Material and Energy Balance Computations
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Lecture –36
Introduction to Energy Balance - VI

Welcome back now to the sixth lecture of our discussion on energy balance as a part of our material and energy balance computations course. So, we had a detailed discussion on phase diagram. So, what type of phase diagram we have learnt. we now know we have an idea about the generic nature of a single component phase diagram. we now know what is so special about the phase diagram of water.

And we have also talked about the phase diagram comprising of two liquids which are heated, and which transform into a vapour phase. So, all these things we have done.

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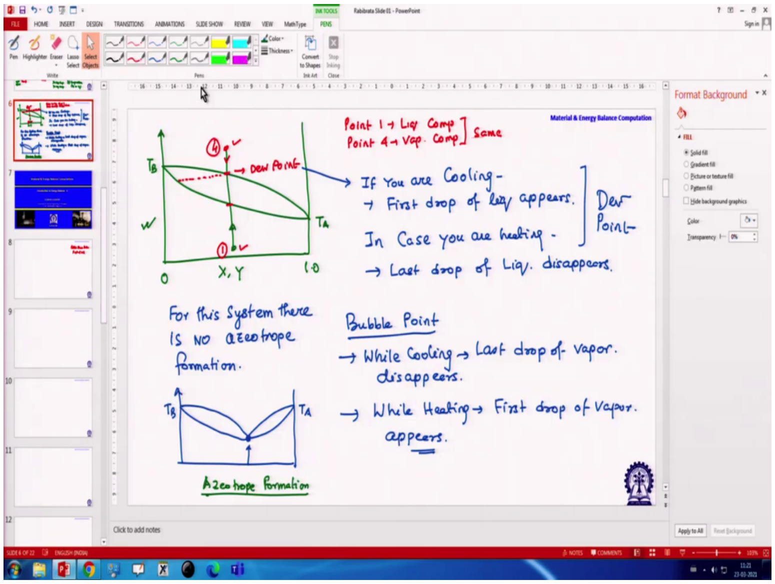

Point 1 → Liq Comp
Point 4 → Vap. Comp] Same

If You are Cooling -
→ First drop of Liq appears.
In Case you are heating -
→ Last drop of Liq. disappears.
] Dew Point

For this System there is no azeotrope formation.

Bubble Point
→ While Cooling → Last drop of vapor disappears.
→ While Heating → First drop of Vapor appears.

And let us also just have a quick look at one of these points. So, looking at the Gibbs phase rule, we have covered this entirely in the previous class just one thing I forgot to mention. So, what we understood that at any point in the bulk region of the phase diagram, the degree of freedom (F) is 3 but on any of these boundaries either on the T-X plot or on the T-Y plot F=2. This happens as P = 2 and C=2 on the phase boundary for a mixture of two liquids. And, one of the degrees of freedom has to be here the composition and the other one is pressure. So, it means that if you are in the two-phase region and you specify the composition then temperature is automatically fixed for T-X-Y plot. So, you cannot independently choose temperature and composition separately.

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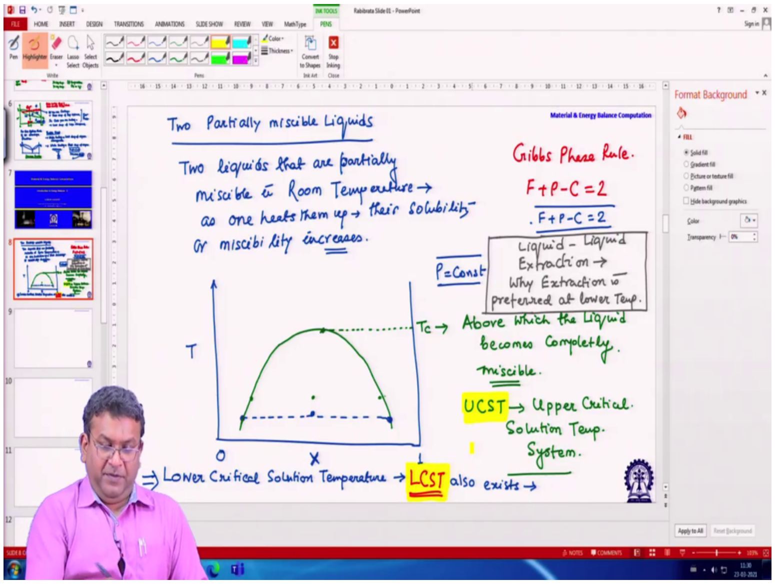

Two Partially miscible Liquids

Two liquids that are partially miscible ō Room Temperature →
as one heats them up → their Solubility or miscibility increases.

