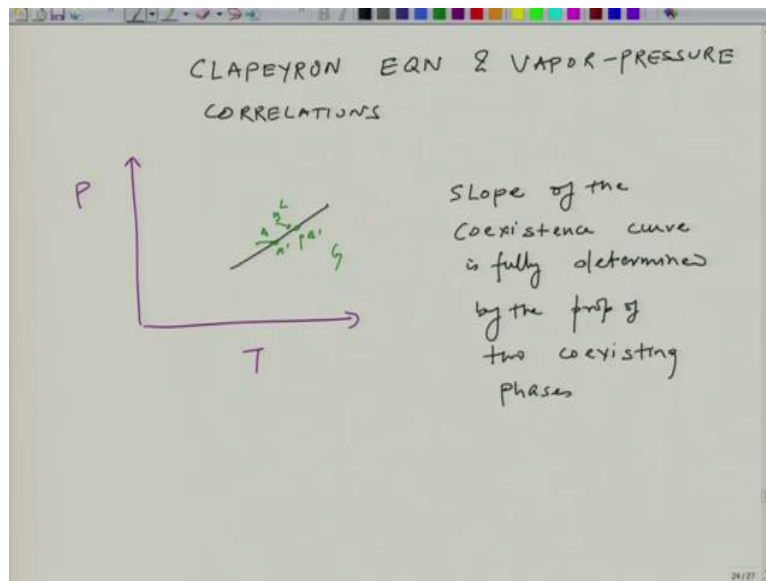


**Chemical Engineering Thermodynamics**  
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**Department of Chemical Engineering,**  
**Indian Institute of Technology, Kanpur**  
**Lecture 29**

**Clapeyron Equations and Vapor Pressure Correlations**

Welcome back. In today's lecture we are going to look at Clapeyron Equation and Vapor Pressure Correlations, okay.

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So, we will start with the PT diagram and I am only going to draw the vaporization line. So, essentially I will just draw kind of straight line and here our interest is to consider the equilibrium states, so in this case let us see this is a point where A, you have A from the liquid side and this is gas and A dash from the vapor side. Similarly, you have this B and B dash okay.

Now, this slope here which will come up with this exercise we will show that this slope of the co-existence curve is fully determined by the property of, by the property of the two co-existence phases, okay. So, this is something we want to show. Now, we will start with basic fundamental equation or the conditions or the criteria of co-existence.

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is fully determined  
by the prop of  
two coexisting  
phases

$$\mu_A = \mu_A'$$
$$\text{or } dG_A = dG_A'$$
$$\text{or } dg_A = dg_A'$$
$$\downarrow$$
$$-S_A dT + v_A dp = -S_A' dT + v_A' dp$$
$$\text{or } (S_A' - S_A) dT = (v_A' - v_A) dp$$

So, in this case you will have,

$$\mu_A = \mu_A'$$

$$\text{or, } dG_A = dG_A'$$

$$\text{or, } dg_A = dg_A'$$

Now, from here we can write down the basic equation.

$$-S_A dT + v_A dP = -S_A' dT + v_A' dP$$

$$\text{or, } (S_A' - S_A) dT = (v_A' - v_A) dP$$

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Handwritten derivation on a whiteboard:

$$\text{or } (S_{A'} - S_A) dT = (v_{A'} - v_A) dP$$
$$\left(\frac{dP}{dT}\right)_{\text{coexs}} = \frac{S_{A'} - S_A}{v_{A'} - v_A} = \frac{\Delta S}{\Delta v}$$

Similarly for B, B'

$$g = u + pv - TS$$
$$= h - TS$$
$$\Delta g = \Delta h - T\Delta S \quad \text{at const } T$$

$$\left(\frac{dP}{dT}\right)_{\text{coexs}} = \frac{\hat{S}_A - S_A}{\hat{v}_A - v_A} = \frac{\Delta S}{\Delta v}$$

Similarly, it can be done for B, B'.

Now, let us try to find out what is a delta S because delta S is not that easy to measure and that is why we can represent the delta S in terms of something like delta H. So, let us look at again the definition of g, okay. The g is nothing but U plus P V minus T S or H minus T S so, that means delta g is going to be delta H minus T delta S at constant T, okay at the co-existence condition.

$$g = u + pv - TS = h - TS$$

$$\Delta g = \Delta h - T\Delta s \quad \text{at const } T$$

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The image shows a whiteboard with handwritten mathematical derivations. At the top, the Gibbs free energy  $g$  is defined as  $g = u + pv - TS = h - TS$ . Below this, the change in Gibbs free energy is given as  $\Delta g = \Delta h - T\Delta s$  at constant temperature. For a coexistence state,  $\Delta g = 0$ , which leads to  $\Delta h = T\Delta s$  or  $\Delta s = \frac{\Delta h}{T}$ . Finally, the slope of the coexistence curve is derived as  $\left(\frac{dp}{dT}\right)_{\text{coex}}$  is equal to  $\frac{\Delta h}{T\Delta v}$ , which is also equal to  $\frac{\Delta H}{T\Delta v}$ .

