# Thermal Physics
**Prof. Debamalya Banerjee**
**Department of Physics,**
**Indian Institute of Technology, Kharagpur**

## Module No # 11
## Lecture No # 55
## Gibb's Phase Rule and Basics of Second Order Phase Transion.

Hello and welcome back to the last lecture of week 11 of this NPTEL course on thermal physics. Now in the last class we talked about the second latent equation which is also called Clausius Clapeyron equation. And today we will complete our discussion on phase transition and for that we have two important topics to cover one is the Gibb's phase rule which is an extremely important rule in phase transition.

And the second one is the second order phase transition and there is something called Ehrenfest equation which describes the pressure temperature the locus of second order phase transition point equilibrium curve along a T-P temperature pressure diagram. So but before that let me start with the last problem of classroom problems that we of week 11.

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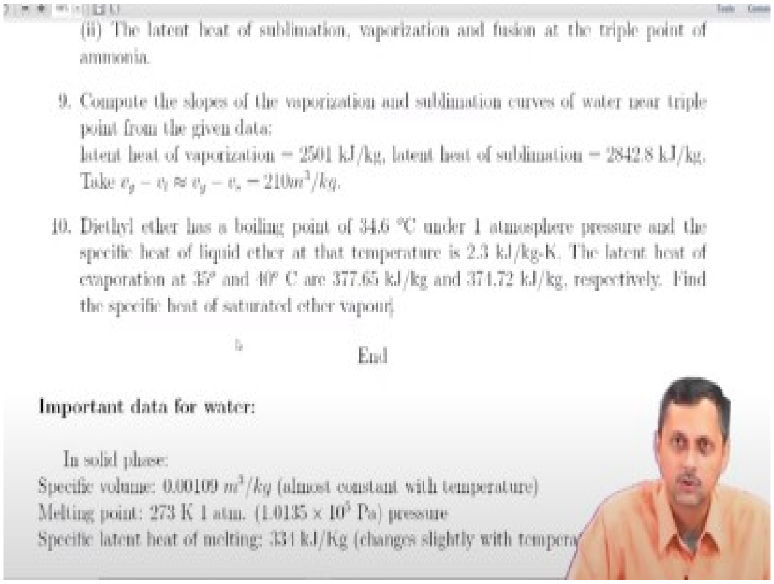

(ii) The latent heat of sublimation, vaporization and fusion at the triple point of ammonia.

9. Compute the slopes of the vaporization and sublimation curves of water near triple point from the given data:
latent heat of vaporization = 2501 kJ/kg, latent heat of sublimation = 2842.8 kJ/kg.
Take $v_g - v_l \approx v_g - v_s = 210m^3/kg$.

10. Diethyl ether has a boiling point of 34.6 °C under 1 atmosphere pressure and the specific heat of liquid ether at that temperature is 2.3 kJ/kg-K. The latent heat of evaporation at 35° and 40° C are 377.65 kJ/kg and 371.72 kJ/kg, respectively. Find the specific heat of saturated ether vapour.

End

**Important data for water:**

In solid phase:
Specific volume: 0.00109 $m^3/kg$ (almost constant with temperature)
Melting point: 273 K 1 atm. ($1.0135 \times 10^5$ Pa) pressure
Specific latent heat of melting: 331 kJ/Kg (changes slightly with tempera

That is the problem where we have to compute the latent the specific heat of saturated ether vapour from the given data. So for diethyl ether the boiling point is 34.6 degree centigrade under

1 atmosphere pressure and the specific heat of liquid ether at that temperature is 2.3 kilojoules per kg k.

So the specific heat is given the boiling point is given the latent heat of evapouration at 35 degree and 40 degree centigrade are 377.65 kilojoules per kg and 374.72 kilojoules per kg respectively find the specific heat of saturated ether vapour. So once again it is a liquid vapour transition so we can use the simplified form of the Clausius Clapeyron equation.

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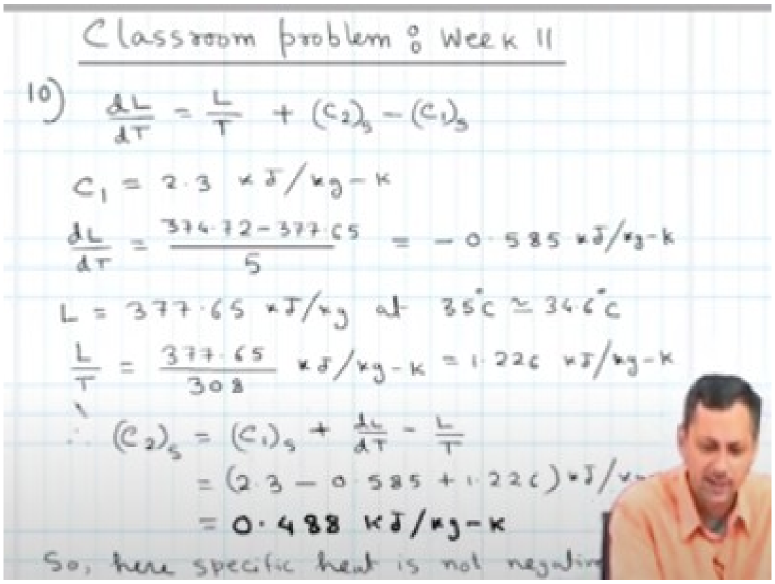

Classroom problem : Week 11

10) $\frac{dL}{dT} = \frac{L}{T} + (c_2)_s - (c_1)_s$

$c_1 = 2.3 \text{ kJ/kg-K}$

$\frac{dL}{dT} = \frac{374.72 - 377.65}{5} = -0.585 \text{ kJ/kg-K}$

$L = 377.65 \text{ kJ/kg}$ at $35^\circ C \simeq 34.6^\circ C$

$\frac{L}{T} = \frac{377.65}{308} \text{ kJ/kg-K} = 1.226 \text{ kJ/kg-K}$

$\therefore (c_2)_s = (c_1)_s + \frac{dL}{dT} - \frac{L}{T}$

$= (2.3 - 0.585 + 1.226) \text{ kJ/}$

$= 0.488 \text{ kJ/kg-K}$

So, here specific heat is not negati

So let us try start with that so we can say d l d t = l by t + c 2 s - c 1 s. Now c 1 is given as 2.3 kilo joules per kg k dL dT is not given directly. But if you if you look at this problem here the specific the latent heat of evapouration or specific latent heat of evapouration is supplied at two temperatures. One is at 35 degree centigrade and one is at 40 degree centigrade and which are 377.65 and 374.72 kilojoules per kg.

So once again we see the latent heat decreases with increasing temperature. So from this we can actually compute the approximate slope around this boiling point under one atmosphere pressure. So d L dT will be roughly equal to well not exactly maybe but roughly equal to 374.72 minus 377.65 divided by 5 which is minus 0.585 kilojoules per kg k. Now L at 34.6 degrees is something that we need to find out of course we have L given as at 35 degree centigrade which is a very close to 34.6 degree centigrade.

