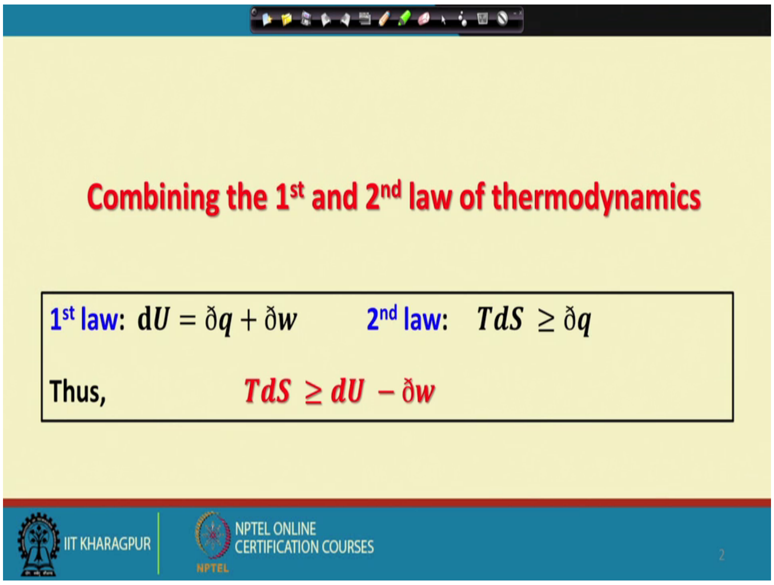
Introduction to Molecular Thermodynamics
Prof. Srabani Taraphder
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture - 04
Thermodynamic Potentials (Contd.)

Welcome. Let us now continue our discussion of using the Thermodynamic Potentials in predicting the final equilibrium state of a given system that may or may not be connected to the reservoir.

(Refer Slide Time: 00:31)



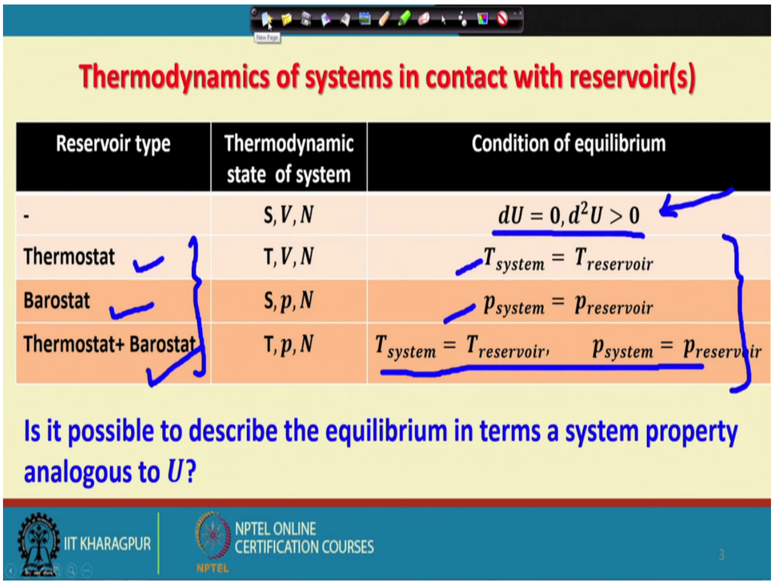
Combining the 1st and 2nd law of thermodynamics

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

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

So, once again the basis of our discussion is the combination of the first and the second law of thermodynamics; where we say that whatever the process maybe, I should have this condition valid. The inequality sign is valid when I am looking for a spontaneous change in state and the equality sign is valid, when the system has attained equilibrium.

(Refer Slide Time: 01:01)



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	$T_{system} = T_{reservoir}, \quad p_{system} = p_{reservoir}$

Is it possible to describe the equilibrium in terms a system property analogous to U?

IIT KHARAGPUR

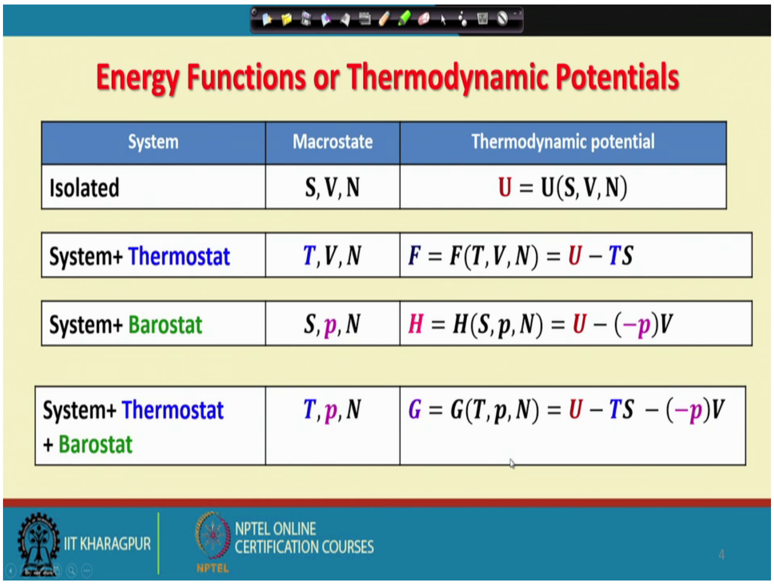
NPTEL ONLINE CERTIFICATION COURSES

Now, the basic question that we are asking is this; is it possible to describe the system in equilibrium; the condition of equilibrium in a system that is in contact with the reservoir? And once that system property has become equal to the reservoir property, can I use an energy function just like U to describe the condition of equilibrium? So, to be more specific for an isolated system; we have already seen that it is a minimization of internal energy that characterizes the condition of equilibrium.

But when I have added a thermostat to the system or a barostat to the system or if I am maintaining the system at a constant temperature or pressure; I understand that within my measurable setup, I must be having the temperature of the system and the reservoir equal in this case; the pressures between the system and reservoir equal in this case. And both the temperature and the pressure must satisfy the equality condition, when I have attached the system to a thermostat and barostat.

But please note that all of these quantities that I mentioned here; these are intensive variables. On the other hand, in the original isolated system I was talking about the equilibrium condition in terms of a system property and this is the internal energy. So, the question is for all the other systems; is it possible to describe the condition of equilibrium using some other energy function that would be entirely a property of the system?

