and R and T, R is the universal gas constant and T is any temperature. For the permanent gases the typical diffusivity value is in the order of 10 to the power minus 10 metre square per second.

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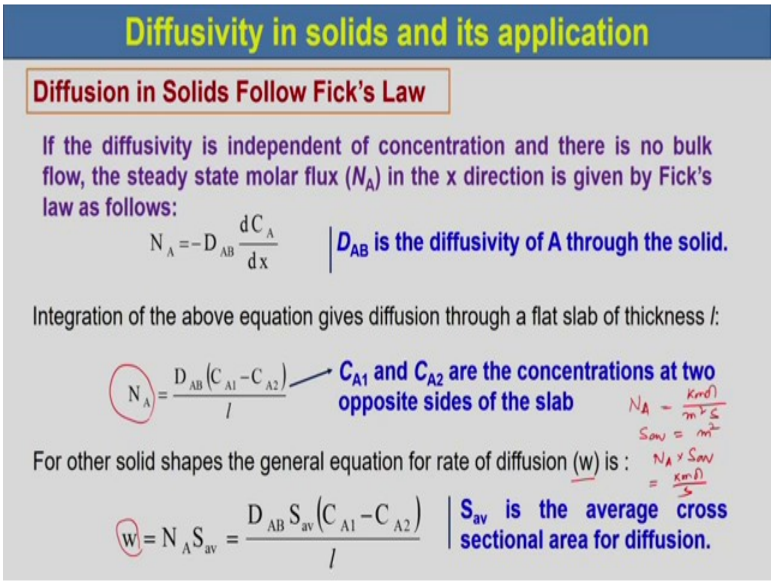

Diffusivity in solids and its application

Diffusion in Solids Follow Fick's Law

If the diffusivity is independent of concentration and there is no bulk flow, the steady state molar flux (N_A) in the x direction is given by Fick's law as follows:

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

D_{AB} is the diffusivity of A through the solid.

Integration of the above equation gives diffusion through a flat slab of thickness *l*:

$$N_A = \frac{D_{AB}(C_{A1}-C_{A2})}{l}$$

C_{A1} and C_{A2} are the concentrations at two opposite sides of the slab

$N_A - \frac{kmol}{m^2 s}$

$S_{av} = m^2$

For other solid shapes the general equation for rate of diffusion (w) is :

$N_A \times S_{av}$

$= \frac{kmol}{s}$

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

S_{av} is the average cross sectional area for diffusion.

So, this is the typical value, but it varies from 10 to the power minus 5 metre square per second to 10 to the power minus 13 metre square per second. Now, if the diffusivity is independent of concentration and there is no bulk flow, the steady state molar flux N A in the x direction is given by Fick's law as follows. N A would be equal to minus D AB d C A d x. Here D AB is the diffusivity of A through the solid. Now integration of this equation gives diffusion through a flat slab of thickness l. So, if we integrate this with a thickness of the slab of solid materials l, we can write N A would be equal to D AB C A 1 minus C A 2 divided by l. Here C A 1 and C A 2 are the concentration at two opposite sides of the slab.

For other solid shapes general equation for rate of diffusion is which is defined by w would be equal to N A into S average would be equal to D AB into S average into C A 1 minus C A 2 by l. So, S average is the average cross sectional area for diffusion. So, basically this w has a unit of mole or kilo mole per second and N A is the flux which is kilo mole per metre square second. So, if you take N A which unit is K mole per metre square second and S average the cross sectional area is in the unit of metre square. So, if we multiply N A into S average, it would be kilo mole per second. So, this is the rate of diffusion or diffusion rate in terms of kilo mole per second.