At coexistence,  $\Delta g = 0$  or,  $\Delta h = T\Delta S$


$$\text{or, } \Delta S = \frac{\Delta h}{T}$$

$$\left(\frac{dP}{dT}\right)_{\text{coexis}} = \frac{\Delta h}{T\Delta v} = \frac{\Delta H}{T\Delta v}$$

Here, if you note that these are all molar properties, you can also see in many textbook this you can also be written as or are written as in different textbook in this way, so this underline is indicative of molar property. Now, in this particular expression which is called Clapeyron equation, is there any approximation?

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CORRELATIONS



Slope of the coexistence curve is fully determined by the properties of two coexisting phases

$$\mu_A = \mu_{A'}$$

$$\text{or } d\mu_A = d\mu_{A'}$$

$$\text{or } dg_A = dg_{A'}$$

$$\downarrow$$

$$-s_A dT + v_A dp = -s_{A'} dT + v_{A'} dp$$

Phases

$$\mu_A = \mu_{A'}$$

$$\text{or } d\mu_A = d\mu_{A'}$$

$$\text{or } dg_A = dg_{A'}$$

$$\downarrow$$

$$-s_A dT + v_A dp = -s_{A'} dT + v_{A'} dp$$

$$\text{or } (s_{A'} - s_A) dT = (v_{A'} - v_A) dp$$


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$$\left( \frac{dp}{dT} \right)_{\text{coex}} = \frac{s_{A'} - s_A}{v_{A'} - v_A} = \frac{\Delta S}{\Delta V}$$

$$\left( \frac{dp}{dT} \right)_{\text{coex}} = \frac{s_{A'} - s_A}{v_{A'} - v_A} = \frac{\Delta S}{\Delta V}$$

Similarly for B, B'

$$g = u + pV - TS$$

$$= h - TS$$

$$\Delta g = \Delta h - T\Delta S \quad \text{at const } T$$

At coexist  $\Delta g = 0 \Rightarrow \Delta h = T\Delta S$

$$\text{or } \Delta S = \frac{\Delta h}{T}$$

$$\left(\frac{dp}{dT}\right)_{\text{coex}} = \frac{\Delta H}{T\Delta V} = \frac{\Delta H}{T\Delta V}$$

CLAPYRON EQN

- is exact
- valid for coexis between phases of any type

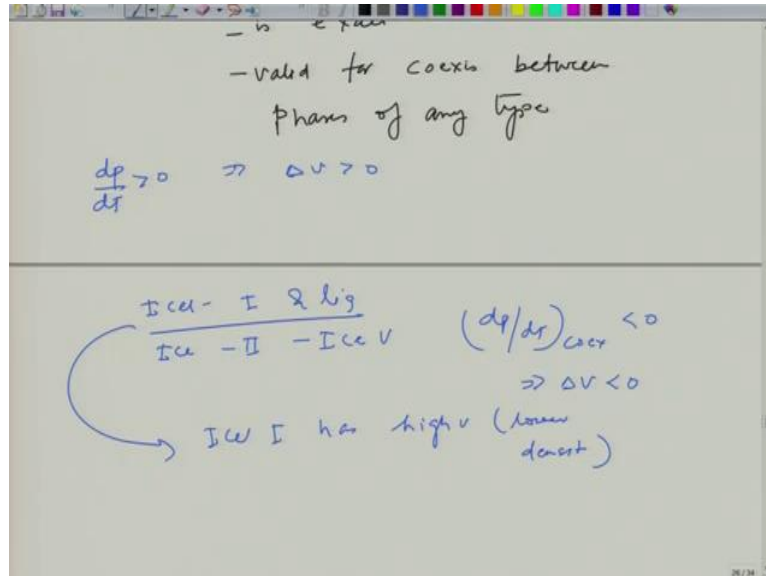
$$\frac{dp}{dT} > 0 \Rightarrow \Delta V > 0$$

So, if you look at it from basic definition, we started with a condition of equality and then we written the expression, thermodynamic expression, we rearrange this thing and then we took the expression of  $g$  again consider that for a constant  $H$  which is the condition of the co-existence and put the condition that is of course  $\Delta g$  is going to be zero for co-existence and then we obtain  $\Delta A$ .

