Chemical Principles II
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Legendre Transformation of Thermodynamic Potentials

Ok, so we have introduced new quantities while talking about the spontaneity of reactions for example we talked about Helmholtz free energy A as U minus TS and Gibbs free energy G as H minus TS and also U also H enthalpy as U plus PV we talked about enthalpy before but in the context of spontaneity we talked about enthalpy in the last lecture. Now we are going to tell you that these different things like enthalpy, Helmholtz free energy, Gibbs free energy they are not some quantity is just for spontaneity itself they have a deeper connections with the thermodynamics because they are all thermodynamics potentials.

So how do you understand that? So in order to understand why they are thermodynamic potentials and why they are important because again if they are criteria for spontaneity means of course they have some role to play in determining the change of matter which direction it will go and all.

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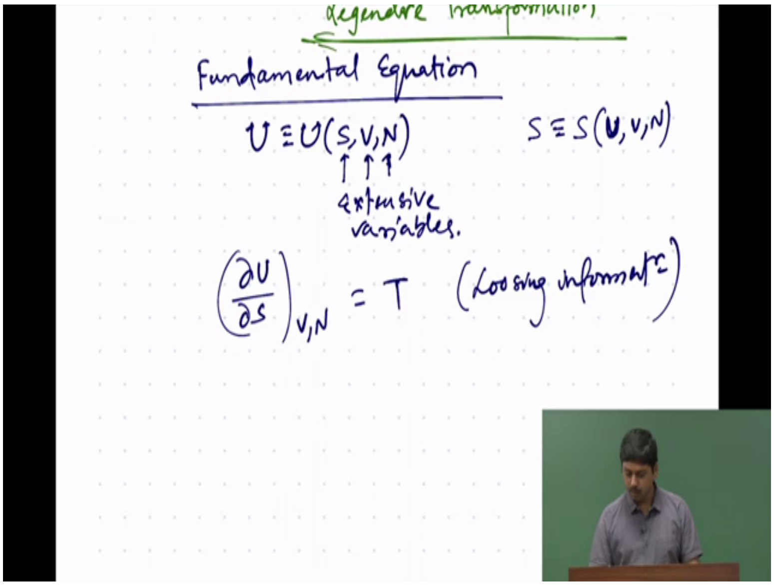

Legendre transformation

Fundamental Equation

$U \equiv U(S,V,N)$ $\qquad$ $S \equiv S(U,V,N)$

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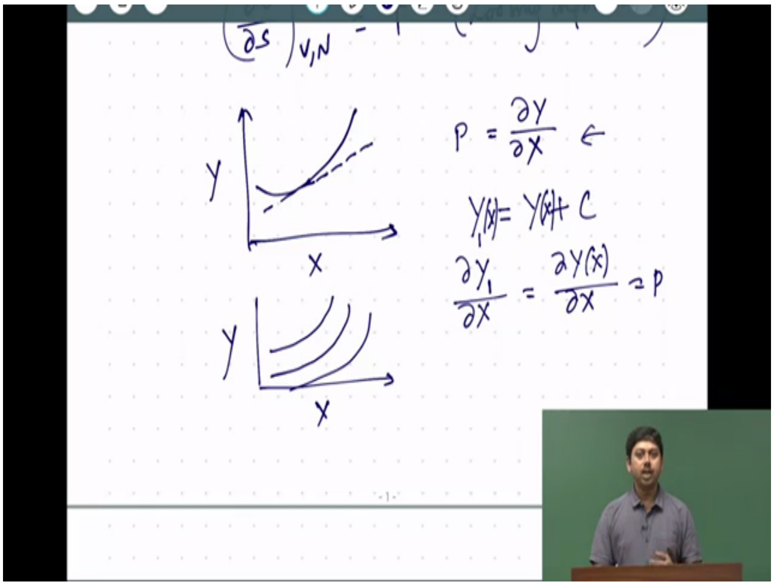
extensive variables.

$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T$ (Loosing informatn)



So we are going to talk to you we are going to show you that how these quantities arrive and that is typically known as Legendre Transformation, so the reason that Legendre transformation is important or it came up because if you look at the fundamental equation, so fundamental equation in U depends on S, V and N. In fundamental equation of U which is called energy fundamental equation there is also corresponding entropy fundamental equation where S is a function of U V and N.

So if you see the fundamental equation U depends on S V and N all are extensive variables and it is not always easy to measure the (expen) extensive variables often we want to have quantities parameters that depends on intensive variables like temperature, pressure and things like that and because they are easy to measure in experiment. So therefore it would be good to have a function that depends on intensive variables however you know that if we do that if we take the derivative of the function for example if I take dU by dS as (use) as you saw earlier at a constant V and N it will give you the intensive variable temperature.

