Principles and Practices of Process Equipment and Plant Design

Prof. Gargi Das
Department of Chemical Engineering
Indian Institute of Technology, Kharagpur

Module – 02
Lecture – 05
Phase Equillibrium

Well, hello everybody. So, today we have come to the second class on the mass transfer processes. Now just to recollect what we had discussed in the previous class we had mentioned that we are primarily concerned with the interphase mass transfer; where between two phases some particular components get transferred from say phase A to phase B where phase B can be created from phase A either by the addition of some form of energy or pressure reduction or there can be an addition of an external phase.

Whenever the two phases come in contact and mass transfer occurs between these two phases till the two phases attain equilibrium. In this particular case of interface mass transfer, what is important? The two phases must be far removed from equilibrium if we want the interface mass transfer to go on. This differentiates the interface mass transfer from the mass transfer which occurs inside any particular phase.

Inside a phase, the mass transfer occurs due to the concentration difference of any particular component between two points in that particular phase. In this particular case, what do we find? The mass transfer occurs because the composition of the transferable component is such that the two phases are not in equilibrium or the chemical potential of the two phases is not the same.

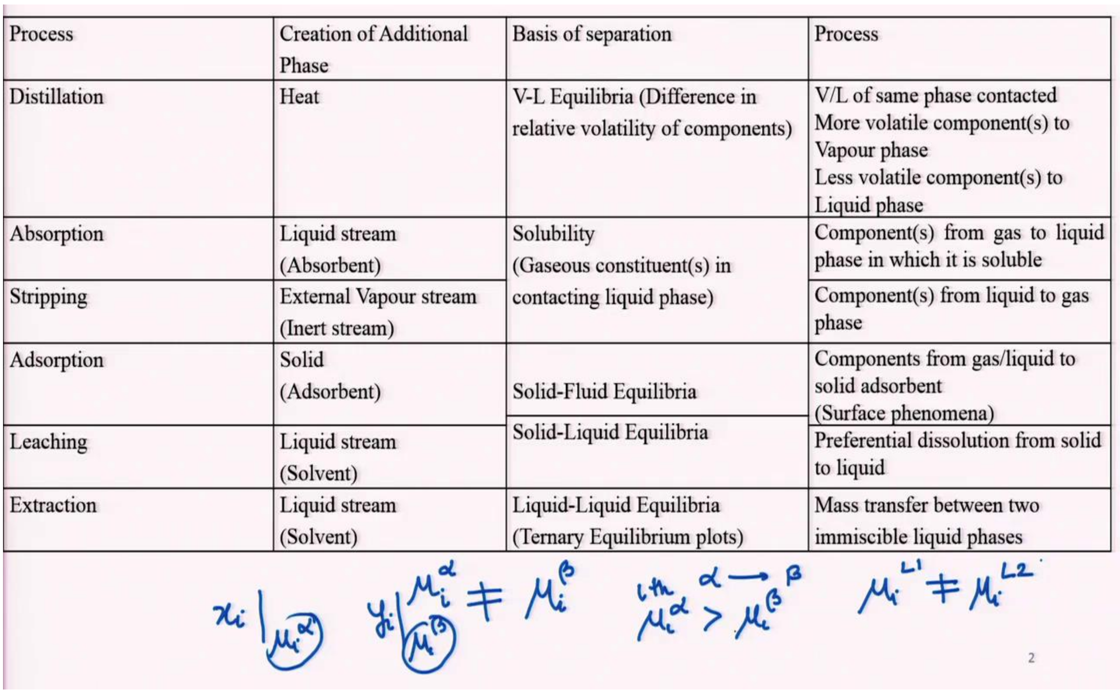
Whether the mass transfer is going to occur or not, is going to depend on the value of the chemical potential corresponding to the two phases. Therefore, the compositions which correspond to equality of chemical potential signifies that the two phases are in equilibrium with respect to the transferable component. Now, here I would just like to mention that equilibrium and steady-state have a basic difference. What is the difference?

Under equilibrium conditions, we consider that in the entire phase A and the entire phase B, the concentrations are uniform throughout. In phase A and phase B, the concentrations may be different. But in the entire phase A and the entire phase B, the compositions have to be the same. Instead, in steady-state what do we assume?

We assume that inside phase A at every particular point the composition does not change with time, but the compositions may vary from point to point. So, therefore, this means that under equilibrium composition the composition within a particular phase neither varies with time nor with any axial position.

