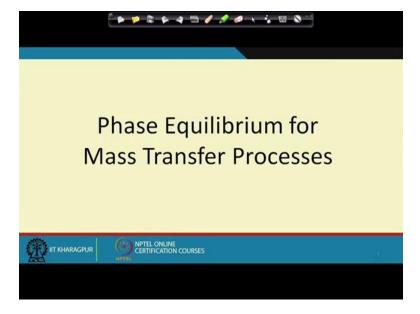
## Course on Phase Equilibrium Thermodynamics By Professor Gargi Das Department of Chemical Engineering Indian Institute of Technology Kharagpur Lecture No 52 Phase Equilibrium for Mass Transfer

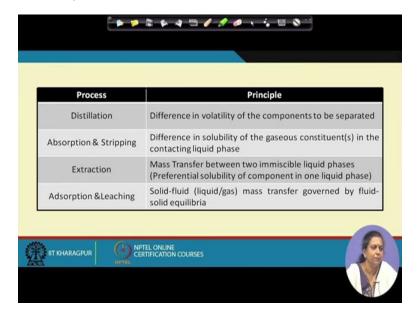
Processes (Refer Slide Time: 0:39)



Well, so this is the last class we are going to have in the course of phase equilibrium thermodynamics till now we have had a large amount of discussions on vapour liquid equilibrium solution for different systems. Now for all these systems we found that vapour liquid equilibrium phase diagrams and the equations for both ideal and non ideal solutions they cover a wide range and this is primarily important for the design of distillation columns.

Now apart from distillation there are also a also a large number of other mass transfer operations and I felt that a small or a brief discussion regarding the phase equilibrium relationships which govern the other mass transfer operations, if they are not at least touched upon, the topic of phase equilibrium thermodynamics remains unfinished or incomplete. So therefore in the last class I have decided to touch upon the phase equilibrium relationships which are important for other mass transfer operations the phase equilibrium relationships other than vapour liquid equilibrium data which is important for distillation columns.

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Now let us see what are the other mass transfer operations that usually a chemical engineer deals with? Definitely distillation we know that the principle underlying distillation or the mechanism of separation which is the used in the distillation processes is that it exploits the difference in volatility of the 2 components to be separated. Apart from distillation we have absorption and stripping, what happens under this phase? There is a gas phase we bring it in contact with the liquid and the liquid absorbs the gas from a mixture of gases or from a pure component gas.

The most common example is absorption of carbon dioxide or sulphur dioxide using sodium hydro caustic soda or caustic potash solutions. Now in this case also we cannot have the complete absorption or maybe suppose we have some amount of sulphur dioxide or carbon dioxide, there is a limit to which this gas can be absorbed in the sodium hydroxide or any other solvent that you use and the maximum amount of absorption that can take place that depends upon the equilibrium concentration of sulphur dioxide in the caustic soda solution or any other solvent that you're going to use and this is governed by the solubility of that particular gas in the solvent that we are going to use.

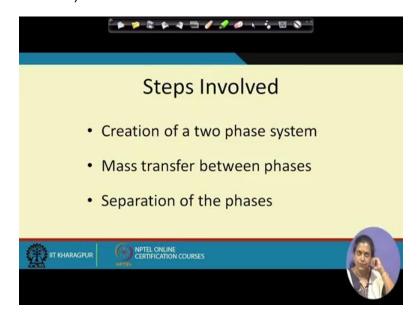
Naturally since sulphur dioxide is more soluble in caustic soda solution as compared to water. So definitely we will have a greater separation or a greater purification of the gas phase if we use caustic soda solution in place of water. So this is governed or the process of absorption is governed by the difference in or rather by the solubility of the gaseous constituent in the contacting liquid phases.

Now in stripping, mass transfer occurs in the reverse direction, in this case mass transfer occurs from the liquid to the gas phase or the vapour phase and in both absorption and stripping, since it is a mass transfer between a gas phase and a liquid phase both of them they depend upon solubility of the gaseous constituent in the contacting liquid phase, accordingly the equilibrium relationship in this case is the solubility of the particular gas in the liquid under constant temperature and pressure conditions.

