Chemical Engineering Thermodynamics
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Lecture 19
Generalized thermodynamic potential – I

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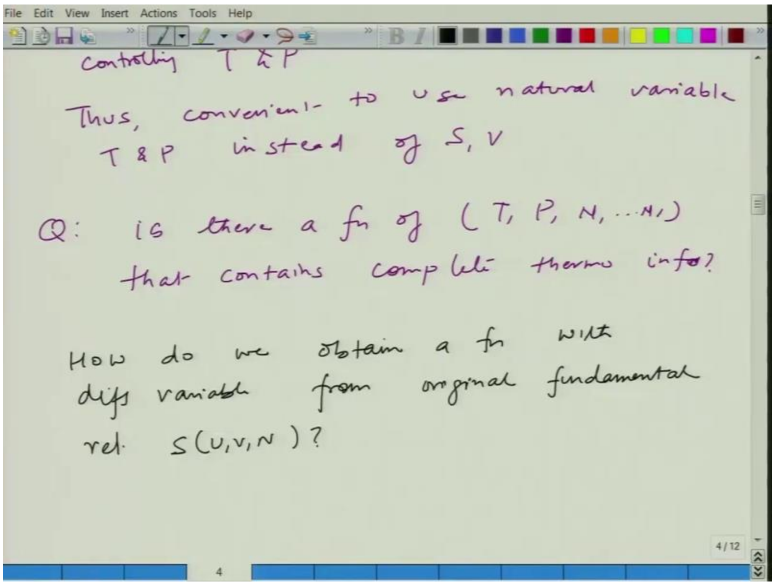

Welcome back. Last class we went through mathematical properties of fundamental equations particularly Euler equation and Gibbs–Duhem (expressions) or equations.

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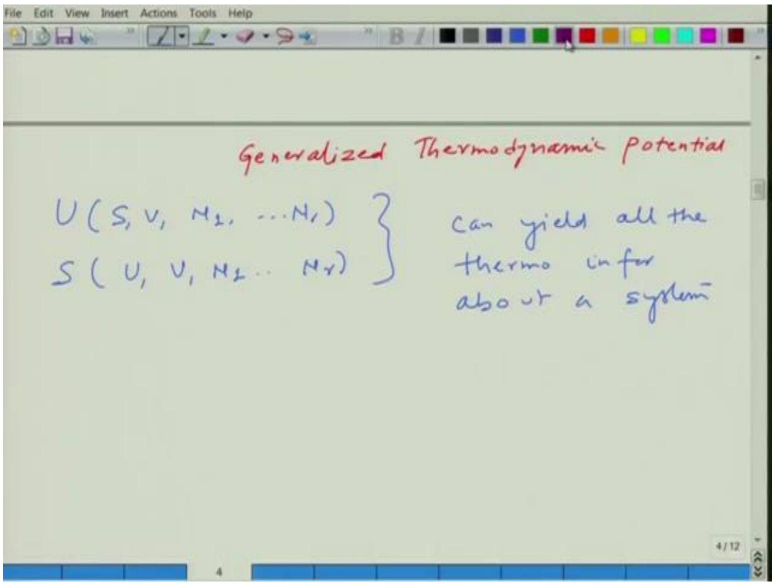

So today we are going to talk about Generalized Thermodynamic Potential. Okay start with this, essentially, we are going to focus on Generalized Thermodynamic Potential. So why are we interested in this Generalized Thermodynamic Potential? One of the reasons is that till date we have just discussed in the class only U and S. So U is a function of S, V, N 1 till N r and S is a function of U, V. So these are natural variables corresponding to U and S, okay. This essentially can yield all the thermodynamic properties of the system whether it is mechanical or thermal equation of state.

So this can yield all the thermo info about a system, okay so one can do this exercise for a given system. One can use this expression of U and variety of different constraints which you have looked into to come up with some equation of state, thermal or mechanical. But the problem is that most of the experiments which we conduct are not under a constant entropy or volume or constant internal energy of volume in moles. We mostly are, mostly conduct those experiments at a constant temperature and pressure.

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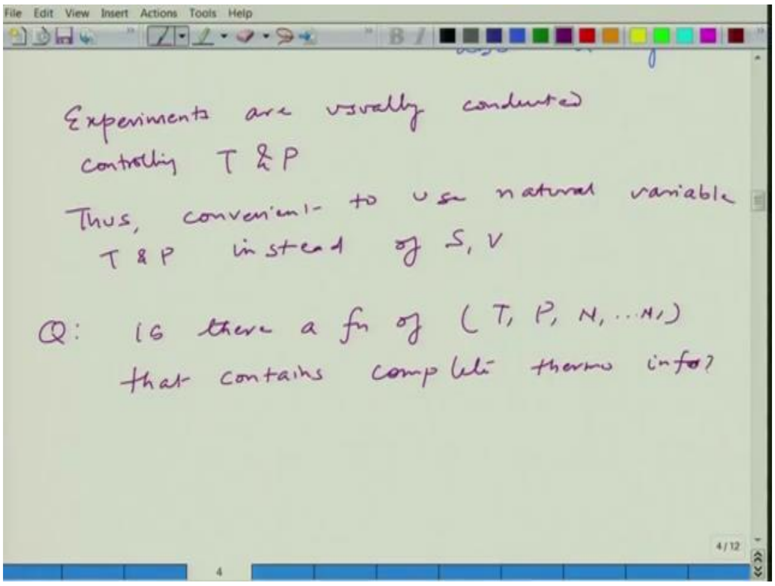

So that brings the question that what will be the appropriate thermodynamic function when we have only temperature, pressure and moles for example constant? Okay so usually experiments are usually conducted by controlling T and P. So thus, the question is that it would be convenient if we can find appropriate thermodynamic function where the natural variable is T and P, okay, convenient to use natural variable T and P instead of, let us say, instead of S and V okay. So this is something which we would like to find thermodynamic function where the natural variable is T, P.