While under steady-state conditions the composition or for that matter all thermodynamic properties are invariant with time, but they vary from location to location which implies that equilibrium comprises or encompasses steady-state operations, but steady-state operations are not equilibrium operations.

(Refer Slide Time: 04:13)



Process	Creation of Additional Phase	Basis of separation	Process
Distillation	Heat	V-L Equilibria (Difference in relative volatility of components)	V/L of same phase contacted More volatile component(s) to Vapour phase Less volatile component(s) to Liquid phase
Absorption	Liquid stream (Absorbent)	Solubility (Gaseous constituent(s) in contacting liquid phase)	Component(s) from gas to liquid phase in which it is soluble
Stripping	External Vapour stream (Inert stream)		Component(s) from liquid to gas phase
Adsorption	Solid (Adsorbent)	Solid-Fluid Equilibria	Components from gas/liquid to solid adsorbent (Surface phenomena)
Leaching	Liquid stream (Solvent)	Solid-Liquid Equilibria	Preferential dissolution from solid to liquid
Extraction	Liquid stream (Solvent)	Liquid-Liquid Equilibria (Ternary Equilibrium plots)	Mass transfer between two immiscible liquid phases

$x_i \,\Big|\, \boxed{\mu_i^{\alpha}}$ $\quad y_i \,\Big|\, \boxed{\mu_i^{\beta}}$ $\quad \mu_i^{\alpha} \neq \mu_i^{\beta}$ $\quad$ ith $\alpha \rightarrow \beta$ $\quad \mu_i^{\alpha} > \mu_i^{\beta}$ $\quad \mu_i^{L1} \neq \mu_i^{L2}$

So, therefore, the basic operations which we had discussed in the last class and the operations which will be discussing in much more detail in the subsequent classes, for example, distillation absorption, adsorption, extraction, etc.

So, all these operations are the interface mass transfer operations where the second phase is either created by the addition of energy primarily in the form of heat or maybe by pressure reduction and or by the addition of a second phase. Whatever be the condition, there have to be two phases and there have to be some components that will be transferred from phase 1 to phase 2.

Now, when will this transfer occur? This transfer will occur as I had mentioned in the last class when the chemical potential of that particular component 'i' that is in the phase α that is not equal to the chemical potential of the component in the β phase. Only when this happens then your component 'i' will diffuse from the α phase to the β phase, provided "$\mu_i^\alpha > \mu_i^\beta$".

If the reverse thing happens then the ith component will move from the β phase to the α phase. So, therefore, the rate of mass transfer and how much amount of mass transfer is going to occur that is going to depend on how much different μ_i^α is different as compared to μ_i^β. When $\mu_i^\alpha = \mu_i^\beta$, the mass transfer to stop or not to happen.

What I mean to say is that suppose 'i' say that in alpha phase 'i' denote the composition as x_i right. So, x i corresponding to μ_i^α and for the beta phase suppose I assume that the composition is denoted by y_i. So, y_i corresponding to μ_i^β, now these two compositions are important and mass transfer will stop when $\mu_i^\alpha = \mu_i^\beta$.

So, for this particular condition whatever x_i and y_i compositions are there, they are known as the equilibrium compositions. It can always happen that x_i and y_i are equal yet mass transfer is occurring. Because even when x_i and y_i are equal, we find that $\mu_i^\alpha \neq \mu_i^\beta$.

It can also happen that y_i is much higher than x_i yet we find mass transfer occurs of component 'i' from α to β phase. This is because even if y_i is higher it is lower compared to the equilibrium composition of y_i which is in equilibrium with x_i.