And naturally if you're dealing with solubility of the gas it's quite natural then we will be more concerned about the mathematical equations which will be governing this is the ideal dilute solution law, the Henry's law in contrast to Raoult's law which used to govern vapour liquid equilibrium for distillation cases. There is another mass transfer operation which we have which is known as extraction, in this case what we have? We use a second liquid phase to extract any particular component from a from one particular liquid phase for example suppose we have acetic acid in toluene we would like to purify to toluene or would like to remove acetic acid from toluene we use water we bring the 2 phases in contact and we try to see rather we try to purify toluene from acetic acid to the maximum extent possible.

Now what is this maximum extent? Definitely it depends upon the relative solubility of acetic acid in toluene and in water. So therefore in extraction we find that the mass transfer between the 2 immiscible liquid phases it depends upon the preferential solubility of the desired component which is to be separated in the 2 liquid phases. Then we have another mass transfer operation which concerns solid liquid or solid gas mass transfer that's known as adsorption and the reverse is leaching.

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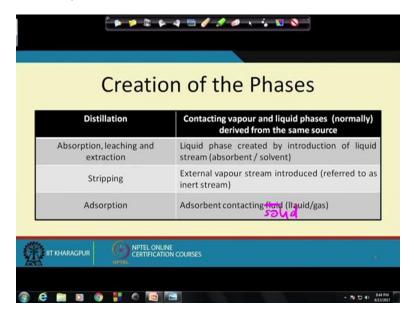


In adsorption a solid phase it absorbs either a gas or a liquid phase and in this case naturally the mass transfer is governed by fluid solid equilibria and in leaching the mass transfer occurs in the reverse direction. Now for all these mass transfer operations what do we need to do? First we need to create 2 phases and then we need to have mass transfer between the 2 phases, how do we create the 2 phases?

For distillation we find that creation of the 2 phases is just by heat we have the component in the liquid phase we apply heat we have a vapour phase naturally the vapour phase is richer in the more volatile component the liquid phase is richer in the less volatile component and we keep on contacting them and separating them and again contacting them, in this process the liquid progressively becomes richer in the less volatile component, the vapour becomes richer in the more volatile component and in this way we can get a substantial good amount of separation.

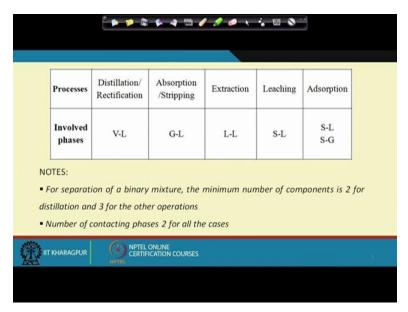
In absorption, leaching in extraction we find that we need, in fact apart from distillation for all other mass transfer operations we find that we need a third component in order to create the same phase or rather in order to create the second phase unlike distillation where the contacting vapour and liquid phases are derived from the same source, for all other mass transfer operations a third phase is required in order to affect separation. For example in absorption, leaching and extraction this third phase is the liquid phase created by introduction of a liquid stream.

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Liquid stream is often termed as the absorbent in absorption or it is termed as the solvent in case of extraction, leaching and also in absorption we often call it as a solvent. In stripping the third phase is an external vapour stream it is often referred to as an inert stream and in adsorption it is the adsorbent contacting it is actually the solid phase which creates the adsorption this is this is wrongly written this should be the solid phase which creates the medium where the liquid or the gas is preferentially adsorbed.

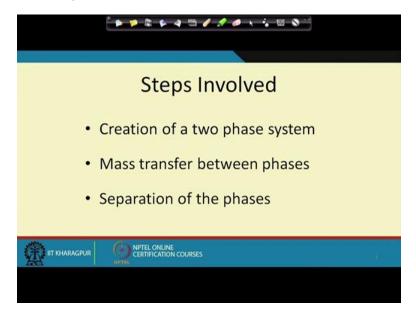
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Now in all these particular in all this all this mass transfer operations we find that for separation of a binary mixture for distillation the minimum number of components is 2 and for all other operations it is 3 and for all operations number of contacting phases is 2, what

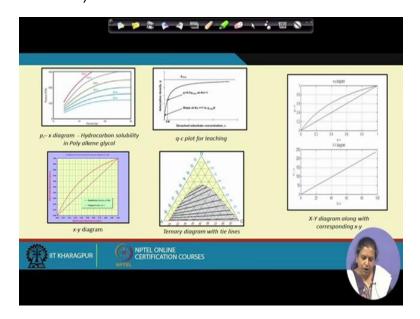
are these 2 phases? For distillation or rectification it is the vapour and liquid phase of the same component, in absorption and stripping it is a gas phase and a liquid phase. In extraction it is the 2 immiscible liquid phases, in leaching it is a solid and a liquid phase. In adsorption it is either a solid liquid or a solid gas phases.