So, this expression is exact, okay that means there is no approximation, okay. And the other question is that, is it only valid for vapor liquid phase? Though I have drawn it for vaporization line but in principle, if you look at it from this expression, this is invariant to any specific combination of the phases. So, this it is true for any or valid for, for co-existence between phases of any type.

So now, given this now, we can start building of other, so now also we may add on to the information that most of the time you will find that  $D P$  by  $D T$  is greater than 0. This is something which you going to find it, okay. For most of the phase transitions, in that case is indicating the  $\Delta V$  is greater than 0, okay because  $\Delta H$  is a latent heat and essentially this would be your always positive or in general this would be positive.

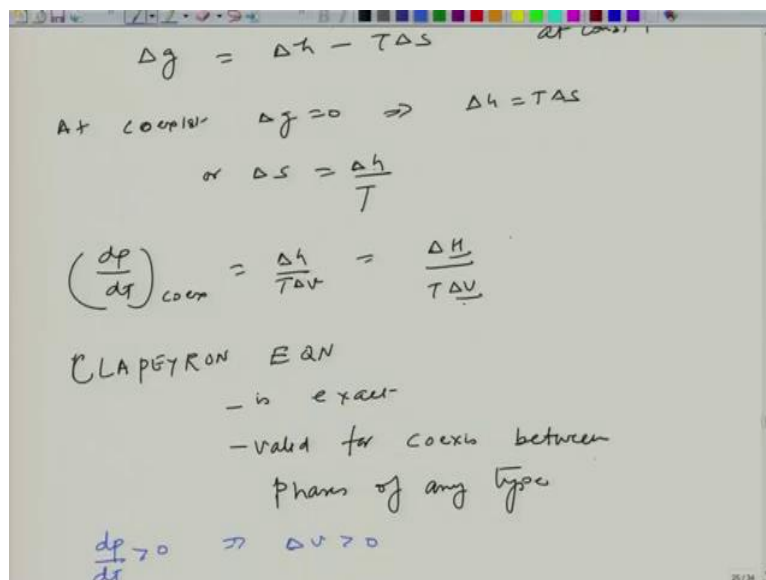
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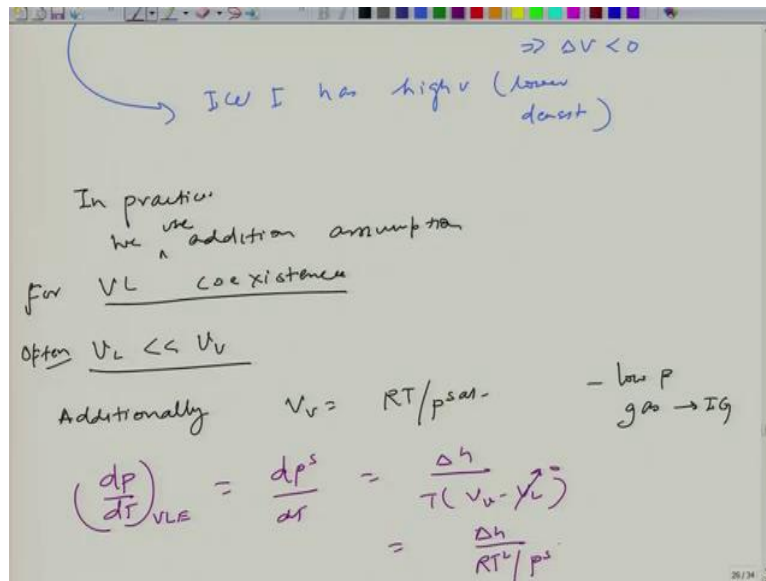
But in the case of specific phases such as ice 1 and liquid or ice 2 and ice 5, you will see that D P by D T co-existence is less than 0. This indicate delta V has to be less than 0 okay.

So, for the case of this you know already ice 1 which we see at the atmospheric pressure that you know ice 1 has higher volume or lower density, right? So that is something which we know for the case of water.

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$$\frac{dP}{dT} > 0 \text{ or, } \Delta v > 0$$



Now, this particular expression is practically not often used, okay. For practical cases we make use of some approximation. So, in practice we make use of some kind of additional views, additional assumptions or in this case assumptions, so consider vapor liquid coexistence, okay. So, for vapor liquid co-existence we know that the volume of liquid is extremely small compared to the volume of vapor.