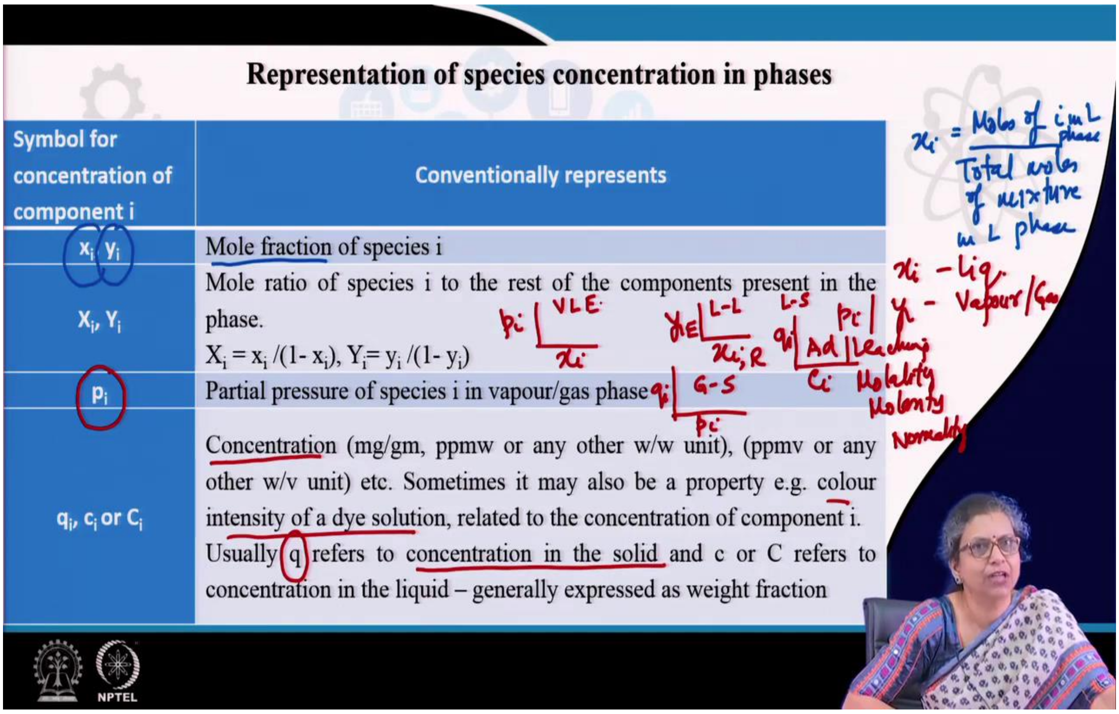
So, therefore, what I would like to say is it is very important to consider the equilibrium conditions and then to relate the compositions corresponding to equilibrium or rather this is known as the generation of equilibrium data that is something very important to understand interface mass transfer operations.

So, quite naturally when we will be dealing with distillation, vapor-liquid equilibrium is going to be important when the vapor and liquid correspond to the same set of components. When it is absorption, here also vapor-liquid or gas-liquid equilibrium is important, but in these cases, naturally, the gas and the liquid phase do not comprise of all the components are not the same. In other words, the gas phase comprises of several noncondensable components.

The same thing applies to stripping as well. For adsorption and leaching definitely, the solid-liquid and the solid-gas equilibrium is important. For extraction, it is the equilibrium between two liquid phases that are not miscible with each other to the total extent.

That means, the two liquid phases may have some miscibility and they usually have some miscibility with one another, but they form two distinct immiscible phases. There is one component or more than one component which diffuses from one liquid phase to the other liquid phase just because the mu of that component “i" in liquid one say is not equal to mu of that component in the second liquid phase.

(Refer Slide Time: 10:08)



Representation of species concentration in phases

Symbol for concentration of component i	Conventionally represents
x_i, y_i	Mole fraction of species i
X_i, Y_i	Mole ratio of species i to the rest of the components present in the phase. $X_i = x_i/(1-x_i)$, $Y_i = y_i/(1-y_i)$
p_i	Partial pressure of species i in vapour/gas phase
q_i, c_i or C_i	Concentration (mg/gm, ppmw or any other w/w unit), (ppmv or any other w/v unit) etc. Sometimes it may also be a property e.g. colour intensity of a dye solution, related to the concentration of component i. Usually q refers to concentration in the solid and c or C refers to concentration in the liquid – generally expressed as weight fraction

So, how do we express the concentration of component “i", where I assume that component “i" is the component which is being transferred from one phase to the other, in that particular case how do we express the composition of component “i"?

Now, the most common way of expressing is the mole fraction or in other words, mole fraction means, moles of “i" in some particular phase divided by the total moles of the mixture. So, if I assume that x_i refers to the composition say in the liquid phase then in that case it is moles of “i" in the liquid phase divided by total moles of the mixture in the liquid phase.

Likewise, y_i by convention generally refers to the mole fraction of component “i" in the vapor phase. If there are two liquids then it refers to the component rather than the composition of component “i" in the phase which is extracting or rather this we call it as the solvent ok.

So, for most of the cases, we usually express the species concentration either in terms of mole fraction of the species “i" or with respect to some property that is proportional to the mole fraction.

For example, in the gas phase normally we use the partial pressure of the species “i" in the vapor phase or the gas phase. For the liquid phase, what do we do? We can either use the mole fraction or else we can use we can express the liquid phase composition in terms of the concentration.

