Thermodynamics of Fluid Phase Equilibria
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Lecture – 15
Criteria for Phase Equilibria

Welcome back, we will continue our exercise, of deriving thermodynamic relations and making use of thermodynamics calculus. So, we will start with the criteria of equilibrium, in terms of intensive property.

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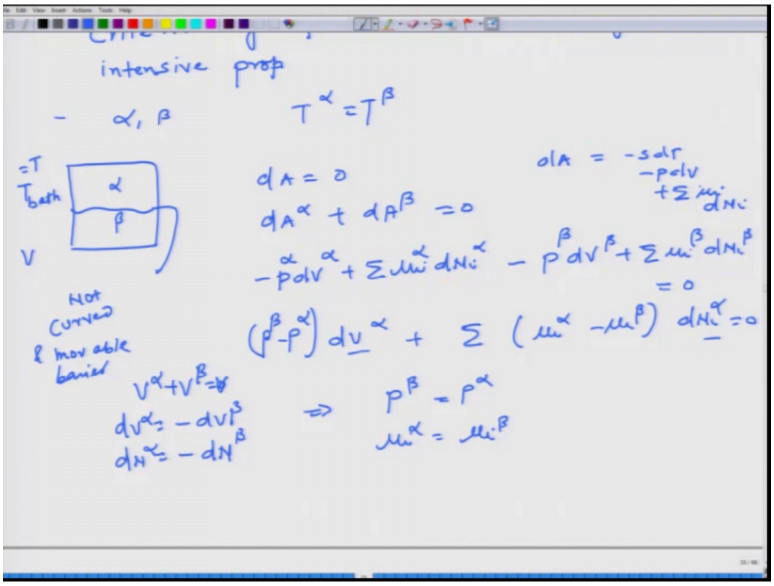

intensive prop

- α, β

$T^\alpha = T^\beta$

$dA = 0$

$dA^\alpha + dA^\beta = 0$

$dA = -SdT - PdV + \Sigma \mu_i dN_i$

$-P^\alpha dV^\alpha + \Sigma \mu_i^\alpha dN_i^\alpha - P^\beta dV^\beta + \Sigma \mu_i^\beta dN_i^\beta = 0$

Not curved & movable barier

$(P^\beta - P^\alpha)\, d\underline{V}^\alpha + \Sigma (\mu_i^\alpha - \mu_i^\beta)\, d\underline{N_i}^\alpha = 0$

$V^\alpha + V^\beta = V$

$dV^\alpha = -dV^\beta$

$dN^\alpha = -dN^\beta$

$\Rightarrow P^\beta = P^\alpha$

$\mu_i^\alpha = \mu_i^\beta$

We are well aware of the 0th law of thermodynamics, ok. And it is basically the property of temperature that, whenever 2 system, let us say, alpha and beta are in thermal equilibrium, then the temperature of that is going to be at equilibrium or will be same.

Now, consider this fluid alpha and beta which is enclosed let us say, enclosed in the rigid container and maintained at a temperature T, ok? So, at equilibrium we know, that considering this rigid the volume is also fixed. So, dA need to be 0; now, dA is being extensive. We can write this as dA alpha plus dB dA beta, this is going to be 0. What is dA? DA is going to be minus SdT in differential form PdV plus summation mu i dNi. So, we can write this for alpha and beta, ok. There is a certain assumption here that, this particular interface is basically movable boundary and it is not curved. So, this is not curved and it is movable barrier ok.

So; that means, you can change the volume of individual component slightly now. So, we going to put this expression. So, this considering the temperature is constant. So, this dA alpha is going to be minus PdV alpha plus summation mu i alpha dNi alpha minus of PdV beta plus summation mu i beta dNi beta ok. And this must be equal to 0.

