Material and Energy Balance Computations
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Lecture –34
Introduction to Energy Balance - IV

Welcome back. we just started to discuss about the Gibb's phase rule. and we now understand what the constituent terms in the phase rule are, which is the degrees of freedom (F), the number of phases (P) and the number of components (C).

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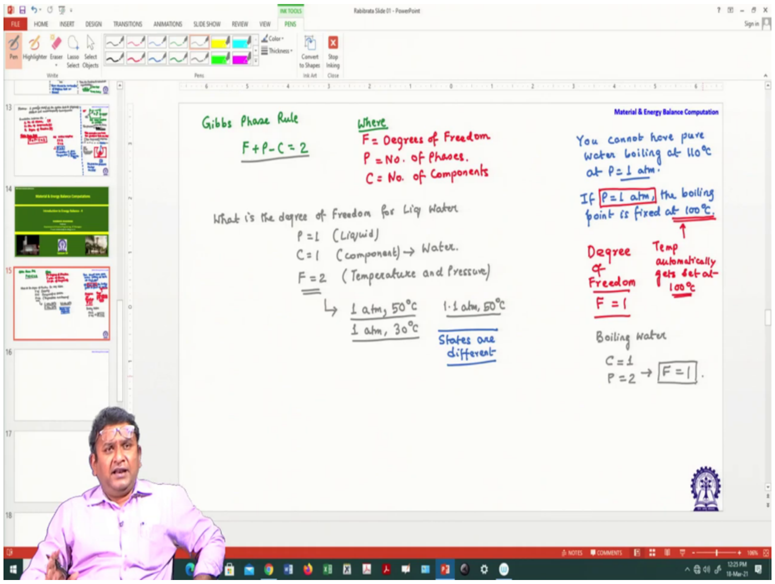

Material & Energy Balance Computation

Gibbs Phase Rule

$F + P - C = 2$

Where
F = Degrees of Freedom
P = No. of Phases.
C = No. of Components

What is the degree of Freedom for Liq Water
P = 1 (Liquid)
C = 1 (component) → Water.
F = 2 (Temperature and Pressure)
↳ 1 atm, 50°C
1 atm, 30°C
1.1 atm, 50°C
States are different

You cannot have pure water boiling at 110°C at P = 1 atm.

If P = 1 atm, the boiling point is fixed at 100°C.

Degree of Freedom F = 1

Temp automatically gets set at 100°C

Boiling water
C = 1
P = 2 → $\boxed{F = 1}$.

And we in the previous class we discussed in detail what exactly is meant by degrees of freedom. It is the number of independent state variables that is required to fully define a system. So, we know for example, if you want to define the condition of water let us say at 30°C. So, when we are talking about a single component system, C=1, and essentially number of phases (P) =1 also, because water is in the liquid state. So, we get F= 2. So, you need to independently define two parameters which are temperature and pressure.

Now, let us say if you would like to talk about the boiling point at 1 atm pressure. What happens at boiling point? Water boils and forms steam. So, we know that at 1 atm pressure, the boiling point is 100°C. So, it means that you can have liquid water at 1 atm pressure 50°C or at 1atm pressure 30°C. So, all these conditions will represent liquid water. But what is actually different amongst these waters. Their states are different. Why? because the associated values of the state variables. Some or all state variables are different. So, their states are different. So, from here you get a very clear idea what exactly is state. Now let us say, we are talking about water that is boiling at and that if the pressure is kept one atmosphere, we all know that water will boil only at 100°C. You cannot have pure water boiling at 110°C at P= 1atm. In other words, if pressure is one atmosphere, the boiling point is fixed at 100°C. So, how do you justify? So, that means that here once your assigned pressure or fixed pressure at 1atm, the temperature automatically gets set.

So, essentially how do you explain this in terms of 'degrees of freedom'? For this system, it turns out the degree of freedom F is actually 1, it is not 2. Why? How do you justify this from the phase rule? Because when you have the example of boiling water its water. So, water and steam both are H_2O. So, component (C) =1, but you have two phases, the liquid phase and the vapor phase. Therefore, P = 2 and if you substitute in phase rule, you get is F =1 only.

