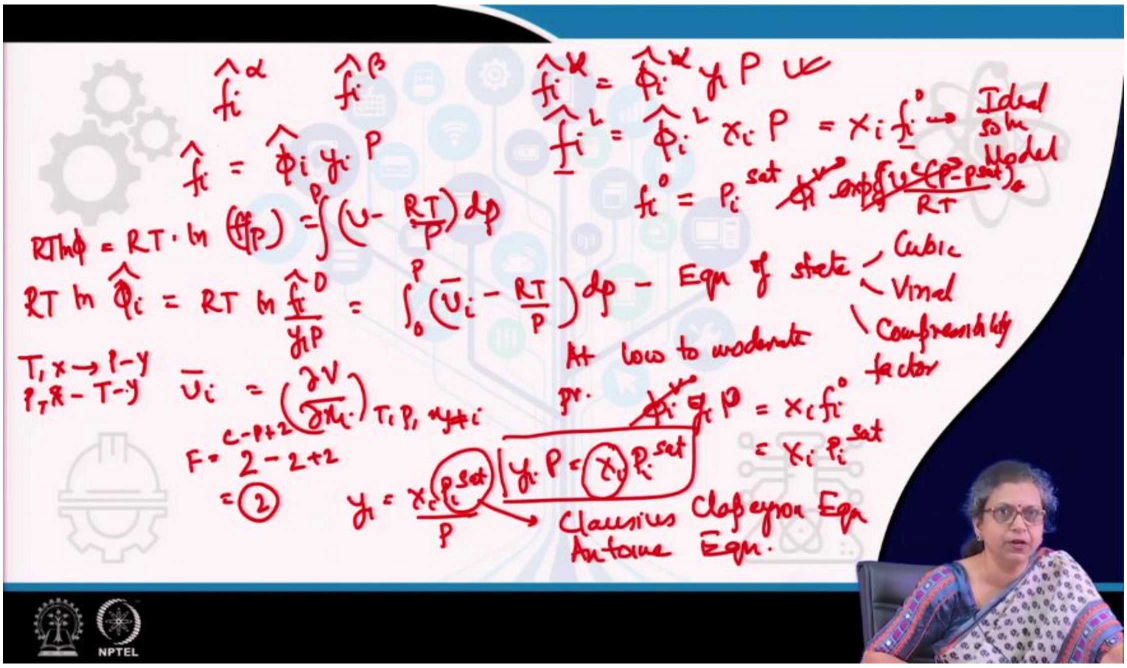
`Principles and Practices of Process Equipment and Plant Design
Prof. Gargi Das
Prof. S Ray
Department of Chemical Engineering
Indian Institute of Technology, Kharagpur

Module - 02
Lecture - 06
Phase Equillibrium (Contd.)

We continue with our discussions regarding the Phase Equilibrium which we had already started in the last lecture. Where did we stop? We stopped by defining the vapor liquid equilibrium under ideal conditions.

(Refer Slide Time: 00:54)



$\hat{f}_i^{\alpha}$ $\hat{f}_i^{\beta}$

$\hat{f}_i = \hat{\phi}_i y_i P$

$RT\ln\phi = RT \cdot \ln\left(\frac{f}{P}\right) = \int^{P}\left(v - \frac{RT}{P}\right)dp$

$RT\ln\hat{\phi}_i = RT\ln\frac{\hat{f}_i^{v}}{y_i P} = \int_0^P\left(\bar{v}_i - \frac{RT}{P}\right)dp$ - Eqn of state < Cubic, Virial, Compressibility factor

$T, x \to P-y$

$P, x - T-y$

$\bar{v}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}}$

$F = C-P+2 = 2-2+2 = ②$

$y_i = \frac{x_i P_i^{sat}}{P}$ $\boxed{y_i P = x_i P_i^{sat}}$ → Clausius Clapeyron Eqn, Antoine Eqn.

$\hat{f}_i^{v} = \hat{\phi}_i^{v} y_i P$ ✓

$\hat{f}_i^{L} = \hat{\phi}_i^{L} x_i P = x_i f_i^{o}$ → Ideal soln Model

$f_i^{o} = P_i^{sat}\cancel{\phi_i^{v}}\exp\left\{\frac{v^{L}(P-P^{sat})}{RT}\right\}$

At low to moderate pr. $\cancel{\hat{\phi}_i^{v}} y_i P = x_i f_i^{o} = x_i P_i^{sat}$

We can find out y_i as a function of x_i. When we are dealing with vapor liquid equilibrium suppose in distillation, we use y_i vs x_i equilibrium data. We find that the number of components suppose it is a binary mixture. So, for a binary mixture, the total degrees of freedom is equal to 2 as per the following equation.

$$F = C - P + 2 = 2 - 2 + 2 = 2$$

So, therefore, if we know 2 number of intensive properties the other properties can be found out.

By convention, either we know T vs x and we can express P vs y or maybe we know P vs x and we can express T vs y. In this particular way, we can find out the vapor-liquid equilibrium under different conditions.

