Introduction to Molecular Thermodynamics
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Lecture - 03
Thermodynamic Potential

Welcome. We are now discussing the Basic Principles of Thermodynamics, and we are addressing the energy functions and their relationship to the condition of spontaneity and equilibrium in isolated as well as non-isolated systems.

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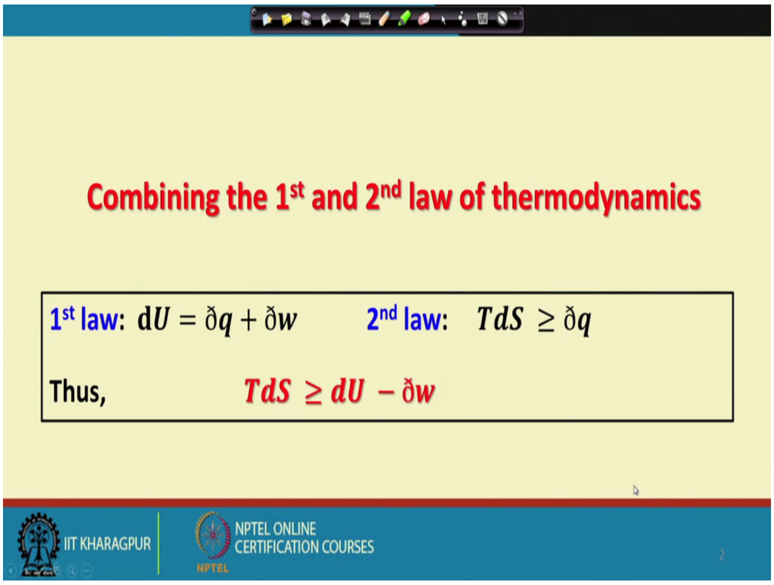

Combining the 1st and 2nd law of thermodynamics

1st law: $dU = \eth q + \eth w$ 2nd law: $TdS \geq \eth q$

Thus, $TdS \geq dU - \eth w$

Now we have already discussed that, if I combine the first and the second law of thermodynamics, in that case there is a single relationship that we find which is valid to predict the condition of spontaneity and equilibrium that is associated with a change in entropy d s, I will change in internal energy d U and d w is the infinitesimal amount of work that is being done by the system or on the system. Depending on these, we are next going to think about what are the kinds of systems that we see in the real world. If we walk into a chemistry laboratory this is what you would see.

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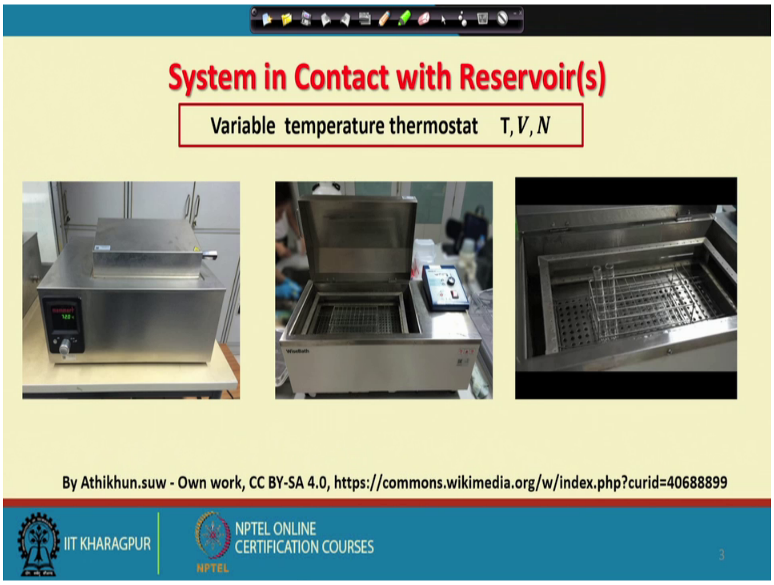

System in Contact with Reservoir(s)

Variable temperature thermostat T, V, N

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You will see huge chests like this these are the commercially available thermostats. If I open the lid, what you find is there is a compartment inside which can be filled with water and can be heated electrically, and the temperature that you want in that can be controlled from this digital pad.

And then you can put in some test tube inside these cages and then you close the lid, and the condition that you have is you are using a variable temperature thermostat. And you can carry out your chemical reactions in the at the condition of constant temperature, constant volume as well as a constant number of particles; that is because you have a lid on and no particle can escape from the system during the process.

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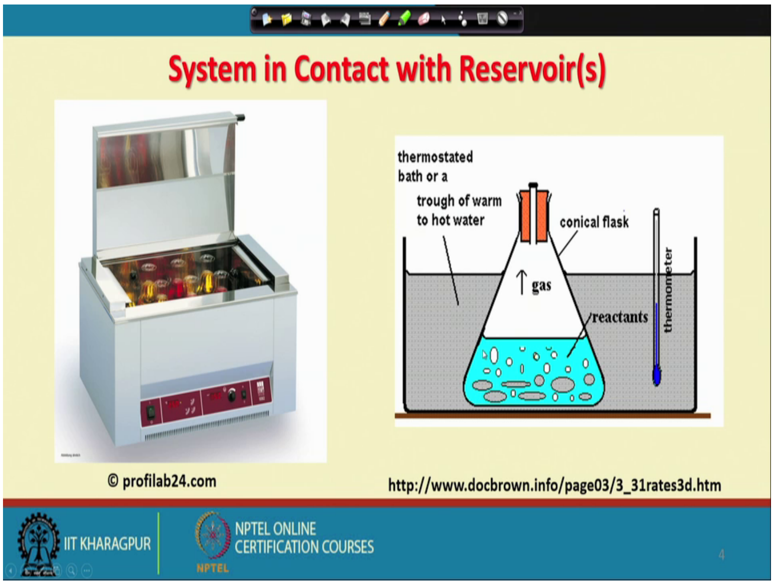

System in Contact with Reservoir(s)

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You can also have the chemical reaction being conducted under the condition, where it is connected to the rest of the universe or the surroundings.