So, this is the utility of the Gibbs phase rule. We can actually do some thought experiments like this. We start with ice and then keeping the pressure constant, we can progressively heat it up. So, we all know that it will remain solid ice at till 0°C if the pressure is 1atm. Then you can supply more heat from outside. But there is going to be no rise in temperature because at 0°C, the ice is going to undergo phase change and therefore it is now accepting the latent heat instead of the sensible heat. So, it accepts the latent heat transforms into water and only when the entire amount of ice has got converted into water and you keep on applying more heat from outside the temperature will increase again. Eventually the temperature will reach 100°C with further heating and then we will again see is no change in temperature for some time, because now the water is getting converted into steam. So, this way you can generate data and collectively what you can come up with is what is known as the typical 'phase diagram'.

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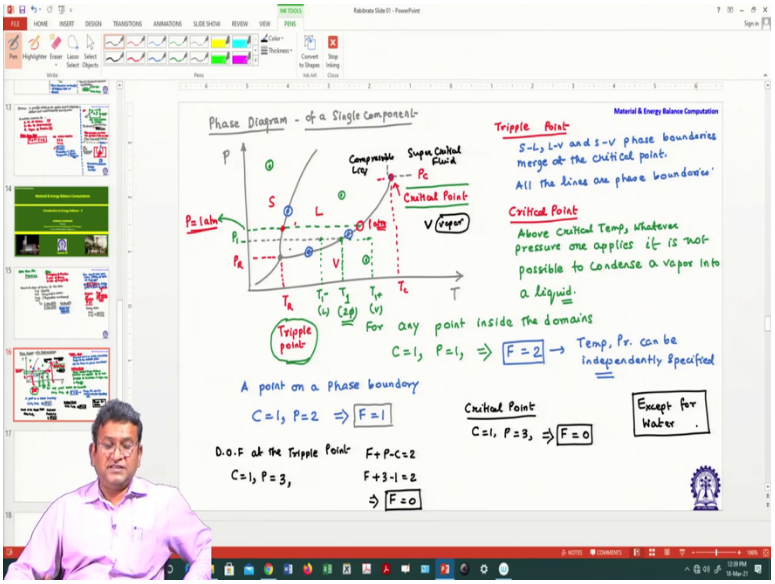

Phase Diagram - of a Single Component

Tripple Point

S-L, L-V and S-V phase boundaries merge at the critical point.

All the lines are phase boundaries.

Critical Point

Above Critical Temp, whatever pressure one applies it is not possible to condense a vapor into a liquid.

For any point inside the domains

$C=1,\ P=1,\ \Rightarrow \boxed{F=2} \rightarrow$ Temp, Pr. can be independently Specified

A point on a Phase boundary

$C=1,\ P=2\ \Rightarrow \boxed{F=1}$

Critical Point

$C=1,\ P=3,\ \Rightarrow \boxed{F=0}$

Except for Water.

D.O.F at the Tripple Point

$C=1,\ P=3,$

$F+P-C=2$

$F+3-1=2$

$\Rightarrow \boxed{F=0}$

So, I guess all of you have some idea about phase diagram now. So, let us have a quick look what phase diagram is. So, if it is a single component phase diagram; typically, what we have that for a single component. If it is in a single-phase region, we have already seen that we have degree of freedom, F= 2. So, generally the axes are temperature and pressure. So, you can independently specify the temperature and pressure.

So, here it is and let us draw a typical nature of a phase diagram. So, what are the critical points or the invariant points as you can say for a system. So, what you have is these two points: the first one is what is known as the ‘triple point’ where the solid liquid and vapor phases merge. So, in other words below the triple point if you heat up a solid it is going to directly transform to a vapour and there is going to be no liquid phase. Specifically, the three phase boundaries merge. So, SL, LV and SV phase boundaries merge at the triple point. So, we typically have a triple point and all these lines are essentially phase boundaries each of this zone is a pure vapor, pure liquid and pure solid as shown in the above slide.