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Now for all these phases again the way I had told you the first thing which we need to do is to create the 2 phase system. I have already discussed how we create the 2 phase system, in distillation it is created by heat for all other cases it is created by a addition of a third component then we have to effect mass transfer between the phases once the mass transfer separation occurs when we try to separate the 2 phases.

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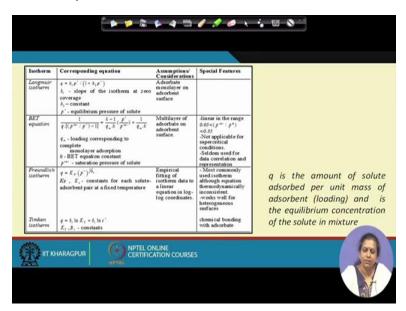


Now this mass transfer is governed by phase equilibrium, we cannot have as much mass transfer as we need and the mass transfer under constant temperature pressure conditions it is limited by the phase equilibrium considerations and this phase equilibrium is denoted in different ways for different mass transfer operations and just like we have we have already discussed we can have graphical representation of phase diagrams and we can also have mathematical equations for the phase diagrams.

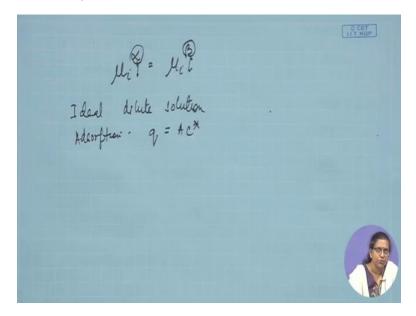
Remember for all phase equilibrium problems the governing equation is the same, what is the governing equation? For each component i, the chemical potential in phase alpha and in phase beta have to be the same this alpha and beta they can be maybe one is the gas phase the other is the liquid phase, both of them can be 2 different liquid phases, one can be a solid phase other can be a liquid or a gas phase whatever be the case the condition of thermodynamic equilibrium remains the same it is the equality of chemical potentials of each component in the 2 phases.

And therefore how do we be develop mathematical equations? For developing mathematical equations we try to express the chemical potential of each component i in the 2 phases in terms of the compositions of component i in the corresponding phases and those particular equation is when they are equated we get mass or rather we get phase equilibrium relationships.

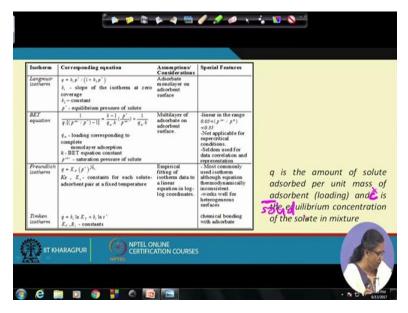
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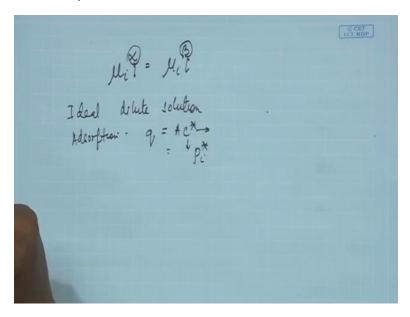


Now tell me for absorption what is the standard equation? For absorption as I have mentioned the ideal dilute solution or in other words Henry's law is the governing equation in case of absorption. For adsorption if we see for adsorption the basic equation the simplest equation it is of the Henry's law type where the equation is given as q equals to A into C star. Now the first question is what q is and what is C star?

So well, q it is the naturally in the, for adsorption it is the solid phase as well as a liquid or gas phase. So q it is a amount of solute adsorbed per unit mass of the adsorbent that is the amount of sol solute which is adsorbed it can be a liquid phase or it can be a gas phase which is adsorbed per unit mass of the adsorbent and C star it is the equilibrium concentration of the

solute phase the C star it is the equilibrium concentration of the solute in the mixture, that means in the gaseous mixture if it is a gaseous mixture then a conventional way is to express the concentration in terms of partial pressure of the gas.

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So therefore usually if it is a gaseous mixture then we prefer to replace C star with Pi star and if it is a liquid mixture then we express it in terms of concentration where the concentration can be either in terms of weight per unit volume or weight per unit weight or maybe moles per unit volume etc.