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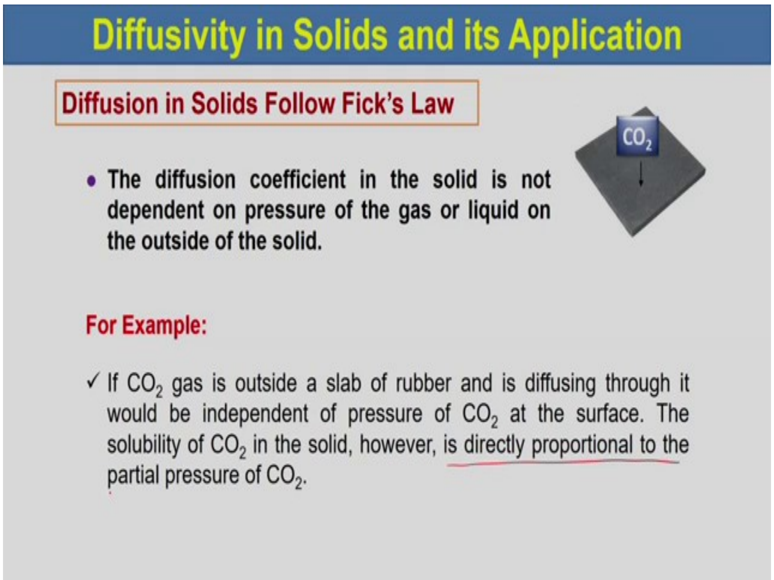

Diffusivity in Solids and its Application

Diffusion in Solids Follow Fick's Law

- The diffusion coefficient in the solid is not dependent on pressure of the gas or liquid on the outside of the solid.

For Example:

✓ If CO_2 gas is outside a slab of rubber and is diffusing through it would be independent of pressure of CO_2 at the surface. The solubility of CO_2 in the solid, however, is directly proportional to the partial pressure of CO_2.

Now, diffusion in solid follow Fick's law. The diffusion coefficient in the solid is not dependent on pressure of the gas or liquid on the outside of the solid. For example, if carbon dioxide gas is outside a slab of rubber and is diffusing through it, would be independent of pressure of carbon dioxide at the surface. The solubility of carbon dioxide in the solid; however, is directly proportional to the partial pressure of carbon dioxide.

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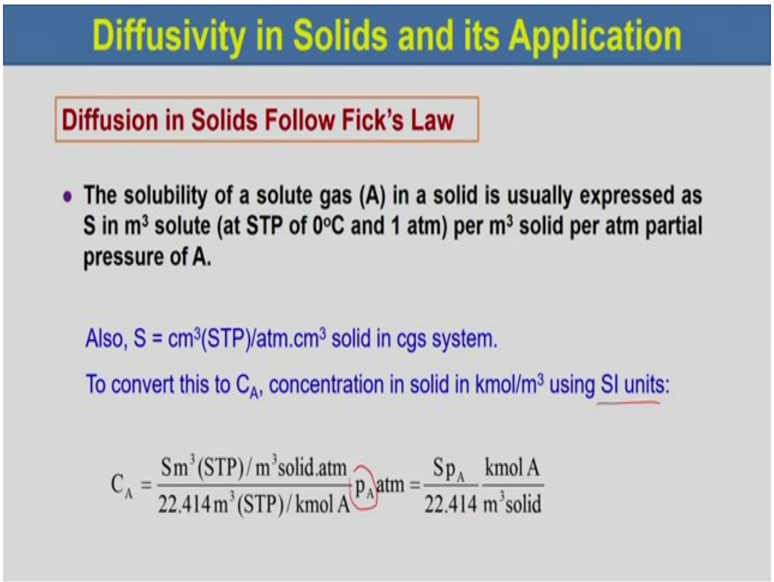

Diffusivity in Solids and its Application

Diffusion in Solids Follow Fick's Law

- **The solubility of a solute gas (A) in a solid is usually expressed as S in m^3 solute (at STP of 0^{o}C and 1 atm) per m^3 solid per atm partial pressure of A.**

Also, S = cm^3(STP)/atm.cm^3 solid in cgs system.

To convert this to C_A, concentration in solid in kmol/m^3 using SI units:

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

So, the solubility term of a solid gas A in a solid is usually expressed as S in metre cube solute at STP of 0 degree centigrade and 1 atmosphere pressure per metre cube of solid per atmosphere partial pressure of A.

So, S has the unit of centimetre cube STP per atmosphere centimetre cube of solid in CGS system. To convert these to C A that is concentration in solid in kilo mole per metre cube using SI unit, we can write C A would be equal to S metre cube STP divided by the metre cube solid into atmosphere divided by 22.414 metre cube STP divided by kilo mole of A into P A atmosphere the partial pressure of component A. So, it would be a S into P A by 22.414 kilo mole of A divided by the metre cube of solid.

