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Lecture - 14 Interphase mass transfer

Welcome to the sixth lecture of module 2 on mass transfer operations. In this module we are mainly discussing the Mass Transfer coefficient. So, let us have a small recap on our last lecture, in our last lecture we have mainly considered two things.

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Recap
Penetration Theory $k_{\lambda} = 2 \sqrt{\frac{D_{AB}}{\pi \theta}}$
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One is penetration theory and in which we have seen that, the gas bubbles or a liquid droplets which are coming to the surface and there is intimate contact between the gas and liquid, and in this case it is considered the exposure time is theta. And, based on this theory we can calculate the mass transfer coefficient of the liquid phase is equal to 2 into root over D AB by pi theta. So, that is mass transfer coefficient is square root dependence with the diffusion coefficient. We have also considered the equal surface renewals in this case. Now, in this lecture we will consider mostly on the Interface mass transfer.

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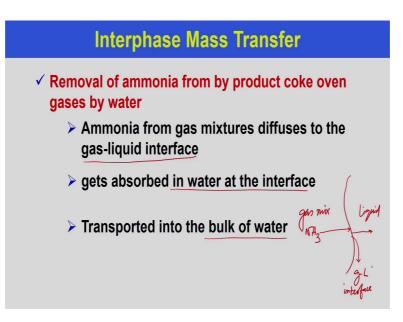
Interphase Mass Transfer

- The theoretical principles of diffusion and mass transfer from one point to another in a single phase or in homogeneous medium.
- Most mass transfer operations in practice involve transport of one or more solute between two insoluble phases.
- Example
 - Removal of ammonia from by product coke oven gases by water

We have discussed the theoretical principles of diffusion and the mass transfer from one point to another in a single phase or in a homogeneous medium. But, mass transfer operation in practice if we look, it involve transport of one or more solutes between the insoluble phases. That means, if there are two phases involved and both the phases are insoluble to each other then, the transfer of components generally happens from one phase or to the other phase, or it involves between the phases and that is called the interface mass transfer.

For example, if we consider removal of ammonia from a by product coke oven gas by water; if we take the coke oven gas the majority of it contains the ammonia and it has to be removed before it released to the atmosphere. And, the best way to remove that component by contacting the ammonia or contacting the product of the coke oven gas by water, so that the water selectively absorb ammonia and basically it forms the ammonium hydroxide and the affinity of ammonia in water is quite high.

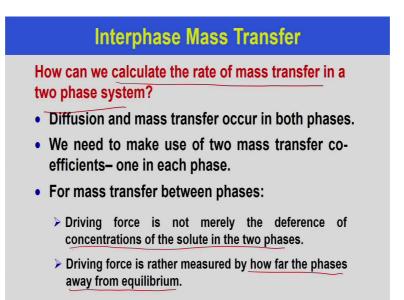
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So, how it occurs? The ammonia from gas mixture diffuses to the gas liquid interface. So, from the gas phase it goes to the gas liquid interface and then it gets absorbed in water at the interphase. So, in the first case it diffuses from the gas phase to the gas liquid interface and then it is absorbed in water at the interface, and then it transport into the bulk of water.

So, transport of these components happens to the bulk of water. The gas mixture if you take over here. So gas mixture mainly ammonia in this case it will go to the gas liquid interface. So, this is the gas liquid interface, and then this is the liquid site. So, it absorbed at the interface and from the interface it transported to the liquid bulk.

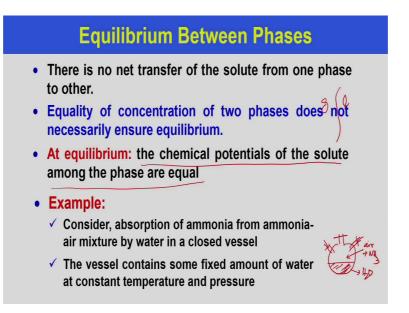
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Now, how can we calculate the rate of mass transfer in a two phase system? Diffusion and mass transfer occurs in both the phases in this case for interface mass transfer. So, we need to make use of two mass transfer coefficient- one in each phase. Since the diffusion and the mass transfer are not same in both the phases because the phases are different, which is gas and in liquid. So, we need to have two different mass transfer coefficient, one in each phase, one in the gas phase and another in the liquid phase.

