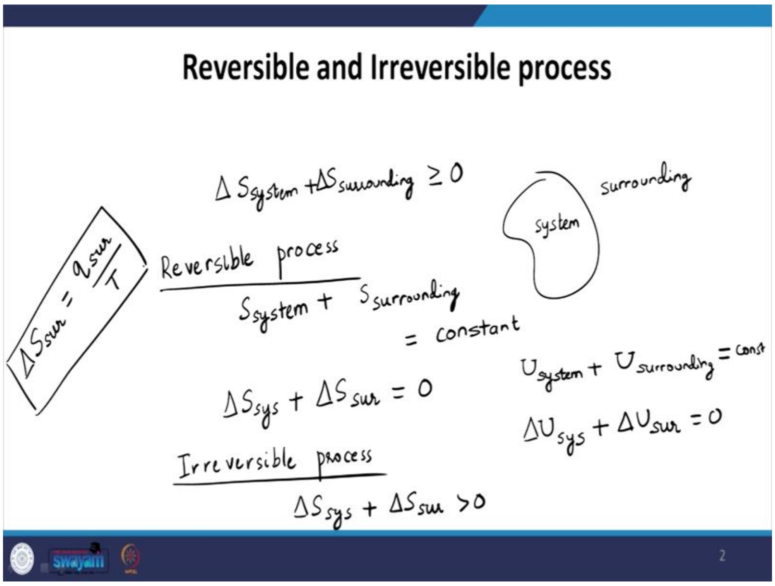
Advanced Thermodynamics and Molecular Simulations
Prof. Prateek Kumar Jha
Department of Chemical Engineering
Indian Institute of Science – Roorkee

Lecture 07
Reversible and Irreversible Processes: Third Law: Legendre Transformation; Thermodynamic Functions for One component System

Hello all of you so in the last lecture we have been discussing the idea of entropy being the driving force when we discuss the first and second laws of thermodynamics. In this particular lecture we will take that argument a bit further. And then I will talk about reversible and irreversible processes and after that I will discuss the idea of thermodynamic functions.

(Refer Slide Time: 00:51)



Reversible and Irreversible process

$\Delta S_{system} + \Delta S_{surrounding} \geq 0$

Reversible process

$S_{system} + S_{surrounding} = \text{constant}$

$\Delta S_{sys} + \Delta S_{sur} = 0$

$\boxed{\Delta S_{sur} = \frac{q_{sur}}{T}}$

$U_{system} + U_{surrounding} = \text{const}$

$\Delta U_{sys} + \Delta U_{sur} = 0$

Irreversible process

$\Delta S_{sys} + \Delta S_{sur} > 0$

So we already have established that if I look at any particular system I always look with a surrounding saying that the system plus surrounding makes my universe clearly surrounding is huge in comparison to the system and then what we established using the first law of thermodynamics is that the internal energy of the system plus internal energy of the surrounding is constant, or in other words we can say for any process-

$$\Delta U_{sys} + \Delta U_{surr} = 0$$

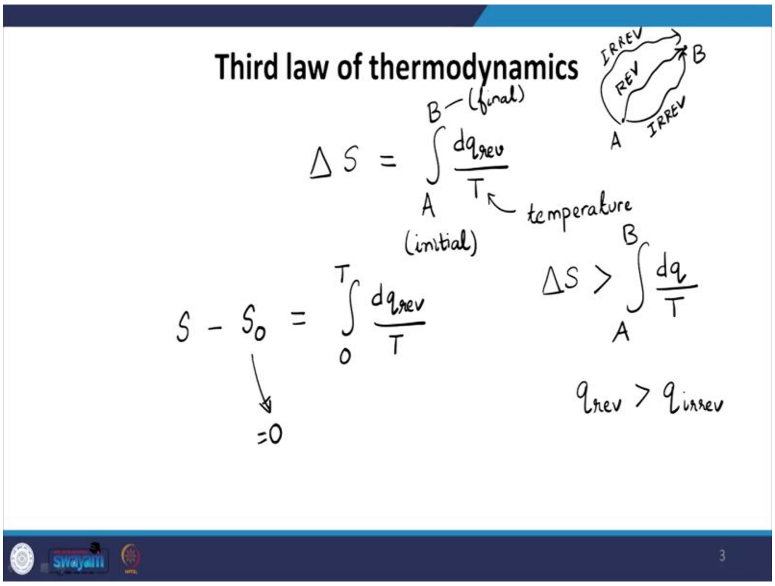
However the entropy of the system plus the entropy of the surrounding should increase in reality there is a greater than equal to 0 thing there is a possibility that a process does not bring in a change in the entropy of universe or it’s possible that entropy increases what is more likely in all situations is that entropy is increasing for the universe.