Now in that case we are losing information I can give you an example of one dimensional function let us say Y depends on X and let us say this is the function that we are talking about and you know the derivative of the function which means slope I can obtain at any point by let us say you know calculating slope of the function P which is let us say define by dY by dX.

So if you see at this particular function slope then this P is not really an unique quantity because P can be obtained so P is unique quantity but it can be obtained from multiple values of Y for example if Y is expressed as Y plus C or let us say yeah Y plus C so let us say a function of another function of Y 1, X depends on Y, X plus C in that case del Y 1 by del X is same as del Y by Del X.

So P will be same in the cases of so many different functions which are created by adding some constant value. So therefore P will be same for a series of functions, so now if I draw a series of function like this which are all like parallel and shifted by C then all of them will give the same P, so therefore whenever you take the derivative we are no longer going to get the same fundamental equation because remember the fundamental equation has all the information however derivative of the fundamental equations which we call as equation of state that does not have all the information because we are projecting on to a particular lesser dimension.

For example what I mentioned here that many of many functions will give the same value of P at that.

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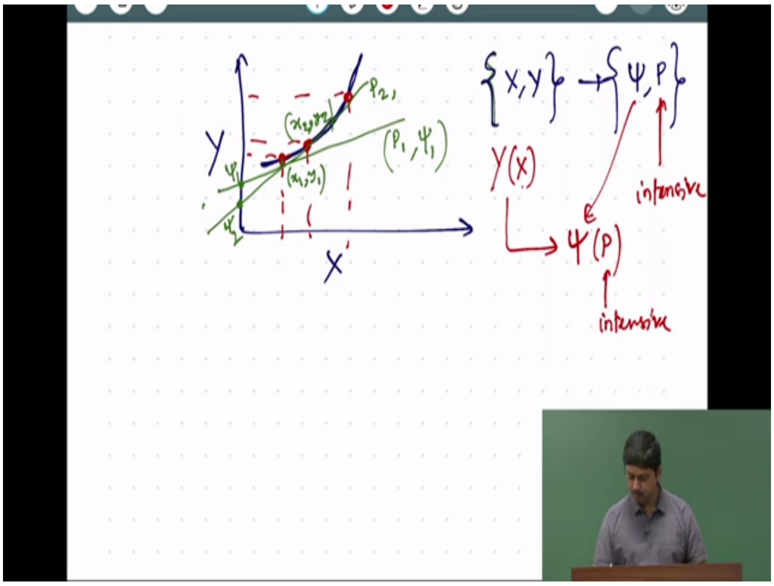

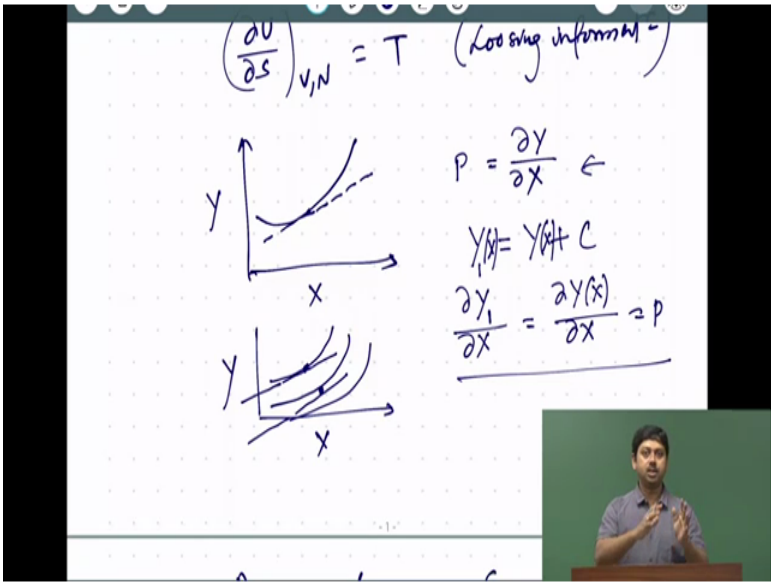

$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T$ (Loosing informat

$P = \frac{\partial Y}{\partial X} \leftarrow$

$Y_1(X) = Y(X) + C$

$\frac{\partial Y_1}{\partial X} = \frac{\partial Y(X)}{\partial X} = P$

So therefore the concept of Legendre transformation is that he want to keep the same information however you want to express same information that is there in the function Y, X by something else. So for example so let us say this is my Y and this is my X and all the different points represent for a given value of X a particular value of Y or all possible values of X and Y is our particular graph and in that this graph represent that for a given value of X what is the value of Y? For a given value of X what is the value of Y? For a given value of x what is the value of Y?

