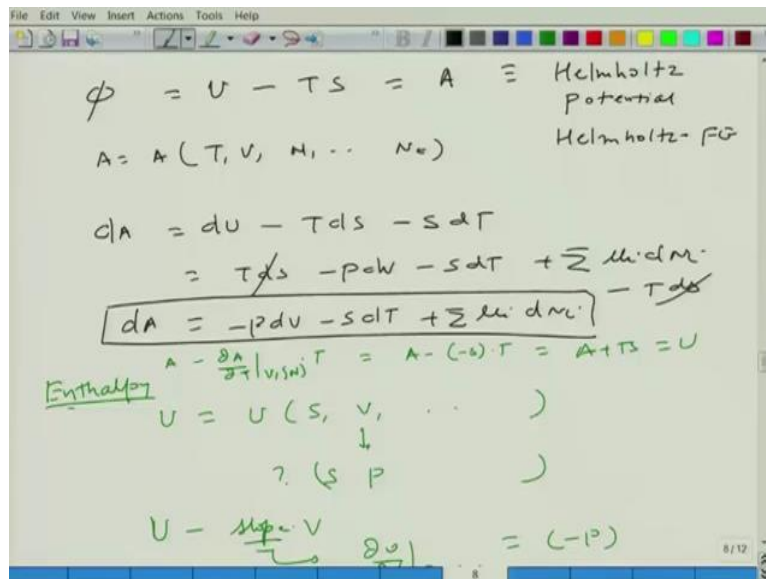


Chemical Engineering Thermodynamics
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Lecture 20
Generalized thermodynamics potential - II

Okay welcome back so in the last class we were working on transformation in order to obtain the Thermodynamic functions where the natural variables are something which you would like to control such as T or pressure and volume and so forth.

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$$\phi = U - T_s = A \text{ (Helmholtz potential or Helmholtz free energy)}$$

$$A = A(T, V, N_1, \dots, N_e)$$

$$dA = dU - Tds - sdT = Tds - P_0W - sdT + \sum(\mu_i dN_i) - Tds$$

$$dA = -Pdv - sdT + \sum(\mu_i dN_i)$$

$$A - \frac{\partial A}{\partial T} |_{V, \{N_i\}} = A - ST = A + TS = U$$

$$U = U(S, V) \rightarrow U(S, P)$$

$$U - \text{slope } V = -P$$

So we have developed two expressions, one for Helmholtz free energy where the natural variables is T, V hence and the other one is basically the enthalpy where the natural variable is SP.

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Gibbs potential or Gibbs FE

$$U(S, V, N_1, \dots, N_k); \quad dU = T ds - P dV + \sum \mu_i dn_i$$

↓

? (T, P, N₁, ..., N_k)

$$\left. \frac{\partial U}{\partial S} \right|_{V, \{N_i\}} = T; \quad \left. \frac{\partial U}{\partial V} \right|_{S, \{N_i\}} = -P$$

$$\phi = U - \left. \frac{\partial U}{\partial S} \right|_{V, \{N_i\}} \cdot S - \left. \frac{\partial U}{\partial V} \right|_{S, \{N_i\}} \cdot V$$

$$G = U - TS + PV$$

Now we will extending this exercise for the case where essentially we would like to change S, V, N1 to something like T, P, N1 so forth, okay. So what would be the function appropriate for that? So in this case we have two variables which we are trying to change. So in the sense it is multivariable, so that means that we have to worry about two specific slopes.

The first one is: $\frac{\partial U}{\partial S} |_{V, \{N_i\}} = T$; $\frac{\partial U}{\partial V} |_{S, \{N_i\}} = -P$

$$\phi = U - \frac{\partial U}{\partial S} |_{V, N_i} S - \frac{\partial U}{\partial V} |_{S, N_i} V = U - TS - (-P)V$$

$$G = U - TS + PV$$

So we have two specific slope which is available now in order to obtain the Legendre transformation function we are going to use U minus the first slope okay $\text{del } U$ by $\text{del } S$ multiplied by the variable which we would like to change which is S minus the second slope multiplied by the variable which is V , okay. So this is the Legendre transformation Φ , so this is going to be U minus $T S$ minus of minus $P V$ okay and that is U minus $T S$ plus $P V$ and this particular function is often called G . So G is nothing but the Gibbs potential or Gibbs free energy we call it.