Now in this case we find for absorption while the Henry's law was the most common equation or it is the ideal equation which is used we have already discussed Henry's law and in this particular case the I will just write down the equation for convenience one, it is the Pi star equals to Hixi which you already know.

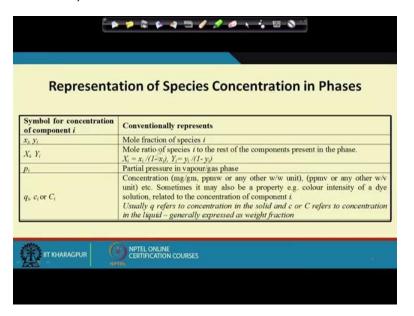
Well, there is one thing which I should be mentioning before I proceed further that is the different unit in which the concentrations are mentioned for the different mass transfer operations. Let us see the different concentrations before I go to the other mathematical equations. We find that while we were discussing vapour liquid equilibrium the mole fraction was the typical concentration ratio typical concentration unit that we were using.

We were using the mole fraction in the vapour phase and the mole fraction in the liquid phase, the mole fraction in the vapour phase was denoted by y the mole fraction in the liquid phase was denoted by x and usually we had Txy diagram, Pxy diagrams and xy diagrams.

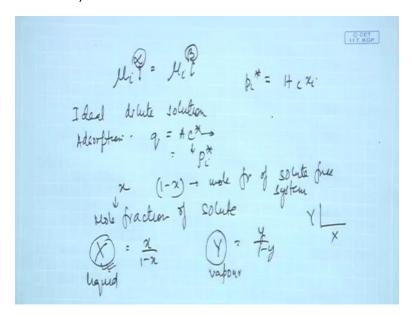
Often for

absorption we use the mole ratio but mole fractions but more common is the usage of mole ratios.

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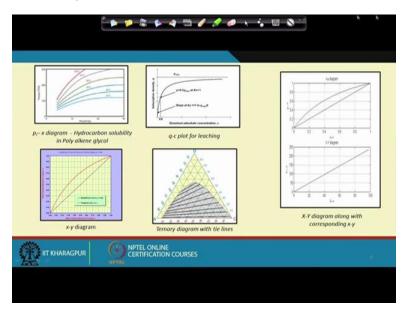
What is the mole ratio? As I have already mentioned in this in this table it is the moles of species i divided by the moles of species free i, isn't it? So therefore if I have a total solution where x is the mole fraction, naturally 1 minus x is the mole fraction of solute free system and x is the mole fraction of solute.

So in this particular case the mole ratio which is denoted by capital X or capital Y, naturally capital Y refers to the vapour phase and capital X refers to the liquid phase the given as x by 1 minus x

and Y is given by y by 1 minus y the reason for often preferring your mole ratios to mole fractions are that these often lead to linear plots Y versus X often leads to linear plot as compared to small y versus small x and once more I will try to emphasize that when we are dealing with gaseous components then very frequently the concentration unit which we prefer is the partial pressure.

So therefore the partial pressure in the vapour phase or the gas phase is often preferred for absorption, stripping and adsorption as well as leaching and when we are dealing with liquid phases say in liquid-liquid extraction or in adsorption of a liquid by a solid under that condition usually we prefer to use concentration or any particular property related to concentration and here I would just like to mention that usually the concentration and the solid phase is denoted as small q and the concentration in the liquid phase is denoted by either a small c or a capital C.

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So therefore the first thing which is which is important for you to remember are the different mass transfer operations and for the different mass transfer operations are concerned with and the second thing is for all these mass transfer operations the separation is guided by phase equilibrium considerations and these phase equilibrium considerations are obtained from phase diagrams or from mathematical relations relating the different equilibrium properties and these particle phase diagrams they are denoted either in terms of mole fractions like we have already seen in distillation or they're denoted this is one in terms of mole fraction or they are denoted in mole ratios the advantages immediately evident while we have a curved xy relationship we have a linear mole ratio relationship.

They can also be denoted by partial pressure as a function of mole fraction this is usually the case for absorption and stripping where the partial pressure of the gas over the solution is plotted with the equilibrium concentration of the gas in the liquid solution. Here I think this has been plotted as a function of temperature and as we know gas solubility decreases with temperature as a result of which the isotherms they become steeper as we go to higher temperatures.

