Advanced Thermodynamics
Prof. Nanda Kishore
Department of Chemical Engineering
Indian Institute of Technology – Guwahati

Lecture – 1
Introduction of Phase Equilibrium

Welcome to the MOOCs course advanced thermodynamics. The title of this lecture is introduction of phase equilibrium. In this particular lecture, we will be discussing a few basics of phase equilibrium problems as well as will be recapitulating a few fundamentals of classical thermodynamics.

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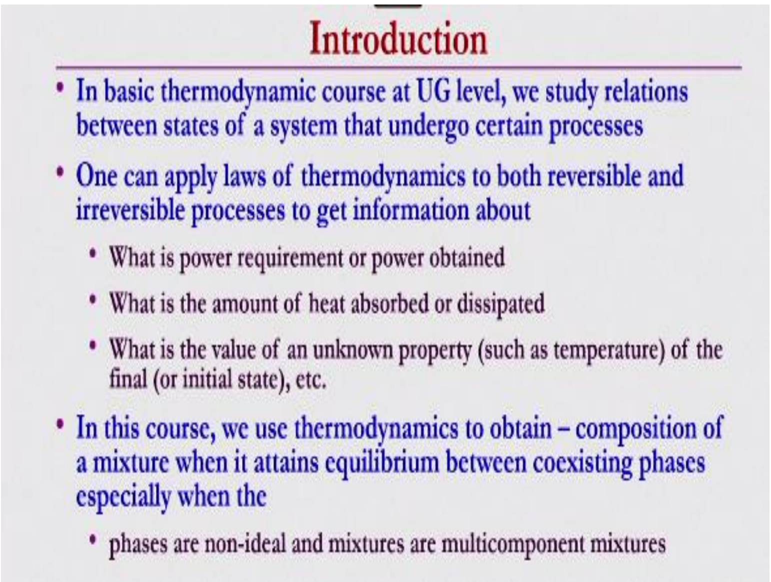

Introduction

- In basic thermodynamic course at UG level, we study relations between states of a system that undergo certain processes
- One can apply laws of thermodynamics to both reversible and irreversible processes to get information about
  - What is power requirement or power obtained
  - What is the amount of heat absorbed or dissipated
  - What is the value of an unknown property (such as temperature) of the final (or initial state), etc.
- In this course, we use thermodynamics to obtain – composition of a mixture when it attains equilibrium between coexisting phases especially when the
  - phases are non-ideal and mixtures are multicomponent mixtures

So, basically in thermodynamics course at UG level, what we study? We study relations between states of a system that undergo certain kind of processes. That is, one can apply thermodynamic principles to both reversible and irreversible process to get the information about what is the power requirement or power obtained? What is the amount of heat absorbed or dissipated? What is the value of an unknown property of a final or initial state such as temperature, etc, pressure, etc.? Those kinds of things one can obtain by using the basic thermodynamic principles. That is what we study in general in basic UG level thermodynamics course.

In this course, we will use principles of thermodynamics to obtain composition of a mixture when it attains equilibrium between co-existing phases, especially when the phases obey non-ideality and mixtures are a kind of multi-component mixtures, not simply binary mixtures, not simply ideal phases, when these phases obey the non-ideality and the mixtures are multi-component mixtures. Under such conditions, if the phases are co-existing and there exists an equilibrium amongst those co-existing phases. What is the equilibrium composition of a given species? Those things we are going to calculate. We are going to study how to obtain those kinds of equilibrium composition for a given system, where two or more than two phases are co-existing and there exists an equilibrium amongst those phases.

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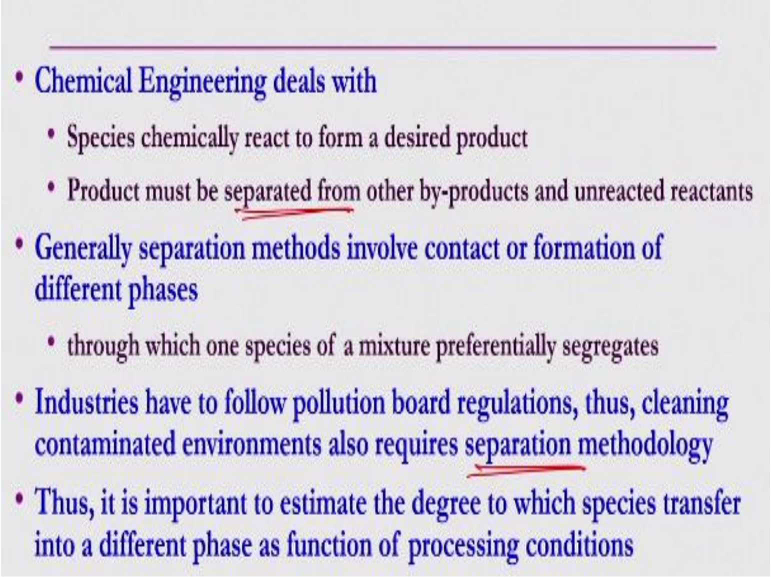

- Chemical Engineering deals with
  - Species chemically react to form a desired product
  - Product must be separated from other by-products and unreacted reactants
- Generally separation methods involve contact or formation of different phases
  - through which one species of a mixture preferentially segregates
- Industries have to follow pollution board regulations, thus, cleaning contaminated environments also requires separation methodology
- Thus, it is important to estimate the degree to which species transfer into a different phase as function of processing conditions

So, then why do we need to study such equilibrium problems being a chemical engineering student? Because in chemical engineering, in general what we study? We study species chemically react to form a desired product and separation of product from other by-products as well as unreacted reactants, etc., those things basically generally we expect to occur in chemical engineering processes or any chemical plant. So, that means, there is a kind of separation as well occurring, not only reaction, but there is a separation.

Further, separation methods involve contact or formation of different phases, wherein, through which one species of a mixture preferentially segregates. And also, industries have to follow pollution board regulations, thus, cleaning contaminated environments also requires separation methodology, right? The separation is occurring, that means definitely one species is going to transfer from one phase to the other phase. Those kind of transfer of species occur from one phase to the other phase, so then at what rate are they occurring?

Is it possible to calculate or what is the equilibrium composition of those species, where the two or more phases are co-existing, are these things possible to calculate or not? Those things you know important to know, right? So, because of this importance of separation of species or transfer of species from one phase to the other phase is unavoidable in any chemical plant. Because of that reason, it is important to estimate the degree to which species transfer into a different phase as function of processing conditions of specified temperature and pressure those kind of things.

So, because of this reason, being a chemical engineering student, it is important to know how to do phase equilibrium calculations.

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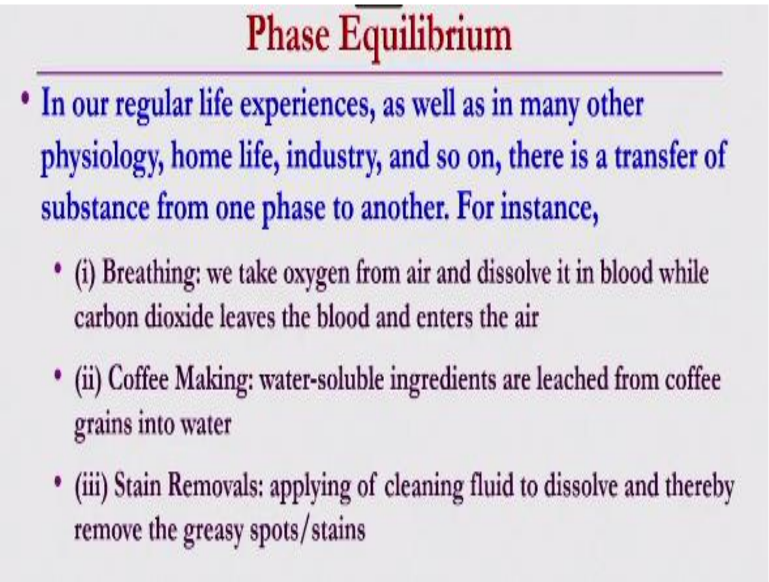

Phase Equilibrium

- In our regular life experiences, as well as in many other physiology, home life, industry, and so on, there is a transfer of substance from one phase to another. For instance,
  - (i) Breathing: we take oxygen from air and dissolve it in blood while carbon dioxide leaves the blood and enters the air
  - (ii) Coffee Making: water-soluble ingredients are leached from coffee grains into water
  - (iii) Stain Removals: applying of cleaning fluid to dissolve and thereby remove the greasy spots/stains

So then, what is phase equilibrium? Before defining the phase equilibrium, in general we see some kind of examples where we often come across these kind of transfer of species from one phase to the other phase. Let us say in our regular life experiences as well as in many other physiology, home life, industry, and so on, there is a transfer of substance from one phase to the other phase.