So for every value of X there is a particular value of Y and that is what the graph is and this graph let us say contains information about the system of you know thermodynamic system. So in that case if I just take the slope as you see that it will not be possible to exactly determine the all the information about the system however let us say instead of slope if we also calculate one more quantity and that is intercept of the function, so in that case this particular point X, Y let us say I call it X, Y 1, X 1 ,Y 1 will give a particular value of P 1 slope and a particular value of intercept let us call it psi 1.

So every point X, Y 1, Y 1 on the graph will correspond to a particular point let us say this point is X 2, Y 2 will give us a particular point of P 2 and psi 2. So therefore we can map the function X, Y to psi P and that is what the Legendre transformation is, so given a graph X, Y where for every value of X we have some value of Y we can always have all the information is contained in the graph be represented by another pair of points psi and P.

So for every value of this thing we will get that and therefore we are not compromising on any information as soon as we put the psi it will be no longer same as for all possible parallel lines because as you can see in this particular case if I have a slope here it will have a particular intercept and this slope will have a different intercept. So if you talk about only slope they may be similar but intercepts will be different for these parallel lines therefore keeping both the slope and the intercept we are going to map the complete information from X, Y point to a psi P point and as you know the P as you as I have discussed that P is an intensive variable now because it comes as a derivative and psi is now a function of that intensive variable P.

So therefore we can represent thermodynamic function Y, X where X is an extensive variable to be cast into another function where that function is a function of intensive variables, so this is intensive and this is extensive and reason is just that we want to express a function in terms of intensive variable for our convenience because it is convenient to measure temperature you know that right (thumb) you know several ways to measure temperature but there is no way to measure the entropy of a system.

So therefore if you cannot measure the entropy of a system we cannot get the value of U but if we cast the same information into something else where we can measure temperature and get the information about that then we get the information about the thermodynamic system much more easily. So that is the reason of converting this one to one set of pairs of points two another set of pairs so points.

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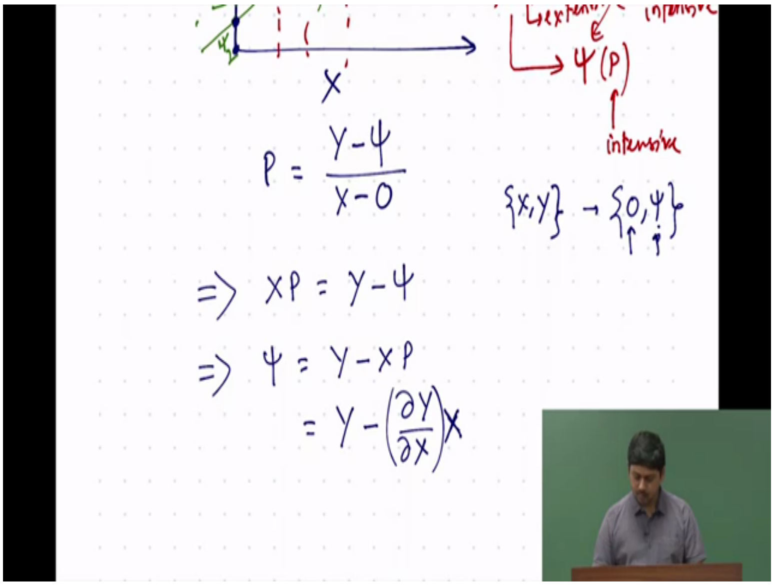