However there is a special class of processes for which entropy of universe is equal to constant and in that case we call the process a reversible process. So essentially for a reversible process we have $S_{system} + S_{surrounding}$ = constant value and we always talk about a change in the entropy. So more precisely the previous expression would be ΔS and ΔS where we always talk from a reference state when we define a process. So we talk about changes in the entropy as opposed to the entropy values. So what we mean to say is that the ΔS of the system + the ΔS of surrounding = 0 only if the process is reversible. If you have an irreversible process which is more common in the universe what we will have is ΔS of system + ΔS of surrounding is higher than 0.

Now whether it is a reversible process or an irreversible process the argument of Clausius was the surrounding is like always very huge in comparison to the system. So instead of talking about number of ways of distribution in the surrounding we can talk in terms of the heat that is added to the surrounding or minus of the heat that is added to the system and define the entropy of the surrounding or the entropy change of the surrounding in terms of the heat that is added to the surrounding.

So with this particular idea, we can now define a reference state for the entropy as well and that reference state is what we have earlier said is the 0Kelvin state.

(Refer Slide Time: 05:20)



Third law of thermodynamics

$$\Delta S = \int_{\underset{(initial)}{A}}^{B\,-\,(final)} \frac{dq_{rev}}{T} \quad \leftarrow \text{temperature}$$

$$\Delta S > \int_A^B \frac{dq}{T}$$

$$\underbrace{S - S_0}_{S_0 = 0} = \int_0^T \frac{dq_{rev}}{T}$$

$$q_{rev} > q_{irrev}$$

However we make a small detail ah to the argument there and the detail is the following, that we say that now I can define the; ΔS of whether the system or a surrounding but we are more concerned about the system in general. So ΔS can be written as the-

$$\Delta S = \int_A^B \frac{dq_{rev}}{T}$$

Where T is my temperature and the integration is done over the initial and the final states. So A is my initial state and B is the final state keep in mind that the definition is only true when the process is reversible. If on the other hand if we have an irreversible process then-

$$\Delta S > \int_A^B \frac{dQ}{T}$$

So in general the q reversible is always higher than q irreversible. Let’s say so if I am going from state A to state B and there is only one reversible process and there can be multiple irreversible processes for going from A to B and for all those processes the heat that is being added is always lower in comparison to the heat that is added in the case of a reversible process.