So thus the question is, is there a function of T, P, N 1 and N r that contains the same complete thermodynamic function as in U and S, contains the complete thermodynamic, thermodynamic information, okay? So that is a very simple question which we are trying to raise, that you know we would like to find the appropriate thermodynamic function where the natural variables are T, P and which contains the same complete information as in U and S.

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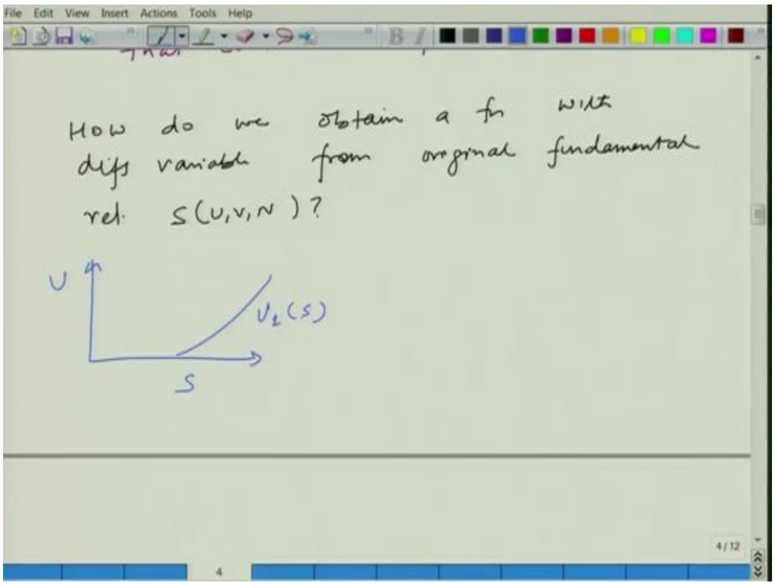

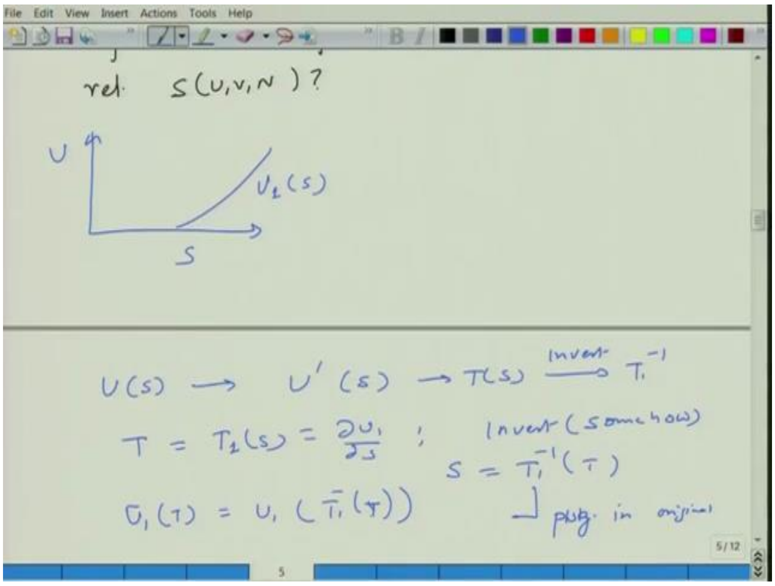

So the question is how do we obtain a function with different variable from the original fundamental relation, okay? So that is the question. So let us consider a very naive approach.

$$U(S) \rightarrow U'(S) \rightarrow T(S) \rightarrow T_1^{-1}$$

$$T = T_1(S) = \frac{\partial U_1}{\partial S}; \quad S = T_1^{-1}(T) \; (plug\ in\ original)$$

$$\overline{U_1}(T) = U_1\left(\overline{T}_1(T)\right)$$

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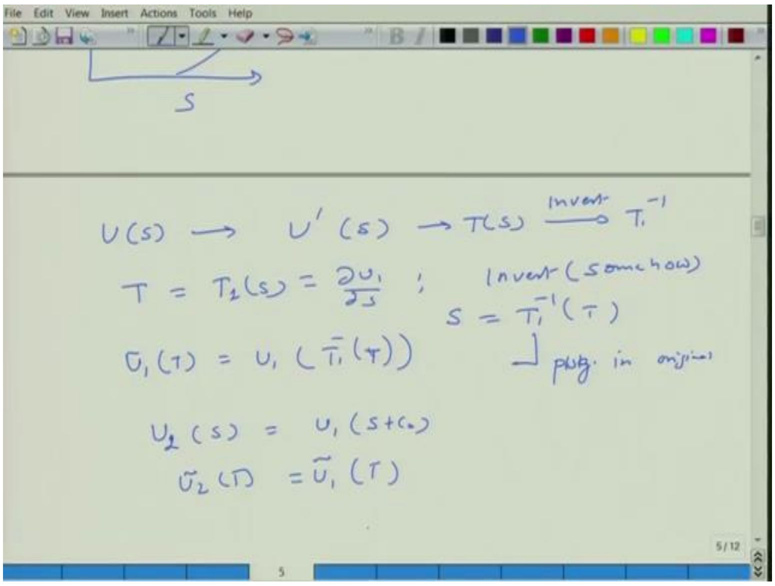

