Thermodynamics of Fluid Phase Equilibria
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Lecture – 18
Thermodynamics of Phase Equilibrium

In this lecture, we are going to start a new topic basically thermodynamics or phase equilibria that itself is a topic. So, we will start summarize what we have gone through last few lectures.

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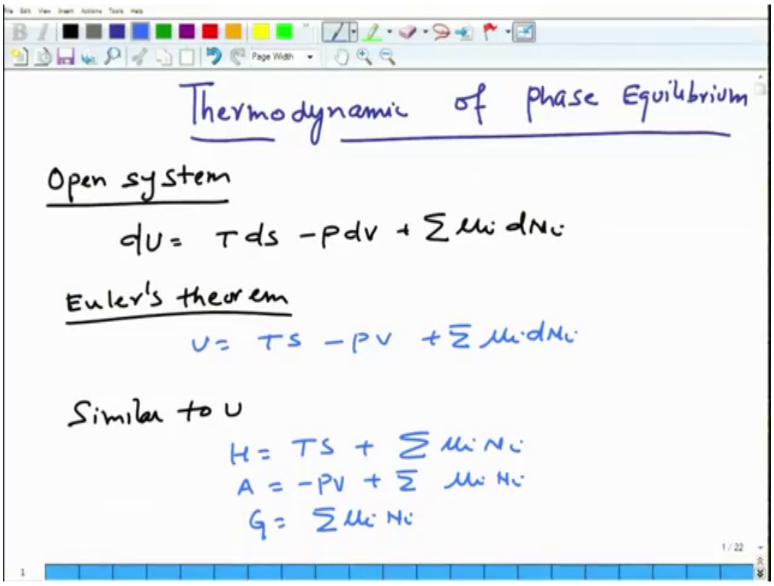

Thermodynamic of phase Equilibrium

Open system

$$dU = Tds - pdv + \sum \mu_i dN_i$$

Euler's theorem

$$U = TS - PV + \sum \mu_i dN_i$$

Similar to U

$$H = TS + \sum \mu_i N_i$$
$$A = -PV + \sum \mu_i N_i$$
$$G = \sum \mu_i N_i$$

We have discussed that for an open system that the differential form of U can be written as T ds minus P dv plus summation of mu i d N i. So, this is for an equilibrium system ok.

And we also know from the Euler's theorem that U is equal to T S minus P V plus summation mu i d mu i; this should be N i ok. So, what we have done is basically we have integrated this and using the extensive property, we got this expression similar to U; you can show that H is also T S plus summation mu i N i; A is also minus P V plus summation mu i an i and G is summation mu i n i. So, that is what we know that ok.

Now, making use of this and as well as the differential equation; what you can do our differential expression of the potentials, what we can do is we can come up with an expression calls Gibbs Duhem equation; equation or relation.

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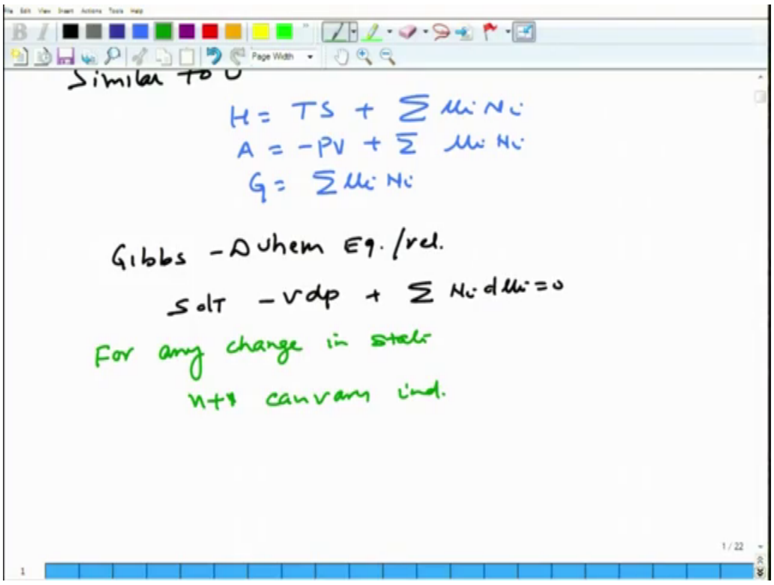

Similar to U

$H = TS + \sum \mu_i N_i$

$A = -PV + \sum \mu_i N_i$

$G = \sum \mu_i N_i$

Gibbs -Duhem Eq./rel.