For instance, breathing, when we take oxygen from air and dissolve it in blood while carbon dioxide leaves the blood and enters the air, there is a transfer of species, right? Similarly, coffee making, when we take these coffee grains into warm water or hot water, what happens? Water soluble ingredients are leached from the coffee grains into the water. So, there is a transfer of species from coffee grains to water phase, right? Similarly, stain removers, applying of cleaning fluid to dissolve and thereby, removing the greasy spots, stains, etc. So, here also there is a kind of transfer of species phases from one phase to the other phase. These are a few general applications or generally we may come across in our regular life. And in industries, there are huge number of applications where the transfer of species takes from one phase to the other phase depending on the applications. So, it is not over exaggerating to say that in chemical plants, there is a huge amount of phase equilibrium problem existing, where these transfer of species takes place from one phase to the other phase. So, then there may also exist a kind of equilibrium and when there is an equilibrium existing amongst those phases, what is the equilibrium composition, those calculations become very much important, both from the design as well as the operational point of view as well, okay?

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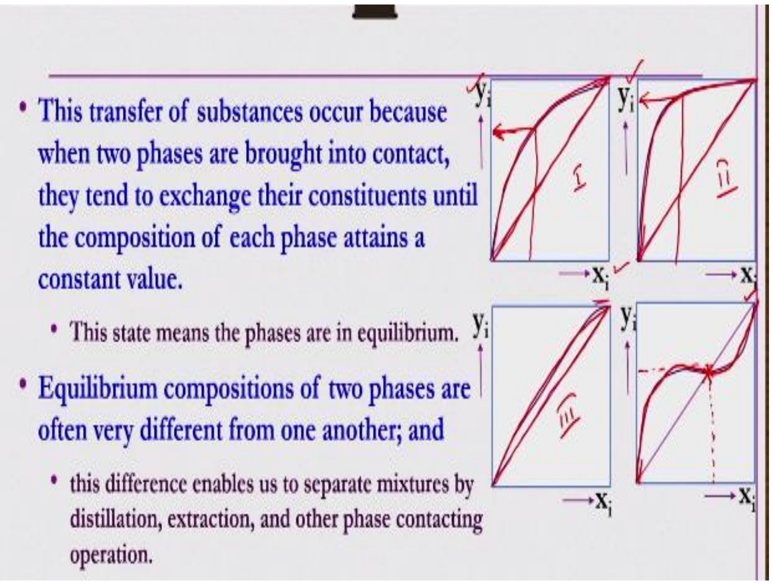

- This transfer of substances occur because when two phases are brought into contact, they tend to exchange their constituents until the composition of each phase attains a constant value.
  - This state means the phases are in equilibrium.
- Equilibrium compositions of two phases are often very different from one another; and
  - this difference enables us to separate mixtures by distillation, extraction, and other phase contacting operation.

So then, this transfer of substances occur because when two phases are brought into contact, they tend to exchange their constituents until the composition of each phase attains a constant value. So, composition of the constituents that is being transferred from one phase to the other phase, that becomes constant in each phase. In each phase that becomes constant but they are not equal to each other, okay? So, we will see some examples as well. So, this state means the phases are in equilibrium. When the composition of each phase attains a constant value that means there is no further tendency to transfer of those species or constituents from one phase to the other phase that means the composition in each phase becomes constant and that state means nothing but phases are in equilibrium. Equilibrium composition of two phases are often very different from one another, and this difference enables us to separate mixtures by distillation, extraction, or any other phase contacting operations in general.

Indeed the difference between equilibrium composition that defines how easy or how difficult of a given separation process. Let us say, if you have a kind of you know methanol water system and then what is the equilibrium curve of this system depends on that one you can decide at a given temperature pressure whether the separation of methanol water mixture into methanol pure or almost methanol pure and almost pure water separate phases, is it possible or not? Those things one can understand, okay?

So, let us say if you have two phases, the composition of i^{th} species in one phase is y_i and then composition of the same species in another phase is x_i, then the equilibrium curve between these two phases, if it is like this as given like this, okay? So, then we can say the separation is possible because at any x_i, what we can see that y_i is different from x_i value and then the difference is large enough sufficiently large enough, that means we can say the separation is possible. So, this line is a kind of diagonal line, right?

So, how much this difference between diagonal line and then equilibrium curve is there that defines you know how easy or difficult given separation process is going to happen, right? If the equilibrium curve is close to the diagonal line, that means we can say that the separation is going to occur very difficult, is going to occur, but it is going to be very difficult or the severity of the conditions may be required to get such kind of separations.

Let us say if you have an equilibrium curve like this, further like you know this curve here in the second picture, we can see the equilibrium curve of that composition whatever the i^{th} component composition in one phase is y_i, another phase is x_i, the difference between these two values are very large and we can understand how far it is from the diagonal line. So, we can see now here you know the difference between x_i and y_i is very much higher.

So, compared to the first case, in the second case, the separation is going to be much easier because the y_i and x_i values are very much different from each other, okay? So, let us say if you have an equilibrium curve like this here as shown in this third picture here. So, this is very much close to the diagonal line, so that means, the separation is going to be very difficult for this, it is possible, but you know severity of conditions may be high that separation cannot occur easily.

So, we have to use severe operating condition to get this separation to take place. Further if you have an equilibrium composition curve like this given here. So, here at certain point what happens, what you can see here? So, this is the equilibrium composition curve. So, at this particular point, the composition of the species i in one phase is equals to the other phase because the point is lying on the diagonal point. So, that means under such conditions, the separation is not possible.

One has to make sure that this point moves away from the diagonal, such a kind of changes in the operating conditions or changes in the you know feed mixture one has to do such a way that this point moves away from this diagonal point, so that the separation can take place okay? So, this difference whatever is there between the equilibrium compositions, this enables us to separate mixtures by different types of phase contacting operations such as distillation, extraction, absorption, etc., those kind of things.

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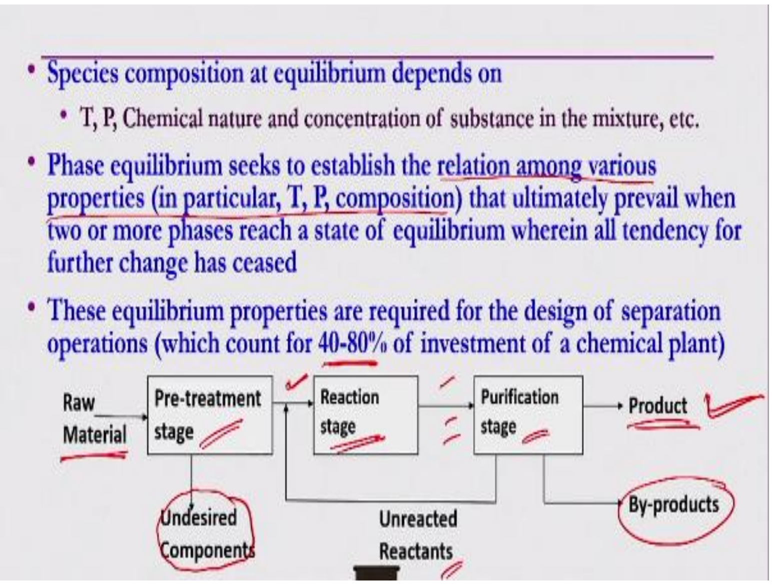

- Species composition at equilibrium depends on
  - T, P, Chemical nature and concentration of substance in the mixture, etc.
- Phase equilibrium seeks to establish the relation among various properties (in particular, T, P, composition) that ultimately prevail when two or more phases reach a state of equilibrium wherein all tendency for further change has ceased
- These equilibrium properties are required for the design of separation operations (which count for 40-80% of investment of a chemical plant)

Raw Material

Pre-treatment stage

Reaction stage

Purification stage

Product

Undesired Components

Unreacted Reactants

By-products

Species composition at equilibrium depends on temperature, pressure, composition and chemical nature of the substance in the mixture, etc. Then, what we need from phase equilibrium point of view? Phase equilibrium seeks to establish the relation among various properties such as you know temperature, pressure, composition that ultimately prevail when two or more phases reach a state of equilibrium wherein all tendency for further change has ceased.

