Chemical Engineering Thermodynamics
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Lecture-28
Phase Transitions

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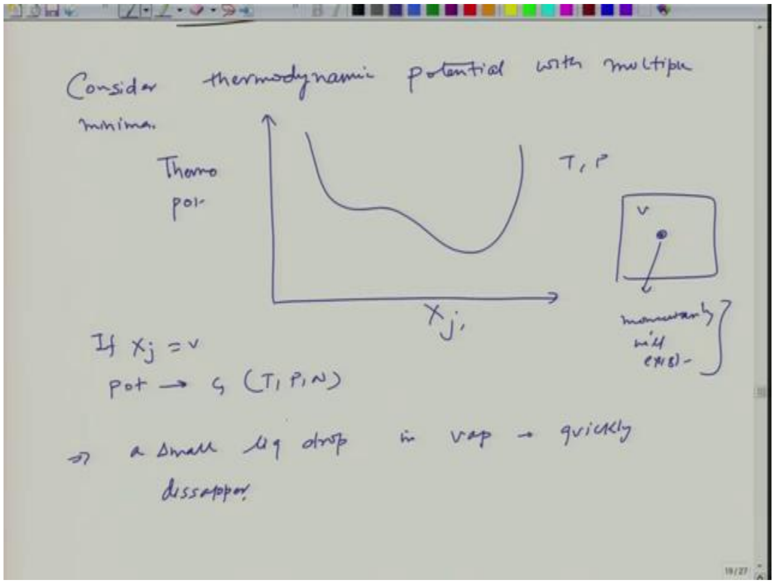

Consider thermodynamic potential with multiple minima.

If $x_j = v$

pot → G (T, P, N)

⇒ a small liq drop in vap → quickly dissapper

momentarily will exist

Welcome back. In today's lecture, I am going to talk about Phase Transition and particularly the order of phase transitions. So, consider a thermodynamic function where you have multiple minimas. So, this is one minima and this is of course another minima, if you have only two and this would be your global minima and this is another variable, so if we consider this to be a volume then essentially this could be written as G of temperature, this potential could be a simply temperature T, P, N okay.

So, in this case or if X is equal to V, we can and let us say potential is G then consider this case where a small liquid drop is present in a let us say a vapor, in vapor okay. So, let us say you have liquid drop, so this is a vapor because the volume is large. So if in this vapor phase if the liquid drop appears then it will quickly disappears because of the fact that the vapor is more stable at this condition which we can say at a given temperature and pressure (or) okay.

So, because of the fact that, in this condition the vapor is more stable hence a small presence of let us say so this is vapor and small present of drop here of liquid will momentarily stay, will exists, but it will disappear. Because of the that fact that the barrier to convert from vapor to liquid is considerably large, but you can change these thermodynamic conditions, the temperature and pressure and eventually at certain point you might see that there is a phase transition going form vapor to liquid. Let me just try and illustrate or elaborate more on this.

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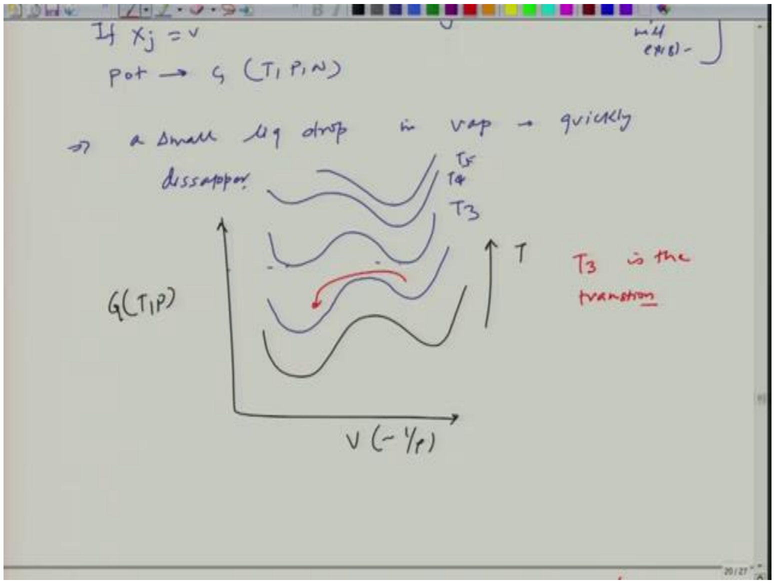

So, now let me draw specifically G as a function of temperature and pressure and this is V, a volume which is nothing but inverse of density and what we interested is that okay, let me change the temperature, so that means I fix the pressure and here you have multiple; so here of course at a very low temperature the liquid is stable, that is why it has lower free energy, it should be stable because of the fact that the free energy is minimum for the case of liquid.

Now, if you increase the temperature, I may get something like the still is fine. At certain point, I may get like this where, you have these equal free energies, for both the phases. Let us say it is T3 and subsequently; so, this may be T4, T5 okay, so from here the analysis you can clearly see that T3 is the transition.

So, if you are cooling temperature here then of course you can clearly see that vapor is more stable here, vapor is more stable and vapor co-exist with liquid and subsequently the vapor becomes unstable. If the fluctuations is large then it will move to, to the liquid phase. But at T3 the equal minima is there and that is transition point.

