Material and Energy Balance Computations
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Lecture –35
Introduction to Energy Balance - V

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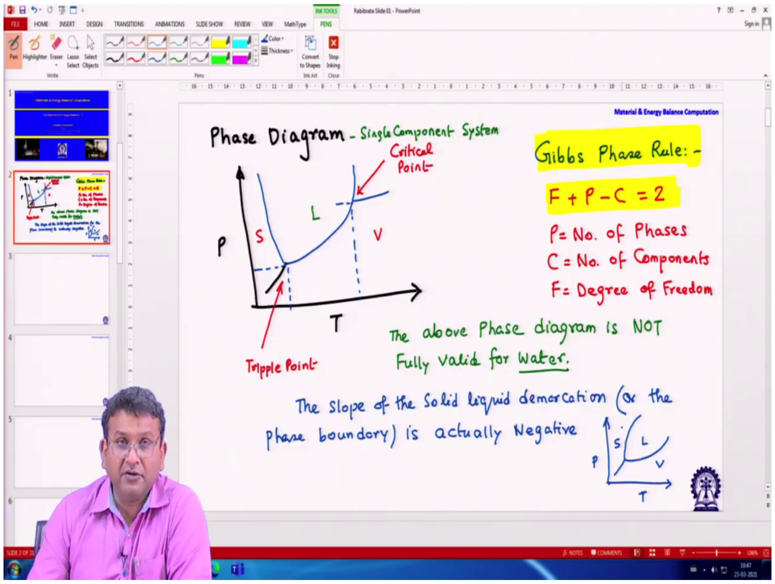

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Phase Diagram - Single Component System

Gibbs Phase Rule: -

$F + P - C = 2$

P = No. of Phases

C = No. of Components

F = Degree of Freedom

The above Phase diagram is NOT Fully valid for Water.

The Slope of the Solid liquid demercation (or the phase boundory) is actually Negative

Welcome back to the 5th lecture of the energy balance module of our course on introduction to materials and energy balance computation. So, in the previous lectures we did talk about the so-called phase rule or the Gibbs phase rule and I guess all of you now understand pretty well what the phase rule stands for. More importantly, one critical concept is the degrees of freedom and based on that we have developed the typical phase diagram of a single component system. So, what is shown in the slide is not a typical phase diagram.

A typical phase diagram is not exactly valid for water and it is interesting. What are interesting aspects of water? We know that there is hydrogen bond in liquid water. But the most interesting aspect is that ice, its solid form actually is lighter than the liquid. That is the reason we all know that ice floats on water. All of you can recapitulate your memories about the titanic disaster.

So, what exactly is the change in the phase diagram of water? The slope of the solid-liquid line demarcation or the phase boundary is actually negative; this is in clear contrast to any regular phase diagram where we have seen that the solid-liquid phase diagram has a positive slope. Generally, a given temperature if you increase the pressure the molecules are actually coming closer to each other and their binding should get even tighter. So, one can say that their density increases. But here in case of water what happens is exactly the opposite.

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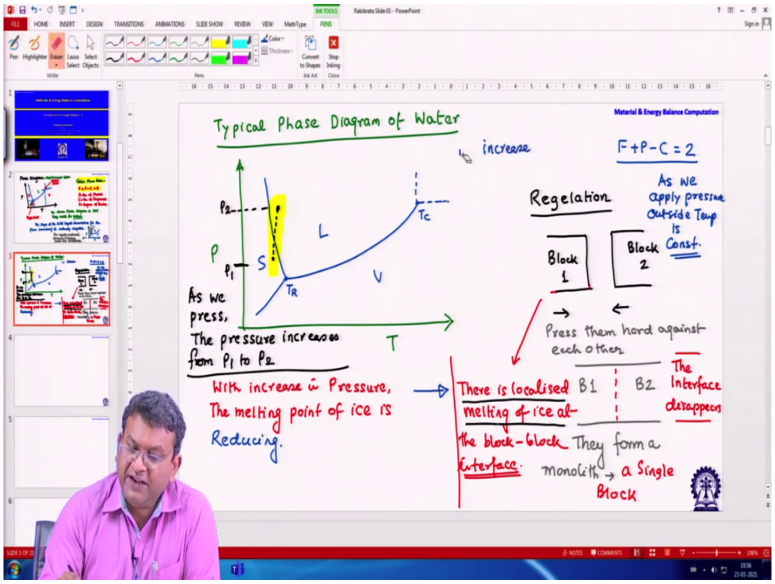