(Refer Slide Time: 03:08)



Energy Functions or Thermodynamic Potentials

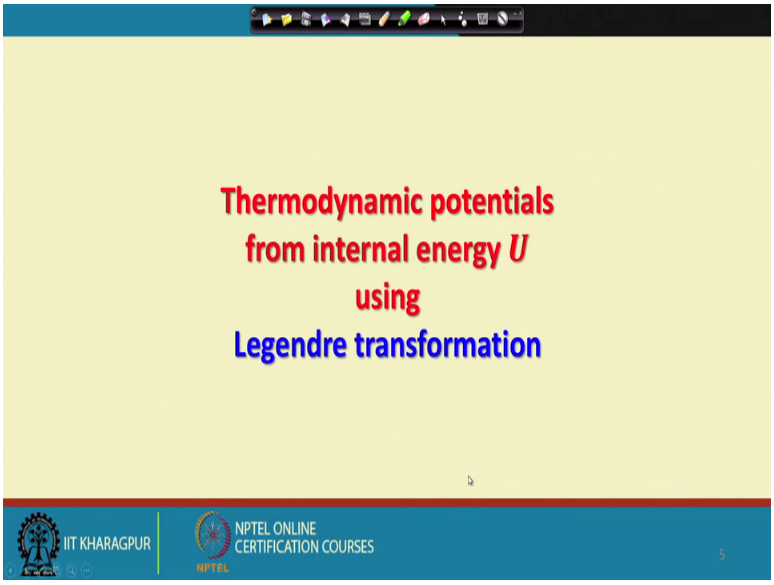
System	Macrostate	Thermodynamic potential
Isolated	S, V, N	$U = U(S, V, N)$
System+ Thermostat	T, V, N	$F = F(T, V, N) = U - TS$
System+ Barostat	S, p, N	$H = H(S, p, N) = U - (-p)V$
System+ Thermostat + Barostat	T, p, N	$G = G(T, p, N) = U - TS - (-p)V$

IIT KHARAGPUR

NPTEL ONLINE CERTIFICATION COURSES

In order to do that, I am going to show you a little mathematical trick that is extremely important in connecting the different energy functions that we have come across so far. So, that different energy functions that we have defined so far are internal energy, Helmholtz free energy, enthalpy as well as the Gibbs free energy.

(Refer Slide Time: 03:28)



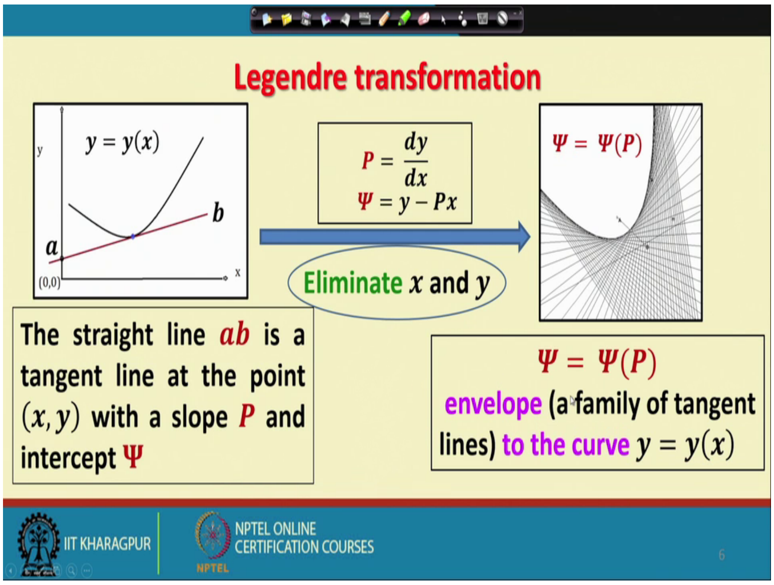
Thermodynamic potentials
from internal energy U
using
Legendre transformation

IIT KHARAGPUR

NPTEL ONLINE CERTIFICATION COURSES

Now, I am going to show you how these thermodynamic potentials can be derived from the internal energy U, using a mathematical method which is known as Legendre transformation.

(Refer Slide Time: 03:46)



Legendre transformation

$$P = \frac{dy}{dx}$$
$$\Psi = y - Px$$

Eliminate x and y

The straight line ab is a tangent line at the point (x, y) with a slope P and intercept Ψ

$\Psi = \Psi(P)$ envelope (a family of tangent lines) to the curve $y = y(x)$

So, let us have a look at this method; now many of you must be quite familiar with this kind of a picture. So, what I have here is along this axis; I am plotting my independent variable x and along this axis I am plotting a dependent variable y and the dependence of y on x is expressed in terms of some kind of a mathematical equation; that has been shown here y is a function of x.

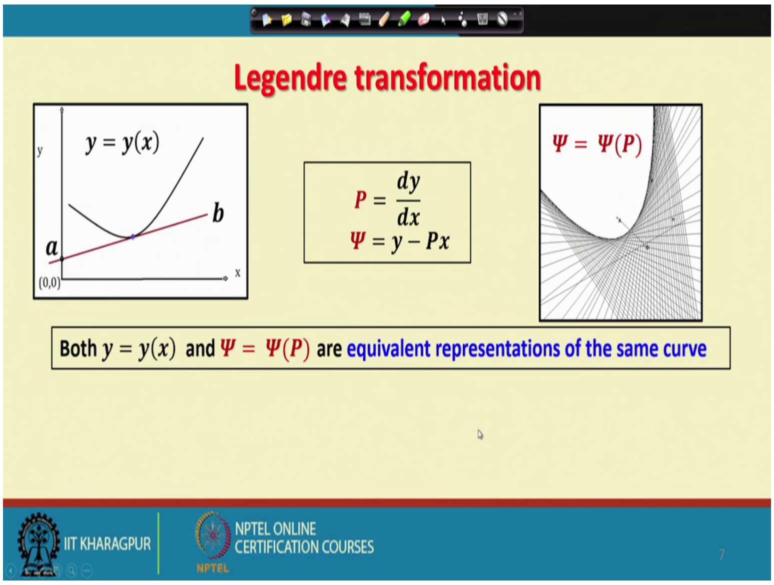
Now let me concentrate on a given point on this curve; this curve on all points of this curve; this functional relationship is satisfied. Now, let me consider this particular point where I have drawn a tangent line. So, a; b is the tangent to this curve at the point where the independent variable has a value x and the corresponding value of the dependent variable is given by this expression.

So, the straight line a b is a tangent line at the point x y; let us say that the slope of this straight line is P and the intercept is psi. Now I can very easily define what P and psi are; so P by definition can be obtained as dy; dx, since I know y as a function of x; I should be able to obtain this for well behaved functions and then psi becomes equal to y minus P x and using this, I can now think of carrying out a transformation which I call the Legendre transformation.

So, what I do is; I have three equations, one equation is this; I have this is my first equation and I have this is my second equation and this is my third equation. Between these three equations, if I eliminate x and y; what would I get? I would get a functional relationship between P and psi. So, let us have a look at what we get? So all we get when you plot psi as a function of P this is known as an envelope or a family of tangent lines to the original curve y as a function of x. So, what is the difference between this and this representation?

Both of them are representing the same points in the two dimensional space, but here I am using the x y representation and here I am using the envelope representation.

(Refer Slide Time: 06:51)



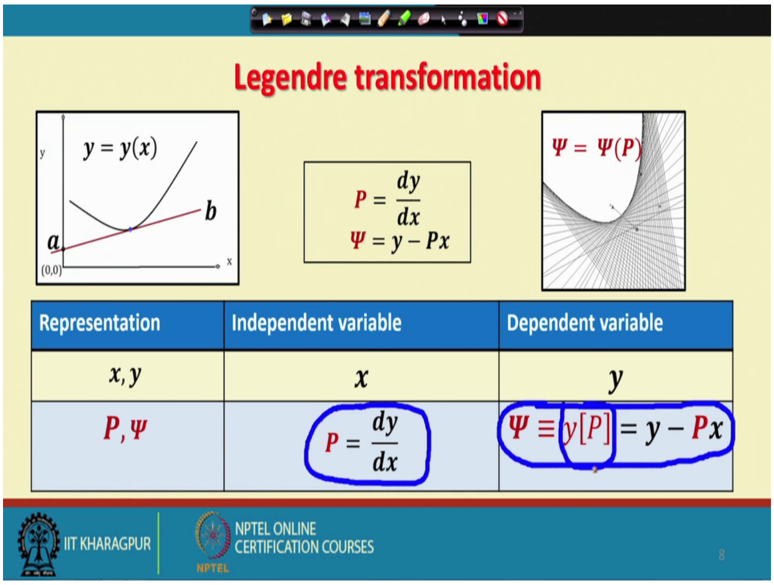
Legendre transformation

$$P = \frac{dy}{dx}$$
$$\Psi = y - Px$$

Both $y = y(x)$ and $\Psi = \Psi(P)$ are equivalent representations of the same curve

And therefore, I would say that both the equations y as a function of x and psi as the function of P are equivalent representations of the same curve.

