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Module - 1 Diffusion Mass Transfer Lecture - 7 Diffusion coefficient: Measurement and Prediction (Part 2)

Welcome to the seventh lecture of module one which is on diffusion mass transfer. So, before going to this lecture, let us have recap on the previous lecture what we have discussed.

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Recap () Gras-phase diffusivity Measurement (A) Twin Bulb Melkod (B) Stefan Tube Melkod

In our previous lecture, we have considered the diffusion coefficient measurements and predictions. First, we have considered the gas phase diffusion coefficient measurements. As we have discussed, that there are several methods available to measure the gas-phase diffusivity, but we have considered only two simple methods to determine experimentally the gas-phase diffusivity; one is twin bulb method, and the second one we have considered is Stefan tube method. So, for both the cases we have obtained the governing equations to calculate the diffusivity from the experiments, and we have explained both the methods with relevant examples. So, in this lecture we will continue

with our discussion of gas-phase diffusivity prediction by different correlations available in the literature.

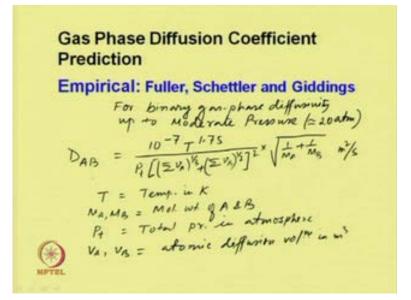
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Module 1: Lecture 7 **Diffusion Coefficient:** Measurement and Prediction (ii) Liquid-phase diffusivity prediction (iii) Liquid-phase diffusivity Measurement (iii) Liquid-phase diffusivity Arediction

In this lecture we will consider gas-phase diffusivity prediction, and then we will consider liquid-phase diffusivity measurements, and liquid-phase diffusivity prediction. Let us consider the first case gas-phase diffusivity predictions.

Although there are several experimental data available for different gaseous components, there are many components, which are required experimental data or shortage of experimental data. In those cases, instead of experimental data we can use the empirical correlations by which we can determine the diffusivity of the gas-phase components.

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A very simple, and reasonably accurate empirical equations which was suggested by Fuller, Schettler and Giddings in 1966 for binary, binary gas-phase diffusivity, gas-phase diffusivity up to moderate pressure, say up about 20 atmosphere.

The correlations they proposed is diffusivity of component A to diffusivity in B is equal to 10 to the power minus 7 T to the power 1.75 divided by P t into summation over V A to the power one-third plus summation over V B to the power one-third whole square multiplied by square root of 1 by M A plus 1 by M B and the unit in meter square per second, where T is equal to temperature in Kelvin; M A, M B, these are the molecular weights of A and B; P t, total pressure in atmosphere; V A and V B are the atomic diffusion volume in meter cube. So, the diffusivity obtained from this relation is in meter square per second.

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Example 7.1
For mixtures of carbon monoxide and hydrogen, predict the diffusivity using the fuller et al. (1966) formulae for the following conditions:
(i) at 1 atmosphere pressure and 100°C temperature
(ii) at 2 atmosphere pressure and 100°C temperature
(iii) at 1 atmosphere pressure and 200°C temperature

Now, let us take an example to calculate the diffusivity from this correlation. For example, for mixtures of carbon monoxide and hydrogen, predict the diffusivity using Fuller et al. 1966 formula for the following conditions. The first one is at 1 atmosphere pressure and 100 degree centigrade temperature; the second problem is at 2 atmosphere pressure and 100 degree centigrade temperature and the third one, at 1 atmosphere pressure, 200 degree centigrade temperature.

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Example 7.1: Solution  $b_{AB} = \frac{10^{-7} T^{175}}{P_{t} \left[ (\Xi V_{s})^{1/2} (\Xi V_{s})^{1/2} \right]^{2} \sqrt{M_{A}^{1+1}} M_{B}$ Atomic values can be obtained from Let A = CO,  $B = H_2$   $\sum v_a = 1.(C) + 1.(O) = 1.216.5 + 1.45.48$ text book MA = 1×12+1×16 = 28 Kg/Kmol Z VB = 2×H = 2×2.31= 4.62 MB = 2×1 = 2 ×g/×mol

So, let us consider the first one at 1 atmosphere presser and 100 degree centigrade temperature. We know that diffusivity D AB will be equal to 10 to the power minus 7 T to the power 1.75 divided by P t summation over V A to the power one-third plus summation over V B to the power one-third whole square and into root over bar 1 by M A plus 1 by M B. So, the atomic values, values, can be obtained from text book.