So, this relation, the relation between temperature, pressure, composition that we have to obtain that is what the essence of this phase equilibrium and then those relations we have to solve to get the solution of equilibrium composition, etc., okay? So, these equilibrium properties are required for the design of separation operations, which count almost 40 to 80% of investment of chemical plant. So, such high is their presence, right?

Out of the chemical plant you know whatever the amount that is invested in designing and then installing a chemical plant, out of which 40 to 80% cost is dedicated or you know required for this kind of separation processes. Such important is the kind of separation processes in chemical plants. So, because of that reason, you know it is required to establish these equilibrium properties, so that design of separation operation can take place efficiently. So, in general if you have a kind of chemical plant, what we have? We have raw materials, which may be having the required reactants, in addition to that, there may be several unrequired or undesired components should be there. So, there will be a kind of pretreatment stage where separation takes place, and then because of that separation, what we can do? We can take out the undesired components from the raw materials and then the desired ones we can take to the reaction stage, second stage, and then from here what we get? We get the products and then by-products we get in general, okay?

There may also be some unreacted reactants as well, right. So then we go to the purification stages or separation stage where you know unreacted reactants would be separated and if required, they can be sent back to the reaction stage and then products would be further separated from the by-products. So, again separation is involved here. So, this chemical plant, the flow sheet of a common simple chemical plant indicates how much important the separation process is.

Since separation processes are very much essential in any of the given plant, it is very much required to find out the equilibrium composition if at all there exists the equilibrium amongst those you know amongst different phases within the separation units.

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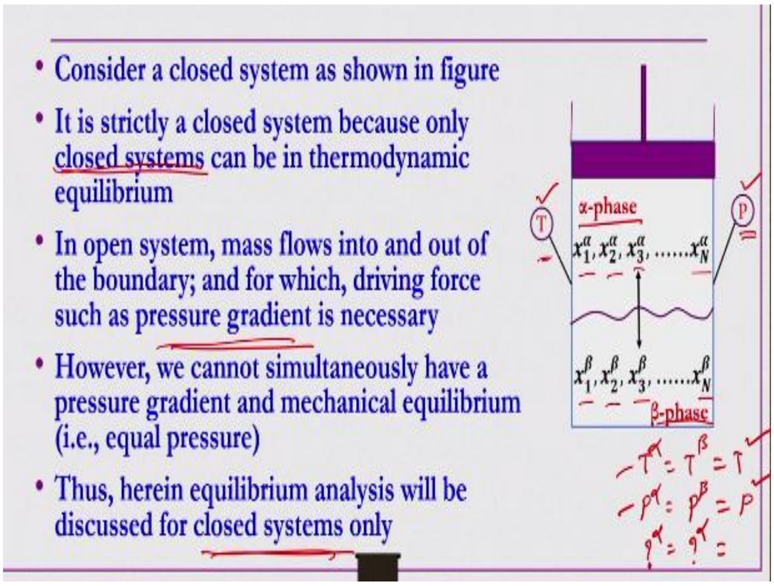

- Consider a closed system as shown in figure
- It is strictly a closed system because only closed systems can be in thermodynamic equilibrium
- In open system, mass flows into and out of the boundary; and for which, driving force such as pressure gradient is necessary
- However, we cannot simultaneously have a pressure gradient and mechanical equilibrium (i.e., equal pressure)
- Thus, herein equilibrium analysis will be discussed for closed systems only

Now, let us consider a closed system, okay? So, here we consider a closed system where there are two phases, α phase and then β phase. The temperature is T and then pressure is P. So, this system is you know kind of equilibrium, right? So, we have a kind of closed system, within this closed system, we have 2 phases, α phase and β phase and there exists a kind of equilibrium between these 2 phases, and then once the equilibrium has been established, the equilibrium composition are given as x_1^{α}, x_2^{α}, x_3^{α} and so on so x_N^{α}. There are N number of components. These are in equilibrium with x_1^{β}, x_2^{β}, x_3^{β},…, x_N^{β}. So, there is an equilibrium, right?

So, when we know if a thermal equilibrium is established, the temperature has to be equal in either of the phases. So, that is the reason temperature we have only one, we are not writing T^{α}, T^{β} separately, because this diagram depicting a closed system where two phases are in equilibrium. So, when there is an equilibrium, temperature has to be same in both the phases, so that is the reason only one T is shown here.

Similarly, when there is a kind of you know a mechanical equilibrium between these two phases, co-existing phases in this closed system, then pressure has to be same in either of the phases. So, that is the reason pressure also we have represented only one, we have not written P^{α}, P^{β} separately, okay? Now, there is a transfer of species, mass transfer is also occurring from one phase to the other phase.

So, then what should be that composition, that we have to find out, but how to represent that you know equilibrium because of the mass transfer, because thermal equilibrium we know that $T^\alpha = T^\beta = T$, so, only one T we are writing, right? Similarly, in mechanical equilibrium we know that $P^\alpha = P^\beta$, so, that is only one P we are representing. Similarly, when there is a transfer of species, so then what is this? Is it a composition?

Composition of that species is that indicating the potential for the transfer of species that we have to find out. For that, we are going to see know what is it, is it measurable like temperature pressure? If it is not measurable, then what is it? Then how to make a relation between measurable properties, etc., those kind of things we are going to see now, okay?

Consider a closed system as shown in figure. It is strictly a closed system because only closed systems can be in thermodynamic equilibrium. It is not possible to have a kind of equilibrium in open system because in open system mass flows into and out of the boundary and for which driving force such as pressure gradient is required. If the mass has to flow into and out of the boundary of the system, that is in a kind of open system, then obviously there should be a kind of pressure gradient, then only mass will flow into or out of the boundary, okay? So, then if there pressure gradient is required for this mass to flow in and out of the boundary as per the requirement then, obviously, there will not be a kind of mechanical equilibrium.

Obviously, if there is a pressure gradient, that means you are saying the pressure is not same everywhere. If the pressure is not same everywhere or the pressure is not same in either sides of the boundary that means you are saying that you know pressure gradient is existing. Pressure gradient is existing that means you cannot say that there is a kind of a mechanical equilibrium, okay? So that means, however, we cannot simultaneously have a pressure gradient and mechanical equilibrium. That is, mechanical equilibrium means equal pressure should be established at either side of the boundary in open system where the transfer of species the mass flow is taking place in and out, okay? So, that is not possible. If you want to have a mass flow in and out, there should be a kind of pressure gradient. If there is a pressure gradient, you cannot say that this system is in mechanical equilibrium.

So, if it is not in mechanical equilibrium, you cannot say that the system is in equilibrium, right? So, that is the reason the equilibrium problems are valid only for closed systems. Thus, here in equilibrium analysis will be discussed only for closed systems.