Typical Phase Diagram of Water

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increase

$F+P-C=2$

As we press, The pressure increases from P_1 to P_2

With increase in Pressure, The melting point of ice is Reducing.

Regelation

As we apply pressure Outside Temp is Const.

Press them hard against each other

There is localised melting of ice at the block-block interface.

The Interface disappears

They form a monolith → a Single Block

To explain this, we can take an example that is ‘Regelation’. So, what is this? This is if you take two blocks of ice and you press them hard against each other; they simply form a monolith. What does monolith mean? Monolith means it forms a single block. Or, they simply join up. Or, in other words the interface between them disappears. So, what exactly is happening. in order to explain what exactly is happening.

Let me just give you an example that if you bring two drops of liquid and make them touch each other then the interface disappears but if you bring two solid blocks and bring them. let us say identical solid blocks and bring them or press them against each other they remain two distinct entities. this we all know. However, again I repeat that if you bring two drops of liquid together there is no interface between them.

So, what actually happens here, as you press the two blocks against each other there is localized melting of ice at the block-block interface and you actually have a layer of water. And now since the both the ice blocks are now covered with thin layers of water there is no interface between this water layer and now when you again withdraw the pressure there is this ice again solidify.. this liquid again solidifies back to ice. This is what is happening.

So, what exactly is happening. The phenomena that is happening is with increasing pressure the melting point of ice is reducing. that is why and only under this condition this is possible that there is localized melting as you apply pressure. So, as you apply pressure at a constant temperature, the melting point of ice is reducing while the atmospheric temperature remains constant. Now if you look into the regular phase diagram, you will see that as you apply pressure, at a given temperature as you apply pressure the boiling temperature or the melting temperature reduces. Because you can see as pressure increases you can see from here as pressure increases melting temperature increases.

So, for regular material with increase in pressure, melting point melting temperature increases. However, the phenomena of Regelation clearly explain that it is possible only when with increase in pressure the melting temperature reduces. And, that is only possible if you have a negative slope. So, it the situation becomes like this. So, here is the starting point let us say, and now you apply pressure. So, with application of pressure, suppose you have increased the pressure of the system from P_1 to P_2 by pressing the blocks against each other.

So, as we press, the pressure increases from P_1 to P_2 and now since the solid-liquid demarcation curve has a negative slope therefore it crosses over to the liquid regime and this is only possible for water. So, now at P_2 the interface between the two blocks is actually a liquid. So, whatever we have mentioned there is localized melting you can clearly see the signature of localized melting in the form of this curve.

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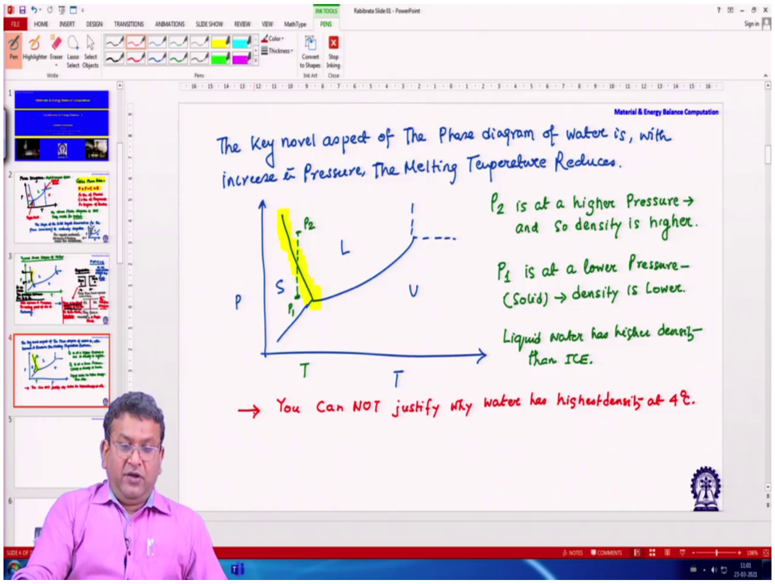