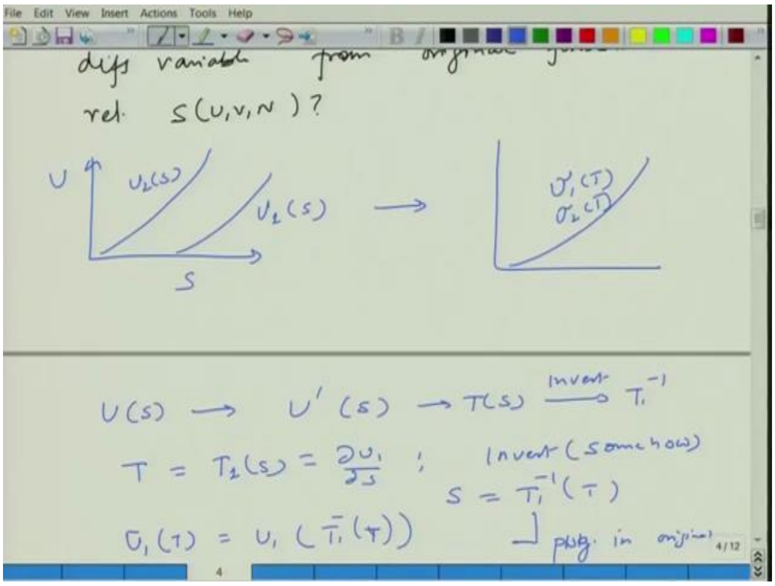

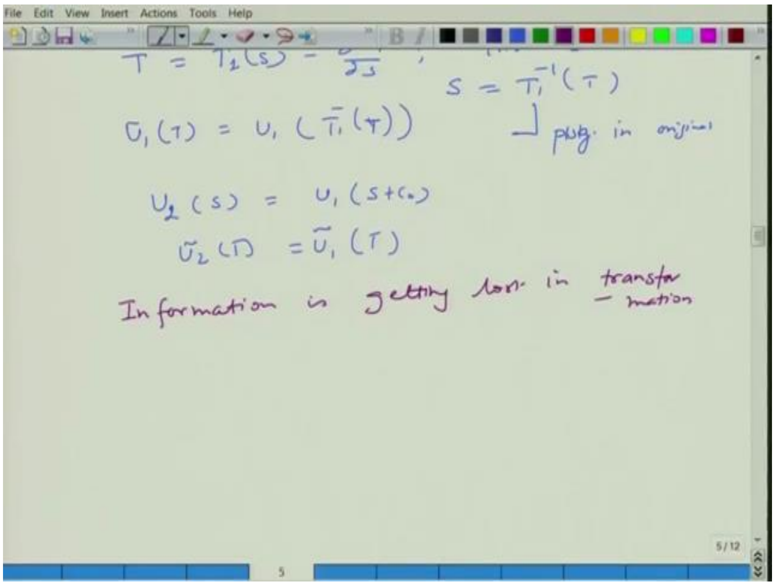

$$U_2(S) = U_1(S + C_*)$$

$$\widetilde{U_2}(T) = \widetilde{U_1}(T)$$

Now with this kind of very simple derivative-based inversion the problem is that let us say if you have two function, U 1 which you have considered this and U 2 let us say is also function of S, which is nothing but the simple shift here. In that case if you take this derivative inversion process which is a naive approach you are going to get same as U 1.

So if you try to take a derivative, obtain inversion and then you invert it back somehow plug in the inversion you are going to lose the information that is what it says if it is a simple approach like this where you consider 2 function which is just a separated by constant then this would be the case where we are considering U 1 T as well as U 2 T, okay. So a simple approach like this is not going to work, okay. So we need to think in little more clever approach. So this kind of approach which you have used here, here what is happening is information is getting lost in transformation, okay.

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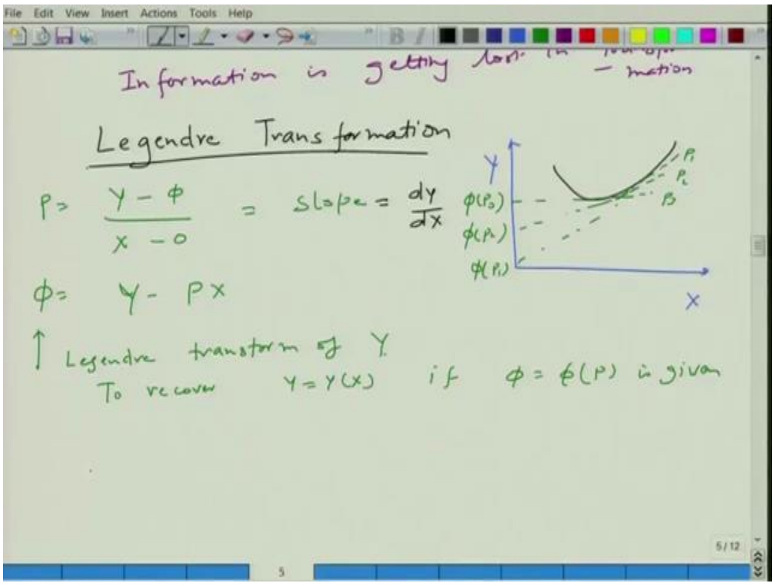

So in order to obtain a suitable function we will be making use of some mathematical approach and that is called Legendre Transformation. So I am going to now describe that. Okay, so the idea behind is that let us consider this is a function which is y as a function of x and you have this, this is let us say the curve and what we are trying to do is now, we are trying to define the slope at different points, okay.