So, this is one such example where you see schematically that we have a chemical process going on, and a gas being liberated as a result of it, but in this case the gas cannot escape to the surrounding. So, what kind of thermodynamic environment does this chemical reaction face? It has been placed in a trough of warm hot water and this trough acts as a thermostat for this system. And what is the temperature at equilibrium that you can safely measure using a analog thermometer as shown here. In the more modern setups these are controlled electrically and measured with using the digital display port. Now if you pick off this lead, in that case the gas can escape into the surrounding, and the reaction system becomes an open system.

In general in the chemistry laboratory, one would like to carry out chemical reactions at different temperatures and you may not even see the standard commercially available the digitally controlled variable temperature thermostats. So, what one does in those cases?

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System in Contact with Reservoir(s)

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Low temperature
thermostat
T, V, N

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Variable temperature thermostat
+
Constant atmospheric pressure
$T, p, N/T, V, \mu$

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Here is an example that is a very simple thermostat that has been made by placing an ice bowl and carrying out the chemical reaction inside a round bottom flask by putting it in this ice bowl. So, in general this chemical reaction will occurred at a constant temperature constant volume as well as a constant number of particles condition, because the outlets of the flask these have been totally covered. And if it so happens that you are trying to carry out your chemical reaction in an open environment you are basically looking at a setup like this.

In here when you are heating up the system, there is no lead and the particles can move away. And therefore, you can have this chemical reaction occurring at a given temperature, at the atmospheric pressure. And if all the components of the system are in volatile or non-volatile, in that case they will this reaction will occur at constant temperature, constant pressure and constant number of particles.

On the other hand if some of the components are volatile here, in that case what you will find is the thermostat will maintain a constant temperature condition. The constant volume condition is maintained by having the entire beaker filled with the reaction mixture, but then the some of the particles are escaping into the environment. And therefore, at equilibrium the equilibrium state will be defined by giving a constant value to the chemical potential of each of the components present in the system; now when you are dealing with systems that are non-isolated. Then the question obviously comes can we use thermodynamics to predict the outcome of any change in state of such systems that is in first and the second is can we extract some energy, when the system is in contact with a reservoir.

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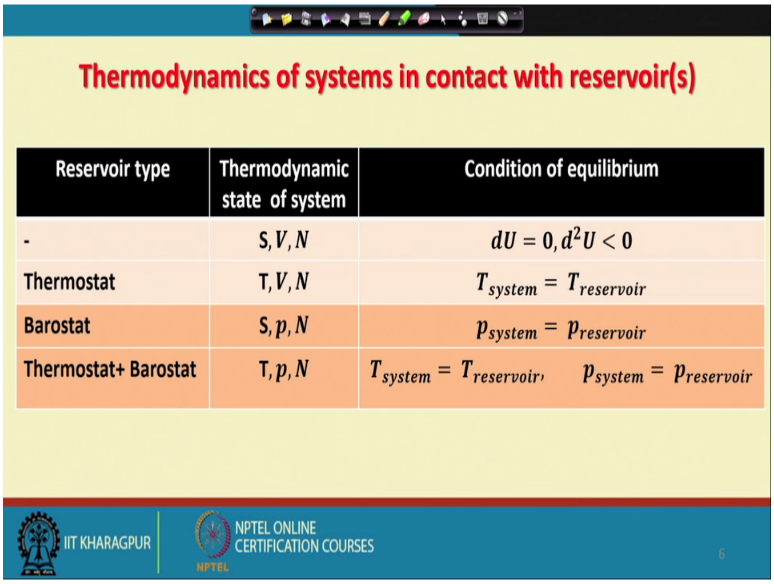

Thermodynamics of systems in contact with reservoir(s)

Reservoir type	Thermodynamic state of system	Condition of equilibrium
-	S, V, N	$dU = 0, d^2U < 0$
Thermostat	T, V, N	$T_{system} = T_{reservoir}$
Barostat	S, p, N	$p_{system} = p_{reservoir}$
Thermostat+ Barostat	T, p, N	$T_{system} = T_{reservoir}, \quad p_{system} = p_{reservoir}$

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So, let us take these two questions step by step and first let me show you how we define the thermodynamic state of a system, when first it is isolated and we already know that for an isolated system if you define a given value of s which is the maximum value of entropy under the given condition, the volume of the system and number of particles. One specific value to each of these three variables will define the thermodynamic state of an isolated system.

And in this case the condition of equilibrium requires that the associated energy, that is the internal energy that is a minimum, this is going to be a greater than sign. Now if we attach a thermostat to the system, which is otherwise isolated, this means that now I have a system like this.

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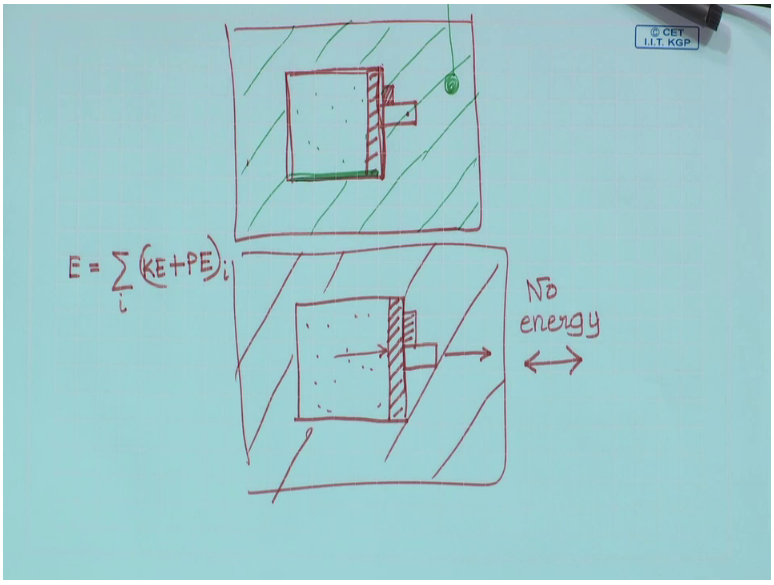

So, initially I had a system which is surrounded by adiabatic, rigid and impermeable wall.