(Refer Slide Time: 07:05)



Legendre transformation

$P = \frac{dy}{dx}$

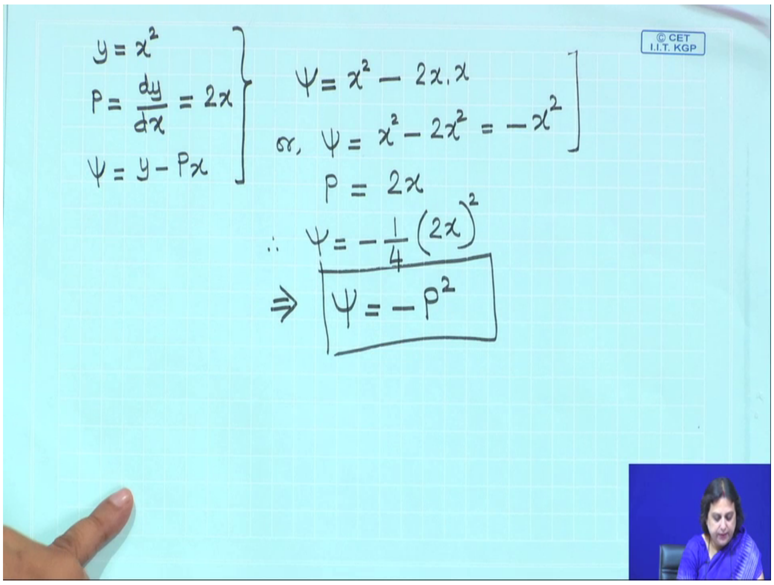
$\Psi = y - Px$

Representation	Independent variable	Dependent variable
x, y	x	y
P, Ψ	$P = \frac{dy}{dx}$	$\Psi \equiv y[P] = y - Px$

And this also tells me that what kind of representation that I am talking about; in the first representation the independent variable was x and the dependent variable was y. In my new representation, I have as my independent variable; the slope of the curve P. So, P is defined as dy; dx or the first derivative of the dependent variable with respect to the independent variable.

So, now what happens to the dependent variable? The dependent variable is now given this kind of representation; this is the standard way of representing psi, it says that now I have a new form of y; where instead of x I am now using P as the independent variable. So, what is psi? This is nothing, but y minus P x. Once you understand this, we can take a very simple example and see how this works.

(Refer Slide Time: 08:20)



$$\left.\begin{aligned} y &= x^2 \\ P &= \frac{dy}{dx} = 2x \\ \psi &= y - Px \end{aligned}\right\} \quad \left.\begin{aligned} \psi &= x^2 - 2x.x \\ \text{or, } \psi &= x^2 - 2x^2 = -x^2 \end{aligned}\right]$$

$$P = 2x$$

$$\therefore \psi = -\frac{1}{4}(2x)^2$$

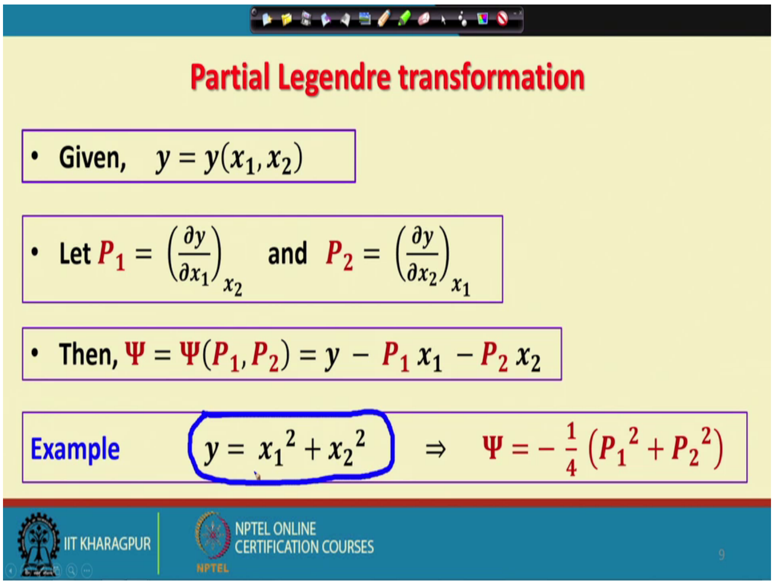
$$\Rightarrow \boxed{\psi = -P^2}$$

Let me take this a very simple expression that y is equal to x square. In that case if I define P; P is dy; dx and its trivial to show that P is equal to 2 x. Now what would be equal to psi? psi is going to be equal to y minus P x. Now between these three I am going to eliminate x and y; in order to do this, the first thing that I do is I write psi as; what is y? y is x square minus P; P is 2 into x multiplied by x or psi is equal to x square minus 2 x square that is equal to minus x square.

If that is so; then only half of my transformation is over, now I know P as a function of x and I know psi as a function of x. Therefore, what is psi as a function of P? I can very easily say that I am going to eliminate x between these two relations and I am going to get psi as one fourth of 2 x whole square. Or in other words, psi is going to be equal to minus P square.

So, the original curve; which is a parabola that has a new representation now in terms of its envelopes, which is a family of tangent lines to the original parabolic curve but this is geometry; I mean how is this useful in interpreting a realistic system, that is placed in a thermostat like the test tube full of your chemical reactants and put it in that thermostat with variable temperature facility? In order to do this connection, let us go and have a look at; before I do that let us have a look at, what is meant by a partial Legendre transformation?

(Refer Slide Time: 10:35)



Partial Legendre transformation

- Given, $y = y(x_1, x_2)$
- Let $P_1 = \left(\frac{\partial y}{\partial x_1}\right)_{x_2}$ and $P_2 = \left(\frac{\partial y}{\partial x_2}\right)_{x_1}$
- Then, $\Psi = \Psi(P_1, P_2) = y - P_1 x_1 - P_2 x_2$

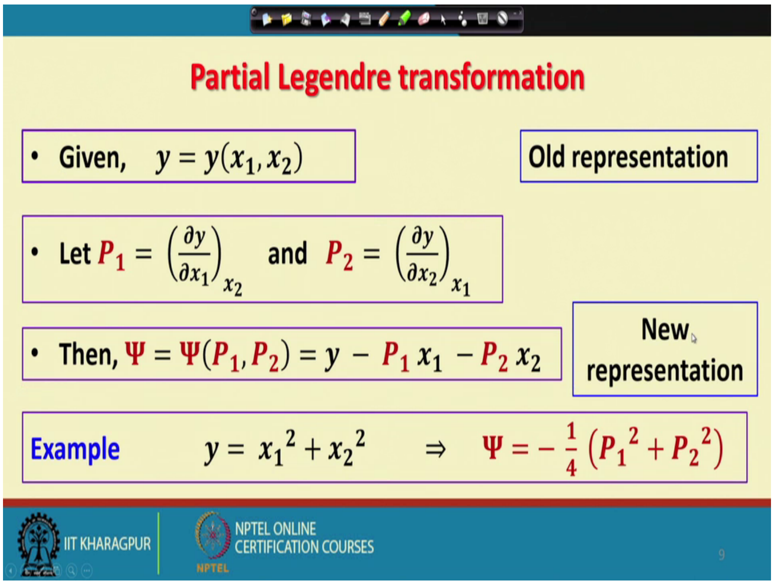
Example $y = x_1^2 + x_2^2 \Rightarrow \Psi = -\frac{1}{4}\left(P_1^2 + P_2^2\right)$

Now, a partial Legendre transformation is applicable; when your dependent variable y is determined by more than one independent variables; as in this case y is a function of two independent variables x 1 and x 2.