So this, okay so, okay so we have now, let us say, P 1, P 2, P 3, this is a kind of slope and the corresponding intercept would be phi, okay. So this is a kind of a slope. So if you consider generic definition of slope here, P would be something like this.

$$P = \frac{Y - \phi}{X - 0} = slope = \frac{dY}{dX}$$

$$\phi = Y - PX\ (legendre\ transform)$$

$$To\ recover, Y = Y(X)\ if\ \phi = \phi(P) is\ given$$

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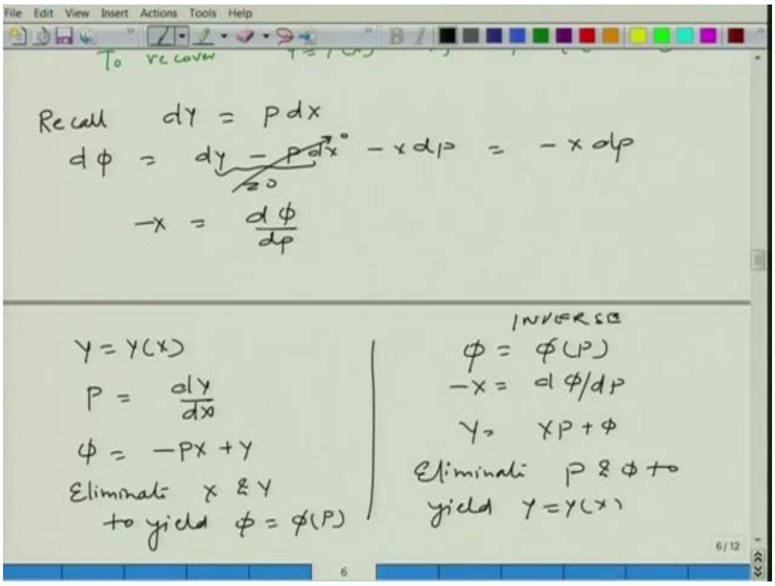

$$dY = PdX$$

$$d\phi = dY - PdX - XdP = -XdP$$

$$-X = \frac{d\phi}{dP}$$

So let us try to summarize here these two approaches or this particular approach that in the case of y given as y of x, the definition we have to make use of is the definition of the slope. This is the Legendre Transformation, minus P x plus y and now here we are going to eliminate x and y to yield phi is equal to phi of P.

$$Y = Y(X)$$

$$P = \frac{dY}{dX}$$

$$\phi = -PX + Y$$

$$Eliminate\ X\ \&\ Y\ to\ yield\ \phi = \phi(P)$$

Now in the case of inverse, to recover the function we are going to use phi is equal to phi of P, the definition is minus of x is d of phi by d P and y now can be written as x P plus phi. So here we are going to eliminate P and phi to recover or to yield y is equal to y of x. So this is the Legendre transformation which we are interested in. So let us now try to extend this for multiple variables. It is not just dependent on only on x, but many other variables. So that is what we can now generalize this.

$$\phi = \phi(P)$$

$$-X = \frac{d\phi}{dP}$$

$$Y = XP + \phi$$

$$Eliminate\ P\ and\ \phi\ to\ yield, Y = Y(X)$$

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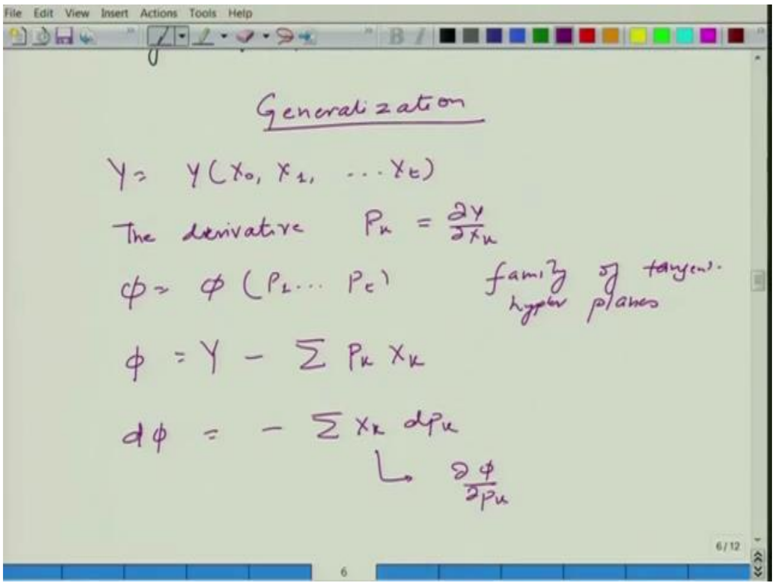