The Key novel aspect of The Phase diagram of water is, with increase in Pressure, The Melting Temperature Reduces.

P_2 is at a higher Pressure → and So density is higher.

P_1 is at a lower Pressure – (Solid) → density is Lower.

Liquid water has higher density than ICE.

→ You Can NOT justify why water has highest density at 4°C.

The key difference in case of water phase diagram is with increase in pressure the melting temperature reduces though the other part of the phase diagram remains same. Of course, the transition points etcetera varies from material to material. So, this is the most interesting aspect of a negative or the of a water phase diagram where you have essentially a negative slope of the solid liquid curve. this also explains that with increase in with or why one can use this phase diagram also to justify.

So, many of you many of many people would say that yeah this is justified because water or ice floats on water but how? the answer to that is the logic is that as we increase pressure what happens is the molecules come closer to each other. So, as the molecules now comes closer to each other the density automatically increases because you are packing the molecules if you look from a material standpoint you are packing the molecules more densely.

So, the density increases and now here you can see with the type of transition we talked about at a particular temperature if you increase the pressure from P_1 to P_2 you can clearly see that P_2 is at a higher-pressure and. So, density is higher on the other hand P_1 is at a lower pressure. So, density and solid and density is lower. So, with this type of a transition or this type of a line if you draw you can clearly justify where why liquid has higher liquid water has higher density than ice.

So, I hope this is clear to all of you must also understand the limitations of whatever concepts you are discussing. And please do remember by looking at the generic shape of the phase diagram you cannot justify why water has maximum density at 4°C. This cannot be justified from the generic shape of the phase diagram.

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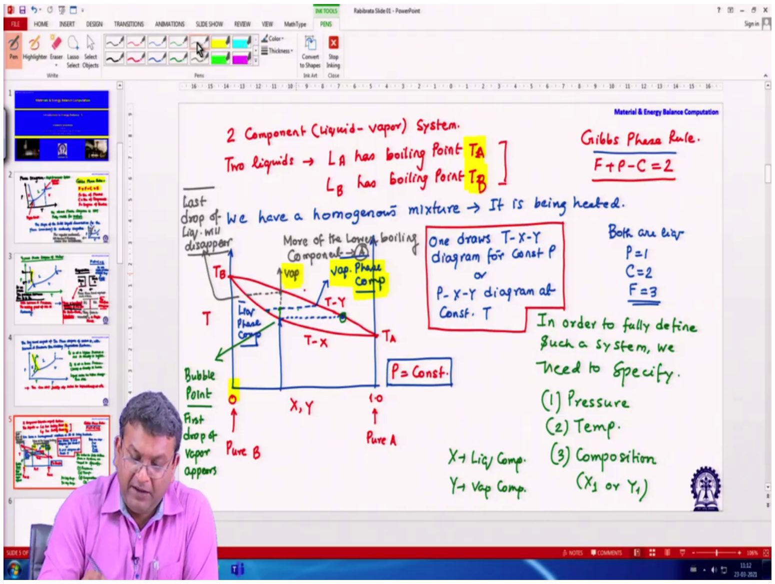

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2 Component (Liquid-vapor) System.

Two liquids → L_A has boiling Point T_A
L_B has boiling Point T_B

Gibbs Phase Rule.
$F+P-C=2$

We have a homogenous mixture → It is being heated.