Gibbs Phase Rule.

$F+P-C=2$

$. F+P-C=2$

P=Const

Liquid - Liquid Extraction →
Why Extraction is preferred at lower Temp.

Tc → Above which the Liquid becomes Completely. miscible.

UCST → Upper Critical. Solution Temp. System.

⇒ Lower Critical Solution Temperature → LCST also exists →

Now, we move on further to another interesting type of phase diagram. And that is the phase diagram for two partially miscible liquids. This is something you will be needing later when you will study extraction. So, if you have two liquids which are immiscible or partially miscible in room temperature and as you heat them up, their solubility or miscibility increases.

This is also valid for many solid liquid systems. For example, if you want to mix sugar in water, it will mix with hot water much faster or much better than in cold water. So, you are making coffee for example, if you add the instant coffee powder in cold water probably you will not get good quality coffee, but you always can make good coffee with hot water. But here let us focus only on to the liquid-liquid system. So, it is a two-component system but a single phase. So, from F + P - C = 2 => F+1-2=2 => F=3; and we get anywhere in the bulk the ‘degrees of freedom’ (F) is 3. So, you can independently choose the pressure, temperature and the composition typically in this type of phase diagram.

So, this type of a phase diagram will look very interesting. So, here again you have the composition but here you only have liquid composition because you do not have any transition from the liquid to the vapour phase we are only talking about the liquid phase. So, what we have is at low temperature let us say the liquids are partially miscible. So, if you take any composition like this the liquid splits up into two phases one is a ‘A’ rich phase and one is a ‘B’ rich phase.

And if you do experiments at different temperature the liquid splits up like this and essentially what you get is a boundary between the single phase and the two phase region and typically what happens as you as you progressively heat up the miscibility increases that means that the span of the immiscible region reduces and there is a temperature a maximum temperature a critical temperature one can say above which the liquid becomes completely miscible.

So, such a system is called the UCST system or the Upper Critical Solution Temperature system. such a system is called the UCST system or the Upper Critical Solution Temperature System is an important thing we are not going to have more discussion on this. But much later when you study extraction liquid-liquid extraction in mass transfer or in many colleges in mass transfer 2 you will realize why extraction is preferred at lower temperature why extraction is preferred at lower temperature.

This you will realize because in extraction you actually would like to have maximum immiscibility that favors extraction or separation of the 2 components for extraction. So, in the previous lecture we talked about the azeotrope formation as a special case of a liquid-liquid system. So, probably many of you know that if there is azeotrope formation in your system you cannot apply distillation.

And extraction is one such mass transfer method which one can use to circumvent in case there are azeotrope formation and associated complications like this. So, just for the sake of completeness let me just point out that theoretically or there are some very few unique examples which I am not going to talk about something called Lower Critical Solution Temperature or LCST is also possible or also exists I would say.

So, as you can probably imagine in an LCST system what happens is it is very unique that at lower temperature the two liquids are miscible and above a critical temperature the liquids start to become immiscible. So, it is a very not a very common system this LCST but yes LCST systems also do exist. So, it is good to know anyway. So, LCST systems also do exist. So, it is good to know. And that sort of brings us to the end of our discussion on phase diagram we will not have any more discussion on phase diagram, and we will move on to other topics.