Often,  $v_L \ll v_v$

Additionally,  $v_v = \frac{RT}{p^{sat}}$  (low P, ideal gas)

$$\left(\frac{dP}{dT}\right)_{VLE} = \frac{dP^s}{dT} = \frac{\Delta h}{T(v_v - v_L)} = \frac{\Delta h}{\frac{RT^2}{p^s}}$$



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for VL Coe Exon

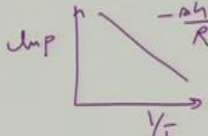
Often  $V_L \ll V_V$

Additionally  $V_V = RT/p^{sat}$  - low P  $g \rightarrow IG$

$$\left(\frac{dp}{dT}\right)_{VLE} = \frac{dp^s}{dT} = \frac{\Delta h}{T(V_V - V_L)}$$

$$= \frac{\Delta h}{RT^2/p^s}$$

$$\frac{dp^s}{d(1/T)} = -\frac{\Delta h}{R}$$

Imp 

CLAUSIUS - CLAPEYRON EQN

$$\frac{dP^s}{d\left(\frac{1}{T}\right)} = -\frac{\Delta h}{R}$$

So this is the Clausius Clapeyron Equation. So the major expect or the key expect of this equation is the following that if you plot LN P by 1 by T, we are going to get a straight line, right? with a slope minus delta H by R. So, this is a popular equations and most of the experimental data thus for fit into such a kind of Clapeyron Clausius Equation but there is usually the some kind of deviation.

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Deviation 7% - 20%

An empirical modification of the clausius - Clapeyron eq known as Antoine eq is used

$$\log_{10} p^s = a - \frac{b}{T+c}$$

$a, b, c$  are empirical parameters to rep. p. data over T range.

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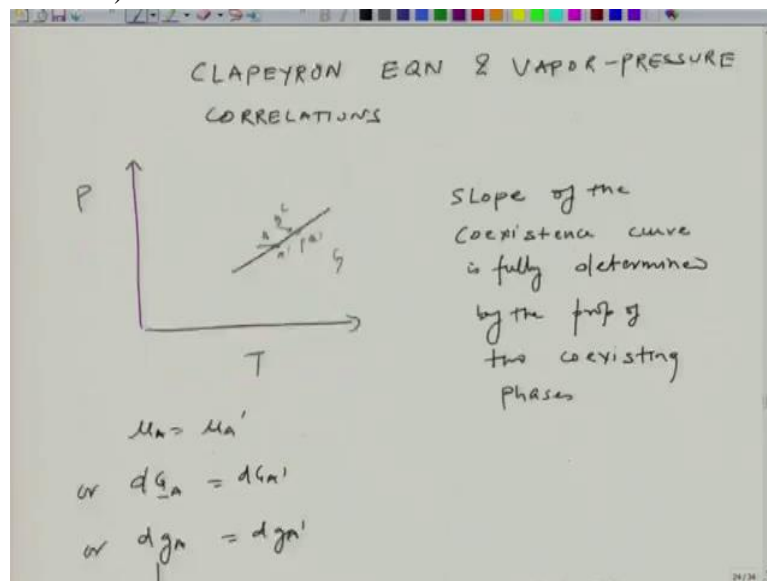
So, deviation from this expression can range from 7 percent to 20 percent but most of the common experimental, common gases and common fluids can be modelled through this Clausius Clapeyron Equation for the V L E part. So, if you want further, if you want to enhance the accuracy and then there has be some work to do that, where the data, experimental data has been fit, fitted to obtain much better level of accuracy.

So, in that case an empirical modification of the Clausius Clapeyron relation has been developed or empirical modified Clausius Clapeyron Equation is often called Antoine Equation.