For mass transfer between phases, the driving force is not merely the difference of concentration of the solute in the two phases. So, what is the driving force in these cases if it is not the concentration driving force between the two phases? The driving force is rather measured by how far the phases are away from equilibrium. So, we need to understand the departure from the equilibrium and the departure will give the driving force for this mass transfer. So, we need to understand what is the equilibrium when there is more than one phase involves or the two phase systems.

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So, we need to understand the equilibrium between the phases. So, when we say the systems is in equilibrium it means that or when there is more than one phase involved the equilibrium means that there is no net transfer of the solute from one phase to the other. So, basically if there is two phases involves gas and liquid there will be no net transfer of the component or the solute from one phase to the other.

So, this equality of concentration of two phases does not mean necessarily ensure equilibrium. So, if we see the concentration of both the phases, if they are same we cannot say that the system reached the equilibrium. So, what happens at equilibrium? At equilibrium the chemical potential of the solute among the phases are equal, because as we said at the beginning in our module 1, to describe the true driving force for mass transfer and we consider that it is the chemical potential. Because, the chemical potential when there is two phases involve they are not similarly related with the chemical potential in both the phases, like in liquid phase or in the gas phase they are not similarly related with the concentration.

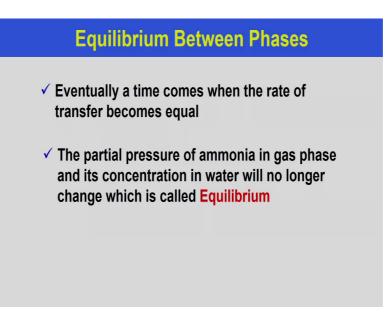
Now, let us take an example consider, an absorption of ammonia from ammonia air mixture by water in a closed vessel. So, if we take a now closed vessel, and you have taken air plus ammonia and you have some liquid which is water. So, the vessel contains some fixed amount of water at constant temperature and pressure. So, temperature and

pressure are set at a particular values and it is closed container, initially there was water and then we have inserted air and ammonia.

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Equilibrium Between Phases
• Example (contd.):
 An amount of ammonia-air mixture is introduced in the vessel
 Ammonia is soluble in water and hence some amount of ammonia will be transferred from gas to the liquid
 Simultaneously, some ammonia molecule will escape back into the gas
 The process of ammonia transfer continues but not necessarily at the same rate.

So, what happens an amount of air ammonia mixture which is introduced into the vessel is will be soluble in water and hence some amount of ammonia will be transferred from gas to the liquid. So, ammonia once it is soluble which are available at the gas liquid interface, they will soluble in the water and then some amount of ammonia will be transferred from the gas phase to the liquid phase. Simultaneously some ammonia molecule will escape back into the gas phase. So, it will dissolve; the process of ammonia transfer continues, but not necessarily at the same rate. (Refer Slide Time: 10:17)



So, this process will continue for a certain period of time, and at time will come when the rate of transfer becomes equal; that means, the transfer of solute from one phase to the other will be equal from the liquid phase to the gas and gas phase to the liquid. The partial pressure of ammonia in gas phase and its concentration in water will no longer change which is called equilibrium. So, if we measure the partial pressure in the gas phase and then its concentration in the liquid phase this will not change when the system will reach in equilibrium.