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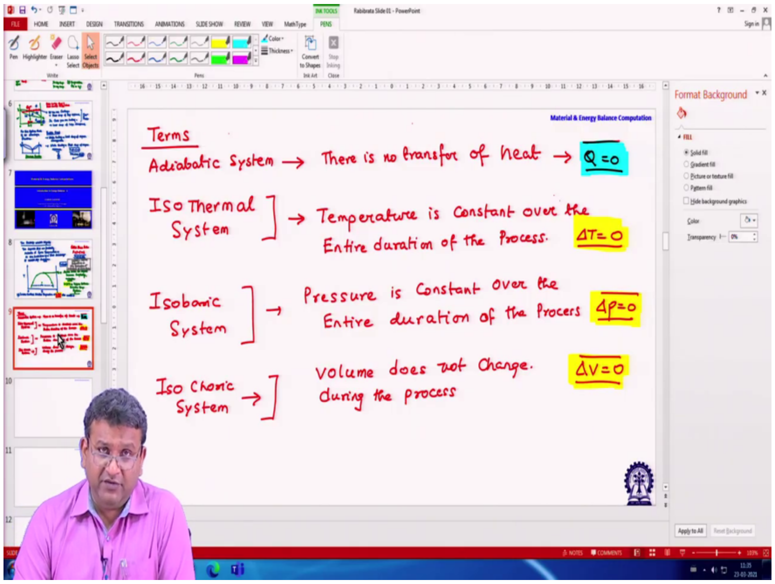

Material & Energy Balance Computation

Terms

Adiabatic System → There is no transfer of heat → $Q = 0$

Iso Thermal System → Temperature is Constant over the Entire duration of the Process. $\Delta T = 0$

Isobaric System → Pressure is Constant over the Entire duration of the Process $\Delta P = 0$

Iso Choric System → Volume does not Change. during the process $\Delta V = 0$

So, before we move on. So, we have learnt a lot of things already about energy balance the basic terminologies etcetera and so, we now know intensive property extensive property etcetera several things we now know the phase diagram we know what is a system we see what is a boundary what is a surrounding we know about open close and isolated systems. We know about intensive property and extensive property.

So, we know about state, equilibrium and the other important terminologies now. There are some standard thermodynamic terms which are important such as (a) adiabatic system: where the system does not exchange any heat with the surrounding during a process. It is a perfectly insulated system and there is no transfer of heat or Q = 0; (b) Isothermal system: where essentially temperature is constant over the entire duration of the process or ΔT = 0; (c) Isobaric system: where pressure is constant over the entire duration of the process or ΔP = 0 and (d) Isochoric system: where the volume is invariant. The volume does not change during the process or ΔV = 0.

So, I guess all of us understand about these processes. A quick note over here that I would like to point out. Here we are writing ΔP =0 or ΔV =0 but we are writing Q = 0 and not ΔQ = 0. We are coming to address this issue in a minute. So, agreeing to these terms that different type of systems you can have which are adiabatic, isothermal, isobaric and isochoric system.

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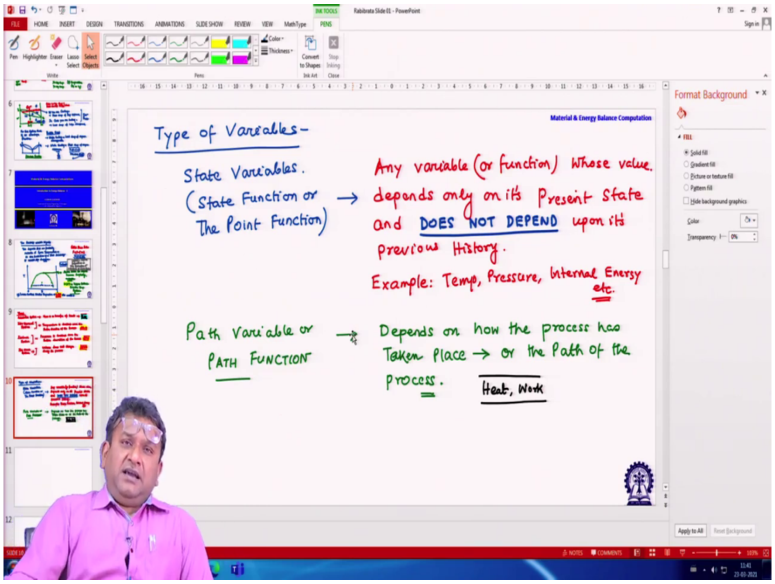

Type of Variables–

State Variables. (State Function or The Point Function) → Any variable (or function) Whose value depends only on it's Present State and DOES NOT DEPEND upon it's previous History.

