Advanced Thermodynamics
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Lecture – 2
Classical Thermodynamics of Phase Equilibria

Welcome to the MOOCs course advanced thermodynamics. The title of this lecture is classical thermodynamics of phase equilibrium. In this lecture, we will be discussing a few definitions of classical thermodynamics, as we will be discussing a few equations of classical thermodynamics in addition to phase equilibria concepts. So, classical thermodynamics of phase equilibria, what is the main problem of thermodynamics of phase equilibria?

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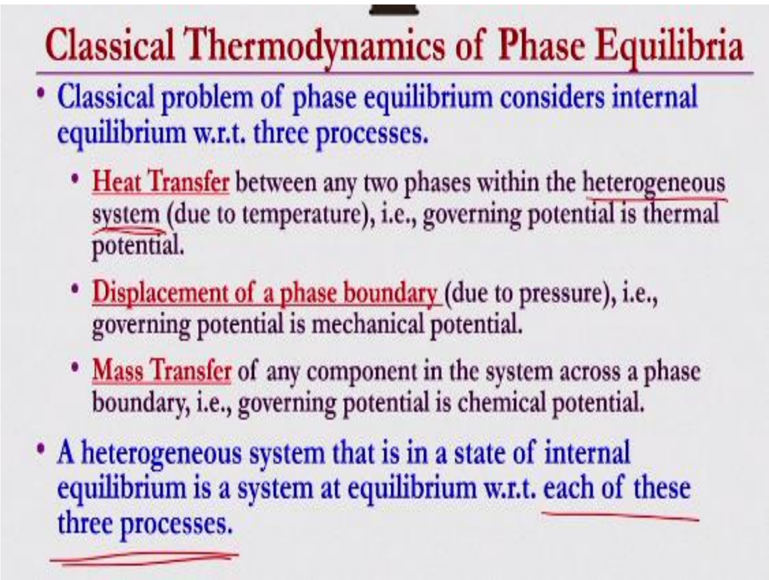

The classical problem of phase equilibria considers internal equilibrium with respect to 3 processes. Three processes, that is heat transfer, mass transfer, and then there is a kind of displacement due to the mechanical balance, right? So, that is you know will be having the heat transfer between any two phases within the heterogeneous system due to the temperature, that is, governing potential is thermal potential. Another process is displacement of a phase boundary due to pressure, that is, governing potential in such case is mechanical potential. And then third important one is the mass transfer of any component in the system across a phase boundary, that is, the governing potential is chemical potential. So, that is if you wanted to ensure that the phase equilibrium or equilibria amongst different phases has been established, you have to make sure that all these 3 equilibrium processes are established. That is, there should be you know thermal equilibrium, there should be mechanical equilibrium, and there should also be chemical equilibrium.

That is all 3 processes should be at equilibrium, then only we can say that internal equilibrium within the system has been established, then only we can use the phase equilibria principle for such kind of problems. Let us say if you have a kind of thermal equilibrium and then chemical equilibrium, then but mechanical equilibrium is not there. If the mechanical equilibrium is not there, that means there is a kind of you know pressure difference, pressure gradient was existing, so under such conditions it is possible that you know the material may be flow in and out of the system.

So, then under such conditions, you cannot have a kind of equilibrium established. If the material is flowing in and out of the system, then it is not possible to have a kind of you know equilibrium established within the closed system, because we know that this phase equilibria problem are valid only for the closed system because the closed system only can ensure a kind of a complete equilibrium with respect to all these 3 processes, that is thermal equilibrium, mechanical equilibrium, and then chemical equilibrium, right?

So, then here what we are talking? We are talking about the heterogeneous system. So, these terminologies also we are going to discuss here in this particular lecture. So, a heterogeneous system that is in a state of internal equilibrium is a system at equilibrium with respect to each of 3 processes, that is, you know having the thermal equilibrium, mechanical equilibrium as well as the chemical equilibrium.

Then, what is homogeneous closed system? Because as I mentioned, we are going to see a few basics of thermodynamic principles which may be useful in order to solve the problems in coming lecture, so, it is a kind of recapitulation of some of these definitions. So, homogeneous closed system, what do you mean by homogeneous closed system?

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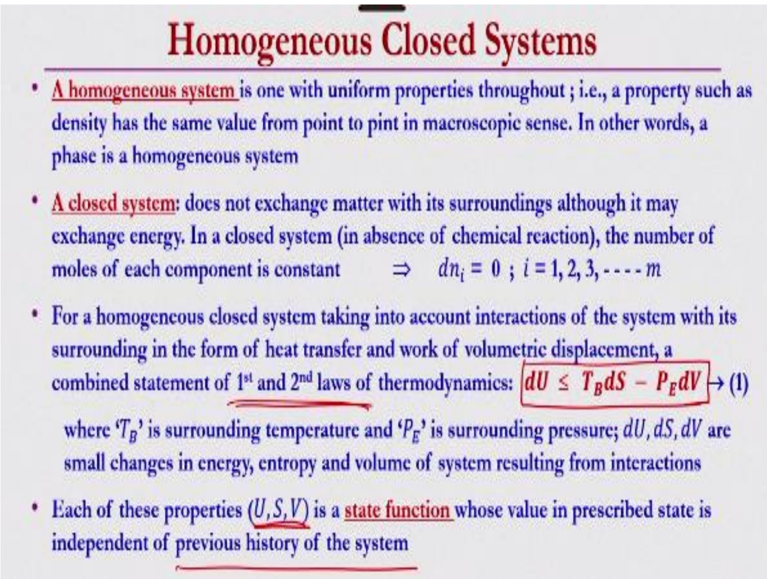

So, here 2 two terminologies are there, one is the homogeneous, another one is the closed system. Homogeneous system in the sense the properties are uniform everywhere in the system that we have taken and then closed system that means, the system that allows the transfer of the energy, exchange of energy is allowed, but the exchange of matter is not allowed. If the exchange of matter is not allowed, but the exchange of energy is allowed in a system, then we can call that system as a kind of closed system.

So, a homogeneous system is one with uniform properties throughout, that is, a property such as density has the same value from point to point in macroscopic point of view. In other words, a phase is a kind of homogeneous system, right? Because within a phase if you have a kind of liquid phase, then let us say if you water, water in a kind of container and then the water is uniform everywhere, so then property, the density of that water is uniform everywhere in the system that you have taken, okay?

So, that is what in other words what we can say? A phase is a kind of homogeneous system in macroscopic sense. A closed system does not exchange matter with its surroundings, although it may exchange energy. In a closed system that is in the absence of chemical reaction, the number of moles of each component is constant, that means dn_i should be 0, n_i is the number of moles of i^{th} component that is present in the system.

So, change in number of moles of that i^{th} component or any other component is 0 in a closed system because it does not allow any exchange of matter with the surroundings. If there is no exchange of matter, so then the number of moles are going to be constant for any component that is present in the system, okay? For a homogeneous closed system taking into account interactions of the system with its surroundings in the form of heat transfer and work of volumetric displacement, a combined statement of first and second laws of thermodynamics will provide us this relation, right?

If you write the first law of thermodynamics and then if you write the second law of thermodynamics, if you combine both of them, then you can derive this relation

$$dU \leq T_B dS - P_E dV$$

Where, T_B and P_E are nothing but the surrounding temperature and surrounding pressure respectively. If equality is there, that is $dU = T_B dS - P_E dV$, then we can say that the process is reversible process. If it is $dU < T_B dS - P_E dV$, then we can say that processes irreversible process, those definitions also we are going to see now, right?

So, here dU, dS, dV are nothing but change in energy, entropy, and volume of the system because of interaction between the system and the surroundings, okay? And then each of these properties whatever U, S, V are known as a kind of state function whose value in a given state is independent of previous history of the system. That is the reason these are known as the state functions because their value at a given specified state is independent of its previous history of the system. Then what do you mean by equilibrium state? These are the terminology we need to understand before going into details of the course.

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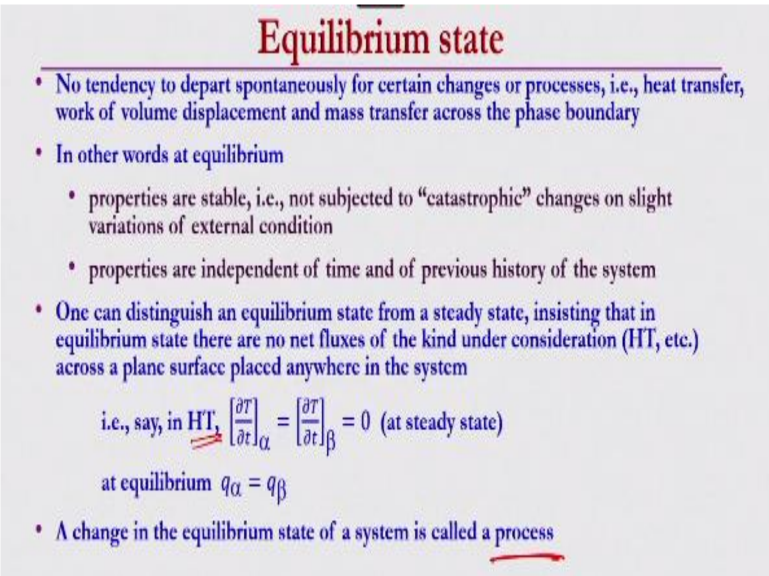

Equilibrium in the sense there is no tendency to depart spontaneously for certain changes or processes that is heat transfer, work of volume displacement, and mass transfer across the phase boundary. Whatever the process you take, actually if the heterogeneous system all these 3 equilibrium processes should exist, then only we can say that heterogeneous system is under equilibrium conditions and for none of these processes, there will be a kind of tendency to spontaneously change from one value to other value.