Then you have essentially what is known as the ‘critical point’, generally marked as T_C and P_C. So, what is the utility of the Critical point (T_c,P_c)? One of the key concepts of critical point is above critical point liquefaction of a gas or a vapor is not possible. So, above critical point above critical temperature whatever pressure one applies it is not possible to condense a vapour into a liquid.

You may start thinking why it happens. I will tell you why exactly it happens in one of the subsequent classes. So, that is it. And now let us examine this phase diagram. So, if you take any point in deep within these domains as shown in the slide, what you have is essentially any point deep within the domains which is not on the phase boundary. Where we have one component, one phase and consequently what you get is degree of freedom, F=2. So, you have to specify temperature and pressure to independently describe the state. However, if you have a point on a phase boundary, what will happen? It's a single component system. So, C =1 and P= 2, because on a phase boundary you are essentially talking about a system which is undergoing a phase change. So, for example water is boiling. So, when you are talking about a system which is boiling you actually have liquid water as well as you have steam. Consequently, what you have is degree of freedom now reduces to one. what does it mean? It means in very simple terms is you already have a line.

So, if you just follow the line for a point on that particular line we know very well from our knowledge of Cartesian coordinate system if you fix that pressure for example you would like to have a phase change what it means if you would like to have a phase change at a particular pressure. So, how do you do go about it? We have to find out at that particular pressure where is that specific point on the phase boundary lies.

So, let us say we want to have the phase transition only at P 1 and that will happen only for temperature that will correspond to a temperature T 1. For pressure P 1 and any other temperature, let us say T 1 minus or let us say T 1 plus you will have a single-phase system. So, for example at T 1 minus you will have a pure liquid and let us say for T 1 plus you will have a vapour. So, I hope it is clear to all of you. Therefore, on any of the phase boundaries what you have is, F=1.

So, we have marked the critical point and the triple point on the graph or phase diagram but we have not marked the normal boiling point and normal melting point. So, what is normal boiling point? and what is normal melting point? It is something we identify for our own convenience. Normally, we are used to an world where pressure is one atmosphere. So, essentially what we do is normal melting point and normal boiling point are nothing but points on the phase boundary for P =1 atm. So, it is a very simple concept. So, each of these points are no way different than any point that lies on the phase boundary but here what you are doing by specifying that it is a normal boiling point or normal melting point or whatever you are just specifying that the pressure is equal to 1 atmosphere and nothing else. Of course, for any of these points these points also lie on your phase boundary therefore degree of freedom is actually 1. And what is the degree of freedom? that degree of freedom also is actually specified in this particular case and that is equal to 1 atmosphere. So, the moment you specify that your pressure is one atmosphere automatically let us say for water the boiling point the melting point automatically has to be 0°C.

So, pure water at 1 atm pressure, it is not possible for water to melt at -10 °C or 10°C. That is the whole idea about these phase boundaries. Now what about the degree of freedom on the critical point. So, at triple point, component (C)=1 but now you have all three phases here. So, P = 3. And if you now put it in your phase rule what you get, F + P - C = 2. So, F + P = 3 -1 =2 and this leads to F =0. So, for critical point, degree of freedom is zero. Therefore, this is an invariant point.

So, if you take a material, if you take a specific system its triple point is fixed. you cannot alter it. It depends on the material property. So, that means that the moment you specify a material your triple point is automatically fixed. So, that is why it is an invariant point. now what about critical point. So, the critical point is again a point where you have component is one, here many people make this mistake because what happens is you typically mark this phase to be the vapor phase, but what actually happens is we have compressible liquid here we have super critical fluid here and we have vapor here. So, here for critical point also the number of phases equal to 3 and correspondingly for the critical point also the degree of freedom is equal to 0. So, therefore for critical point is also an invariant point.

The phase diagram is a very generic phase diagram for a single component system except that for water. There is a subtle difference. So, can I use it for water? The answer to it is ‘no’. there is a small difference when you draw the phase diagram of water. So, let us try to find out what is so special about the phase diagram of water.