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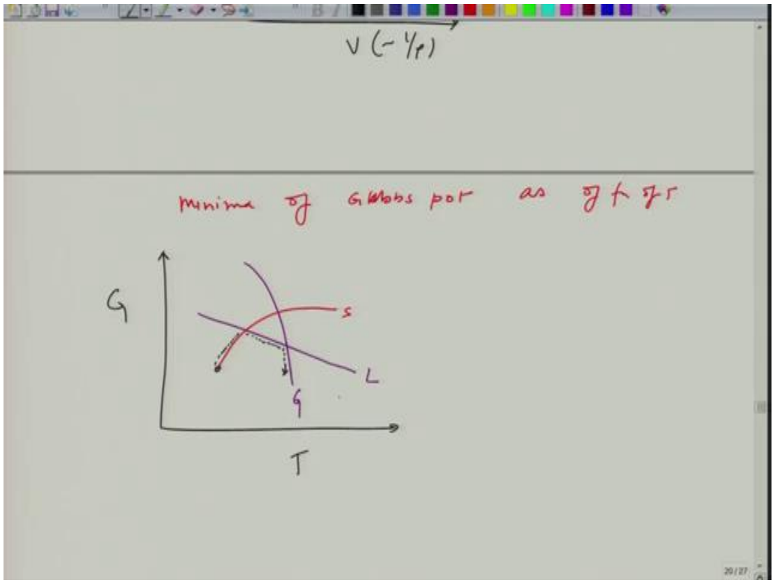

Now, you consider case where, you looking at a minima of Gibbs potential as a function of T. So, what we are trying to do is we are looking at these different minima here, here, here this is for the vapor phase. Similarly, for the liquid phase and you plotting this as a function of temperature okay, so this is how it looks.

For the pure system and that a simple system, so this is for the gas or vapor, this is for the liquid and this is for the solid. Now, you can clearly see that if you are increasing the temperature from the very low and then essentially at certain point the right curve if you look at it, it starts from here because this is a lowest free energy. So, this could be somewhere here but it will as you increase the temperature, it may follow this line and then it has to change because essentially the lowest free energy is now in the liquid phase.

If you go very fast, then you may cross the barrier and stay it for some time in the solid phase but eventually it has to drop down to liquid phase. And then at certain point, you have to follow the gas phase. So, this is how it will look like, of course the slope here is very high but of course at a certain point it will be at higher temperature, it will be something like this.

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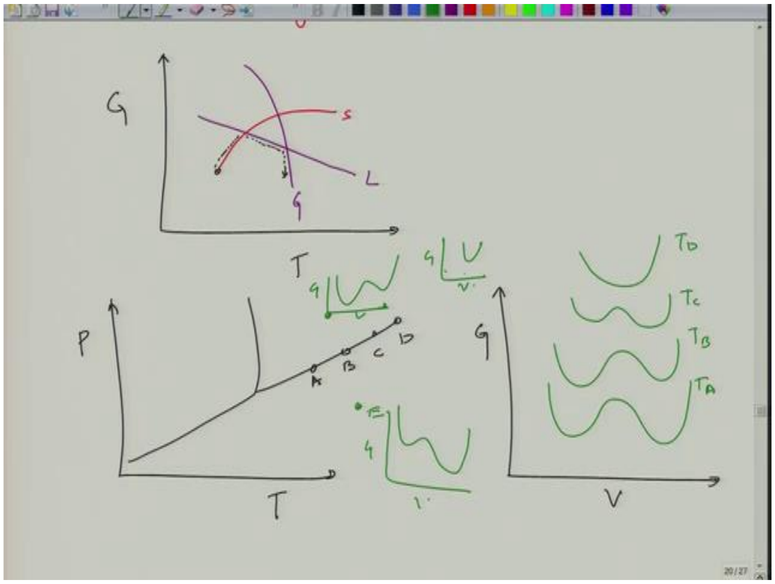

Now, this gives you an idea about this as far as the free energy is concerned, I also can plot another here but now in terms of the PT diagram, this is what we know for simple system and this is a vaporization line, so what would be the nature of your free energy curve, Gibbs free energy curve at this different coexisting point.

So, I can draw this for A it will be something like this, for B again, for C and for D. So, this is your TD okay, temperature TD, TC, TB and TA. So, this is how it will look as far as the Gibbs free energy is concerned. You can also consider specific points here for example what will be the point here? Let us say this is E, now what will be the free energy here? So, here this is a gas phase, so you expect that the free energy of the gas will be lower, hence the plot should look like something like this.

Whereas here, the free energy of the liquid will be lower hence, the plot should look like this. Where you are talking about G as a function of V. And somewhere here, of course it should be something like this, because there is only one phase. So, having got this so far where we have illustrated the free energy with respect to the change in the extensive variable in this case of volume and understanding that, the how this behavior change particularly in terms of change in the temperature. We can now look at little bit of how to define the order of phase transition and this is something which would become very useful to quantify the type of the natures in terms of the order of the phase transition.

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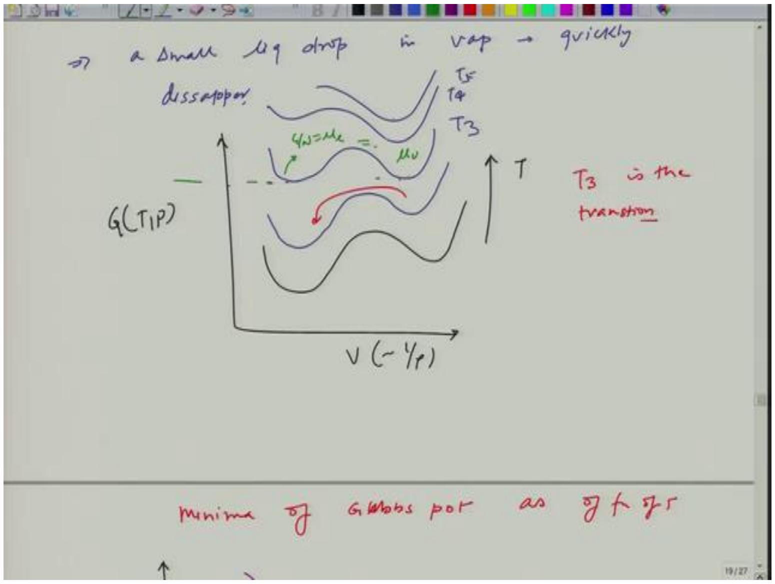

So, we know that at a given or equal phases of course a free energy is equal, if you divide by the number of moles you can identify this as; for example, in T3 this I also means that, that G by N that is a chemical potential here, if we divide this as G by N this is chemical potential of the liquid and this is a chemical potential of the vapor here this must be same.