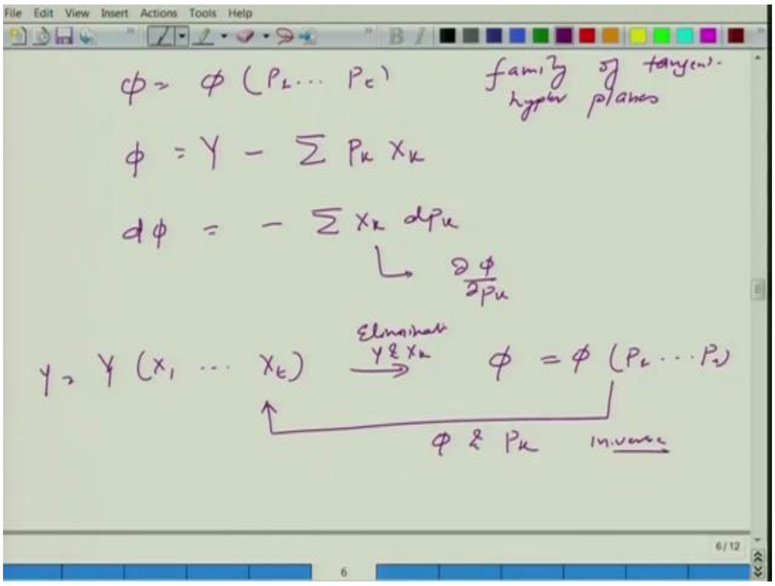

$$Generalization, Y = Y(X_0, X_1, \dots, X_t)$$

$$The\ derivative, P_k = \frac{\partial Y}{\partial X_k}$$

$$\phi = \phi(P_1, \dots, P_t) \quad family\ of\ tangent\ hyper\ planes$$

$$\phi = Y - \sum(P_k X_k)$$

So this is by definition here. So if you take the derivative here:

$$d\phi = -\sum(X_k dP_k) \quad X_k = \frac{\partial \phi}{\partial P_k}$$

$$Y = Y(X_1, \dots, X_t)\ \ eliminate\ Y\ \&\ X_k \rightarrow \phi = \phi(P_1, \dots, P_t)$$

$$\phi = \phi(P_1, \dots, P_t)\ eliminate\ \phi\ and\ P \rightarrow\ Y = Y(X_1, \dots, X_t)$$

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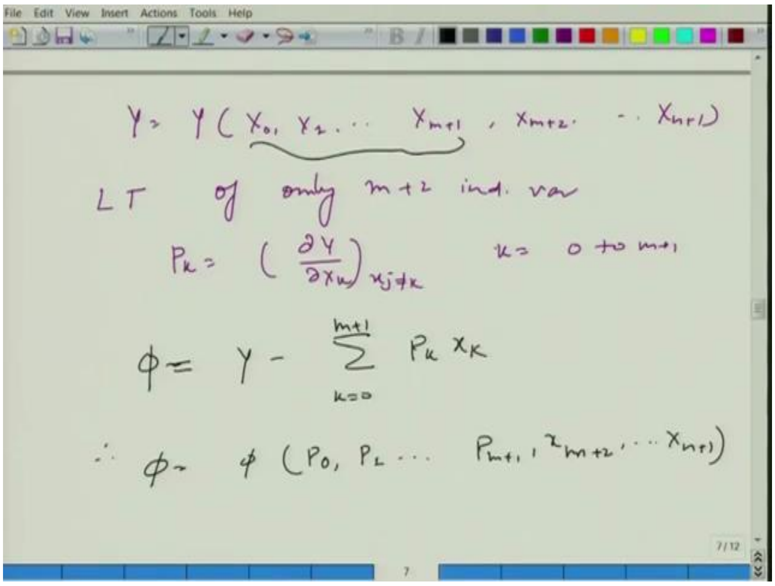

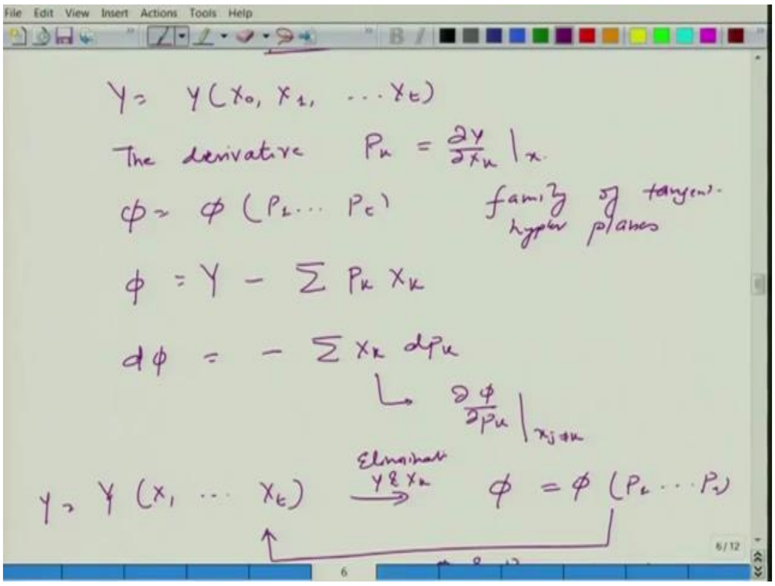

Now you may have situation where only not only all the variables you would like to change only, let us say m plus 2 are independent variable and in that case the function, let us say is Y:

$$Y = Y(X_0, X_1, \ldots, X_{m+1}, X_{m+2} \ldots X_{n+1})$$

So if you are interested let us say in some situation you might like to just take a Legendre Transformation of only m + 2 independent variables.

So that means you would like to only change this, okay. Or m plus 2 would be okay m plus 2 would be only this, okay. So if you are interested in only this aspect or to take the Legendre Transformation then your P k is going to be:

$$P_k = \left(\frac{\partial Y}{\partial X_k}\right)_{X_{j \neq k}} \quad k = 0\ to\ (m+1)$$

$$\phi = Y - \sum_{k=0}^{m+1} P_k X_k$$

So this is by definition. But when k varies from 0 to m plus 1 for this specific k where, because we are only interested to take Legendre Transformation of only m plus 2 independent variable, okay. So this is m plus 2. So in that case what would be Legendre Transformation function?

$$\phi = \phi(P_0, P_1 \dots P_{m+1}, X_{m+2}, \dots X_{n+1})$$

So we have been using a generic symbol such as y but we can now interpret this y as some kind of energy function such as U or S. So let us now try to use this Legendre Transformation concept for transforming the variables from our basic fundamental relation expressions of U to something which we desire as far as the independent variables are concerned.