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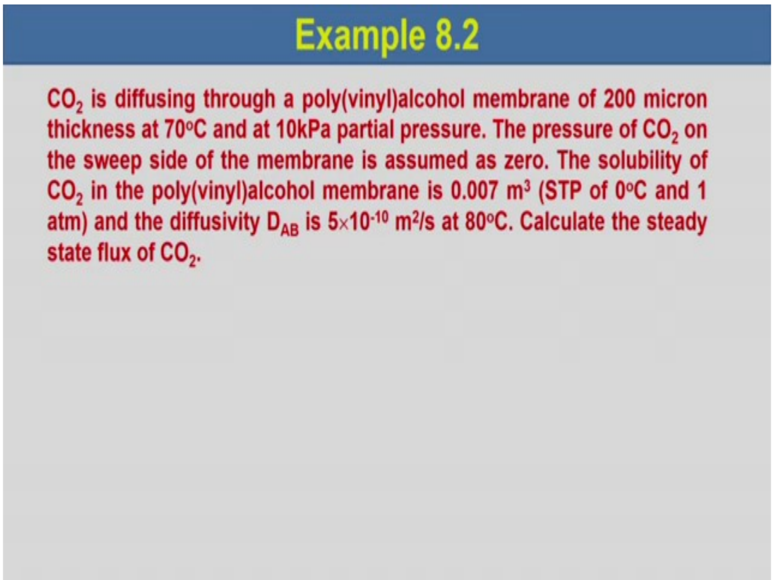

Example 8.2

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.

Now, let us consider another example, carbon dioxide is defusing through a polyvinyl alcohol membrane of 200 micron thickness at 70 degree centigrade and at 10 kilo Pascal partial pressure.

The pressure of carbon dioxide on the sweep side of the membrane is assumed as 0, the solubility of carbon dioxide in the polyvinyl alcohol membrane is 0.007 metre cube STP of 0 degree centigrade and 1 atmosphere pressure. And the diffusivity of D AB, the diffusivity of component A that is carbon dioxide into the solid is 5 into 10 to the power minus 10 metre square per second at 80 degree centigrade. Calculate the steady state flux of carbon dioxide.

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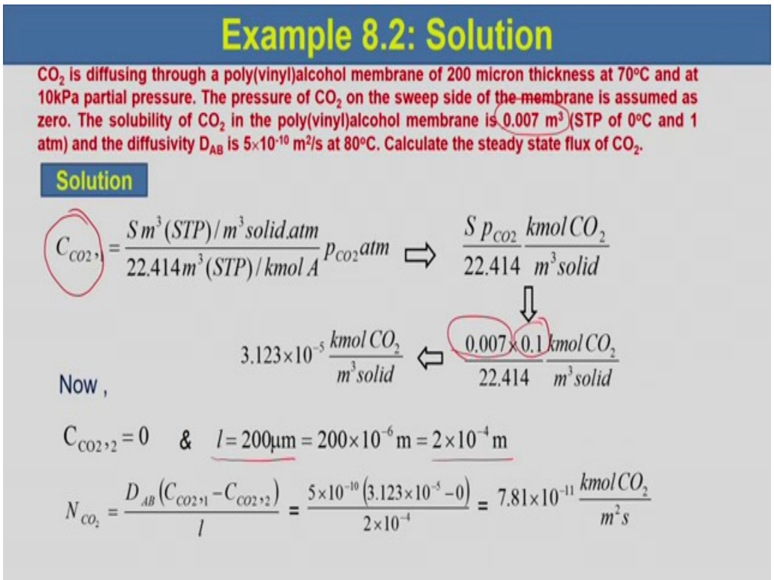

Example 8.2: Solution

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.

Solution

$$C_{CO2,1} = \frac{S\, m^3(STP)/m^3 solid.atm}{22.414 m^3(STP)/kmol\, A} p_{CO2} atm \Rightarrow \frac{S\, p_{CO2}}{22.414} \frac{kmol\, CO_2}{m^3 solid}$$

$$\Downarrow$$

$$3.123 \times 10^{-5} \frac{kmol\, CO_2}{m^3 solid} \Leftarrow \frac{0.007 \times 0.1}{22.414} \frac{kmol\, CO_2}{m^3 solid}$$

Now ,

$$C_{CO2,2} = 0 \quad \& \quad l = 200 \mu m = 200 \times 10^{-6} m = 2 \times 10^{-4} m$$

$$N_{CO_2} = \frac{D_{AB}(C_{CO2,1} - C_{CO2,2})}{l} = \frac{5 \times 10^{-10}(3.123 \times 10^{-5} - 0)}{2 \times 10^{-4}} = 7.81 \times 10^{-11} \frac{kmol\, CO_2}{m^2 s}$$

So, we can write C carbon dioxide that is concentration of carbon dioxide at side 1 is equal to S metre cube STP by metre cube solid into atmosphere divided by 22.414 metre cube STP per kilo mole A into p CO 2 atmosphere.