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Equilibrium Between Phases

- If small samples of the phases are taken and analyzed for NH₃ contents, we get the equilibrium partial pressure (p_{NH3}) in the gas phase and the corresponding mole fraction (x_{NH3}^*) in the liquid phase.
- If we inject some more NH₃ into the vessel and sufficient time is allowed, the system will reach a new equilibrium state and we get another set of equilibrium values, (p_{NH3}, x_{NH3}*)

If we takes small amount of samples of the phases and analyse the ammonia content and we get the equilibrium partial pressure p NH3. So, taking very small amount from the gas phase as well as the liquid phase, we can analyse the partial pressure in the gas phase of that component like small p NH3 is the partial pressure of the ammonia. And the amount corresponding to this partial pressure of ammonia how much dissolve, the mole fractions of ammonia in the liquid phase which is defined as small x NH3 star.

So, this is the equilibrium value at that temperature and pressure in the liquid phase, that is x NH3 star. Now if we inject some more ammonia into the vessel what will happen and if you allow the system to reach certain period of time or sufficient time is allowed, so that the system reach the equilibrium state again, because we have injected more amount of ammonia into the system. Then we can again once the equilibrium is reached after a certain period of time, we can take out samples like in the first case and we can analyse their concentration for both the phases; gas and liquid phase. And, we can calculate the partial pressure in the gas phase and the mole fractions in the liquid phase corresponding to that partial pressure.

Note that this partial pressure in the second case will be injected more amount of ammonia and the no, partial pressure which we have obtained earlier are not same because, we have inserted more amount of ammonia. So, the partial pressure will be different and the new equilibrium will reach. So, we will get another set of equilibrium values at this condition

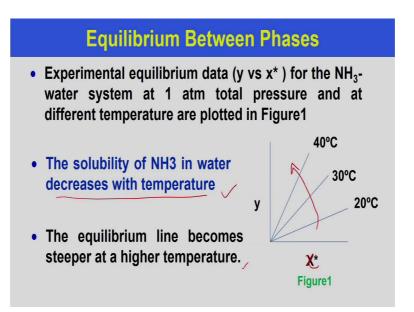
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Equilibrium Between Phases

- Set of $(p_{NH3,} x_{NH3}^*)$ values at a constant temperature and at a constant total pressure generated in this way are called the equilibrium data for a particular system.
- A plot of these data is called the <u>equilibrium line</u> or equilibrium curve.
- Equilibrium data may also be expressed in mole fraction(y_{NH3} vs x_{NH3}) or mole ratio (X_{NH3} vs Y_{NH3}) units

Now, the set of no partial pressure and no its mole fraction in the liquid phase at constant temperature and constant pressure; we can generate in this way and which we generally called the equilibrium data for a particular system. Now if we plot of this data is called the equilibrium line or equilibrium curve. Now, how to express the no equilibrium data it is either we can express in terms of the mole fractions that is small y NH3 and x NH3 that is, it is in the gas phase concentration in terms of the mole fraction. And, it is liquid phase concentration in terms of the mole fractions or we can write in terms of the mole ratio which is capital X NH3 versus capital Y NH3. So, it is in the mole ratio unit and this is in the mole fractions unit.

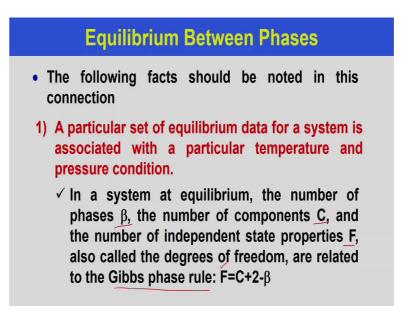
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If we just plot experimental equilibrium data y versus x star for ammonia and water system at 1 atmosphere total pressure and at different temperature, which can be seen in the figure. So, it looks like this. So, h no y and this is small x. So, this is at 20 degree centigrade and this is at 30 degree centigrade and this is at 40 degree centigrade and you can could see as we increase the temperature the slope of the curves becomes steeper; that means, the solubility decreases.

So, the solubility of ammonia in water decreases with temperature. The equilibrium line becomes steeper at higher temperature. So, this is the two observation we can see from this figure where we plot the mole fractions of that component in the gas phase and with the liquid phase.

