Advanced Thermodynamics and Molecular Simulations

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Lecture - 21

Mixing and Phase Separation, Phase Equilibrium of a Multiphase Multicomponent system, Gibbs phase Rule

Hello, all of you so in the last few lectures we have been discussing the idea of thermodynamic ensembles. So, we have looked at how can we define ensembles and how can we find thermodynamic properties in different ensembles and basically if I have to summarize the discussion in the last few lectures.

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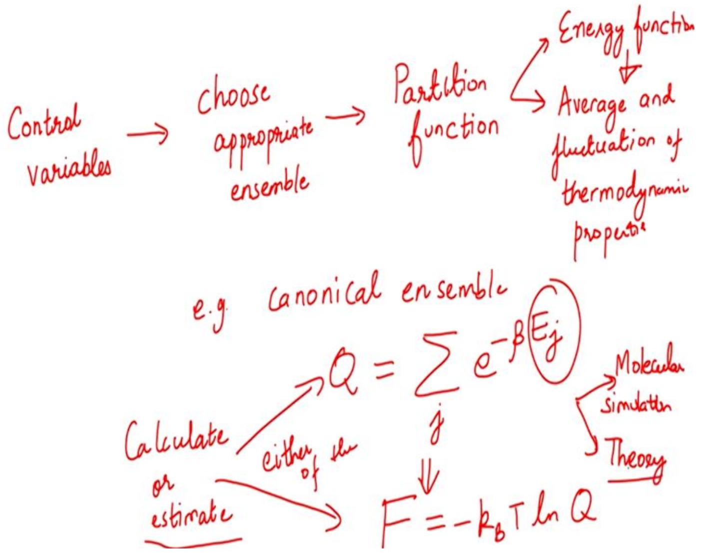

The idea is, if I want to find thermodynamic properties the first thing is to determine what are the control variables in my problem? And once we have figured out the control variables, then we should choose appropriate ensemble which can be various types like that we have discussed like. For example, if N V E are the control variables we go for the micro canonical ensemble, if N V T is a control variable we will go for the canonical ensemble. If N P T is a control variable we will go for the isothermal isobaric ensemble. If chemical potential volume temperature mu VT is the control variable we will go for the grand canonical ensemble.

But, nonetheless in all of them ultimately the goal is to first find the appropriate partition function and then using the partition function we can find, for example the appropriate energy function for the ensemble. Let us say for example for the micro canonical ensemble we will find the entropy canonical ensemble we find the Helmholtz free energy and so on nd not only that we can also use the partition function to get the average and fluctuations of thermodynamic properties and we should reiterate here, that we will find the average and fluctuations for the properties that we are not controlling because for the control variables the property values are constant let us say if we are in the canonical ensemble then in that case N V T is the same for all the states.

On the other hand the energy, the pressure and the chemical potential are going to fluctuate or different for different states in the ensemble and it is for those properties that we will find the average and fluctuations we have already earlier established that we could get that also using the energy function for the ensemble.

So, we can begin with the partition function that is more convenient if I start with ensemble kind of an idea and find the energy function and using that I can find the evidence and fluctuations or I can find it directly from the partition function because energy function is anyway a function of the partition function.

So, this is I would say the broad approach that we have been telling you but there is one small catch with this approach is that let us say if I want to apply to a problem. We have said what is the mathematical form of the partition function? But if you look at that form it is not something that I can evaluate so easily for any system. Let us say for example if I am looking for the canonical ensemble, I know that the partition function is-

$$Q = \sum_j e^{-\beta E_j}$$

Now the problem is even if we have the mathematical expression we do not know what are the available energy states. So, although the approach appears to be rigorous it is still not complete in some sense, because we still need to find what are the energy levels in the ensemble? So, in other words we have a method to proceed for different control variables, but we still need to figure out what are the energy levels for that particular problem. In a similar manner if I look at the Helmholtz free energy then we know that the Helmholtz free energy is a function of Q. But since I do not know, the energy levels since I do not know what are the possible energy levels we do not know what is the value of F, if we can figure out Q or if we can figure out F, then we can go ahead and find the average and fluctuations, but how will we figure it out we still have not seen in the discussion so far because if you recall the discussion has been quite general we were not looking at specific systems the energy levels are going to be different for different systems.