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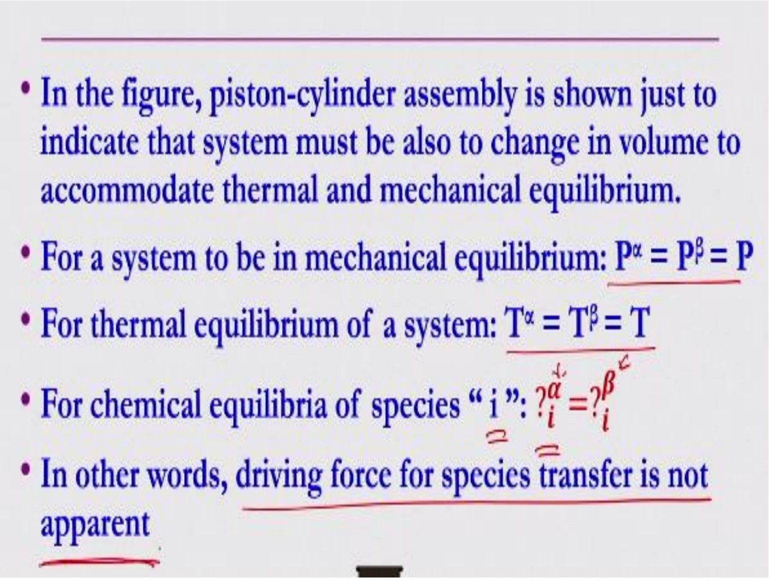

- In the figure, piston-cylinder assembly is shown just to indicate that system must be also to change in volume to accommodate thermal and mechanical equilibrium.
- For a system to be in mechanical equilibrium: $P^{\alpha} = P^{\beta} = P$
- For thermal equilibrium of a system: $T^{\alpha} = T^{\beta} = T$
- For chemical equilibria of species " i ": $?_i^{\alpha} = ?_i^{\beta}$
- In other words, driving force for species transfer is not apparent

Now, in the figure, piston-cylinder assembly shown just to indicate that the system must also allowed to change in volume to accommodate thermal and mechanical equilibrium if at all there is a change, So, it has to accommodate you know thermal and mechanical equilibrium. So, because of that reason, just for kind of understanding, this piston-cylinder assembly is shown to indicate that the system must also change in volume to accommodate the thermal and mechanical equilibrium.

For the system to be in mechanical equilibrium, we know that $P^{\alpha} = P^{\beta}$, so that is equals to one constant P. Similarly, for a system to be in thermal equilibrium, then T^{α} is equals to T^{β} is equals to some constant temperature T. So, that is in both phases temperature is same, in both the phases pressure is same if mechanical equilibrium is also there. For chemical equilibrium of species, so then what is this? Let us say i^{th} species, whatever this system that we have taken is having more than two components, let us say one component we are taking i, okay?

For that component, what is it? What is it in the α phase should be equals to what is it in the β phase that we have to make sure. If you think as a kind of mole fraction, then is it reliable or not? That is what we are going to do or in other words, driving force for species transfer is not apparent. Why is it not apparent? That we will see now.

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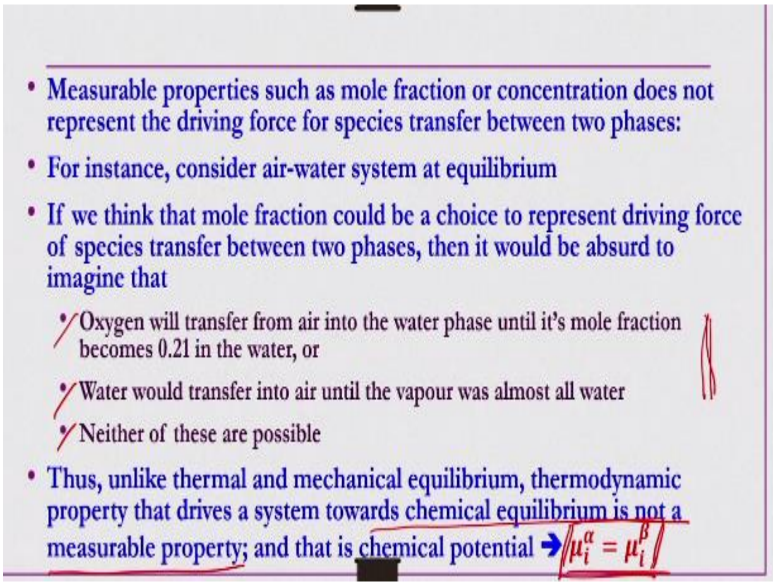

- Measurable properties such as mole fraction or concentration does not represent the driving force for species transfer between two phases:
- For instance, consider air-water system at equilibrium
- If we think that mole fraction could be a choice to represent driving force of species transfer between two phases, then it would be absurd to imagine that
  - Oxygen will transfer from air into the water phase until it's mole fraction becomes 0.21 in the water, or
  - Water would transfer into air until the vapour was almost all water
  - Neither of these are possible
- Thus, unlike thermal and mechanical equilibrium, thermodynamic property that drives a system towards chemical equilibrium is not a measurable property; and that is chemical potential → $\boxed{\mu_i^\alpha = \mu_i^\beta}$

Measurable properties such as mole fraction or concentration does not represent the driving force for species transfer between two phases, why? Because, for example, if you take air-water system at equilibrium, then if you see this problem as a kind of transfer of oxygen from one phase to the other phase, then in the air, the mole fraction of oxygen is 0.21. That means, if we think that mole fraction could be a choice to represent driving force of species transfer between two phases. Then, it would be absurd to imagine that oxygen will transfer from air into the water phase until its mole fraction becomes 0.21 in water. That is not possible. If that is the case, then in the water as well as in the air, the mole fraction of oxygen has to be equals to 0.21, but that is not true in any system that you take, okay? Or otherwise if you think that water would be transferring into air, then the vapor was almost all water because water is almost pure like pure water you are taking, air is having oxygen and nitrogen, other constituents are also there.

If you think like you know water is transferring into the air phase as a kind of in the vapor form, then see water is evaporating and then getting into the air phase or vapor phase. So, it has to transfer until the entire vapor phase has to become full of water. That is also not possible, okay? So, because of this reason, it is not possible to say that some measurable property like you know mole fraction or concentration of a system in two phases that can be used to represent the equilibrium of the species that is the chemical equilibrium between two phases, okay?

That is the reason we do not represent the chemical equilibrium in terms of mole fractional or concentration. So, then what is it? So because obviously, we know neither of these are possible for this case of air water. If you take any system, these arguments are going to be valid for any system that you are going to take. We have just discussed air water system because we know in the air water system like if you have the oxygen transferred in the air, you know that oxygen mole fraction is 0.21. So, that system we have taken.

Likewise, if you take any system, it is not possible to represent a chemical equilibrium of a system by mole fractions or concentration or in terms of mole fraction or concentration it is not possible to represent chemical equilibrium. Thus, unlike thermal and mechanical equilibrium, thermodynamic property that drives a system towards chemical equilibrium is not a measurable property and that is chemical potential. So, that non-measurable property for the time being, let us call it as a chemical potential, okay?

So, unlike in thermal and mechanical equilibrium, thermodynamic property that drives a system towards chemical equilibrium is not a measurable property and that non-measurable property for the time being, let us take it as a chemical potential or let us name it as a chemical potential. So, chemical potential of ith component in α phase should be equals to chemical potential of same ith component in the β phase if there exists a kind of a chemical equilibrium between these two phases, α and β. So, we are going to see more details about these chemical potentials and all those in coming slides anyway.