Let us consider A is equal to carbon monoxide and B is equal to hydrogen. Now, summation of V A would be 1 into carbon plus 1 into oxygen, so this will be equal to 1. The molecular volume of carbon is 16.5 plus for oxygen it is 5.48, so it will be equal to 21.98. And molecular weight of carbon monoxide M A would be 1 into 12 plus 1 into 16, would be 28 kg per kmol. Similarly, for molecular volume for V B would be 2 into hydrogen, 2 into molecular volume 2.31, it is 4.62 and M B is 2 into 1 is equal to 2 kg per kmol.

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Example 7.1: Solution  

$$T = 100^{\circ}c = (100 + 273) & x = 373 & x \\ P_{4} = 1 \text{ atm} \\ D_{AB} = \frac{10^{-7}(373)}{1 \times [(21.98)^{3} + (1.4)^{3}]^{2}} & \sqrt{\frac{1}{28} + \frac{1}{2}} & \frac{1}{3} & \frac{1}{3} \\ = 1.159 \times 10^{-4} \text{ m}^{2}/\text{s} \\ \hline D_{AB} \propto \frac{1}{P_{4}} \frac{1}{9} & \frac{D_{ABD}}{D_{AB}} = \frac{P_{4}}{P_{4}} \\ \hline \end{array}$$

The temperature is given as 100 degree centigrade, is equal to 100 plus 273, this much Kelvin, so 373 Kelvin. And P t is given 1 atmosphere, so if we substitute, D AB would be equal to 10 to the power minus 7, 373 temperature to the power 1.75 divided by 1 pressure into molecular volume of A is 21.98 to the power one-third plus, for hydrogen 4.62 to the power one-third whole square into root over 1 by 28 plus 1 by 2 meter square per second. So, this will give you 1.159 into 10 to the power minus 4 meter square per second.

Now, let us consider the second problem, that is, at 2 atmosphere and 100 degree centigrade temperature. So, for this case, since we have already determined for the same system the diffusivity at a particular temperature and pressure, there is no need to calculate the diffusion coefficient for the same system at different conditions from scratch. So, we can use the diffusion coefficient determined in the earlier problem and calculate with respect to the temperature and pressure corrections.

So, keeping all the properties same for the components in problem two, at constant temperature, which is temperature is 100 degree centigrade remains same, the diffusivity D AB from the Fullers equation is inversely proportional with the total pressure. So, we can write, at that temperature it is inversely proportional with pressure, so we can write D AB1 or D AB2 by D AB1 will be P t 1 by P t 2.

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Example 7.1: Solution  $D_{AB2} = \frac{P_{t_1}}{R_2} \times D_{AB1}$   $P_{t_1} = 1 \text{ atm} D_{AB} = 1.156 \times 10^{-14} \text{ m}^2/\text{s}$   $P_{t_1} = 2 \text{ atm} D_{AB} = 1.156 \times 10^{-14} \text{ m}^2/\text{s}$   $D_{AB2} = \frac{1}{2} \times 1.152 \times 10^{-14} \text{ m}^2/\text{s}$   $= 0.58 \times 10^{-14} \text{ m}^2/\text{s}$ (iii)  $T_2 = 200^{\circ}\text{c}, \quad P_{t_2} = 1 \text{ atm}.$   $D_{AB} \propto T^{1.75}, \quad \frac{D_{AB2}}{D_{ABM}} = \left(\frac{T_0}{T_1}\right)^{1.25}$ 

So, in this problem we can write D AB2 will be equal to P t 1 by P t 2 into D AB1. So, P t 1 is 1 atmosphere, P t 2 is 2 atmosphere, and D AB is we have obtained 1.156 into 10 to the power minus 4 meter square per second. So, we can calculate D AB2 is equal to 1 by 2 into 1.156 into 10 to the power minus 4 meter square per second, which is equal to 0.58 into 10 to the power minus 4 meter square per second.