Let us say for example if I compare an ideal gas with a Vander Waals gas or for example a liquid or a solid the energy levels I can access are going to be different, not only that they will depend on the temperatures and other conditions that are there out there.

So, we will now see how can we will find that or in other words how can we calculate or estimate either of these two, because once I know either of the two I can find the properties that I am interested in. If I know the partition function clearly I can generate all the properties of interest, but even if I know the Helmholtz free energy I can do the same thing because ultimately Helmholtz free energy is a function of the partition function.

So, there are two ways to get there, one way is that I can do molecular simulation with an objective to estimate the partition function, the point that I am saying is estimate is very important because we have said that the number of states are endless. So, theoretically speaking we can sum over all the states but since the number of states are very large because the number of molecules are very large that is will be a very intensive kind of an affair, so if we can estimate it to a good approximation that is still good enough.

So, we can try to estimate either the Q or the F from a molecular simulation and using that I can find the properties of interest. The other approach is to apply some kind of theory and we looked in the last couple of classes that we can do pretty good job for the case of an ideal gas for example within certain approximations we can find what is known as the equation of state and once we have the equation of state we have in some sense the energy function.

So, whenever we are doing a theoretical analysis we have to keep in mind that is within certain approximations. In molecular simulations we may have fewer approximations but nonetheless, we are only going to estimate in most cases the partition function or the Helmholtz free energy for very small number of molecules we can get that exactly, but in thermodynamics we are dealing with large number of molecules.

So, in the next part of this particular course, we are going to look at both these approaches with certain examples. So, I will first discuss how can we theoretically proceed for certain systems and then I will tell you how can we proceed using molecular simulations. and so I was telling you that we can do a Monte Carlo simulation or a molecular dynamic simulation we will get there.

But let us first start looking at this particular thing from a theoretical perspective and try to see what kind of theories we can do. We already have done the ideal gas case, but as chemical engineers we are more interested in things which are liquid or solid or generally we are interested in all kinds of fluids or in complex fluids in general. So, we need to have some mechanism to also simulate or estimate the properties of liquids and solids and so on particularly liquid is the one that I will focus on.

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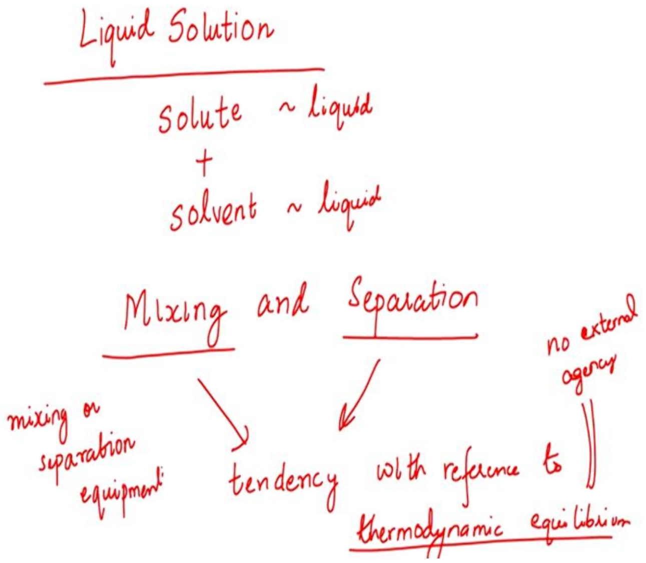

So, the particular problem that I will now look at is of a liquid solution and keep in mind that until so far our treatment have been quite general I do not specify that whether we have a solid, a liquid or a gas when I was doing the ensembles. But now whatever I am doing is applicable for the liquid solution. When I go to the next case I will tell you what system I am trying to simulate.

So, for a liquid solution I am looking at typically a solute and a solvent. Now the solute itself can be a solid, liquid or a gas, and the solvent itself again can be a solid liquid or a gas. But we are mostly looking at right now when the solute is a liquid and solvent is a liquid. We will make certain approximations that are only valid for liquids when I want to extend it for example, for gaseous solutes or for gaseous solvents we have to relax those assumptions. I will tell you where the liquid part comes in the derivation but keep in mind that whatever we are doing we are trying to specifically model a liquid solution. So, the similar approach can be applied for other cases but we need to look at the assumptions more carefully.