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The image shows a handwritten derivation on a digital whiteboard. At the top, it states $G = G(T, P, N_1, \dots, N_t)$. Below this, the differential dG is derived from the differential of internal energy dU . The first line is $dG = dU - Tds - sdT + PdV + VdP$. The second line shows $dU = Tds - PdV + \sum \mu_i dN_i$, with arrows indicating the substitution of Tds and $-PdV$ into the first line. The final boxed equation is $dG = VdP - sdT + \sum \mu_i dN_i$. At the bottom, it shows the transformation $G(T, P, N_1, \dots, N_t) \rightarrow U(S, V, N_1, \dots, N_t)$. The whiteboard interface includes a menu bar (File, Edit, View, Insert, Actions, Tools, Help) and a toolbar with various drawing tools. The page number '10' is visible in the bottom right corner.

Now G is a function of T, P, N_1 till N_t .

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

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

$$G(T, P, N, \dots, N_t) \rightarrow U(S, V, N, \dots, N_t)$$

So you may also like to test whether we are going to get the original expression if you do inverse, so let us do that so we have to get back the G that means from G, T, P, N_1 till N_t to U, S, V, N_1 till N_t okay, so this is the transformation you would like to have it and check whether we are going to return get back you are not if you this change T and P to S, N, V .

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The image shows a digital whiteboard with the following handwritten text:

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

$$G - \underbrace{\frac{\partial G}{\partial T} \Big|_{P, \{N_i\}} \cdot T}_{(-S)} - \underbrace{\frac{\partial G}{\partial P} \Big|_{T, \{N_i\}} \cdot P}_V$$

$$G + ST - VP = U = U(S, V, \dots)$$

$$G - \frac{\partial G}{\partial T} \Big|_{P, \{N_i\}} T - \frac{\partial G}{\partial P} \Big|_{T, \{N_i\}} P$$

$$G + ST - VP = U = U(S, V, \dots)$$

So we get back the original function by doing this inverse approach. So you can also consider not just these two variables but you can also try to get H because H is nothing but a function of S and P.

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

$$\phi = H - \frac{\partial H}{\partial S} \Big|_{P, \{N_i\}} S = H - TS = U + PV - TS$$

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

$$\downarrow$$

$$\phi = \phi(T, P, N_1, \dots, N_k)$$

$$= H - \frac{\partial H}{\partial S} \Big|_{P, \{N_i\}} \cdot S = H - TS$$

$$= U + PV - TS$$

$$\phi = U - \frac{\partial U}{\partial S} \Big|_{V, \{N_i\}} \cdot S + \frac{\partial U}{\partial V} \Big|_{S, \{N_i\}} \cdot V$$

$$G = U - TS - (-P)V = U + PV - TS = H - TS$$

$$G = G(T, P, N_1, \dots, N_k)$$

$$dG = dU - Tds - sdT + PdV + VdP$$

$$= Tds - PdV + \sum N_i dN_i - Tds - sdT + PdV + VdP$$

$$\boxed{dG = VdP - sdT + \sum N_i dN_i}$$

$$G(T, P, N_1, \dots, N_k) \rightarrow U(S, V, N_1, \dots, N_k)$$

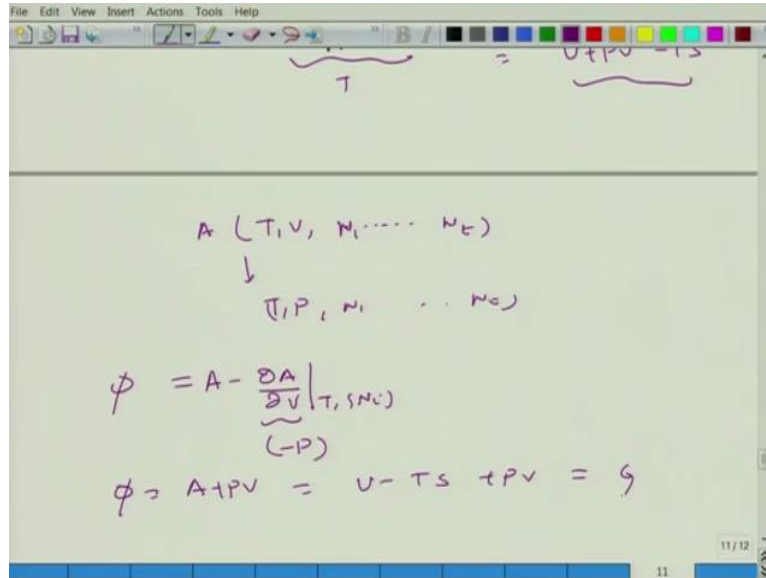
$$G = \frac{\partial G}{\partial T} \cdot T - \frac{\partial G}{\partial P} \cdot P$$

So let me try that and show this demonstrate that part, so what I am trying to say here is that we can also try this H to T, P, N1, Nt and this is a function G okay which means we are talking about G is equal to nothing but H minus del H by del S or rather I would say some function let us say which should be same as G okay. So this could be Phi again this H minus del H by del S at constant P, Ni and this is H, so if you look at that differentiation or the derivative expression or expression of H in the differential form it is dH here so the derivative of this with respect to S keeping the rest constant is nothing but T.