$S\,dT - V\,dp + \sum N_i\,d\mu_i = 0$

For any change in state

n+1 can vary ind.

So, what it does? It gives you a constraint between intensive variables ok. So, it tells you that considering that this is a constraint and you can obtain from either of this either of the potential function ok.

So, it tells you that there n plus 2 for any change in state you need n plus 2 variable intensive variable, but only n plus 1 can vary independently ok. Now what we are going to do is; we are going to apply this to the equilibrium conditions. Let us just consider that you have a phase many phases can be considered at equilibrium ok.

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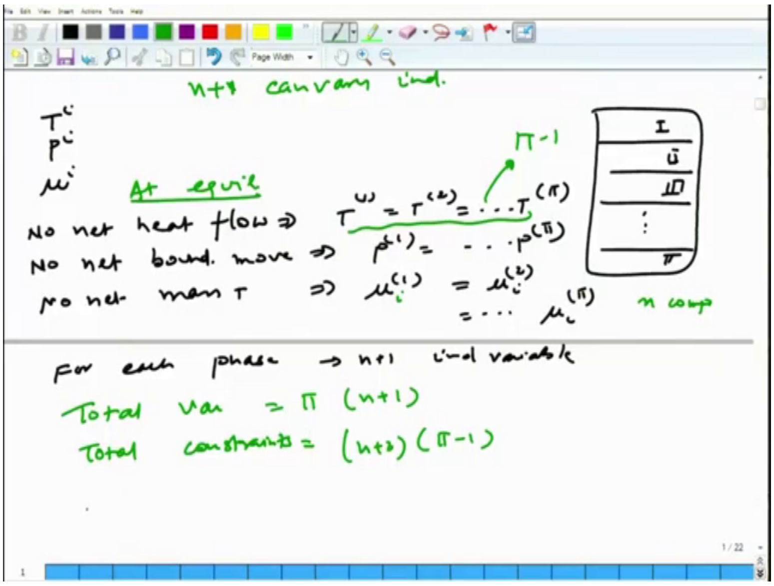

n+1 can vary ind.

T^i

P^i

μ^i

At equi.

No net heat flow $\Rightarrow$ $\underbrace{T^{(1)} = T^{(2)} = \cdots T^{(\pi)}}$ $\Pi - 1$

No net bound. move $\Rightarrow$ $p^{(1)} = \cdots p^{(\Pi)}$

No net mass T $\Rightarrow$ $\mu_i^{(1)} = \mu_i^{(2)} = \cdots \mu_i^{(\Pi)}$ n comp

For each phase $\rightarrow$ n+1 ind variable

Total var = $\Pi\,(n+1)$

Total constraints = $(n+2)(\Pi-1)$

So, you can have phase I phase II phase III and so, forth and phase pi ok. So, there could be this many because there is no condition of that maximum number is limited to 2 or 3 as far as the equilibrium phases are concerned, you can consider let us say arbitrary pi phases which are at equilibrium.

But considering the thermal mechanical and chemical equilibrium that for each phases; if I consider that say T i is the temperature of the phase i; P i for a pressure of the phase i and mu i , then at equilibrium what are the conditions? There is no net heat flow ok; there is no net movement of the boundary and there is no net mass exchange.

So, no net heat flow would tend to give us this condition that T 1 is equal to T 2 and this is same as T of pi no net boundary movement would give us P 1 P pi known that mass transfer would give us V 1 o; instead of this we need to also define because there i; if they are let us say n component right.

Then you have to define mu i in phase I that should be same as mu 2 in phase II; mu i in phase II and that should be same as mu i in phase, but ok. So, this is the condition we have; now if you want to find out the number of variables, which you can independently vary that is what we call the degree of freedom, then we can make use of this equation. So, how many conditions of the constraints we have been put here for the equilibrium? If they are pi phases, then they are pi minus 1 equation T 1 independent equation T 1 equal to our constraints T 1 is equal to T 2 T 2 is equal to T 3 and so, forth right and they are enters to here number of variables ok.