(Refer Slide Time: 02:18)

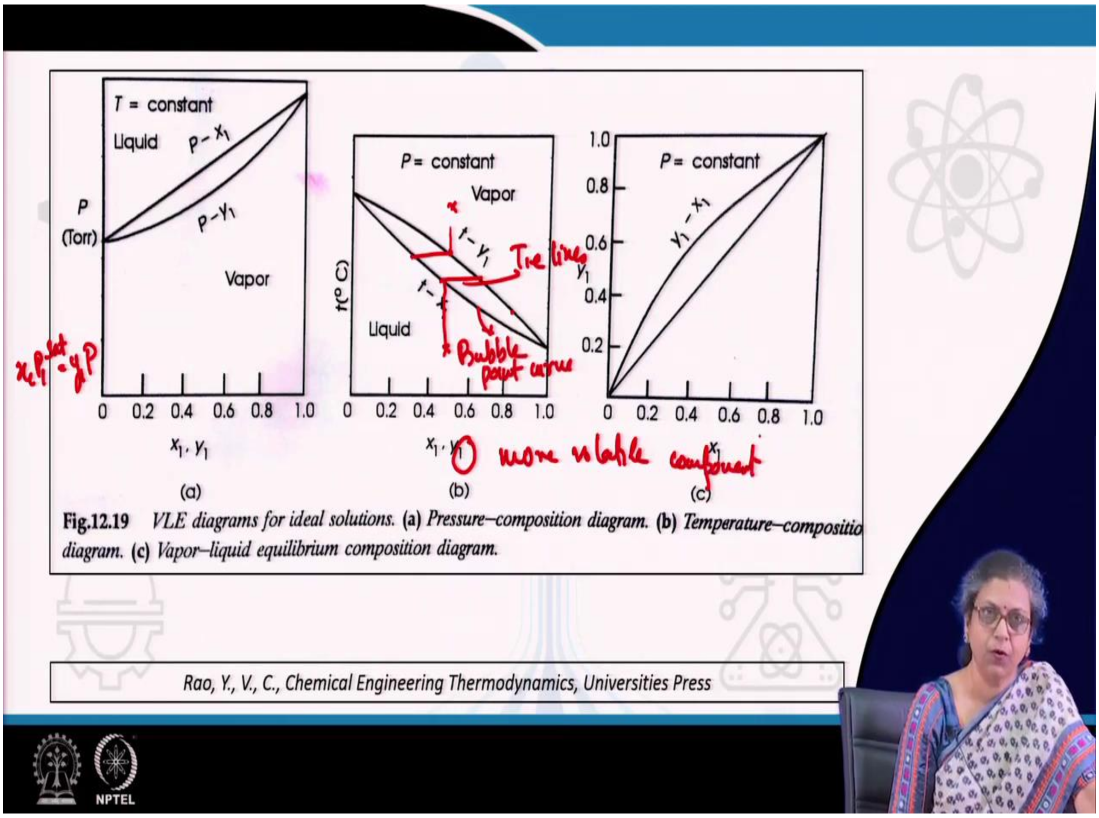


Fig.12.19 *VLE diagrams for ideal solutions.* **(a)** *Pressure–composition diagram.* **(b)** *Temperature–compositio diagram.* **(c)** *Vapor–liquid equilibrium composition diagram.*

Rao, Y., V., C., Chemical Engineering Thermodynamics, Universities Press

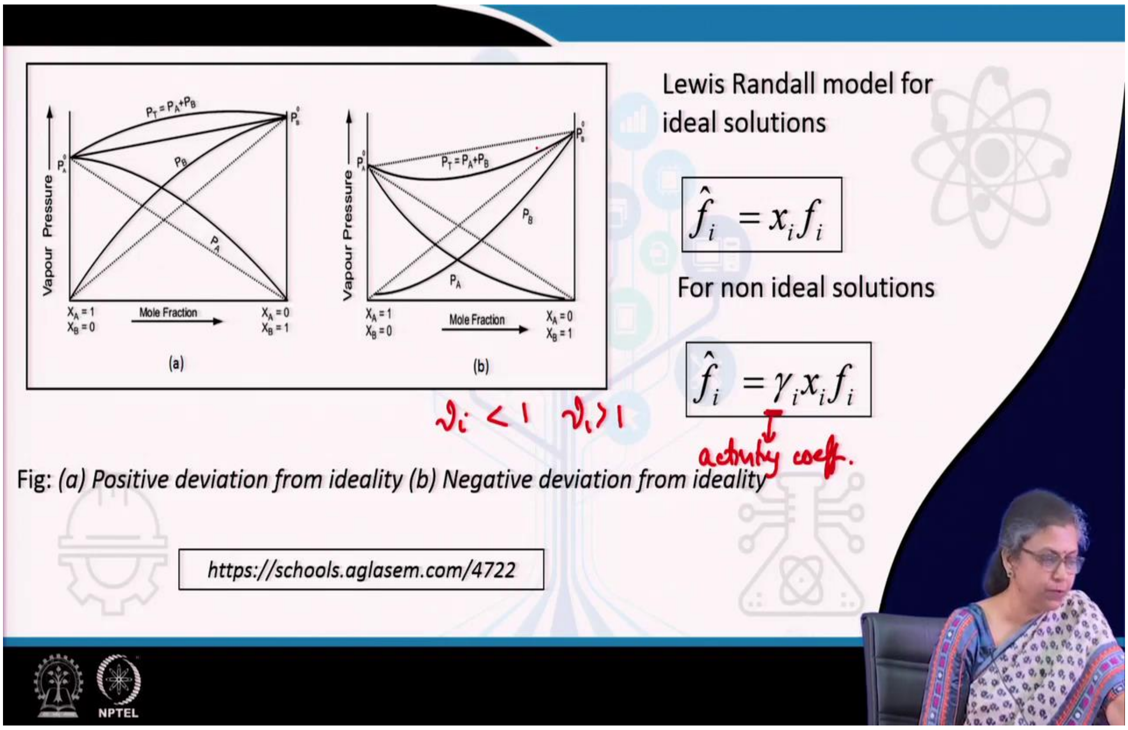
Let us consider P-x-y data. We discussed that

$$x_iP_i^{sat} = y_iP$$

Which automatically means that the pressure (P) varies linearly with the composition in the liquid phase (x_1) as a result of which we find that P versus x_1 is linear. P vs y_1 is something of this sort. Above this, we are having a liquid. At higher pressures, there is liquid and at lower pressures, there is vapor.