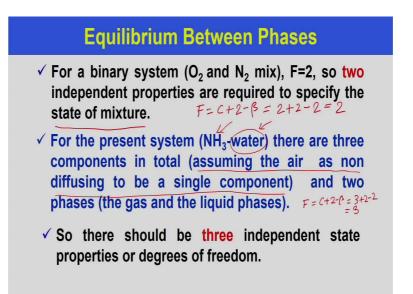
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Now, the following facts should be noted in these connections. A particular set of equilibrium data for a system is associated with a particular temperature and pressure condition. When we say the equilibrium data for a particular system, we have to define the temperature and pressure for that system. So, at that conditions you will get a equilibrium curve.

In a system at equilibrium the number of phases that is beta the number of components involves that is C, and the number of independent state properties that is F, also called the degrees of freedom are related with the Gibbs phase rule that we know is F is equal to C plus 2 minus beta. So, that is the degrees of freedom would be equal to the number of components plus 2 minus the number of phases involved.

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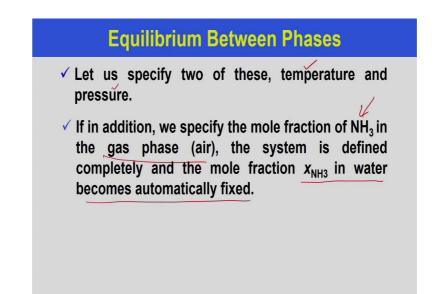


So, if we take the examples of a binary system, that is oxygen and nitrogen mixture. If 2 component systems binary systems and we have 2 component, so the number of phases is 2, if we apply the phase rule F is equal to C plus 2 minus beta. In this case for 2 component systems, it is 2 plus 2 minus beta is two phase system. So, it is 2 hence, F is equal to 2. So, the degrees of freedom is 2 and, so we need 2 independent properties to specify the state of this mixture.

Now, for the present systems where we have considered ammonia in air and water mixtures; in this case there are 3 components in a total where we assume that the air which is non-diffusing and as a single component. So, here we have assumed air as a non-diffusing to be a single component, and ammonia is another component, and water is another component in the liquid phase. So, we have 3 component systems, now if we apply the phase rule over here.

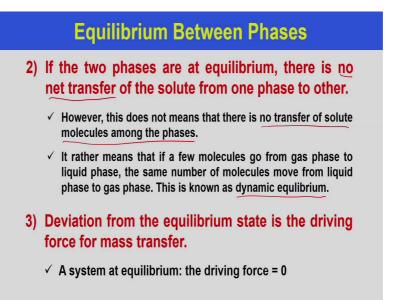
So, if it will be F is equal to C plus 2 minus beta would be equal to 3 plus 2 minus 2. So, F degrees of freedom would be 3. So, there should be 3 independent state properties or degrees of freedom to define this system.

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So, what are these three independent state properties? Let us specify two of this, one is temperature and pressure. So, temperature and pressure we can specify for a particular system. Now, in addition if you specify the mole fractions of ammonia in the gas phase that is in the air. So, the system is then defined completely and the mole fractions of ammonia in water becomes automatically fix. So, if you just fix the ammonia concentration in the gas phase, corresponding to that concentration what would be the liquid phase concentration we can calculate from the equilibrium relations. So, that would be fixed.

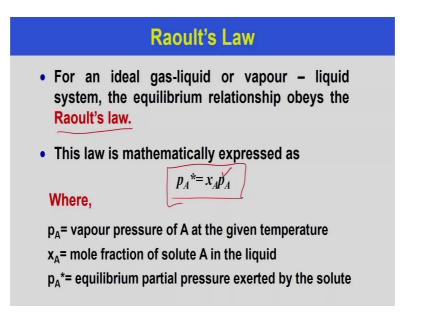
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Now, if the two phases are at equilibrium there is no transfer of the solute from one phase to the other. However, this does not mean that there is no transfer of solute molecules among the phases. We said if the two phases are at equilibrium there is no net transfer of the solute from one phase to the other. So, this does not mean that there is no transfer of solid molecules among the phases. It rather means if a few molecules go from gas phase to the liquid phase, the same number of molecules move from the liquid phase to the gas phase. This is known as dynamic equilibrium. That means, although we see that the equilibrium reached and net transfer of the solute ceases.