So, what I can write is for each phase you have n plus 1 independent variable so; that means, the total number of variable is why the n plus 1? Because you have the 1; which is constrained by the Gibbs Duhem equation, so, for each phase you have n plus 1 variable. So, total number of variables are pi multiplied by n plus 1 ok, but these are total number of variables and how many constraints we have?

Constrains that would be; so, if you look at it these equations are pi minus 1 and this number of variables are because. So, this is two temperature pressure is 2 and this i is n ok; that means, n plus 2 multiplied by this constant, this is pi minus 1 for each variable we have pi minus 1 constraint so; that means, total constraints are these. So, degree of freedom is total number of variables minus the number of constraint.

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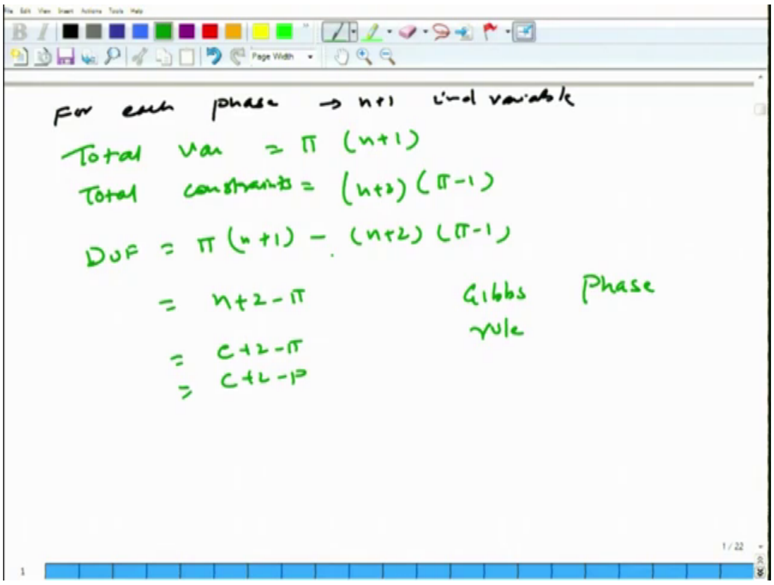

For each phase → n+1 ind variable

Total var = $\pi(n+1)$

Total constraints = $(n+2)(\pi-1)$

$$\text{DoF} = \pi(n+1) - (n+2)(\pi-1)$$

$$= n+2-\pi$$

$$= c+2-\pi$$

$$= c+2-P$$

Gibbs Phase rule

So, this gives you n plus 2 minus pi and n is number of components, someone can also write let us say c plus 2 minus pi or c plus 2 minus P; these are same thing right because this is number of component ok. So, this is what do you call it Gibbs phase rule alright since we have defined this particular expression ok; this is something which was defined using Euler theorem for thermo dynamic function, which was basically all these are extensive functions. We can generalize this by considering arbitrary E as a function which is extensive function.

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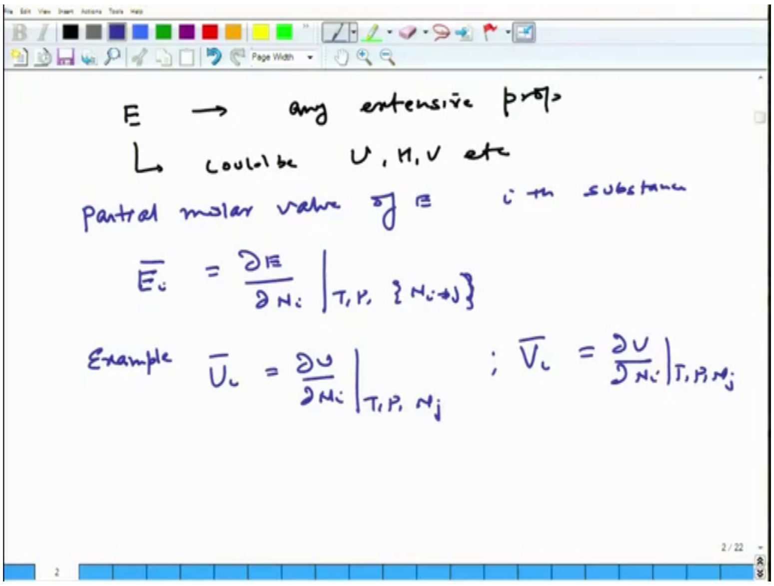