And here this is the typical XY diagram which we have already dealt, this is distillation, this is absorption and this is this is also absorption and this is a typical isotherm for adsorption. Adsorption we plot or rather we construct the phase diagram with the fraction or the amount adsorbed in by the solid phase and the equilibrium concentration of the adsorbate in the remaining gas phase or in the remaining liquid phase.

If it is a liquid phase I repeat, we denote the coordinates with concentration and if it is a gas phase we denote it with partial pressure and this is a typical phase equilibrium diagram for liquid-liquid extraction, we will be discussing or rather I will be giving some time on it because it is different as we see, why is it different let us understand? When we are dealing with the other mass transfer operations, what do we see?

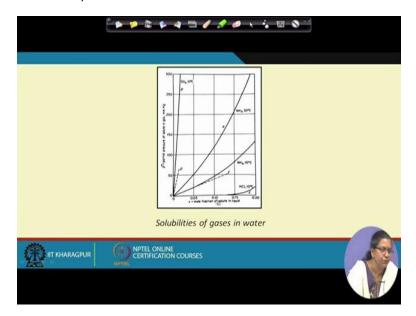
We usually consider that there is only one component which is being transferred from phase a to say phase b, in distillation it's either from liquid to vapour or vapour to liquid. In absorption it is from vapour to liquid, stripping liquid to vapour. Adsorption it's from liquid or gas to solid, leaching solid to liquid or gas but when we are considering liquid-liquid extraction, what happens?

We find that there is one particular liquid for a component is dissolved we bring another particular liquid and although we consider that the 2 liquids they are completely immiscible in practice we hardly get any liquid where which are completely immiscible with one another. So basically in practice what happens? The solute which has to be extracted suppose we have A is one particular solvent where the component C is dissolved we bring B to it such that it extracts C from A.

Now C therefore it dissolves in A, C it dissolves in B and even if A and B they have got very less mutual solubility there will be some amount of solubility between A and B. So therefore there has to be equilibrium between AC, BC and AB in order to show all these equilibrium in

a single curve usually we take the help of a Ternary equilibrium plot which I will be explaining after I discuss the other parts.

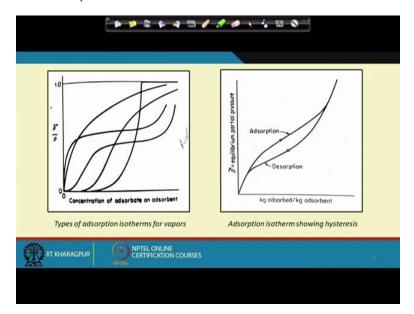
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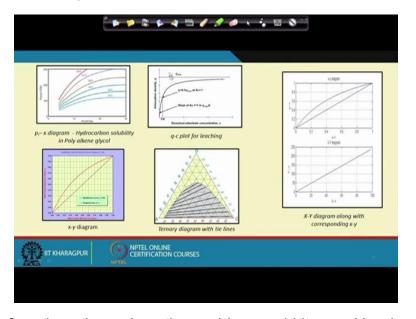
And so therefore this is a typical solubility curve for gases in water here we find that in this particular case the coordinates are partial pressure of solute in gas as a function of the mole fraction of the solute in liquid and we find that the steepness of the curves that we get, they denote the extent of solubility. For example we find that there is a the partial pressure is very high at a low mole fraction for the case of sulphur dioxide which shows that sulphur dioxide under this particular condition is relatively insoluble in water.

While on the other hand the partial pressure is much less at higher mole fraction for HCl solution which shows that HCl is much more soluble in water. So therefore the steepness of the curve gives you an idea of the solubility of that particular component and from there we know that whether the absorption with this particular solute is going to be feasible or not. If the solubility is very low then there is no point in using this particular solvent for extracting or absorbing this particular gas.

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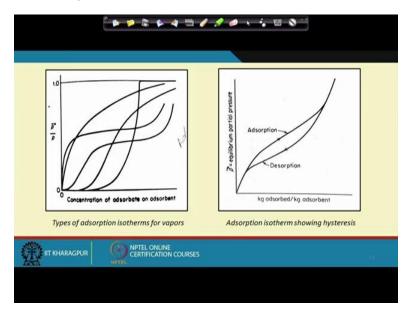
Now let us go for adsorption, adsorption as I have said it can either be a q versus C as have shown here this is for adsorption of a liquid. We can also have in terms of partial pressure as we have shown here. Now from this particular curve it is quite evident that adsorption isotherms they are called adsorption isotherms because mostly they are plotted at constant pressure they are not always concave upwards we can have a wide variety of adsorption isotherms as we can see here.