So, let us say if I have two substances A and B. It can be water and alcohol, it can be for example water and oil, it can be for example oil and alcohol and whatsoever and we clearly know that not every two substances mixed together. For example if I mix try to mix water and oil you will find that oil tends to stay above water because oil has a low density and oil does not mix with liquid. On the other hand if I try to mix liquid, with liquid water with alcohol, let us say for example if I try to mix ethanol and water they are perfectly miscible they will not tend to fail separate not only because the density is somewhat similar but also and more importantly because they have a tendency to mix together.

So, if I want to look at that behavior of mixing and separation thermodynamics can be extremely useful to determine which substances have a tendency to mix and which substances have a tendency to separate. And when I call a thing like tendency we are talking in terms of the system that is considered to be going towards an equilibrium state and when that is happening, we are implicitly assuming that there is no external driving force.

So, although I said that oil and water does not mix it is not that I cannot make them mix together, I can stir them and I can keep stirring and you will see that the water and oil is mixed together as long as am stirring it.

On the other hand if I remove the stirring or if I do not stir, then the water and oil will separate from each other in the case of the water and alcohol mixture that is not true. We can stir it in the beginning that may make the mixing slightly faster but even if we do not do that the system will get mixed over time so, we are referring to the tendency with reference to the thermodynamic equilibrium that is what is going to happen if I am looking at the thermodynamic equilibrium condition and that implicitly means no external force or agency that is working on the system.

So, even if we have an external force then also this thing has a meaning, why because if the tendency of the system is to mix together then if I apply any external agency if I apply some stirring clearly that may make that mixing faster but nonetheless system is already going towards equilibrium. So, the amount of effort I need to put will be relatively less in comparison to the case where the thermodynamic equilibrium says that the system wants to separate when the system wants to separate, then to keep it mixed we need to provide more energetic effort.

And it is that energetic effort that determines the power cost for a chemical engineers that how much power do I have to apply or how much energy do I have to spend for a mixing or separation equipment. It so happens that the mixing and separation equipment particularly the separation equipment in any chemical process industry is actually one of the most energetic intensive applications in fact that goes beyond chemical process industry, if I look at the total energy cost that is going towards separation processes in chemical process or other industries that separation cost is much more in comparison to energy expense in many other things. So, a large fraction of the world energy cost is actually going into separation processes and it is there the thermodynamics can help us because if I know the equilibrium state I know what is the tendency of the system and if I know what is the tendency we know how much is going to be the effort to go towards it or go against it that is if I want if it wants to mix at equilibrium if I want to separate I have to put effort if I want to if it wants to separate at equilibrium we have to put an effort to keep it mixed and that is essentially the energy cost that we are putting into this.

So, essentially as chemical engineers we look at this particular problem in terms of phase equilibrium. So, before I get into the molecular thermodynamics kind of an approach that we have been following let us first look at how chemical engineers look at it or how you may have read in your undergrad chemical engineering thermodynamics or any other thermodynamics course that you may have done

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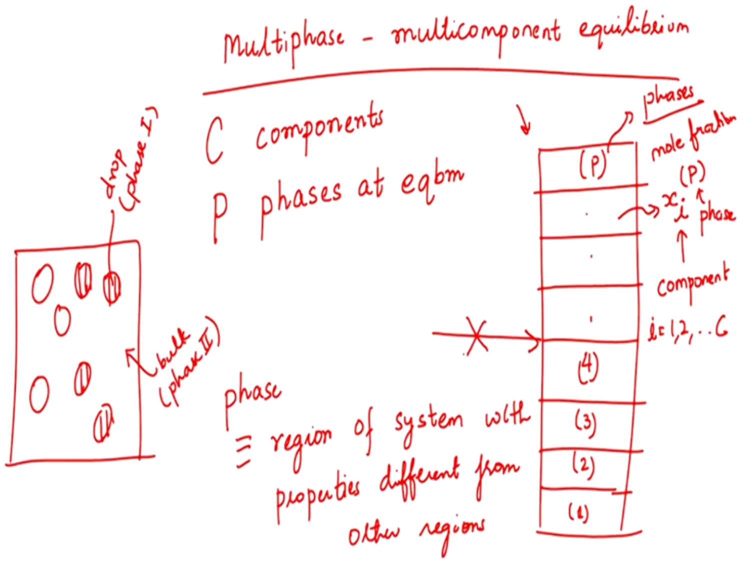

So, the way to look at it is we typically look at what is known as a Multiphase - multicomponent equilibrium and we start with saying that let us say for example we have a system that has certain number of components let us say some C components. I am not defining here what is a solute and a solvent whichever is more is going to be the solvent, whichever is less is going to be solute.