E → any extensive prop

↳ could be U, H, V etc

Partial molar value of E i th substance

$$\bar{E}_i = \frac{\partial E}{\partial N_i}\bigg|_{T,P,\{N_{j\neq i}\}}$$

Example $\bar{U}_i = \frac{\partial U}{\partial N_i}\bigg|_{T,P,N_j}$; $\bar{V}_i = \frac{\partial V}{\partial N_i}\bigg|_{T,P,N_j}$

So, I am trying to now relate this and define something called E which stands for any extensive property ok. So, what I am trying to do is basically connect the chemical potential to partial derivatives of this extensive properties ok. And from there, we would like to get some idea how to get this chemical potential and then we will realize that this is more ambiguous or as difficult to do that. And then we will try to introduce something called fugacity ok.

So, let us consider E V stand for any extensive propertyhe could be anything you; could be E energy U H V etcetera; it could be U H V etcetera. Now I am going to define partial molar value of E let us say for i th substance or ith component in the mixture ok. So, this is the definition is basically partial derivative of E with respect to N i ok; keeping temperature pressure and all other components amount of components fixed; that means, N i is not equal to N j ok.

So, example could be U i which is del U by del N i; T P and for all possible js such as j is not equal to A. Similarly you can also come up with V i ok; so, this is something which you have you already aware of it right. So, what I am trying to do with this definition.

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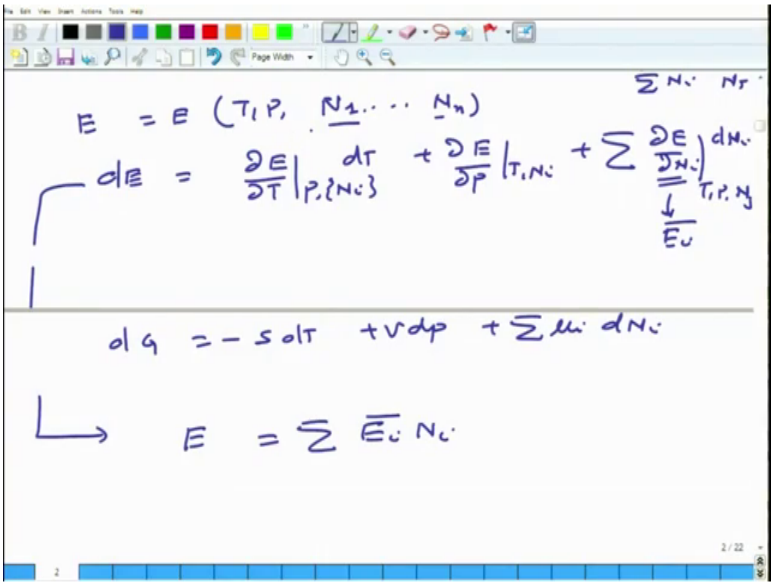
$\sum N_i \quad N_T$

$$E = E(T, P, \underline{N_1} \ldots \underline{N_n})$$

$$dE = \left.\frac{\partial E}{\partial T}\right|_{P,\{N_i\}} dT + \left.\frac{\partial E}{\partial P}\right|_{T,N_i} + \sum \underbrace{\left.\frac{\partial E}{\partial N_i}\right|_{T,P,N_j}}_{\overline{E_i}} dN_i$$

$$dG = -SdT + VdP + \sum \mu_i dN_i$$

$$E = \sum \overline{E_i} N_i$$

Is to write expression E which is a function of T P N 1 till N n and come up with a differential form a general differential form ok.

I will show that that you can also obtain a generic expression what we have got into differential form for other known thermodynamic functions; for any extensive property. Now remember that for total or the molar value or molar properties typically, let us say for small e; we defined as a molar property which is like E divided by total number of moles or E divided by N T ok.

So, I we are going to use small variables to define molar properties ok, where is the partial molar properties are the big symbols with a bar on top of it ok. So, let me just write this a this E which is basically a function of T P. So, let us assume that this is a function of T P and all this moles of different component. So, d E is of course, as we are going to take it as partial derivatives ok.