In that case, you will have to define two new independent variables; P 1 and P 2 which are the partial derivatives of y with respect to x 1, keeping x 2 constant and partial derivative of y; with respect to x 2, keeping x 1 constant. In this case the Legendre transformation of y is going to be psi and given by y minus P 1; x 1 minus P 2; x 2. So, as I see that if you take this very simple example, you will find that this curve; the original curve that you had y equal to x 1 square; plus x 2 square with x 1 and x 2 as the independent variables and y as the dependent variable; is now being transformed, x 1 is replaced by P 1; x 2 is replaced by P 2 and in the new representation y has been replaced by psi.

So, next question that we ask is; how do I relate this kind of old representation to the new representation?

(Refer Slide Time: 12:05)



Partial Legendre transformation

- Given, $y = y(x_1, x_2)$

Old representation

- Let $P_1 = \left(\frac{\partial y}{\partial x_1}\right)_{x_2}$ and $P_2 = \left(\frac{\partial y}{\partial x_2}\right)_{x_1}$

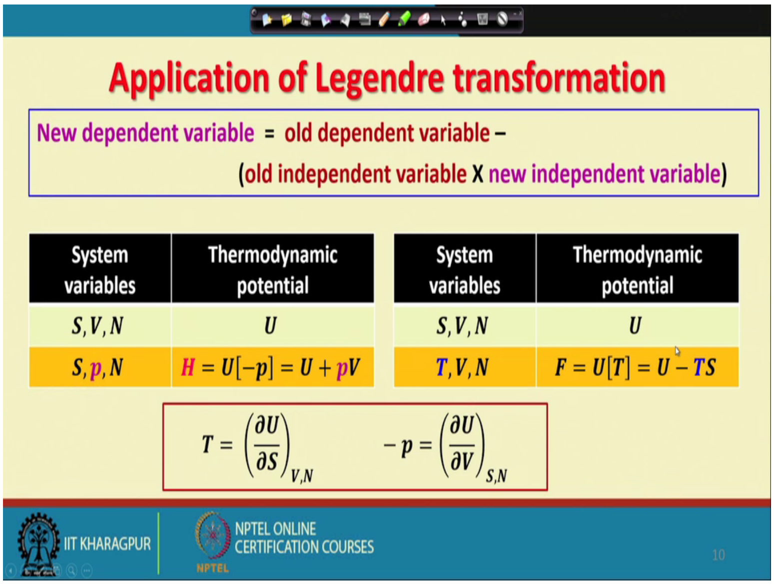
- Then, $\Psi = \Psi(P_1, P_2) = y - P_1 x_1 - P_2 x_2$

New representation

Example $y = x_1^2 + x_2^2 \Rightarrow \Psi = -\frac{1}{4}\left(P_1^2 + P_2^2\right)$

So, when I discuss the application of Legendre transformation.

(Refer Slide Time: 12:15)



Application of Legendre transformation

New dependent variable = old dependent variable – (old independent variable X new independent variable)

System variables	Thermodynamic potential
S, V, N	U
S, p, N	$H = U[-p] = U + pV$

System variables	Thermodynamic potential
S, V, N	U
T, V, N	$F = U[T] = U - TS$

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

There is only one result from this mathematical treatment that I need to take care of very carefully. Look at this, so when I carry out the Legendre transformation; I find that the new dependent variable is nothing, but the old dependent variable minus a correction term. Now what is this correction term? This correction term is obtained by multiplying the old independent variable with the new independent variable. So, once you understand this; the rest becomes fairly easy. Now, let us have try and think; what are the different slopes that we know of when I am describing the internal energy?

Do you remember what the slopes are? Del U, del S that gives you T; if I am taking the derivative keeping, the volume and number of particles constant. Similarly, minus P is the slope of del U, del V; keeping S and N constant. Now, let us have a look at this situation; in an isolated system, I had this representation S, V, N and the dependent on these independent variables was the thermodynamic potential U.

Let me carry out a simple Legendre transformation, where I am replacing V by p. Now what is p? By definition; I know that p is the slope of U; is a derivative of U with respect to V. Therefore, it is like x being replaced by the corresponding derivative; the capital P, if I do that then what will happen to U? The Legendre transform of u with respect to minus p will be; what is the old dependent variable? That is U. What is the correction term? So, you will have a negative here, then I have a correction term.

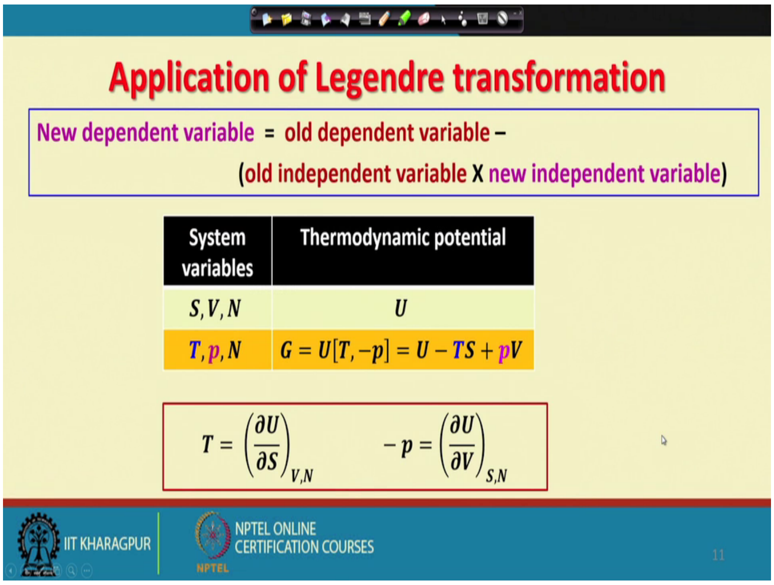
So, this is the correction term; what is that correction term? The old independent variable multiplied by the new independent variable. So, what was your old independent variable? That was V, so I have put in V here. What is your new independent variable? Although, I write p here, the actual new independent variable is minus p. So, I put minus p here and both the negative signs make this as a positive.

And therefore, I find that if I represent the macroscopic state of the system as S, V, N; which is an isolated system and I try to use this representation in another case, where V has been replaced by p; then whatever role U was playing in this case, will be played by H; that is the enthalpy of the system. Now, let us next have a look at the situation where I am trying to construct the thermodynamic potential of a system that is in contact with a thermal reservoir.