Let us say if you take the heat, and so temperature will not change spontaneously by certain small changes that is occurring in the system, okay? So, in other words, we can say that the properties are stable, that is not subjected to catastrophic changes on slight variations of external conditions. Otherwise, properties are also independent of time and of previous history of the system, then we can say the equilibrium state is being established.

One can distinguish an equilibrium state from a steady state, insisting that in equilibrium state that there are no net fluxes of the kind under consideration across the plane surface placed anywhere in the system. In general, there is a kind of confusion amongst the students what is the difference between steady state and equilibrium conditions. So, if it is steady state, the variation with respect to the temperature in the property or in general considered as 0, then we can say the steady state.

Let us say if you have heat transfer problem, then $\frac{\partial T}{\partial t}$ = 0, capital T is the temperature and the small t is standing for the time. Then we can say that the steady state is established, right? So, if there are 2 phases interacting, $\left[\frac{\partial T}{\partial t}\right]_{\alpha}$ = 0 as well as $\left[\frac{\partial T}{\partial t}\right]_{\beta}$ = 0, then we can say that both phases are at you know steady state conditions, but if you wanted to ensure that there is also equilibrium in addition to the steady state condition, then what you can say, you can say that the net fluxes are 0 or there is no net flux.

So, in other words, $q_{\alpha} - q_{\beta} = 0$ or $q_{\alpha} = q_{\beta}$. This is, I have taken as a kind of heat transfer example. So, similarly, any transfer process one can establish such kind of relations for you know equilibrium. So, a change in the equilibrium state of the system is in general known as the process in the thermodynamics. How do you define a process? Simply it is a change in the equilibrium state of the system is called a process.

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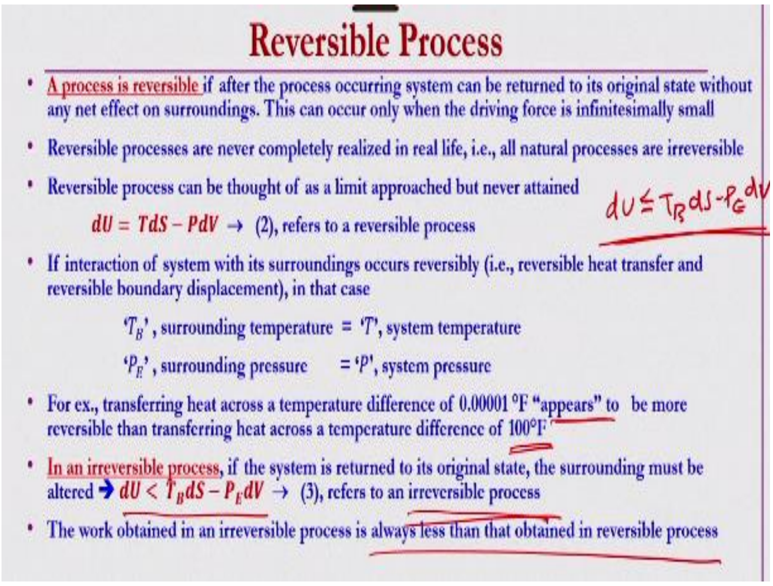

Then what is reversible process? Reversible process is the one upon occurring in the system when the process is stopped and if the system is coming back to its original state, then we can call it as a kind of a reversible process. That is a process is reversible if after the process occurring system can be returned to its original state without any net effect on the surroundings, that is important, it has to return to its original state, and while returning to its original state, there should not be any net effect on the surroundings, then only we can call it as a kind of reversible process.

In general, almost all processes in the nature are irreversible processes. None of the processes are reversible in general. However, these reversible processes can be established by having the driving forces, very small driving forces. Let us say if you have the heat transfer process, if the driving force that is delta T is very very small order of 10 to the power of -4 or 10 to the power of -5 degrees Fahrenheit, then it is possible that the reversible process can be established, right?

Let us say you have a temperature T_1 is you know 2 into 10 to the power of -5 degree Fahrenheit and then there is a processes occurring. So, because of the temperature is decreasing to 1 into 10 to the power of -5 degrees Fahrenheit. So then, without making any changes in the surrounding or without causing any net effect on surroundings, it is possible that temperature may be getting back to 2 into 10 to the power of -5 degrees Fahrenheit.

That is possible in general without making much changes or without making any changes to the surroundings okay or without causing any effect on the surroundings that is possible, but if you have the temperature, same heat transfer problem, but if you have the temperature difference of order of 10 to the power of 2 or 10 to the power 1 something like that, then it is not possible. That is let us say initial temperature is 100 degrees Fahrenheit and then there a process is occurring.

So, the temperature has raised to 200 degrees Fahrenheit, then it is not possible that temperature to come back to the initial temperature of 100 degrees Fahrenheit without causing any changes in the surroundings, it may come back, but definitely that will be causing some kind of effects on the surrounding by the transferring of heat to the surroundings, then only temperature would be coming down from 200 degree Fahrenheit to 100 degrees Fahrenheit.

So, here also, that may come but that may cause some kind of effect on the surroundings, okay? So, if the process is getting back to its original state without causing any kind of effect on surroundings, then we can call it as a kind of irreversible processes and almost all natural processes are irreversible, that is none of the natural processes are reversible, okay? And then reversible processes can be established only when the driving force is infinitesimally small. So, other way reversible process can be thought of as a limit approached, but never attained.

So, if you have $dU = TdS - PdV$, the same equation just a few slides before we have written as $dU = T_BdS - P_EdV$, but now here we are writing $TdS - PdV$, and if there is a kind of equality, this equation we have written, or equality is there then that process we call it as a kind of a reversible process. If the interaction of system with surrounding occurs reversibly, that is reversible heat transfer and reversible boundary displacement. In that case, what we can have?

We can have that the surrounding temperature is equal to the system temperature and similarly surrounding pressure should be equal to the system pressure, that is the reason we have written here without the subscript B and E for temperature and pressure, because T and P are nothing but the system temperature and system pressure respectively, whereas T_B and P_E are nothing but the surrounding temperature and then surrounding pressure respectively, right?

When the process is reversible, these conditions, surrounding temperature and system temperature are equal, similarly surrounding pressure and system pressure are equal. For example, as I mentioned transferring heat across a temperature difference of order of 10 to the power of -5 degrees Fahrenheit appears to be more reversible than transferring the heat across a temperature difference of 100 degrees Fahrenheit without causing any net effect on surroundings that is the important condition.

In an irreversible process if the system is returned to its original state, the surrounding must be altered, then in such case, $dU < T_B dS - P_E dV$, then under such conditions whatever the process is known, that is known as the irreversible process, that is it cannot go back to its original state without causing any effect on the surroundings, okay? That means surroundings must be altered in order to make the conditions to get back or the system to get back to its original state, right? In order to bring back that system, let us say the same example 100 degrees Fahrenheit initial temperature of the system is there and then some changes occur in the process, there awesome process has occurred. So, the temperature has increased to 200 degrees Fahrenheit, it can come back to the 100 degrees Fahrenheit only some of the heat is you know dissipated to the surroundings. So, that means surrounding has been changed. So, some kind of effect has occurred on the surrounding, then only it is coming back to its initial state, so then because of that reason, this processes are called as irreversible process.

If without causing any change on the surroundings or without causing any net effect on the surrounding if the process is coming back to its initial state, then we call it as a kind of a reversible process. If reversible process is there, then equality is there between dU and TdS - PdV. If there is an irreversibility, then inequality symbol, that less than symbol should be there, okay?

That means, the work obtained in an irreversible process is always less than that obtained in reversible process because in reversible process $dU = TdS - PdV$, whereas in irreversible process $dU < T_B dS - P_E dV$. That is the reason whatever the work obtained in irreversible process is always going to be less than the work that is obtained in a reversible process.

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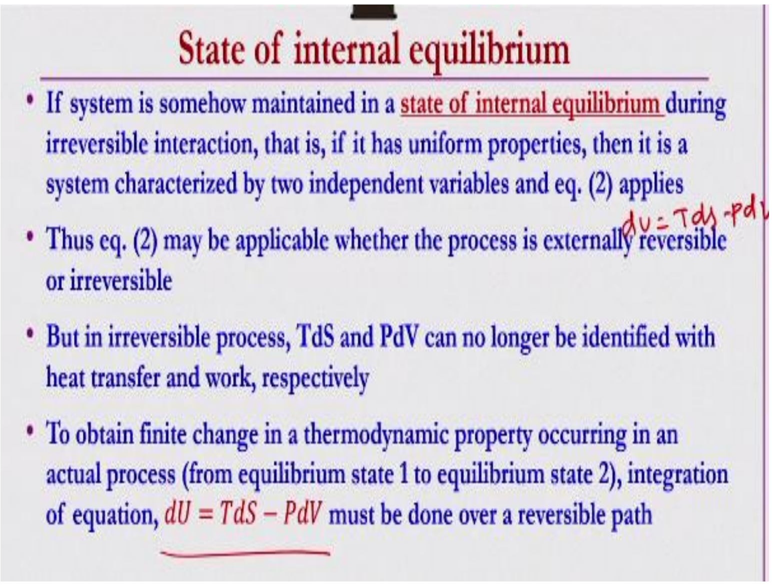

So, then what is state of internal equilibrium? If system is something maintained in a state of internal equilibrium during irreversible interaction, that is, if it has uniform properties, then it is a system characterized by 2 independent variables and equation 2 applies. The equation 2 is nothing but the dU = TdS - PdV, this equation will apply, right? So, equation 2 may be applicable whether the process is externally reversible or irreversible. If the state of internal equilibrium is maintained.