If we have many of these components then you can have a collection of solutes in a solvent and vice versa the distinction of solute and solvent is not particularly important. When the two components become similar in amount because I mean let us say if you have 40% water and 60% alcohol then it does not really matter whether water we call as solute or the alcohol because both are present in large amount solvent typically is used in the context when the amount of solute is much lesser than the amount of the solvent. In that case we call that a solvent. We are using that to dissolve the solute. So, we will not really be using the word solute and solvent here we will come back to that when we do a binary system next, but for the time being we say we have some C components and let us say, we have some P phases at equilibrium.

So, we do not know what is going to be the value of P to begin with. So, P can be one when all the C components form a homogeneous phase. P can be two when we form a two phase mixture, P can be three when we have a three phase mixture. And all that but assuming that we have certain number of phases. Let us say P phases we can draw a picture like this within any of the separation equipment that we have and let me call these phases 1, 2, 3, 4 to P.

So, these refers to my phases and all these phases in principle, contains all the components, the amount of the component in every phase is going to be different but in principle they contain all the component. It may be that one of the component is absent in one of those phases but in general they contain all the components and since we are dealing with the liquid we can represent the composition of a phase as something like this where x_i is a mole fraction, we can also work in terms of the volume fraction or a weight fraction but mole fraction is typically used. So, i that is subscript here indicate the component. And clearly I can take values 1, 2 to C because C is total number of component and P refers to the phase there. So, keep in mind that although I have drawn a picture like this it should not always look like that. So, it is not that every face should be on top of each other that is not what I mean from the on the picture here.

It can very well be that you can have the phase as one of the phases as let us say some drop that forms one phase and the other phase can be the bulk. So, as long as whatever we define the phase like it can be drop suspended in a fluid we can think of other possibilities as well. As long as the phase that I define is having thermodynamic properties different from the other phases we can say it is a phase. So, a phase so as to speak is the reason of system with properties different from other regions and the reason why this particular point is very important here because, the notion that we typically present is something like this but this will only happen when you will have a clear difference in the density of the P phases.

So, for a water oil mixture you will always see water oil going to top and water coming at bottom for significant amount of oil but that is because oil and water has different density. On the other hand oil and something else may have a similar density. But they can still form a two phase system because some other property is different. So, density is not the only thermodynamic property you can have other properties which can be different in the two phases and then as well we will say that they are forming two phases. And if the density is more or less similar clearly we will not see one phase going on top of the other but since the other property is different we can say that they are forming two phases. So, we should first clear out that notion that this drawing does not always mean that we have a density difference. A density difference is not necessary for the condition of a multiphase equilibrium.

So, with this particular idea, we can now write the equations for a multiphase - multicomponent equilibrium and before that I want to re-emphasize that we are looking at the equilibrium condition that means there is no external agency that is acting here. So, there is for example no flow into the system let us say if I look at a continuous process then there are inflows and outflows when the inflow and outflow is happening that means that the system is not in a state of equilibrium. I may still assume that the system is in a state of equilibrium, I can call it a pseudo equilibrium, but rigorously speaking the system is in a state of equilibrium only when there is no external agency that means absence of flows absence of any other kind of external energy like heating cooling or whatsoever.

In a real chemical process equipment that is never happening. So, therefore, we always assume an equilibrium condition in a chemical process equipment but in reality we never have a true equilibrium so as to speak. So, we need to take this equilibrium idea more kind of a limiting behavior in those conditions where you have inflows and outflows and heating and cooling and all those things equilibrium is only valid rigorously speaking when there is no external agency.

So, even let us say for the flow is small and heating is small and cooling is small, it may be such that the conditions are similar to equilibrium condition or near the equilibrium condition, but true equilibrium is only attained when there is no external agency and we have waited long enough. So, let us say for example, if I put everything together then clearly in the very beginning the system is not in a state of equilibrium, system will eventually go towards that equilibrium state

So, whenever we talk about an equilibrium we mean these two things that there is no external agency and we have waited long enough. Again rigorously speaking it is infinite time, but in most typical situations we get very close to equilibrium in relatively small time let us say 1 hour, 2 hour, 3 hour and how much time it takes to get there depends on the system under consideration.