So, once again I start with an isolated system I understand that there the thermodynamic potential is U. Now I want to look at the situation where the system variables are T, V and N. So, what is the difference between this representation and this one? I have replaced S by T; how are S and T related? T is the slope of U with respect to S.

Therefore, how will the thermodynamic potential change? So, U will now be replaced by F. Now what is F? F is the old dependent variable minus some correction term. So, what is this correction term? The old independent variable; which is S and the new independent variable, which is T and this is how; you see that we arrive at the definition of the thermodynamic potential S, which we already have seen to be playing a very important role in deciding the direction of a spontaneous change in state; as the system is maintained under isothermal condition.

(Refer Slide Time: 17:28)



Application of Legendre transformation

New dependent variable = old dependent variable − (old independent variable X new independent variable)

System variables	Thermodynamic potential
S, V, N	U
T, p, N	$G = U[T, -p] = U - TS + pV$

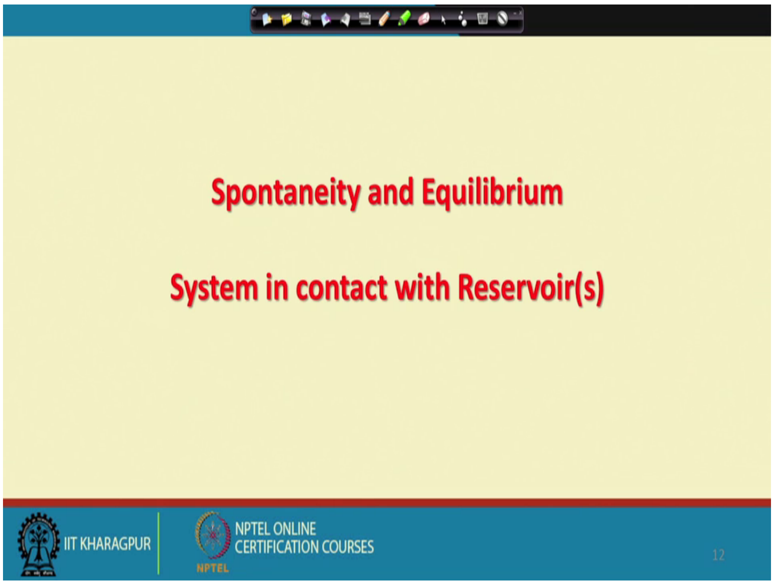
$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \qquad -p = \left(\frac{\partial U}{\partial V}\right)_{S,N}$$

Now, of course, I should be able to generalize this in the case of the isothermal isobaric condition. So, once again as I start from the isolated system and I try to derive the representation of a system that is connected to a thermal, as well as a pressure reservoir. I see that the representation of the system is now T, p, N in terms of these three independent variables. And the change over that I see from here is that S has been replaced by T, V has been replaced by actually minus p and N remains constant.

Then we ask the question that then what would be the corresponding thermodynamic potential? So, now instead of U; I will be having the old dependent variable U, which is this; then correction terms which appear from the combination of T and S and the combination of p and V; minus p and V. So, in total what I get is the thermodynamic potential for this representation must be U minus T S plus p V.

So, this actually shows that knowing a little bit of mathematics is not harmful at all because that gives you some idea about why and how we arrive at those specific definitions of F, H and G.

(Refer Slide Time: 19:04)

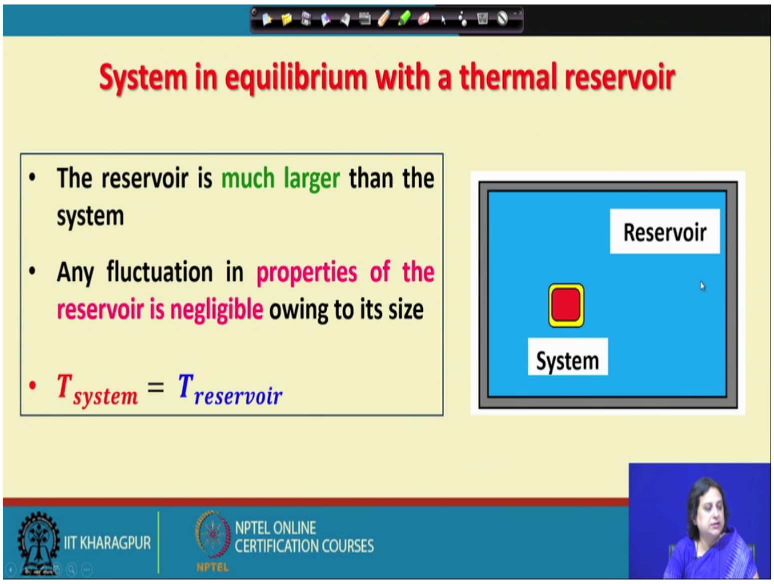


Spontaneity and Equilibrium

System in contact with Reservoir(s)

Let us now have a look at how these thermodynamic potentials can be used to explain in particular, the condition of equilibrium when a system is in contact with a reservoir.

(Refer Slide Time: 19:18)



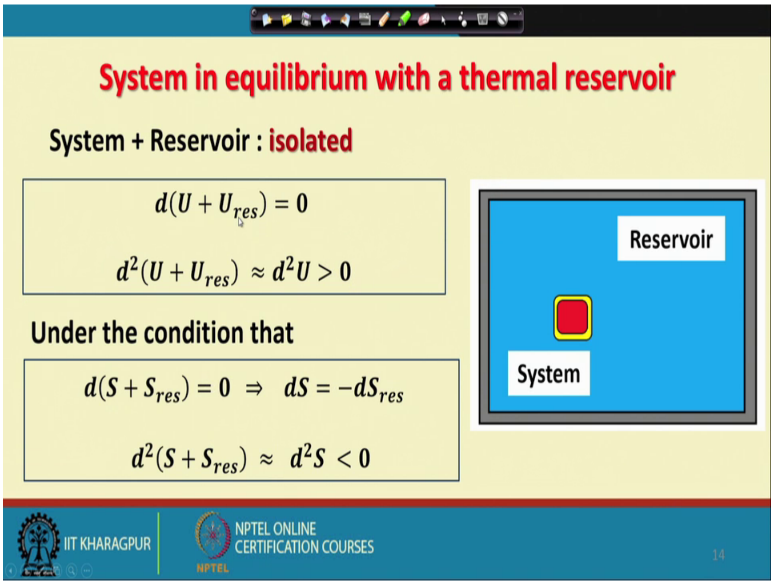
System in equilibrium with a thermal reservoir

- The reservoir is much larger than the system
- Any fluctuation in properties of the reservoir is negligible owing to its size
- $T_{system} = T_{reservoir}$

Now for the sake of simplicity, I am going to focus on a system in equilibrium with a thermal reservoir. So, this is a situation I have in mind; where I have a system, this has been kept in contact with a thermal reservoir so that it is surrounded by our diathermal rigid, but impermeable wall and there is energy exchanged between the system and the reservoir in the form of heat. I also assume that the reservoir is much much larger than the system.

And therefore, whatever properties are fluctuating in the reservoir because of the exchange between the system and itself; these are going to be nominal and we can safely neglect them. And also in whatever I do to the system, I understand the system is going to be having a temperature that is equal to the temperature of the reservoir.