One draws T-X-Y diagram for Const P or P-X-Y diagram at Const. T

Both are liq
$P=1$
$C=2$
$F=3$

In order to fully define such a system, we need to specify.
(1) Pressure
(2) Temp.
(3) Composition (X_1 or Y_1)

X → Liq Comp.
Y → Vap Comp.

And so, we have essentially learnt about the phase diagram of a single component system and with specific emphasis on water. and we will see later that not only the ice-water transition is interesting but another phase the vapor phase of water that is the steam is also very important for our consideration and we will be spending lot of time on steam. So, we will also understand what the difference between saturated steam and super-heated steam is.

But let me tell you one thing at this point steam is not an ideal gas. So, this is another mistake many people I have seen doing that they consider steam equal to ideal stream is an ideal gas and use PV= nRT; that is not the case. So, there can be other type of phase diagrams also which when if you are talking about metallurgy a subject like metallurgy people spend years on phase diagram but for our consideration, I will just look into two more types of phase diagram.

So, one of them is a two component both are liquid system. So, let us say we have two liquids. the first one boiling point T_1 and L_2 boiling point T_2. So, what happens and also let us write down the Gibbs phase rule. So, let us say we have a homogeneous mixture and it is being heated.

So, this is the Gibbs phase rule. So, if you have a homogeneous mixture in the liquid state. Both are liquids.

So, what you have? You have both when both of them are in the liquid state. So, phase is one component is two and therefore what is the degrees of freedom? Degrees of freedom turns out to be equal to 3. So, what are these? So, in order to fully define such a system, we need to specify 3 parameters such as pressure, temperature and composition. So, which one can write as X1. So, X1 is the liquid phase composition or Y1 that is for the vapor composition.

So, if the first phase has a composition of X1 in the liquid phase then of course the first liquid I would I am sorry not phase first liquid has a composition of X1 in the liquid phase then obviously the second liquid has a fraction (1 - X1). Now what can you plot now the problem is that since the degrees of freedom is three you cannot really simultaneously plot all the three variations together in a Cartesian coordinate system.

So, typically what is done, one typically draws either T-X-Y diagram for constant P or P-X-Y diagram at constant T. this is what one typically draws. So, let us focus T-X-Y diagram is the more popular one. So, let us focus on a typical phase diagram P is constant and what you have this axis is the composition axis and this is the temperature axis. So, we have already noted that the pure component boiling points are T1 and T2.

So, what does this one mean? this one means that there is X is zero. So, that means this is pure B or L A let us say an L B let us say. So, this is pure B and this is X equal to 1.0. So, this is pure A. So, here we are just marking T_A and T_B. So, here the boiling point is let us say T_A and here the boiling point let us say is T_B. So, what you get the typical nature of the phase diagram is something like this. So, this is the T-X-Y diagram, and this is the sorry, this is the T-X diagram I am explaining what it means, and this is the T- Y diagram.

So, what happens is we all know that if you have a pure component and at a constant pressure if you are gradually supplying heat then the liquid will get heated up to a temperature of T_A let us say we are talking about pure component A. Then even if you supply heat it is not the temperature is not going to rise the it is going to entirely get converted to the vapour phase and then only. So, essentially whatever heat you are supplying is not used for the sensible per sensible heat purpose it is used for the latent heat purpose.

And, essentially it converts entirely to the vapour phase. But here what happens is a liquid mixture if you take firstly the; what you need to know that the liquid a liquid mixture does not have a fixed boiling point unlike a pure liquid. So, what happens as you progressively heat it up, here is the first point here the first drop of bubble appears, here the first drop of bubble appears, or vapour appears, and this is known as the ‘bubble point’ this is extremely important to note this is known as the bubble point where first drop of vapour appears.

And the vapour phase has a completely different composition as compared to the liquid phase see amongst T_A and T_B, T_A is the lower boiling compound it has its boiling point is less. So, when you heat up a mixture it is more likely it is obvious that more amount of A will first or more easily go to the vapour phase. And therefore, the when the first drop of vapour appears it comprises more A because that is the low boiling compound now you progressively heat it up.