Now, what I have done is, I put this in a reservoir which is much bigger than the size of the system and I have made one part of the wall of the system conducting. So, if I have some gas inside and this is a reservoir then what will happen? The system will be able to exchange energy in the form of heat with the reservoir; under that condition the standard way of measuring the equilibrium condition is that, you measure the temperature of the reservoir and when the temperature becomes independent of time, you say that the system has achieved equilibrium.

Now, coming back to this description therefore, the question is if a system is in contact with a thermostat and it has attained an equilibrium, then how do I define this thermodynamic state of the system. I shall obviously, assign the temperature value as I see from my thermometer or my digital display pad, and the volume of the system because it is now surrounded it is still surrounded by a rigid wall, and a number constant number of particles because the wall surrounding the system is impermeable. And in that case the most accessible condition of equilibrium is that, the system temperature must be equal to the reservoir temperature.

Now, instead of making one wall conducting; let me have another situation where I have a similar system. So, surrounded by adiabatic and impermeable wall put in contact with a reservoir, but what I have done is I have attached a piston on one side of this system. Therefore, this piston can be moved horizontally and while moving this piston, that is no energy its used.

So, it is a massless frictionless piston. So, no energy supplied to the system or no energy is being taken out of the system. So, under what condition will the system attain equilibrium? That is of course when the piston comes to rest. So, let us say that I have some gas over here and the so the gas will try to push the piston out and whatever is holding the piston here, will try to push the piston in.

So, in the final equilibrium state, the piston will acquire an equilibrium position. So, at this stage you will find out how much pressure you require to put the piston in this apparently time independent position and therefore, the condition of equilibrium in that case will be determined by saying that well you have the pressure of the system equal to the pressure of the reservoir and the equilibrium state of the system now is defined in by defining a constant value of the entropy, a constant value of the pressure and the constant number of particles. The more common situation that you come across is the isothermal isobaric situation.

So, now, I have the same system as I had before, but what I have done is, while one wall is adiabatic I have added a movable piston to another wall. So, this is typically the kind of system which is connected to not only a thermal reservoir, but also a pressure reservoir. So, under this condition when do I know that the system has attained equilibrium? So, first the temperature of the system has to become equal to the temperature of the reservoir, and then the pressure of the system has to become equal to the pressure of the reservoir and then the equilibrium state is characterized by giving a value to the temperature of the system, pressure of the system as well as the number of particles.

Now in this particular case, what we see is well in the isolated system we have described the equilibrium condition in terms of an extensive variable what was that? That was internal energy. So, we talked about the condition of equilibrium as minimization of internal energy. Now for the non-isolated systems can we have such energy functions that will give us the condition of equilibrium entirely in terms of system properties that is where we look for alternative forms of energy functions in thermodynamics.

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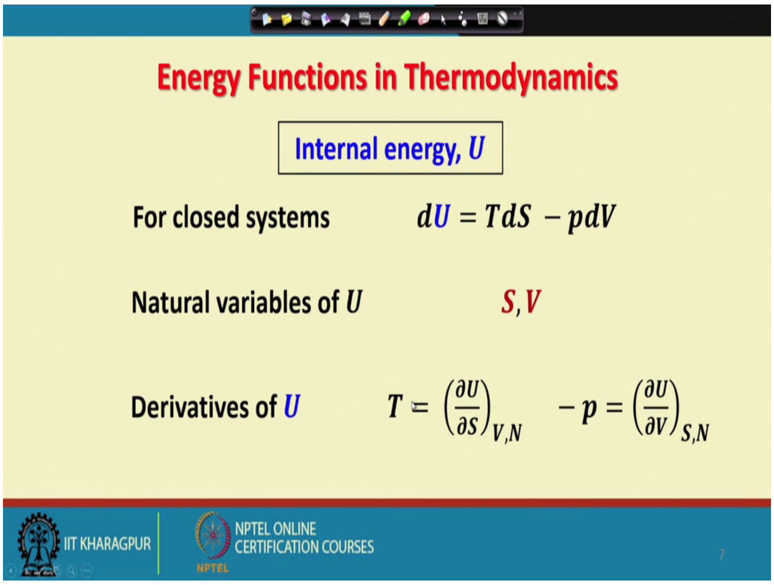

Energy Functions in Thermodynamics

Internal energy, U

For closed systems $dU = TdS - pdV$

Natural variables of U S, V

Derivatives of U $T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$ $-p = \left(\frac{\partial U}{\partial V}\right)_{S,N}$

The first one is of course, internal energy, its very interesting to know that the concept of internal energy was there. From a long time back we knew that a system must contain some property that tells us about its ability to do some work.

And the first law of thermodynamics quantified this idea by introducing the internal energy to us. In the molecular systems if you have a molecular system then what would be its internal energy? The internal energy the instantaneous energy of the system is going to be a summation over the kinetic energy and the potential energy of each particle that you have and then summed over all possible particles now if I have an isolated system then internal energy is this particular energy.

Now what we have learnt is for closed systems d U is TDS minus pdV and this is obtained by combining the first and the second law of thermodynamics. And by the structure of thermodynamics we know that U is a state function and therefore d U must act as a an exact differential and this is typically the form of an exact differential. So, what does it tell us? It tells us that U has two natural variables in a closed system. The first one is s and the second one is V; therefore, if a system whose initial state is defined by assigning some values of s and V and if it undergoes a change in state.

In that case what will happen is the change in state will be characterized by some change d S and some change d V and there will be associated directly a corresponding change in the internal energy. So, once we know that we can also understand what is T and what is

p. Both T and p are intensive variables. So, what we find here is this that, what I shall have is intensive variables and nothing, but the derivatives of the energy function that is internal energy. So, if your equilibrium state of the system the thermodynamic state of the system is defined in terms of s and V, then temperature is a derivative of U with respect to s keeping V and N constant and pressure negative of pressure rather is a derivative of U with respect to V keeping S and N constant.