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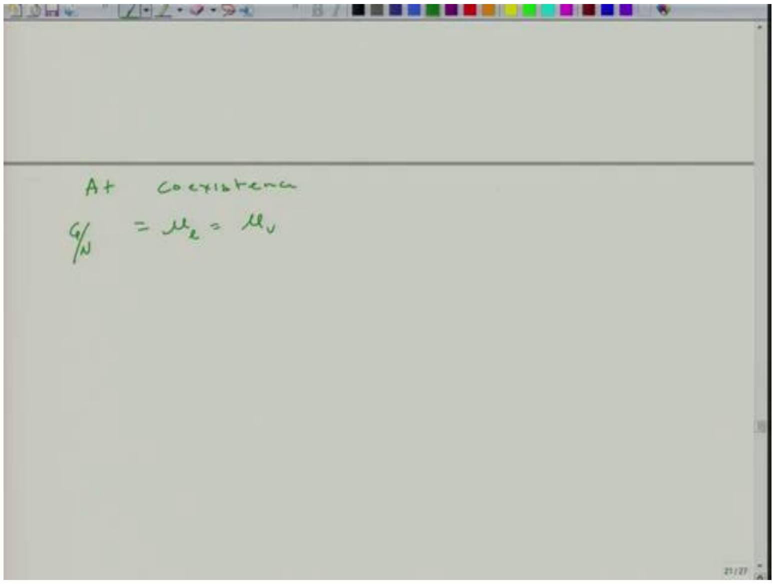

At coexistence

$G/N = \mu_l = \mu_v$

$$At\ coexistence, \qquad \frac{c_p}{N} = \mu_l = \mu_v$$

So, in some sense you are saying that at coexistence we know from our earlier analysis that liquid should be equal to vapor and this is nothing but your G by N. So, that comes also from the diagram.

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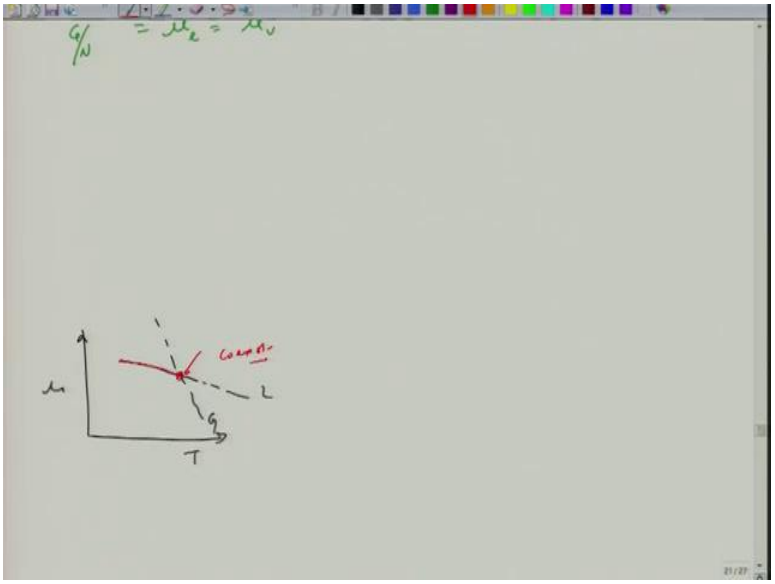

$G/N = \mu_l = \mu_v$

Now, if you at this chemical potential, chemical potential is same in some sense, so essentially if we can draw the chemical potential, it will be something like this, temperature as a chemical potential for the case of liquid and for the case of the gas it will be something like this. So, this is your liquid, this is your gas and this is the reason that it will follow this and at a given coexistence the gas and liquid has to be same and hence this would be the coexistence, conditions or the equality here.

So, the same thing which we have drawn earlier but in a different way. But now, let us look at what is the the derivative of mu, what are the things which are continuous at the coexistence? What are the things which are discontinuous? How do you define this order of phase transitions?

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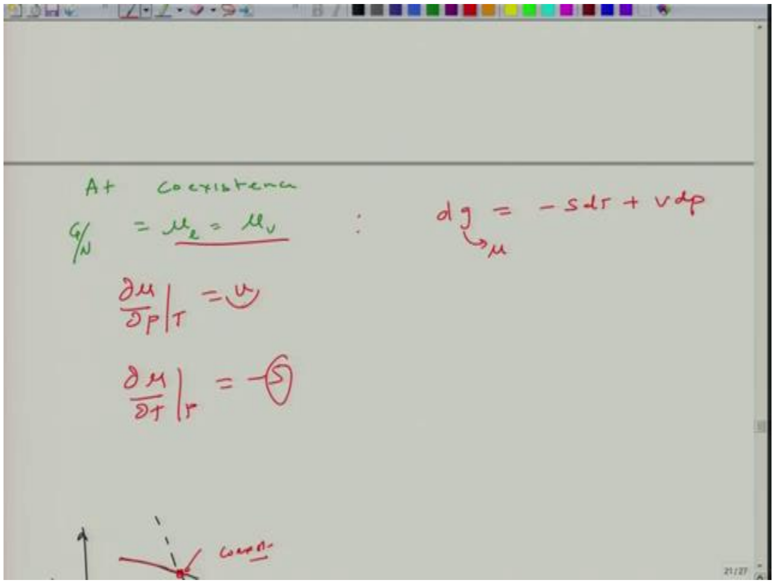