So, if we substitute over here we can write S is 0.007 metre cube. So, 0.007 and then the partial pressure is 10 kilo Pascal which is point 1 divided by 22.414 kilo mole carbon dioxide per metre cube solid. So, this would be equal to 3.123 into 10 to the power minus 5 kilo mole carbon dioxide per metre cube solid. So, we have calculated the concentration of carbon dioxide. Now at 2 that is on the other side the concentration of carbon dioxide is 0 because it is considered no sweep side pressure is 0 and the thickness l is 200 micron. So, we can write 200 into 10 to the power minus 6 metre which is 2 into 10 to the power minus 4 metre.

Now, if you substitute these values in the flux equation, we will have diffusivity of carbon dioxide into the solid which is 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 which is equal to 7.81 into 10 to the power minus 11 kilo mole carbon dioxide per metre square second.

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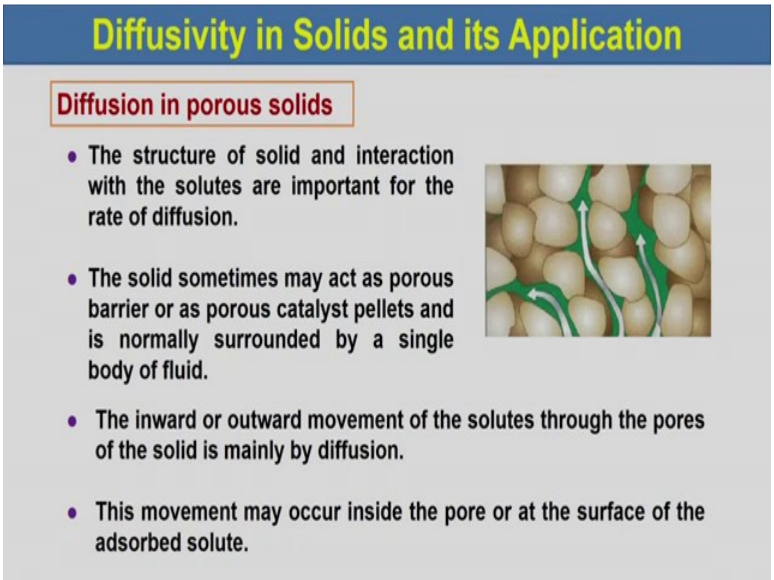

Diffusivity in Solids and its Application

Diffusion in porous solids

- The structure of solid and interaction with the solutes are important for the rate of diffusion.
- The solid sometimes may act as porous barrier or as porous catalyst pellets and is normally surrounded by a single body of fluid.
- The inward or outward movement of the solutes through the pores of the solid is mainly by diffusion.
- This movement may occur inside the pore or at the surface of the adsorbed solute.

Now, diffusion in porous solid. So, if we have the solid materials which is porous in nature, the structure of solid and interactions with the solutes are important for the rate of diffusion. The solid sometimes may act as porous barrier or as porous catalyst palate and is normally surrounded by a single body of fluid. The inward or outward movement of the solutes through the pores of the solid is mainly by diffusion. This moment may occur inside the pore or at the surface of the adsorbed solute.