$$\log_{10} p^s = a - \frac{b}{T + c}$$

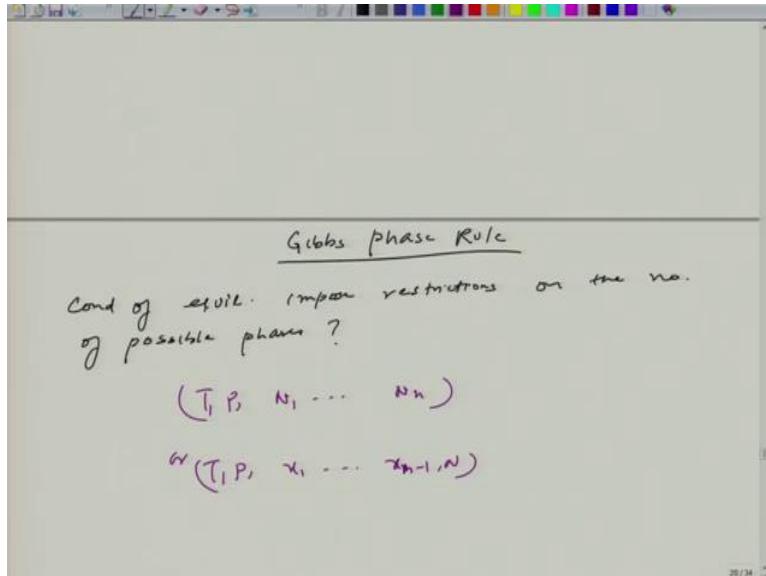
Now, you will find these set of equations or a, b, c's from N I S T data which has fitted this kind of these equations to variety of different gases and different fluids and thus these information is widely available.

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So, that is which something which I wanted to cover as well as Clapeyron Equation and Vapor-Pressure Correlations are concerned. Now, I can take it forward to and try to develop a Gibbs phase rule, okay and so, this is phase rule which provides constraints conditions of equilibrium in terms of number of variables for a given set of phases.

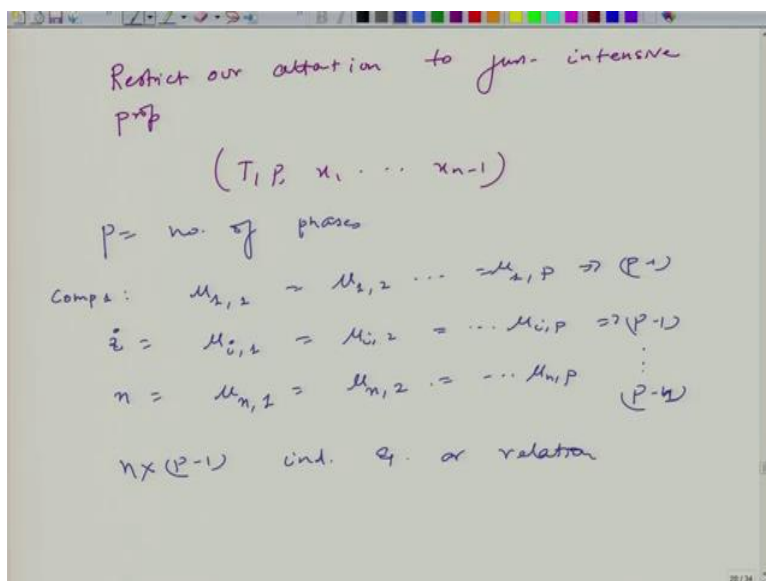
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So, Gibbs Phase Rule is the condition of equilibrium impose restriction on the number of possible phases. So, a Gibbs phase rule talks about that for a given set of phases to have equilibrium what are the number variables which we must have it. So, the question is now, does the condition of equilibrium impose restrictions on a number of possible phases? So, do we have some control on the number of possible phases for to have an equilibrium?

So, let us try to understand this okay, this set of questions. So, consider that you have N component system and the information we have is  $N_1, N_n$  or we can write this as  $X_1, X_n$  minus 1, N number of moles okay.

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*Intensive properties,  $(T, p, x_1, \dots, x_{n-1})$   $p = \text{number of phases}$*

These are independent intensive variable, okay and now what we can do is, we can ask the question, what is a condition of equilibrium for let us say component one? So, we know the condition of equilibrium is of course the temperature has to be same, the pressure but let us focus now on chemical potential because we are keeping temperature same.

So, essentially, we are not bothered by that. So, the chemical potential of component 1 in phase 1 should be equal to chemical potential of component 1 in phase 2 and should be equal to chemical potential of component 1 in phase P.

Similarly, for the  $i$ th component, you should have component  $i$  phase 1, component  $i$  should be equal to phase 2 and so forth the chemical potential component  $i$  in phase P should be equal to the other (comp) other chemical potential and similarly for component  $n$ , chemical potential of  $n$  in phase 1 should be equal to chemical potential of component  $n$  in phase 2 and so forth, okay.

So, if you look at it the number of independent relation equation here, would be  $P$  minus 1 similarly, here also  $P$  minus 1, here also  $P$  minus 1. So, the total number of independent relation would be  $n$  times  $P$  minus 1. This would be independent equation or relation, okay.

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Handwritten notes on a whiteboard:

$$\mu_{n,1} = \mu_{n,2} = \dots = \mu_{n,P} \quad (P-1)$$

$n \times (P-1)$  ind. eq. or relation

No. of variables?