I can rearrange this expression considering that V alpha plus V beta is constant. All dV alpha is nothing but minus dV beta. Similarly, dN alpha is nothing but minus dN beta. So, doing this, we can also, I am going to put alpha here as well, ok? So, doing this, we can rearrange this expression, we can write dV alpha. This is going to be P beta minus P alpha and this summation of mu i alpha minus mu i beta dNi alpha is equal to 0 ok.

Now, these are independent. And thus, this implies, P beta is equal to P of alpha and mu i alpha is equal to mu beta ok. Now, this implies that the pressure here should be same in this 2 phases; 2 fluids; which I had equilibrium. It also implies that, the chemical potential of a component i in alpha phase should be same as chemical potential of i in beta phase, ok.

So, this is a very simple criteria for equilibrium. So, here we have fixed the temperature of the system and that is why, we just took the second 2 terms ok. Now, let me further try to summarize the mathematical relations which comes out of it all this exercise ok. So, I am going to just write down some identities which are going to be useful.

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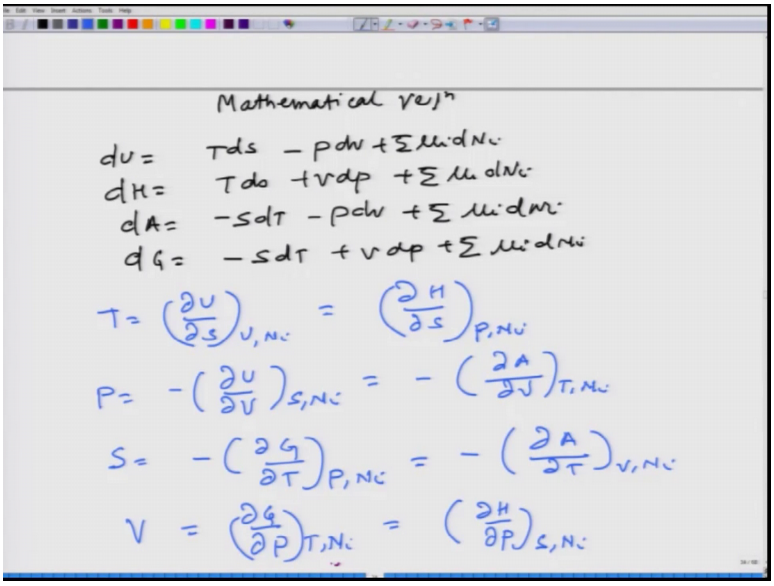

Mathematical relⁿ

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

$dH = Tds + vdp + \sum \mu_i dN_i$

$dA = -sdT - pdv + \sum \mu_i dN_i$

$dG = -sdT + vdp + \sum \mu_i dN_i$

$T = \left(\frac{\partial U}{\partial S}\right)_{V, N_i} = \left(\frac{\partial H}{\partial S}\right)_{P, N_i}$

$P = -\left(\frac{\partial U}{\partial V}\right)_{S, N_i} = -\left(\frac{\partial A}{\partial V}\right)_{T, N_i}$

$S = -\left(\frac{\partial G}{\partial T}\right)_{P, N_i} = -\left(\frac{\partial A}{\partial T}\right)_{V, N_i}$

$V = \left(\frac{\partial G}{\partial P}\right)_{T, N_i} = \left(\frac{\partial H}{\partial P}\right)_{S, N_i}$

So, as we know from the thermodynamic potentials in derivative form, we have dT is equal to TdS minus PdV the summation mu i dNi dH is equal to TdS plus VdP plus summation mu i dNi dA is minus SdT minus PdV plus summation and similarly, dG. Now, what I am going to do is, basically I am going to derive the temperature pressure entropy and volume in terms of the partial derivatives, using these 4 relations thermodynamic potential relations and derivative form.

So, the temperature is going to be here is the temperature to is going to be del U by del S at constant V and Ni. This should be same as del H by del S at constant P and Ni. Similarly, you can obtain pressure P from these 2 equations del U by del V S Ni. This is same as minus of del A by del V T Ni this comes from here ok. This is a partial derivative of del A with respect to V keeping constant temperature and a nice ok.