So, this does not necessarily mean that there will not be any transfer of the solute molecule from one phase to the other, but it means that there will be the equal amount of transfer of solute among the phases. So, that the equilibrium is reached and the system calls the dynamic equilibrium. Now, deviation from the equilibrium state is the driving force for mass transfer. So, what is the deviation when the system at equilibrium this deviation or the driving force would be 0.

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If we considered ideal gas or vapour - liquid no gas liquid mixture, or in a vapour liquid system, the equilibrium relationship obeys the Raoult's Law from which we can calculate the concentration of the phases. This law is mathematically expressed as partial pressure p A star would be equal to mole fractions into p A. So, p A is the vapour pressure of A at a given temperature. So, this is vapour pressure of A at a given temperature, x A is the

mole fractions of solute A in the liquid and p A star is the equilibrium partial pressure exerted by the solute. So, the equilibrium partial pressure can be related with the liquid phase mole fractions of the solute, at a given temperature with the vapour pressure of that solute. So, this is known as Raoult's Law and mathematically it represents with this relation.

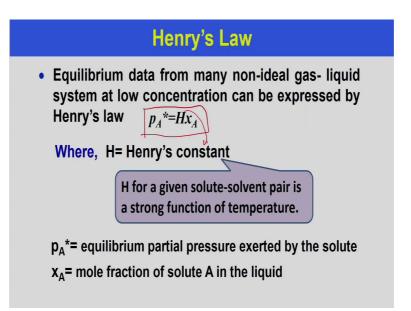
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Raoult's Law	
A solution behaves ideally when	
a. The solute and the solvent molecules have similar sizes and intermolecular forces.	
b. The excess volume of mixing is zero.	
c. The heat of mixing is zero when both the solute and the solvent are liquids.	
• When the solute is a gas, the heat of mixing is equal to the heat of condensation.	

Now, a solution when we say ideal solutions. So, Raoult's Law is applicable for the ideal solution. What does this ideal solution means? A solution which will behave ideally when it meets the certain conditions, what are they? The solute and the solvent molecules have similar sizes and intermolecular forces. So, solute and the solvent molecules have similar sizes and intermolecular forces, then it will form the ideal solution. The excess volume of mixing is zero. Excess volume of mixing is zero, and then third point is that the heat of mixing is zero, when both the solute and the solvents are liquid.

So, if we mix the know solute and solvent, and if they are in liquid then the heat of mixing is should be zero. When the solute is a gas, the heat of mixing is equal to the heat of condensation. In general the most cases the solution which are formed they are non-ideal in nature, but there are certain solutions they form the ideal solution. Certain mixture or some solutions which are nearly ideal and we consider them ideal solutions; like if we take homologous series of hydrocarbons they generally forms ideal solutions.

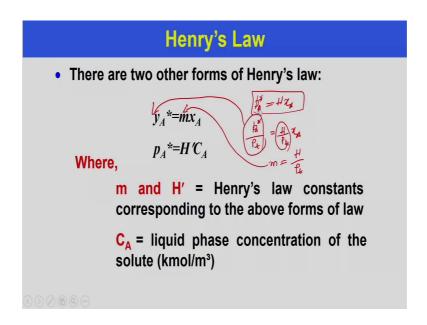
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So, equilibrium data from many non ideal gas liquid systems at low concentration can be expressed by Henry's Law. So, if it is non-ideal gas liquid systems at low concentration we can apply the Henry's Law to calculate the equilibrium data, or to correlate the equilibrium data which is represented by p A star would be equal to H x A. In this case H is the Henry's Law constant and this H for a given solute solvent pair is a strong function of temperature.