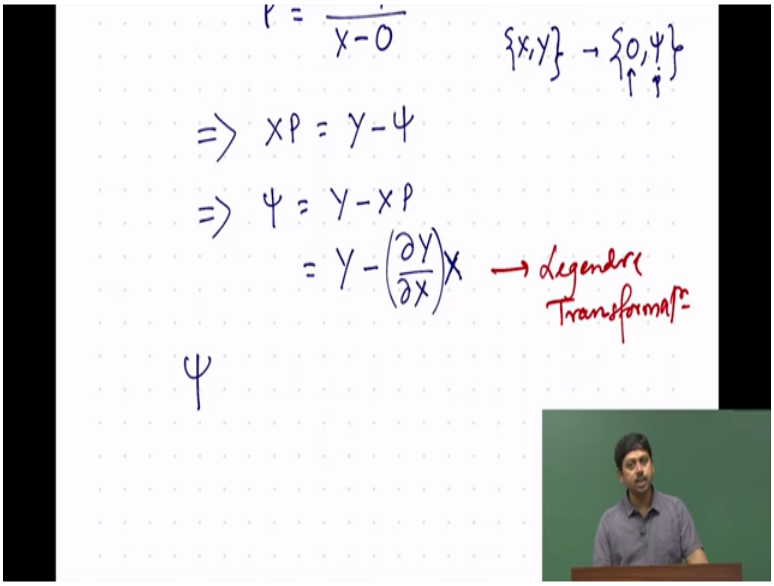
$$P = \frac{Y-\psi}{X-0}$$

$$\{X,Y\} \rightarrow \{0,\psi\}$$

$$\Rightarrow XP = Y-\psi$$

$$\Rightarrow \psi = Y - XP$$

$$= Y - \left(\frac{\partial Y}{\partial X}\right)X$$



$$P = \frac{}{X-0} \qquad \{X,Y\} \rightarrow \{0,\psi\}$$

$$\Rightarrow XP = Y-\psi$$

$$\Rightarrow \psi = Y - XP$$

$$= Y - \left(\frac{\partial Y}{\partial X}\right)X \rightarrow \text{Legendre Transformat}^{n}$$

$$\psi$$

Now how do we do that? It is actually extremely very simple, so for example we know the definition of P, P is a slope, slope means you know the difference in Y I am talking about two points one point is X, Y on the graph and another point is zero 0 and psi because as you know psi is the intercept right, so intercept meaning the value of Y at X equal to 0, so value of Y so this is also X, Y points but value of Y at X equal to 0 is nothing but psi because that is the intercept of the function.

So this is let us say for example this is the value of Y at value of X equal to 0, so therefore I am taking two points one point is this particular point and another point is any of the points that is mentioned here X, Y, so then I am talking about the slope is nothing but dY by dX which is delta Y by delta X, so I am talking about the difference between Y minus 0 divided by Y minus psi divided by X minus 0, so that is the definition of slope.

So then automatically what we get is X P is Y minus psi and what we get from there is psi Y minus XP which is if I write it a little bit in a nicer way P is nothing but slope of the function so del Y by del X into X. So this is for one dimensional function, so you can see that for multi-dimensional function let us say if it depends on more than one variable let us say our Y depends on more than one variable then we have to use a subscript for that, so that we can talk about only slope in one particular variable we are going to show you immediately right now.

So this is what the Legendre transformation is this is what called Legendre transformation. So you see that by doing the legionary transformation we have not compromised anything we have got all the information is at the same time we have cast our function which was dependent on extensive variable to now a function which depends on intensive variable, now we will do that and we will show you that how we can get that.

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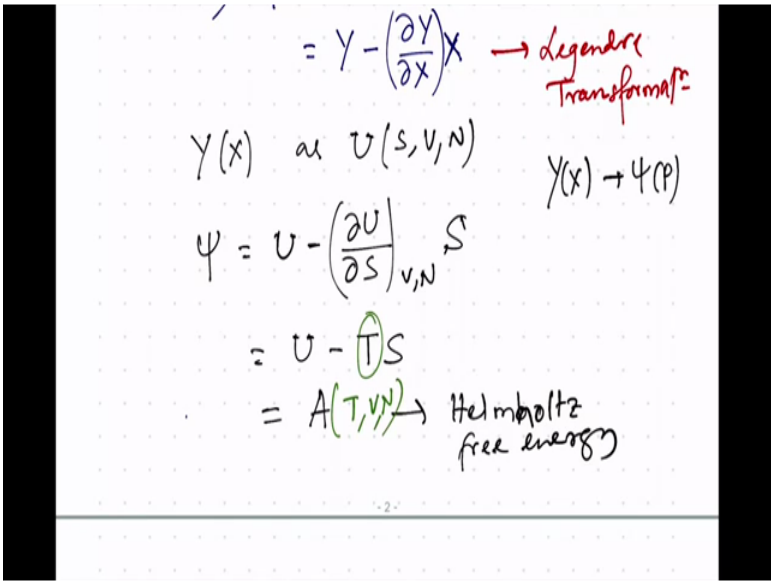

$$= Y - \left(\frac{\partial Y}{\partial X}\right) X \rightarrow \text{Legendre Transformat}^{n}$$

$$Y(X) \text{ as } U(S,V,N) \qquad Y(X) \rightarrow \psi(P)$$

$$\psi = U - \left(\frac{\partial U}{\partial S}\right)_{V,N} S$$

$$= U - \bigcirc\!\!\!\!T\, S$$

$$= A(T,V,N) \rightarrow \text{Helmholtz free energy}$$

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So let us talk about our Y which was a function of X as U as a function of S, V and N, so this is our thermodynamic fundamental equation right. So now we are going to write a function psi which is U minus derivative of U with respect to X, so del U by del S and since it depends on multiple variables I said that we have to use the other variables as constant and then you have to just multiply with S and you know what is dU by dS at a constant V and N right that is nothing but T, so U minus TS and U minus TS we already defined as A.