Similarly, you can get S is minus of del G by del T PNi this is the same as minus of del A by del T keeping V and Ni constant. Similarly, you have G volume. So, volume would be your take it partial derivative of G with respect to P keeping temperature and Ni constant that should be partial derivative of same as partial derivative of S keeping S and Ni constant ok. So, these are the relations, which you can directly obtain from the mathematical thermodynamic functions or this thermodynamic functions which we have derived in derivative form. Now, I can also make use of little bit more exercise and write down some interesting quantities.

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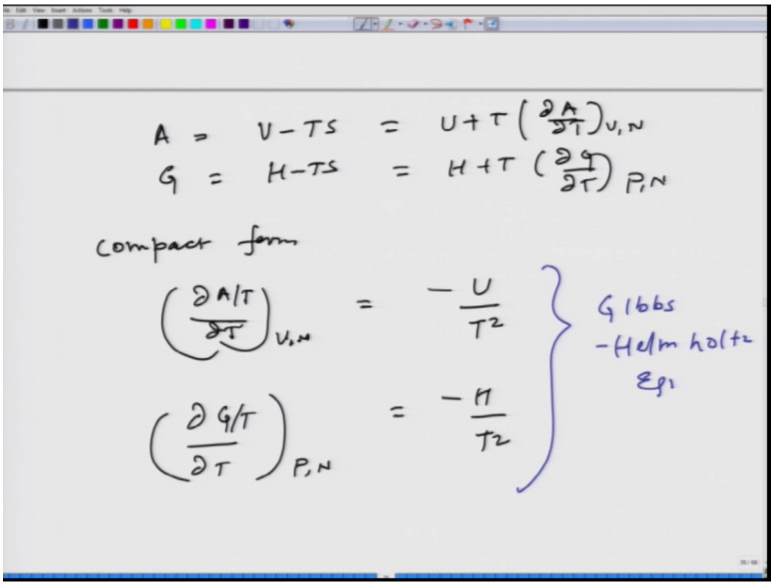

$$A = U - TS = U + T\left(\frac{\partial A}{\partial T}\right)_{V,N}$$

$$G = H - TS = H + T\left(\frac{\partial G}{\partial T}\right)_{P,N}$$

compact form

$$\left(\frac{\partial A/T}{\partial T}\right)_{V,N} = -\frac{U}{T^2}$$

$$\left(\frac{\partial G/T}{\partial T}\right)_{P,N} = -\frac{H}{T^2}$$

Gibbs -Helmholtz Eq.

So, let us take U minus TS. This is nothing but U plus T. Because, S is given as in terms of A. So, I am going to write it del A by del TV N, that is a constant ok. Just for the for the pure system, we can write in this form and this can also be written as in the compact form, which I am going to write later.

Now, similarly, for G H minus TS, I can also write H plus T again S is here del G by del T. So, this is going to be G T P N. Now, you can write this 2 expression in compact form. So, the compact form is del A by T del T V N. This is minus U by T square. And del G by T del T at constant P N is minus H by T square ok. And this, we call it Gibbs Helmholtz equation ok.

Now, these are all energy variables U A H and G. these are all energy variables. Now, we are going to make use of this expression in order to understand a couple of things. So, let us try to get a feel of finding out the change in this energy. Now, energy is never going to be 0 ok. We can only measure the changes in the energy.