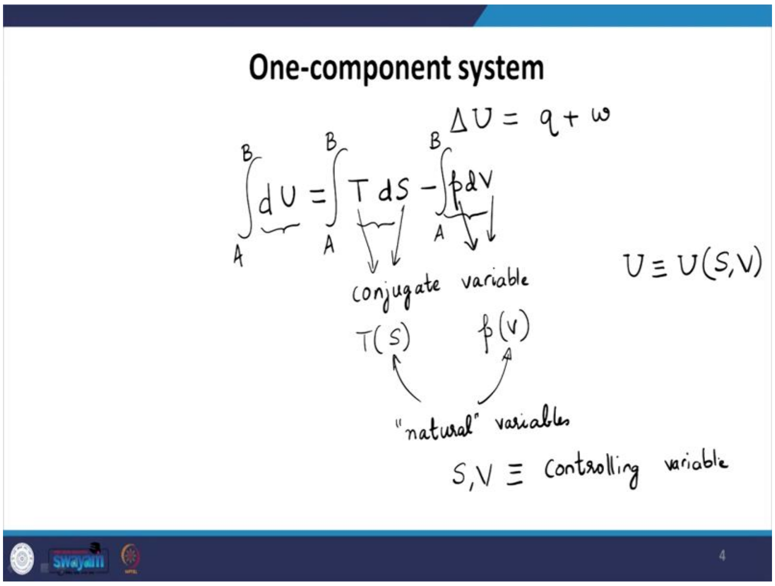
So now using this particular idea if I define my initial state as the 0 Kelvin state I can say that the entropy at any particular temperature-

$$S - S_0 = \int_0^T \frac{dq_{rev}}{T}$$

and by the third law of thermodynamics this particular reference state the entropy at 0 Kelvin is assumed to be 0 that is the state when we do not have any disorder in the system. As we discussed this correspond to a state where all the molecules are in their ground state if I go with the Boltzmann probability argument.

So with this particular idea I can now define the internal energy of the system in the following way.

(Refer Slide Time: 08:25)



One-component system

$$\Delta U = q + w$$

$$\int_A^B dU = \int_A^B T\,dS - \int_A^B p\,dV$$

conjugate variable

T(S) p(V)

"natural" variables

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

S,V ≡ Controlling variable

We have already established that the change in the internal energy is given by the heat added and the work done on the system and in the differential form we can write this as-

$$\Delta U = q + w$$

$$dU = T\ ds - pdv$$

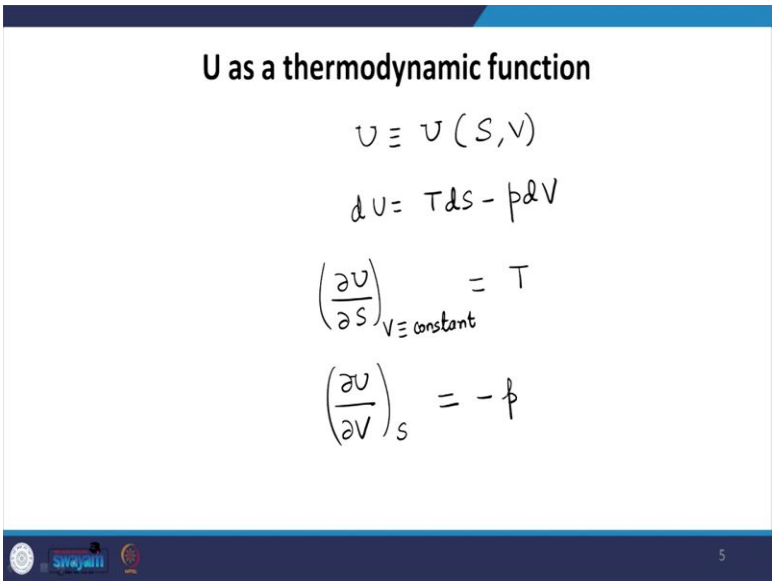
There is a small point here to make that both of these functions are actually path dependent and although we have said that in general the ΔS is higher than the dq by T going from A to B in this expression we have put an equality sign that comes from some cancellations. But the way to understand that is there are two contributions to the change in the internal energy, one contribution relates to temperature and entropy and one contribution ah relates to the pressure and the volume and this temperature and entropy they form like a pair that is called a conjugate variable. And this temperature and entropy they form like a pair that is called a conjugate variable and similarly the pressure and the volume from a pair and they are also called conjugate variable.