But in irreversible process, Tds and PdV can no longer be identified with the heat transfer and work respectively. Then, under such conditions to obtain finite change in thermodynamic properties occurring in an actual process from equilibrium state 1 to equilibrium state 2, integration of equation dU = TdS - PdV must be done over reversible path.

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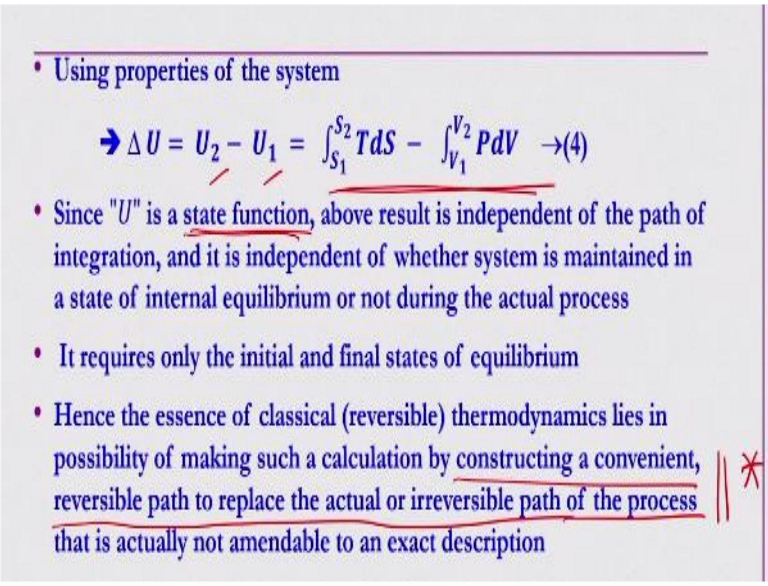

Let us say if you have a 2 equilibrium state, equilibrium state 1, equilibrium state 2, and then these 1 and 2 are in properties they are mentioned as a kind of you know subscripts.

So, $\Delta U = U_2 - U_1 = \int_{S1}^{S2} TdS - \int_{V1}^{V2} PdV$. V_1 is the equilibrium state 1, V_2 is equilibrium state 2, the volume of equilibrium state 1 and then volume of equilibrium state 2.

Since U is a state function as we have already seen, it does not depend on its previous history, right? It does not depend on the previous history, whatever its property is there, that is at that specified state only, at that particular instant only, does not depend on previous history and the result whatever this equation integration we have done, it is independent of the path of the integration and it is independent whether the system is maintained in a state of internal equilibrium or not during the actual process.

So, only thing it requires the initial and final equilibrium states only, it requires only initial and final states of equilibrium. Hence, the essence of classical or reversible thermodynamics lies in possibility of making such a calculation by constructing a convenient reversible path to replace the actual or irreversible path of the process, okay? So, this is very much important, like you know, we know that none of the natural processes are reversible, but having reversible processes is always advantageous from thermodynamics point of view.

So, the essence of classical thermodynamics lies in possibility of making such calculation by constructing convenient, reversible path to replace the actual or irreversible path of the process without making or without causing any kind of net effect on the surroundings.

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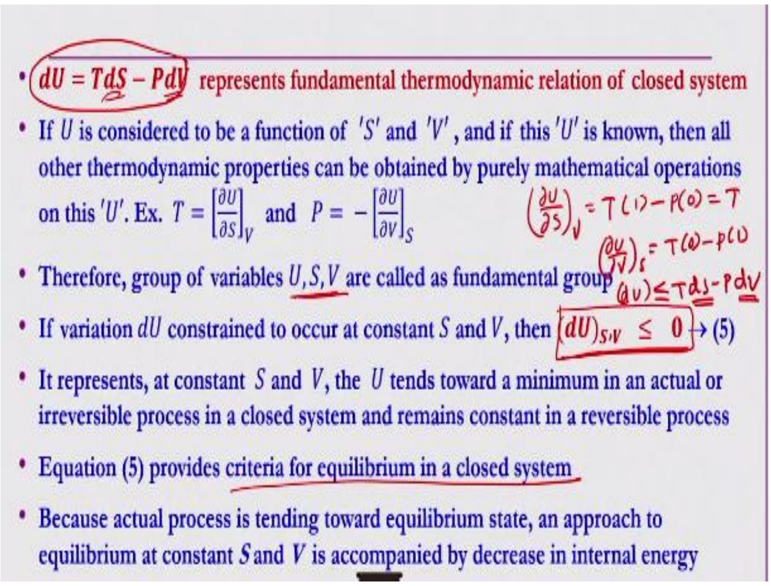

So, whatever dU = TdS - PdV that is known as the fundamental thermodynamic relation of a closed system, okay? It is a closed system because there is no exchange of matter, there is only exchange of energy. So, only the terms related to the energy or work done are only appearing here. So, dU = TdS - PdV is fundamental relation of classical thermodynamics for closed system. So, if U is considered to be a function of s and v, obviously here we can see dU = TdS - PdV.

So, any change in S, any change in V, that is causing some kind of change in U, right? So, that means, U is considered to be a function of S and V. Then if this U is known somehow, then all other thermodynamic properties can be calculated by simply using some kind of mathematical relations, right? So, from dU = TdS - PdV, if this equation if you partially differentiate with respect to S at constant V, then what you can have? You can have $\left[\frac{\partial U}{\partial S}\right]_V = T\left(\frac{\partial S}{\partial S} = 1\right) - P\,(0)$ at constant V. So, that means, $T = \left[\frac{\partial U}{\partial S}\right]_V$.

Similarly, $\left[\frac{\partial U}{\partial V}\right]_S = T\,(dS = 0)$ at constant S - $P\left(\frac{\partial V}{\partial V} = 1\right)$. So, that means, $P = -\left[\frac{\partial U}{\partial V}\right]_S$, such kind of simple mathematical principles one can use to get you know remaining thermodynamic properties if you know what that U as function of S and V is. Therefore, group of variables U, S, V are called as fundamental group.

If variation dU constrained to occur at constant S and V, then if let us say in this equation what we have if you have this you know dS, if S and V are constant, then dS and dV are 0, obviously, right? So, the final equation I have written only the equation for reversible process, if you write common equation, dU ≤ Tds - PdV, right? If you have a constant entropy and constant volume system, then obviously the dU ≤ 0, right?

So, that means, you know, for a system to be at equilibrium, what you have? At constant entropy and volume, change in energy is 0 or it is decreasing okay or in otherwise the energy is remaining constant or it is decreasing, so that dU = 0 or < 0, okay? So, this is one of the criteria to know whether the system is at equilibrium or not, okay? It represents at constant S and V, the U tends towards a minimum in an actual or irreversible process in a closed system and remains constant in a reversible process.

Because dU = TdS - PdV if S and V are constant, then dU = 0 in reversible process. In irreversible process, dU < TdS - PdV. So, again S and V are constant, then dU < 0, okay? So that means in the case of a reversible process, change in energy is going to be 0 or the energy is going to remain constant in a reversible process, whereas in kind of an irreversible process, the energy is going to decrease or it goes towards the minimum.

So that dU < 0 in the case of irreversible process that is what this means by $(dU)_{S, V} \leq 0$, and this provides a criteria for equilibrium in a closed system. The closed system is in equilibrium or not if you wanted to find out, you how to find out $(dU)_{S, V}$ and if $(dU)_{S, V} = 0$, then the reversible process is at equilibrium because actual process is tending toward equilibrium state and approach to equilibrium at constant S and V is accompanied by a decrease in internal energy.

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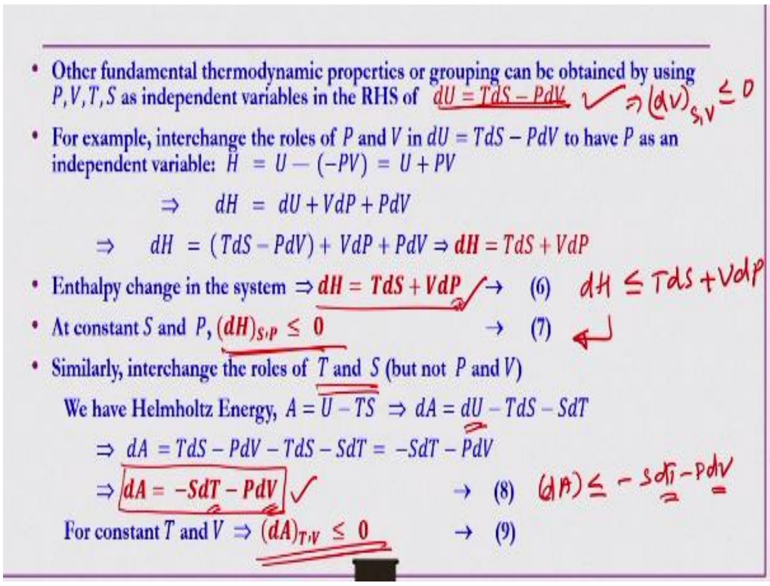

So, similarly other fundamental thermodynamic properties or grouping can be obtained by using P, V, T, S as independent variables in the RHS of $dU = TdS - PdV$, this is one of the fundamental relation for the closed system, like that in terms of enthalpy, in terms of Helmholtz energy, in terms of Gibbs energy also we can develop the fundamental relation for the closed system by using this P, V, T, S as independent variables for different cases.