So we can use this value directly or else what we can do is we can use this slope in order to find out what should be the correction to these values but let me tell you this might be a change in the first decimal place so not worth doing it. So we can simply use L is equal to this value here and we can take T is equal to 35 degree centigrade which is 308 kelvin so L by T will be this which is 1.226 kilojoules per kg k.

And if you let me tell you if you do this precise correction so if you use the slope here in order to compute the latent heat at 34.6 degree centigrade. You might see a change in this instead of 2 6 I do not remember often but it will be probably 2 8 or something so it is a very tiny change so 6 will be 8 or something so it is ok. Now using this above using this data of l by t and d L d T which we have calculated here we can calculate C 2 s is equal to C 1 s plus d L dT minus L by T which is 2.3 minus 0.585 plus 1.226 kilojoules per kg k which is 0.488 kilojoules per kg k.

And please understand that why I have chosen this example this is to show you that the specific heat here is not negative. So what we have calculated the specific heat around the boiling point of water at 100 degree centigrade is negative. That is only I mean it once again it cannot be generalized it is only a special case for water and there are few other substance which also demonstrate negative specific heat around the boiling point.

But diethyl ether for example does have a positive specific heat around boiling point. So that means if we want to increase the ether vapour the temperature of ether vapour by 1 degree around 34 from 34.6 to 35.6 degree centigrade 488 kilo joules per kg heat has to be supplied right okay.

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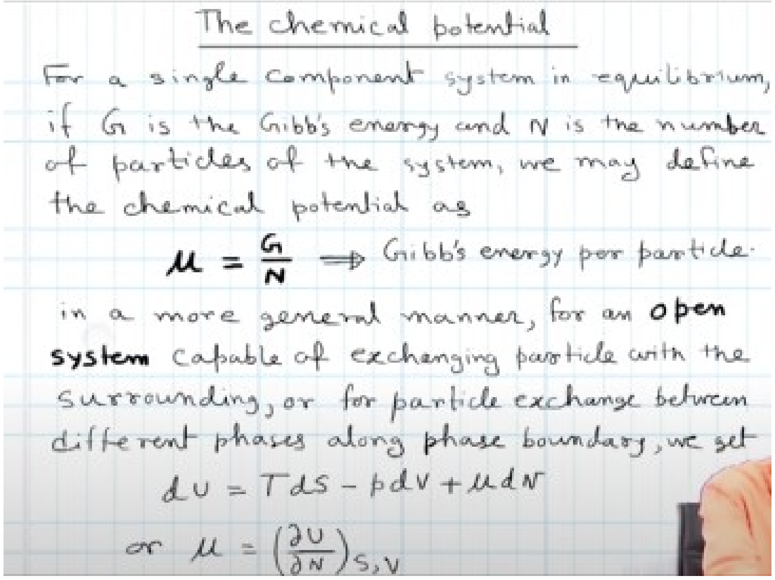

The chemical potential

For a single component system in equilibrium, if G is the Gibb's energy and N is the number of particles of the system, we may define the chemical potential as

$$\mu = \frac{G}{N} \Rightarrow \text{Gibb's energy per particle.}$$

in a more general manner, for an **open system** capable of exchanging particle with the surrounding, or for particle exchange between different phases along phase boundary, we get

$$dU = TdS - pdV + \mu dN$$

$$\text{or } \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

So now let us start our discussion on the Gibbs phase rule so for that first we have to define a quantity called the chemical potential. Now what is chemical potential? There are many different you know many accepted definition for chemical potential we will discuss some of those but the simplest and most easily understood definition is probably. That if we have a system in equilibrium where it is a single let us say there is a single component system in equilibrium where there is total number of N particles into the system.

Then the chemical potential mu is G by N where g is the Gibb's total Gibb's free energy of the system so that means mu is nothing but Gibb's energy per particle. So now in a more general manner if; we have an open system which can exchange particle with the surrounding or maybe we have a system. Let us say we have we are talking about a system in phase equilibrium single component system only it is not exactly an open system

But we have one liquid and vapour phase in equilibrium in a closed environment. And the particles can some particles can go from liquid to vapour phase and some particle can come back from vapour to liquid phase. At equilibrium this number itself please remember it is a dynamic equilibrium so that means some liquid particles are going into vapour and exactly that number of particles are coming back from vapour to liquid right.

So in such cases even this there is a particle exchange if we calculate the for example if we focus on only the liquid phase it behaves like a single open system it is in equilibrium with its own vapour so particle exchange is taking place. So for such cases d u or for that fact any free energy function can be written as a combination of let us say du is equal to T d s minus p d v plus mu d n right. So this mu is the chemical potential and d n is the number of particle exchange.

So d u also has a mu d n contribution so basically this is the energy or internal energy also mu is also equal to the internal energy of this per particle. So for single particle system the energy so basically the mu is energy associated with a single particle of the system so mu can be written as del u del n with s and v constant. Now for even for a closed system maintaining s and v constant is not so easy. I mean maintaining v constant is probably but maintaining it adiabatic completely adiabatic experimentally is not very feasible.

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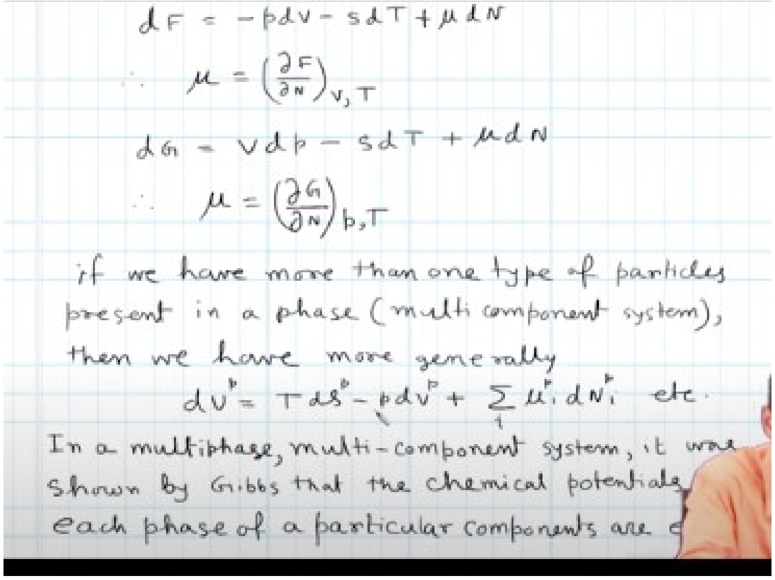

$$dF = -p\,dV - S\,dT + \mu\,dN$$

$$\therefore \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}$$

$$dG = V\,dp - S\,dT + \mu\,dN$$

$$\therefore \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{p,T}$$

if we have more than one type of particles present in a phase (multi component system), then we have more generally

$$dU^{p} = T\,dS^{p} - p\,dV^{p} + \sum_{i} \mu_i^{p}\,dN_i^{p} \quad \text{etc.}$$

In a multiphase, multi-component system, it was shown by Gibbs that the chemical potentials each phase of a particular components are

So we can also define other differential forms so we can write the similar expression for other free energy function for example we can write d F is equal to minus p dv minus s dT plus mu d N and mu is equal to del f del n and v t. So maintain I mean so we have to compute the or basically the specific Helmholtz energy per particle keeping volume and temperature constant. Similarly we can write mu is equal to del G del N p2 or the phase or Gibb’s free energy per particle keeping pressure and temperature constant.