So, for the third problem, similarly, since the temperature T 2 is given as 200 degree centigrade temperature and P t 2 is 1 atmosphere, which is remain same for the first

problem, so we can write D AB is directly proportional to the T to the power of 1.75. So, we can write D AB2 by D AB1 will be equal to T 1, T 2 by T 1 to the power 1.75.

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Example 7.1: Solution T2 = 200+273= 473K DAM = 1. 159 × 10 4 m 3/s T1 = 100 + 273 = 373K  $D_{AB2} = \left(\frac{473}{373}\right)^{1.75} \times \frac{1}{1.154 \times 10^{-4}} \frac{1}{375}$  $= 1.761 \times 10^{-4} \text{ m}^2/\text{s}$ (iii)  $T_2 = 200^{\circ}c$ ,  $P_{12} = 1$  adm.  $D_{AT_3} \propto T^{1.75}$ ,  $\frac{D_{ATA_2}}{T_2} = (\frac{T_0}{T_1})^{1.25}$   $T_2 : 200 + 273 = 473K^{DATA_1} = (\frac{T_0}{T_1})^{1.25}$ 

T 2 is given as 200 plus 273 is equal to 473 K and D AB1 is 1.159 into 10 to the power minus 4 meter square per second and T 1 is 100 degree centigrade, which is 373 Kelvin. So, D AB2 would be 473 by 373 to the power 1.75 into 1.159 into 10 to the power minus 4 meter square per second, which will be about 1.761 into 10 to the power minus 4 meter square per second. So, this is different conditions for the same systems.

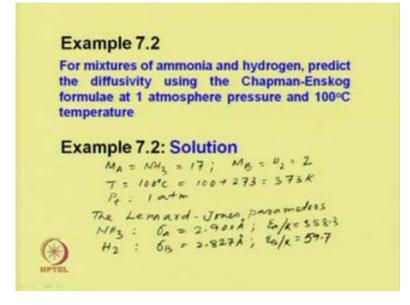
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Gas Phase Diffusion Coefficient Prediction Chapman-Enskog equation  $D_{A,B_{a}} = \frac{1.858 \times 10^{7} \tau^{4S}}{P_{t} 6_{AB}^{2} \Omega_{p}} \times \sqrt{\frac{1}{M_{A}} + \frac{1}{M_{B}}} \times \frac{1}{2}$ T = temp in K MAING = Mol. W/ & A&B Pt : Total pr. in atm. BAR = Characteristic Length & binanyais BAR = Characteristic Length & binanyais RD = collision integral = f(xT/EAB) EAB = JEAEB

There is another important useful correlation, which is Chapman-Enskog equation. In this case, the equation is derived based on the kinetic theory of gasses and the diffusion coefficient calculated from this equation is strongly dependent on binary interaction parameters of the mixture pair.

So the equation, which is given D AB is equal to 1.858 into 10 to the power minus 7 T to the power 1.5 divided by P t sigma AB square omega D into square root of 1 by M A plus 1 by M B, this is in meter square per second, where T is the temperature in Kelvin; M A, M B are the molecular weights of A and B; P t is the total pressure, total pressure, in atmosphere; sigma AB the characteristic length, characteristic length, of binary mixture in angstrom, this we can calculate using sigma A plus sigma B divided by 2, and omega D is the collision integral, integral, which is a function of K T by epsilon AB. This epsilon AB can be calculated from root over epsilon A into epsilon B.

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Now, let us take an example, very simple example of mixture of ammonia and hydrogen for this. Predict the diffusivity using this formula at 1 atmosphere pressure and 100 degree centigrade temperature.

Now, let us consider A is ammonia, so M A is equal to NH 3 is equal to 17 and M B is hydrogen is 2, T is given, 100 degree centigrade, so which is equal to 100 plus 273 So, 373 Kelvin and P t is the total pressure, which is 1 atmosphere.

Now, the Lennard-Jones potential parameters we can calculate for ammonia from the literature, we can, from the text book we can get 2.900 angstrom, so that we can calculate the epsilon A by K is 558.3 and for hydrogen sigma B is 2.827 angstroms and epsilon B by K is 59.7.