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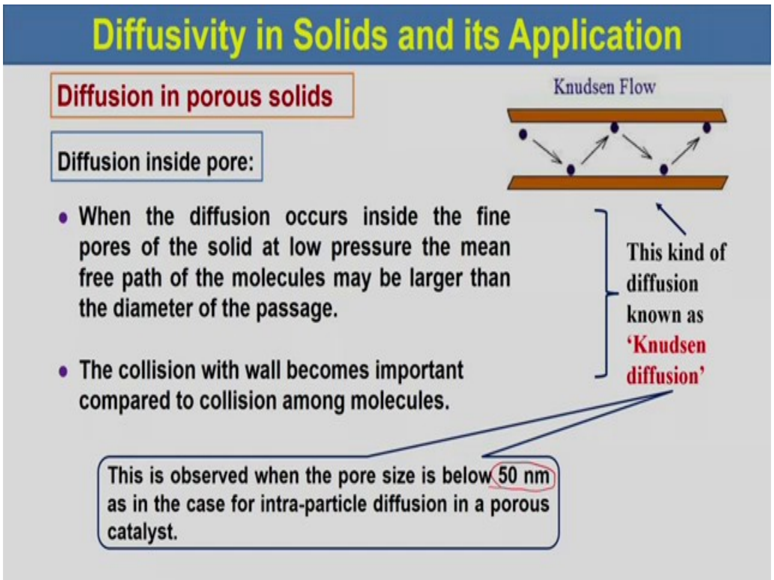

Diffusivity in Solids and its Application

Diffusion in porous solids

Knudsen Flow

Diffusion inside pore:

- When the diffusion occurs inside the fine pores of the solid at low pressure the mean free path of the molecules may be larger than the diameter of the passage.
- The collision with wall becomes important compared to collision among molecules.

This kind of diffusion known as 'Knudsen diffusion'

This is observed when the pore size is below 50 nm as in the case for intra-particle diffusion in a porous catalyst.

Now, diffusion inside the pore: when the diffusion occurs inside the fine pores of the solid at low pressure, the mean free path of the molecules may be larger than the diameter of the passage. The collision with wall becomes important in this case compared to the collision among the molecules. This kind of diffusion is known as the Knudsen diffusion and you can see the solid molecule passes through the channels and collide with the wall of the passage and in this case the mean free path of the molecules is larger than the diameter of the channel.

So, this we can call the Knudsen diffusion and in this case the collision with the wall is important compared to the collision among the molecules. So, this is observed when the pore size is below 50 nanometre as in the case of intra particle diffusion in a porous catalyst. So, when the diameter of the pore is smaller than 50 nanometre Knudsen diffusion becomes predominant.

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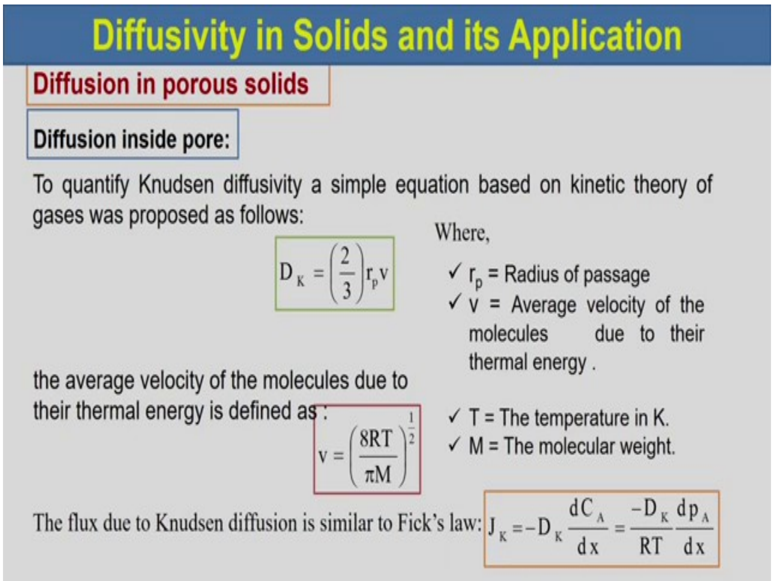

Diffusivity in Solids and its Application

Diffusion in porous solids

Diffusion inside pore:

To quantify Knudsen diffusivity a simple equation based on kinetic theory of gases was proposed as follows:

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

Where,

✓ r_p = Radius of passage

✓ v = Average velocity of the molecules due to their thermal energy.

the average velocity of the molecules due to their thermal energy is defined as:

$$v = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}}$$

✓ T = The temperature in K.

✓ M = The molecular weight.

The flux due to Knudsen diffusion is similar to Fick's law: $J_K = -D_K \frac{dC_A}{dx} = \frac{-D_K}{RT}\frac{dp_A}{dx}$

Now, to quantify Knudsen diffusivity, a simple equation based on kinetic theory of gases was proposed as follows. That is D K would be equal to 2 by 3 into r p into v where r p is the radius of the passage and v this the average velocity of the molecules due to their thermal energy.