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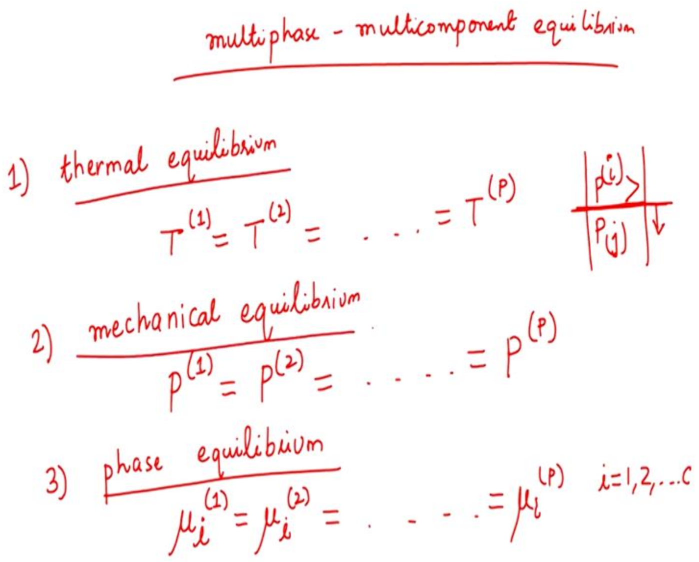

multiphase - multicomponent equilibrium

1) thermal equilibrium

$$T^{(1)} = T^{(2)} = \ldots = T^{(P)}$$

2) mechanical equilibrium

$$P^{(1)} = P^{(2)} = \ldots = P^{(P)}$$

3) phase equilibrium

$$\mu_i^{(1)} = \mu_i^{(2)} = \ldots = \mu_i^{(P)} \quad i = 1, 2, \ldots C$$

So, with this particular idea I can write the equation of a multiphase multicomponent equilibrium as the following. So, this equilibrium entails three separate equilibriums, first of all we say that the temperature of all the phases has to be the same, that is $T^1 = T^2 = \ldots . T^p$ superscripts refers to the phases to what I am discussing here and why is that because if temperatures are different then you have some heat transfer from higher temperatures to lower temperatures. whenever there is a heat transfer happening we can say that we are not in a condition of equilibrium, because at equilibrium you should have the rate of forward process equal to the rate of backward process whenever there is a temperature difference we only have a forward process that is heat transfer from a hotter fluid to a colder fluid. There is no backward process, only when the temperatures become equal we can say that that process has ceased and we have achieved a state of thermal equilibrium that is essential for the idea of equilibrium.

$$thermal\ equilibrium = T^1 = T^2 = \cdots \ldots \ldots . T^P$$

The next thing that must be valid is what is referred as a mechanical equilibrium and that says that the pressures of all the phases has to be the same and again the idea here may seem if pressures are different then what is going to happen- Let us say for example you have two phases i and j for the time being and let us say for example they have different pressure.

So, let us say if Pi is more than Pj now what is going to happen. Since that pressure is higher this particular boundary will have a tendency to go down, because higher pressure to lower pressure we will have a pressure drop and the pressure drop results in a flow. So, a flow will cease completely when the pressures become equal, so, just like the heat transfer we also have to look at the momentum transfer and the net momentum transfer should also be equal to 0 that will happen when the pressures become equal and of course, assuming that there is no inflow and outflow.

$$mechanical\ equilibrium = P^1 = P^2 = \cdots \ldots \ldots . = P^P$$

And finally there is an equation of phase equilibrium and this is the part we discuss in more details in the coming lectures but the key idea is that we assume that the chemical potential of every component and that point is important chemical potential of every component. Let us say if i look at the component i let us say i equal to 1 then the chemical potential of the component one is going to be the same in each of the phases, that is μi^1 is equal to μi^2 that is equal to μi^p. And that is true for every component, so this equation have to be written for i is equal to 1 to c.

$$phase\ equilibrium = \mu^1 = \mu^2 = \cdots \ldots \ldots . = \mu^P$$

So, it is these three equilibrium conditions that determines what is the equilibrium for that system and once we have established that then we can figure out what are the phases that are going to be and what are the compositions going to be in those phases. However, when we talk about the compositions, there is a constraint on the composition and that is since I have defined my x_i as the mole fraction.