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Example 7.2: Solution FN NHS(A) - H2 (B) Pair  $\frac{\pi K}{K} = \left(\frac{\xi_{A}}{k} - \frac{\xi_{B}}{k}\right)^{2} = \frac{2 \cdot 9^{21} + 2 \cdot 8^{27}}{2} = 2 \cdot 8 \cdot 6 \cdot 8 \cdot 5 \times 5^{9} \cdot 7\right)^{\frac{1}{2}} = 182 \cdot 6$   $\frac{\pi K}{K} = \left(\frac{\xi_{A}}{k} - \frac{\xi_{B}}{k}\right)^{2} = \left(\frac{5 \cdot 8 \cdot 5 \times 5^{9} \cdot 7}{182 \cdot 6}\right)^{\frac{1}{2}} = 182 \cdot 6$   $\frac{7}{4} = \frac{373}{182 \cdot 6} = 2 \cdot 0.4$ From the collesim integral GARS = GAHGA = S2D = 1.075

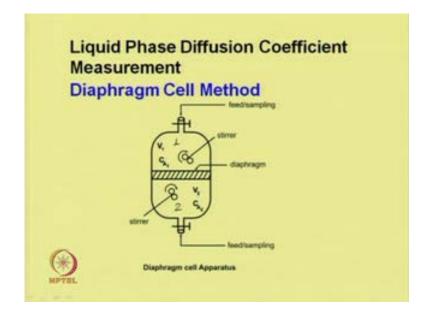
So, using this value for this ammonia-hydrogen pair, for NH 3, which is A and H 2, which is B, this pair, we can calculate sigma AB, which is sigma A plus sigma B by 2 is equal to 2.900 plus 2.827 by 2 is equal to 2.8635 angstrom. So, epsilon AB by K we can obtain, epsilon A by K, epsilon B by K to the power half. So, it will be 558.3 into 59.7 to the power half is equal to 182.6. So, with this value K T by epsilon AB will be 373 by 182.6 will give you 2.04. With these values from the collision integral we can calculate omega D, we can obtain 1.075.

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Exam	ple 7.2: Solution
	$=\frac{1.858\times10^{-7}(373)^{15}}{1\times(2.8635)^{\frac{1}{5}}\times575}\times\sqrt{\frac{1}{17}+\frac{1}{2}}$
	= 1.134 × 10 4 m 7/s
()	

Now, if we substitute all these values in the equation D AB, will be 1.858 into 10 to the power minus 7, T is 100 degree centigrade, is 373 to the power 1.5 divided by 1 into 2.8635 square into 1.075 multiplied by root over bar 1 by 17 plus 1 by 2. So, this will give 1.134 into 10 to the power minus 4 meter square per second.

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Let us consider another technique for liquid phase diffusion coefficient measurements. There are many methods available to calculate the liquid phase diffusivity; one of the simplest methods is known as the diaphragm cell method. In this case, a simple cell is divided into two parts with a diaphragm, this diaphragm (()) porous in nature and in two compartments, compartment 1 and comportment 2. We can take two different concentrations of the liquids and allow them to diffuse between the compartments. After certain period of time take the sample from different compartments and analyze, and then from the mole balance we can calculate the diffusivity.

The assumption is, that one very dilute solution is placed in compartment 1 and relatively little lower concentrations are placed in compartment 2, and molecular diffusions take place through the diaphragm. Let the volume of the compartment 1 is D A1 and the concentration in comportment 1 is C A1 and the volume of compartment 2 is D 2 and the concentration is C A2. Both the comportments are well mixed.

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**Diaphragm Cell Method** hel the area of diaphrogm = A porosity = E Effective area for diffusion = A E Tortusity factor = T Solute come in very low, so the bulk flow term can be neglegted and taken as 2000  $N_{A} = -D_{AB} \frac{dG_{A}}{dh} = \frac{G_{A} - G_{A}}{(h_{2} - h_{1})Z}$  $= D_{AB} \frac{G_{A} - G_{A}}{XZ}, \text{ where } x + h_{2}$ 

Let the area of diaphragm is A, and porosity is epsilon, so effective area for diffusion for diffusion is A epsilon. The diffusion path is not uniform, so to account the nonuniformity of the diffusion path we can use a term tortuosity factor tau, tortuosity, tortuosity factor tau. Since the solute concentration is very low, solute concentration is very low, so the bulk flow term can be neglected and taken as 0. So, in that case we can write flux equation N A will be minus D AB dC A divided by dh, which is equal to C A1 minus C A2 divided by h 2 minus h 1 into tau, which is equal to D AB C A1 minus C A2 by x tau, where x is equal to h 2 minus h 1, the thickness of the diaphragm. (Refer Slide Time: 31:08)

Diaphragm Cell Method Flux equi for both sides of diaphrage - V, dan = AENA V3 dCA2 = A ENA d (4-41) A & DAR (CAT-4 Initial comes are Caro and 4=0. CATO, Gaz = GA2,0 CAN.F.