So with this idea of integration let us say for example if I am looking at the change in the internal energy of a process. I am basically looking at integration of what we have on the hand side. So you have integration of this and you have integration of this that gives me integration of that if I am looking from some state A to B.. So how will I compute this integral? So you may notice that in the first integral on the hand side we have T dS so S is the independent variable. So T therefore should be written as a function of S only then we can integrate with respect to the entropy S. Similarly in the second expression we have p dv so pressure should be written as a function of volume. So we have T as a function of S p as a function of V and the other way to say the same thing is that S and V they become the independent variables in this particular expression or they become what we know as natural variables.

In other words we can say that our energy ‘U’ is a function of I use the word U I use the U again as a function of S and V, I am looking at only one component system. So we are not concerned now what is the effect of different species present will come to that later in one component system you have only one component and this particular case I can write internal energy as a function of entropy and the volume. And why is that true because temperature and pressure does appear in the expression but temperature has to be written as a function of entropy and pressure has to be written as a function of volume because temperature is a conjugate variable of entropy pressure is a conjugate vary variable of volume.

There is one more way of saying this that is become important for the argument here. So let us say for example if I want to evaluate this particular expression what do I have to do? For that particular process I need to evaluate temperature as a function of entropy that means I need to conduct experiments at different entropy and find temperature in those conditions that will give me temperature as a function of entropy. Similarly I need to do experiments at different volume and find pressures in those conditions and therefore I will get the function pressure as a function of the volume and by doing that what essentially we mean to say is that we should have an ability to control the entropy and volume that means by saying that I need to do experiments for different entropy and find temperature what I mean to say that I should have a facility I need to have a way in which I can conduct the experiment at different entropy which means that I need to be able to control entropy at different values and find temperature at those values. Similarly I need to have an ability to control the volume and find the pressure at those particular volumes that point becomes extremely important as we go along.

(Refer Slide Time: 14:16)



U as a thermodynamic function

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

$$dU = Tds - pdV$$

$$\left(\frac{\partial U}{\partial S}\right)_{V\equiv constant} = T$$

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

So now this brings us to the definition of a thermodynamic function, and the first function I am writing is the function U that is the internal energy of the system and this is a function of two natural variables S and V. And I also have the differential expression of the same thing as-

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

$$dU = Tds - pdV$$

So if you are with me so far now what you can also see is since U is a function of S and V. If I want to define derivatives of U, derivatives can be defined with respect to S and with respect to V and these will be partial derivatives. So for example I can say-

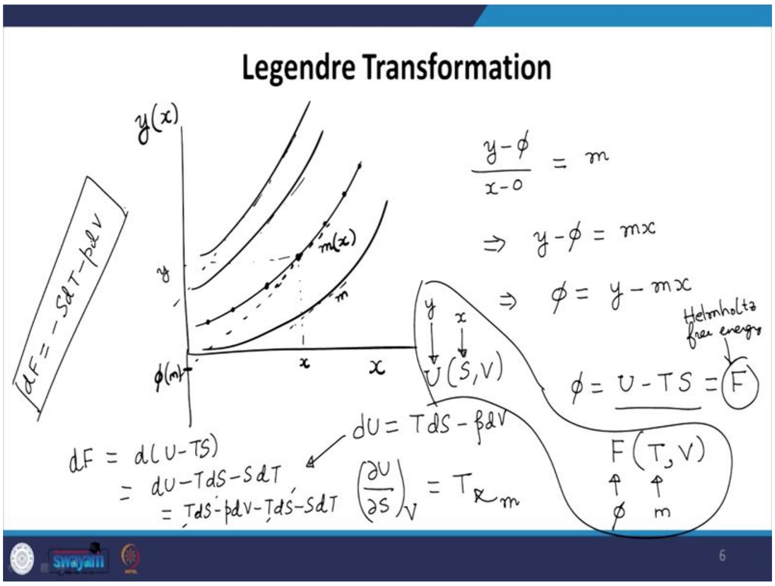
$$\left(\frac{\partial U}{\partial S}\right)_{V\equiv constant} = T$$