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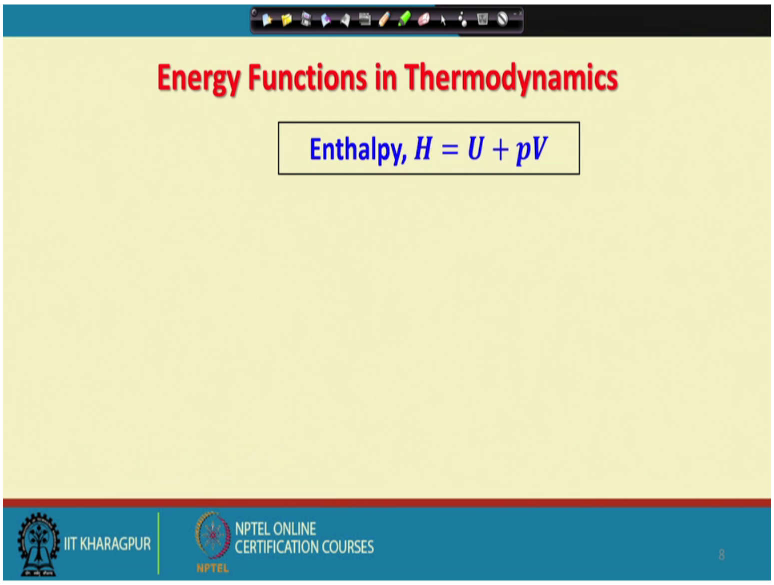

Energy Functions in Thermodynamics

Enthalpy, $H = U + pV$

Now we next come to another energy function that we have seen in the consequence of first law of thermodynamics which is enthalpy. So, by definition enthalpy is H equal to U plus pV.

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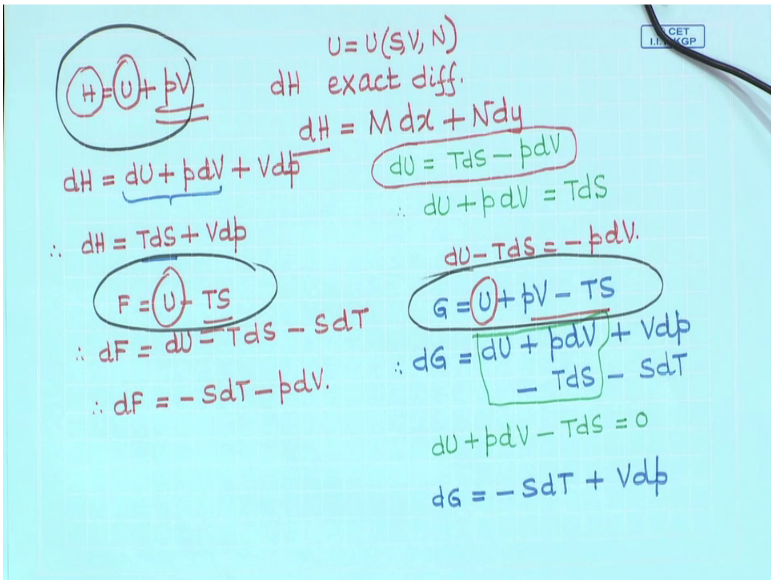

$U = U(S, V, N)$

$H = U + pV$

dH exact diff.

$dH = M\,dx + N\,dy$

$dH = \underbrace{dU + p\,dV} + V\,dp$

$dU = T\,dS - p\,dV$

$\therefore dU + p\,dV = T\,dS$

$\therefore dH = T\,dS + V\,dp$

$dU - T\,dS = -p\,dV.$

$F = U - TS$

$\therefore dF = dU - T\,dS - S\,dT$

$\therefore dF = -S\,dT - p\,dV.$

$G = U + pV - TS$

$\therefore dG = dU + p\,dV + V\,dp - T\,dS - S\,dT$

$dU + p\,dV - T\,dS = 0$

$dG = -S\,dT + V\,dp$

Now I would like to ask the question just as U was a natural function of S, V and N in a closed system, what are the natural variables of H once again please remember.

That H is a state function therefore, d H is an exact differential and therefore, I should expect that d H should be written as something like M d x plus N d y, where x and y are the two independent variables on which H depends . So, now, let us have a look at what is d H. So, d H is equal to d U plus pdV plus Vdp clear. But for any general system if I combine the first and the second law of thermodynamics, I know that d U is equal to TDS minus pdV right therefore, I can write d U plus pdV that is equal to TDS. If I replace this expression in the expression for d H I would get d H is equal to TDS plus Vdp.

And therefore, what I have done is I have replaced this part by this term using the combination of first and the second law of thermodynamics. Now once I know this for a closed system where there is no change in the number of particles.

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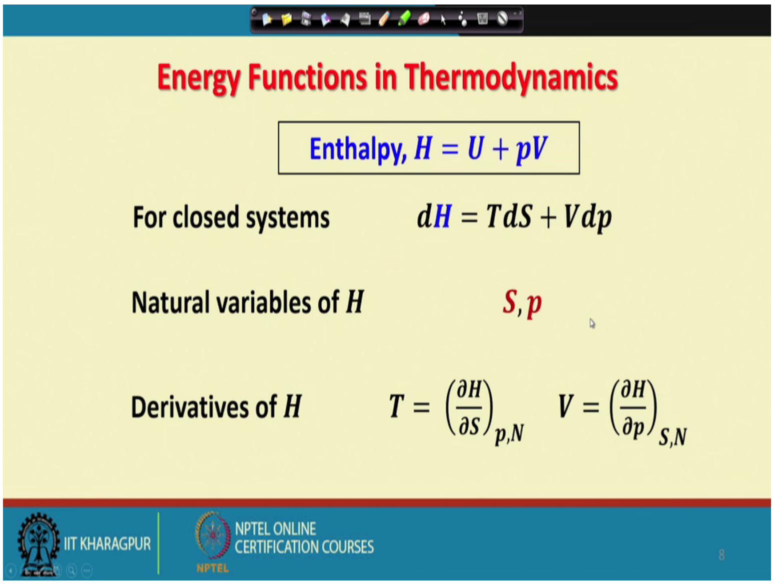

Energy Functions in Thermodynamics

Enthalpy, $H = U + pV$

For closed systems $dH = TdS + Vdp$

Natural variables of H S, p

Derivatives of H $T = \left(\frac{\partial H}{\partial S}\right)_{p,N}$ $V = \left(\frac{\partial H}{\partial p}\right)_{S,N}$

I would immediately conclude that the natural variables of H are s and p, and correspondingly when the thermodynamic state of a system is represented by s p and a constant value of n, then temperature is defined as the derivative of H with respect to s keeping p and n constant, and v is defined as the derivative of H with respect to be keeping s and n constant.