So, this may be basically all of this right dT plus del E by rho P; T N i plus summation del E by T P and N j such that such that N j such that j is not equal to i ok. Now if you compare this expression to the expression of let us say Gibbs free energy in the differential form ok. So, let us compare this to d G value minus SdT plus vdp plus summation mu i d N i ok.

So, it is more or less it basically if you replace A by G; you get exactly the same expression with the partial derivatives of a del E by del i and i is nothing, but mu i ok. So, now given this you can integrate this and we can obtain a generic expression using the i th (Refer Time: 12:14) as nothing, but E partial molar property of E with respect and multiplied by an N i.

So, this is a very straightforward exercise; this you can do that exactly the same as you have done for getting G is equal to summation mu i N i because here this is nothing, but E i bar ok. So, when you integrate this you get exactly this as the same way as we have done for other cases ok. So, this particular exercise can be done for any extensive variable for, but T i in this case the reason why you are getting this because of the fact that what is the component of the extensive variable.

Because here e is T P N 1 to N and so, here the homogeneous function of only n variables. So, you can do this exercise is something which you must have done in your earlier courses also as I said this is true for any extensive property. So, if you replace E by U this would be your U is equal to summation U i bar N i.

If you replace E by H this is going to be similarly E will be replace by partial molar enthalpy ok. So, in other word I can actually use this information to get U as summation U i.

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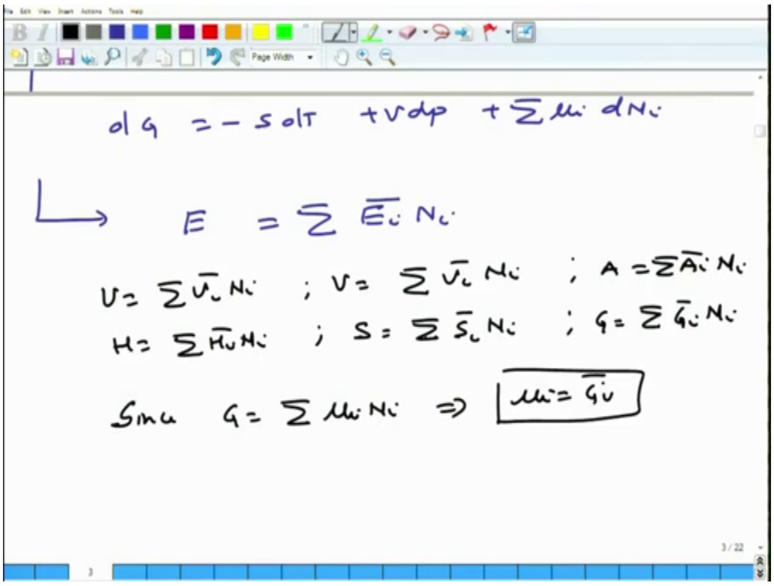

$$dG = -S\,dT + V\,dp + \sum \mu_i\, dN_i$$

$$\hookrightarrow \quad E = \sum \bar{E}_i N_i$$

$$U = \sum \bar{U}_i N_i \; ; \; V = \sum \bar{V}_i N_i \; ; \; A = \sum \bar{A}_i N_i$$

$$H = \sum \bar{H}_i N_i \; ; \; S = \sum \bar{S}_i N_i \; ; \; G = \sum \bar{G}_i N_i$$

Since $G = \sum \mu_i N_i \Rightarrow \boxed{\mu_i = \bar{G}_i}$

N i V S summation V i N i A is summation A i N i. So, we can write now any extensive property as a summation of partial molar property multiplied by the number of moles of that particular component where i or summation is over the number of components it is ok.

Now, since G is summation mu i N i which means basically if you compare this two expression means mu i is G i bar ok. So, chemical potential is nothing, but partial molar Gibbs free energy or space is i ok. So, let me just describe one more thing.