So essentially we have this as T okay so you have H minus TS okay so but H is nothing but U plus PV minus TS and this expression is nothing but the same as the earlier expression when we calculate the function G okay. So if you look at the function G it was U plus PV minus TS which is nothing but H minus TS okay.

So this is the same expression which we obtained here, so this is nothing but G so you can consider by changing sequentially all these variable or you can consider all the variables to be changed by this derivatives that is also feasible in this mechanism, okay.

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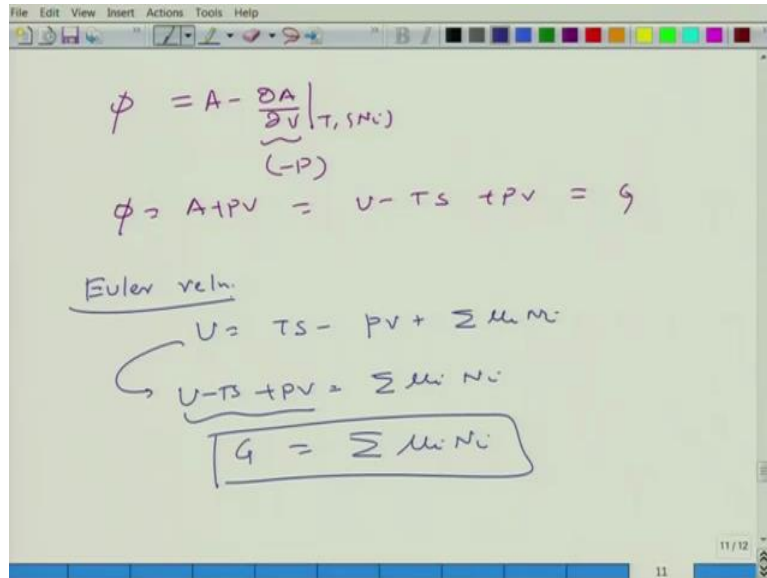
So similarly I can also consider A:

$$A(T, V, N_1, \dots, N_t) \rightarrow A(T, P, N_1 \dots N_t)$$

$$\phi = A - \frac{\partial A}{\partial V} \Big|_{T, \{N_i\}}$$

$$\phi = A + PV = U - TS + PV = G$$

So essentially you get the same expression.



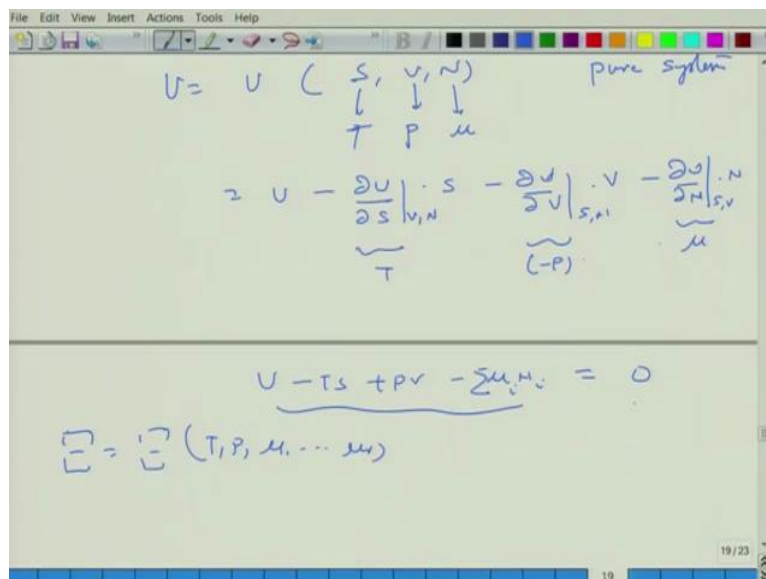
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So if you recall your Euler equation this is the interesting aspect here,