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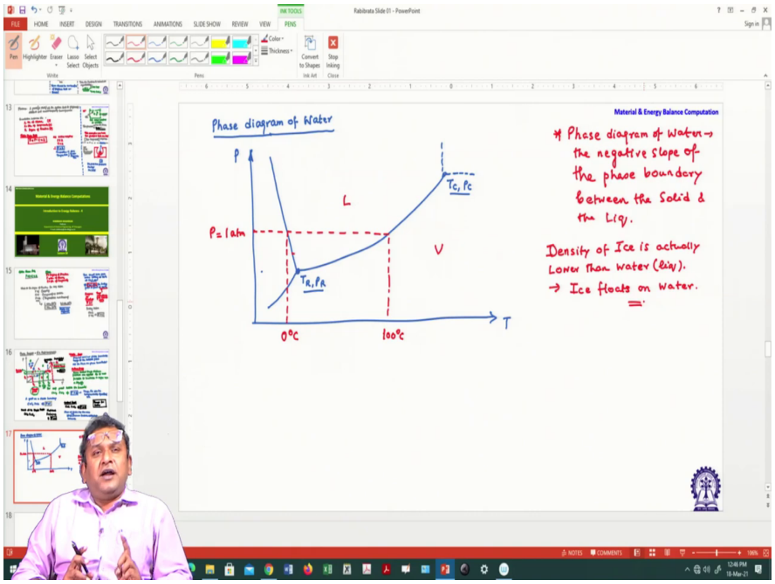

Phase diagram of Water

* Phase diagram of water → the negative slope of the phase boundery between the Solid & the Liq.

Density of Ice is actually Lower than water (Liq).

→ Ice floats on water.

In the phase diagram of water, this solid liquid line does not have a positive slope as shown in the above slide. So, what does this particular positive slope of this solid liquid line mean? It actually means that if you increase pressure, the melting temperature increases. This also has certain other consequences which I think we will be able to capture once we learn a little bit more. So, a slope of this nature for the liquid-vapor line also tells you that if you increase the pressure your boiling temperature increases, and this is something that also happens for water and that is exactly the principle why you would prefer to cook in a pressure cooker.

Now, it turns out that this particular slope of the solid-liquid phase boundary is not positive, it actually has a negative slope in the phase diagram of water. So, this is how the phase diagram of water looks like and instead of just remembering that we have read that the phase diagram of water has an opposite slope.

Please check out in the textbook, what is the value of the pressure and temperature for water at the triple point and at the critical point. I am not much interested in telling you the numbers. Many of you would say that that water has higher density than ice is a proof itself or ice has a lower density than water this is also very unique because of the fact that in most cases we know that the solids are heavier than liquid. But for water, we all know that the density of ice is actually lower than water, liquid and that is why ice floats on water. many would give this as an example. but it is an indirect example. So, you say that yeah ok density of ice is lower than density of water but how does it directly capture this particular negative slope. So, that actually remains unresolved. And so now here comes the example and we are running out of the time.

So, I will continue this discussion in the next class but here is the example I am giving which you can try out at your home. So, if you take two blocks of ice and press them against each other. So, you have a block one, you can just take out two blocks of ice cubes from your mother's refrigerator and just press them hard against each other. Do you know what happens? what will happen is if you release the pressure it will get converted to a single block. this is known as the phenomena of Regelation.

So, in the next class I will start from here how the phenomena of regelation clearly explains a negative slope between the solid and the liquid phase boundaries negative slope of the solid liquid phase boundary. in the meantime, I would strongly encourage all of you to try out doing this and you can post pictures or share pictures with your in the group when the course is running. So, just take two blocks of eyes press them hard against each other for some time, withdraw the pressure and you will see that it has joined up.

You can do regulation experiments in different ways also if I get time, I will discuss that. So, with that I come to an end of this fourth lecture of this series. And I will pick up the thread from here in the next class, thank you very much.