The corresponding t-x-y diagram can be developed from here. We start from a liquid phase and start heating it, then the first bubble will appear on the line of t-x curve. As all the bubble point at different composition appears on this line, this line is called as the bubble point curve. In the same way, if we start from the vapor phase and if we start cooling it then the first dew appears on the line of t- y curve. This particular point is called the dew point. All the dew points for different compositions appear on the t-y curve. This t-y curve is called the dew point curve. The dew composition which is in equilibrium with its corresponding bubble composition can be connected by the horizontal line which is the isobaric, isothermal line. If you remember, you must have studied them in thermodynamics, they are known as tie lines. These correspond to the equilibrium compositions and they can be plotted. If they are plotted, we get another graph like graph C. I would like to remind you that these particular graphs (a,b,c) which have been drawn concerning component-1. Component-1 refers to the more volatile component and as a result of which we get "y vs x" curve in this particular form (Figure C).

(Refer Slide Time: 04:22)



Lewis Randall model for ideal solutions

$$\boxed{\hat{f}_i = x_i f_i}$$

For non ideal solutions

$$\boxed{\hat{f}_i = \gamma_i x_i f_i}$$

activity coeff.

$\gamma_i < 1$ $\gamma_i > 1$

Fig: *(a) Positive deviation from ideality (b) Negative deviation from ideality*

https://schools.aglasem.com/4722

Now, suppose this solution is not an ideal solution under that condition what we do? Non-ideality is applicable for the liquid and the vapor phase always follows the ideal condition. In the liquid phase when the solution is not ideal we modify Raoult's law or rather the Lewis Randall rule by incorporating a parameter gamma (γ) which is known as the activity coefficient.

There can be positive divisions from Raoult's law when $\gamma_i > 1$. There can be negative divisions from Raoult's law when $\gamma_i < 1$. When $\gamma_i > 1$, the total pressure is higher than that calculated from your ideal solution model. When $\gamma_i < 1$, the total pressure is lower as that computed from the ideal solution model.

(Refer Slide Time: 05:21)

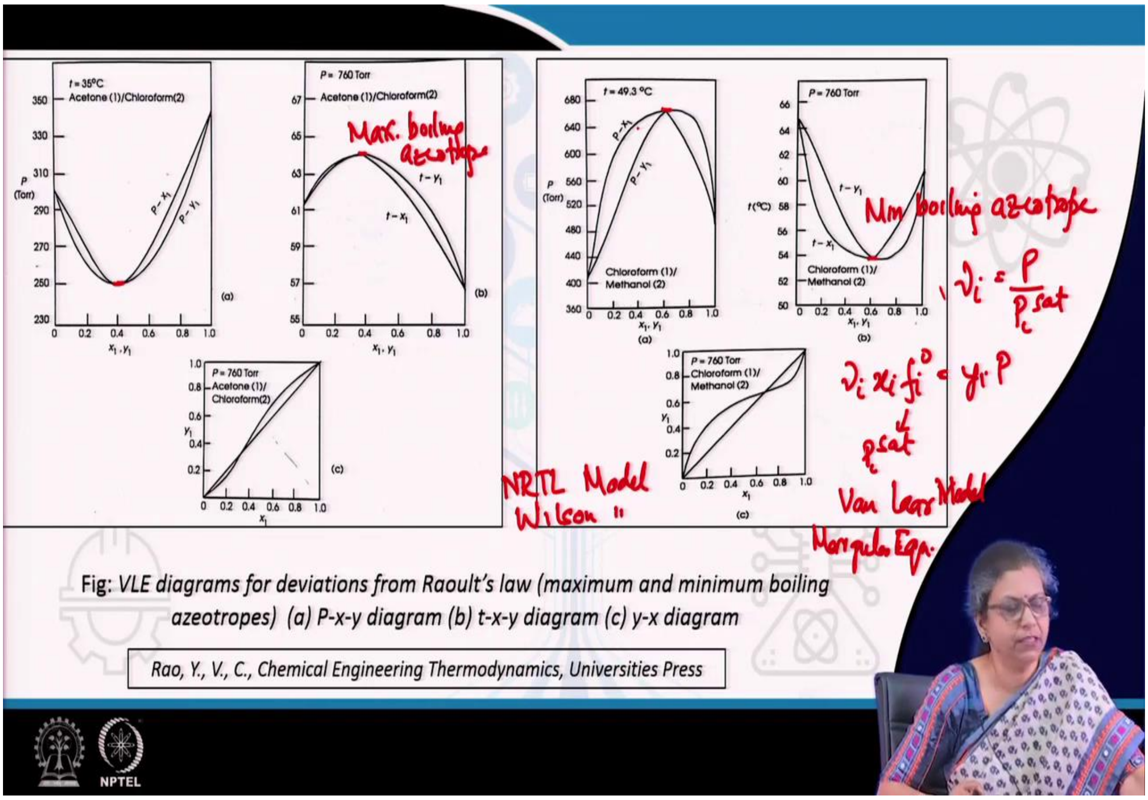


Fig: VLE diagrams for deviations from Raoult's law (maximum and minimum boiling azeotropes) (a) P-x-y diagram (b) t-x-y diagram (c) y-x diagram

Rao, Y., V., C., Chemical Engineering Thermodynamics, Universities Press

So, the P-x-y, t-x-y, and the x-y diagrams get modified for non-ideal solutions in this particular way. The left side figure corresponds to the negative deviation from Raoult's law which forms the maximum boiling azeotrope. At this particular when we find that the two boiling points are not very much removed and the deviation is quite high. For such conditions, the P-x-y exhibits either minima or maxima. There is one particular composition where the mixture boiling point is much higher compare to the boiling point of the pure components and this point refers to the maximum boiling azeotrope which forms when there is a negative deviation from Raoult's law. We also have positive deviations from Raoult's law, we have a minimum boiling azeotrope. Now, in these azeotropic conditions, they are very useful for finding out the gamma (γ). That is why I would like to mention a special reference to it.