$U = TS - PV + \sum(\mu_i N_i)$ using the extensivity of the Thermodynamic function, so we obtained this relation if you recall. Now you can extend this relation to the different thermodynamic function we just derived. So we can demonstrate this for Gibbs free energy, so if you look at the Gibbs free energy definition

$$U - TS + PV = \sum(\mu_i N_i) = G$$

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Now, as of now we just looked into two intensive variable T and P okay we converted S to T and volume to P, but now we can think of another intensive variable which is chemical potential μ so which so which you like to convert the conjugate variable and to its to μ which essentially can be done in a same way that we can demonstrate and let us do this consider S, V, N and the corresponding thermodynamic function which is U and what we want to do is we want to convert this let us say only T. Pure systems only.

$$U = U(S, V, N) \rightarrow U(T, P, \mu)$$

$$= U - \frac{\partial U}{\partial S} \Big|_{V, N} S - \frac{\partial U}{\partial V} \Big|_{S, N} V - \frac{\partial U}{\partial N} \Big|_{S, V} N$$

If it is a multi-component system then we are going to have $\mu_i N_i$ and there will be summation.

So now if you look at Euler equation which we written earlier, the Euler equation which is written here $U - TS + PV - \sum(\mu_i N_i)$ so this clearly means that this function is nothing but 0 and this is sometime we call grand canonical potential which is nothing but a function T, P, μ_i , μ_r okay. So from this expression is basically the Euler expression which we come up with and this expression yields the value 0.

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The image shows a digital whiteboard with the following content:

$U - TS + PV - \sum \mu_i N_i = 0$

$\Omega = \Omega(T, P, \mu_1, \dots, \mu_r)$

Type System	FN Potential	Equil attain
S, V, N	U	S max U min
T, V, N	A	A min
S, P, N	H	H min
T, P, N	G	G min

Now in the later part, what I am going to show is that if you have a system so this is a type of system so if it is S, V, N, we have calculated the function or potential okay thermodynamic

function the corresponding natural variable is U which we are now aware of. The corresponding T, V, N , natural variable is A . A natural function is A , that means for A natural variables at T, V, N , for the case of S, P, N the thermodynamic function, appropriate thermodynamic function is Helmholtz free energy. For the case of T, P, N , the appropriate function is G .

So that means that for U natural variables are S, V, N , for A natural variables are T, V, N , for H natural variables are S, P, N , for G is T, P, N . Now in the earlier stage of this course we described that for equilibrium we looked into the maximum entropy, in the later part we are going to show that equilibrium can be also shown by considering the minimum A, H minimum okay and G minimum. So these are the minimization of these some other function would also attain the equilibrium conditions for the corresponding natural variables.

For the case of S, V, N , okay we had either S maximum okay and later on we are going to show that S maximum or U minimum are equivalent okay to for the case of equilibrium conditions. Okay, so the other set of Legendre transformation we are not going to show those are those cases which we are using S as a function for basically U, V, N . So the bases we have considered here is basically the internal energy as a function and we were trying to transform the variables in our interested variables such as T, P .

Similarly, you could do the same thing for S okay and you may get another function those functions are sometimes called massive function okay, so we are not going to deal with those functions because this is something which we interested.

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Type System	FN Potential	Equil attain
S, V, N	U	S_{max} U_{min}
T, V, N	A	A_{min}
S, P, N	H	H_{min}
T, P, N	G	G_{min}

$U = U(S, V, N)$	$dU = Tds - PdV + \mu dN$
$A = A(T, V, N)$	$dA = -SdT - PdV + \mu dN$
$H = H(S, P, N)$	$dH = Tds + VdP + \mu dN$
$G = G(T, P, N)$	$dG = -SdT + VdP + \mu dN$

$$U = U(S, V, N)$$

$$dU = TdS - PdV + \mu dN$$

$$A = A(T, V, N)$$

$$dA = -SdT - PdV + \mu dN$$

$$H = H(S, P, N)$$

$$dH = TdS + VdP + \mu dN$$

$$G = G(T, P, N)$$

$$dG = -SdT + VdP + \mu dN$$

So to summarize this is basically all the aspect of the new Thermodynamic functions which we have developed for different intensive variables or the changes in the variables which are interested in.

So these are the four generic expressions which we are going to make use of in the later part of the course.

So that is something which I wanted to cover this class, in the next class will be looking at some further expressions or derivations particularly which is relevant in order to get the thermodynamic functions in conditions and that you call it massive relation. Okay, so I will see you in the next class.