In a similar manner I can find-

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

So now I have a very nicely defined function and I can define its derivatives and we have pretty much all the tool box that we need, provided we are able to control S and V in the problem in general that is not always true because you may imagine the experiments you typically do in thermodynamics laboratory. So in those experiments it is probably easier to control temperatures as opposed to entropy and in many cases it is easier to control pressure as opposed to volume. The volume may change in a process but the pressure can be easily controlled it may so happen similarly entropy first of all entropy is rather vaguely defined because it relates the to the disorder of the system. So clearly controlling entropy is not something that comes very naturally as opposed to controlling temperature because we can have some kind of a thermostat and we can control temperature, controlling entropy is not as trivial as controlling temperature. So here is what the other thermodynamics functions come to our skew and we are going towards the definition of functions known as enthalpy and the free energies and the way to do that is purely a mathematical way of representing these functions. And that refers as the legendary transformation.

(Refer Slide Time: 17:37)



Legendre Transformation

$$\frac{y-\phi}{x-0} = m$$

$$\Rightarrow y-\phi = mx$$

$$\Rightarrow \phi = y - mx$$

$$\phi = \underline{U - TS} = \boxed{F}$$

Helmholtz free energy

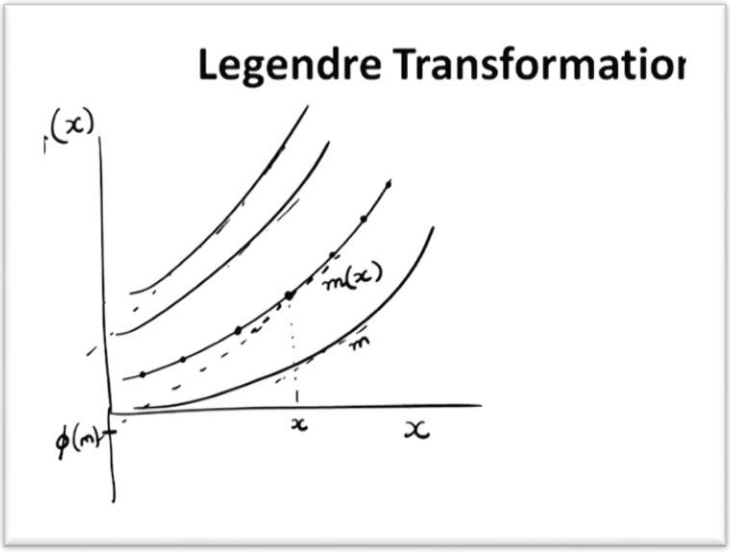
$$dU = TdS - pdV$$

$$dF = d(U-TS)$$
$$= dU - TdS - SdT$$
$$= TdS - pdV - TdS - SdT$$

$$\left(\frac{\partial U}{\partial S}\right)_V = T$$

$$\boxed{dF = -SdT - pdV}$$

So what the Legendre transformation stands for is that if I have for example some function y of some variable x then this function may have some shape. So instead of computing the y at different value of x I can get the same curve if I instead compute the slope of the function at different points x and let me call that slope something like m of x. So instead of writing y x I can write in terms of m of x. So if I know the slope at every point, I can hope to reconstruct the entire curve without knowing the function y itself. However there is a small catch and the catch is that for this particular slope you can have actually a family of curve which are parallel to this particular curve. So for example all this curve they will have the same value of m at this particular value of x if they are parallel to each other. So therefore apart from the slope we also consider the intercept of the slope that means if I take the intercept. Now this intercept is going to be a unique value for different curves in the picture. For example if I have a curve here that will have a different intercept as opposed to the curve in that I have drawn. So therefore instead of writing y as a function of x I can write the function in terms of the intercept and the slope because if I know the intercept and the slope I can uniquely define the curve and that is going to be the same curve as what we had and this whole idea is what is known as a Legendre transformation.