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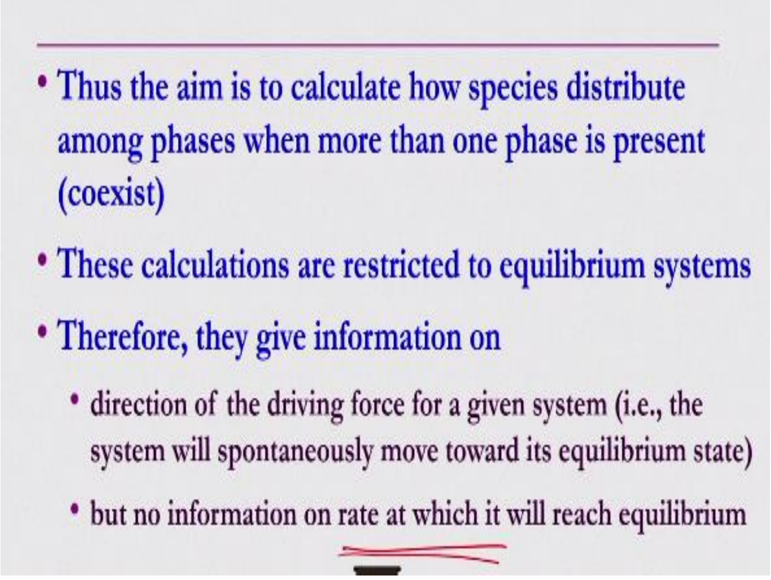

- Thus the aim is to calculate how species distribute among phases when more than one phase is present (coexist)
- These calculations are restricted to equilibrium systems
- Therefore, they give information on
  - direction of the driving force for a given system (i.e., the system will spontaneously move toward its equilibrium state)
  - but no information on rate at which it will reach equilibrium

Thus, the aim is to calculate how species distribute among phases when more than one phase is present or co-existing, that is the point, right? So, the purpose ultimately let us say thermal equilibrium or mechanical equilibrium, the pressure you are measuring or they can be measurable. So, that is straightforward or maybe quite easy compared to the chemical equilibrium case.

In the chemical equilibrium case, there is no such kind of a measurable thermodynamic property, which represents the chemical equilibrium, we call it as a chemical potential, but what is the chemical potential that is unmeasurable? So then, there should be a kind of relation between this unmeasurable chemical potential and other properties like temperature, pressure, composition, etc. So those kinds of things we have to do. The aim is to calculate how species distribute among phases when more than one phase is present or coexist.

These calculations are restricted to equilibrium systems only. Therefore, they give information on direction of the driving force for a given system that is the system will spontaneously move toward its equilibrium state, but that will not give the information rate at which it will reach equilibrium, okay?

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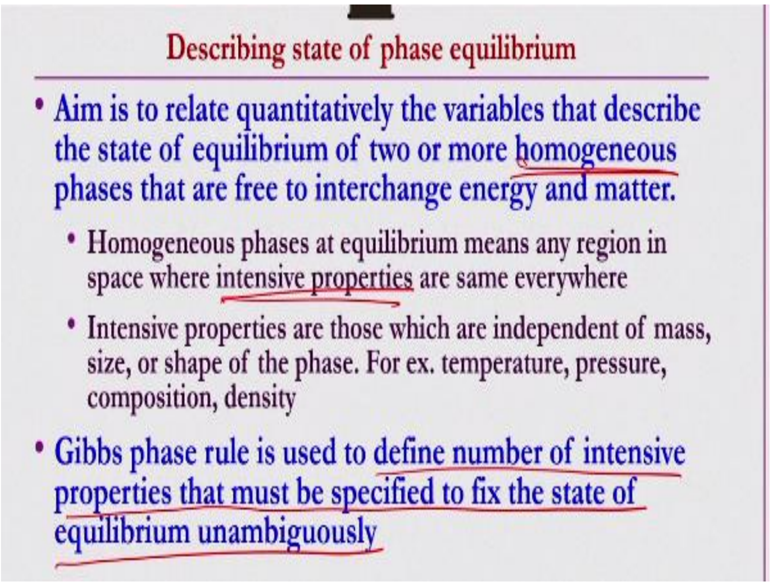

Describing state of phase equilibrium

- Aim is to relate quantitatively the variables that describe the state of equilibrium of two or more homogeneous phases that are free to interchange energy and matter.
  - Homogeneous phases at equilibrium means any region in space where intensive properties are same everywhere
  - Intensive properties are those which are independent of mass, size, or shape of the phase. For ex. temperature, pressure, composition, density
- Gibbs phase rule is used to define number of intensive properties that must be specified to fix the state of equilibrium unambiguously

Now, understanding the importance of phase equilibria especially from chemical point of view and then how to define a chemical equilibrium for a given system, it is also becomes important to describe the state of phase equilibrium especially in terms of thermodynamics, okay? So, how to describe state of phase equilibrium? So, aim is to relate quantitatively the variables that describe the state of equilibrium of two or more homogeneous phases that are free to interchange energy and matter.

Then, what do you mean by homogeneous system here? Homogeneous phases at equilibrium means any region in space where intensive properties are same everywhere then we can say that is a kind of homogeneous, right? So, then what are the intensive properties? Intensive properties are those which are independent of mass, size, and shape of the phase. For example, temperature, pressure, density, composition, etc. okay?

So, while discussing this phase equilibrium, wherever we have this basic thermodynamic terminologies, we are going to define them as well as a kind of recapitulation of what we have studied in our undergraduate course.

So, Gibbs phase rule is used to define number of intensive properties that must be specified to fix the state of equilibrium or the state of phase equilibrium unambiguously. If you fix the state of phase equilibrium, then it becomes easier or straightforward to obtain the phase equilibrium composition, etc. okay? So, that is the reason if you want to describe the state of phase equilibrium, you have to use the phase rule, right? That is, in order to describe the state of phase equilibrium, you have to use Gibbs phase rule.

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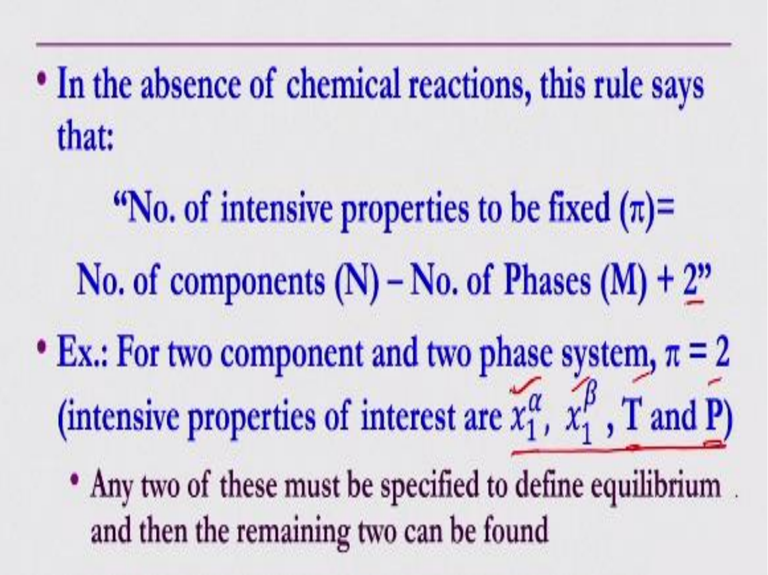

- In the absence of chemical reactions, this rule says that:

  "No. of intensive properties to be fixed (π)=
  No. of components (N) – No. of Phases (M) + 2"

- Ex.: For two component and two phase system, $\pi = 2$ (intensive properties of interest are x_1^α, x_1^β, T and P)
  - Any two of these must be specified to define equilibrium and then the remaining two can be found

What it says in the absence of chemical reactions, (number of intensive properties to be fixed(Π)) = (number of components(N)) – (number of phases(P)) + 2 and this 2 stands for temperature and pressure. So, let us say for example, two component two phase system is there, so, then $\Pi = 2$, okay? So, that means how many intensive properties are there x_1^α, so x_2^α is nothing but $(1 - x_1^\alpha)$ because it is a binary system we have taken. So, this is only intensive property, x_2^α cannot be counted as a separate intensive property, okay?

Similarly, x_1^β two, temperature pressure third and fourth. There are 4 intensive properties that are describing the system, okay? These 4 intensive properties are there, out of which how many if you fix, then you can say that the state of phase equilibrium is described unambiguously, that you can know by the Gibbs phase rule. So, $\Pi = N$ is you know 2 components and P, 2 phases, so 2 - 2 and then + 2 is there, so that is $\Pi = 2$.