This concentration can be weight per weight, may be milligrams per gram, or parts per million weight, or any other weight per weight. It can be volume per volume or it can be weight per volume also and we can also have some particular other types of units.

For example, normality, molarity etc. We can also have normality. We can also express concentration in these particular terms as well. For the solid phase by convention at least for this particular course, we would like to refer to the concentration in the solid phase in terms of q or terms of q_i.

So, what I would like to conclude is when we will be dealing with liquid phase compositions it will either be if we are dealing if we are referring to in terms of the mole fractions then generally in the liquid phase the composition is expressed by x_i and the composition in the gas phase or the vapor phase that is expressed in terms of y_i.

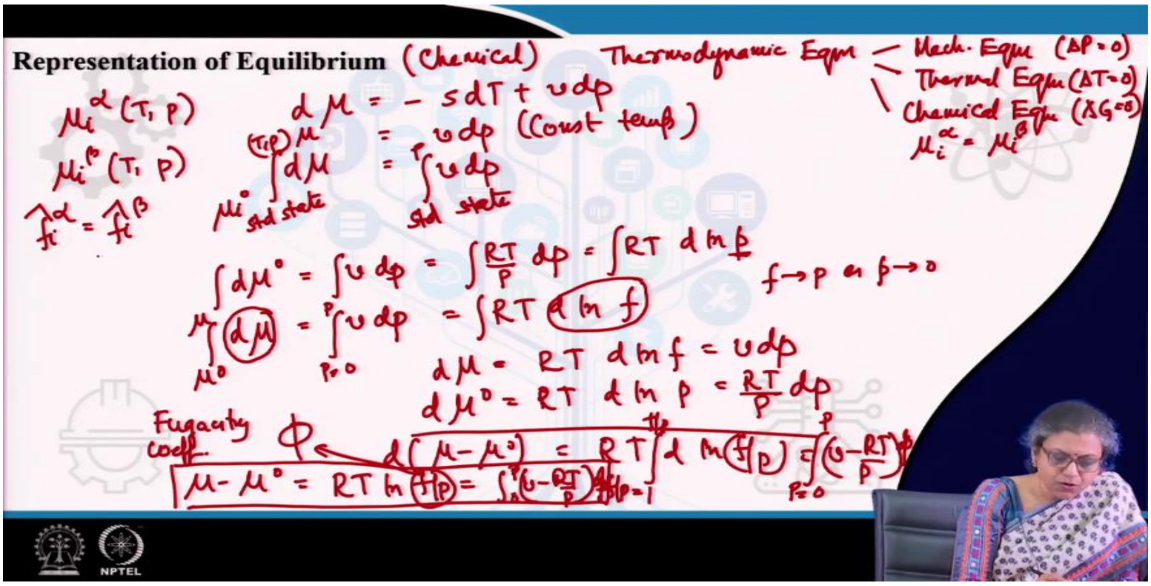
Usually, y_i it is often convenient to express it in terms of partial pressure. In the liquid phase rather than mole fraction, we often use any particular concentration unit. It can also be said, for example, the color intensity of a dye solution which is related to the concentration can be a measure of absorbance or conductance etc.

So, for distillation, it is y_i versus x_i, for absorption, it is all sometimes preferable to use p_i versus x_i. For extraction, we can use something like y_i versus x_i, where y_i refers to the composition of component “i" in the extract phase or the phase where the component has been extracted and x_i refers to the raffinate phase or the phase which is remaining from the feet after the component has been extracted.

When we are dealing with adsorption or maybe leaching for those particular cases we generally represent it as q_i vs c_i. When we are dealing with gas-liquid adsorption under that case we can also represent it as q_i vs p_i.

So, therefore, the equilibrium data can be represented in terms of graphs or tables. We can also have some equations to develop the relationships between x, y or p_i, x_i etc. Just to understand equilibrium, this is not a thermodynamics class, I will not be going into details of equilibrium.