So you see we got Helmholtz free energy just by we name it as Helmholtz free energy but this A is nothing but Legendre transformation of U, now you know that we are going from Y X to psi P, P is a slope so here this is the slope right. So therefore it will depend on T and since we have not changed the variable V it will depend on V and N, so now A depends on T V and N.

So since U was a thermodynamic potential A is also a thermodynamic potential.

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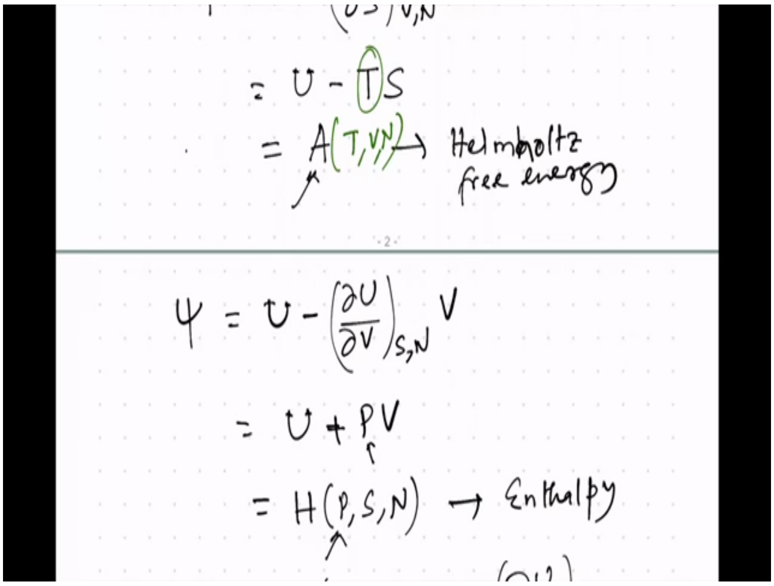


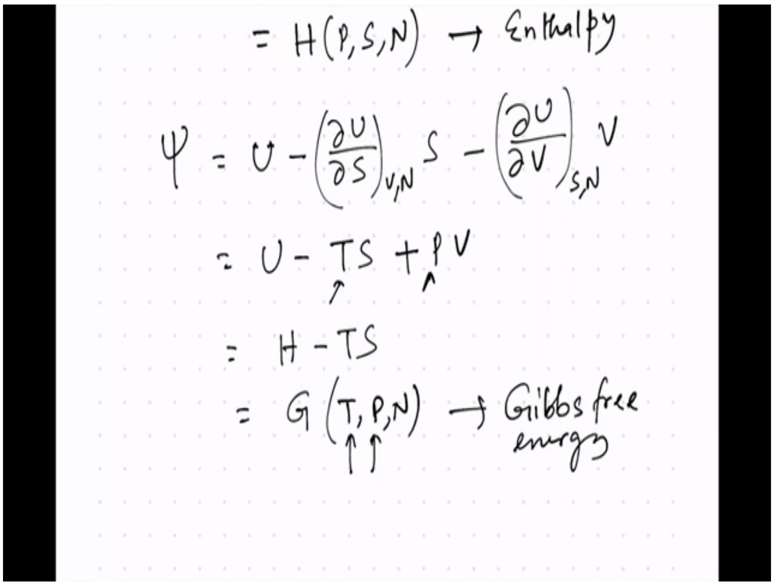
$$= U - TS$$

$$= A(T,V,N) \rightarrow \text{Helmholtz free energy}$$

$$\Psi = U - \left(\frac{\partial U}{\partial V}\right)_{S,N} V$$

$$= U + PV$$

$$= H(P,S,N) \rightarrow \text{Enthalpy}$$



$$= H(P,S,N) \rightarrow \text{Enthalpy}$$

$$\Psi = U - \left(\frac{\partial U}{\partial S}\right)_{V,N} S - \left(\frac{\partial U}{\partial V}\right)_{S,N} V$$

$$= U - TS + PV$$

$$= H - TS$$

$$= G(T,P,N) \rightarrow \text{Gibbs free energy}$$

So let us now do another regenerate transformation which is a different variable, now we do you minus now we are going to do with respect to V, so del U by del V at a constant S N and V and what does that give us U now minus du by DV you know is plus right plus P, U plus P V and we have defined earlier named it as H and what does it depend on? It will depend on the slope which is P and rest of the variables will be constant which is S and N, so H is a function of S and N and we call that as enthalpy.

Now we are going to do one more psi as both the variables so we do now regenerate transformation on both the variables, so del U by del S at a constant V N and S minus del U by del V at a constant S N and V which gives us U minus TS minus plus PV and U plus PV is H minus TS and that is nothing but G and it will depend on which are the slopes T and P, so T and P and N did not was not changed, so N is also there, so this is called Gibbs free energy or we name it as Gibbs free energy.