Now this is by far the most popular definition of chemical potential because as we have already discussed almost. I mean many of the chemical processes we are talking about including phase transition is a constant pressure constant temperature process. So that is why for when we talk about phase transition and related phenomena we always say mu is equal to del G del N so that means.

So basically from this discussion you see that mu is actually the energy per particle so we can add that to the internal energy of the system we can add that to the Helmholtz energy of the system Gibb's energy of the system also to the enthalpy of the system it does not matter. But the most popular definition is mu is equal to del G del N at constant pressure and temperature. Now for a situation for a particular system if we have more than one type of particle, present in a phase.

So which is basically multi component system let us say we have just liquid phase we have water and alcohol mixed together some alcohol mixed together. So that gives you a very good example of a two component liquid phase system. Then for each phase we can write d U p = T d s p + p stands for the phase. By mistake sorry this should be P because phase is always written with T not p that has been a mistake so this should be P and right.

I hope you understand the handwriting is not that great here but you understand what I am saying. So in a multi phase multi component system it was shown that Gibb's by Gibbs himself that the chemical potential of each phase of a particular component are equal. So let us say we have once again going back to the example that we have taken we have alcohol water system in equilibrium with their own vapour. So we have inside a closed container water alcohol mixture which is in equilibrium with the vapour.

So we have essentially two components and two different phases now we have liquid phase we have vapour phase. In liquid phase we have two components water and alcohol also in the vapour phase we have two components water and I mean water vapour and alcohol vapour. Now what Gibb's showed us a Gibb's showed by rigorous mathematical treatment that the chemical potential of alcohol in vapour phase and chemical potential of alcohol in liquid phase has to be equal along the phase, boundary.

Similarly chemical potential of water vapour and chemical potential of liquid vapour along the phase boundary has to be equal. So that means for a single component system we always know that the specific Gibb's energy has to be equal between 2 phases right. Similarly for multi component system it has to be the chemical potential of different phases has to be equal along the phase boundary for the same component right.

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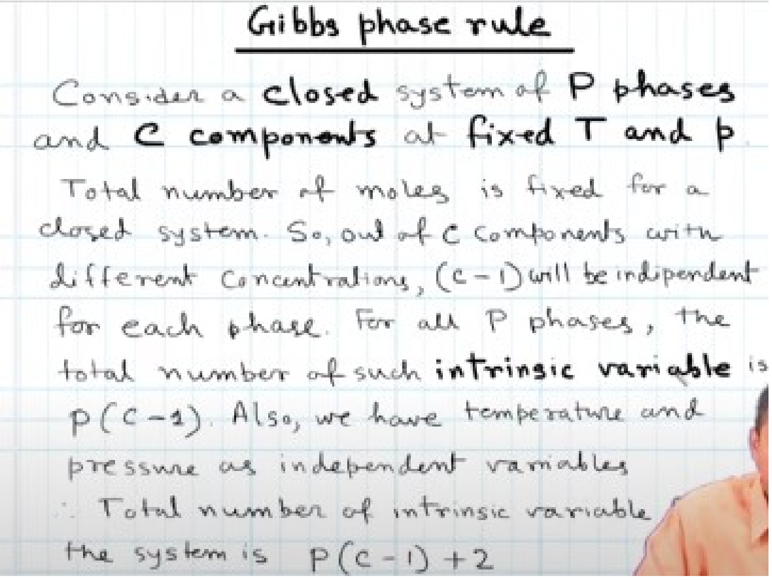

Gibbs phase rule

Consider a **closed** system of **P phases** and **C components** at **fixed T and p**

Total number of moles is fixed for a closed system. So, out of C components with different concentrations, $(C-1)$ will be indipendent for each phase. For all P phases, the total number of such **intrinsic variable** is $P(C-1)$. Also, we have temperature and pressure as independent variables

$\therefore$ Total number of intrinsic variable the system is $P(C-1)+2$

Now let us consider that in a closed system we have P phases and C components at a fixed temperature T and P right. Now total number of moles is fixed for a closed system so that means we cannot add particles from outside. Or we can remove particle from outside but when we have let us say please remember we have taken example so far only for a water alcohol mixture.

But if what if we mix water acetone ethyl alcohol methyl, alcohol these four different liquids together they are absolutely miserable. They will mix up so that means it will be a four component two phase system. And if we take the temperature down at some point all of this water and alcohol and you know acetone they can solidify if we go to low enough temperature. So we can actually have 4 component 3 phase system right.

So in general if we have a c component and p phase system right but then what happens you know if we have a closed system we cannot add more particles from outside or we cannot take out any particles from outside. So out of this c components with different concentration c minus 1 will be independent of each for each phase right. So for all p phases the total number of such intrinsic variable that we are talking about intrinsic variable being pressure including pressure temperature and mole fraction is p into c minus 1 right.

So try to think why mole fraction can be an intrinsic variable and not an extensive variable talk about mole fraction not the number of mole. So we have P into c minus 1 such independent variables that is present in a P phase and c component closed system. Also we have on top of this so these components are predominantly I mean these variables are predominantly the mole fractions of each component in each phase.

And on top of that we have pressure and temperature so all together we have P time's c minus 1 plus 2 numbers of intrinsic variables right. Now also there are certain constraints associated with this system.

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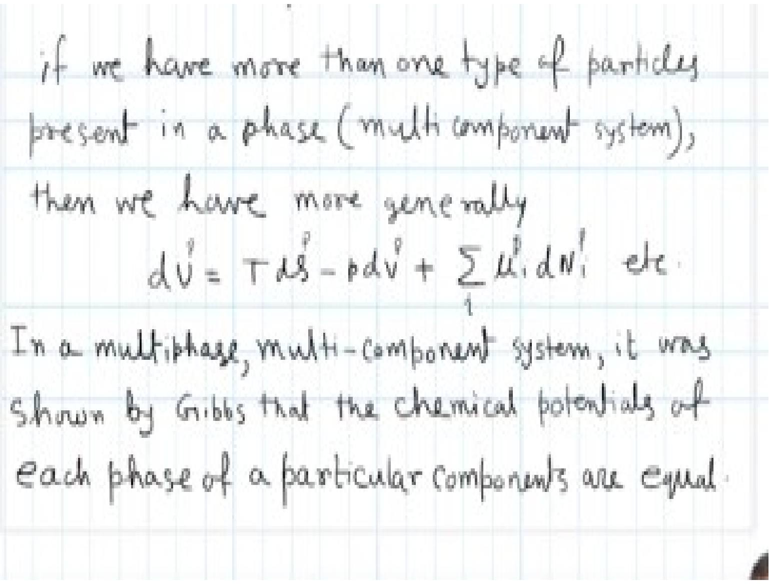

if we have more than one type of particles present in a phase (multi component system), then we have more generally

$$dU^{\alpha} = T dS^{\alpha} - p dV^{\alpha} + \sum_{i} \mu_i^{\alpha} dN_i^{\alpha} \quad \text{etc.}$$

In a multiphase, multi-component system, it was shown by Gibbs that the chemical potentials of each phase of a particular components are equal.