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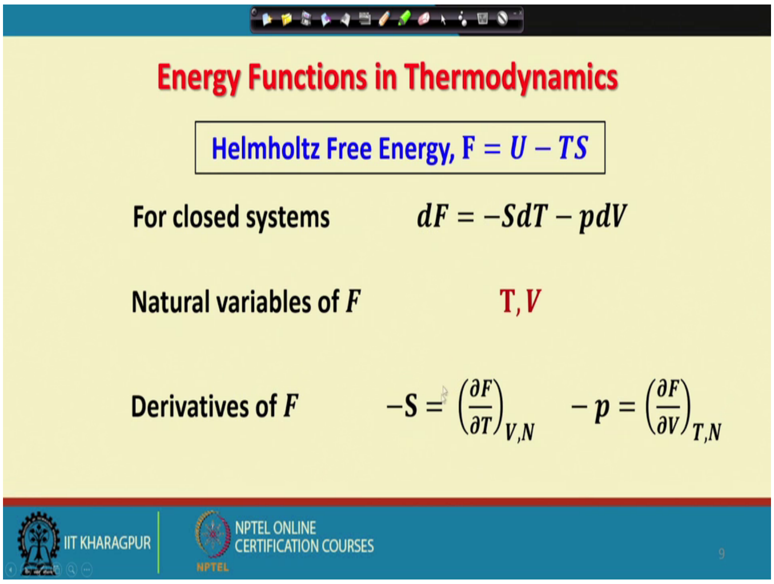

Energy Functions in Thermodynamics

Helmholtz Free Energy, $F = U - TS$

For closed systems $dF = -SdT - pdV$

Natural variables of F T, V

Derivatives of F $-S = \left(\frac{\partial F}{\partial T}\right)_{V,N}$ $-p = \left(\frac{\partial F}{\partial V}\right)_{T,N}$

Now similarly we can think of the Helmholtz free energy which is defined as U minus TS and starting from the definition once again you can show that d F is equal to U minus

TS therefore, d F is equal to d U minus TDS minus sdt right and what is it that we know about d U minus TDS. D U minus TDS from here I can say that this is equal to minus pdV. As a result I can now simplify and say that d f is equal to minus sdT minus pdV. Therefore, can I answer this question, what are the natural variables of f the Helmholtz free energy? The natural variables of F is T and V and of course, we are talking about closed systems and therefore, n is held constant.

And from the expression of dF we can immediately conclude that minus S and minus p are the derivatives corresponding to first partial derivative of F with respect to T keeping V and N constant and del F del V keeping T and N constant. The fourth energy function that we come across is the Gibbs free energy.

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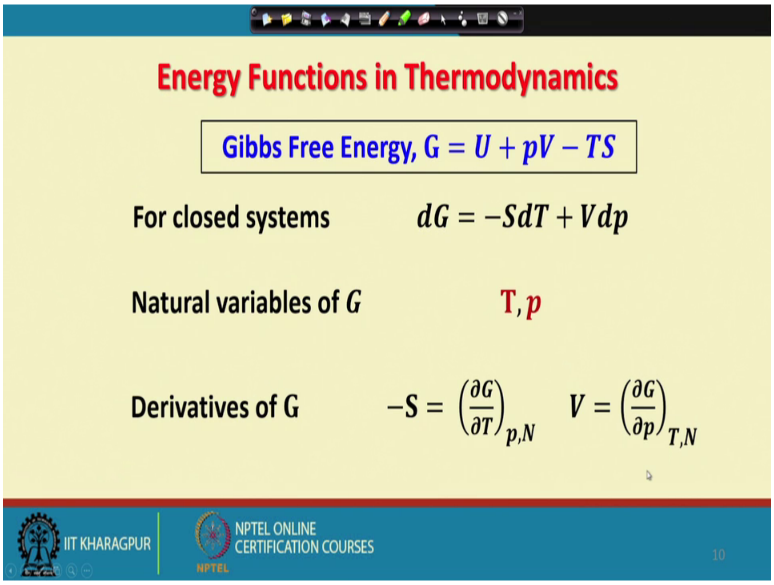

Energy Functions in Thermodynamics

Gibbs Free Energy, G $= U + pV - TS$

For closed systems $dG = -SdT + Vdp$

Natural variables of G T, p

Derivatives of G $-S = \left(\frac{\partial G}{\partial T}\right)_{p,N}$ $V = \left(\frac{\partial G}{\partial p}\right)_{T,N}$

So, how is the Gibbs free energy defined? The Gibbs free energy is defined in as U plus p V minus TS. So, once again let us write it out so G that is equal to U plus p V minus TS therefore, what is dG? DG that is equal to d U plus pdV plus Vdp minus TDS minus Sdt. Now let us look back at what the first law of thermodynamics tell us.

It says that d U is equal to TDS minus pdV therefore, I can very easily say that well in that case I must be having d U plus pdV minus TDS equal to 0; which means that this part of this equation is becoming equal to 0 and I am left with d g that is equal to minus sdT plus Vdp . So, for a closed system can you now tell me what are the natural variables of G. The natural variables of G are t and p and once again you can get if you know the g you can get the negative of entropy as the partial derivative of g as a oh as a with respect to temperature under isobaric conditions, and you can retrieve volume as a partial derivative of G with respect to pressure under isothermal conditions; now that we know the definitions of all these free energies.