So, H is a strong function of temperature, and p A star is the equilibrium partial pressure exerted by the solute and x A is the mole fractions of solute in the liquid. So, in this case it is the, no this H is the Henry's constant and we can correlate with the partial pressure, the equilibrium partial pressure of the solute with the mole fractions in the liquid phase.

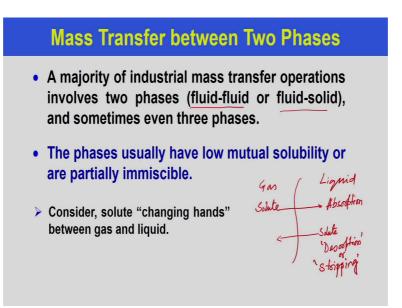
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There are two other forms of the Henry's Law one of them is y A star would be equal to m x A another form is p A star would be equal to H dash C A; m and H dash these are Henry's Law constant corresponding to the above forms of law and C A is the liquid phase concentration of the solute in kilo mole per metre cube. Now if we consider this p A the original form of the Henry's Law is p A star is equal to H x A.

Now, if we divide both sides by total pressure it would be p A star by p t would be equal to H by p t into x A. So, this p A star by p t is nothing, but the mole fractions in the gas phase and H by p t is nothing, but m. So, m is H by p t the total pressure. So, this is m, so y A star would be equal to m x A. So, this is another form which we can derive from the, know the Henry's Law equation.

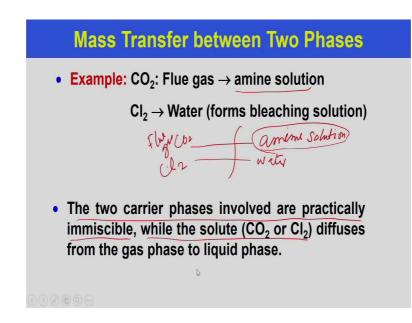
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Now, mass transfer between phases, the majority of the industrial mass transfer operations involve two phases; either fluid-fluid systems or gas fluid solid systems. In this case we can consider gas solid systems or it may be liquid solid system. So, this is the case fluid-fluid and fluid solid systems, and sometimes it may involve the three phase systems as well that is gas liquid solid. The phases usually have low mutual solubility or are partially immiscible. So, then only we say that it is immiscible phases.

Now, if you consider solutes which are changing hands between gas and liquid. So, if we consider a gas liquid system, two phase system and we call the gas solute are changing hands between gas and liquid. So, we have gas and liquid phase. Now, solute transferred from gas phase to the liquid phase, and another case the solute transferred from the liquid phase to the gas phase. So, this is we generally call absorption, we will discuss later in detail and this we call desorption or stripping. So, this is a case of know solute which changing hands between the two phases a gas and liquid phases.

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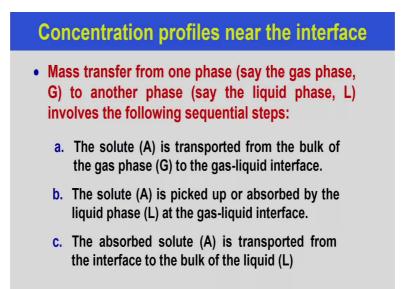


Now, let us consider example say carbon dioxide which is obtained as a flue gas from the power plants, a flue gas generally contains carbon dioxide with other you know impurities along with nitrogen, in a power plants and then when we burn coal or natural gas as a fuel for no power generation. So, what generally it is done the flue gas is contacted with a basic solutions, which is amine solutions and carbon dioxide is selectively transferred from the gas phase to the liquid phase. Another example is no chlorine, which is you know if you have a chlorine gas no it can very high affinity with the water and we forms the bleaching solution. So, when chlorine transfer from the gas phase to the liquid phase.