Now this average velocity due to their thermal energy can be calculated as follows, v is equal to 8 R T by pi M to the power half where T is the temperature in Kelvin, M is the molecular weight and R is the universal gas constant. The flux due to Knudsen diffusion is similar to the Fick's law and we can write J K would be equal to minus D K D CA by d x would be equal to minus D K by R T into d P A by d x.

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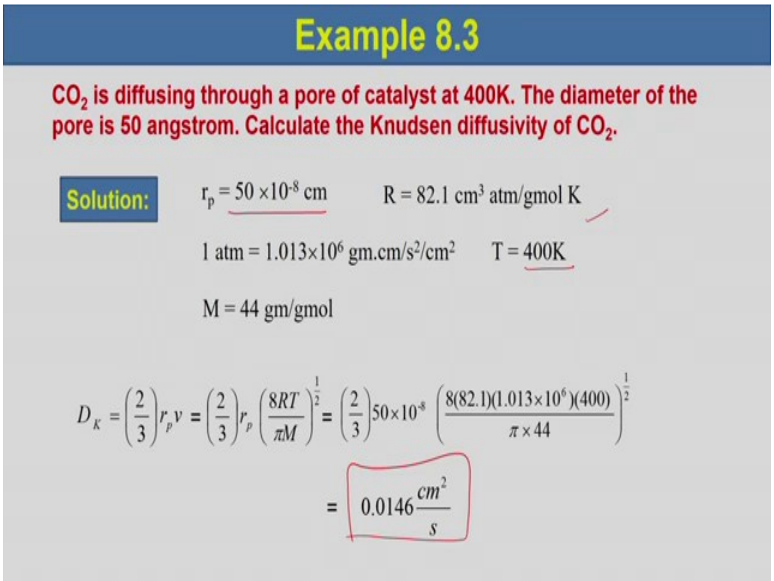

Example 8.3

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 = 400K

M = 44 gm/gmol

$$D_K = \left(\frac{2}{3}\right) r_p v = \left(\frac{2}{3}\right) r_p \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}} = \left(\frac{2}{3}\right) 50 \times 10^{-8} \left(\frac{8(82.1)(1.013 \times 10^6)(400)}{\pi \times 44}\right)^{\frac{1}{2}}$$

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

Now, let us take an example; carbon dioxide is diffusing through a pore of catalyst at 400 Kelvin. The diameter of the pore is 50 angstrom, now we need to calculate the Knudsen diffusivity of carbon dioxide.

So, r p over here the diameter of the pore is 50 angstrom. So, which is 50 into 10 to the power minus 8 centimetre; r is the universal gas constant we know 82.1 centimetre cube atmosphere per gram mole Kelvin. Now one atmosphere we can write in CGS unit 1.013 into 10 to the power 6 gram centimetre per second square per centimetre square. T is the temperature which is 400 Kelvin. Now M is equal to 44 gram per gram mole. If we use the equation for diffusivity D K would be equal to 2 by 3 into r p into v. So, now, if you substitute the equation for b which is 8 R T by pi M to the power half then it would be 2 by 3 into r p 8 R T divided by pi M to the power half. Now if you substitute it would be 2 by 3 into r p is 50 into 10 to the power minus 8 into 8 into 82.1 into 1.013 into 10 to the power 6 into 400 divided by pi into 44 to the power half. So, if we solve it, it would be 0.0146 centimetre square per second. So, this is the values of diffusivity Knudsen diffusivity through the pores.