So now so you see that from one fundamental equation where you use function of extensive variables we have arrived at 3 new fundamental equations and 3 new thermodynamic potentials where now the variables got changed to from extensive variable to intensive variable for example you can see G is function of 2 intensive variables and H here is function of 1 intensive variable because only 1 we changed and Helmholtz free energy is function of 1 intensive variable because one only we change but G is function of 2 intensive variables only 1 extensive variable that is N.

So you see now we call this particular thermodynamic potentials like A H and G are nothing but avatar of the same god because it only appears that they are therefore they are there with a different appearance however with the same identity underlying information contained in this particular thermodynamics potential is always same whether or not we write them in a different way.

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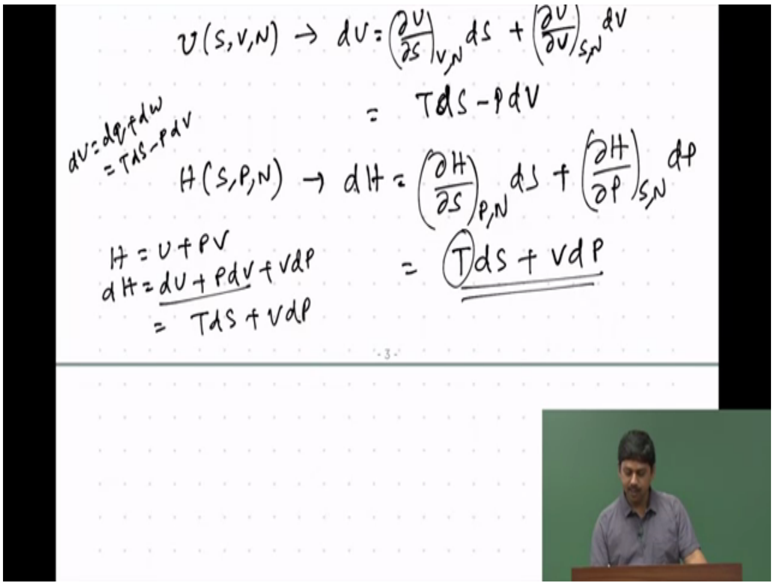


$$U(S,V,N) \rightarrow dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV$$

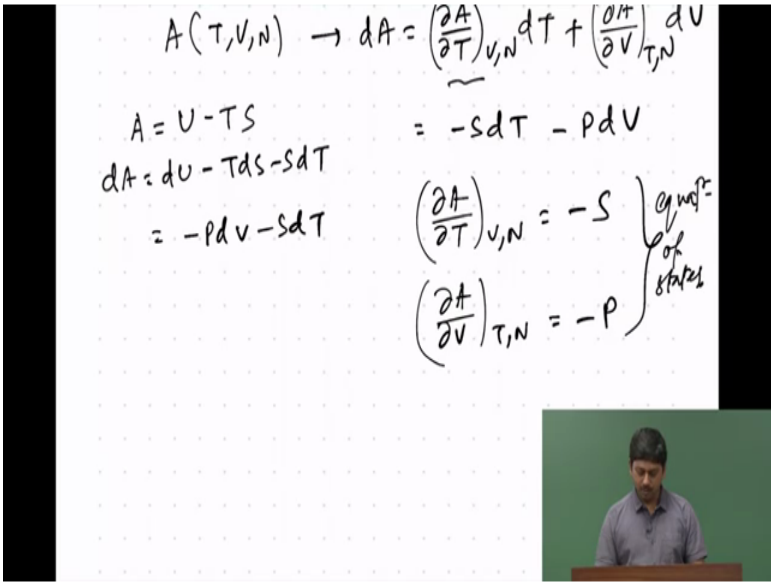
$$= TdS - PdV$$

$$dU = dq + dw$$
$$= TdS - PdV$$

$$H(S,P,N) \rightarrow dH = \left(\frac{\partial H}{\partial S}\right)_{P,N} dS + \left(\frac{\partial H}{\partial P}\right)_{S,N} dP$$

$$H = U + PV$$
$$dH = \underline{dU + PdV} + VdP$$
$$= TdS + VdP$$

$$= \underline{\underline{\textcircled{T}dS + VdP}}$$



$$A(T,V,N) \rightarrow dA = \left(\frac{\partial A}{\partial T}\right)_{V,N} dT + \left(\frac{\partial A}{\partial V}\right)_{T,N} dV$$

$$A = U - TS$$

$$dA = dU - TdS - SdT$$

$$= -PdV - SdT$$

$$= -SdT - PdV$$

$$\left.\begin{aligned}\left(\frac{\partial A}{\partial T}\right)_{V,N} &= -S\\ \left(\frac{\partial A}{\partial V}\right)_{T,N} &= -P\end{aligned}\right\} \text{eqn}^{s} \text{ of states}$$

So once we get that now we will summarize again all thermodynamics potentials, so U is a function of S V and N and we have seen that dU as del U by del S V N dS plus del U by del V S N dV and we are not talking about N now, so that is TdS minus PdV, ok. So now H is a function of S P and N and therefore we can write the dH is del H by Del S P N dS plus del H by del P S and N dP which is del H by del S is constant P and N is nothing but Tds and del H by del P is V, so TdS plus VdP right.