These constraints are Gibb's by Gibb's here which says the chemical potential of each phase of a particular component are equal. So if we have water you know as I said we have water ethanol, methanol, acetone all mixed together. So for and if they are in 2 phases so for 2 phase equilibrium we have 4 such constraint equation right.

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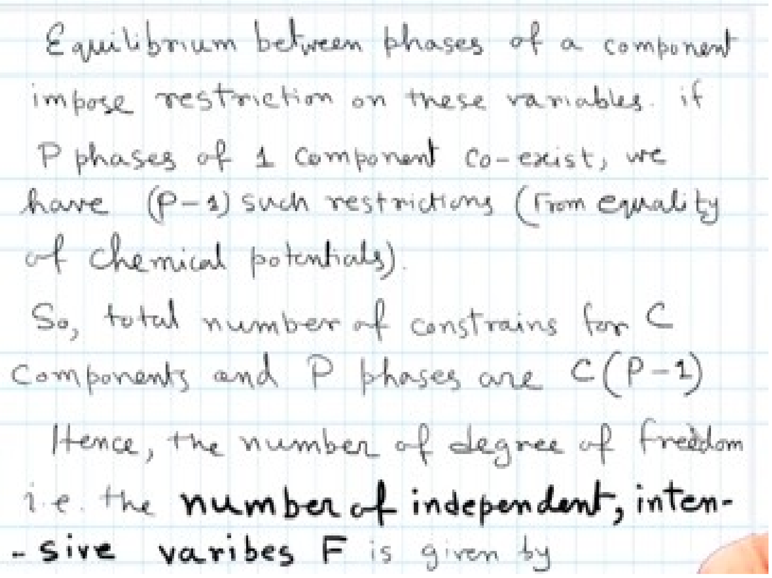

Equilibrium between phases of a component impose restriction on these variables. if P phases of 1 component co-exist, we have (P−1) such restrictions (from equality of chemical potentials).

So, total number of constrains for C components and P phases are $C(P-1)$

Hence, the number of degree of freedom i.e. the **number of independent, intensive varibes F** is given by

So in general if we have we have 2 phase right. So for one single component let us say for water we have water vapour and liquid water at equilibrium along the phase boundary so this is one constraint equation. So if we have 3 phases there should be 2 constraint equations along the liquid vapour and solid vapour boundary right. So altogether if we have P phases, we have P minus 1 such constraint equation for each component. And altogether if we have C number of components then we have C times P minus 1 such constraint equation present.

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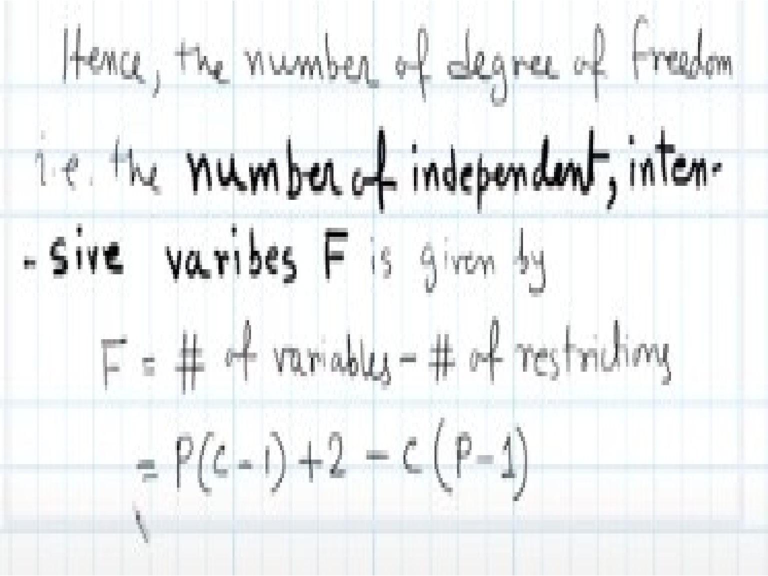

Hence, the number of degree of freedom i.e. the **number of independent, intensive varibes F** is given by

$$F = \#\text{ of variables} - \#\text{ of restrictions}$$

$$= P(C-1)+2-C(P-1)$$

So total number of independent degrees of freedom should be the number total number of variables total number of constraints. Now what we have seen the total number of variables is P times C minus 1 plus 2. Whereas the total number of, constraint is C times P plus 1 so we have sorry P times c minus 1 plus 2 and we have minus C times P minus 1. So if we open the bracket and simplify so this is the number of independent intensive variable is called the degree of freedom so f is equal to this.

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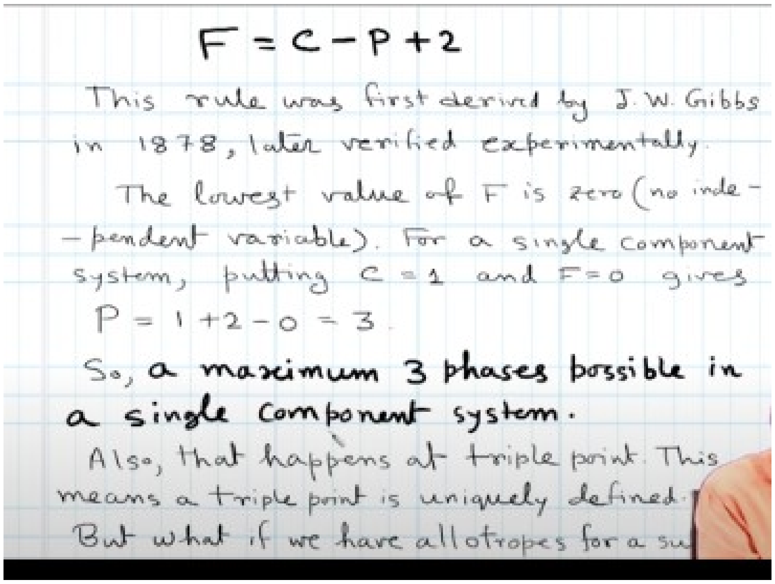

$$F = C - P + 2$$

This rule was first derived by J. W. Gibbs in 1878, later verified experimentally.