(Refer Slide Time: 20:24)



System in equilibrium with a thermal reservoir

System + Reservoir : isolated

$$d(U + U_{res}) = 0$$

$$d^2(U + U_{res}) \approx d^2U > 0$$

Under the condition that

$$d(S + S_{res}) = 0 \Rightarrow dS = -dS_{res}$$

$$d^2(S + S_{res}) \approx d^2S < 0$$

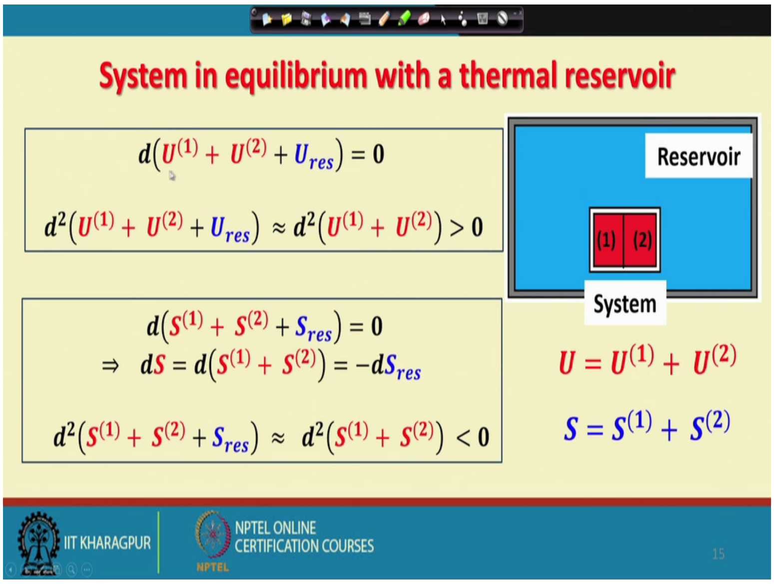
Now, once I have this situation; I understand that the composite of system and the reservoir this; is an isolated system. As a result, I can really easily say that if S is the entropy of the system and S res is the entropy of the reservoir, since system plus reservoir is isolated S plus S res; under the given condition should be a maximum. As a result, any small perturbation to the system we will see that d of this summation to be equal to 0; which means that in as long as the system remains an equilibrium, I must have this condition satisfied that d S is equal to the negative of d of S res.

Similarly, if I look at what happens to this quantity that is a second order differential of S plus S res? I see that this must be d 2 S plus d 2 S res, but I have already said that; any fluctuation in the reservoir property is negligibly small therefore, the second derivative can be safely assumed to be nearly 0. Therefore, this quantity is equal to d 2 S and for an isolated system at equilibrium; the d 2 S must be a maximum, as a result it must be less than 0.

Now, once I understand this then I also must realize that under such condition U plus U res; that also be a constant, therefore, any small perturbation that still retains the system in equilibrium must satisfy the fact the d of this summation, this is going to be equal to 0. And d 2 of this summation, which is essentially d 2 of the internal energy of the system should be greater than 0; why is that so?

That is because when an isolated system is at equilibrium its entropy is constant at a maximum value and its internal energy is constant at a minimum value under the given experimental conditions.

(Refer Slide Time: 23:10)



System in equilibrium with a thermal reservoir

$$d\left(U^{(1)}+U^{(2)}+U_{res}\right)=0$$

$$d^2\left(U^{(1)}+U^{(2)}+U_{res}\right) \approx d^2\left(U^{(1)}+U^{(2)}\right) > 0$$

$$d\left(S^{(1)}+S^{(2)}+S_{res}\right)=0$$

$$\Rightarrow \quad dS = d\left(S^{(1)}+S^{(2)}\right) = -dS_{res}$$

$$d^2\left(S^{(1)}+S^{(2)}+S_{res}\right) \approx d^2\left(S^{(1)}+S^{(2)}\right) < 0$$

$$U = U^{(1)}+U^{(2)}$$

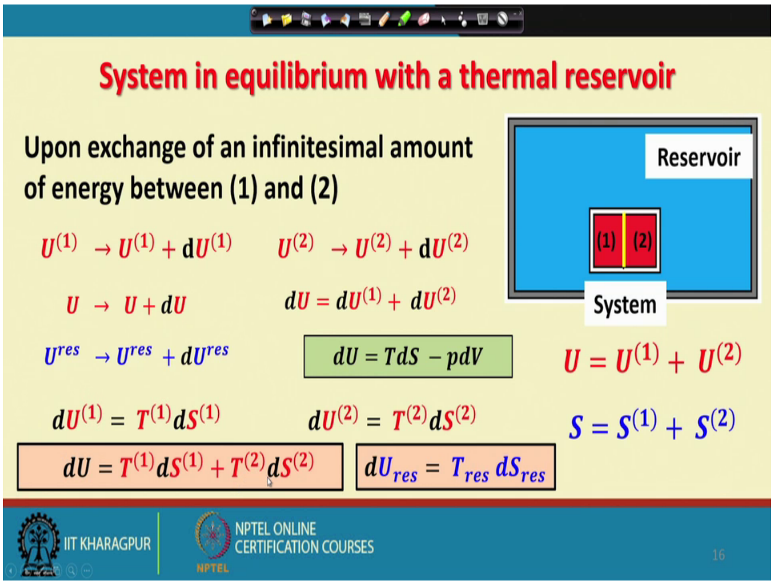
$$S = S^{(1)}+S^{(2)}$$

Once this is understood, we are next going to modify the system a little bit. So, instead of having a simple system; now I have a system which has two compartments, 1 and 2. But it is still in thermal contact with the reservoir and the system and the reservoir, they are constituting a composite set up which is isolated in nature. Now let me then try and explain that whatever I was thinking about as the internal energy of the system is now U 1 plus U 2.

So, what is U 1? U 1 is the internal energy of the compartment 1; U 2 is the internal energy of the compartment 2. Therefore, for any even state of the system; the total internal energy of the system is going to be the sum of these two quantities. Similarly, S which is also an extensive quantity will be a summation of S 1; that is the entropy of compartment 1, plus entropy of compartment 2.

So following the assumption regarding the system plus reservoir given me an isolated setup, now I can write down the equations that I wrote in the previous slide as; I must be having differential of this quantity equal to 0 and the double differential of U 1 plus U 2 will greater than 0. Similarly d S that is now a differential of S 1 plus S 2; must be equal to negative of the reservoir entropy; differential change in this reservoir entropy and this change is a maximum.