So we also know that because you know H is equal to U plus PV, so del H is del U plus PdV plus VdP and dU plus the as you know that dU equal to dq plus dw which is TdS minus PdV, so therefore dU plus PdV is nothing but TdS, TdS plus VdP and that is what we got here and we know that del H by del S is T and del A del H by Del P is V. Similarly we got A as T V and N which we expand as dA del A by del T at a constant V N dT plus del A by del V at a constant T N dV remember we are not doing the N part but otherwise is fine.

Now what is this quantity in order to understand that we have to expand that as U minus TS, so dA is dU minus TdS minus SdT and what is dU minus TdS it is nothing but dU minus dq which is dw which is minus PdV minus SdT, now you just compare and you get minus SdT minus PdV, so therefore we got del A by del T at a constant V and N as minus S and del A by del V at a constant T and N as minus V.

So you see with we are also getting the derivative of the fundamental equations as new quantities these are all again equation of state, so these are also equation of state any derivative of fundamental equation will be equation of states.

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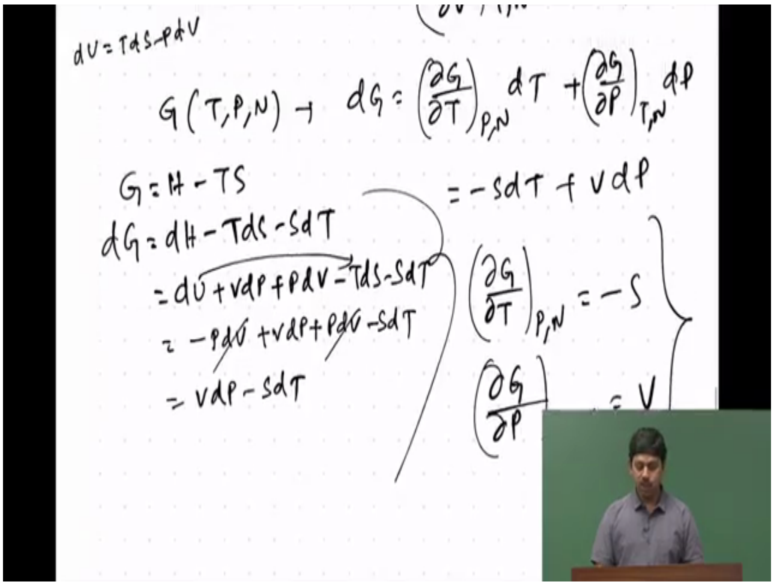


$dU = TdS - PdV$

$$G(T,P,N) \rightarrow dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP$$

$$= -SdT + VdP$$

$G = H - TS$

$dG = dH - TdS - SdT$

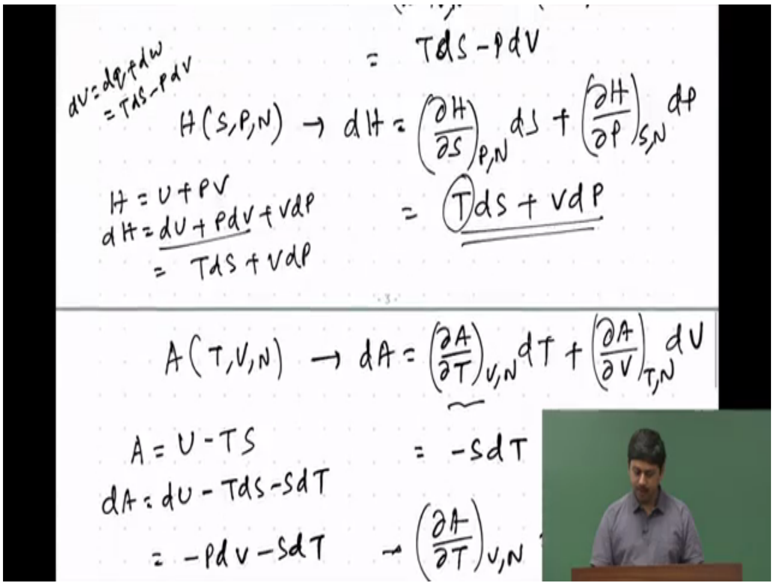
$= dU + VdP + PdV - TdS - SdT$

$= -\cancel{PdV} + VdP + \cancel{PdV} - SdT$

$= VdP - SdT$

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

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



$= TdS - PdV$

$dU = dQ + dW$
$= TdS - PdV$

$$H(S,P,N) \rightarrow dH = \left(\frac{\partial H}{\partial S}\right)_{P,N} dS + \left(\frac{\partial H}{\partial P}\right)_{S,N} dP$$