Now, for non-ideal solutions what do we find? For non-ideal solutions, the vapor-liquid equilibrium condition can be written as follows:

$$\hat{f}_i = \gamma_i x_i f_i^0 = y_i P$$

At low to moderate pressures,

$$f_i^0 \rightarrow P_i^{Sat}$$

Therefore, this gamma i (γ_i) has to be found out from the other available parameters. Normally, there are some activity coefficient models which you must have studied in your thermodynamics class.

Here I would like to mention that mostly for finding out γ_i. The models which are taught in the colleges are usually the Van Laar model and the Margules model. But in reality when we try to find out γ_i, we use some models which correspond to the "NRTL model" or the "Wilson model" or maybe the "UNIQUAC model". Usually, we use these models which normally we do not cover, but you remember that these are the models which are normally used.

At the point of azeotropy

$$x_i = y_i$$

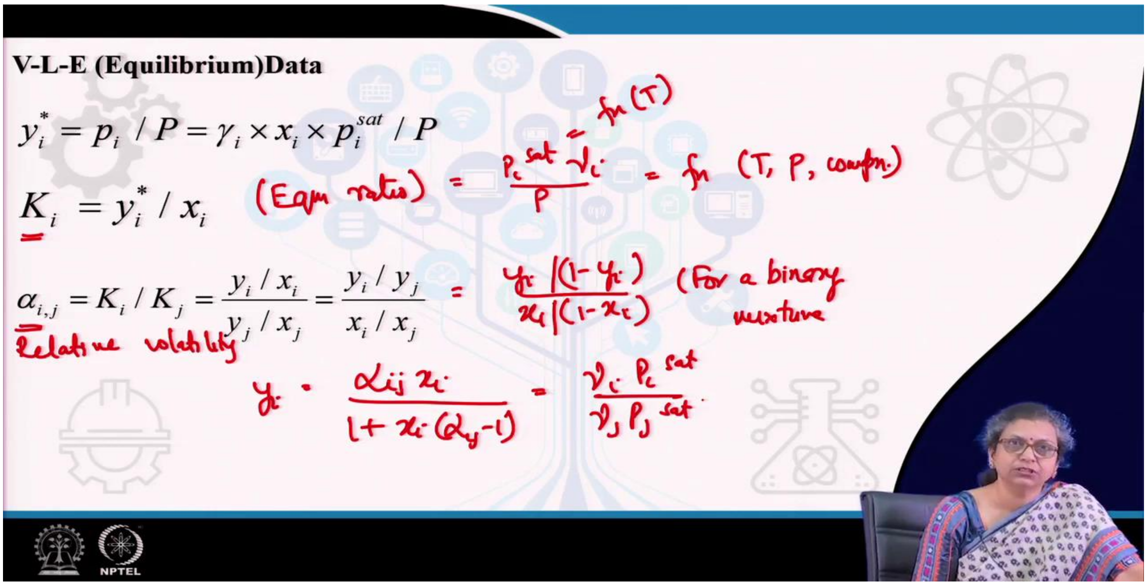
So, under that condition, we find

$$\gamma_i = \frac{P}{P_i^{Sat}}$$

So, therefore, finding out activity coefficients at the point of azeotropy becomes extremely easy. Therefore, it is very important to determine whether we are going to have an azeotrope for two reasons;

1. At the moment we have an azeotrope, we cannot perform further separations by distillation,
2. At the point of azeotropy, we can estimate γ_i.

(Refer Slide Time: 08:31)



V-L-E (Equilibrium)Data

$$y_i^* = p_i / P = \gamma_i \times x_i \times p_i^{sat} / P$$

= fn (T)

$$\underline{K_i} = y_i^* / x_i \quad \text{(Eqm ratio)} = \frac{P_i^{sat}\gamma_i}{P} = fn\ (T, P, \text{compn.})$$

$$\underline{\alpha_{i,j}} = K_i / K_j = \frac{y_i / x_i}{y_j / x_j} = \frac{y_i / y_j}{x_i / x_j} = \frac{y_i / (1-y_i)}{x_i / (1-x_i)}$$

(For a binary mixture

Relative volatility

$$y_i = \frac{\alpha_{ij} x_i}{1 + x_i(\alpha_{ij} - 1)} = \frac{\gamma_i P_i^{sat}}{\gamma_j P_j^{sat}}$$

In vapor-liquid equilibrium, I would also like to mention that it is not only that we find out y_i from x_i, conventionally very frequently what we do? We can often express the vapor-liquid equilibrium data in terms of some equilibrium ratio (K_i).

$$K_i = \frac{y_i^*}{x_i}$$

As we know,

$$y_i^* = \frac{p_i}{P} = \frac{\gamma_i \times x_i \times p_i^{sat}}{P}$$

For this particular case, we will find

$$K_i = \frac{P_i^{sat}\gamma_i}{P}$$

It is a function of P_i^{sat} which is again a function of temperature. So, K_i is a function of temperature, pressure, and composition.

$$K_i = f_n(T, P, composition)$$

So, therefore, very frequently instead of expressing the equilibrium data in terms of K_i what we do? We express it in terms of a parameter which is expressed as α_{ij}, which is the ratio of K_i and K_j. For vapor-liquid equilibrium, this is known as relative volatility.

It simply shows the ease of separation of the two components. You will find that very frequently the equilibrium data are expressed in terms of α_{ij}.

$$\alpha_{ij} = \frac{y_i/y_j}{x_i/x_j}$$

For a binary mixture, α_{ij} can be expressed in the following way.