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$$\sum_i x_i^{(k)} = 1 \quad ; \quad k = 1, 2, \ldots P$$

$$\mu_i^{(k)} \equiv \mu_i^{(k)}\left(T^{(k)}, P^{(k)}, \underbrace{\{x_i^{(k)}\}}_{\Downarrow}\right)$$

$$\left(x_1^{(k)}, x_2^{(k)}, \ldots x_c^{(k)}\right)$$

Degree of freedom (DOF)
= # variables − # equation

$$\boxed{\text{DOF for intensive variables}}$$

If I look at within each of the phases the mole fractions must add to 1, So, let us say if I look at a phase k and if I sum over all the components this is going to be equal to 1 and this has to be written for k is equal to 1 to P.

$$\sum_i x_i^k = 1 \qquad and \qquad k = 1,2, \dots \dots \dots \dots \dots \dots \dots P$$

So, basically we have tried to summarize the conditions of equilibrium for this system now the final thing and that is I would say the most important thing that this system of equation is still not complete and that is because we do not know what is the chemical potential of every component in every phase and this has to come from some sort of an equation of a state and this in some sense has to come from the partition functions and all those things that we have discussed earlier we are not doing a molecular picture here but keep in mind that the chemical potential ultimately has to come from the equation of state more specifically each of these chemical potentials must essentially be a function of the temperature of the phase let us say if I look at a phase k, then temperature of that phase, the pressure of that phase and also the composition of that phase. So, the composition is represented by curly bracket, so this means I am looking at composition of all the component within that particular phase.

$$\mu_i^k \equiv \mu_i^k(T^{(k)}, P^{(k)}, \{x_i^k\}$$

Here,

$$\{x_i^k\} = (x_1^k, x_2^k, \dots \dots \dots \dots \dots x_c^k$$

So, chemical potential is not going to be constant, chemical potential is going to vary as the temperature and pressure changes. So, even for the same component the chemical potential can in principle be different in different phases if they have different temperature and pressure and different composition. So, we have to ensure that the chemical potentials become equal and only then we can say that we have reached a phase equilibrium.

So, in some sense we have listed out all the equations that we have to worry about and let us now find what is known as the degree of freedom of this problem. So, a degree of freedom is defined as the number of variables that we need to find minus the number of the equations. The degree of freedom represents how many variables I am free to control. So, for example, if degree of freedom is equal to one there is one variable in the problem that I can control all the other variables are determined once I control that one variable, if degree of freedom is equal to 0 we have no variable under control. So, that we can also call as the number of design variables because we can choose a value for that variable, so the degree of freedom pretty much determines what is the control that we have what variable we can control and so on.

So, in this case, if you looked at it carefully we have only listed the intensive variable in the problem nothing in our picture so far represents the quantity in the equations. So, I can write first the degree of freedom or DOF for the intensive variables only and we can so I will not really get into there we can show that this is sufficient for characterizing the equilibrium state if for example if I am considering the extensive variables then we have to write for example the material balance and energy balance equations in equilibrium conditions those equations are inconsequential, because there is no inflow and outflow there is no additional energy input or external energy input and therefore those equations need not be considered for the characterizing the equilibrium state.

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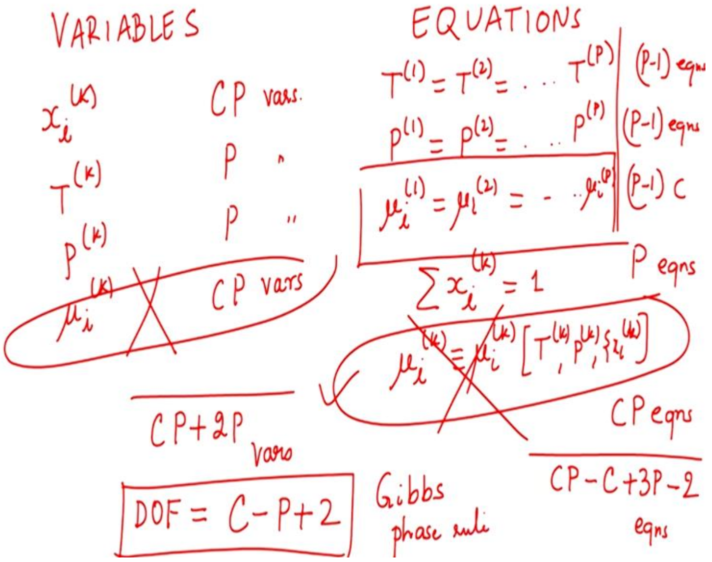

So, let us try to find the degree of freedom of the intensive variable in the problem and the way to do that is we list what are the variables that we have. And we list what are the equations that we have, we count the number of variables and the equations and then take a difference. So, the variables in this problem are the compositions and we have C components in P phases, so we have CP variables which are representing the composition or the mole fraction.