The lowest value of F is zero (no independent variable). For a single component system, putting $C = 1$ and $F = 0$ gives $P = 1 + 2 - 0 = 3$.

So, **a maximum 3 phases possible in a single component system.**

Also, that happens at triple point. This means a triple point is uniquely defined.

But what if we have allotropes for a su

And if we simplify we get the famous phase rule which is F= C – P + 2. So F is the number of independent intensive variable, C is the number of components, P is the number of phases. And 2 is a number which comes from the two independent variable two intensive variables pressure and temperature of the system. Please remember this is valid for a closed system of fixed pressure and constant pressure and constant temperature.

So this rule was first derived by Gibb’s himself in actually it is not exactly 1878 it is a series of publication between 75 and 78 where he has established this rules. And later it was experimentally verified that this rule cannot be bypassed there has to be this. And please remember the one condition for this rule to apply is there is no chemical reaction taking place between the different components.

So we can have let us say liquids dissolved into each other we can have if we add some salt to that system we are talking about we might have some salt going into the system we can still have some solid salt remaining. So this type of solution while mixing and mixing is you know this one is allowed but if we for example add a small amount of lithium metal into this it will vigorously react with water and that is not allowed so that will not come under phase rule.

So when we talk about phase equilibrium the system has to be in thermodynamic equilibrium that means total it will be total thermal chemical and mechanical equilibrium with the surrounding right. Now for a single component system if we put C = 1 and F = 0 that means we can F = 0 means there is no degree of freedom.

So that will give you the maximum number of phases that is possible for a single component system right. Because if in this case if I put F = 0 and C = 1 we get the maximum value for P and we get P = 3.

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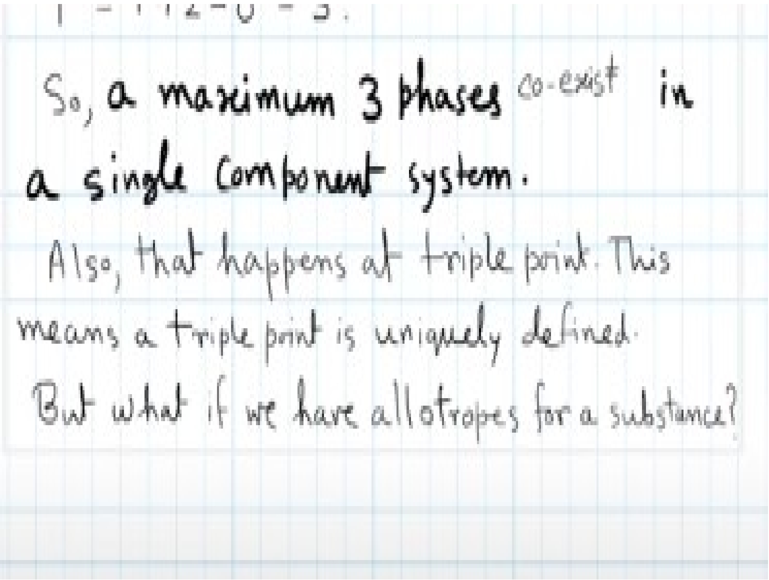

So, a maximum 3 phases co-exist in
a single component system.
Also, that happens at triple point. This
means a triple point is uniquely defined.
But what if we have allotropes for a substance?

So that tells you that given that the Gibb's phase rule is universally valid for any closed system. For a single component system we can have a maximum of 3 phases possible in a single component I mean sorry not possible. I should say maximum of 3 phases coexist not possible of course there could be more phases possible but it should not coexist in a single component system.

So that happens around the triple point this means the triple point is uniquely defined. But let us say we have a certain system where we have allotropes we have discussed in the last class also briefly I have said.

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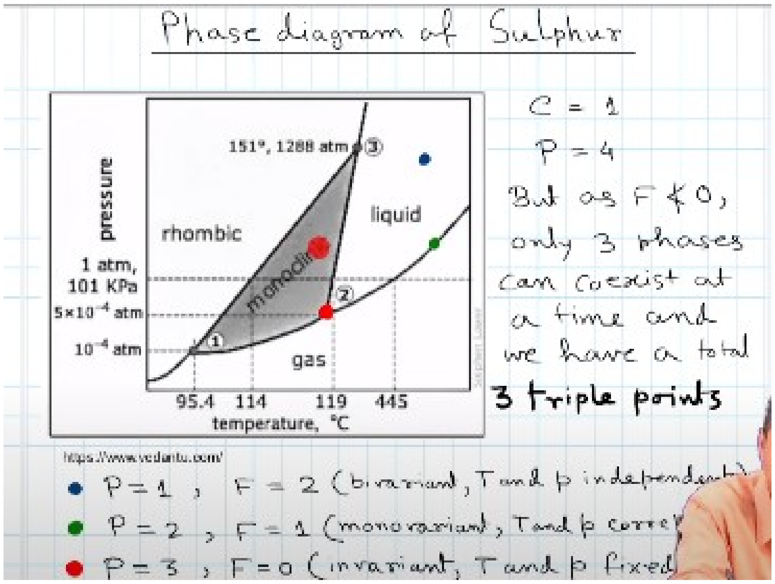

Phase diagram of Sulphur

C = 1

P = 4

But as F ≮ 0, only 3 phases can coexist at a time and we have a total **3 triple points**

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- ● P = 1 , F = 2 (bivariant, T and p independent)
- ● P = 2 , F = 1 (monovariant, T and p corre
- ● P = 3 , F = 0 (invariant, T and p fixed

So let us take the example of sulphur, in sulphur there are 2 types of solid phases one is rhombic and one is monoclinic we can go from 1 phase to the other by changing pressure or temperature or both right. So basically for example if we are in this point and if we increase the pressure from the, we go into from monoclinic we go into the rhombic phase. Or if we add this or if we added this point we increase the temperature keeping the same pressure we go from rhombic to monoclinic phase.

So in such cases we have C = 1 and P = 4 so we have 2 solid phases rhombic, monoclinic and then there is a liquid phase there is a gas phase or vapour phase whatever you might call it. But if we put C = 1 P = 4 we get what F = - 1 but F cannot be equal to less than 0. So that tells you readily that only 3 phases can coexist at a time and we have a total of 3 triple points why? Because at this point the rhombic phase the monoclinic phase and the gas phase coexist.

At this point the rhombic phase sorry the monoclinic phase the gas phase and the liquid phase coexist. And at this point the rhombic, monoclinic and liquid phase coexists so these are actually 3 different triple points. One is at 95.4 degrees one is at 119 and this one is I think something around 154 degree centigrade I do not remember often but you can find this anywhere in any standard textbook have a look.

Now just to show you the usefulness of this little more discussion on this phase rule I have chosen 3 points from this phase diagram I have marked them with blue here green here and red here. Now if we look at the blue point first now in blue point it is inside one liquid phase one phase. So I mean I could have chosen this blue point instead of here we can choose it here also or here also here only thing is it is nowhere close to the phase boundary it is deep inside one given phase.