So, we can write flux equations, flux equations for both sides of the diaphragm. For compartment one it is v 1 d CA 1 dt would be equal to epsilon N A and for compartment 2 will be v 2 d C A2 dt is equal to A epsilon N A. So, combining these two equations we can get, d C A1 minus C A2 dt would be equal to A epsilon D AB by x d tau C A1 minus C A2 into 1 by v 1 plus 1 by v 2.

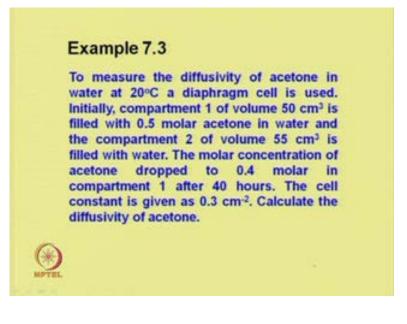
So, if the initial concentrations are between the compartments C A1, 0 and C A2, 0, then with the following conditions at t is equal to 0, C A1 will be C A1, 0; and C A2 will be C A2, 0; t is equal t F, C A1 will be C A1, F and C A2 will be C A2, F.

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**Diaphragm Cell Method** DAB = - X E LE [ + + + ] ] by ( Garo - (+2,0) AB = A E LE [ + + + ] ] by ( Gare - (+2,0) ( Gare - (+2,0))  $= \frac{1}{\alpha' t_F} \left( \ln \left[ \frac{C_{AT,0} - C_{A2,0}}{C_{AT,F} - C_{A2,F}} \right] \right)$  $\alpha' = cell constant$  $= \frac{A \in \left[\frac{1}{V_1} + \frac{1}{V_2}\right]}{\frac{\pi}{4} \frac{2}{C} \left[\frac{1}{V_1} + \frac{1}{V_2}\right]}$  $\alpha' can be obtained using a solute$ of known diffusion coefficient:

Using this condition we can integrate the flux equations and it will give D AB will be x d tau by A epsilon t F 1 by v 1 plus 1 by v 2 inverse ln C A1, 0 minus C A2, 0 divided by C A1, F minus C A2, F, which we can write 1 by alpha t F ln C A1, 0 minus C A2, 0 divided by C A1, F minus C A2, F, where alpha is the cell constant, constant, which is equal to A epsilon by x d tau 1 by v 1 plus 1 by v 2. So, this can be determined, alpha can be obtained using a solute of known diffusion coefficient.

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Now, let us consider a simple example. To measure the diffusivity of acetone in water at 20 degree centigrade a diaphragm cell is used. Initially, compartment one of volume 50 centimetre cube is filled with 0.5 molar acetones in water and the compartment 2 of volume 55 centimetre cube is filled with water. The molar concentration of acetone dropped to 0.4 molar in compartment 1 after 40 hours. The cell constant is given as 0.3 per centimetre square. Calculate the diffusivity of acetone.

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Example 7.3: Solution V1 = 50 cm 3, V2 = 55 cm 3 EF = 40 hours = 40×60×60 S = 144 000 sec oc = 0.3 cm -2 at t=0, GAT,0=0.5, GA2,0=0 al t= bF, Gar, F= 0.9, Gaz, F= ? V, GAI, 0 + V2X GA2, 0 = V, GAI, 5 + V2 GA2, 5 50x 0.5+ 55 ×0 = 50×0.9+ 55× Gaz, CA2,F = 0.09 5 - 1/5 = 1. 11 × 10 1. 11 × 10

So, the data, which are given is, volume of compartment 1 is 50 centimetre cube and for compartment 2 is 55 centimetre cube. t F, total time, which is 40 hours is 40 into 60 into 60 seconds, so it will be 14400 seconds. Alpha cell constant is given, 0.3 centimetre minus 2; at t is equal to 0, C A1, 0 is equal to 0.5 and C A2, 0, because of pure water it is 0. Concentration of acetone is 0 at t is equal to t F, C A1, F is 0.4, dropped in compartment 1 and C A2, F we have to calculate from the material balance.