So, basically this is the examples of no changing from carbon dioxide from flue gas and chlorine to the water and it is in the amine solution. These are the examples of no absorption where transfer of the solute takes place from the gas phase to the liquid phase. Similarly the stripping once the gas is absorbed to make it free we just dissolve it by heating the solution. So, like particularly if you do not want the absorbed carbon dioxide in the amine solutions and if we cannot utilise and we wanted to reutilise the amine solutions; we heat it up dissolve the carbon dioxide take as a pure component and use the amine solutions again for absorption.

So, the reverse state is the stripping. The two carrier phases involves are practically immiscible while the solute, carbon dioxide or chlorine diffuses from the gas phase to the liquid phase.

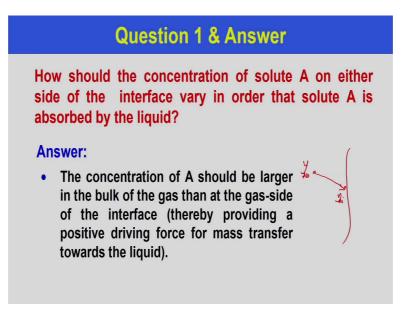
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Now, what would be the concentration profile near the interphase? Mass transfer from one phase say the gas phase G to another phase say the liquid phase L involves the following sequential steps. What are those steps? The solute A is transported from the bulk of the gas phase G to the gas liquid interface. The solute is picked up or absorbed by the liquid phase that is L at the gas liquid interface. The absorbed solute is transferred from the interface to the bulk of the liquid.

So, for transfer of component from one phase to the other phase involves 3 sequential steps. First step the component from the bulk of the gas should be diffuse to the gas liquid interface. It will be absorbed at the gas liquid interface by the liquid. So, step 1 and step 2 and step 3 from the interface on the liquid side it will be transferred to the bulk of the liquid. So, this is the 3 steps involved for the absorption or transfer of components from one phase to the other.

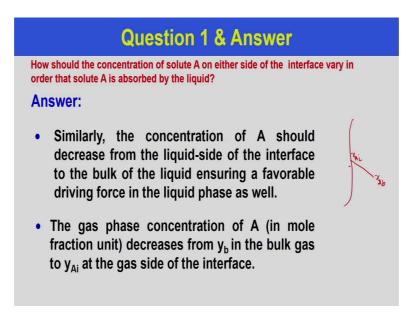
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Now, how should the concentration of solute A on either side of the interface vary in order that solute A is absorbed by the liquid. So, question is how the concentration of solute would vary both in the gas phase and in the liquid phase in order that the solute A is observed by the liquid. The concentration of A should be larger in the bulk of the gas than at the gas side of the interphase. So, if we take the interface and if it is gas the concentration over here of the solute should be higher from the interfacial concentration.

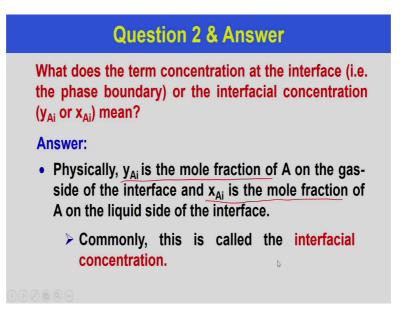
So, that it will diffuse in this gas phase from high concentration, this is gas bulk so it will diffuse from here to the interface, or if I write it is in terms of y b and this is y y this is y Ab and this is y Ai. Similarly so, the interface and the providing a positive driving force for mass transfer towards the liquid. So, driving force will be there in the gas side.