Example: Temp, Pressure, Internal Energy etc.

Path Variable or PATH FUNCTION → Depends on how the process has Taken Place → or the Path of the process.

Heat, Work

It is also important to understand the difference between the types of variables or what are the type of variables you may have? And the type of variables you have are the type of function the state variables these are also called the state function or the point function. So, any variable this is very, very important. So, any variable or function whose value depends only on its present state and this is important does not depend does not depend upon its previous history.

So, example is I will give a very lucid example which will make this concept very, very clear example is temperature, pressure, internal energy etcetera. there are many other examples. but I am focusing on this. very simple example. suppose we have two systems both of which are now at 100°C. So, for both the temperature is 100°C but let us say one system was initially at 50°C and it has been heated up to 100°C and the other system was at 200°C and has been cooled down to 100°C.

You should understand that the present temperature 100°C or the present internal energy of the system if the volumes are same and the material is same does not depend or does not take into account anyway whether this 100°C has been attained by heating or by cooling this is what is meant by state variable. I hope this concept is clear to all of you. So, now the system is at 100 degree centigrade.

So, it depends only on the present state it does not depend on its previous history suppose you are driving a car at 50 km/hr. So, the state variable velocity is a state variable the present state is that the car is moving at 50 kilometers per hour. And it does not take into account the present state does not take into account whether the car has been accelerated from 20 km/hr or decelerated from 100 km/hr.

So, is it clear to all of you? same is the condition with internal energy or pressure. So, therefore these are state variables. The other thing that is very, very important is the path variable or the path function this path variable or the path function. So, this depends on how the process on let us now i do not write definitions anywhere because I am not following or reading out or have prepared any notes from books.

So, this depends on how the process has taken place. So, or the path of the process we will soon understand what exactly this means we will take up with the help of a problem that we will show that where something for example work done depends on the different path you are taking it can become different even if the initial and the final states are same. So, examples of path variable are heat and work heat transfer and work.

So, you can actually correlate this to why we did not have delta Q. I will probably talk about it little later. You can see here that heat is actually a path variable. Unlike others like pressure temperature or volume which are all state variables. So, there is something additional to that why you can you cannot write or in other words heat and work are essentially different forms of energy that are manifested.

So, I mean I think I will not discuss it now because let me describe what is a process and then it will be easier for all of us to understand what exactly these path variables are or why hit and work are path variables. So, with that we further move on now to a very important concept the concept of process and cycle.

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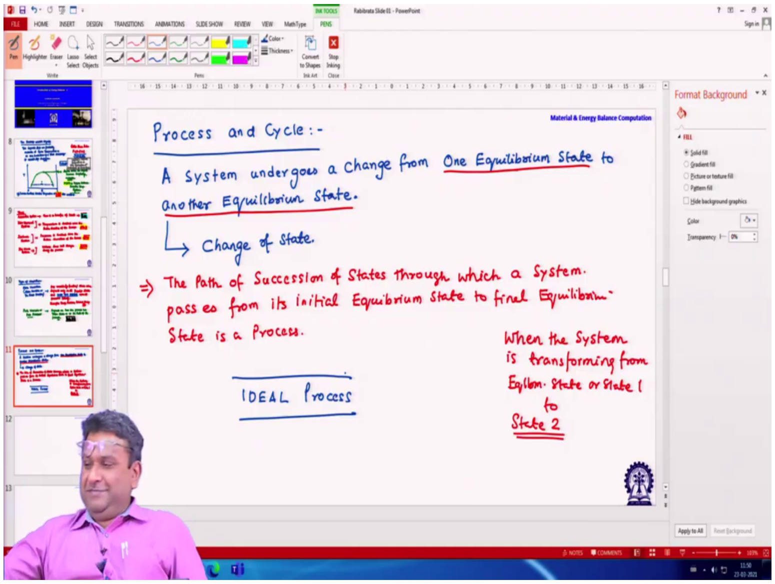

Process and Cycle :-

A System undergoes a change from One Equilibrium State to another Equilibrium State.

↳ Change of State.

⇒ The Path of Succession of States through which a System passes from its initial Equibrium State to final Equilibrium State is a Process.