At coexistence

$G/N = \mu_l = \mu_v$: $dg = -sdT + vdp$

$g \to \mu$

$\left.\frac{\partial \mu}{\partial P}\right|_T = v$

$\left.\frac{\partial \mu}{\partial T}\right|_P = -s$

$$\frac{c_P}{N} = \mu_l = \mu_v$$

$$dg = -sdT + vdP$$

$$\frac{\partial\mu}{\partial P}|_T = u \quad \frac{\partial\mu}{\partial T}|_P = -s$$

So, if you look at carefully, del mu by del P at constant T is nothing but V. It comes directly from the fact that if you consider the molar G this is nothing but minus S T plus Vd P where, G is nothing but mu. Now, if you take the derivative of this del mu by Del P it is nothing but V, similarly del mu by del T at constant P is nothing but minus S.

Now, what happens to the molar entropy at the phase transition? If you look at it these are discontinuous of the phase transitions. On the other hand, chemical potential at the phase transition is not discontinuous as I showed here that has to be equal and hence its continuous in some sense.

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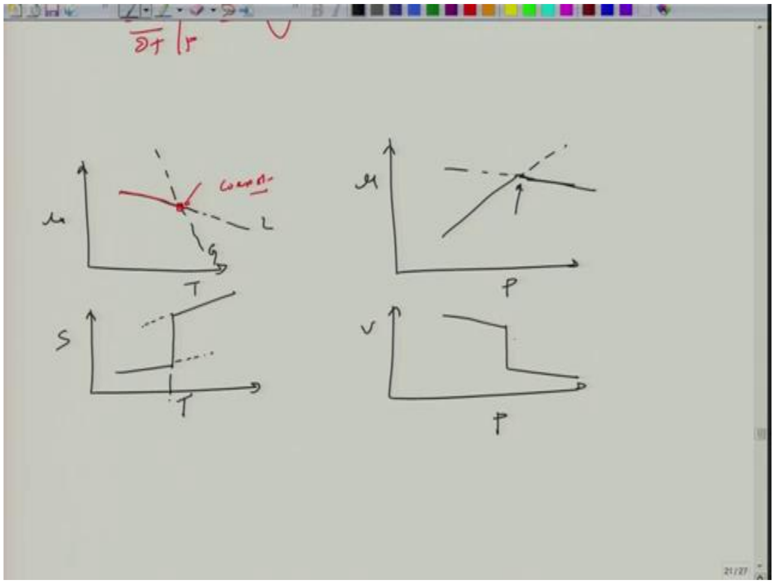

So, if you draw the plot of entropy as a function of temperature is going to be something like this. So, these are two different lines, so this is liquid line, of course dash line indicates this is metastable or unstable and this is a vapor line and this again dash line says that it is metastable or unstable. So, it shows the discontinuity clearly, whereas chemical potential as a function temperature shows like this but a chemical potential as a function of pressure will be something like this. So, it is equal at the phase transition.

So, you do have change in the chemical potential. So, this is your phase transition point. Whereas this here at the T coexistence there is a jump, similarly if you plot volume as a function of pressure you are going to get something like this. Again, a discontinuous V. So, the definition of this phase transition is that there is a discontinuity in the first derivative of the chemical potential hence such a phase transition such as a vapor, liquid are first order phase transitions.

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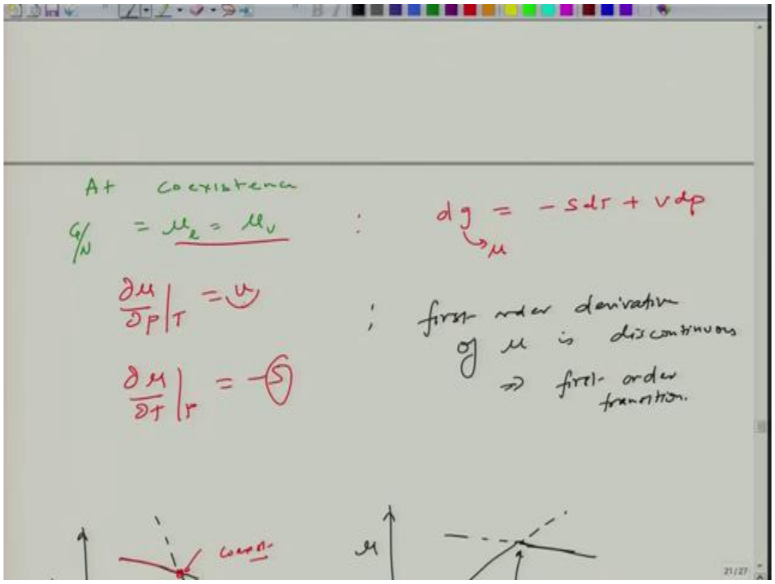

At coexistence

$G/N = \underline{\mu_l = \mu_v}$: $\underset{\hookrightarrow \mu}{dg} = -s\,dT + v\,dp$

$\left.\frac{\partial \mu}{\partial P}\right|_T = \boxed{v}$; first order derivative of μ is discontinuous

$\left.\frac{\partial \mu}{\partial T}\right|_P = -\boxed{S}$ $\Rightarrow$ first order transition.