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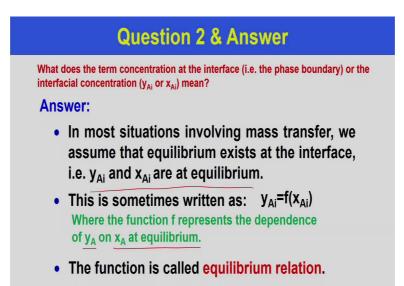
Next similarly the concentration of A should decrease from the liquid side of the interface to the bulk of the liquid ensuring a favourable driving force in the liquid phase as well. That means, in the liquid phase from the interface of the liquid there should be a driving force that is x Ai would be no higher than the x Ab which is in the liquid phase concentration. So, this no driving force should be there, so that the solute which is observed on the liquid should be diffuse to the other side or to the liquid bulk. The gas phase concentration of A in mole fraction unit decreases from y b in the bulk gas to y Ai at the gas side of the interface so, which is already set.

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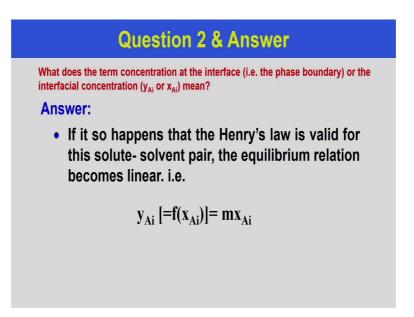
Now, what does the term concentration at the interface that is at phase boundary or the interfacial concentration y Ai and x Ai mean? Physically, y Ai is the mole fractions of A on the gas side of the interface, and x Ai is the mole fractions of A on the liquid side interface. So, x Ai is the mole fraction in the liquid side interphase and y A is the mole fractions of A in the gas side interface.

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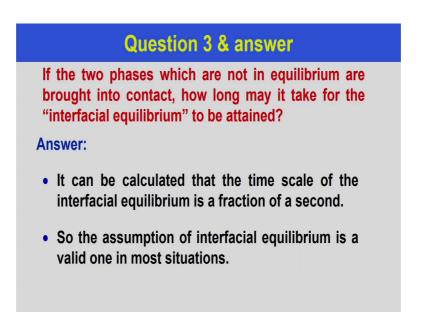
Commonly this is called the interfacial concentration and how to relate the interfacial concentration. In most situation involving mass transfer we assume that equilibrium exist at the interface; that means, y Ai and x Ai are in equilibrium. So, this essentially mean that there is no resistance to mass transfer at the gas liquid interface. So, this is sometimes written in terms of the equilibrium relations y Ai is equal to function of x Ai where the function f represents the dependent dependence of y A and x A at equilibrium. So, this function is called equilibrium relation.

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And it is so happen that the Henry's Law is valid for this solute solvent pair the equilibrium relations become linear, and if no if we can apply the Henry's Law at the interface it will be y Ai would be equal to m x Ai.

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Now, if the two phases which are not in equilibrium are brought into contact how long may it take for a interfacial equilibrium to be attained. So, if they are not equilibrium and they are brought in contact to reach the equilibrium how long it would take? This can be calculated that the time scale of interfacial equilibrium is a fraction of second very very

small time it takes to reach the equilibrium. No fraction of second at the interface and so the assumption of interfacial equilibrium is a valid one in most situation. Since, the time scale to reach that equilibrium at the interface is very small so, the assumptions we take at the interface that is valid one in most of the situations.

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Question 3 & answer

- However, there are cases when equilibrium does not exist at the interface, and we say that there is an "interfacial resistance".
- For example: an accumulation of a surface active agent such as cetyl alcohol at an air-water interface exhibit interfacial resistance.

However, there are cases when equilibrium does not exist at the interface and we say that there is interfacial resistance. If some cases no there is not equilibrium among the, at the interface then we say that the there is some interfacial resistance, but in most of the cases we assume no there is no interfacial resistance. For example, if we consider an accumulation of the surface active agent such as acetyl alcohol at an air water interface exhibit interfacial resistance. This is one of the examples of no where there is resistance exist at the interface, that is at gas liquid interface; acetyl alcohol which accumulate at the surface for a system of air water interface.

So, thank you for your attention to hearing this lecture and we will continue our discussion on the interface mass transfer in the next class.