IDEAL Process

When the System is transforming from Eqlbm. State or State 1 to State 2

So, process is essentially when a system transforms from one equilibrium state to another equilibrium state that is a process. So, in very simple state. So, there is a system let us write in simple terms. System undergoes a change from one equilibrium state to another. So, this is associated with what this is associated with change of state. a process may be associated with phase change a process may be associated with chemical reaction whatever. but a process is always associated with change of state.

So, for example if you heat up water from 30 degree centigrade to 50°C or if you had initial water at 30°C which was at equilibrium that was the first equilibrium state. Now you heat up point to be noted now you heat up to 50°C there is no change in phase there is no chemical reaction there is no vaporization no condensation but the states have changed why the states have changed because the value of one state variable that is the temperature has changed from 30°C to 50°C.

So, is this clear this is what is a process. Now the second important thing to understand is that a system undergoes a change from one equilibrium state to another equilibrium state. Now the system was at equilibrium. So, why on earth the system will undergo a change. So, you need to understand that in order for a process to occur some energy must be supplied from wherever.

So, either some energy is supplied from outside to the system or some energy is extracted out from the system. So, without an energy penalty nothing happens for a without a reason. So, change of state or a process happens because of change in the total energy of the system. this is something you must understand. there must be a causative reason. So, as we said that water is heated from 30 degree centigrade to 50 degree centigrade.

So, heating means that you are actually giving energy to the system and all of you know that if you give this much amount of energy its $mC_p\Delta T$. So, you can calculate the change in state. So, is it clear? a process occurs because the sum the total energy of the system. So, either some energy has been given or some energy has been withdrawn from the system and a process is associated with the transition of a system from one equilibrium state to another equilibrium state.

So, is this concept clear? I hope this concept are clear to all. ah. So, one can also write it very nicely, the path of succession of states through which a system passes from its initial equilibrium state to final equilibrium state is a process which is fine we all understand this is all written in very sophisticated language but we understand what is a process. Now my question is when the system is transforming from equilibrium state or state 1 to state 2 do you know the intermediate stages, or can you know the intermediate stages. think about it.

So, I am telling that the system is transforming from one equilibrium state to the other equilibrium state and is it possible to define the intermediate stages. The answer to this is for most processes it is not possible to define the intermediate states because how can you define state variable or how can you define state, or you can define. So, how do you define a state? you now in order to define a state we now all know about the degrees of freedom.

So, this many number of independent state variables have to be defined but please do understand that you can define the num the state variables only when the system is at equilibrium. So, if you are let us say rapidly changing the temperature or pressure of a system from let us say state one let us say P_1 to P_2 or T_1 to T_2 at the intermediate stages the system is not at equilibrium. Why it is not at equilibrium because it is receiving heat and its temperature is rising.

So, at any instance of time it is not in a state of balance which is the basic criteria of equilibrium since the system does not is not at equilibrium therefore theoretically it is not possible to define the intermediate condition of a system which is undergoing a process because process is defined. So, two entities of the process can be defined at the initial equilibrium state and the final equilibrium state.

But the intermediate stages straight away for any process you cannot define because of the simple fact that in order to define the intermediate stages the system must be at equilibrium during all these intermediate stages and which for regular system regular process is not the case and theoretically. So, you can say that see I am heating the temperature heating water and i have immersed a thermometer and see you are telling all this but I am recording the thermometer that you can get some recording but you can never say that.

So, even if you know the temperature what exactly the pressure is there are many other things which you cannot define. We will come it with a more classical example of the expansion of a piston in the next class. So, what you need to understand that you know the intermediate stages only for a process which never deviates from equilibrium and that is what is the condition or condition of an ideal process that I will take up in the next class.

And this concept is very, very important because this concept will give you an understanding about what is the difference between a real process and an ideal process and we will also see that when you talk about reversible process reversible process are only possible for ideal processes or quasi equilibrium process there is a reason for that which I think I will take up in the next class. So, please go through whatever we have discussed.

So, far and please feel free to write to me if you are enjoying the course if you are understanding or if you want me to revise something or add something through this live sessions and I will be very happy to address your concerns, thank you very much for the time being.