(Refer Slide Time: 16:58)



Representation of Equilibrium (Chemical)

Thermodynamic Eqm — Mech. Eqm ($\Delta P=0$) — Thermal Eqm ($\Delta T=0$) — Chemical Eqm ($\Delta G=0$)

$$\mu_i^\alpha = \mu_i^\beta$$

$$\mu_i^\alpha (T, P)$$

$$\mu_i^\beta (T, P)$$

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

$$d\mu = -s\,dT + v\,dp$$

$$= v\,dp \quad \text{(Const temp)}$$

$$\int_{\mu_{i\,\text{std state}}^{\circ}}^{\mu\,(T,P)} d\mu = \int_{\text{std state}}^{P} v\,dp$$

$$\int d\mu^\circ = \int v\,dp = \int \frac{RT}{p}\,dp = \int RT\, d\ln p$$

$$f \to p \text{ as } p \to 0$$

$$\int_{\mu^0}^{\mu} \boxed{d\mu} = \int_{p=0}^{P} v\,dp = \int RT \boxed{d\ln f}$$

$$d\mu = RT\, d\ln f = v\,dp$$

$$d\mu^0 = RT\, d\ln p = \frac{RT}{p}\,dp$$

Fugacity coeff. Φ

$$d(\mu - \mu^\circ) = RT \int^{f/p} d\ln (f/p) = \int_{p=0}^{P} \left(v - \frac{RT}{p}\right) dp$$

$$\boxed{\mu - \mu^\circ = RT \ln (f/p) = \int_0^P \left(v - \frac{RT}{p}\right) dp} \quad f/p = 1$$

But just to as a recap of the thermodynamics course that you have already done. I would just like to represent or just like to recall a few things that we had already discussed in your thermodynamics class. Whenever we represent equilibrium let me be very specific, we are talking about chemical equilibrium right.

I will just mention and this is not a part of this particular course nevertheless that thermodynamic equilibrium is satisfied when we have a combination of mechanical equilibrium ($\Delta P=0$), thermal equilibrium ($\Delta T=0$), and chemical equilibrium ($\Delta G=0$). The Gibbs free energy Change, $\Delta G = 0$, implies that $\mu_i^\alpha = \mu_i^\beta$ (i= any particular component).

Suppose there are two phases alpha and beta then μ of each component should be equal in the two phases. Let us recollect that how to express because if we know how to express μ in terms of composition, temperature and pressure then in that case suppose there is any particular way of finding out μ of component “i" under the conditions of temperature and pressure existing in phase alpha.

In other words what I mean to say that if there is a way of expressing μ_i^α in terms of temperature and pressure and there is a way of expressing μ_i^β as a function of temperature and pressure. If we have those particular relationships then, in that case, using those relationships we can find out μ_i^α and we can find out μ_i^β.

If we find that $\mu_i^\alpha > \mu_i^\beta$, then “i" moves from alpha to beta phase, if $\mu_i^\alpha < \mu_i^\beta$ then “i” moves from the beta to the alpha phase.

Now, you must be recollecting that for a pure component

$$d\mu = -sdT + vdp$$

At constant temperature, dμ equals as follows:

$$d\mu = vdp \text{ (at const temp)}$$

So, what we find is that if we want to find out μ under any particular temperature and pressure then this particular equation has to be integrated from some particular standard state to the temperature and pressure conditions which are existing in the alpha phase. So, accordingly, this equation also has to be integrated from some particular standard state to the pressure since the temperature is constant.

$$\int_{std\ state}^{(T,P)} d\mu = \int_{std\ state}^{p} vdp$$

Now, the point is that if you have to use this equation and find out μ_i^α or μ_i^β using this particular relationship. Then we need to know μ_i at some particular standard states. Is not it? Let, μ_i at standard state can be called as μ_i^0. So, we need to know μ_i^0 with the help of this, we can find out μ under the particular condition.

Now, I will tell you this is one particular very important problem of thermodynamics is that more than the equations it is very difficult to understand that most of the equations which express properties in terms of measurable properties are differential equations. So, therefore, if we want to find out the absolute value of any property we need to know the value of that property under some particular standard conditions. Now, μ itself is an abstract quantity.

So, how to find out the value of μ at any particular standard state? We just do not have any clue about that. Now, whenever we become so clueless we immediately resort to one particular thing that is the ideal gas state. Since the ideal gas state is based on the kinetic theory of gases in which most of the equations are quite well defined.

So, denoting the ideal gas state with the superscript 0, what do we find? In the ideal gas state $d\mu^0$ can be written as follows:

$$\int d\mu^0 = \int v dp = \int \frac{RT}{P} dp = \int RT d(lnP)$$

So, therefore, we find that for an ideal gas we know that the change in μ in going from one state to the other is related to the change in the ln p. So, there is a very famous scientist G N Lewis who felt that why not retain this particular same expression for μ for any other substance other than the ideal gas merely by replacing P with f and keeping in mind that this f becomes equal to P when this particular substance behaves as an ideal gas.