Let us say for example, interchange the roles of P and V in $dU = TdS - PdV$ to have P as an in an independent variable, then what we have this H is nothing but U plus PV, right? Then under conditions

$$dH = dU + VdP + PdV$$

Now, substitute: $$dU = TdS - PdV$$

Then, $$dH = TdS + VdP$$

So, this is another relation that is enthalpy change in the system, $dH = TdS + VdP$. Now, pressure is independent variable. Here in the case of $dU = TdS - PdV$, volume is independent variable in addition to the entropy, right?

So, like this if you keep on changing the independent variables, different fundamental relations you can get for a closed system. Now, we have 2 relations. Similarly, here also from this relation also if you have the constant entropy and constant pressure, then $dH \leq 0$, this equation has been written here only for the reversible process. If you write the same equation for irreversible process, then you are going to have this equation as like this, and then at constant entropy and constant pressure, you are going to have this $dH \leq 0$.

This is another condition for equilibrium established in the closed system or not to check. Now, similarly, interchange the roles of T and S, but not P and V in the above equations, then we have Helmholtz energy A:

$$A = U - TS$$

Then, $$dA = dU - TdS - SdT$$

Now substitute, $$dU = TdS - PdV$$

$$dA = - SdT - PdV$$

Now, here temperature and then a volume are a kind of independent variables, right?

If the independent variables are temperature and volume, then what the fundamental relation for the closed system is, it is nothing but $dA = - SdT - PdV$. Now, this is also written for a kind of reversible process. If you write the same equation for irreversible process, then you have dA = - SdT - PdV, so there would be a kind of inequality, less than or equals to. If it = 0, then reversible, if it < then it is a kind of irreversible process.

So here again, if the temperature is constant and then volume is constant for a given system, then $(dA)_{T, V} \leq 0$, right? Now, we have 3 relations, 3 fundamental relations for closed system and then 3 conditions. From here what we got? We got $(dU)_{S, V} \leq 0$, 3 conditions for you know checking the equilibrium in a closed system, right? Any of them can be used.

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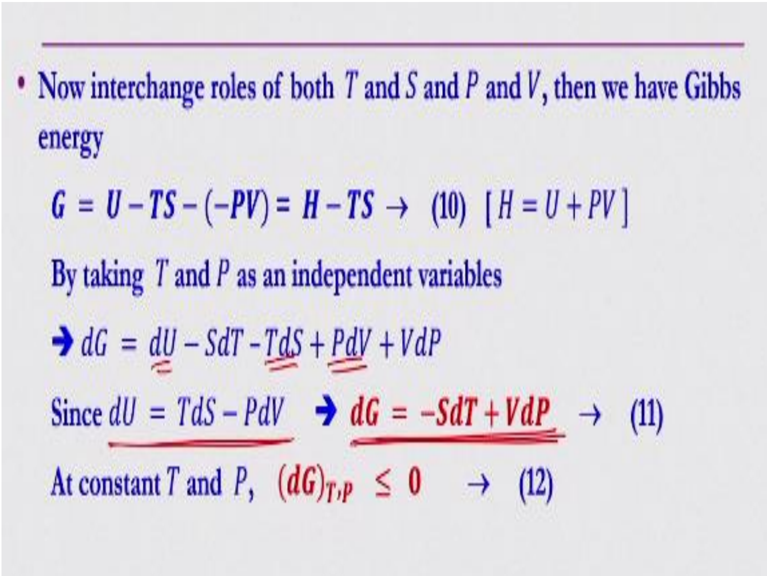

Now, we can have one more relation that is in terms of Gibbs energy. So, here now, both the roles of T and S and P and V are interchanged, then we can have Gibbs energy

$$G = H – TS$$

Now, here actually $H = U + PV$.

By taking T and P as independent variables, you can have

$$dG = dU – SdT + TdS + PdV + VdP.$$

Now, here rearrange this equation such that dU -TdS + PdV are on one side,

Because this $dU = TdS - PdV$

So, $dU - TdS + PdV$

These 3 terms together will become 0 because dU = TdS - PdV. Then, what we have? We have the remaining 2 terms dG = - SdT + VdP. This is another relation and then this relation also we have written for the reversible process. If you write for irreversible process, there will be less than symbol, right? And again at the constant temperature and pressure, we can have $(dG)_{T, P} \leq 0$ in order to check whether the closed system is equilibrium or not?

This is the condition for the equilibrium of a closed system. So, now, we have 4 fundamental relations depending on the independent variables, sometimes T and P, sometimes S and V independent variables, like that T, S, P, V we have changed, different independent variables we have changed and then different fundamental relations we are having for the closed system. So, this H, A, G are also known as thermodynamic potentials, so that is about the closed system.

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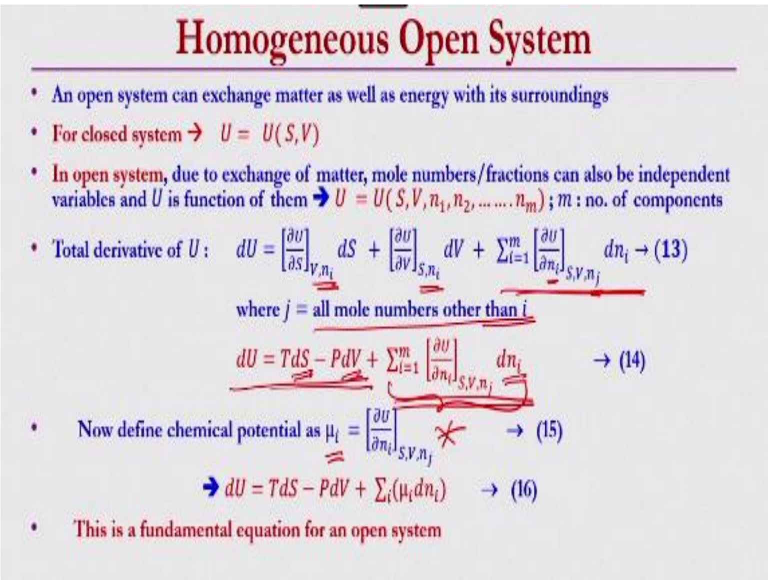

Now, we see a few basics about the open system as well, homogeneous open system. Open system is the one which can allow the exchange of matter as well as the energy with its surroundings. In the closed system, only exchange of energy with surroundings is allowed, but in a kind of open system, in addition to the energy, exchange of matter is also allowed with the surroundings, then we can call such system as a kind of open system.

Then in the closed system, we have seen that this U is function of S and V, that is entropy and volume, but in a kind of open system there is an exchange of matter, so number of moles are also there. So, that is the reason here this U is a function of S and V, in addition to that one, it is also a function of n_1, n_2, and so on so depending on the number of components, whereas n_1, n_2, etc are known as the number of moles of those competent 1, 2, etc., okay? Because now exchange of matter is allowed, so then number of moles of each component should also come into the picture, okay?

So, that means, if you do the total derivative of U, Then, $dU = \left[\frac{\partial U}{\partial S}\right]_{V,\, ni} dS + \left[\frac{\partial U}{\partial V}\right]_{S,\, ni} dV + \sum_{i=1}^{m} \left[\frac{\partial U}{\partial ni}\right]_{S,\, V,\, nj} dn_i$

n_j is counting for all other moles other than the n_i moles because here we are differentiating with respect to the n_i. So, all such like you know ∂ by ∂n_1 at constant S, V, n_2, n_3 and so on would be there plus ∂U by ∂n_2 at constant S, V, n_1, n_3, n_4 like that all those things will be there.

So, all those things we can do a kind of summation as a kind of here $\sum_{i=1}^{m} \left[\frac{\partial U}{\partial ni}\right]_{S,\, V,\, nj} dn_i$.

This is the total derivative of U for an open system, right? Now, j is standing for all mole numbers other than i because with respect to i, we are differentiating. So, other than i whatever all other moles are there, number of moles are there, so they have to be kept constant in addition to entropy and volume for this part, okay? So now, $\left[\frac{\partial U}{\partial S}\right]_{V,\, ni} = T$.

Similarly, $\left[\frac{\partial U}{\partial V}\right]_{S,\, ni} = P$ coming from the Maxwell relation. So, $dU = TdS – PdV$

$$\left[\frac{\partial U}{\partial V}\right]_{S,\, ni} = - P \text{ okay?}$$

So, $$dU = TdS – PdV + \sum_{i=1}^{m} \left[\frac{\partial U}{\partial ni}\right]_{S,\, V,\, nj} dn_i$$

So, now $dU = TdS - PdV$ is what? It is nothing but the fundamental relation for the closed system.

Now, we are doing for the open system, there is an exchange of matter. Because of that exchange of matter, there should be additional term. That additional term is coming here like this, that is $\sum_{i=1}^{m} \left[\frac{\partial U}{\partial ni}\right]_{S,\, V,\, nj} dn_i$ and this is not one term, they depend on, let us say 10 components are there, then there will be 10 such kind of terms would be there, all terms are added together like this in a generalized manner, okay? Now, what should we observe here? The coefficient of dS is what T, so that is nothing but related to something like you know thermal potential, right? And then here coefficient of d is nothing but P, that is nothing but you know something related to the mechanical potential.

Now, here this is dn_i and then whatever the coefficient of dn_i is there should be a kind of you know chemical potential because n stands for the number of moles of that particular matter okay and whatever the component that is present in this system, i^{th} component. So, analogous to that one, what we can say that $\left[\frac{\partial U}{\partial ni}\right]_{S,\, V,\, nj}$ is nothing but chemical potential, right? So, that is now defined chemical potential $\mu_i = \left[\frac{\partial U}{\partial ni}\right]_{S,\, V,\, nj}$. This is analogously we are doing.