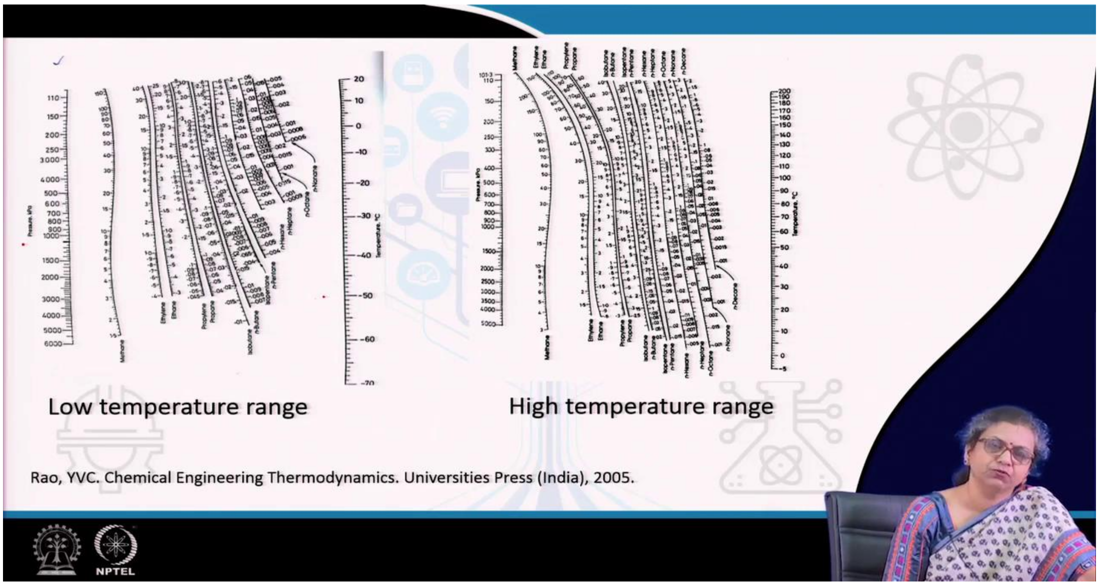
$$\alpha_{ij} = \frac{y_i/(1-y_i)}{x_i/(1-x_i)}$$

So, therefore, for a binary mixture if we know the value of α_{ij} and you know the value of x_i then you can find out y_i. We can use the following equation for this purpose.

$$y_i = \frac{\alpha_{ij}x_i}{1+x_i(\alpha_{ij}-1)} = \frac{\gamma_i p_i^{sat}}{\gamma_j p_j^{sat}}$$

The ratio of K_i for the two for the different components can be expressed in terms of the relative volatility for a vapor-liquid or gas-liquid equilibrium data. Accordingly, we can express it in this particular form as mentioned above. Conventionally Ks are used for ideal solutions.

(Refer Slide Time: 11:43)



Low temperature range

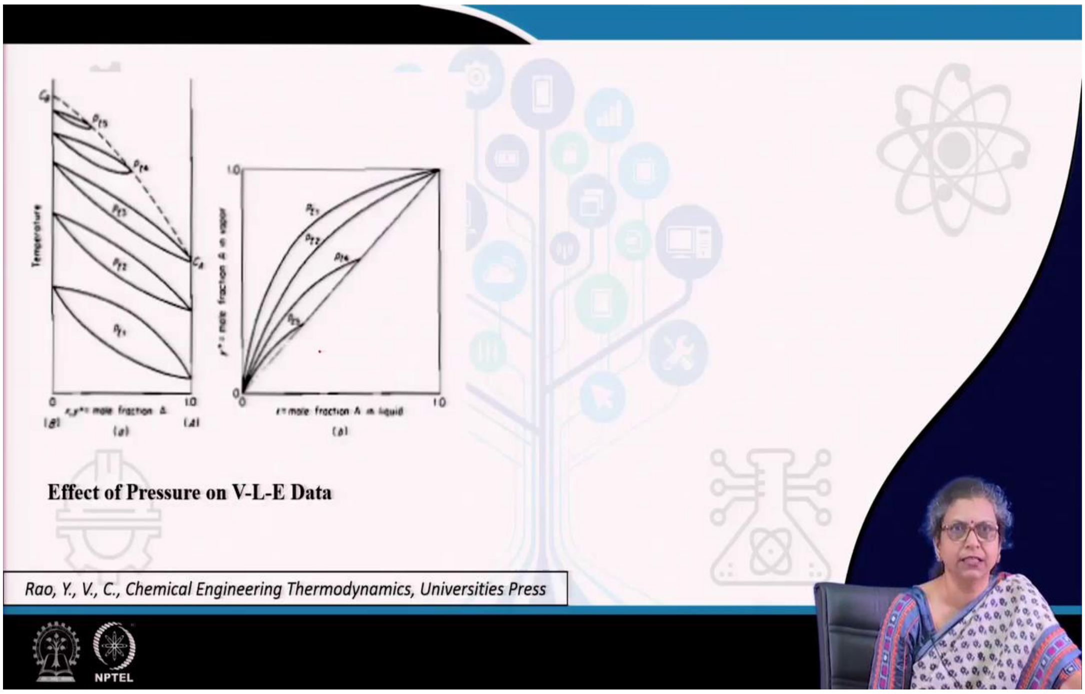
High temperature range

Rao, YVC. Chemical Engineering Thermodynamics. Universities Press (India), 2005.

You have already studied, they are ideal for adjacent members of homologous series and isomers etc. So, therefore, the K values are available for hydrocarbons. So, typical K values which are available have been shown in this particular slide. Here if you know the pressure (P), temperature (T), then for the different hydrocarbons you can out the K values.

Once you can find the K values you can find the α_{ij} values and you can generate the vapor-liquid equilibrium data. For other substances, as we go into distillation. You will find that quite often we give you the data on α_{ij} and there can also be some situations where you will find that the equilibrium data either in terms of t-x-y or in terms of x-y.