Now in this case P = 1 F = 2 because if we put into this equation where is it if we put see C is always equal to 1 C = 1. If we put P = 1 so 1 - 1 = 0 so f gives you it will give you F = 2. That means this point is an example of a bi-variant point where pressure and temperature are independently changeable. So you can change either this pressure or the temperature or both and around this point and you will still be inside this liquid phase only.

So there is no you know so it the phase rule actually talks about the degree of freedom in a given phase right. So in this phase inside this liquid deep inside this liquid phase or deep inside this, gas phase or monoclinic or rhombic space. When you are well within that phase you are free to change the pressure and temperature as per your will so both behaves as two independent parameters right.

Now we take the green point where the green point? Green point is at the liquid gas phase on the liquid gas phase equilibrium line. So on that we have two phases coexisting P = 2 that immediately tells you F = 1 from the phase rule that means it is a mono variant point. So, where only 1 degree of freedom there is effectively 1 degree of freedom now if we have to maintain the 2 coexisting phases on the, this point has to be maintained on the phase boundary.

We already know pressure and temperature they are correlated by the first latent heat equation so thereby no means independent of each other and that is exactly what is reflected into this F = 1. Now let us look at the last point that is the red point on this curve which is one of the triple points. How many phases are there? There are 3 phases from monoclinic gas and liquid that gives you F = 0 so this is an invariant point where temperature and pressure is fixed.

So that is why I say for a triple point for a given system. It there could be more than one triple point but each triple point has a uniquely defined pressure and temperature and that is also given by the phase rule when we get F = 0. So my suggestion would be I mean we have not discussed much about the phase rule. But I think we have discussed enough at least for a single component system so that you can understand the basic application and principle behind the phase rule.

My suggestion would be please go back take your take any standard textbook or if possible take more than one textbook and try to read through the relevant chapter so that you will understand it little better.

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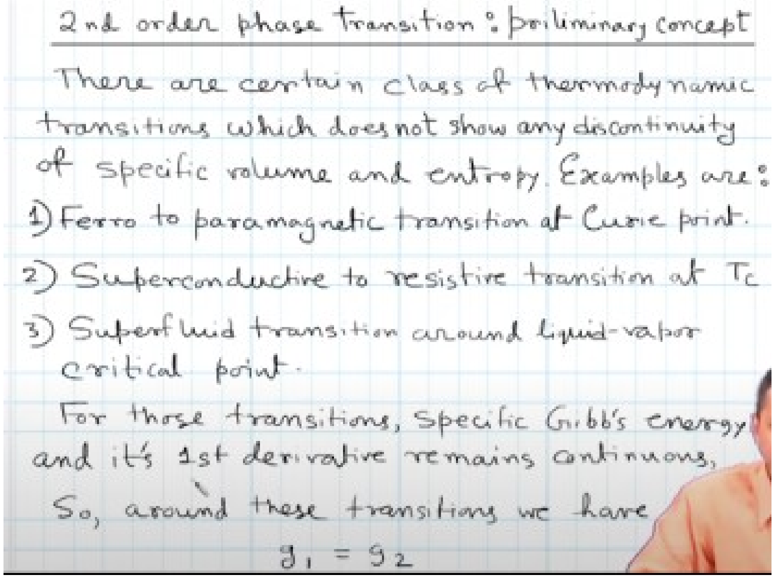

2nd order phase transition : priliminary concept

There are certain class of thermodynamic transitions which does not show any discontinuity of specific volume and entropy. Examples are:

1) Ferro to paramagnetic transition at Curie point.
2) Superconductive to resistive transition at $T_c$
3) Superfluid transition around liquid-vapor critical point.

For those transitions, specific Gibb's energy and it's 1st derivative remains continuous,

So, around these transitions we have

$$g_1 = g_2$$

For the last topic of this week's lecture we take second order phase transition and let me tell you why the second order phase transition is necessary at all. So it has been found experimentally there are certain classes of phase transition in thermodynamics. For example Ferro to paramagnetic; transition at Curie point or superconductive to resistive transition at critical point. Or let us say the super fluid transition that takes place around the liquid vapour critical point.

This transition around I mean across this transition the specific Gibb's energy and its first derivatives remain continuous. Now what are these first derivatives we are talking about we are talking about pressure the specific volume and specific entropy. So in a first order phase, transfer typical first order phase transition that we have discussed so far. We have either of specific I mean both of specific volume and specific entropy around this across this phase transition becomes discontinuous. So we have around the phase transition we have g 1 = g 2.

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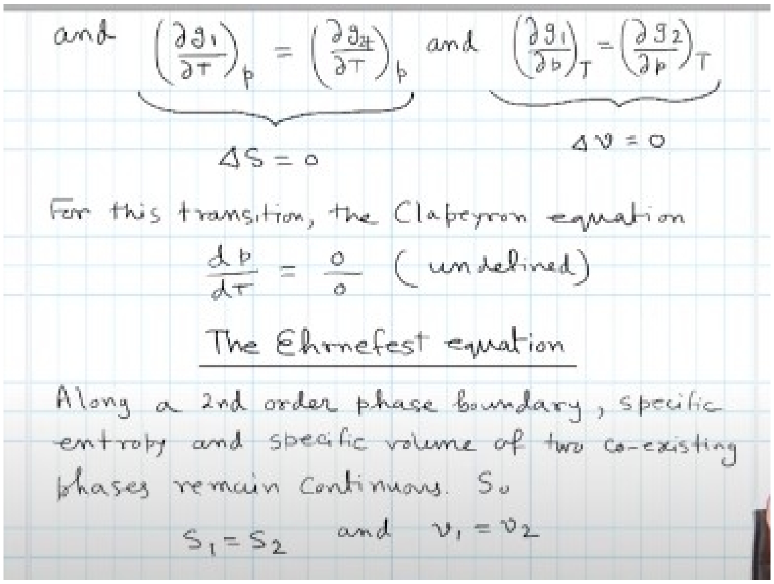

and $\underbrace{\left(\frac{\partial g_1}{\partial T}\right)_p = \left(\frac{\partial g_2}{\partial T}\right)_p}_{\Delta S = 0}$ and $\underbrace{\left(\frac{\partial g_1}{\partial p}\right)_T = \left(\frac{\partial g_2}{\partial p}\right)_T}_{\Delta v = 0}$

For this transition, the Clapeyron equation

$$\frac{dp}{dT} = \frac{0}{0} \quad \text{(undefined)}$$

The Ehrnefest equation

Along a 2nd order phase boundary, specific entropy and specific volume of two co-existing phases remain continuous. So

$$S_1 = S_2 \quad \text{and} \quad v_1 = v_2$$

And now for a for this particular class of transition which we are discussing here we have g 1 = g 2 and del g 1 del Tp is equal to del g 2 it should be 2 actually del g 2 del Tp which means delta S = 0. And del g 1 del pt is equal to del g 2 del pt which means delta v = 0. Now for this, such transition now for a first order transition the Clapeyron equation we have d p d t = delta S by delta v. But in this case it becomes a in a coming into a 0 by 0 form which makes no sense I mean it is not defined then we have to apply some other rule.