So the way of doing that is the following. So I can apply some geometry, so what I can do is that I can find the slope as-

$$\frac{y-\phi}{x-0}=m$$

$$y-\phi=mx$$

$$\phi=y-mx$$

So let us apply it in the case that we just had so I knew that-

$$U(S,V)$$

$$dU=TdS-pdV$$

$$\left(\frac{\partial U}{\partial S}\right)_V=T$$

So let us say for example I call this U as the function y that we have and I call this S as the variable x that we have then for this choice of variables this becomes my m. And therefore I can find the corresponding Φ as-

$$\phi=U-TS$$

So this means that instead of defining U, I can define a function U - TS and U - TS is no longer going to be a function of S and V instead U - TS is going to be a function of T and V. So both y and x I am replacing with Φ and m. So this function let me call this function f so this function is going to be a function of T and V. So this becomes-

$$F(T,V)$$

This transformation that we have done is what is known as the Legendre transformation. So I have changed the variables from yx to Φm and we have pretty much the same description of the curve. But in terms of thermodynamics you can see what advantage do have I got the advantage I have got is now the natural variables are no longer S and V the natural variables become T and V. So therefore the experiments I have to do now I have to do different temperatures and find entropy as those temperatures as opposed to what I had earlier where I was doing experiments at different entropy and computing temperatures at those entropy. So now we have temperature as a controlling variable earlier we had entropy as a controlling variable and this particular function is what is known as the Helmholtz free energy which is also a thermodynamic function just like the U.

So now I can also find the df by definition we have-

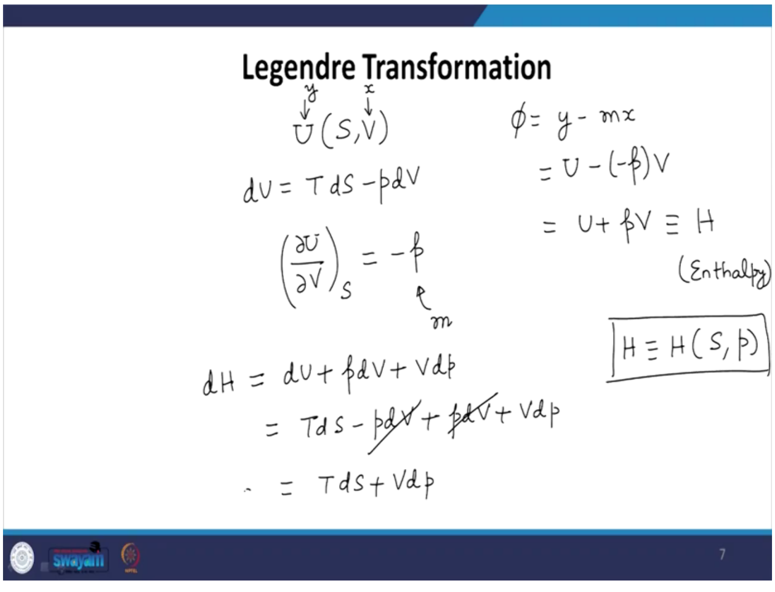
$$dF = d(U - TS)$$
$$= dU - TdS - SdT$$
$$= TdS - pdV - TdS - SdT$$

So we have cancellations and therefore we establish-

$$dF = -SdT - pdV$$

and we have successfully been able to define a new thermodynamic function that has temperature and volume as the controlling variable and it should not come to you as a surprise that both of them have pretty much similar meaning both U and F have pretty much similar meaning only the variable I am controlling has changed because both represent the same curve. In one case I am using y and x in other case I am using the intercept and the slope pretty much both are describing the same thermodynamics only the variable I am writing in terms of is changing, only the natural variables are changing everything else remains the same.