And something very unique to adsorption which I should be mentioning here is that for all other mass transfer processes see we can extract the phase equilibrium data either while we are increasing the concentration or while we are decreasing the concentration and we find that

usually for all the cases we get the same equilibrium concentration. For example in case of absorption, say carbon dioxide being absorbed in water, okay.

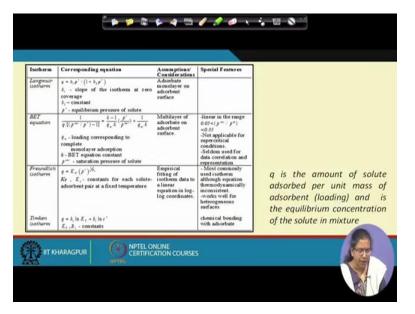
We can either start with a highly saturated value of carbon dioxide in water we can keep on changing the pressure so that the solubility keeps on decreasing and we can record the solubility as a function of pressure or a function of temperature or else we can start with pure water we can keep on dissolving carbon dioxide and increasing the temperature or the pressure and finding out the equilibrium concentration, for both the cases usually we get the same equilibrium concentrations but this is not the case for adsorption.

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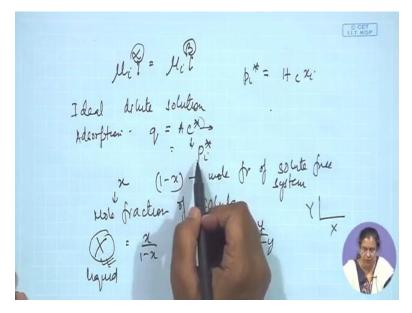


If we generate the adsorption isotherm during adsorption and during desorption usually we find that the 2 curves they do not coincide with one another as a result of which it exhibits the phenomena of hysteresis which is mostly exhibited by adsorption and not by other mass transfer processes and during this exhibition of this phenomena of hysteresis which is usually exhibited over a particular range of concentration we always find that the desorption equilibrium pressure is always lower than the adsorption equilibrium pressure.

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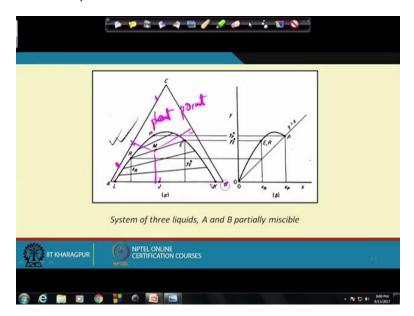


Well, as far as the mathematical equations are concerned I have already mentioned for absorption it is the Henry's law and for adsorption the simplest equation is something like the Henry's law it denotes a linear relationship between the amount which is adsorbed per unit mass of adsorbent and equilibrium concentration in the liquid phase or the or the equilibrium partial pressure in the vapour phase.

Apart from that we find that several other equations are available to predict the adsorption isotherms under different conditions, the equations and the special features are mentioned here it's not important for you to remember all these equations it is just important for you to remember that since absorption it so very erratic as I've shown you the isotherm as have

shown you the phenomena of hysteresis therefore several equations are needed in order to predict adsorption under different conditions.

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Well, the last which I would like to discuss with you is liquid-liquid extraction. In this case as I have already mentioned that what happens when we are dealing with liquid vapour cases? The gas phase is always miscible, liquid phase it may be miscible it may not be miscible, so therefore usually a two-dimensional plot of the 2 equilibrium concentrations under different conditions of temperature and pressure are sufficient to generate an equilibrium plot.

But in liquid-liquid equilibrium as I have mentioned or taught while ago, we find that they have mutual solubility's among the different components, let us take a concrete example say we have A where C is dissolved and we add up B in order to and here what we do? We add up B in order to extract C from A, we know that C is soluble in A and C is soluble in B, right? And also A is soluble to small extent in B and B is soluble to a small extent in A.

Now how to represent such a type of phase diagram? What we do? We usually represent them on an equilateral triangle where the 3 apexes of the triangle refer to pure components, so this apex it refers to pure A, this is pure C and this is pure B and all the sides of the triangles they refer to binary solutions this denotes solution of C in A, this denotes solution of C in B, this denotes the liquid-liquid mixture of A and B.