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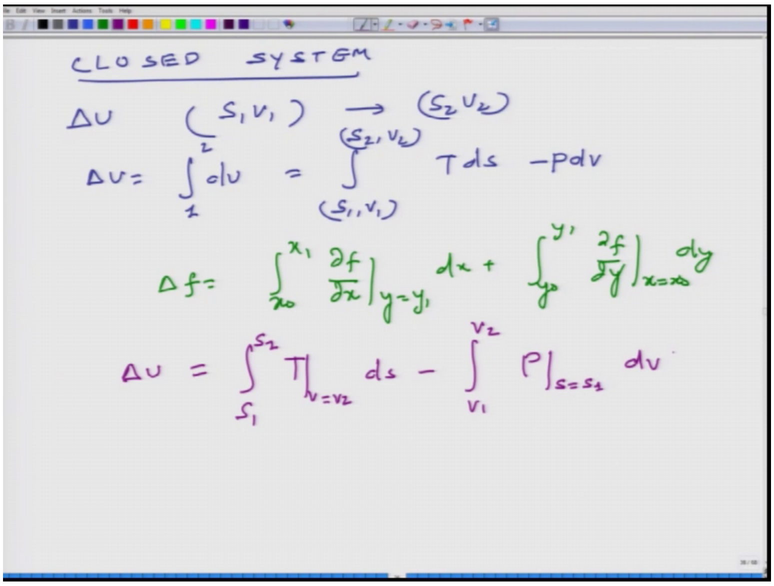

CLOSED SYSTEM

$\Delta U \quad (S_1, V_1) \rightarrow (S_2 V_2)$

$$\Delta U = \int_1^2 dU = \int_{(S_1,V_1)}^{(S_2,V_2)} T\,ds - p\,dv$$

$$\Delta f = \int_{x_0}^{x_1} \left.\frac{\partial f}{\partial x}\right|_{y=y_1} dx + \int_{y_0}^{y_1} \left.\frac{\partial f}{\partial y}\right|_{x=x_0} dy$$

$$\Delta U = \int_{S_1}^{S_2} T\Big|_{v=v_2} ds - \int_{v_1}^{v_2} P\Big|_{s=s_1} dv$$

So, let us consider a closed system. And what we are interested now is, change in the internal energy delta U in going from S 1 V 1 state to S 2 V 2. So, I have just considered the pure system as of now, ok? So, and I have dropped it and what I am interested is basically delta U from 1 to 2 ok.

So, this I can write as S 1 V 1 S 2 V 2 TdS minus PdV, ok. So, notice that the left-hand side is, delta U is basically independent of the part, but, this is going to be dependent on the part individual turns, but together they are not, ok. So, using the earlier result which we have derived that your delta f is x 0 x 1 del f by del x y is equal to y 1 dx plus y 0 y 1 del f by del y x is equal to x 0 dy, we can make use of this to get delta U S 1 S 2 T at V is equal to V 2 d S minus S 1 V 2 P S is equal to S 1 dV ok.

So, this is how we are going to get the expression.

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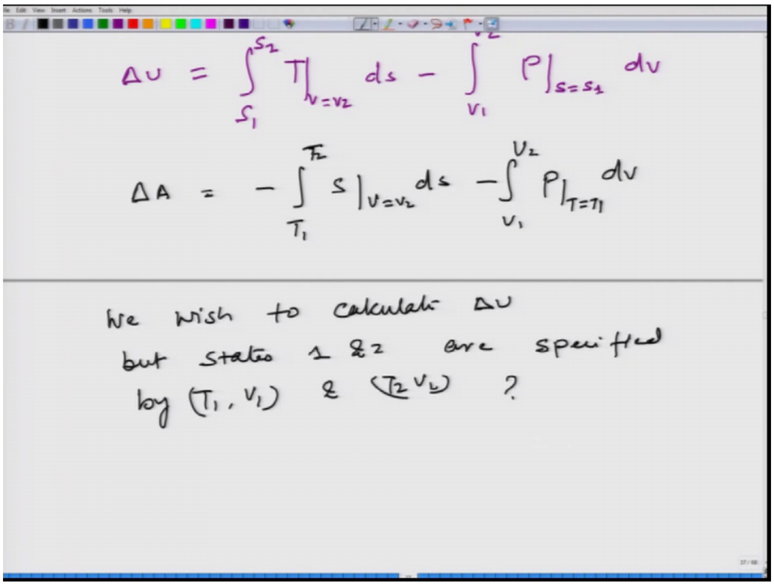

$$\Delta U = \int_{S_1}^{S_2} T\Big|_{V=V_2} ds - \int_{V_1}^{V_2} P\Big|_{S=S_1} dV$$

$$\Delta A = -\int_{T_1}^{T_2} S\Big|_{V=V_2} ds - \int_{V_1}^{V_2} P\Big|_{T=T_1} dV$$