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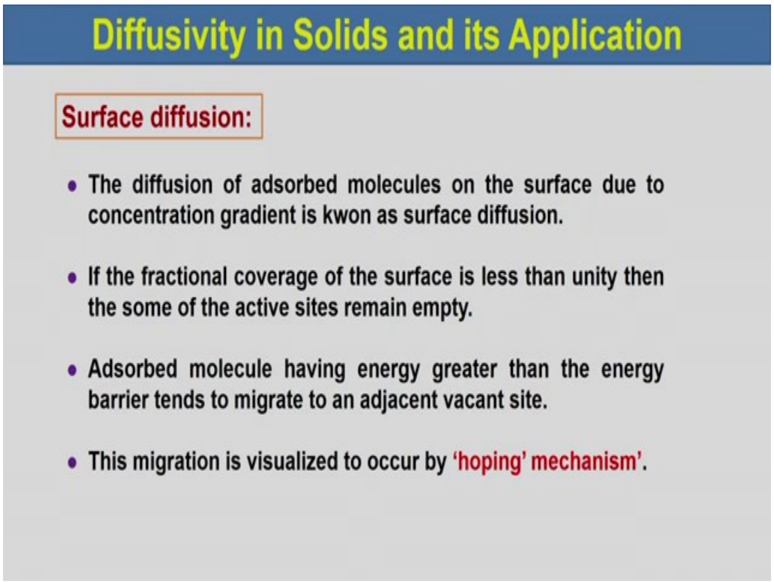

Diffusivity in Solids and its Application

Surface diffusion:

- The diffusion of adsorbed molecules on the surface due to concentration gradient is kwon as surface diffusion.
- If the fractional coverage of the surface is less than unity then the some of the active sites remain empty.
- Adsorbed molecule having energy greater than the energy barrier tends to migrate to an adjacent vacant site.
- This migration is visualized to occur by 'hoping' mechanism'.

Now, another thing is the surface diffusion. The diffusion of adsorbed molecules on the surface due to concentration gradient is known as the surface diffusion.

If the fractional coverage of the surface is less than unity, then some of the active sites remain empty. So, in that case what happens? Adsorbed molecules having energy greater than the energy barrier tends to migrate to an adjacent vacant side. So, this migration is visualized to occur by hoping mechanism. So, this type of diffusion is known as surface diffusion, where the molecules diffuse from one active site to the other active sites or adjacent active sites which are vacant, through the hoping mechanism.

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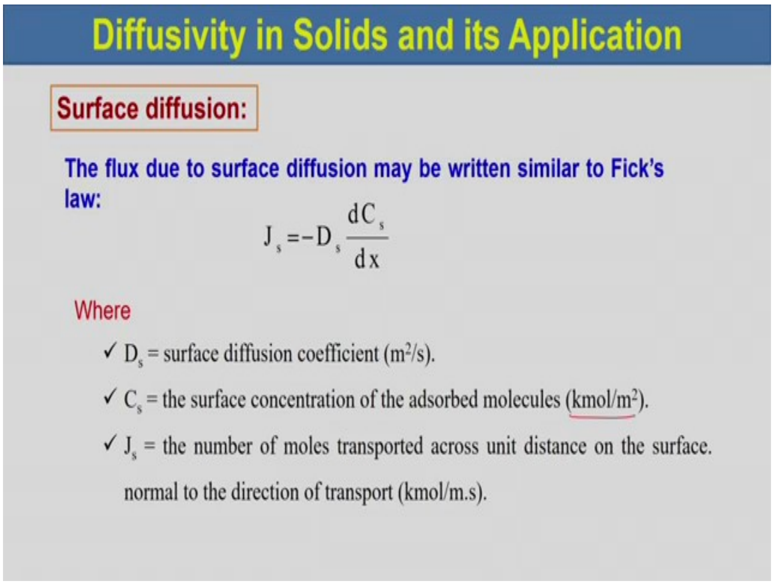

Diffusivity in Solids and its Application

Surface diffusion:

The flux due to surface diffusion may be written similar to Fick's law:

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

Where

✓ D_s = surface diffusion coefficient (m^2/s).

✓ C_s = the surface concentration of the adsorbed molecules ($kmol/m^2$).

✓ J_s = the number of moles transported across unit distance on the surface. normal to the direction of transport (kmol/m.s).

The flux due to surface diffusion may be written similar to Fick's law which is J s would be equal to minus D s into d C s by d x.

Here D s is the surface diffusion coefficient and its unit is metre square per second. C s is the surface concentration of the adsorbed molecules which is kilo mole per metre square. So, please note that the surface concentration unit compared to the bulk concentration unit. The bulk concentration we generally defined by the unit of kilo mole per metre cube, but surface concentration is defined by kilo mole per metre square, that is the unit surface area. So, J s the number of moles transported across unit distance on the surface, normal to the direction of transport is in the unit of kilo mole per metre second.

So, thank you for attending this lecture and we will discuss in the next module that is module 2 is the interface mass transfer.