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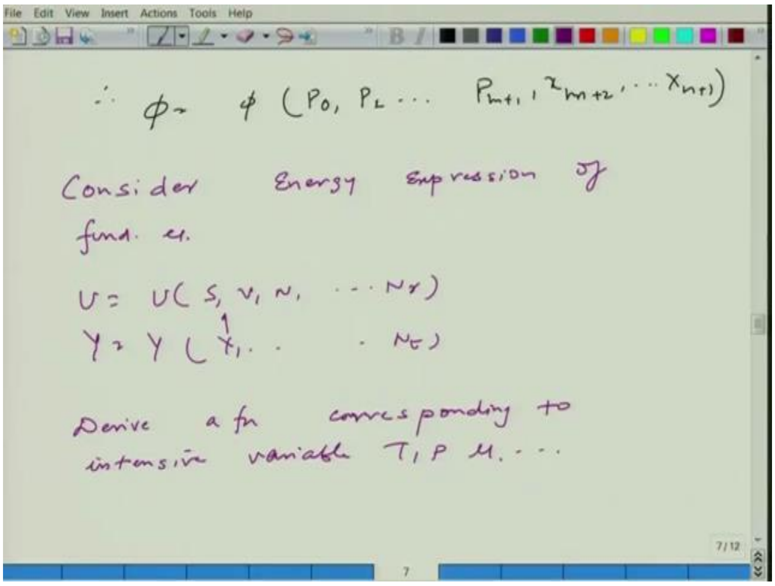

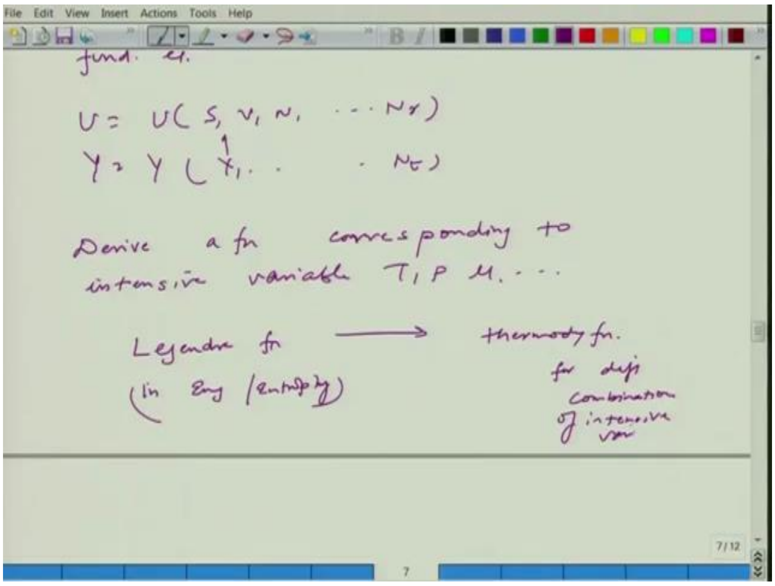

So let us look at it. So if we interpret this function. Now let us say we consider, consider the case of energy, okay consider energy expression or, okay or energy expression of fundamental equation, okay. So U is U S 1, you know and the V or N 1 till N some r, okay. So this is nothing but if you look at it, y is equal to function of y, x 1 and so forth, right. So here basically x is this. These are the natural variables for basically the U. So what we want is to derive a corresponding two intensive variable.

So what you want is to derive an expression or function, derive a function corresponding to intensive variable T or P or mu okay, so this is what we want to do. So let us look at it and essentially what you are going to see that all the derivation has simply this particular kind of transformation where we are using Legendre function or transformation, okay in energy or entropy and essentially we are going to get the thermodynamic function, okay.

So we are going to apply this thing and we are going to get thermodynamic function which we call potential functions for different kind of independent variables and that is something which we would like to see there.

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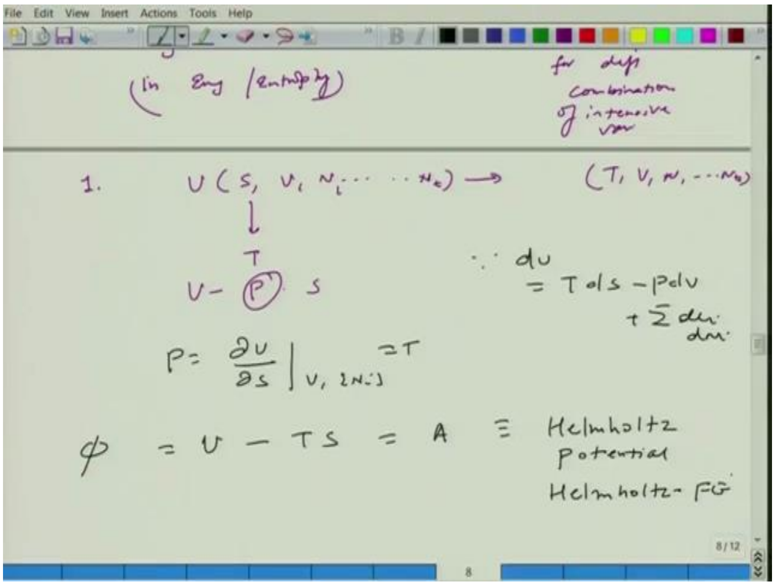