We wish to calculate ΔU
but states 1 & 2 are specified
by (T_1, V_1) & $(T_2 V_2)$?

Now, similarly, you can also calculate that is, the delta A which will be minus T 1 T 2 S V is equal to V 2 d S V 1 V 2 P T is equal to T 2 which is T is equal to T 1 TV. So, this would be the case where, delta A going from T 1 V 1 to T 2 V 2, all right. Now, this these are very simple case where, because what we have done is, we have changed the state which is based on the natural variables. What if you have been asked to calculate delta U?.

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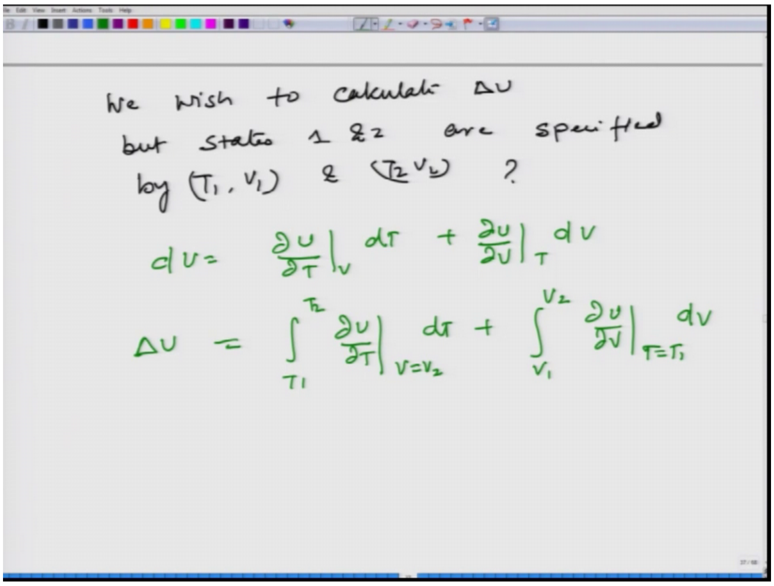

We wish to calculate ΔU
but states 1 & 2 are specified
by (T_1, V_1) & $(T_2\, V_2)$?

$$dU = \left.\frac{\partial U}{\partial T}\right|_V dT + \left.\frac{\partial U}{\partial V}\right|_T dV$$

$$\Delta U = \int_{T_1}^{T_2} \left.\frac{\partial U}{\partial T}\right|_{V=V_2} dT + \int_{V_1}^{V_2} \left.\frac{\partial U}{\partial V}\right|_{T=T_1} dV$$

So, let us say, we wish to calculate delta u, but states 1 and 2 are specified not in S and V terms, but specified by only T 1 V 1 and T 2 V 2. Now, in that case, how are we going to calculate? Ok, that is where the challenge is, ok. And this is where all these relations which we are derive will come into play, ok.

So, let us try so; that means, U in this case is a function of TV. So, we are going to write down a differential form del U by del T at constant V dT plus del U by del V at constant T dV, ok. So, using this expression, we can get del U delta U as integral of T 1 T 2 del U by del T at V is equal to V 2 dT plus V 1 V 2 del U by del V at T is equal to T 1 dV, ok. Now, this is a chosen path of course, we can get this the expression the using other path, now the challenge is to get this expression ok.