(Refer Slide Time: 12:39)



Effect of Pressure on V-L-E Data

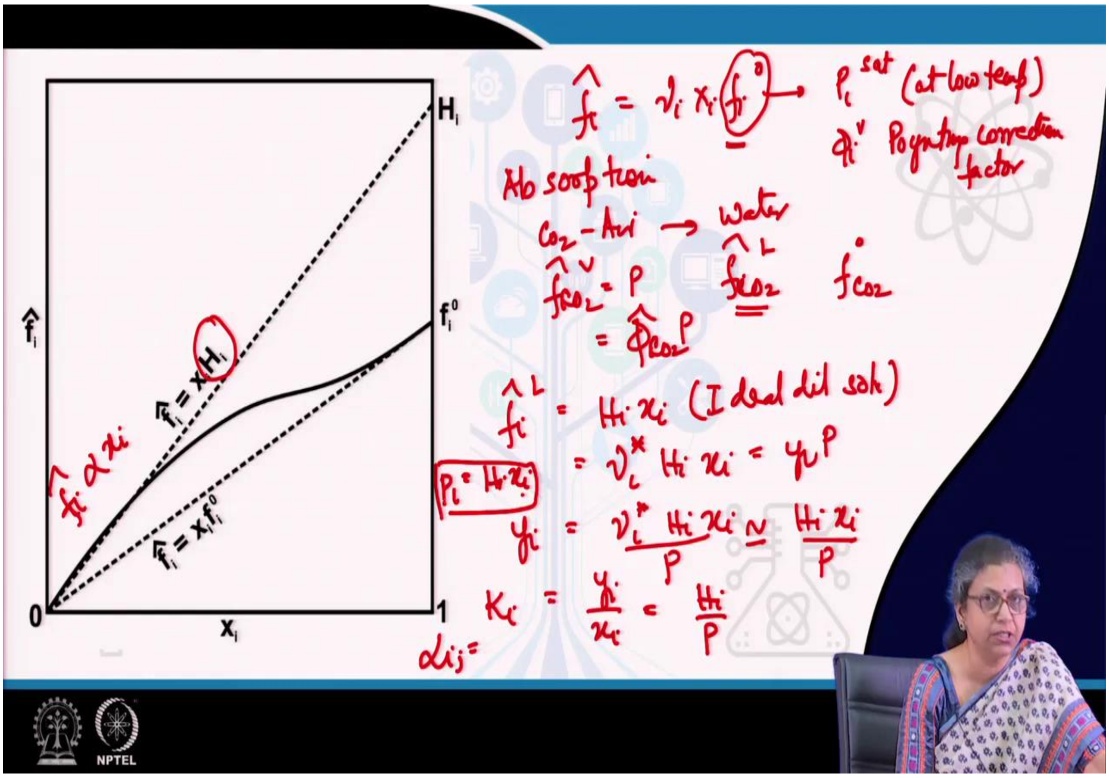
Rao, Y., V., C., Chemical Engineering Thermodynamics, Universities Press

I would just like to show you that how does pressure effect the t x y data. This we will be doing in much more detail when we do distillation. What do we find in this particular case? We find if you observe, you find that more or less the difference between the bubble point and the dew point becomes narrower and narrower as we go for higher pressure conditions in this particular case these are for higher pressure conditions.

When this becomes narrow what it means? It means that the relative volatility between the two phases becomes closer and therefore, separation by distillation becomes more difficult. Also, you will find that once we exceed the critical conditions of the more volatile component, then we find that the curve becomes looped and therefore, the range of conditions where separation can occur by distillation that becomes smaller and smaller.

So, these things the effect of pressure and V-L-E data is something which we will need to remember when we decide upon the pressure in which we would like to operate the distillation column that we are going to design.

(Refer Slide Time: 14:05)



$\hat{f}_i = \gamma_i x_i f_i^0 \rightarrow P_i^{sat}$ (at low temp)

ϕ_i^v Poynting correction factor

Absorption

CO_2 - Air → water

$\hat{f}_{CO_2}^V = P \quad \hat{f}_{CO_2}^L \quad f_{CO_2}^0$

$= \hat{\phi}_{CO_2} P$

$\hat{f}_i^L = H_i x_i$ (Ideal dil soln)

$= \gamma_i^* H_i x_i = y_i P$

$\boxed{p_i = H_i x_i}$

$y_i = \frac{\gamma_i^* H_i x_i}{P} \simeq \frac{H_i x_i}{P}$

$K_i = \frac{y_i}{x_i} = \frac{H_i}{P}$

$\alpha_{ij} =$

When we were dealing with vapor-liquid equilibrium, we had assumed that all the components exist in the liquid phase, over the entire range of compositions right. Then what we did? We assumed the ideal solution model and then we modified the ideal solution model.

So, if we consider the modified form of the ideal solution model.

$$\hat{f}_i = \gamma_i x_i f_i^0$$

Finding out f_i^0 is not at all a problem because this corresponds to the pure component fugacity at the temperature and pressure of the system. So, therefore, if you know the temperature and pressure of this solution you can very well find out f_i^0. f_i^0 will correspond to the saturated vapor pressure at low temperatures. Otherwise, you can very well find it out, once if you know ϕ_i^v and also the pointing correction factor.

Suppose, the liquid is in equilibrium with noncondensable gases. It means that at the condition of the solution, the gas does not exist as a liquid. In this case f_i^0 for the non-condensable gas that becomes a fictitious state. Finding out fi^0 becomes difficult under that condition. This is the case which we encounter for the process of absorption.

So, what do we do? See we have to find out $\hat{f}_i$ for the liquid phase and to calculate the equilibrium conditions. If we want to remove carbon dioxide from air and we add water whether at all any removal will happen or not we have no idea.

So, by some means, we need to find out $\hat{f}_{CO_2}^L$ in the water phase or the liquid phase. we also need to find out $\hat{f}_{CO_2}^V$ in the vapor phase. Then, we need to compare to find out whether at all we can do absorption or not.