Why are we defining this one as a chemical potential? Because it is analogously, here whatever the coefficient of dS there that is T, so that T represents something to thermal potential, right? And then whatever the coefficient of V is there, so change in volume dV, so that coefficient of dV is nothing but you know change in volume in general occurs because of the change in pressure. So, that pressure that stands for the mechanical potential, right?

Similarly, change in number of moles dn_i so that stands for the change in the number of moles of the competent that is present in the system, that is the change in mass that is occurring or that is related to mass transfer, so its coefficient should be analogous to these two, it should be a kind of chemical potential, because if coefficient of dS is you know thermal potential, similarly coefficient of dV is mechanical potential analogous to these two, the coefficient of dn_i should be chemical potential that is the reason we define the $\left[\frac{\partial U}{\partial ni}\right]_{S,\, V,\, nj} = \mu_i$.

So, then this equation can be written as $dU = TdS - PdV + \sum_i (\mu i \; dni)$ and this is known as the fundamental relation for the homogeneous open system, okay? Likewise in terms of dH, dA, dG also we can derive this relation that we can see now, okay?

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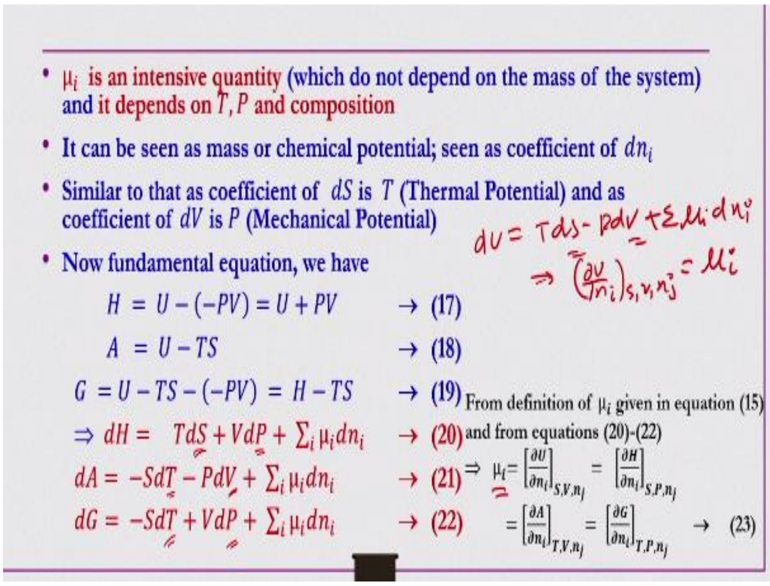

The μ is an intensive quantity, which do not depend on the mass of the system, intensive quantity that means intensive property is what? It is a property, which does not depend on the size of the system or the mass of the system, right? And it depends only on the temperature, pressure, and composition. It can be seen as a mass or chemical potential, seen as coefficient of dn_i similar to that as coefficient of dS in T and as coefficient of dV is P, okay? Analogous to the one.

So, now, fundamental equations we have already seen that you know H = U +PV, A = U - TS and G = U - TS + PV like that we have already seen. If you differentiate dH, dA, dG and then substitute $dU = TdS - PdV + \sum_i(\mu i\, dni)$ and then simplify, then we have this relations.

$$dH = TdS + VdP + \sum_i(\mu i\, dni)$$

Similarly,

$$dA = - SdT - PdV + \sum_i(\mu i\, dni)$$

$$dG = - SdT + VdP + \sum_i(\mu i\, dni)$$

Only difference is here S and P are independent variables here in this equation number 20, in equation number 21 T and V are independent variables.

And the equation number 22, T and P are independent variable, whereas in the previous equation $dU = TdS - PdV + \sum_i(\mu i\, dni)$, here you know S and V are independent variables. Now, let us say from here if you take you know constant S and V, then what we can have from here if constant S and V, then dS, dV = 0, so $\left[\frac{\partial U}{\partial ni}\right]_{S,\,V,\,nj} = \mu_i$, simple mathematical relation at constant S and V. Similarly from here also at constant S and P, you can have one equation for μ_i in terms of dH.

Similarly in terms of dA and dG also you can have one expression for μ_i. So, those relations are given here, okay? So, this is how you know chemical potential can be defined in terms of thermodynamic terminology.

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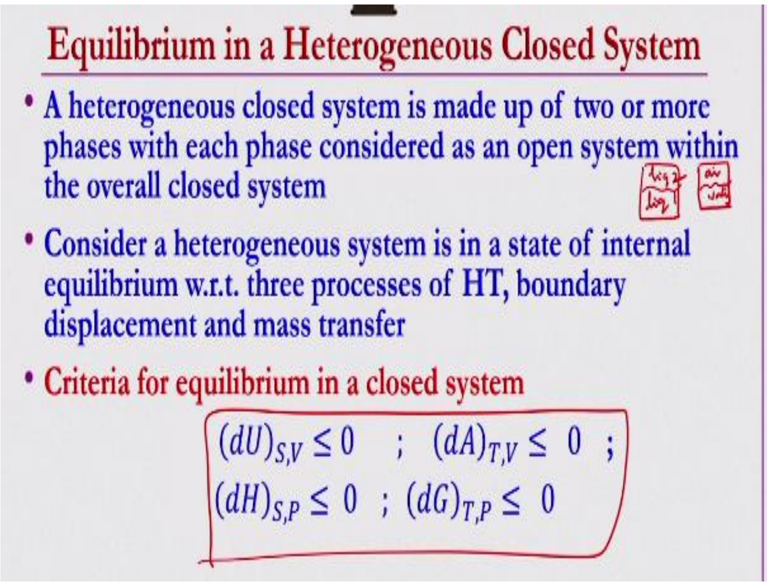

So, equilibrium in a heterogeneous closed system. What is heterogeneous closed system? Heterogeneous closed system is the one in which you may be having two are more homogeneous open system, right? Then if those homogeneous open systems are at equilibrium, then the entire heterogeneous closed system would also be at equilibrium, right. So, a heterogeneous closed system is made up of two or more phases with each phase considered as an open system within the overall closed system, okay?

Let us say you have a kind of closed system, in this closed system you have a you know water and then some air kind of thing it is closed. So, these are the 2 different phases okay. So, water is the liquid phase, homogeneous liquid phase, and then it is open system, some constituents may be going into air. Similarly, air is a homogeneous system, here homogeneous phase and then it is also open system because some constituents of air may be going into the water.

So, this entire system is a closed system and such system if you have, you can call them as a kind of heterogeneous system or similarly you can have a kind of liquid-liquid system to immiscible liquids are there, liquid 1 and liquid 2. There is a kind of transfer of species of particular component from liquid phase 1 to the liquid phase 2 and then vice-versa. So, those individual liquid phases are kind of homogeneous phases and they are open system because they are transferring their constituents to the other phases, but these two are constrained within a kind of a one single closed system.

So, that such kind of closed system which is having two or more homogeneous open system, then we can call that a heterogeneous closed system. For this heterogeneous closed system, consider a system is in a state of internal equilibrium with respect to 3 processes of heat transfer, boundary displacement, and mass transfer. So, criteria for equilibrium in a heterogeneous closed system we have already seen that this relations we have already derived. So, these relations will also hold for heterogeneous closed system as well. These are the criteria for equilibrium in closed system.

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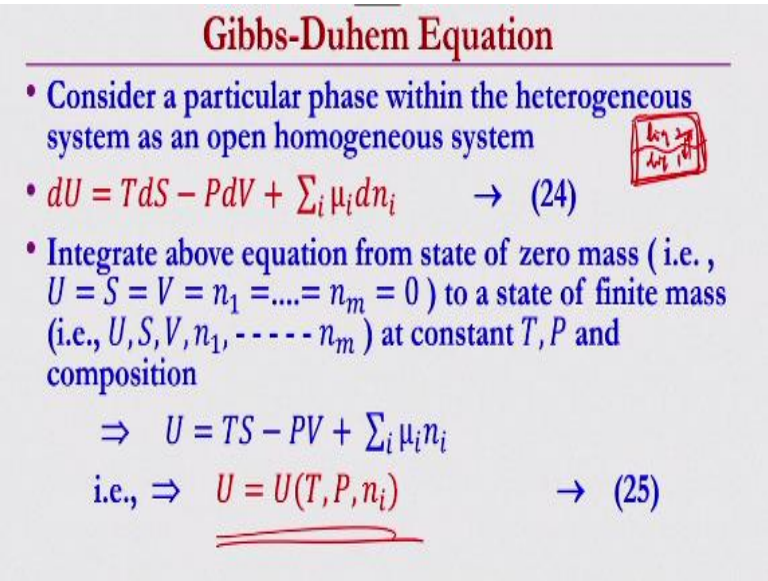

Now, we derive Gibbs-Duhem equation. This is one of the important equations which may be used later on to check the thermodynamic consistency of the data that has been produced experimentally those kinds of things, okay? So, consider a particular phase within the heterogeneous system as an open homogeneous system as I mentioned, water air in a closed container, liquid 1, liquid 2 which are immiscible into each other, they are taken in a kind of closed container.

So, that kind of heterogeneous system you take and then whatever the system phases are present within the heterogeneous system they are open homogeneous system, right? For such kind of systems as a just expand, let us say we have liquid 1 and liquid 2, two liquid phases, they are homogeneous open system, right? So, their properties are constant throughout within each phase, but they are transferring their constituents also from one into other until the phase equilibrium is established, right?