That means, out of this 4 intensive properties, right? That is x_1^α, x_1^β, T and P. Out of these 4 intensive properties if you fix any two, remaining two you can find out without any difficulty using this phase equilibrium problems. Next, let us say if you have a methanol water system, right? And then you are fixing temperature and pressure, assume in this methanol and water system the vapor and the liquid phases are at equilibrium. So, what are you trying to do? You are trying to separate them into almost pure methanol and then almost pure water kind of 2 separate phases that you are trying to do, right? So then, obviously for this purpose, what are you trying to do? You are applying certain pressure and temperature, right? Let us say pressure is 1 atmospheric pressure and then temperature is let us say 60°C if you are fixing, for example. Then, by heating at this temperature and keeping 1 atmospheric pressure fixed in the closed system where you have taken this methanol water mixture, then you know obviously the phase separation will occur, that is vapor phase will take place because of the evaporation of the more volatile component and you know the more volatile component will get into vapor phase and less volatile component will be present in a kind of liquid phase, right? So, then what is the equilibrium composition?

Without doing experiment, we can find out if that vapor phase that has formed is a kind of let us assume an ideal phase. Similarly, that liquid phase which is there after separation is also going to be let us assume as a kind of ideal phase. Then, we can use this relation y_i into P is equals to x_i into P_i^{sat}, right? Pressure is anyway fixed, for a given temperature P_i^{sat} you can find out and then from here y_i, x_i you can directly find out. For 2 components if you write, what will happen? I have written a generalized one, so that for 2 components, $y_1*P = x_1*P_1^{sat}$. Similarly, $y_2*P = x_2*P_2^{sat}$. So, now here, in place of y_2, you can write $(1 - y_1)$, in place of x_2, you can write $(1 - x_1)$, right? y_1, x_1 are the two unknowns, okay? Then P is known and then P_1^{sat}, P_2^{sat} you can know from this given temperature expression, right? So, Antoine equation you can use and then you can find out the saturation pressure, etc, at a given temperature for a given species. So, these are known, so then from here, these 2 equations are there, 2 unknowns x_1 and y_1 are there.

So, those things you can calculate without doing any experiments that is the point of this phase equilibrium problem. Even if you have a kind of non-ideality in these phases, then we have ϕ_1, γ_1 and then ϕ_2, γ_2. So, this we can calculate, we can obtain this ϕ_1, ϕ_2, γ_1, γ_2 describing the non-ideality of vapor and then liquid phases and then we can substitute here and then again y_1 and x_1 we can find out, okay? This is how you describe the state of phase equilibrium.

Once you describe the state of equilibrium without any ambiguity like this, so, we can use this phase equilibrium relations to get the phase equilibrium composition without any difficulty, for example. So, not necessarily you need to fix temperature and pressure to get the x_1^α and x_1^β for this case. You can fix x_1^α and T and then you can find out x_1^β and P. Like that any 2 intensive properties you can fix, so that remaining 2 you can obtain from the phase equilibrium relations.

So, any two of these must be specified to define equilibrium and then the remaining two can be found. This is described only for a binary system and then two component binary mixture and then two phase system, right? But the same is true or holds good for any number of phases, any number of components that are present in the system, okay?

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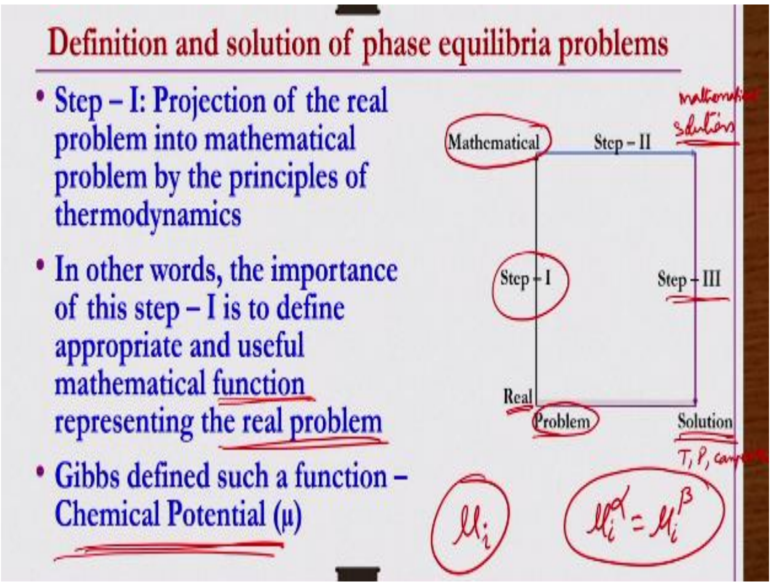

Definition and solution of phase equilibria problems

- Step – I: Projection of the real problem into mathematical problem by the principles of thermodynamics
- In other words, the importance of this step – I is to define appropriate and useful mathematical function representing the real problem
- Gibbs defined such a function – Chemical Potential (μ)

Now, definition and solution of phase equilibrium problems. So, we have seen the requirement, importance of the phase equilibrium problems in chemical plant. We have also seen the chemical potential, how to you know define a chemical equilibrium in terms of chemical potential that we have seen. We have also seen describing the state of phase equilibrium. So, once you describe the state of phase equilibrium problem, then it becomes important to define and then find out the solution of phase equilibrium problems as well.

Then only we can have a kind of proper justification of studying this phase equilibrium problems. So, let us say we have a real life problem, okay? So, this real life problem, what we have to do? We have to convert in a kind of mathematical form representing the real life physical problem, okay? That we call it as a first step, where we are transforming the real life problem into a kind of mathematical you know form, mathematical equation. So, there should be a kind of functions to define this real life problem in terms of mathematical functions. So, what are those mathematical functions, etc, we have to find out.

Then once you find out appropriate mathematical form or function of the real life problem, then we have to find out the solution of those mathematical problem. First, the real problem, we have to convert into a mathematical problem by using proper mathematical functions, then those mathematical problems we have to find out their solutions, right? So, then when you have the mathematical solution which would be in terms of some kind of mathematical or thermodynamic variables or properties, so that is not kind of real life measurable property. So, whatever the mathematical solution is there, that again has to be transformed into a kind of form of the solution which is having a real essence of physical life, or real life physical meaning that solution should have, such kind of transformation should we do in step three, right?

So, what do you mean by having a solution in terms of real life essence or the having meaning in real life essence, that is nothing but having the solution something like in terms of temperature, pressure, and then composition, etc., because these are the things that you can measure. These are the things you can measure in a given phase equilibrium system in general. So, your solution should also be in terms of this one, then only you can find out whether the mathematical solution is correct or not?

Is it you know compatible or is it validating with the experimental results or not? That you can find out only if it is having a kind of you know solution in the form of measurable properties such as temperature, pressure, and composition. That means, in this step 1, what we are trying to do? Projection of the real problem into mathematical problem by the principles of thermodynamics, in other words, the importance of this step 1 is to define appropriate and useful mathematical function representing the real problem.

So, what is the mathematical function that is again very much important? Until and unless you know what is a mathematical function, you are not going to represent this physical real problem into the mathematical form and then especially if there is a kind of chemical equilibrium, it is very difficult to have a kind of mathematical function in terms of you know measurable property, something like mole fraction or concentration, etc., and then we have seen that mathematical function is nothing but the chemical potential if there exist chemical equilibrium amongst the phases, okay?

So, this has been disclosed by the Gibbs that is Gibbs defined such a function as chemical potential. Now stands surprisingly, what you have to see here this step 1, the mathematical function is chemical potential, right? And then, we have to find out solutions for this mathematical function and then solution we have already found, it is already known through the phase equilibrium problem or the chemical potential. When we describe the chemical potential, we have seen the chemical potential of component i has to be same in all co-existing phases.

So, that is the solution, μ_i^α is = μ_i^β, like that, okay? So, now surprisingly, you can see that μ_i itself is a kind of a function that defines the real problem into the mathematical form, rather it transforms the real problem into the mathematical form and that function is nothing but the chemical potential and again the solution for that mathematical form of the problem is again nothing but the chemical potential which should be equal for a given component in all the phases, okay?