---


$$\mu_{1,1} = \mu_{1,1}(T, P, x_{1,1}, x_{2,1}, \dots, x_{n-1,1})$$

$$\mu_{1,2} = \mu_{1,2}(T, P, x_{1,2}, \dots, x_{n-1,2})$$

$$\mu_{1,3} = \mu_{1,3}(T, P, x_{1,3}, x_{2,3}, \dots, x_{n-1,3})$$

$$\vdots$$

$$\mu_{n,P} = \mu_{n,P}(T, P, x_{1,P}, x_{2,P}, \dots, x_{n-1,P})$$

Now, what about the number of variables? So, let us look at this, so number of variable for the case of let say chemical potential 1 in phase 1 this would be a function of  $T$ ,  $P$  and all composition is phase 1, so this will be your  $X_{1,1}$ , component 2 in one and similarly, component  $n$  minus 1 is 1 because component  $n$  comma 1 would be dependent on the rest of this. So, do

you have these independent variables for this or this chemical potential depends on these particular variables.

Similarly, I will have  $\mu_n$  in 1 should also be  $\mu_n$  in one, T, P1, X1 to 1 and Xn minus 1, 1 okay. So, this is the nth component one should also function of this. Similarly, I can write this  $\mu_1$  in 2 should be  $\mu_1$  in 2 that is the chemical potential of component 1 in the phase 2 is a function of T P then you have this chemical (potential) composition of 1 in 2, composition of 2 in 2 and so forth. Composition of n minus 1 in 2 that is phase 2 and so forth I can keep writing it and this is component n in phase P this would be your function of T, P, X of 1 in P, X of 2 in P and so forth.

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$$2 + (n-1) \times P = \text{no. total variables}$$

$$\text{Dof} = \text{Total no. of variable} - \text{no. of constraints}$$

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

So, this way, how many variables intensive independent or how many total number of variables are there? T P is common, so we have 2 plus this is n minus 1 variable, okay and this we can multiply by because this is a common for just 1 phase okay and similarly, you will have P phases this will lead to these many variables plus the 2, so these are the number of total variables.

So, remember this 1 to n will have the same set of variables, so this will be common hence for just one phase you have this n minus 1 variable plus 2, okay. For the second phase of course T P is already taken into account hence the remaining is n minus 1 variable and so forth and hence you will have these many number of variables which are compositions plus the temperature and pressure.

So, let us define the degree of freedom okay the degree of freedom that means the number of variables which you have to impose to find out the conditions of the phases would be the total number of variables minus number of constraints or the independent relations which we have obtained. So, this way we will be having 2 plus n minus 1 P minus n times P minus 1.

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$p = \text{no. of phases}$   
 Comp:  $\mu_{1,2} = \mu_{2,2} = \dots = \mu_{1,p} \rightarrow (P-1)$   
 $i = \mu_{i,1} = \mu_{i,2} = \dots = \mu_{i,p} \rightarrow (P-1)$   
 $n = \mu_{n,1} = \mu_{n,2} = \dots = \mu_{n,p} \rightarrow (P-1)$   
 $n \times (P-1)$  ind. eq. or relation  
No. of variable?  
 $\mu_{1,2} = \mu_{1,1} (T, P, x_{1,1}, x_{2,1}, \dots, x_{n,1}) ?$

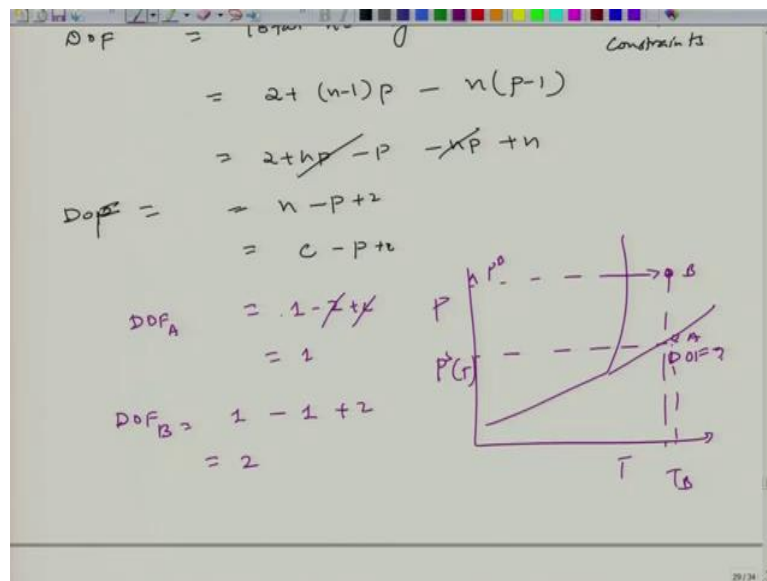
So, n times P minus one came from this relation, independent equations of relations which was nothing but the constraints, the equality constraints.