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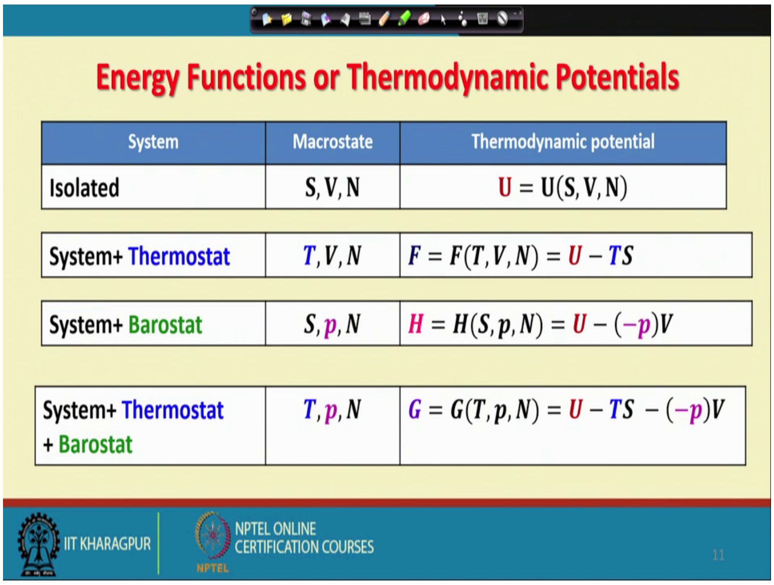

Energy Functions or Thermodynamic Potentials

System	Macrostate	Thermodynamic potential
Isolated	S, V, N	$U = U(S, V, N)$
System+ Thermostat	T, V, N	$F = F(T, V, N) = U - TS$
System+ Barostat	S, p, N	$H = H(S, p, N) = U - (-p)V$
System+ Thermostat + Barostat	T, p, N	$G = G(T, p, N) = U - TS - (-p)V$

Let us just now summarize what we have obtained here. Now if you have an isolated system then there are three independent variables which are S V and N that would describe the equilibrium state of a given system and of these three independent variables if you want to see the corresponding thermodynamic potential, which directly depend on them then I would say that you are going to have internal energy as the thermodynamic potential corresponding to the isolated system. So, what is the thermodynamic potential?

A thermodynamic potential is an energy function for the thermodynamic system that or the macroscopic state that we are talking about, and this is going to be a function of the three variables with which you are defining the macroscopic state of the system. Now if I have a system and thermostat, then the macro state is defined in terms of temperature volume and number of particles and the energy function, which has these three variables as its natural independent variables is the Helmholtz free energy. If I have a system and the barostat in that case we come across the enthalpy, and this is defined as U plus p V. Now if I have a system in contact with both the temperature and pressure reservoir, in that case this is how I will define the macro state of the system or the thermodynamic state of the system and the corresponding thermodynamic potential is going to be the Gibbs free energy.

obviously, the question arises as to why am I interested in thinking about these different energy functions, can I finally, use them to predict the direction of a spontaneous change in state or can I determine the condition of equilibrium in terms of these energy functions.

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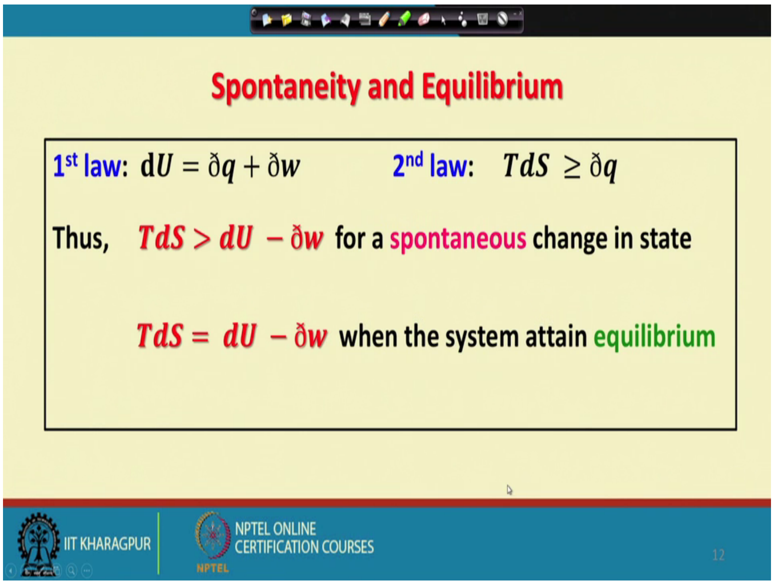

Spontaneity and Equilibrium

1st law: $dU = \eth q + \eth w$ 2nd law: $TdS \geq \eth q$

Thus, $TdS > dU - \eth w$ for a spontaneous change in state

$TdS = dU - \eth w$ when the system attain equilibrium

So, let us next have a look at what we can do about predicting this condition of spontaneity and equilibrium in terms of these energy functions, but please remember all we know at this stage is the presence of the combination of the first law and the second law of thermodynamics, whereby if I am looking for a spontaneous change in state TDS must be greater than d U minus del w.

And when the system attains equilibrium then I must be having TDS becoming equal to d U minus del w. Now with this background in mind let us go and have a look at is a at our spontaneous change in state Where the condition is minus d U plus TDS is greater than minus del w.