For the vapor phase, it is not at all a problem. We know that it will either be equal to pressure or in other words it will be equal to $\hat{\phi}_{CO2} \times P$ depending upon the composition.

$$\hat{f}_{CO_2}^V = P \text{ } or \text{ } \hat{\phi}_{CO_2} P$$

So, therefore, how to find out $\hat{f}_{CO_2}^L$? If we cannot find out $\hat{f}_{CO_2}^0$ in the pure state.

So, when we refer to the graph of by the partial fugacity with composition, we find that the just like at very large compositions f_i is proportional to x_i. The proportionality constant is f_i^0.

$$\hat{f}_i = x_i f_i^0$$

We find that at very low compositions also f_i that is proportional to x_i, but the proportionality constant this is not equal to f_i^0, but it is Henry's law constant (H).

$$\hat{f}_i = x_i H_i$$

So, for absorption, we can write down that f_i^L in the liquid state is equal to Hi^*x_i for an ideal dilute solution. If it is not an ideal dilute solution, we are going to modify it by activity coefficient. Where this activity coefficient which I have denoted with γ_i^*that corresponds to the deviation from the ideal dilute solution model right.

$$\hat{f}_i^L = H_i x_i = \gamma_i^* H_i x_i$$

Again, at equilibrium condition, $\hat{f}_i^L = y_i P$

From the above equations, we can write

$$y_i = \frac{\gamma_i^* H_i x_i}{P}$$

For. Ideal liquid condition, the above equation can be further reduced to

$$y_i = \frac{H_i x_i}{P}$$

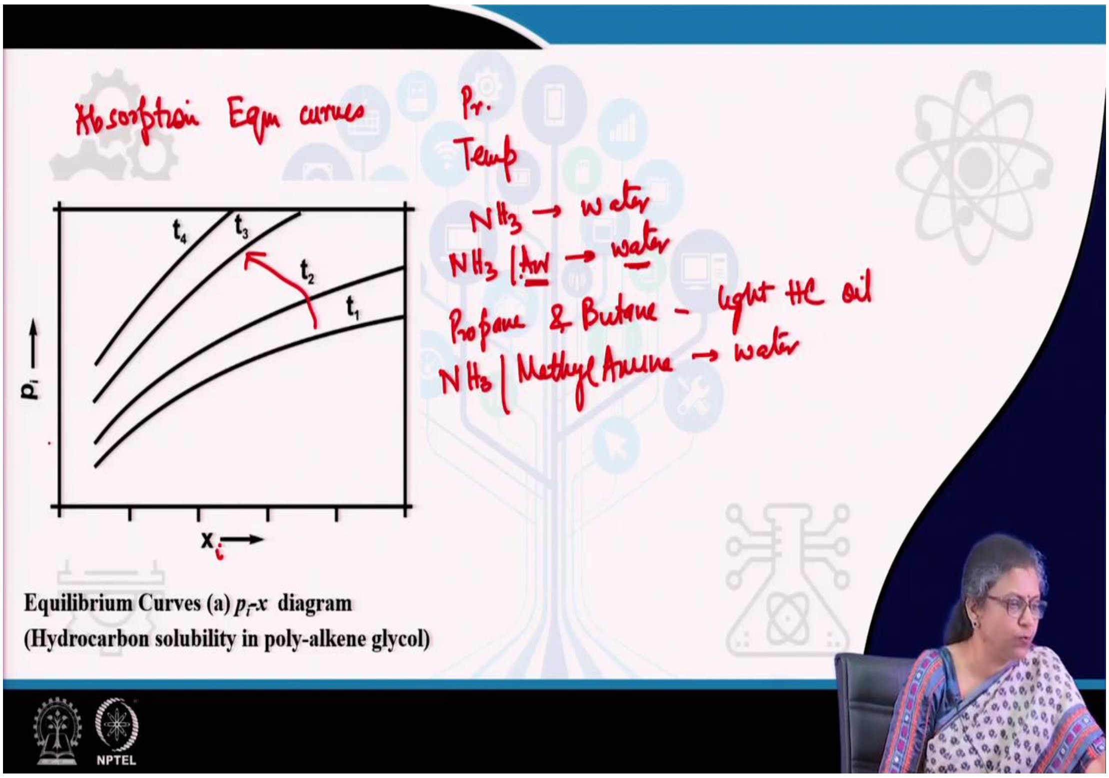
So, for absorption equilibrium constant can be expressed by the following equation.

$$K_i = \frac{y_i}{x_i} = \frac{H_i}{P}$$

We find that for and accordingly you can find out α_{ij}. Accordingly, once we can find out y_i and x_i definitely for different x_i values we can find out y_i values. We can start generating the data. But as I have told you that conventionally we express the data in terms of partial pressure (p_i) and x_i.

So, therefore, to do that we find that p_i corresponds to Hi*x_i.

(Refer Slide Time: 19:44)



Absorption Eqm curves

Pr.

Temp

$NH_3 \rightarrow$ water

NH_3 | Air $\rightarrow$ water

Propane & Butane - light HC oil

NH_3 | Methyl Amine $\rightarrow$ water

Equilibrium Curves (a) p_i-x diagram

(Hydrocarbon solubility in poly-alkene glycol)

So, once you know x_i, we can generate the partial pressure data. We can generate the p_i versus x data for different conditions. Here the p_i vs x data has been shown for hydrocarbon solubility in poly-alkene glycol. This is just a typical curve and the same thing exists for different situations as well.

Now, for this p_i versus x curve which corresponds to the vapor-liquid equilibrium curves. When the non-condensable gas is in contact with the liquid, we need to think particular cases how does the measurable parameters influence it? How does pressure influence the p_i versus x curve when we increase pressure quite naturally the solubility increases.

So, therefore, with the application of pressure the solubility increases. How does temperature inference? See with an increase in temperature if suppose any particular process is there which liberates heat then, in that case, the rate of the rather the process becomes slower as we go for higher and higher temperature. This is from “Van't Hoffs law”.