In other words, what was felt is that for any particular substance why do not we write this as integral RT d ln f, where we know that f becomes equal to P under the ideal gas state. When does any particular substance behave as an ideal gas? When the pressure is very low. So, therefore, what does this mean? This means that we have simply replaced this function dμ with RT dlnf knowing fully well that f becomes equals to P as P tends to 0. In equational form it can be summarized as follows:

$$\int_{\mu_0}^{\mu} d\mu = \int_{p=0}^{p} v dp = \int RT dlnf$$

Where f→p when p→0.

So, therefore, the defining equation for fugacity the purpose of doing this is that we did not know the lower limit or the standard state based on which μ should be calculated, but if we replace this equation in the ideal gas equation if we relate this particular P with “f” then we know the value of “f” under some particular standard state which corresponds to the ideal gas situation. So, therefore, what is the defining equation for fugacity?

The defining equation for fugacity is written in this particular form that; so, what we do? If we want to find out μ under any particular condition we simply write it in these particular terms and from here we know that d of mu minus mu 0 that is equal to RT d ln f by P which is equals to v minus RT by P dp. And now what we can do? We can integrate this equation. From what state? f by P equals 1. Under what condition that happens? When P=0.

$$d\mu = RTdlnf = vdp$$

$$d\mu^0 = RTdlnf = \frac{RT}{p}dp$$

$$d(\mu - \mu^0) = RT\int_{\frac{f}{p}=1}^{f/p} dln(\frac{f}{p}) = \int_{p=0}^{p}\left(v - \frac{RT}{p}\right)dp$$

$$\boxed{\mu - \mu^0 = RTln\left(\frac{f}{p}\right) = \int_{0}^{p}\left(v - \frac{RT}{p}\right)dp}$$

This is the defining equation for fugacity. This particular ratio (f/p) is called the fugacity coefficient which was denoted by ϕ.

We know fugacity under some conditions, so, therefore, it was felt that μ with fugacity and just we can write down all the things which were written in terms of μ just in terms of “f”.

For the equilibrium condition of any particular component “i” in pure form,

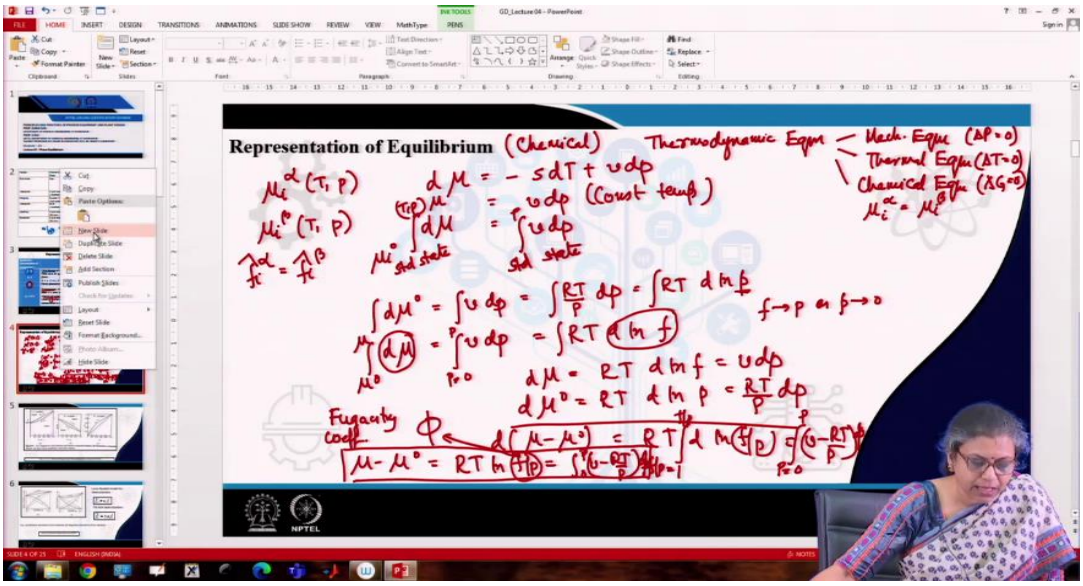
$$f_i^\alpha = f_i^\beta$$

For, the component in mixture or solution, the equilibrium condition can be written as:

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

Therefore, the entire problem of determining equilibrium in terms of chemical potential boils down to finding out the fugacity of that particular component in the particular mixture.