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$2 + (n-1) \times P = \text{no. total variable}$   
 $Dof = \text{Total no. of variable} - \text{no. of constraints}$   
 $= 2 + (n-1)P - n(P-1)$   
 $= 2 + nP - P - nP + n$   
 $Dof = n - P + 2$   
 $= C - P + 2$

So, this gives us the information 2 plus n P minus P minus n P plus n. So is n minus P plus 2 this is your degree of freedom, okay. Sometimes, we also write is like C minus P plus 2 where C is the component. So, here n is a number of component. So, what it did tells? It tells you that if you have a system such as a vapor liquid, okay.

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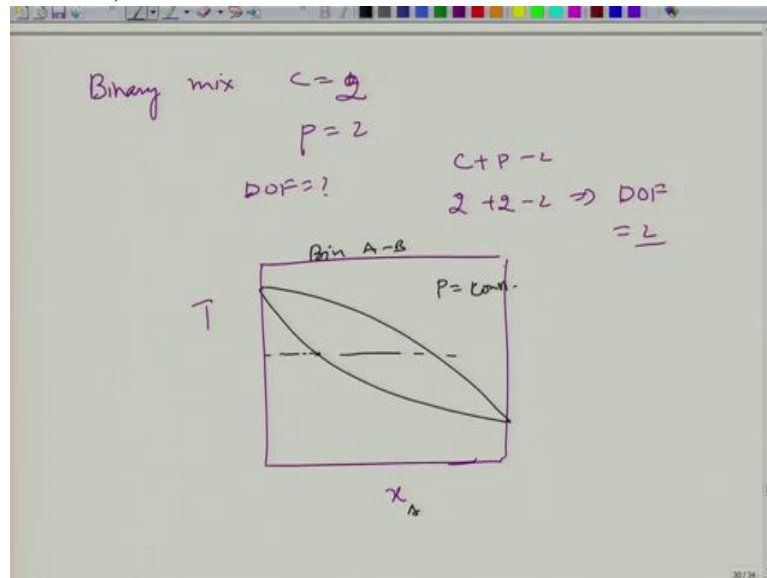
So, these are pure system but this is if you are looking at only the saturation lines so let us say this is a co-existence line for vapor liquid then what would be the degree of freedom in such case?

In such case for the pure component is 1 for let us say A would be 1 minus their 2 phases 2 plus 2 that is 1. So, that means the only 1 variable is independent. So, once you fix P okay so you fix P automatically, T is fix. So, for a given P sat there is a specific T or T sat, okay.

Similarly, that will be the case for the solid liquid co-existence line, that will be case of the vapor solid coexistence line, right? So, degree of freedom will always be 1 in such case. What about here B? So, in this case degree of freedom B is going to be again for the pure phase is 1 the number of phases, well there is only 1 phase, 1 plus 2. So there is 2, the degree of freedom for the case of B is 2.

It means that well, in order to find out the state B you need to define P but also you need to define a specific temperature and that is corresponding to this, okay. So, you need to define T of B and P of B so once you define it you obtain this specific set. On the other hand, saturation line once you define P, you automatically have fixed it because (you) this is the P of the saturation, okay. So, that means a corresponding T is fixed.