So this rule is called the equation that we get is called the Ehrnefest equation. Now along the second order phase boundary specific entropy and specific volume of 2 coexisting phases are equal. So that means S 1 = S 2 and v 1 = v 2. Now this gives you so from this first relation we get d s1 = d S2 similarly dv 1 = d v 2. Please remember we all already have d g1 I mean g 1 = g 2 that means dg 1 = dg 2. And we have applied that property already in order to compute the first order phase the Clapeyron equation in the first latent heat equation.

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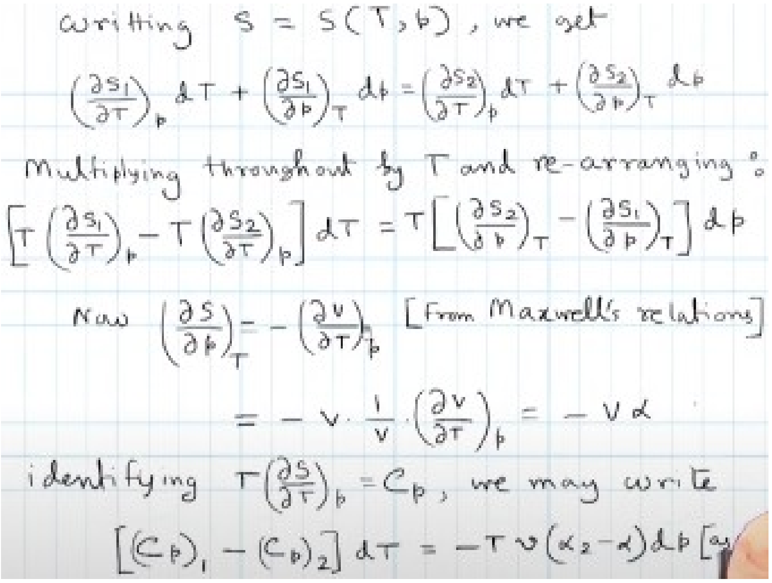

writting $S = S(T, p)$, we get

$$\left(\frac{\partial s_1}{\partial T}\right)_p dT + \left(\frac{\partial s_1}{\partial p}\right)_T dp = \left(\frac{\partial s_2}{\partial T}\right)_p dT + \left(\frac{\partial s_2}{\partial p}\right)_T dp$$

Multiplying throughout by T and re-arranging :

$$\left[T\left(\frac{\partial s_1}{\partial T}\right)_p - T\left(\frac{\partial s_2}{\partial T}\right)_p\right] dT = T\left[\left(\frac{\partial s_2}{\partial p}\right)_T - \left(\frac{\partial s_1}{\partial p}\right)_T\right] dp$$

Now $\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$ [From Maxwell's relations]

$$= -v \cdot \frac{1}{v} \cdot \left(\frac{\partial v}{\partial T}\right)_p = -v\alpha$$

identifying $T\left(\frac{\partial s}{\partial T}\right)_p = C_p$, we may write

$$\left[(C_p)_1 - (C_p)_2\right] dT = -Tv(\alpha_2 - \alpha)\,dp\,[$$

And actually also the second latent heat equation because secondary equation also starts from the, you know the basic equation where dp dT = l by T v 2 - 1 right. So we have d s 1 = d s 2 now writing s is as a function of temperature and pressure. We get d del S 1 del T p dT + del S 1 del p t dT = del s 2 del T p d p + del S 2 del p T dp. D sorry this should be d T my mistake it should be d T right.

Now multiplying both sides by T and rearranging we get t del S 1 del T p - t del S 2 del T p d T = T del S 2 del p T - del S 1 del p T d p. From Maxwell's relation we know s del s del p t = - del v del T p which is equal to - of v times 1 by v del v del T p = - v alpha. And we identify this T del s del T p = c p we can write del p c p 1 - c p 2 times d T = T times v alpha to minus alpha 1 d p which because v 1 = v 2.

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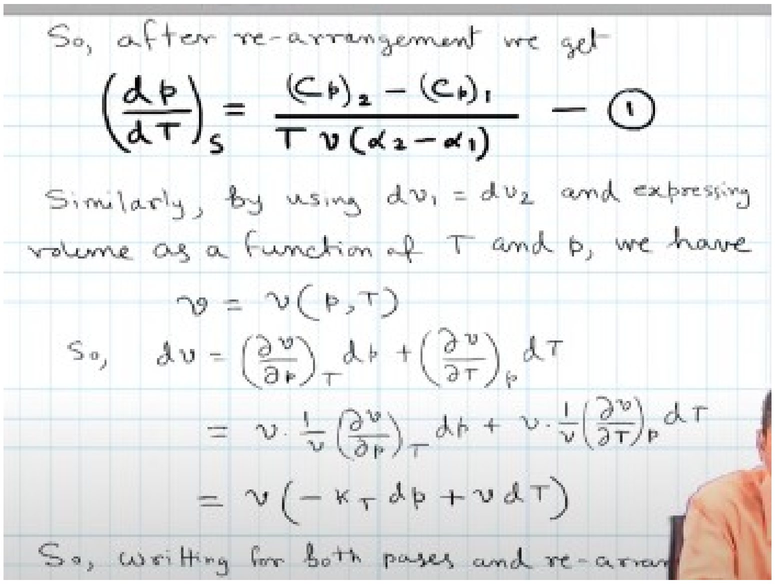

So, after re-arrangement we get

$$\left(\frac{dp}{dT}\right)_S = \frac{(C_p)_2 - (C_p)_1}{T\, v\, (\alpha_2 - \alpha_1)} \quad — ①$$

Similarly, by using $dv_1 = dv_2$ and expressing volume as a function of T and p, we have

$$v = v(p, T)$$

$$\text{So,} \quad dv = \left(\frac{\partial v}{\partial p}\right)_T dp + \left(\frac{\partial v}{\partial T}\right)_p dT$$

$$= v \cdot \frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T dp + v \cdot \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p dT$$

$$= v\left(-\kappa_T\, dp + v\, dT\right)$$

So, writting for both pases and re-arran

Now we can rearrange and get d p d T = c p 2 – c p 1 divided by T v times alpha 2 - alpha 1. Now this S here this is for I mean this is nothing to do, with saturated. This is there because we got this relation from keeping entropies of 2 phases or using the relation d S 1 = d S 2. So this s here is the indication that we got this d p d T relation by entropy.

I mean it could be misleading but just to I mean it is not actually necessary. We can just remove this from here but it is just says entropy of these 2 phases are equal. Similarly by using d v 1 is equal to d v 2. Once again we can write v is equal to v of p and T and from there we can write d v = – v, v times minus k T dp plus v dT. Where k t is the isothermal compressibility so writing for both phases and rearranging we get another relation.