(Refer Slide Time: 25:03)



System in equilibrium with a thermal reservoir

Upon exchange of an infinitesimal amount of energy between (1) and (2)

$U^{(1)} \rightarrow U^{(1)} + dU^{(1)}$ $U^{(2)} \rightarrow U^{(2)} + dU^{(2)}$

$U \rightarrow U + dU$ $dU = dU^{(1)} + dU^{(2)}$

$U^{res} \rightarrow U^{res} + dU^{res}$ $\boxed{dU = TdS - pdV}$ $U = U^{(1)} + U^{(2)}$

$dU^{(1)} = T^{(1)}dS^{(1)}$ $dU^{(2)} = T^{(2)}dS^{(2)}$ $S = S^{(1)} + S^{(2)}$

$\boxed{dU = T^{(1)}dS^{(1)} + T^{(2)}dS^{(2)}}$ $\boxed{dU_{res} = T_{res}\, dS_{res}}$

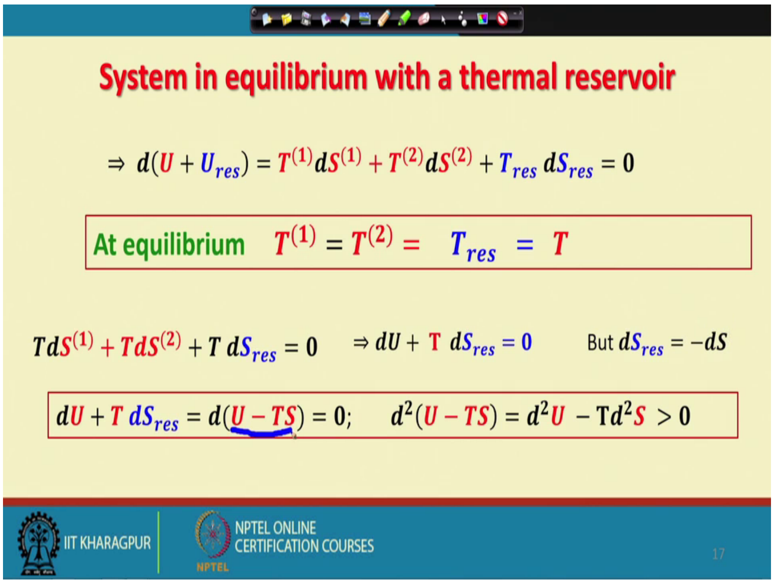
Now, I am going to introduce a small perturbation; which is a small perturbation in the sense that it is going to allow an infinitesimal exchange of heat between the compartment 1 and the compartment 2. So, what is going to be the result of this? I will have the internal energy of compartment 1 changing over to sum U 1 plus d U 1. Similarly, U 2 will change to U 2 plus d U 2; correspondingly I will have the internal energy of the system if initially it was U, now it will be U plus d U, where what is d U? d u; obviously, is d U 1 plus d U 2.

This is a fairly simple and then at the same time the system is exchanging heat with the compartment 1 as well as compartment 2. And therefore, U res will change from to this value, U res plus d U res. But we know that for any system which is undergoing a change in state; d U can be equated to TdS minus pdV by the combination of the first law and the second law of thermodynamics.

So, this is exactly what I have written over here and once you know this, look back at the kind of process that you have; if I have some material in the compartment 1. it has undergone a change in state by exchanging energy with this, material in the second compartment. And let us say that; that has given rise to d U, now looking at this change what do you think is going to contribute to the change in internal energy in compartment 1? Not pdV; because it did not exchange volume either with compartment two or with the reservoir.

Therefore, whatever change in internal energy that I will see in compartment 1 or in compartment 2 or for that matter in the reservoir is entirely going to be attributed to this term and therefore, I can very easily write that d U 1; should be T 1; d S 1, d U 2 would be T 2; d S 2. And correspondingly the net differential change in internal energy of the system, it is going to be T 1; d S 1 plus d 2; d S 2 and d U res. The change in the reservoir internal energy is going to be given by T res into d S res.

(Refer Slide Time: 28:06)



System in equilibrium with a thermal reservoir

$$\Rightarrow d(U + U_{res}) = T^{(1)}dS^{(1)} + T^{(2)}dS^{(2)} + T_{res}\,dS_{res} = 0$$

$$\boxed{\text{At equilibrium} \quad T^{(1)} = T^{(2)} = T_{res} = T}$$

$$TdS^{(1)} + TdS^{(2)} + T\,dS_{res} = 0 \qquad \Rightarrow dU + T\,dS_{res} = 0 \qquad \text{But } dS_{res} = -dS$$

$$\boxed{dU + T\,dS_{res} = d(\underline{U - TS}) = 0; \qquad d^2(U - TS) = d^2U - Td^2S > 0}$$

Once I have this then let me go back and see the consequence of these results on the fact that the system plus the reservoir is an isolated setup. If we look back at this, now this condition is translated into the fact that I must be having this combination equal to 0; if the system even after this small infinitesimal change in state is still at equilibrium, so that is equilibrium condition that I am talking about.

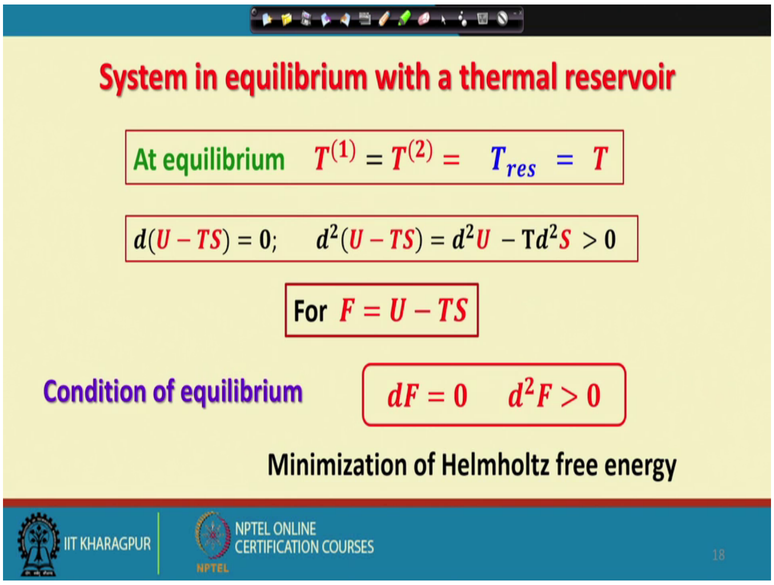
Once I understand that, I also understand that my experimental situation is such that T 1 is equal to T 2; equal to T res and equal to some constant value of T. So, if I incorporate this into this expression, then the condition of equilibrium turns out to be T into d S 1; T into d S 2, plus T into d S res is equal to 0. What does it imply? It implies that what is this quantity? That is nothing, but d U; so d U plus T into d S res is equal to 0.

But we already know that d S res is equal to minus d S and therefore, the condition of equilibrium now boils down to this. So, d U plus T into d S res can be written as a differential of this quantity U minus T S. And the I understand that when if the system even on this infinitesimal perturbation, still remains an equilibrium; this quantity U minus TS is going to attain an extremum. Now the question is; is this a minimum or a maximum; in order to understand that, we will have a look at the second order differential d 2 of U minus T S. Now if I evaluate this, I find that it depends on d 2 U and d 2 S.

But already I know the signs of this; now d 2 U because the system plus the reservoir is isolated then this quantity is greater than 0 and this quantity is less than 0. And therefore, since temperature is always a positive quantity; I must be having that this combination must be greater than 0. So, now we have identified this quantity U minus T S; which is the function of system properties only.

And under the condition that their system maintains a constancy of temperature with a reservoir, I find that this combination U minus T S is going to reach a minimum at equilibrium.