So now, solution is also in terms of μ_i, right? We do not know what μ_i is? It is unmeasurable. So, then we have to convert it in terms of some kind of a measurable properties or you know some kind of properties which are close to the real life situations, if not exactly in terms of measurable properties. We cannot write in terms of measurable properties because already we have decided, we have discussed, we have seen that this chemical potential is non-measurable thermodynamic properties unlike you know temperature and pressure. Temperature and pressure you can measure, but chemical potential you cannot measure.

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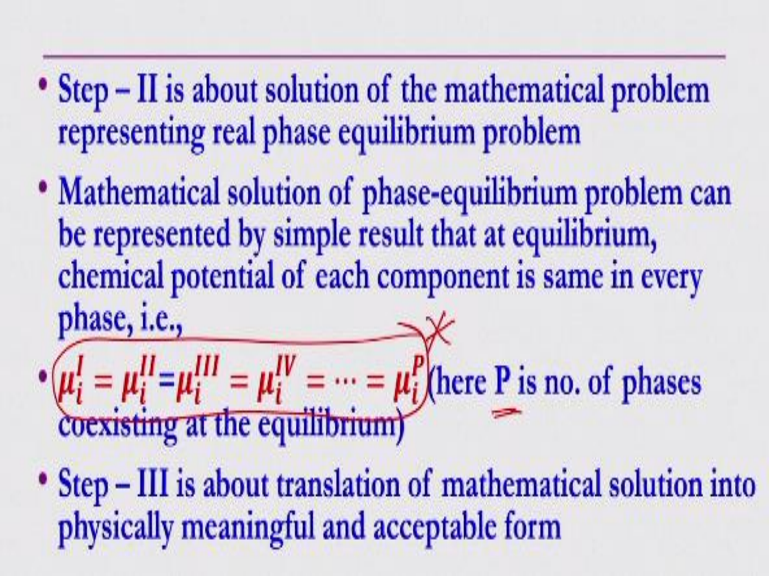

- Step – II is about solution of the mathematical problem representing real phase equilibrium problem
- Mathematical solution of phase-equilibrium problem can be represented by simple result that at equilibrium, chemical potential of each component is same in every phase, i.e.,
- $\mu_i^I = \mu_i^{II} = \mu_i^{III} = \mu_i^{IV} = \cdots = \mu_i^P$ (here P is no. of phases coexisting at the equilibrium)
- Step – III is about translation of mathematical solution into physically meaningful and acceptable form

So, step 2 is about the solution of the mathematical problem representing real phase equilibrium problem. So, mathematical solution of phase equilibrium problem can be represented by a simple result at equilibrium that is chemical potential of each component is same in every phase. That is, if there are P number of phases, $\mu_i^I = \mu_i^{II} = \mu_i^{III} = \mu_i^{IV} = \ldots = \mu_i^P$ if there are a number of phases co-existing at equilibrium or there are P number of phases and there is equilibrium amongst all those P number of phases. So, this is the solution.

Now, step 3 is a word translation of mathematical solution into physically meaningful and acceptable form. Now, we got the solution, this is nothing but the solution of the phase equilibrium problem, but this is not having any physical meaning or acceptable form in terms of measurable properties, etc. So, the solution is as useless as nothing has been done unless if you have a kind of translation of this solution into a kind of physically meaningful and acceptable form, right? So, how to do that one?

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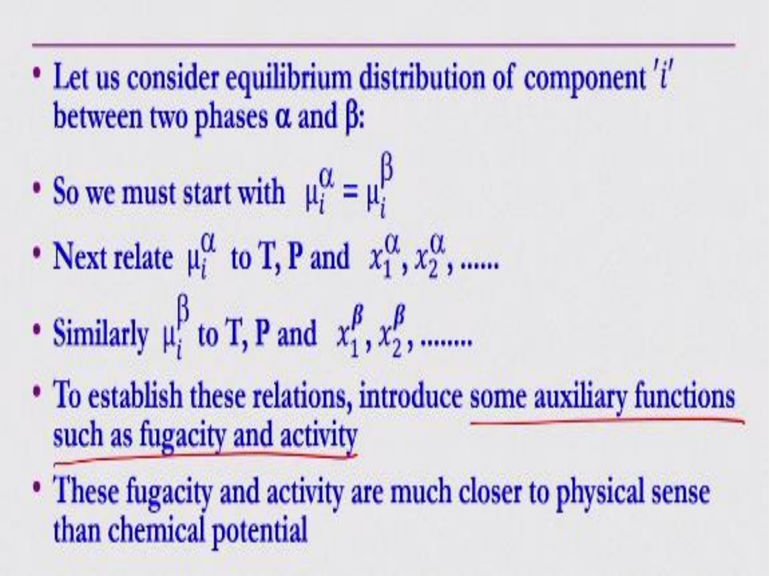

- Let us consider equilibrium distribution of component 'i' between two phases α and β:
- So we must start with $\mu_i^{\alpha} = \mu_i^{\beta}$
- Next relate μ_i^{α} to T, P and $x_1^{\alpha}, x_2^{\alpha}, \ldots\ldots$
- Similarly μ_i^{β} to T, P and $x_1^{\beta}, x_2^{\beta}, \ldots\ldots..$
- To establish these relations, introduce some auxiliary functions such as fugacity and activity
- These fugacity and activity are much closer to physical sense than chemical potential

Let us consider equilibrium distribution of component i between 2 phases α and β. Then, μ_i^{α}, μ_i^{β} you are having so that you must start with $\mu_i^{\alpha} = \mu_i^{\beta}$ and this μ_i^{α} you how to make a relation or relate μ_i^{α} to temperature, pressure, x_1^{α}, x_2^{α}, x_3^{α}…, depending on the number of components present. Similarly, you have to relate μ_i^{β} to temperature, pressure, and x_1^{β}, x_2^{β}, x_3^{β}… depending on the number of components present in that phase, right?

This relation you how to make first, then only you can have some kind of physically meaningful and acceptable form of the solution. Now, to establish this relations what we do, we introduce some auxiliary functions such as fugacity and activity, right? This fugacity and activity are much closer to physical sense than chemical potential.

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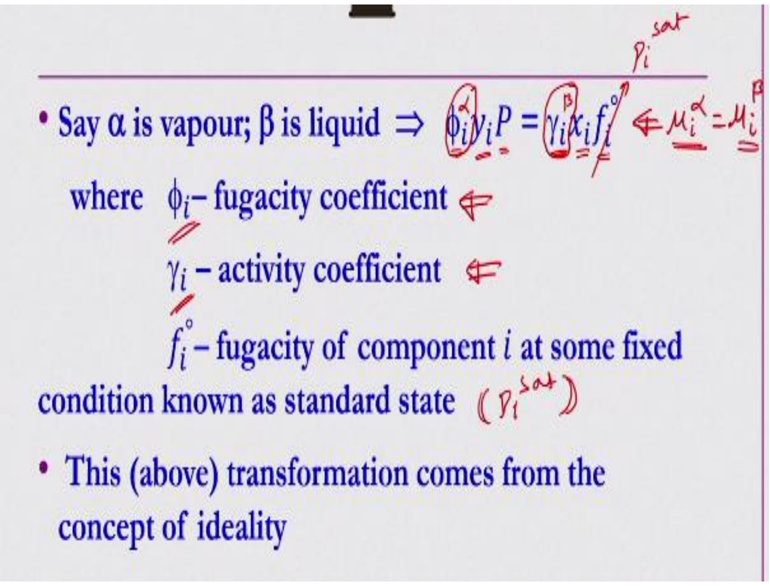

- Say α is vapour; β is liquid ⇒ $\phi_i^{\alpha} y_i P = \gamma_i^{\beta} x_i \overset{p_i^{sat}}{f_i^{\circ}} \Leftarrow \mu_i^{\alpha} = \mu_i^{\beta}$

  where ϕ_i – fugacity coefficient ⇐

  γ_i – activity coefficient ⇐

  f_i° – fugacity of component i at some fixed condition known as standard state (p_i^{sat})
- This (above) transformation comes from the concept of ideality

So, that means let us say if you take a vapor-liquid phase or there is an equilibrium between vapor and liquid phase, which is having you know i number of components. So, let us assume α is a vapor phase, β is a liquid phase and let us take component i and there may be N number of components. So, for ith component actually we can write it as $y_i*P*\phi_i = x_i*f_i^\circ*\gamma_i$, right? So, actually this is nothing but $\mu_i^\alpha = \mu_i^\beta$. So, if you want you can have a kind of α here for ϕ_i^α and γ_i^α. You can have a kind of β like this for indication.