So, you can say first order derivative of mu is discontinuous, this is means first order transition, where mu is continuous. Now, there could be a second order transition some other cases where, the second order phase, second order derivative of the chemical potential be 0; not the first one. So, first order chemical (potential) first order derivative of chemical potential will not be 0 in such cases, only the second order derivatives will be 0, those would be the examples of second order phase transitions and these are something call; but of course in this course we will not be looking into this, so that is why I am not going into those details. So, in addition to mu, S and V sometimes we also interested in getting the C P / V

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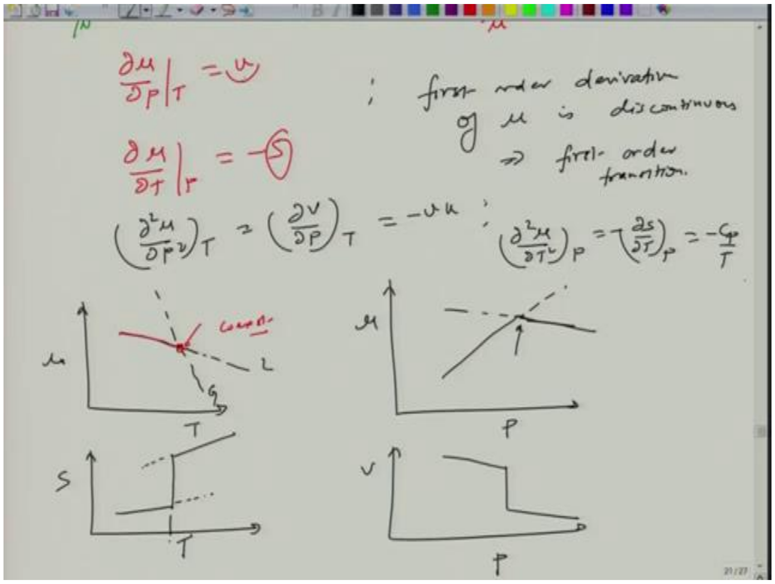

$\left.\frac{\partial \mu}{\partial P}\right|_T = v$; first order derivative of μ is discontinuous

$\left.\frac{\partial \mu}{\partial T}\right|_P = -S$ $\Rightarrow$ first order transition.

$\left(\frac{\partial^2 \mu}{\partial P^2}\right)_T = \left(\frac{\partial v}{\partial P}\right)_T = -vk$; $\left(\frac{\partial^2 \mu}{\partial T^2}\right)_P = -\left(\frac{\partial S}{\partial T}\right)_P = -\frac{c_p}{T}$

$$\left(\frac{\partial^2 \mu}{\partial P^2}\right)_T = \left(\frac{\partial v}{\partial P}\right)_T = -uk\ ;\ \left(\frac{\partial^2 \mu}{\partial T^2}\right)_P = -\left(\frac{\partial S}{\partial T}\right)_P = -\frac{c_p}{T}$$

So, let me just look at the second derivative of mu, this is del V by del P are constant t, this because minus V K, isothermal compressibility that is the second derivative of mu with respect to the pressure, if you take second derivative with respect to temperature at a constant pressure, this is going to be del S by del T at constant pressure, this is minus C P by T. So, you can also look at the second derivative property.

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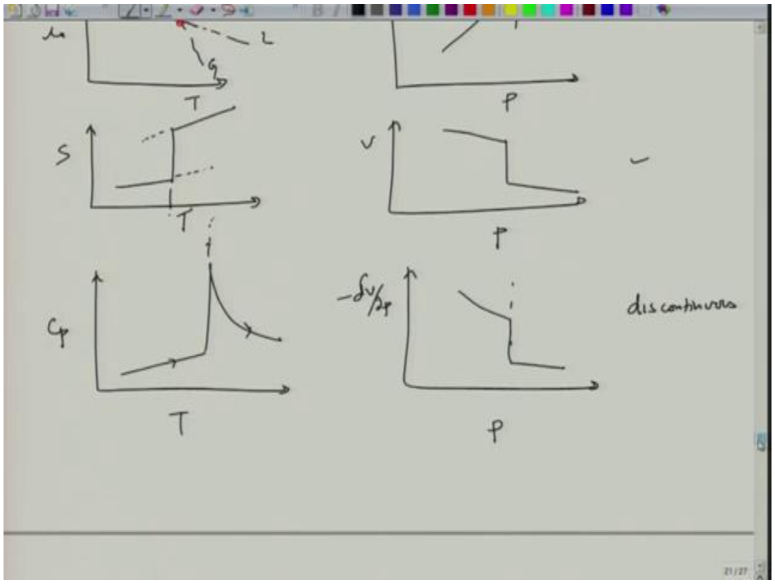

So, second derivative property is K and C P and you can also draw that. They will be also discontinuous at the phase transition. But since the first derivative is the first one which is discontinuous in such case hence this called first order derivative, first order transition in such case. So, this is how it looks, so this goes to infinity, if you increasing the temperature, this is the behavior and for the case of the ideal gas which is nothing but del V by del P minus here and this is pressure, the following is same here.

So, this is infinity and this. So, second order derivatives also discontinuous and same with the this one but since this is the minimum order of derivatives which is discontinuous hence this is called first order transitions. In some cases, the second order becomes the first order which gets discontinuous, in those cases it will be a second order transitions. I hope, I was clear in providing this information and but you can also look into the advance thermodynamic books in order to get the clarity on this phase transitions and order of the phase transitions.