(Refer Slide Time: 27:54)



Representation of Equilibrium (Chemical)

Thermodynamic Eqm < Mech. Eqm ($\Delta P = 0$), Thermal Eqm ($\Delta T = 0$), Chemical Eqm ($\Delta G = 0$)

$\mu_i^{\alpha} = \mu_i^{\beta}$

$\mu_i^{\alpha}(T, P)$

$\mu_i^{\beta}(T, P)$

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

$d\mu = -s\,dT + v\,dp$

$= v\,dp$ (Const temp)

$\int_{\mu_i^0 \text{ std state}}^{\mu (T,P)} d\mu = \int_{\text{std state}}^{P} v\,dp$

$\int d\mu^0 = \int v\,dp = \int \frac{RT}{P}\,dp = \int RT\, d\ln p$

$f \to p$ as $p \to 0$

$\int_{\mu^0}^{\mu} d\mu = \int_{P=0}^{P} v\,dp = \int RT\, d\ln f$

$d\mu = RT\, d\ln f = v\,dp$

$d\mu^0 = RT\, d\ln p = \frac{RT}{P}\,dp$

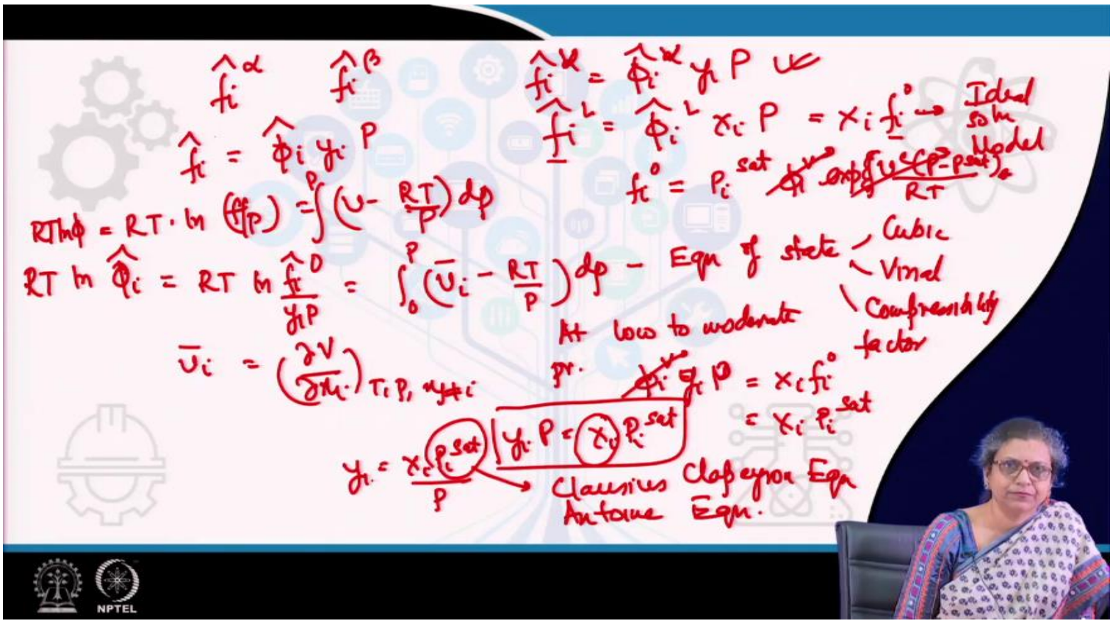
Fugacity coeff ϕ

$d(\mu - \mu^0) = RT \int^{f/p} d\ln (f/p) = \int_{P=0}^{P} \left(v - \frac{RT}{P}\right) dp$

$\boxed{\mu - \mu^0 = RT \ln (f/p) = \int_0^P \left(v - \frac{RT}{P}\right) dp} \quad f/p = 1$

So, therefore, if I can insert one more slide and I can show you.

(Refer Slide Time: 28:06)



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

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

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

$RT \ln \hat{\phi}_i = RT \ln \frac{\hat{f}_i^{0}}{y_i P} = \int_0^P \left(\bar{v}_i - \frac{RT}{P}\right) dp$ – Eqn of state < Cubic, Virial, Compressibility factor

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

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

$\hat{f}_i^{L} = \hat{\phi}_i^{L} x_i P = x_i f_i^{0} \to$ Ideal soln Model

$f_i^{0} = P_i^{sat}\, \cancel{\phi_i^{v}}\, \cancel{\exp\left\{\frac{v_i (P - P^{sat})}{RT}\right\}}$

At low to moderate pr.