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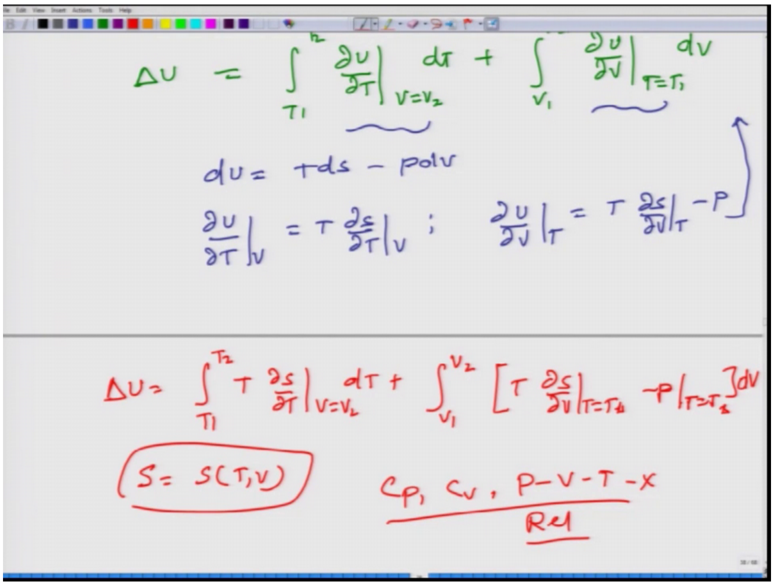

$$\Delta U = \int_{T_1}^{T_2} \underbrace{\left.\frac{\partial U}{\partial T}\right|_{V=V_2}} dT + \int_{V_1} \underbrace{\left.\frac{\partial U}{\partial V}\right|_{T=T_1}} dV$$

$$dU = TdS - PdV$$

$$\left.\frac{\partial U}{\partial T}\right|_V = T\left.\frac{\partial S}{\partial T}\right|_V ; \quad \left.\frac{\partial U}{\partial V}\right|_T = T\left.\frac{\partial S}{\partial V}\right|_T - P$$

$$\Delta U = \int_{T_1}^{T_2} T\left.\frac{\partial S}{\partial T}\right|_{V=V_2} dT + \int_{V_1}^{V_2} \left[T\left.\frac{\partial S}{\partial V}\right|_{T=T_1} - P\Big|_{T=T_1}\right] dV$$

$$\boxed{S = S(T,V)} \qquad \underline{C_P,\ C_V,\ P-V-T-x}$$

$\underline{\text{Rel}}$

The challenge is to get this expression and that is where, we are going to understand this need to make use of this different relation. So, let me just try again here, let us say, we have taken dU is equal to TdS minus PdV. This is our basic thermodynamic relation based on the first law. So, if you take the partial derivative of T with respect to partial derivative of U with respect to T at constant V, we get Td S at constant V ok. Similarly, if we use del U by del V at constant T, which is what we are interested here, this is going to be T del S by del V at constant T minus P.

So, we can plug these relations in this expression. Now, what we get delta U S T 1 T 2 T multiplied by del S del S by del T at constant V dT plus V 1 V 2. Now, we plug in here this expression this comes out to be T del S by del V T is equal to T 1 minus P which is at T is equal to T 1 and this is going to be dV ok. Now, if you clearly look at it, this depends on the information of S as a function of TV ok.

Then only, we can find it out. So, this information we do not know. So, what we have access to us typically is, the experimental accessible quantities. So, what are the experimental accessible quantities? These are heat capacities CP CV and of course, the relation of TP X. So, we have CP CV PVT and X relation. These are the relations which are available to us. So, in order to evaluate delta U, we must convert or make use of the experimentally known observation or the properties in this and replace this partial derivative of S by those properties.

And that is where, the maximal relation comes into the picture, which we are going to now summarize those relations.

So, I will stop here and basically in the next lecture, we will take up the Maxwell relation and summarize other relevant thermodynamic relations.