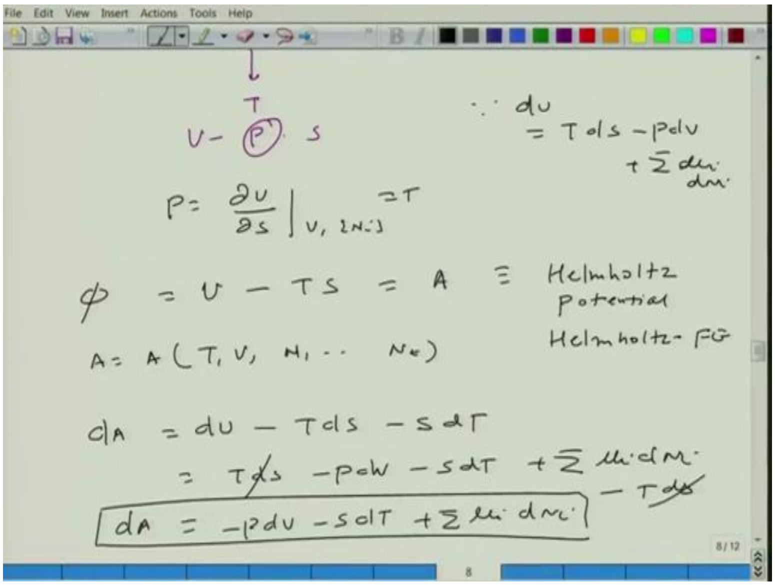

So let us take a case and let us say, okay so let us take a case first where we are going to look at U, S, V, N, N 1 till N, let us say t and then we would like to get a function such as it is T, V, N 1, N t, okay. So essentially what we are trying to do is we are trying to change one of the variable, this to T, okay.

Now if you look at it, the way we have done it in the expression here, that if you are interested in, let us say m plus 1 variable to be Legendre transformed then essentially we multiply the slope corresponding to the kth variable multiplied by the variable x. So this is what we are going to do that because here it is only one variable S to be converted to T so essentially our function should be something like this, the variable S. So we do not know what is S at this point. So let us first come up with the slope S, slope P.

$$U(S, V, N_1 \ldots N_t) \rightarrow (T, V, N_1, \ldots, N_t)$$

$$Since, dU = TdS - PdV + \sum(\mu_i dN_i)$$

$$P = \frac{\partial U}{\partial S}|_{V,\{N_i\}} = T$$

$$\phi = U - TS = A \ \ (Helmholtz\ potential\ energy)$$

So the P here is nothing but the derivative of del U by del S at a function of V and all Ni are constant, okay. So this is the slope, right by definition and this value if you look at the basic thermodynamic function in differential form is d U is T d S minus P d V plus summation mu i d N i. So for the case of V, N i is constant. d U by d S is nothing but T, okay. So what we have is now a thermodynamic Legendre Transformation function which is nothing but U minus T S and this is what we define. So this is phi now.

This is what we are defining is, in order to differentiate this with different Legendre function which we are going to get. So this is, this function is now we call it A. Okay so this is nothing but it is Helmholtz Potential. Sometimes this is also called Helmholtz Free Energy. So this Free Energy concept will come little later but I am going to just write it down, okay.

So now you have a function A which is nothing but U minus T S and remember now A is a function with T V, N 1 till N t right. So if you take the differentiation of this A or differential form this is going to be d A is equal to d U minus T d S minus S d T, right. Now you can use here the basic definition of d U. This will be T d S minus P d V minus S d T plus summation mu i d N i. So there is another term here, minus T d S, okay so this get canceled, this and this. So what you have is minus P d V minus S d T plus summation mu i d N i. So this is the differential expression of Helmholtz Free Energy or Potential, okay. That is something which we came, okay.

$$A = A(T, V, N_1, \ldots, N_t)$$

$$dA = dU - TdS - SdT = TdS - PdV - SdT + \sum(\mu_i dN_i) - TdS$$

$$dA = -PdV - SdT + \sum(\mu_i dN_i)$$

So now we have a function which basically has a natural variable T, V, N and that is what A is, okay, the Helmholtz Free Energy. Now this is one thermodynamic function, okay. Now what about others?

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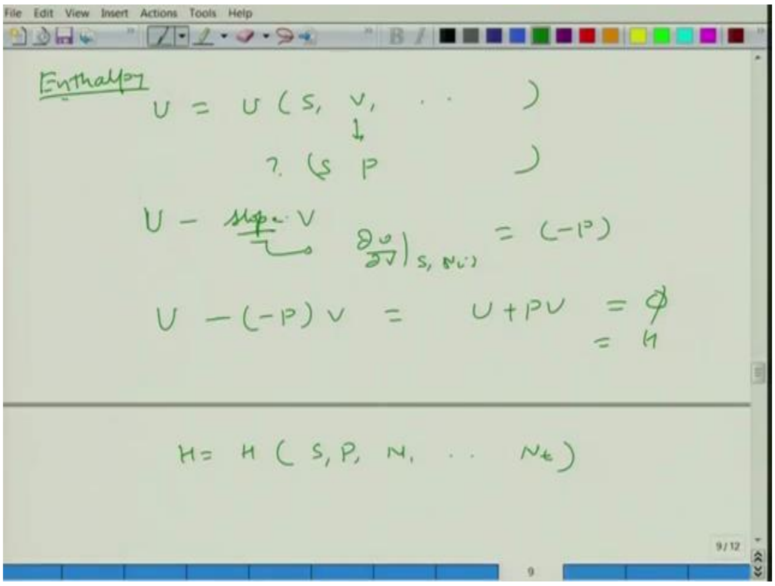