So, therefore, most of the absorption cases, are accompanied by the release of heat. In other words, they are exothermic. Therefore, for most of the cases we find that as we increase the temperature, the curve becomes steeper and steeper and the solubility of the gas decreases with increase in pressure.

Then, we also find that these particular absorption equilibrium curves are also a function of the type of gas. I would like to mention in this particular case that when a mixture of gases is brought in contact with the liquid.

Say for example, when we have pure ammonia which is contacted with water and we generate this particular curve where the ammonia and in this particular case naturally it will be the pressure of ammonia and in contact with the water right.

Again suppose we have an ammonia-air mixture and we contact it with water and we try to generate the curve. If we find that we express the equilibrium curve in the terms of p_i and x_i, then we find that if the ammonia is mixed with some particular component that is sparingly soluble in the solvent then in that case when we bring ammonia-air in contact with water the x_i remains almost constant. It does not change.

Therefore, if the same equilibrium curve can be applicable whether we are dealing with a pure component or with a component in a mixture with some other components which are very sparingly soluble in the solvent provided we have expressed it in terms of p_i.

We find that suppose there is a mixture of several gases of an all of which are soluble or several which are soluble in the solvent then under that condition. We can use the equilibrium curve for each particular solute provided all of them form ideal solution with the solvent. If they do not form an ideal solution with the solvent then definitely you know that Henry's law constant changes and under that condition we cannot use this pi versus xi curve.

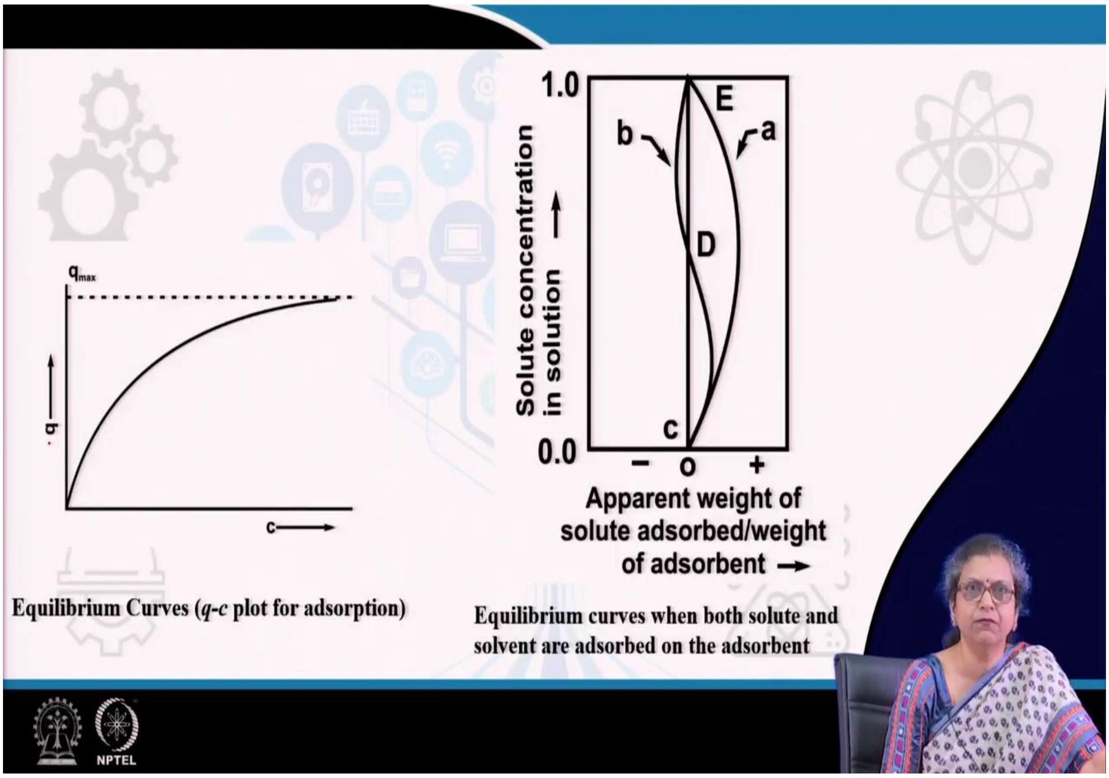
But we can use this p_i versus x_i curve for any component i if the component other components along with i they form either ideal solutions with the solvent or they are almost insoluble in that particular solvent. Also, it is important to note that suppose in the solvent say there is a nonvolatile solute dissolve for example, in water suppose we add some salt quite naturally under that condition also this particular equilibrium curve is not going to be applicable under that particular case. For example I would like to tell. We have propane and butane. Both of them can be absorbed by light hydrocarbon oil. Now for this particular case, we find that in this since each of the component they form an ideal solution. So, therefore, for propane also if we have this p_i versus x_i curve that is going to be applicable for pure propane as well as in this particular mixture the same thing is also true for butane as well.

But suppose we have a mixture of ammonia and say methylamine say for example, and I am absorbing it say in water. In this particular case, the equilibrium curve generated for ammonia or ammonia air is not going to be applicable for a mixture of or rather for absorption of ammonia in water in presence of methylamine.

So, therefore, these are the few things that we need to remember and usually this is the reason why normally we express the absorption equilibrium curves in terms.

I would like to tell you that whenever there is a gas phase we always prefer to express the concentration in the gas phase in terms of partial pressure be it absorption, be it gas-solid adsorption we usually prefer this right.

(Refer Slide Time: 26:15)



Equilibrium Curves (*q-c* plot for adsorption)

Equilibrium curves when both solute and solvent are adsorbed on the adsorbent

The next thing which I would like to discuss is adsorption. So, in adsorption and in extraction what happens that we will be discussing in the next class. Thank you very much.