So now, whatever the μ_i^α is there that is related to its composition, its pressure and then ϕ_i is anyway obviously function of temperature, pressure, and composition that we are going to find out, okay? And then similarly, for the liquid phase that is β phase, so what we have is now this μ_i^β which is related to its composition x_i, okay? And then f_i°, it is kind of related to some fugacity at reference state. f_i° can be taken in general as P_i^{sat} also, the saturation pressure of the component related to the temperature and then some auxiliary function γ_i^β activity coefficient. So, this fugacity coefficient, this activity coefficient are a kind of auxiliary functions, we are using to relate this chemical potential to temperature, pressure, and then composition of the system. Further, this auxiliary functions fugacity and activity are coming from the concept of ideality, ideal behavior or ideal phase kind of thing, how it is that we can see.

ϕ_i is nothing but fugacity coefficient and then γ_i is nothing but the activity coefficient, f_i° is fugacity of component i at some fixed condition known as standard state, so in general it is taken as P_i^{sat} for many cases as a standard reference, okay? And this transformation comes from the concept of ideality. That means, this whatever the fugacity coefficient, activity coefficient they are not only some kind of auxiliary functions used to transform the chemical potential, so that to relate them to the temperature, pressure, and composition, but also they tell something about the ideality of the phases also.

If the vapor phase is ideal phase, then fugacity coefficient is going to be 1. If the liquid phase is a kind of ideal liquid mixture, then activity coefficient is going to be 1 for that component. So, that means, if this ϕ_i and γ_i are deviating away from value of 1 that means, there is a kind of a nonideality in the vapor and liquid phases respectively, okay? So, what is the point? What is the importance of this activity coefficient and fugacity coefficient?

First, they are the kind of auxiliary functions used to relate chemical potential to the temperature, pressure, and then composition of the system plus they are also a kind of indication about the degree of non-ideality that is present in vapor and liquid phases respectively. If they are equals to 1, that means vapor and liquid phases are ideal mixtures.

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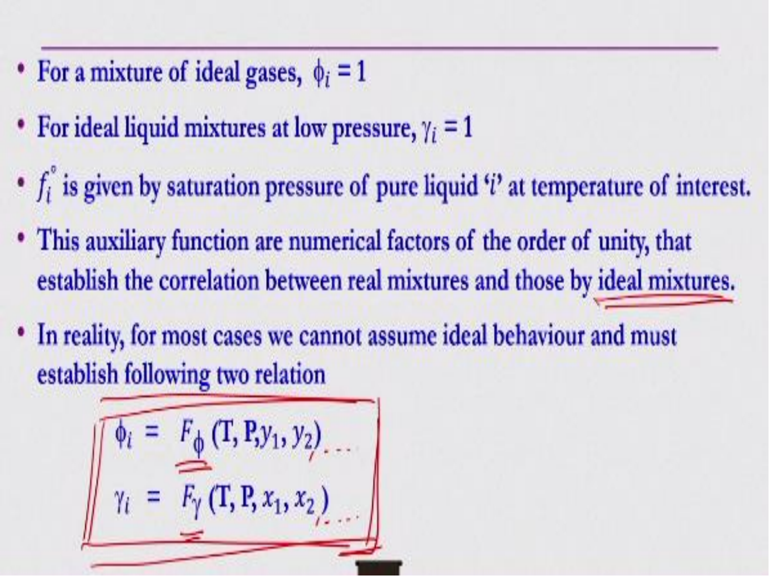

- For a mixture of ideal gases, $\phi_i = 1$
- For ideal liquid mixtures at low pressure, $\gamma_i = 1$
- f_i° is given by saturation pressure of pure liquid 'i' at temperature of interest.
- This auxiliary function are numerical factors of the order of unity, that establish the correlation between real mixtures and those by ideal mixtures.
- In reality, for most cases we cannot assume ideal behaviour and must establish following two relation

$$\boxed{\begin{aligned} \phi_i &= F_\phi(T, P, y_1, y_2)\ldots \\ \gamma_i &= F_\gamma(T, P, x_1, x_2)\ldots \end{aligned}}$$

For a mixture of ideal gases, ϕ_i equals to 1. Similarly, for an ideal liquid mixtures at low pressures $\gamma_i = 1$ as I mentioned. If these are equals to 1 that means these phases are ideal phases. The $f_i°$ is given by saturation pressure of pure liquid i at temperature of interest in general. This auxiliary function or numerical factors of the order of unity that establish the correlation between the real mixtures and those by ideal mixtures, okay?

Without this information of ϕ_i and γ_i, we cannot have a kind of phase equilibrium problems or we cannot solve the phase equilibrium problems where these phases are having non-ideality. If you have a phase equilibrium problems with non-ideality, then you must have some kind of provision to obtain this ϕ_i and γ_i relations. Those things we are going to do in subsequent lectures anyway. In reality for most cases, we cannot assume ideal behavior and must establish following 2 relations, that is $\phi_i = F_\phi$ function of T, P, y_1, y_2 and so on so if it is binary mixture.

Similarly, $\gamma_i = F_\gamma (T, P, x_1, x_2\ldots)$. It is not necessarily for the binary mixture, it is also valid for the multi component mixtures as well. So, if you wanted to solve the phase equilibrium problems with certain degree of non-ideality, before solving those problems you have to establish these relations, what is this is F of ϕ, what is F of γ, these relations you have to establish. So, that is the primary part of this course for the first 5 to 6 weeks.

So, we are going to establish these relations for many vapor and then liquid mixtures having non-ideality and those non-ideality defined by different types of models.

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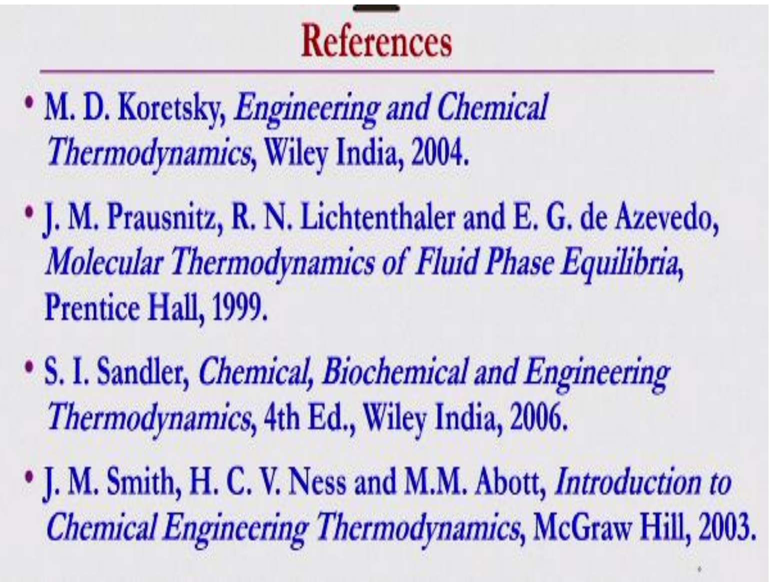

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So, the references for this lecture are Engineering and Chemical Thermodynamics by Koretsky, Molecular Thermodynamics of Fluid Phase Equilibria by Prausnitz et al., Chemical, Biochemical and Engineering Thermodynamics by Sandler, Introduction to Chemical Engineering Thermodynamics by Smith et al.

Thank you.