So, any points over here if you see you are now going to have a mixture of liquid and vapour any intermediate point within this dome you are going to have a mixture of liquid and vapour. So, this, this point gives the vapour phase composition and this point gives the liquid phase composition and these two compositions this vapour composition and this liquid composition at that particular pressure and temperature are at equilibrium and the two compositions are different.

So obviously, the vapor phase composition will have more amounts this is also important. So, once you follow this lecture carefully and try to understand everything will become clear. So, obviously the vapour phase will have more of the lower boiling component that is A and the liquid will have more of the higher boiling component. So, this is how it goes, till you keep on progressively heating. So, this is the point where the last drop of liquid will disappear.

So, here the last drop of liquid will disappear. here the last drop of liquid will disappear, and if you heat it further it is now a pure vapor. I hope this is clear to all of you. So, this is the typical scenario when you heat up a two-phase mixture. So, you do not have. So, what is important to note for a two-phase mixture for a two-component liquid mixture. So, here are the key summaries.

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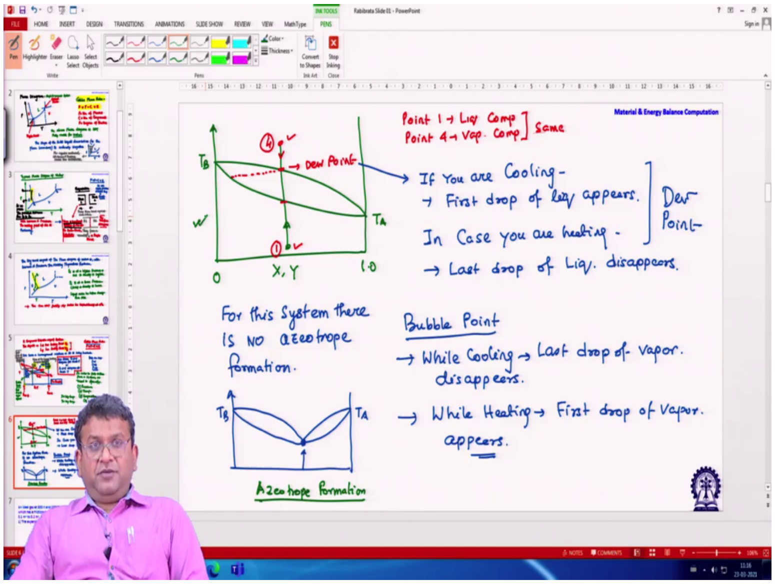

Point 1 → Liq Comp] Same
Point 4 → Vap. Comp]

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.

So, if you now heat up a liquid composition from the liquid phase let us say to this particular temperature which is at a vapor phase over here and here the compositions are same. So, let us say at point 1 and at point 4, point 1 liquid composition and point4 vapor composition are same however if you are looking into a point anywhere between the bubble point and this is called the dew point incidentally. So, how do you define dew point if you now do the opposite process.

So, if you start with a vapour at point four and gradually cool it down dew point is the point where the first drop of liquid appears. So, now you can understand if you are cooling it down here the first drop. So, one can define dew point as if you are cooling first drop of liquid appears; in case you are heating the last drop of liquid disappears. So, this is what is known as the 'dew point' and for 'bubble point' while cooling last drop of vapour disappears and while heating first drop vapor appears.

Of course, this is a system where there is no azeotrope formation. In case there is azeotrope formation. I will not go into the detail you will do it in some subsequent courses. there is a constant boiling composition is there. So, this is the azeotropic compositions it. So, this is the typical phase diagram in case there is azeotrope formation and therefore based on distillation you cannot separate any composition into the two pure constituent liquids which is possible to do here.

So, with that I will stop this lecture and we will touch a little bit of more about phase diagram in the next lecture and move on to some additional stuff, thank you very much.