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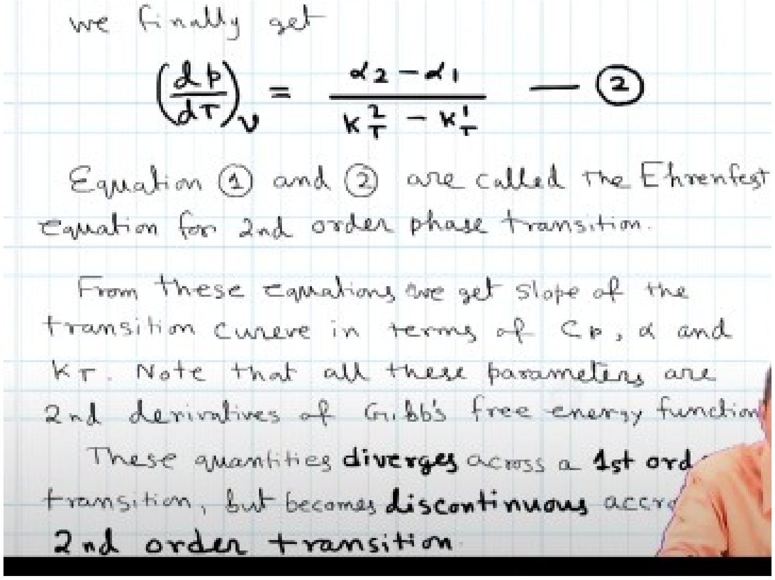

we finally get

$$\left(\frac{dp}{dT}\right)_V = \frac{\alpha_2 - \alpha_1}{k_T^2 - k_T^1} \quad — ②$$

Equation ① and ② are called the Ehrenfest equation for 2nd order phase transition.

From these equations we get slope of the transition curve in terms of Cp, α and $K_T$. Note that all these parameters are 2nd derivatives of Gibb's free energy function

These quantities **diverges** across a **1st ord** transition, but becomes **discontinuous** accr **2nd order transition**

That is this time v remains i mean we use the equality of volume in both phases that dp dt is equal to alpha 2 minus alpha 1 k T square minus k T 1. So these equations are called the Ehrenfest equation and this is the equation that describes the phase boundary of a second order phase transition. Now this, equations we from this equations we see that we get the slope of this transition curve in terms of the quantity.

Like compressibility and expansion coefficient or C p or for example here we get from C p in terms of C p all these quantities these are actually second derivative of the Gibb's free energy. And all this quantity they actually diverge along a first order phase transition. But for the second order phase transition they become discontinuous across a second order phase transition but never diverge.

So the difference of alpha 2 minus alpha 1 or c p 1 minus c p 2 is defined for a second order phase transition which is actually in defined for a first order transition.

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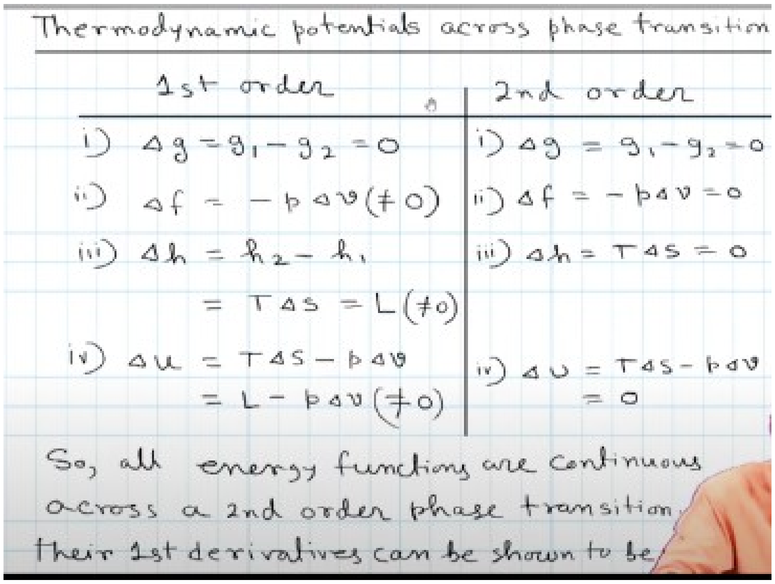

Thermodynamic potentials across phase transition

| 1st order | 2nd order |
|---|---|
| i) $\Delta g = g_1 - g_2 = 0$ | i) $\Delta g = g_1 - g_2 = 0$ |
| ii) $\Delta f = -p\Delta v \ (\neq 0)$ | ii) $\Delta f = -p\Delta v = 0$ |
| iii) $\Delta h = h_2 - h_1$<br>$= T\Delta s = L \ (\neq 0)$ | iii) $\Delta h = T\Delta s = 0$ |
| iv) $\Delta u = T\Delta s - p\Delta v$<br>$= L - p\Delta v \ (\neq 0)$ | iv) $\Delta u = T\Delta s - p\Delta v$<br>$= 0$ |

So, all energy functions are continuous across a 2nd order phase transition, their 1st derivatives can be shown to be

Now so these are the equations we are not going into the details of a second order transition but it will be interesting to see what happens to the other chemical potentials or other thermodynamic potential function. So for first order we see delta g = g 1 – g 2 between the specific energy of two phases which is equal to 0. But delta f is equal to minus p delta v which is not equal to 0 because delta v is not equal to 0.

Delta h is equal to t delta s which is actually l the latent heat which is once again not equal to 0 for a first order transition. And delta u = T d s – p d v that means l minus p delta v which is once again a combination of this and this and definitely not equal to 0. So now when we look at the second order transition we anyway we have d g delta g is equal to 0. But delta f which is p delta v and please remember in a second order phase transition there is no discontinuity in specific volume.

So this is equal to 0 delta h is equal to T delta s which is equal to 0 that means no latent heat involved in a second order phase transition that is a very important result. And delta u is equal to T delta s minus p delta v once again equal to 0. So all the energy functions are continuous across a second order phase transition and also it can be shown that the first derivative of this energy functions are also continuous across the second order phase transition.

Where it shows discontinuity across the first order transition now I am leaving that to you to prove or see whether the first derivatives are of this energy functions are continuous or not. Just to give you a hint you can actually express delta v and delta s in terms of first derivatives of certain energy function. Similarly you can do that and that will definitely tell you that the first derivative of because delta s is equal to 0 and delta v is equal to 0 in a second order transition.

That tells you the first derivatives of certain energy functions must be continuous across the second order phase transition. So that concludes our discussion on phase transition and we have learned about certain aspects of we focus primarily on first order phase transition but also we have discussed in brief the second order phase transition. The most important result for second order phase transition is probably what we have discussed is there is no latent heat involved in here.

And also we have seen what happens to the thermodynamic potentials across a first order and a second order phase transition. So that concludes this week's lecture next week we will be focusing primarily on you know that is the last week of the lecture series and we will be primarily focusing on the radiation till then thank you.