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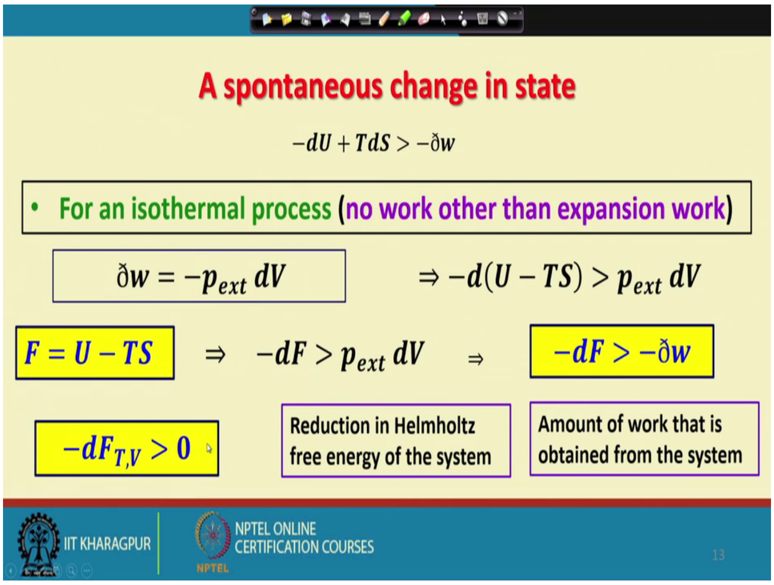

A spontaneous change in state

$$-dU + TdS > -\eth w$$

- For an isothermal process (no work other than expansion work)

$$\boxed{\eth w = -p_{ext}\,dV} \qquad \Rightarrow -d(U - TS) > p_{ext}\,dV$$

$$\boxed{F = U - TS} \quad \Rightarrow \quad -dF > p_{ext}\,dV \quad \Rightarrow \quad \boxed{-dF > -\eth w}$$

$$\boxed{-dF_{T,V} > 0}$$

Reduction in Helmholtz free energy of the system

Amount of work that is obtained from the system

Now let me consider a system initially at equilibrium which is undergoing an isothermal process. And this isothermal process is it involves only expansion work, in that case I can very easily say that the work that appears on the right hand side of this equation is nothing, but minus p external into d V that is one of the fundamental equations in thermodynamics.

Now then once you know this you can use it to go further and say that how will this relationship be modulated for an isothermal process, where del w is given by this expression and the temperature is constant. If the temperature is constant; obviously, on the left hand side you can take t inside the differential and you can write the left hand side as negative of differential of this quantity U minus TS and for a spontaneous change in state, it must happen that minus d of this quantity must be greater than p external into d V, but we already know that this U minus TS what is U? U is the internal energy of the system what does T? T is the temperature under which the system is maintain in equilibrium with the thermostat and S is the entropy of the system and f is given by U minus TS and.

Therefore it follows that for a spontaneous change in state to occur minus d f must be greater than p external into d V and this means that whenever a system is undergoing a change in state by performing some expansion work pv work in that case there will be some decrease in the Helmholtz free energy. And this decrease in Helmholtz free energy must be greater than whatever work that is being extracted from the system. And therefore, this slide the take home message from this slide is that, minus d F is a reduction in the Helmholtz free energy of the system, and minus d w is the amount of work that is being obtained from the system. And if you have a process where the system is undergoing a change in state under the constant temperature and constant volume condition then what is the condition for and irreversible spontaneous process.

The condition is then given by minus d F T, V greater than 0 can you guess where this 0 came from? If you keep the volume constant in that case del w is going to be 0 because there will be no change in volume. As a result for a constant temperature constant volume process if the system undergoes a change in state it will do so spontaneously in the direction which decreases the Helmholtz free energy of the system.

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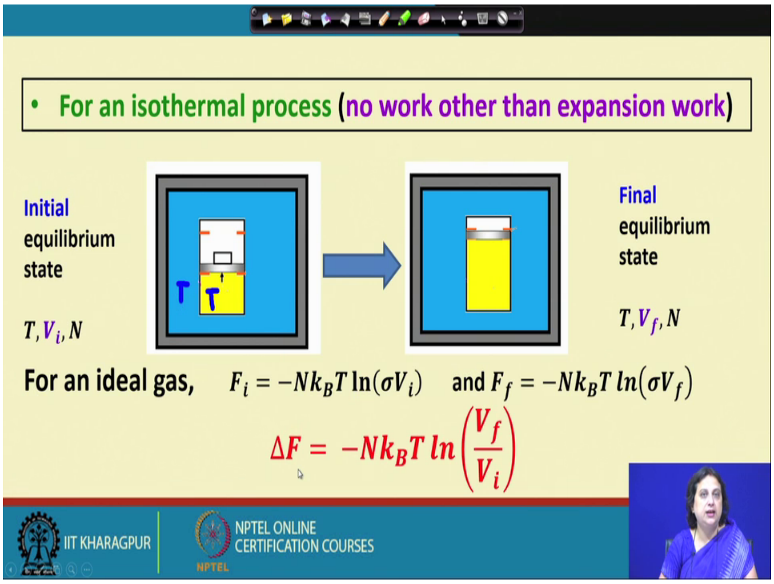

- For an isothermal process (no work other than expansion work)

Initial equilibrium state

T, V_i, N

Final equilibrium state

T, V_f, N

For an ideal gas, $F_i = -Nk_BT\ln(\sigma V_i)$ and $F_f = -Nk_BT\,ln(\sigma V_f)$

$$\Delta F = -Nk_BT\,ln\left(\frac{V_f}{V_i}\right)$$

Now let me take an example of what I mean by an isothermal process, where there is no work other than the expansion work. So, let me think of a system like this.

What I am trying to show you here is as follows; this is my system and this system is immersed in a reservoir and the system plus the reservoir they are surrounded by a rigid adiabatic impermeable wall. So, the composite setup of the system and the reservoir this is isolated. Now let us focus on the system, this system initially it has some kind of an ideal gas and this is kept with the volume of V i at a given temperature T and this temperature T is the temperature of the reservoir as well as the temperature of the gas.

Now I allow this system to expand and when the system expands, we find that the final equilibrium state is now characterized by some volume Vf under the given experimental condition please try to understand that this expansion work is being carried out while the system maintains this isothermal condition such that its temperature is equal to the temperature of the reservoir.