So, such system we are taking and then for those kind of system, we know that the equations are already dU = TdS - PdV +$\sum_i$(μi ni), right? Now, what we do, integrate above equation from a state of 0 mass, that is if the 0 mass is there, then U, S, V, n_1, etc all should be 0 to a state of finite mass, then that finite mass let us say U, S, V, n_1 and so on at constant T, P, and composition. Then what we get? We simply get U = TS – PV +$\sum_i$(μi ni). That means, U = U (T, P, n_i). So, this is already we know, we do not need to go through all these things because we already know it.

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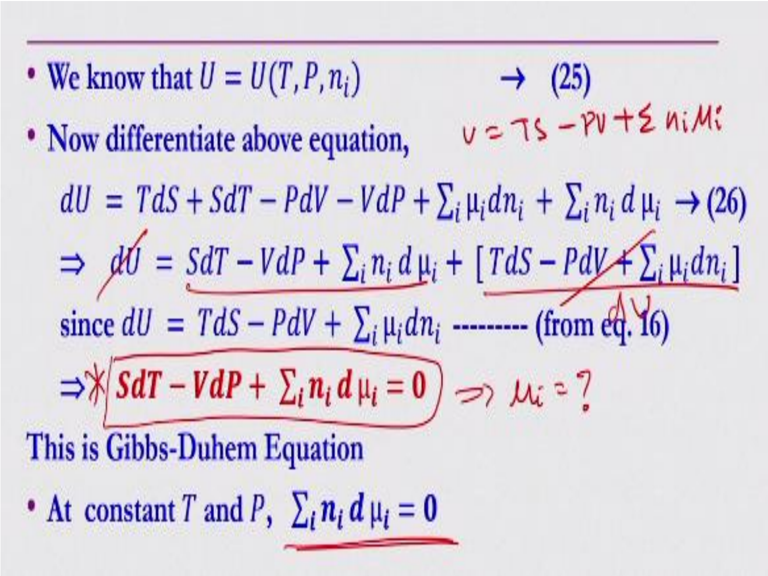

Since we know this one, U is equals to U function of T, P, n_i what we do? Now we differentiate this above equation, right? So, dU = TdS - SdT, whatever this above equation that equation number 25 it is there U = TS - PV +$\sum_i$(μi ni). So, this equation we differentiate. U = TS - PV +$\sum_i$(μi ni). This equation if you differentiate, then you have dU = TdS + SdT - PdV - VdP + $\sum_i$(μi dni) +$\sum_i$(ni dμi).

Now, rearrange this equation such a way that dU = SdT - VdP + $\sum_i$(ni dμi) as 3 terms and then remaining 3 terms TdS - PdV +$\sum_i$(μi dni) = dU. That means, this one and the left hand side dU is cancelled out, so that you have you know this equation SdT - VdP + $\sum_i$(ni dμi) = 0, this is known as Gibbs-Duhem equation and this is going to be very much important equation in order to know what is this chemical potential. So far, what we have done?

We have developed several relation for you know chemical potential, but none of the relations are you know having kind of a form that we can derive some kind of information about the μ_i because all those equations are having $\sum_i$(μi dni) those kind of terms, okay? So, that is not possible to get what is μ_i, especially you know in terms of measurable properties, right? Now, here from this equation simply, what you can say if the temperature and pressure is constant or there is no change in temperature or pressure of the system, then dT = 0, dP = 0.

Then what we can have, $\sum_i$(ni dμi) = 0, right? So, this equation probably can be used in order to get some kind of information about the chemical potential for a system, okay? So, that is the reason this equation is going to be important for next few slides.

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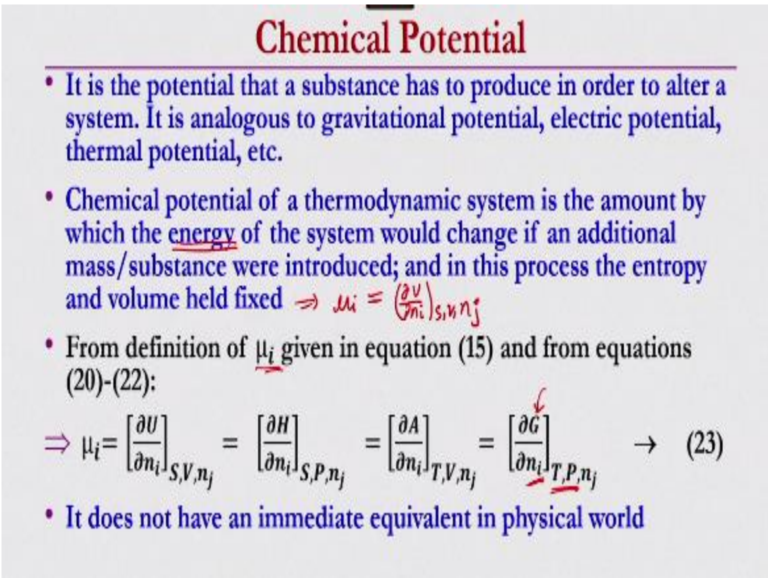

So, chemical potential, what we have seen? It is the potential that a substance has to produce in order to alter a system. It is analogous to gravitational potential, electrical potential, thermal potential, etc. In other words, chemical potential of a thermodynamic system is the amount by which the energy of the system would change if an additional mass or substance were introduced; and in this process the entropy and volume held fixed.

That is this statement is nothing but you know mathematical form of this statement is nothing but $\left[\frac{\partial U}{\partial ni}\right]_{S,\ V,\ nj}$. If you maintain constant entropy and volume, then if you introduce some additional mass into the system, then whatever the change in the energy of the system is there, that change in the energy of the system is known as the chemical potential, whatever the change dU is there by some change in n_i number of moles from n_i to dn_i is known as the chemical potential, okay?

So, there are other equations, other expressions for the μ_i as we have already seen like this. So, in other words, these chemical potential letters if you wanted to define like this, you know, the chemical potential of thermodynamics system is the amount by which Gibbs energy of the system would change if additional mass and substance were introduced in the system, while maintaining the temperature and pressure constant amongst the other moles of n_j as well. So, like this we can define the chemical potential, but from here you know you can have a kind of mathematical form, but it is not having direct physical sense.

This chemical potential is not having any physical sense as of now, it does not have any immediate equivalent in physical world. So, that is what we are going to do. In order to develop a relation between chemical potential and then physically measurable properties such as temperature, pressure and composition, etc., we may require to use Gibbs-Duhem equation that is the reason Gibbs-Duhem equation is important equation.

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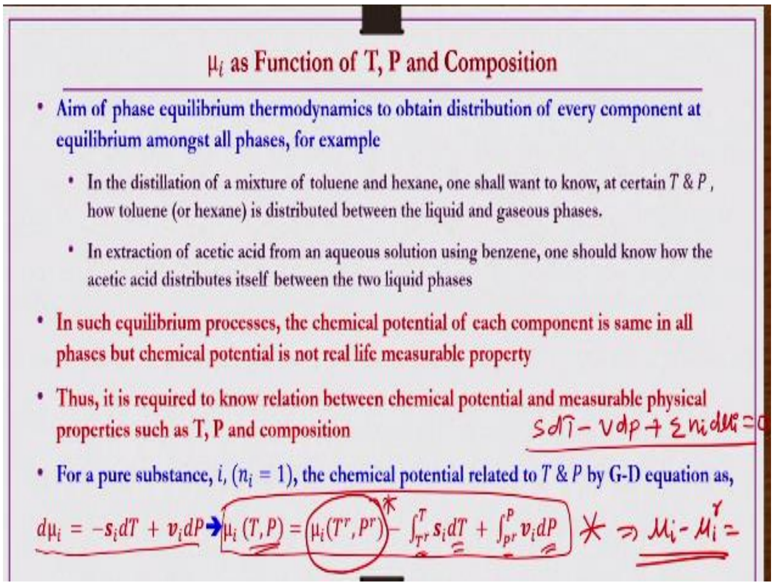

So, now chemical potential as function of temperature, pressure, and composition. So, the aim of any phase equilibrium problem is to find out or is to obtain the distribution of every component at equilibrium amongst all phases. How a particular component is being distributed amongst all the phases? How a particular species that is present in the system is distributed amongst different phases which are co-existing at phase and then there is a kind of phase equilibrium established? That one has to find out, that is the primary aim of this phase equilibrium thermodynamics, right?

That is, in other words, equilibrium composition one has to find out that is the primary aim. So, that is the reason you know one has to have a kind of relation, something like you know distillation of mixture of toluene and hexane, how these 2 components are being distributed between liquid and gases phases at certain temperature and pressure that one has to know. So, then can we use this phase equilibrium thermodynamics in order to know those things or not? Similarly, we have extraction of acetic acid from aqueous solution by using benzene.

Then one should know how the acetic acid distributes itself between the 2 liquid phases of aqueous phase as well as the benzene that one has to know, that can we have a kind of relation through this phase equilibrium thermodynamics, so that to get this information or not? That is the primary aim of this phase equilibrium thermodynamics or equilibrium thermodynamics, okay? So, that is what we are going to see in the rest of the course but now, we see few basics.

Now, in such equilibrium processes, we know that the chemical potential of each component is same in all phases. If there are P number of phases and then let us say there are i number of components, then $\mu_{i1} = \mu_{i2} = \mu_{i3}$ ….. μ_{iP}. That is, in all phases, 1, 2, 3 up to P phases, the chemical potential of i^{th} component should be same that we already know but this chemical potential is not a measurable property in real life that is the reason we need to establish relation between chemical potential and measurable physical properties.