So, if you do the material balance, v 1 C A1, 0 plus v 2, plus v 2 into C A2, 0 will be v 1 C A1, F plus v 2 C A2, F. So, 50 into 0.5 plus 55 into 0 will be equal to 50 into 104 plus 55 into C A2, F, so C A2, F is equal to 0.091.

So, then diffusivity D AB we can use, 1 by alpha t F ln concentration of C A1, 0 minus C A2, 0 by C A1, F minus C A2, F. Now, putting the value 1 by 0.3 into 144000 seconds ln 0.5 minus 0 divided by 0.4 minus 0.091, so this will give 1.11 into 10 to the power minus

5 centimetre square per second, so which is equal to 1.11 into 10 to the power of minus 9 meter square per second.

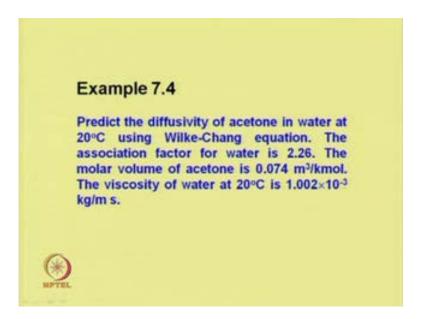
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Liquid Phase Diffusion Coefficient Prediction Wilke-Chang Equation DAB = 1.173 × 1516 (\$ MB) Ma 2.0.6 of association factor MB = molecular with & solvent B T = temp in K solt visusity Kg/ms las volume it nor K mal

There is some empirical correlations available to determine the liquid phase diffusivity and one of the simplest correlations, which is known as Wilke-Chang equation and it gives D AB is equal to 1.173 into 10 to the power minus 16 phi M B to the power 0.5 into T divided by mu B v A to the power 0.6 in meter square per second.

Here, D AB is the diffusivity of solute A in B, solvent B; phi is the association factor M B is the molecular weight of solvent B, solvent B, and T is the temperature in Kelvin; mu B is the solution viscosity in kg per meter second; v A is the molar volume at normal boiling point in meter cube per kmol.

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So, let us consider simple example to predict the diffusivity of acetone in water at 20 degree centigrade using Wilke-Chang equation. The association factor for water is given 2.26, the molar volume of acetone is given 0.074 meter cube per kmol and viscosity of water at 20 degree centigrade is 1.002 into 10 to the power minus 3 kg per meter second.

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Example 7.4: Solution DAB = 1.173×10-16 (+ MB) × T MA VAO.6  $T = 20^{\circ}C = (20 + 273)k = 243k$   $\varphi = 2.26, \qquad M_{5} = 18 \qquad ...5$   $D_{AB} = \frac{1.173 \times 10^{-16} \times (2.26 \times 18) \times 253}{(1.002 \times 15^{-5}) \times (0.074)^{0.6}}$   $= 1.04 \times 10^{-9} \text{ m}^{2}/\text{S}$ 

So, using this values we can calculate, D AB will be 1.173 into 10 to the power of minus 16 into phi M B to the power 0.5 into T divided by mu B v A to the power 0.6. The temperature is 20 degree centigrade, which is 20 plus 273 Kelvin, so 293 Kelvin. So, if

you substitute, D AB would be 1.173 into 10 to the power of minus 16 into association factor phi is given 2.26 and M B is 18 for water. So, substituting 2.26 into 18 to the power 0.5 into 293 divided by viscosity is given, 1.002 into 10 to the power minus 3 multiplied by the volume, molar volume is given 0.074 to the power 0.6. This will give 1.04 into 10 to the power minus 9 meter square per second.

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Liquid Phase Diffusion Coefficient Prediction Stokes-Einstein Equation DAB M = constant

There is another correlation, which is Stokes-Einstein equation, which also says that the liquid phase diffusivity for different components varies linearly with absolute temperature, and inversely proportional to the viscosity of the medium. So, we can write D AB mu by T as constant. So, this is end of lecture 7 and in the next lecture we will continue diffusivity for the multi-component mixtures.

Thank you.