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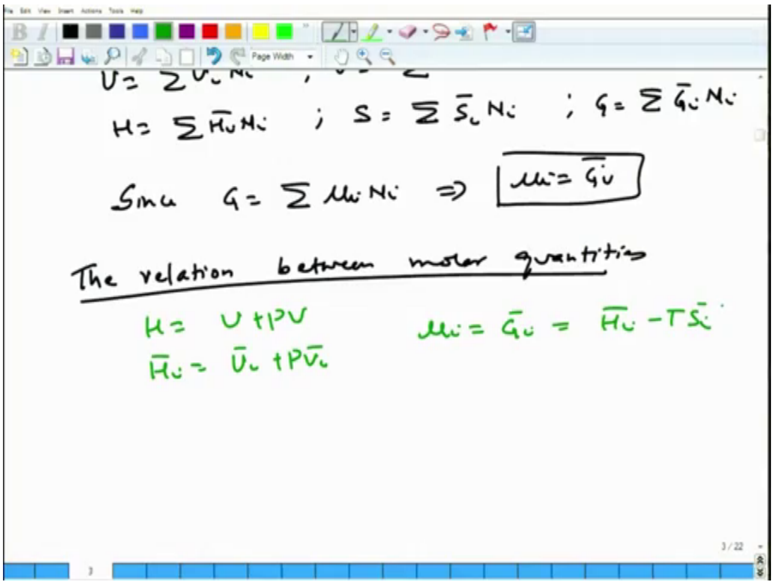

$U = \sum U_i N_i$

$H = \sum \bar{H}_i N_i \; ; \; S = \sum \bar{S}_i N_i \; ; \; G = \sum \bar{G}_i N_i$

Since $G = \sum \mu_i N_i \Rightarrow \boxed{\mu_i = \bar{G}_i}$

The relation between molar quantities

$H = U + PV$

$\bar{H}_i = \bar{U}_i + P\bar{V}_i$

$\mu_i = \bar{G}_i = \bar{H}_i - T\bar{S}_i$

So, there is a relation between this molar quantities you know H is equal to U plus P V.

If you want to write those in the partial molar quantities in the form of that you can simply write H i bar is U i bar plus P V bar similarly you can write mu i which is basically G i bar is nothing, but H i bar minus T S i bar ok. Because G is equal to nothing, but H minus T yes; so, you can write in the same form I can try to exploit this and this is something which I am going to get this expression in of partial derivative of mu in terms of the; so, variables which are experimentally accessible ok.

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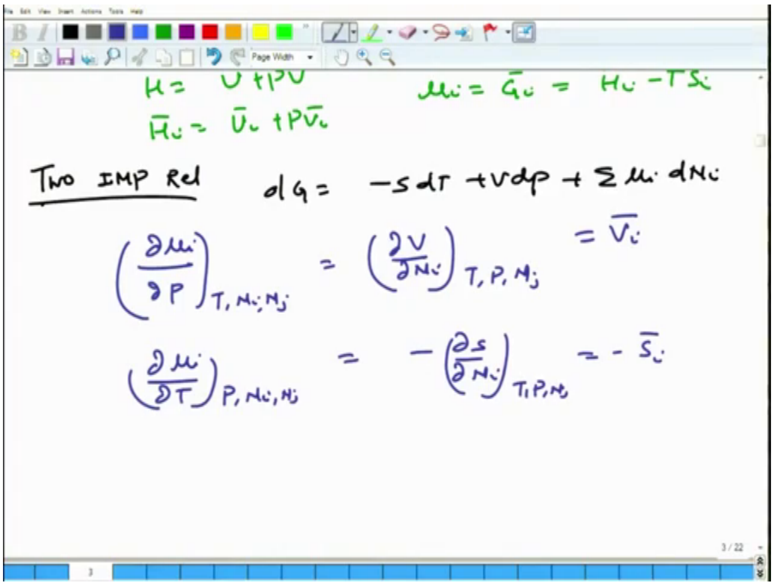

$H = U + PV$

$\bar{H}_i = \bar{U}_i + P\bar{V}_i$

$\mu_i = \bar{G}_i = H_i - T\bar{S}_i$

Two IMP Rel

$dG = -SdT + VdP + \sum \mu_i dN_i$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T, N_i, N_j} = \left(\frac{\partial V}{\partial N_i}\right)_{T, P, N_j} = \bar{V}_i$$

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P, N_i, N_j} = -\left(\frac{\partial S}{\partial N_i}\right)_{T, P, N_j} = -\bar{S}_i$$

So, let me just come up with the two important relation ok. So, let us let me start with d G is equal to minus S dT plus V dP plus summation mu i dNi I can make use of a Maxwell's relation ok. Now I am come up with this expression that del mu i by del P at constant T N i. And all other j this should be equal to del V by del N i temperature pressure and keeping N j constant ok.