That is the reason it is required to establish the relation between chemical potential and measurable physical properties such as temperature, pressure, and composition. But let us say if you have a pure substance, then chemical potential may be related to the temperature and pressure by using Gibbs-Duhem equation because we know that you know SdT - VdP $+\sum_i$(ni dμi) = 0, this is the Gibbs-Duhem equation we know, right? Now, let us say if you have a pure substance, only one component is there, then we can say that you know and this S, V, etc we can write for the molar properties, right?

Then, we can have this equation as you know, $S_i dT - V_i dP + d\mu_i = 0$ that means $d\mu_i = - S_i dT + V_i dP$. Then if you integrate this equation, then you can have μ_i at certain temperature and pressure at which we wanted to know the chemical potential, then there should be a reference state = $\mu_i (T_r, P_r)$. T_r, P_r are nothing but the temperature and pressure a certain reference standard state

$$\mu_i (T, P) = \mu_i(T_r, P_r) - \int_{Tr}^{T} Si \, dT + \int_{Pr}^{P} Vi \, dP$$

This temperature and pressures are varying from P_r to P and T_r to T. Some reference state to the temperature, pressure of required level, okay?

So, now here at least we have some relation that is the reason why I was mentioning Gibbs-Duhem equation is important. Now, whether it is useful or not, we have some relation, some equation for chemical potential in terms of measurable properties, temperature and pressure as a kind of independent variables, okay? We see further how we can make use of this equation. So, here S_i and V_i are nothing but molar entropy and volume respectively and then superscript r stands for some reference state, right?

But this equation again, it is though is having a kind of you know relation with measurable properties temperature and pressure as independent variables, but this is as useless as nothing has been done unless you know what is this μ_i (T_r, P_r), right? We cannot know what this is? If you know this μ_i (T_r, P_r), then only this equation is more useful. This is one of the major drawback of phase equilibrium thermodynamics. Because of that one, we cannot extensively use the thermodynamics to real life application problems.

However, what we can have? We can have change in these properties, let us say μ_i it is certain temperature pressure minus μ_i at certain reference temperature, reference pressure. This change we can have, then it is possible. So, you may not able to measure absolute chemical potential, but you can measure change in chemical potential with respect to some reference state by using this equation okay? So, that is the reason the reference state is going to be very much essential, you cannot arbitrarily choose any temperature and pressure conditions as a reference state.

Let us say if you are measuring chemical potential at low to moderate pressure, then it is always better to have a pressure tends to 0 as a kind of reference state because pressure tends to 0 is a kind of ideal gas state. So, like that, one has to be very judicious while selecting this referenced state. So, this reference state is also going to have a kind of very important factor in solution of this chemical potential. However, we need not to worry about this reference state, etc., because all those are anyway going to be cancelled out while doing the calculations.

So now, we understand that you know chemical potential is not a directly measurable property, but we can have a kind of relation for it with respect to relation with temperature, pressure and the composition of the system just through a Gibbs-Duhem equation we have seen for pure component, right? So, but it is still not a completely measurable property. So, if we have a kind of of some relations which is you know close to the measurable property or related to that one is going to be very much useful.

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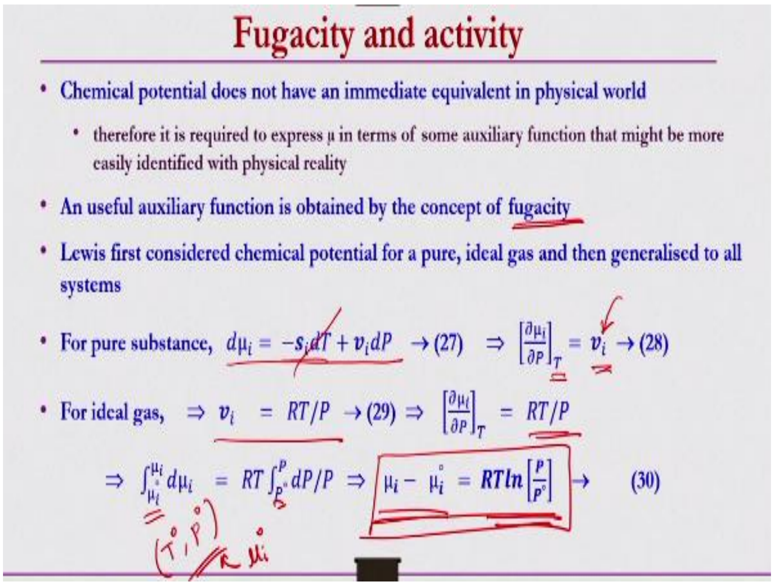

So, fugacity and activity. Chemical potential does not have an immediate equivalent in physical world. Therefore, it is required to express μ in terms of some auxiliary function that might be more easily identified with physical reality, what are those we have to see. So, a useful auxiliary function is obtained by the concept of fugacity. Lewis first considered chemical potential for a pure ideal gas, then generalize to all systems, right? This is the basic.

So, for pure systems, just now we have seen this equation from Gibbs-Duhem equation for pure substance or pure component, we know $d\mu_i = - S_i dT + V_i dP$. Now, at constant temperature, if the temperature is constant, so then this term is gone, then we can have from this equation $\left[\frac{\partial \mu i}{\partial P}\right]_T$ = V_i because right hand side we have $V_i\left(\frac{\partial P}{\partial P} = 1\right)$, so we have V_i. Now, for ideal gases, pure ideal gas what is V_i that we know, RT by P.

For ideal gas $V_i = \frac{RT}{P}$ if you substitute here, $\left[\frac{\partial \mu i}{\partial P}\right]_T = \frac{RT}{P}$. That means, if you integrate this equation from some reference state having some reference temperature T°, P° as a reference state, then corresponding chemical potential whatever is there, that we are calling it as μ°, okay? So, then

$$\int_{\mu i^\circ}^{\mu i} d\mu i = RT \int_{P^\circ}^{P} dP/P$$

$$\mu_i - \mu_i^\circ = RT\ln\left[\frac{P}{P^\circ}\right]$$

Now until a few slide before, we do not have any information about you know chemical potential relation to the measurable property temperature, pressure, etc. Now we have a relation at least, may not be absolute chemical potential, but change in chemical potential you can measure in terms of you know some measurable properties like you know pressure here.

But this is only for pure gas, but we have a kind of basis from here onwards we can develop on to develop a relation which is useful for generalized any gas, any liquid, any solid system whether pure or mixture.

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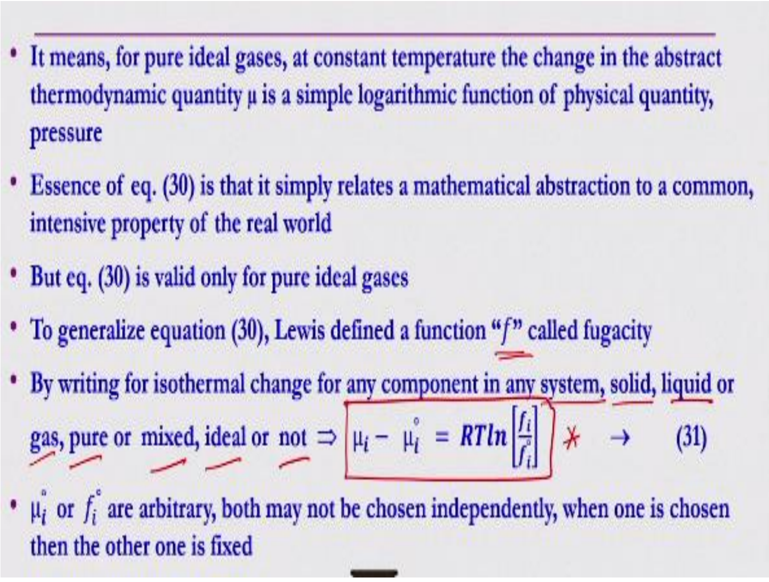

It means for pure ideal gases at constant temperature, the change in the abstract thermodynamic chemical potential is a simple logarithmic function of physical quantity, pressure.

That is $\Delta\mu = RT\ln\left[\frac{P}{P^\circ}\right]$that is what it means. The essence of this equation is that it simply relates the mathematical abstraction to a common intensive property of the real world that is pressure, but it is valid only for pure ideal gases but Lewis defined a function f fugacity, so that to generalize that equation whatever we have just develop $\Delta\mu = RT\ln\left[\frac{P}{P^\circ}\right]$.

So, that can be generalized using fugacity f that is auxiliary function. Now, by writing for isothermal chain for any component in any system whether solid, liquid, or gas, whether it is pure or mixed, ideal or not, then we can have a kind of generalized expression that

$\Delta\mu = RT\ln\left[\frac{fi}{fi^\circ}\right]$. f_i is the fugacity of the component at the required temperature and pressure, f_i° is a kind of fugacity at reference temperature, pressure T°, P° something like that and this is valid for liquid, solid, gas, pure, mixture, ideal, or nonideal whatever.

Only thing is corresponding f_i, $f_i°$ one has to use here depending on the phase, depending on the mixture or pure component like that, right? And this $\mu_i°$ and $f_i°$ are arbitrarily both may not be chosen independently. If you choose one, other will obviously be fixed.