The variable here also are temperature, we have P variables, the variables here are the pressure again we have P variables. And there is if you look at it there is no other variable in the problem we have assumed the P. So, P is not a variable in this particular case the chemical potential we can find as a function of the temperature pressure and the mole fraction. So, the chemical potential is also not a variable in other words we are essentially looking at only the independent variable not the dependent variables in the problem and we have pretty much listed out all the variables.

Now let us look at how many equations do we have- so, we have the temperature equality-

$$T^{(1)} = T^{(2)} = T^{(3)} \ldots\ldots\ldots\ldots\ldots . T^{(P)}$$

and this gives me P minus 1 equation, because I can write $T^1 = T^2$, $T^1 = T^3$ and so on we will have in total P minus 1 equations. Similarly for pressure we are going to have P minus 1 equations-

$$P^{(1)} = P^{(2)} = P^{(3)} \ldots\ldots\ldots\ldots\ldots . P^{(P)}$$

Similarly for chemical potentials-

$$\mu^{(1)} = \mu^{(2)} = \mu^{(3)} \ldots\ldots\ldots\ldots\ldots . \mu^{(P)}$$

now that is written for every value of i, so we have P minus equation for every i value multiplied with C and then we have said we have-

$$\sum_i x_i^k = 1$$

and we are writing it for each phase, so in total we have p such equations and finally we have the equations for the chemical potentials and that again is going to give me some CP equations.

$$\mu_i^{(k)} \equiv \mu_i^k \left[T^{(k)}, P^{(k)}, \left\{x_i^{(k)}\right\}\right] \; CP\ equations$$

So, we have figured out what are the variables in this particular problem, we have figured out what are the equations in this problem and then, we can find the degree of freedom for this particular problem.

So, we have to be a bit careful here when I do that and that is because of the last equation that we have written, so what is that equation for? So, I am writing equation for the chemical potential. I have earlier said that the chemical potential is a function of the temperature, pressure and composition. So, therefore we have already not counted chemical potential as a separate variable. So, this equation-

$$\mu_i^{(k)} \equiv \mu_i^k \left[T^{(k)}, P^{(k)}, \left\{x_i^{(k)}\right\}\right] \; CP\ equations$$

therefore should also not be considered if I am doing that because I know that equation that is a property relation to find the chemical potential. Once we have figured out the temperature, pressure and the mole fraction then we can figure out the chemical potential in other words I could have said that chemical potential is an extra variable and we have additional CP variable here that is going to give you the same answer, because the number of variables of the chemical potential that I will list the CP variable will match the number of equations that I have written there that will not make any difference to the degree of freedom and that is why I will not count them here. So, you can either not count them as variables and equations or you can count them as both variables and equation and you will get the same answer.

However this equation-

$$\mu^{(1)} = \mu^{(2)} = \mu^{(3)} \ldots\ldots\ldots\ldots\ldots.\mu^{(P)}$$

because if you think about it, the mole fractions are determined by these equations that are on the board the chemical potentials have to be equal and that is what will give rise to different mole fractions. So, we will find the mole fraction using that equation and therefore we need to count those equations there, but chemical potential equations as the last one in the list here need not be counted if we are counting it, we should also count the chemical potential as the variables.

So, if I list them then we have CP + 2P variables on the right side we will have CP - C plus 3P - 2 equations. And if I do number of variables minus the number of equation we can see that the degree of freedom is given as C - P + 2 and that is what is known as the Gibbs phase rule.

And that tells me what is the number of degree of freedom referring to the intensive variables that characterizes the multiphase multicomponent equilibrium of a system.

So, in the next lecture we will see what are the consequences of this equation and then we will go towards trying to have a molecular explanation of why we need to have equality of chemical potential. And first of all what is a chemical potential? How can we relate the ideas that we have learned earlier in your undergrad thermodynamics with the advanced notion of thermodynamics that we are trying to do in this particular course.

So with that I conclude this lecture.