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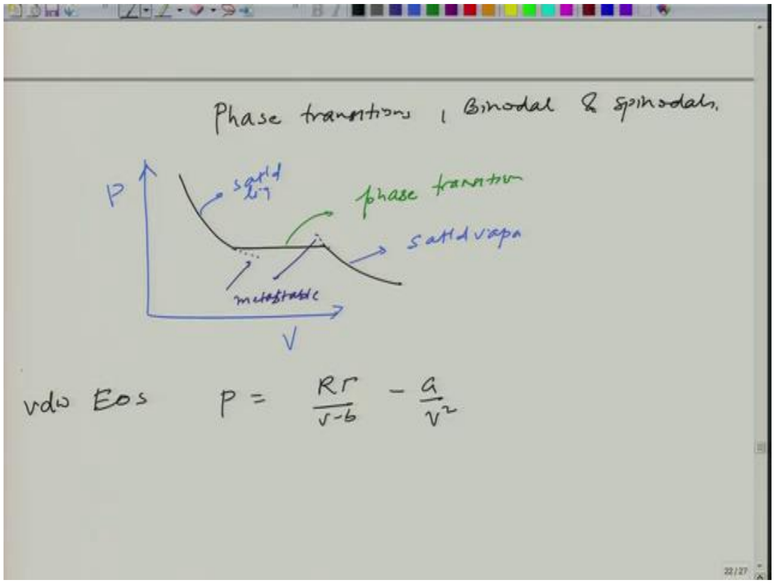

$$vdw\ EOS \quad P = \frac{RT}{v-b} - \frac{a}{v^2}$$

So, let me just extend this exercise and now, what I am interested is I will be looking into the phase transition bi-nodal as spi-nodal here. So, let us look at P V, so again this is our typical phase transition, this is your (saturation) saturated liquid, this is your saturated vapor and this is a phase transition and this would be if you go pretty fast then essentially this would be your meta stable. So, in this case you can measure, if you can avoid the nucleation. Now, this specifically does exist in reality and sometimes is very difficult to model such a thing.

But equation of the state such as Van der Waal equation of state is quite useful to produce isotherm that connects the liquid-vapor branch by a smooth curve and also captures these unstable regions. So, this is a Van der Waal equation of the state.

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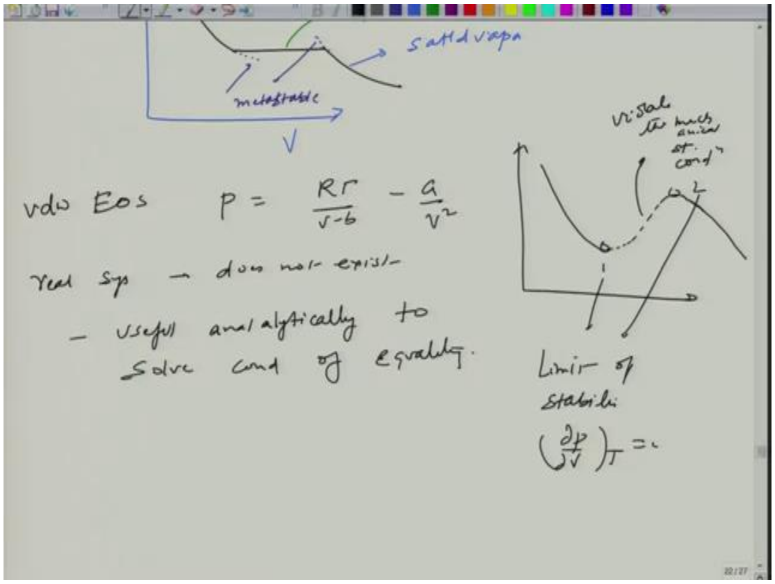

vdw Eos $P = \frac{RT}{v-b} - \frac{a}{v^2}$

real sys → does not exist

- useful analytically to solve cond of equality.

Limit of stabili

$\left(\frac{\partial P}{\partial V}\right)_T = 0$

So, with this I can actually come up with a curve which looks like this, the same curve. So, this part, here to here is this and this part, the saturated liquid is this but I am connecting now with a dash line which violates the mechanical stability but it can be captured stability condition.

So, but it can be captured using this kind of equation of states. So, real system, of course real system will not have this kind of unstable region. So, in real system this dash region does not exist, but is useful analytically to solve the condition of equality or rather the like for example the chemical potential equality we could be, we should be able to solve it or the conditions for the thermodynamic coexistence. So, is useful analytically to solve condition of equality.

Now, if you look at this 1 and 2 this will be your limit of stability that means the del P by del V at constant T is equal to 0. So, what we can do is we can extend this and find out the conditions particularly making use of the fact that the chemical potential is going to be equal.

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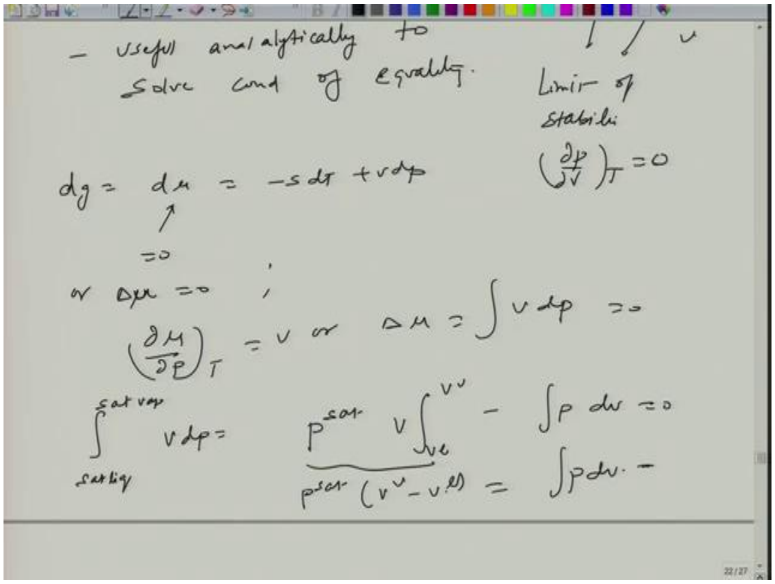

- useful analytically to solve cond of equality.