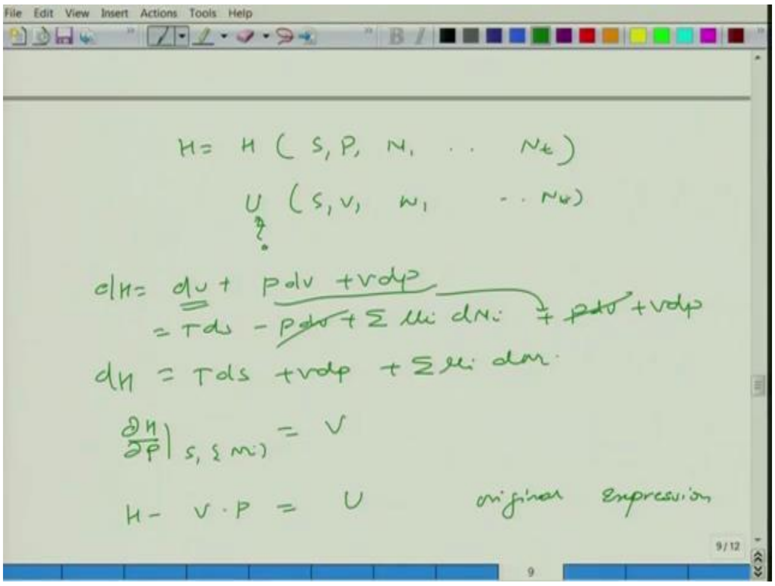

So let us consider another function.

$$U(S, V, N_1 \dots N_t) \rightarrow (S, P, N_1, \dots, N_t)$$

$$Since, dU = TdS - PdV + \sum(\mu_i dN_i)$$

$$Slope = \frac{\partial U}{\partial V}|_{S,\{N_i\}} = -P$$

$$\phi = U - (-P)V = U + PV = H \ \ (Enthalpy)$$

Now, if you want to show that this, one of the important thing in the Legendre Transformation is to obtain the original information using the inverse approach so that, that means the transformation back to the original does not lose any information. So we should try and check whether we are getting the same if you redo this thing here and here if I try this thing to get S and V back, okay using the same approach here, okay so do we get this U, okay? So we can try that.

$$H = H(S, P, N_1, \dots, N_t)$$

$$dH = dU + PdV + VdP = TdS - PdV + \sum(\mu_i dN_i) + PdV + VdP$$

$$dH = TdS + VdP + \sum(\mu_i dN_i)$$

Now d H here is going to be d U plus P d V plus V d P, okay and d U we know. This is nothing but T d S minus P d V plus summation mu i d N i plus this here, P d V plus V d P. Now this gets canceled. So you have the expression T d S plus V d P plus summation mu i d N i. So if you look at the derivative of this function so because we want to change P to its derivative so that means we are talking about del H by del P and S and rest are constant. Then this is nothing but, if you look at this expression, okay then this is nothing but your V okay, right.

So we have a function now H minus V times T and this is nothing but, if you look at the original expression by definition, H minus P V is nothing but U. So essentially you are getting back the original expression, okay. So that means we are not losing any information. This is the transformation, so it makes perfect in a value to our mathematical means to convert from one variable to another variable.

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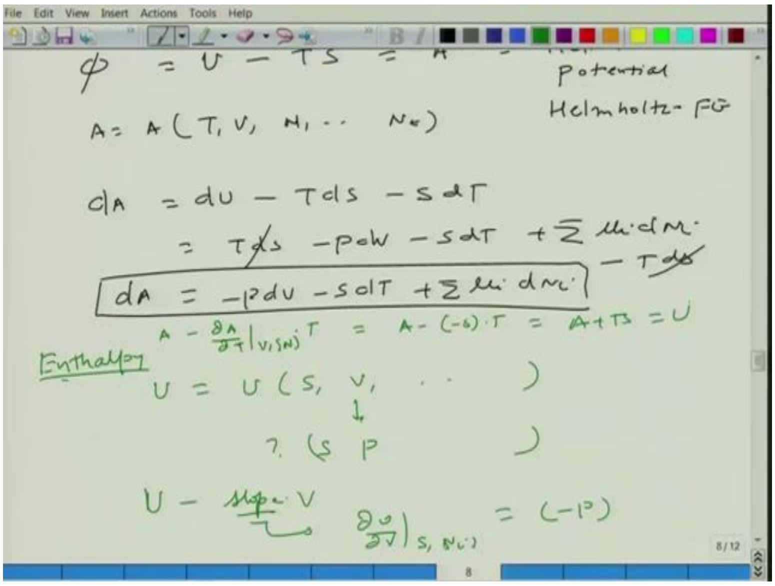

Okay, so same thing we could have done that for A also. So you can get back A minus del A by del T at constant V and N multiplied by T and this is going to be A minus del A by del T is nothing but minus of S and T and this is by definition A plus T S and this is nothing but, if you look at the definition of A, here A plus T S is nothing but, so you could do the same exercise for the Helmholtz Free Energy also, okay.

Now I can take it further for the case where we would like to change not just one variable but another variable. So I will, but that could be done in the next class. I will take a break here and then we will continue this exercise for obtaining the thermodynamic function appropriate of A's natural variables are T P, okay and then we will try to summarize this exercise. Okay, so I will see you in the next class.