Now for an ideal gas the initial free energy value of the system will be minus NkT log of some constant into V i the where V i is the initial volume, and the final Helmholtz free energy is going to be dependent on V f therefore, as the system passes from this initial equilibrium state to the final equilibrium state you see that the net change in Helmholtz free energy this is dependent on minus NkT log of V f by V i. Here k t k B is the Boltzmann constant, temperature is the constant temperature under which this process is occurring and as you see that under the given condition.

The gas is going to expand provided V f; provided this initial volume is initial condition is such that upon withdrawal of this excess pressure, V f becomes greater than V i. It is only under that condition that the delta f becomes less than 0 and the process is accompanied by a reduction in the Helmholtz free energy.

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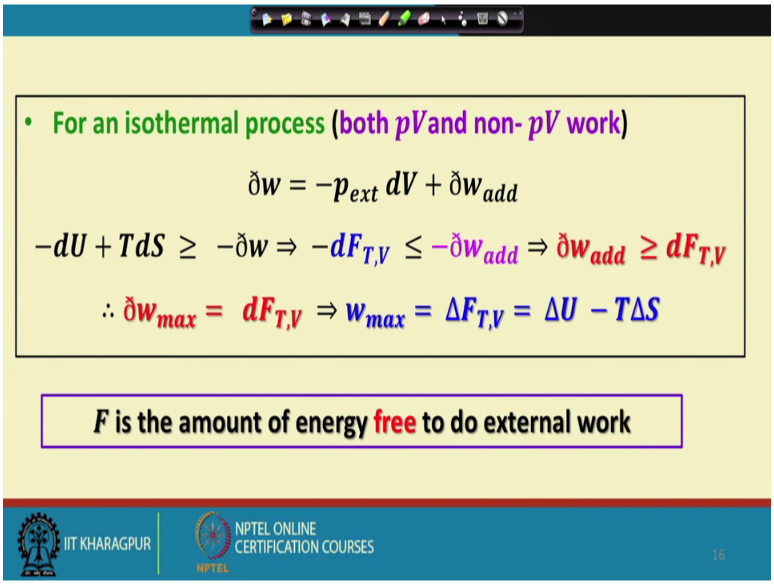

- For an isothermal process (both pV and non- pV work)

$$\eth w = -p_{ext}\, dV + \eth w_{add}$$

$$-dU + TdS \geq \; -\eth w \Rightarrow \; -dF_{T,V} \leq -\eth w_{add} \Rightarrow \eth w_{add} \geq dF_{T,V}$$

$$\therefore \eth w_{max} = \; dF_{T,V} \Rightarrow w_{max} = \Delta F_{T,V} = \Delta U \; - T\Delta S$$

F is the amount of energy free to do external work

And further what I can talk about is if you have both p v and non p v work, in that case even if you are carrying out a isothermal and isobaric process we will be able to show very easily that what I find is the maximum work that can be extracted from the system is actually related to the decrease in Helmholtz free energy under such condition.

And therefore, we would like to say that F is the amount of energy free to do the external work, under the condition where a constant temperature is being maintained between the system and the surrounding.

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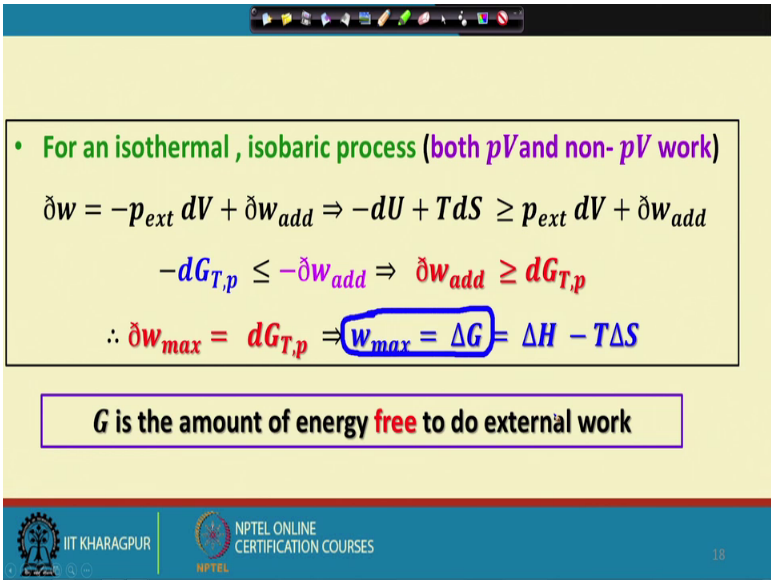

- For an isothermal , isobaric process (both pV and non- pV work)

$$\eth w = -p_{ext}\, dV + \eth w_{add} \Rightarrow -dU + TdS \geq p_{ext}\, dV + \eth w_{add}$$

$$-dG_{T,p} \leq -\eth w_{add} \Rightarrow \eth w_{add} \geq dG_{T,p}$$

$$\therefore \eth w_{max} = dG_{T,p} \Rightarrow \boxed{w_{max} = \Delta G} = \Delta H - T\Delta S$$

G is the amount of energy free to do external work

I will leave you to work on this test case where there is an isothermal and isobaric process with only pressure volume work. In that case it is very easy to show that you must be having this particular condition valid that the decrease in this particular quantity should be greater than or equal to 0, but we already know that what is this quantity it is nothing, but the Gibbs free energy and therefore under isothermal and isobaric condition, process a system will undergo a spontaneous process provided the corresponding change in Gibbs free energy is negative. If I think of an additional work being done by the system over and above the pressure volume work. Then again you can very easily show that this additional work is going to be equal to this additional work when it is done under reversible condition, that is maximum value and this is going to be equal to the change in Gibbs free energy.

Under the given conditions and therefore, G as defined here is the amount of energy free to do external work under isothermal and isobaric condition. Now, that we know that there are different forms of energy. Then let us ask this question we have introduced these definitions like H is equal to U plus p V h f is equal to U minus TS or G is equal to U plus p v minus TS all of them originate from U all of them have U in them and then some correction term which is appearing over here.

In the next lecture we are going to see how these additional terms come and how they control the condition of equilibrium.

Thank you.