Limit of stabili

$$\left(\frac{\partial p}{\partial v}\right)_T = 0$$

$$dg = \underset{=0}{d\mu} = -s\,dT + v\,dp$$

or $\Delta\mu = 0$;

$$\left(\frac{\partial \mu}{\partial p}\right)_T = v \quad or \quad \Delta\mu = \int v\,dp = 0$$

$$\int_{sat\,liq}^{sat\,vap} v\,dp = \underbrace{P^{sat}\, v\Big|_{v^l}^{v^v}}_{p^{sat}(v^v - v^l)} - \int p\,dv = 0$$

$$p^{sat}(v^v - v^l) = \int p\,dv \;-$$

$$dg = d\mu = -sdT + vdp \quad or, \Delta\mu = 0\,;$$

$$\left(\frac{\partial\mu}{\partial P}\right)_T = v \qquad or, \qquad \Delta\mu = \int vdP = 0$$

$$\int_{sat\ liq}^{sat\ vap} vdP = p^{sat}\int_{v^l}^{v^v} v - \int Pdv = 0$$

So, if you consider d g is equal to d mu is equal to minus d S T plus this for the coexistence condition this has to be 0 or or in other words, I can actually get delta mu that must be 0. I can come up with a volume because volume we are changing here, so I can write this as del mu by del P at constant T this is V or del mu is integral of V d P right. So, this has to be 0. So now, you have a curve where the integral of V d P across the region for coexistent condition this should be 0.

So, what we can do, we can use this chain rule and the following can be written that from saturated liquid to saturated vapor V d P is something which we can integrate by chain rules where, we can write this as P saturation V integral from V liquid to V vapor minus P dV K is equal to 0. So, this means is P sat V vapor minus V liquid this will be integral of P d V. So, this comes from the simple exercise.

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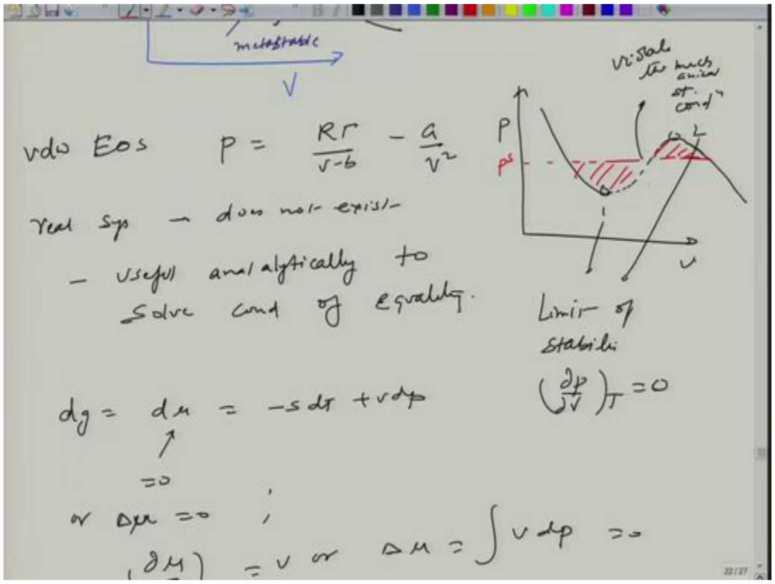

vdw EoS $P = \frac{RT}{v-b} - \frac{a}{v^2}$

real sys → does not exist

– useful analytically to solve cond of equality.

$\left(\frac{\partial P}{\partial V}\right)_T = 0$

$dg = \underset{\substack{\uparrow \\ =0}}{d\mu} = -s\,dT + v\,dP$

or $\Delta\mu = 0$;

$\left(\frac{\partial \mu}{}\right) = v$ or $\Delta\mu = \int v\,dP = 0$

This pressure and volume here, you need to have a P sat somewhere here, P sat somewhere here, which divides such that the area under these two curves must be equal.

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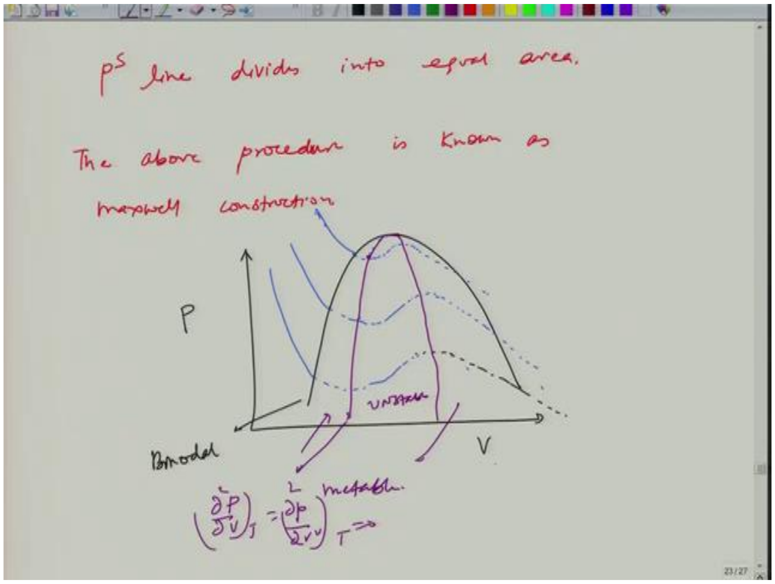

P^s line divides into equal area.