(Refer Slide Time: 25:37)



Legendre Transformation

$$\overset{\overset{y}{\downarrow}}{U}(S,\overset{\overset{x}{\downarrow}}{V})$$

$$dU = TdS - pdV$$

$$\left(\frac{\partial U}{\partial V}\right)_S = \underset{\underset{m}{\uparrow}}{-p}$$

$$\phi = y - mx$$
$$= U - (-p)V$$
$$= U + pV \equiv H$$

(Enthalpy)

$$\boxed{H \equiv H(S,p)}$$

$$dH = dU + pdV + VdP$$
$$= TdS - \cancel{pdV} + \cancel{pdV} + Vdp$$
$$= TdS + Vdp$$

So now we can extend this idea and look at for example the other variable that I want to change. Let us say for example, I again go back to this U and we have-

$$dU = TdS - pdV$$

but now instead of S I want to replace the volume as the natural variable. So U becomes-

$$\left(\frac{\partial U}{\partial V}\right)_S = -p$$

$$\phi = y - mx$$

$$= U - (-p)V$$

$$U + pV \equiv H$$

which we know as h or the enthalpy. And just like what we have done earlier we can again define-

$$dH = dU + pdV + Vdp$$

$$= TdS - pdV + pdV + Vdp$$

$$dH = TdS + VdP$$

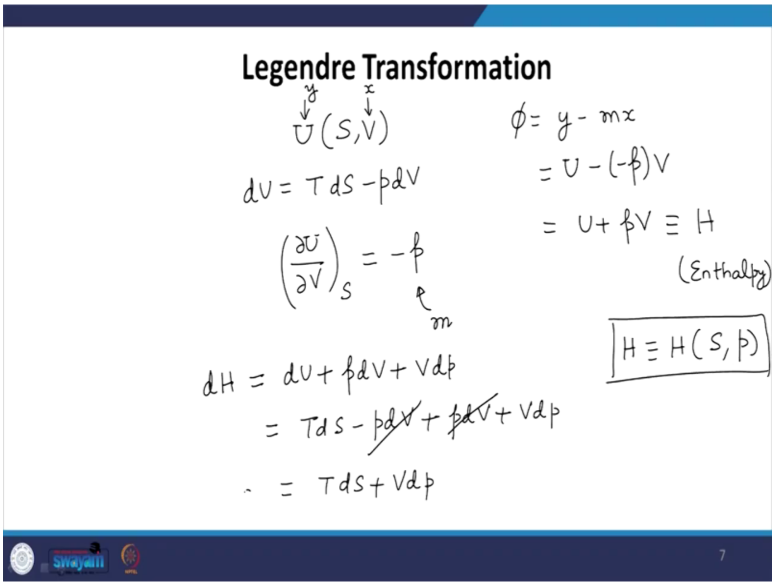
So we have H defined as a function of S and p that means the controlling variable has changed from v to p. So we have H defined as a function of S and p that means the controlling variable has changed from v to p.

So now I can do experiments at different pressures and find volume what I was doing earlier I was doing experiments at different volume and finding the pressure. Again it is a new thermodynamic function that we have defined and it has the following differential form-

$$dH = TdS + VdP$$

So if this is clear we can extend this idea to multiple slopes together.

(Refer Slide Time: 25:37)



Legendre Transformation

$$\overset{\overset{y}{\downarrow}}{U}(S,\overset{\overset{x}{\downarrow}}{V})$$

$$dU = TdS - pdV$$

$$\left(\frac{\partial U}{\partial V}\right)_S = \underset{\underset{m}{\uparrow}}{-p}$$

$$\phi = y - mx$$
$$= U - (-p)V$$
$$= U + pV \equiv H$$

(Enthalpy)

$$\boxed{H \equiv H(S,p)}$$

$$dH = dU + pdV + Vdp$$
$$= TdS - \cancel{pdV} + \cancel{pdV} + Vdp$$
$$= TdS + Vdp$$