$\cancel{\hat{\phi}_i^{v}}\, y_i P = x_i f_i^{0}$

$= x_i P_i^{sat}$

$\boxed{y_i P = x_i P_i^{sat}}$

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

So, therefore, in this particular case what we find is that our entire problem then boils down to finding out the fugacity of the component i in say the alpha phase and to find out the fugacity of component i in the beta phase. Where what is f i?

In the vapor phase or in any particular phase the relationship between fugacity and fugacity coefficient can be expressed as follows:

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

We know from the previous derivation that for pure component we can write

$$RTln\varphi = RTln\left(\frac{f}{P}\right) = \int_0^p (v - \frac{RT}{P})dp$$

Therefore for a mixture the above expression can be written as follows:

$$RTln\hat{\varphi}_i = RTln\left(\frac{\hat{f}_i^0}{y_i P}\right) = \int_0^p (\bar{v}_i - \frac{RT}{P})dp$$

So, therefore, to find out f_i^α, what should it be? Say, α is a vapor phase then the following expression can be followed:

$$\hat{f}_i^v = \hat{\varphi}_i^v x_i P$$

For the liquid phase, the above expression will be

$$\hat{f}_i^L = \hat{\varphi}_i^L x_i P$$

So, what do I need to do? For finding out f_i^L and f_i^v, we need to compute these parameters.

Now, for the vapor phase, it can be done. How it can be done? The expression can be obtained from here and this particular expression we can find out from any particular equation of state. Mostly for gases, we know that they conform to Amagat’s law of additive volume and Dalton’s law of partial pressure and therefore, the partial molar volume is equal to the molar volume of that particular component and molar volume can be obtained from any particular equation. It can be a cubic equation, it can be a “virial equation” of state, it can also be the compressibility factor chart. So, from anywhere we can find it out.

But, when we try to find it out for the liquid phase what we find is that in the liquid phase finding out or evaluating this particular integral is slightly difficult ($\int_0^p(\bar{v}_i - \frac{RT}{p})dp$).

Because we know that this particular partial molar volume can be expressed in the following way:

$$\bar{v}_i = \left(\frac{dv}{dx_i}\right)_{T,p,x_{j\neq i}}$$

So, therefore, it varies with composition, and this particular variation we are required to know at every pressure starting from 0 pressure to P pressure. Now, this becomes finding out this becomes very difficult. So, therefore, other than a vapor phase finding out f_i^L, it is very difficult when component “i” is in a solution.

So, just to eliminate this particular difficulty an ideal solution model has been assumed in the liquid phase which states that the molar the partial fugacity of component i in the liquid phase it is proportional to the composition in the liquid phase and the pure component fugacity of that particular component in the liquid phase provided the f_i^0 and the f_i^L are evaluated at the same conditions of temperature and pressure.

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

Now, this particular model is known as an ideal solution model, and in this particular usually to find out f_i^l we use this particular ideal solution model.

To find out the pure component fugacity of i in the liquid state

$$f_i^0 = p_i^{sat}\varphi_i^v \exp\left(\frac{v^c(P - P^{sat})}{RT}\right)$$

If you would recall this was equal to the saturated pressure into the fugacity coefficient of the vapor in equilibrium with the liquid into a pointing correction factor which arises because the pressure is far removed from the or rather this is not required since I assume Vc = const.

So, therefore, the f_i^0 is a summation, or rather it is a product of these three things right. So, therefore, at low to moderate pressures what do we find?

$\varphi_i^v = 1$, exp $\left(\frac{v^c(P-P^{sat}}{RT}\right) = 1$, because P is close to P saturated Vc is constant.

Then, the above expression reduces to$f_i^0 = p_i^{sat}$.

So, therefore, at low to moderate pressure what do we find?

For a vapor-liquid equilibrium,

$$\varphi_i^v y_i P = x_i f_i^0 = x_i p_i^{sat}$$

At low to moderate pressure, $\varphi_i^v = 1$.

So, therefore, we get Raoult's law at low to moderate pressures and the x, y data are generated from this particular equation.

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

This P_i^{sat} , we can find out either from the Clausius Clapeyron equation or we can find it out from the Antoine equation. We can construct the different curves corresponding to VLE data which we are going to discuss in the next class.

Thank you very much.