The above procedure is known as maxwell construction

$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$

So, that means this Ps line which essentially means that Ps line divides into equal area. Now, this above procedure or the procedure where to in order to find it analytically or graphically the P sat given this P V curve from let us say equation of state and you can come up with a Ps line such that it divides this region equally so, that you can have equal area. The shaded region should be same, such a construction is called ‘Maxwell construction’.

So, let me draw again a P versus V curve. Now, this is typical saturation liquid and saturation vapor, sometimes also called bi-nodal.

Now, we will consider the isotherm then I can write this. Similarly, so and the dash lines are basically to reflect the changes in a region here. So ideally, I should draw in a way, which should be something like this. So, I am using the different color here. Now, I can write this as okay; similarly, I can do the same for here, here it is going to be right, so what is in order to find this unstable and meta stable, so I am going to connect this points where this derivative of this or the point is that I can join all this points which provides the limit of stability.

And this we can do that essentially, I have a region where it is unstable and this is a region which is meta stable and this provides the limit of stability where the first derivative a volume and the second derivative, the second derivative are 0. So, this is something which we can get here.

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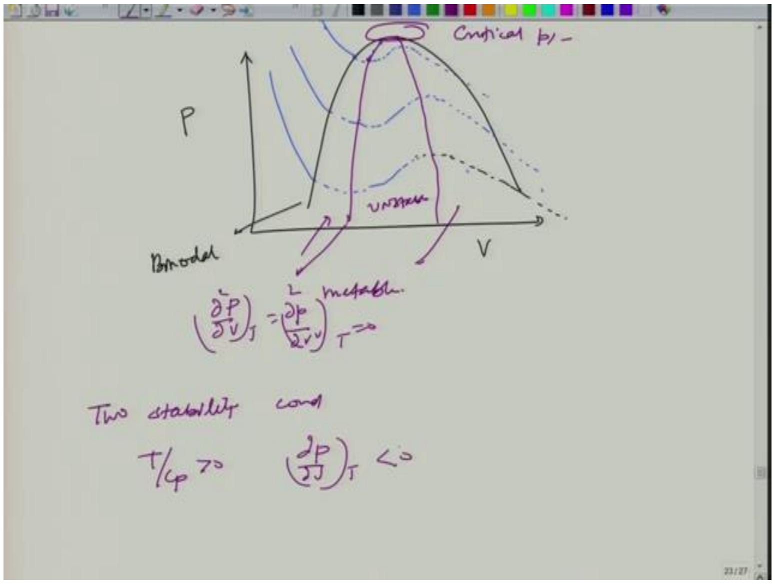

$$Two\ stability\ conditions:$$

$$\frac{T}{c_p} > 0 \quad \left(\frac{\partial p}{\partial v}\right)_T < 0$$

The other thing which would be interesting is, what happens to the properties at this critical region? So, if you consider these two stability criteria, which are T by C P is greater than 0 and del P by del V, these are equivalent.

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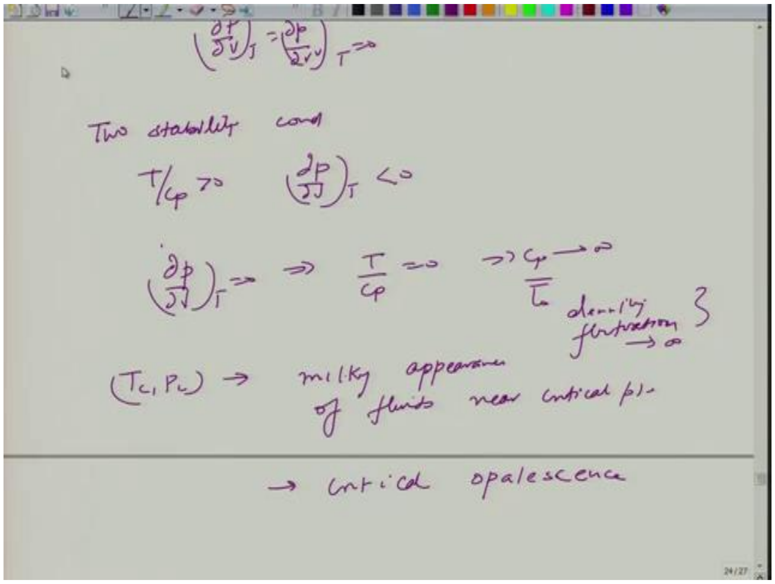

$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$

Two stability cond

$T/C_p > 0$ $\left(\frac{\partial P}{\partial V}\right)_T < 0$

$\left(\frac{\partial P}{\partial V}\right)_T = 0 \Rightarrow \frac{T}{C_p} = 0 \Rightarrow C_p \to \infty$

$= T_c$ density fluctuation $\to \infty$ }

$(T_c, P_c) \to$ milky appearance of fluids near critical pt.

$\to$ critical opalescence

And you can show that at critical point del P by del V should be equal to 0, as it approaches there, which indicates that T by C P is 0, which indicates C P goes to infinity. So, this is true also because the density fluctuation here is very large and usually the size of the molecules are shorter (then) smaller than the wavelength of the light and this is the reason that you cannot come up with any specific analytical expression to capture the critical point and is not easily measurable also because at T C, P C because of this very large fluctuation, which is also given by this information which you can make use of the statistical mechanics to get this fact that the density also fluctuates then the T C, P C what happens because of the fact that the size is small, molecule smaller than the wavelength of light.

And there is a large fluctuation and hence you always get some milky appearance of fluids near criticality, critical point. So, this is also sometimes called ’Critical Opalescence’. So, I think for now we can stop here and we will take up this understanding analysis and extend it in the next lecture, probably by next lecture we will be able to finish the questions which we started with from the last lecture onward. So, I will see you in the next lecture.