$$= \boxed{T} dS + VdP$$

$H = U + PV$

$dH = dU + PdV + VdP$

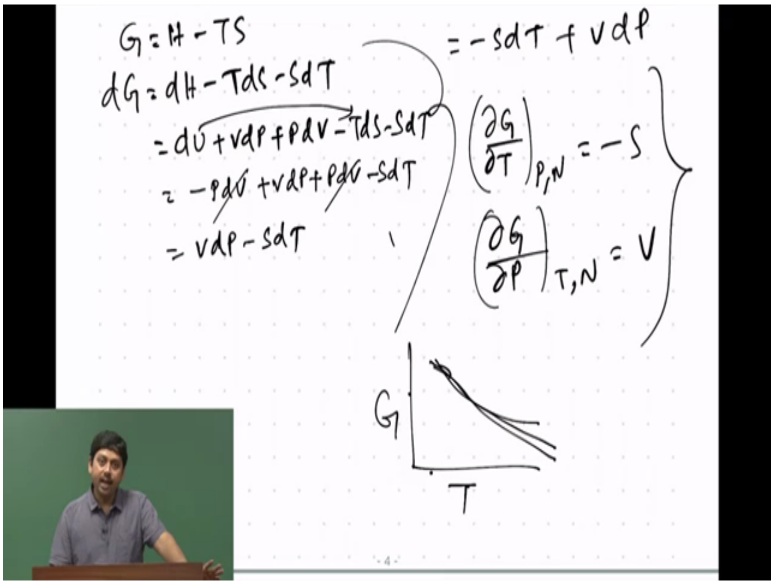
$= TdS + VdP$

$$A(T,V,N) \rightarrow dA = \left(\frac{\partial A}{\partial T}\right)_{V,N} dT + \left(\frac{\partial A}{\partial V}\right)_{T,N} dV$$

$A = U - TS$ $\qquad = -SdT$

$dA = dU - TdS - SdT$

$= -PdV - SdT \rightarrow \left(\frac{\partial A}{\partial T}\right)_{V,N}$



$G = H - TS$ $\qquad = -SdT + VdP$

$dG = dH - TdS - SdT$

$= dU + VdP + PdV - TdS - SdT$

$= -\cancel{PdV} + VdP + \cancel{PdV} - SdT$

$= VdP - SdT$

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

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

Now comes the last one of the thermodynamic potentials which is G which is T, P and N, so dG is del G by del T at a constant P and N dT, so as you see that after the fundamental equation we have not assumed anything we know the first law of thermodynamics which is dU equal to dq plus dw we know the second law of thermodynamics which is dq reversible by TdS is DS we know that after that everything else comes from naturally from just the manipulations of the derivatives.

So del G by del P at a constant T N dP, now what is G? G is H minus TS, so dG is dH minus TdS minus SdT and dH is nothing but H is U plus PV, so it is dU plus VdP plus PdV minus TdS minus SdT. Now dU plus PdV now we have to see that like dU is equal to TdS minus PdV we know that from first law of thermodynamics, so let me see so dU minus TdS is minus PdV, so this is nothing but minus PdV plus VdP plus PdV minus SdT this cancels giving us VdP minus SdT, so minus SdT plus VdP, so from here what we get that del G by del T at a constant P and N is minus S and del G by del P at a constant T and N gives us V.

Now we get several such relations of like now we can get entropy by now several different ways, we can get entropy from Gibbs free energy, we can get entropy from Helmholtz free energy like here we can get entropy also from other thermodynamics potential as well are many different ways, ok. So all these relations of thermodynamics potential are there to help us measure a certain particular quantity and compare that with the desired ones.

So for example we cannot measure entropy directly, so therefore we can measure the free energy change with respect to temperature, so let us say we calculate the free energy which can be calculated by calculating the binding constant there are ways to do that and if you do that a different \temperature from there from the slope of that, so from the slope of G with respect to T let us say the plot is like this we can get from the slope of that we can get the expression of entropy as you can see here minus of that slope will give us the information about entropy.

So that means now using some measurable quantities we will be able to get something which is immeasurable and that is the sole purpose of calculating and performing this several you know different thermodynamic relations.