So just like what we did earlier was we had y as a function of x and I defined a slope and I defined an intercept Φ but in reality what you have is a multivariable function. So you have U as a function of both S and V that means I need to define two slopes in terms of two variables that we have in the problem x1 and x2. So I can extend this idea and what we then have and you can derive it is I can define the intercept as-

$$\phi = y - \sum_{j=all\ variables} m_j x_j$$

And you can see how it will be applied. So in this case if I start with this function U as a function of S and V this becomes-

$$m_1 \equiv \left(\frac{\partial U}{\partial S}\right) = T$$

$$m_2 \equiv \left(\frac{\partial U}{\partial V}\right) = -p$$

$$\phi = U - TS + pV$$

So we have V so we have defined a new thermodynamic function which is known as G or the Gibbs free energy and just like what we had done earlier I can find-

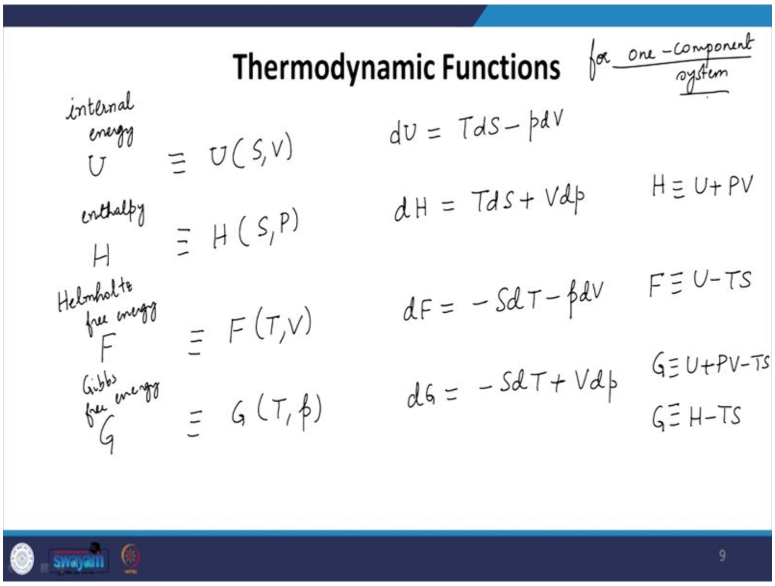
$$dG = dU - TdS - SdT + pdV + Vdp$$

$$dG = TdS - pdV - TdS - SdT + pdV + Vdp$$

$$= -SdT + Vdp$$

and G therefore becomes a natural function of temperature and pressure.

(Refer Slide Time: 30:50)



Thermodynamic Functions

for one-component system

internal energy $U \equiv U(S,V)$ $\quad dU = TdS - pdV$

enthalpy $H \equiv H(S,P)$ $\quad dH = TdS + Vdp$ $\quad H \equiv U + PV$

Helmholtz free energy $F \equiv F(T,V)$ $\quad dF = -SdT - pdV$ $\quad F \equiv U - TS$

Gibbs free energy $G \equiv G(T,p)$ $\quad dG = -SdT + Vdp$ $\quad G \equiv U + PV - TS$ $\quad G \equiv H - TS$

So to summarize our discussion we have defined four thermodynamic functions and what was different in them was the controlling variables that we used otherwise both are representing the same thermodynamics it is simply coming from a mathematical operation and these are U H F G namely internal energy, enthalpy, Helmholtz free energy and Gibbs free energy. These are functions of different variables U is a function of S and V, H is a function of S and p, F is a function of T and V and G is a function of T and p these are defined in differential form as-

$$U \equiv U(S,V); dU = TdS - pdV$$

$$H \equiv H(S,p); dH = TdS + Vdp$$

$$F \equiv F(T,V); dF = -SdT - pdV$$

$$G \equiv G(T,p); dG = -SdT + Vdp$$

We can also write-

$$H \equiv U + PV$$

$$F \equiv U - TS$$

$$G \equiv U + PV - TS$$

$$G \equiv H - TS$$

So this completes the thermodynamic functions for one component system.

In the next lecture we will see how this extends when we are looking at a multiple component system a multi component system where we will also have one additional variable that we know as the chemical potential.

So with that I want to conclude here thank you and see you next class.