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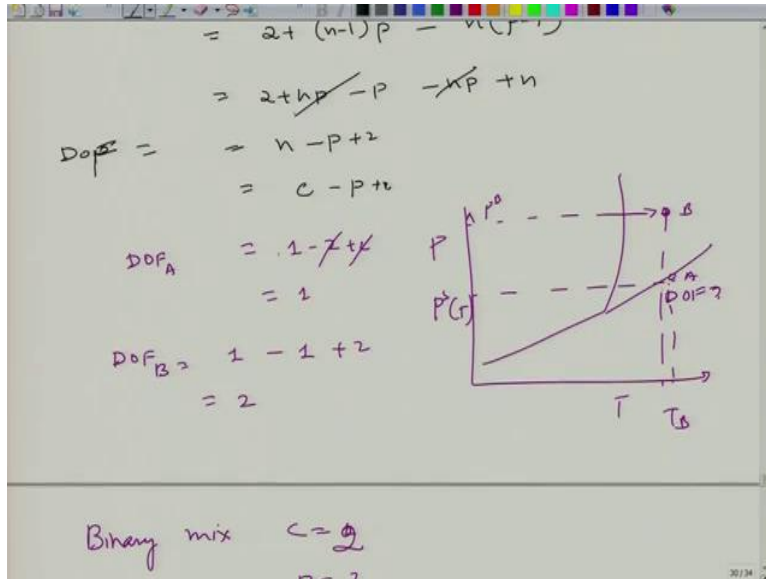
So, if you consider now a different case. In this case let us say you have temperature is a binary mixture. If it is a binary mixture, that means the C is 1, sorry C is 2, C or N the number of components and let us consider again a 2 phase system so that means the P is pressure, sorry that means the P is 2, so what would be the degree of freedom D O F is? Okay.

So, if you look at that equation Gibbs phase rule, it says C plus P minus 2, C is 2, P is 2 minus 2 this means degree of freedom is 2. So, you need to define 2 variables in binary mixtures, so this, it can be represented in the following way. So, this is a T X diagram for a given P, P is constant, okay. And now this is for a binary mixture let us say A, B and this could be composition of A.

So, in order to find out the specific state you have to define not only T but also because this can have many composition, so you have to define not only T but as well as specific composition in order to find out the specific state, okay.

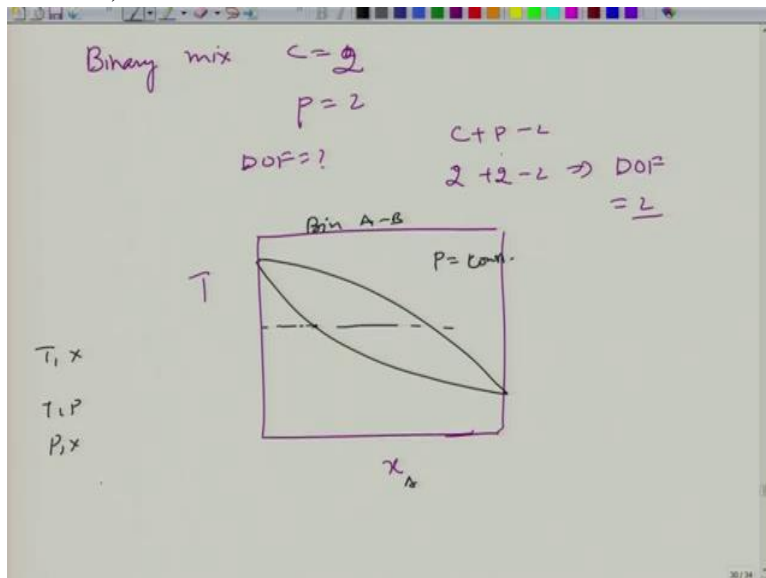


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So, in this case, this is completely different from the one where you just fixed your temperature and you obtain your temperature independent variable on a co-existence line but in this case where your binary mixtures you have 2 independent variables okay.

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So, either it could be T, X, so it could be T X, it could be T, P okay it could be P, X so these are independent variables for the binary mixtures, okay.

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$$\mu_{1,2} = \mu_{1,2}(T, P, x_{1,2}, x_{2,2}, \dots, x_{n-1,2})$$

$$\vdots$$

$$\mu_{n,p} = \mu_{n,p}(T, P, x_{1,p}, x_{2,p}, \dots, x_{n-1,p})$$

$$2 + \underbrace{(n-1) \times p}_{\text{no. total variables}} = \text{no. total variables}$$

$$\text{Dof} = \text{Total no. of variable} - \text{no. of constraints}$$

$$= 2 + (n-1)p - n(p-1)$$

$$= 2 + \cancel{np} - p - \cancel{np} + n$$

$$\text{Dof} = n - p + 2$$

$$= C - P + 2$$

$p^{\circ} \rightarrow p, \beta$

So, I think this point I can stop, so in the next lecture I would be starting new set of topic it will be based on equation of state and particularly intermolecular interactions. So, this understanding what we have done in today's lecture, in the previous lectures we have used a Maxwell relations and once we understand equation of state then we can come up with a derivative expressions of those and plug in to the, to the, to the expressions which we have developed in order to find out the change in the variables such as delta U or delta H, so I will be illustrating those examples.

So, next lecture will get little bit inside of the equation of state and basically how it is being developed and what are the key parameters in those equation of states, okay. So, I will see you in the next class.