So, this is if you look at this expression you can directly get this expression from this Maxwell relations ok; what you are doing is you are you are taking the derivative of this with respect to P keeping temperature constant. And all other constant this should be same as what the if you are keeping N j constants the what remains is basically mu i dNi and that does you should be getting del mu by del P that should be equal to del V by del i Ni.

So, remember this conjugate variable which may try to make use of it now given this expression this is nothing, but V i bar ok. Similarly using the same fundamental equation we can also write ok. So, again using the Maxwell relation; here we are getting this that minus of partial molar entropy of component i is nothing, but the partial derivative of the chemical potential with respect to the temperature ok. And partial molar volume of component i is nothing, but partial differentiation of chemical potential with respect to pressure ok.

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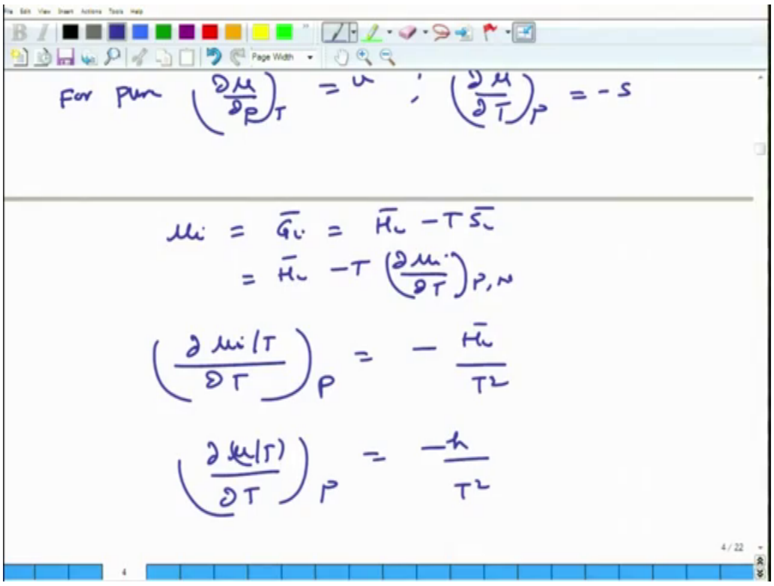

For pure $\left(\frac{\partial \mu}{\partial P}\right)_T = v \; ; \; \left(\frac{\partial \mu}{\partial T}\right)_P = -s$

$$\mu_i = \bar{G}_i = \bar{H}_i - T\bar{S}_i$$

$$= \bar{H}_i - T\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N}$$

$$\left(\frac{\partial \mu_i/T}{\partial T}\right)_P = -\frac{\bar{H}_i}{T^2}$$

$$\left(\frac{\partial \mu/T)}{\partial T}\right)_P = \frac{-h}{T^2}$$

Now, for a pure system of course, you can write this as for pure del mu by del P at T; this is molar volume and del mu by del T at P is minus molar entropy and we are going to use this to expression in the later case. Now let me and this part of this discussion by considering the fact that I can also connect the partial derivative of mu to something which is more measurable ok. So, not just in trophy and how I am going to do that by considering that mu i is nothing, but G i bar is equal to H i minus T S i bar ok.

And now S i bar is this expression this; so, I can write this as H i bar minus T del mu i by del t at P and N constant ok. So, if you rearrange this expression I should be able to derive this in this form minus H i bar by t square ok. For a pure system, this is equivalent to saying that this is nothing, but minus molar property for a pure system right.

Now, in this case whatever what we have done is we have connected the changes in the chemical potential with respect to temperature to something which we can measure enthalpy. Truly speaking this only enthalpy change which we can measure; now this brings to a question about chemical potential ok.

So, stop here and the next part we will continue with the chemical potential and its relation with the fugacity.