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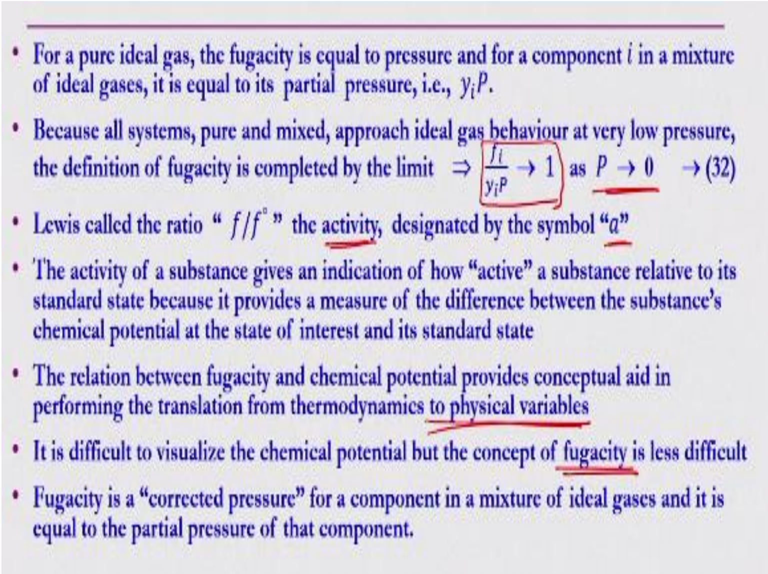

For the pure ideal gas, the fugacity is equal to pressure and for a component i in a mixture of ideal gases, it is equal to its partial pressure that is y_iP. That means, you know by using this limitation, one can complete the definition. Because all systems with a pure or mixed, approach ideal gas behavior at very low pressure, the definition of fugacity may be completed by this limiting condition f_i by y_iP tends to 1 when pressure tends to 0. Then further Lewis called $\left[\frac{f}{f°}\right]$, whatever that equation $\Delta\mu = RT\ln\left[\frac{f}{f°}\right]$ that f by f° Lewis referred it as activity and designated by the symbol a.

It signifies how active the substance to move from one phase to the other phase is? The activity of the substance gives an indication of how active a substance related to its standard state because it provides a measure of the difference between the substance's chemical potential at the state of interest and its standard state. The relation between fugacity and chemical potential provides conceptual aid in forming the translation from thermodynamics to physical variables, right?

It is difficult to visualize the chemical potential, but the concept of fugacity is less difficult because it is coming from $\left[\frac{P}{P°}\right]$we are replacing by $\left[\frac{f}{f°}\right]$ in order to generalize. That means we can call fugacity as something like corrected pressure or modified pressure or you know something like that. So, but appropriate word is here fugacity is a corrected pressure for a component in a mixture of ideal gases and it is equal to the partial pressure of that particular component.

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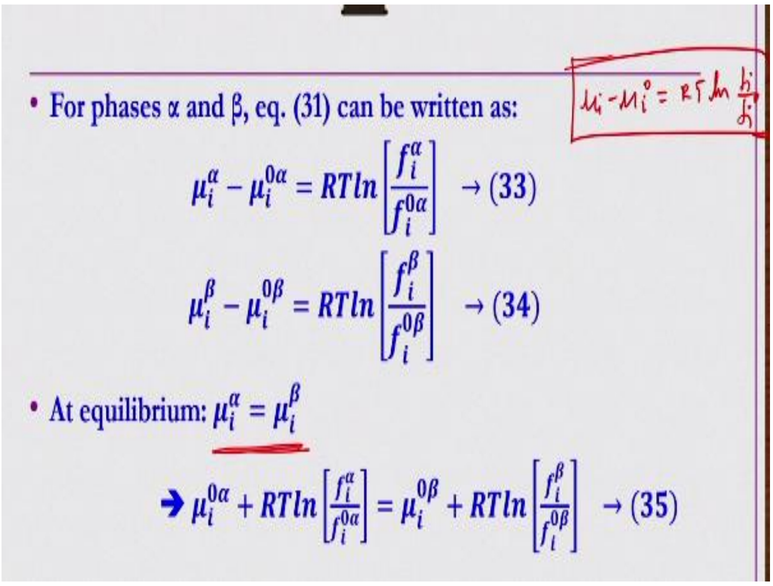

Now, let us say this equation whatever the μ_i - μ_i° = RTln$\left[\frac{fi}{fi^{\circ}}\right]^{\circ}$, this equation now this is commonly we have written. Now, we apply for two different phases and phases which are at equilibrium. Assume there are 2 phases, alpha and beta phases. They are at equilibrium and those equilibrium phases, we are going to write this relation. So, alpha phase, you can write this equation μ_i^{α} minus $\mu_i^{\circ\alpha}$ = RTln$\left[\frac{fi\alpha}{fi^{\circ}\alpha}\right]$, alpha superscript alpha stand for alpha phase.

Similarly, for beta phase, we can write like this. So, at equilibrium, we know that $\mu_i^{\alpha} = \mu_i^{\beta}$, right? Then, we have this relation, that is $\mu_i^{\circ\alpha}$ + RTln $\left[\frac{fi\alpha}{fi^{\circ}\alpha}\right]$ = $\mu_i^{\circ\beta}$ + RTln$\left[\frac{fi\beta}{fi^{\circ}\beta}\right]$. Why are we trying to do? We have an equilibrium at this relation, can we have such kind of relation in terms of fugacity or not? In order to check that one, we are doing this calculation now. Now in order to check that one, we need to have 2 different cases.

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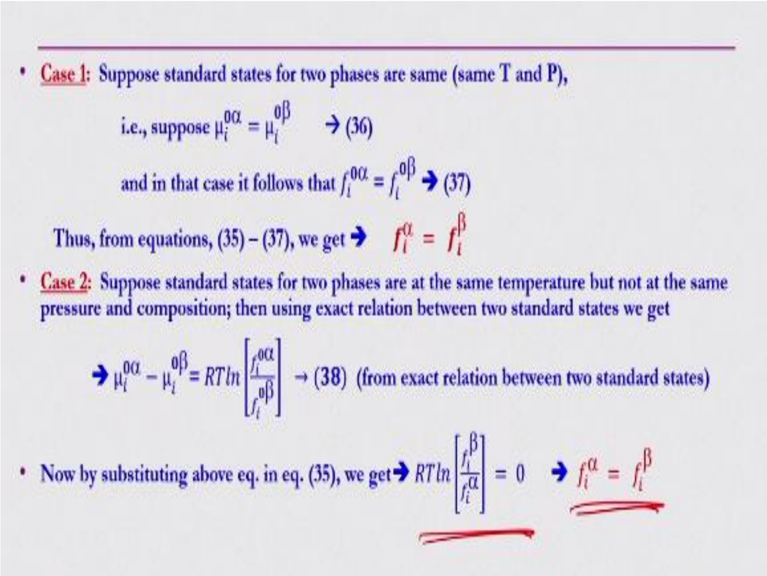

First case. Suppose standard states for 2 phases are same, that is same temperature and pressure are there for both alpha and beta phases as the reference states, then from the definition, $\mu_i^{o\alpha} = \mu_i^{o\beta}$ because the reference states are equal. Then in that case, we will be getting $f_i^{o\alpha} = fi^{o\beta}$. When you use this equation in the equation number 35, then you will get fi^{α} is equals to fi^{β}.

That means at equilibrium, not only chemical potentials of a component are equal amongst different phases, but also fugacity of that particular component are also equal amongst different phases which are at equilibrium, which are coexisting and which are at equilibrium. Another case, suppose the standard states for 2 phases are at the same temperature, but not at the same pressure and composition, then using exact relation between 2 standard states, we get this relation, right?

This is from the exact relation between 2 standards states, this is what we get. Now, this equation if you make use in the equation number 35, after simplification you will get RTln $\left[\frac{fi\beta}{fi\alpha}\right]$ = 0 that means $f_i^{\alpha} = f_i^{\beta}$. So, whether the reference states are same for both the phases or all the phases are not, it is true that not only the chemical potential's of that component are equal amongst all the phases, but also fugacity's of that particular component are also equal amongst all phases which are coexisting and which are at equilibrium.

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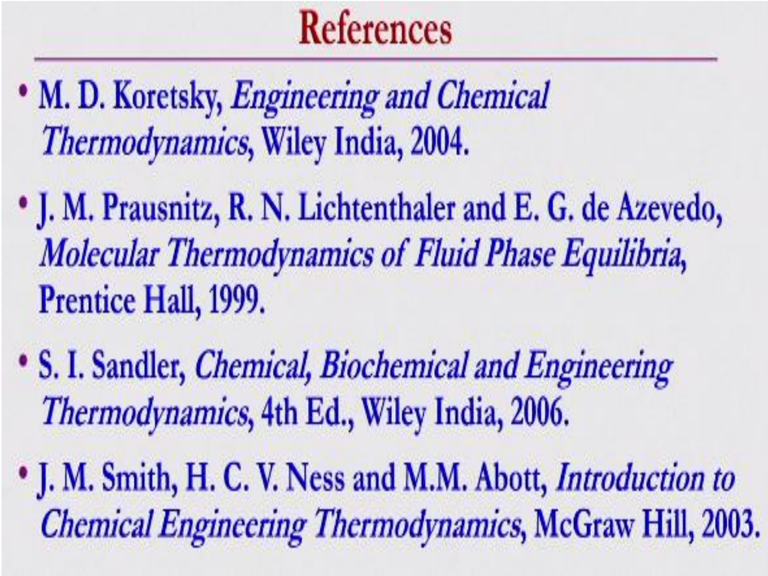

The references are given for this lecture, one can go through.

Thank you.