Along this particular site, the relative proportions of A and C is denoted by the particular point where we select for example a point here it has got a small amount of A, a large amount

of C where as the point here is a small amount of C and a large amount of A. Now we know C, C and A form a completely miscible system C and B form a completely miscible system, A and B their solubility's are very low in one another. So therefore they form 2 immiscible systems which are denoted by point L and point K.

If the systems are highly immiscible point L and point K they shift more and more towards A and towards B. So therefore this particular range it shows the extent of miscibility of A and B and we find that between L and K there is a dome, what does it represent? This particular side from L to P it denotes that A and B they are mutually insoluble and with the addition of C the change in the mutual solubilities of A and B are denoted by this particular dome.

So within this region, this region it is heterogeneous region comprising of 2 phases, outside this region it is a single phase liquid solution and solubility of C in A and the solubility of C in B both of them they meet at a point P which is known as the plait point and within this particular dome any particular point say point M it comprises of 2 liquid phases one liquid phase comprises of solution of C in A and the other liquid phase comprises of a solution of C in B, the compositions of the 2 phases are denoted by the Tie lines which pass through M and intersects this particular dome.

So therefore at M in reality we have a solution of A and C corresponding to composition R and the solution of C in B corresponding to a composition E and we find that all these Tie lines they are usually not parallel to one another they are usually not horizontal they gradually change their slope but the sign of the slope more or less remains the same there are few cases where we see that the sign of the slope changes and we find that the slope gradually from negative slope it becomes horizontal and then it becomes slightly on the other side such systems are known as Solutropic system but the systems are not very common in one another.

So therefore we find that, in this particular case if we find the solution of **C** in B is much richer as compared to the solution of C in A this is also denoted by this particular phase diagrams which automatically suggests that B has got a higher or rather C has got a higher affinity for B and therefore B can serve as a proper solvent for extracting C from A and again another thing I would like to mention that any point inside the triangle we can know the proportions of A, B and C here, how can we know it? We know that sum of the perpendicular dropped from this point on the 3 sides they equal to the sum of the altitude, so what do we do?

We assume that the altitude is 100 percent, so therefore these 3 they sum up to 100 percent and the perpendicular distance dropped from M on AC it represents the mole fraction or the fraction of B, the perpendicular which has been dropped from M on BC represents the mole fraction of A and the perpendicular of M from AB represents the mole fraction of C. So accordingly by this process we can find out for any particular point inside the triangle the composition of the liquid mixture corresponding to that point when it is inside the triangle it is a it comprises of all the 3 components, when it is along the sides of the triangle it comprises of 2 components and when it forms any particular apex of the triangle it refers to that particular pure component.

So therefore this completes our discussions on phase equilibrium thermodynamics, we have not only dealt with vapour liquid equilibrium but also other equilibrium considerations which are which are important for other mass transfer operations which we will be covering in the course of your chemical engineering curriculum. From here we could understand how phase equilibrium is important for all mass transfer operations and in what way phase equilibrium relationships or phase equilibrium diagrams should be represented for different mass transfer operations and it's also important to remember that the units in which we express the phase diagrams they are also different for different systems that we consider.

Usually mole fractions are used or preferred, mole ratios are preferred to obtain linear phase equilibrium curve and partial pressure is a much more relevant unit when gas phase is concerned just because it is easier to measure partial pressure or the pressure as compared to concentration, for any liquid phase involved or for any solid phase involved it is the concentration which is important. Usually concentration is denoted by C in the liquid phase and by Q in the solid phase.

And it is also important to remember that in adsorption equilibrium isotherms they are often marked by the phenomena of hysteresis and therefore adsorption isotherms they're comparatively difficult to obtain and they are mainly based on equilibrium experimental data and several curve fitting of experimental data as have been proposed by the different adsorption isotherms that we have discussed and such ternary liquid such ternary equilibrium plots they are not only common in liquid-liquid equilibrium data they can also be common for adsorption or other mass transfer operations when more than one particular component gets transferred

or in other words when all the components involved with one another gets transferred into one another but usually ternary plot is much more relevant for liquid-liquid extraction processes. So with this I wish you good luck and I really hope you have enjoyed journey of phase equilibrium thermodynamics. We have been solving your doubts and queries and we are there for addressing further doubts that you have before your exams. So good luck and good day to all of you