(Refer Slide Time: 31:14)



System in equilibrium with a thermal reservoir

At equilibrium $T^{(1)} = T^{(2)} = T_{res} = T$

$d(U - TS) = 0; \quad d^2(U - TS) = d^2U - Td^2S > 0$

For $F = U - TS$

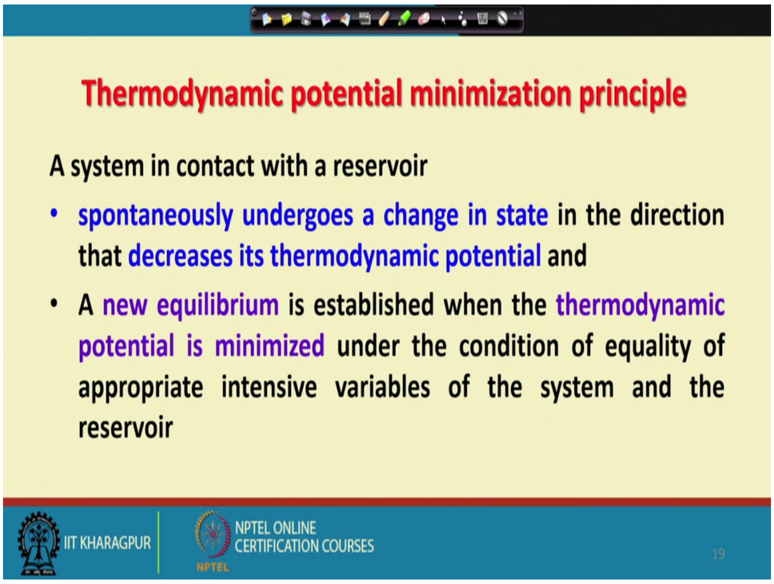
Condition of equilibrium $dF = 0 \quad d^2F > 0$

Minimization of Helmholtz free energy

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES

And therefore, what we find is that; if a system is in equilibrium with a thermal reservoir and if the temperature is uniform all throughout the system and the reservoir, then if I define the Helmholtz free energy as F which is U minus T S, then the condition of equilibrium is F should be a minimum. So, this is the demonstration of the minimization of Helmholtz free energy, when a system is at equilibrium.

(Refer Slide Time: 31:46)



Thermodynamic potential minimization principle

A system in contact with a reservoir

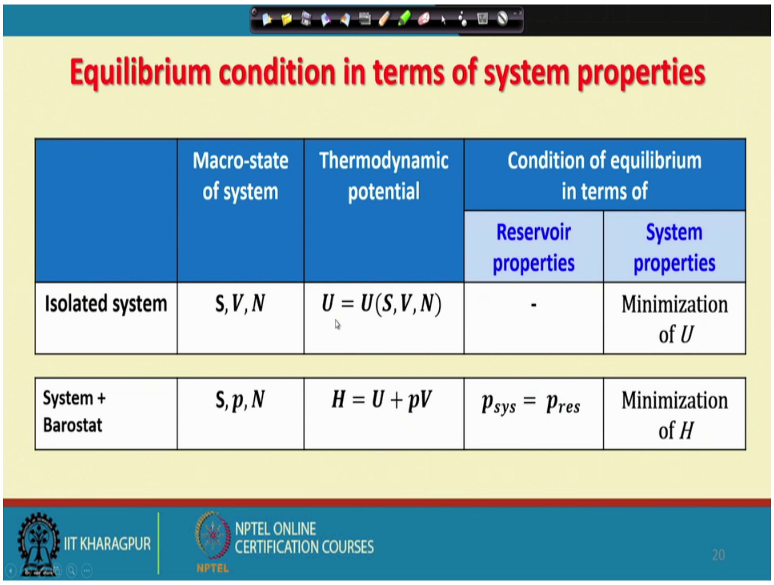
- spontaneously undergoes a change in state in the direction that decreases its thermodynamic potential and
- A new equilibrium is established when the thermodynamic potential is minimized under the condition of equality of appropriate intensive variables of the system and the reservoir

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES

In general, one can say that if a system is in contact with a reservoir; then first we have already seen that it can spontaneously undergo a change in state in the direction that decreases its thermodynamic potential. And now we have shown that if the system is at now finally, at equilibrium; we can perturb it to a very small degree by allowing one part of the system to exchange; for example, heat with another part of the system while maintaining the constancy of temperature.

And then I find that even such small infinitesimal changes will result in the minimization of the Helmholtz free energy or in the case of isothermal condition or the appropriate thermodynamic potential, if the system still remains in equilibrium.

(Refer Slide Time: 32:48)



Equilibrium condition in terms of system properties

	Macro-state of system	Thermodynamic potential	Condition of equilibrium in terms of	
			Reservoir properties	System properties
Isolated system	S, V, N	$U = U(S, V, N)$	-	Minimization of U
System + Barostat	S, p, N	$H = U + pV$	$p_{sys} = p_{res}$	Minimization of H

IIT KHARAGPUR

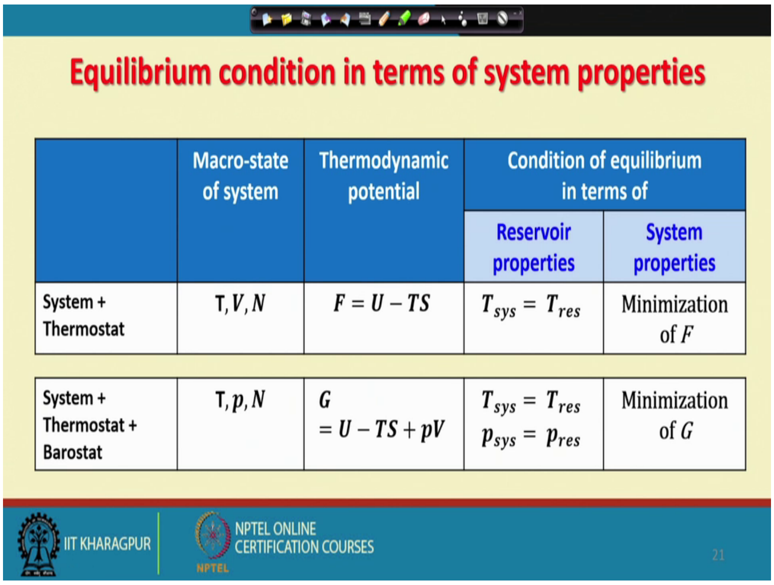
NPTEL ONLINE CERTIFICATION COURSES

20

So, now the conclusion is as follows in an isolated system I understand that the macroscopic state of the system that is at a length scale of about 1 meter, where I can see the system with my naked eye; the equilibrium state is given can be defined in terms of the entropy; volume and a number of particles. And the energy function which is a natural function of these three variables is U and there is no reservoir.

As a result of which, you see that the condition of equilibrium is described entirely in terms of system property and it says that; if the system undergoes a change in state; it will proceed in the direction of decreasing U and at the final equilibrium state, the U will be minimized. Similarly, for the system in contact with a barostat; this is the representation of the thermodynamic or the macro state of the system. And this is a thermodynamic potential which has S, p, N as its natural variables and here you define the equilibrium in terms of reservoir properties by saying that the system pressure must be equal the reservoir pressure and this should lead to minimization of enthalpy.

(Refer Slide Time: 34:21)



Equilibrium condition in terms of system properties

	Macro-state of system	Thermodynamic potential	Condition of equilibrium in terms of	
			Reservoir properties	System properties
System + Thermostat	T, V, N	$F = U - TS$	$T_{sys} = T_{res}$	Minimization of F
System + Thermostat + Barostat	T, p, N	$G = U - TS + pV$	$T_{sys} = T_{res}$ $p_{sys} = p_{res}$	Minimization of G

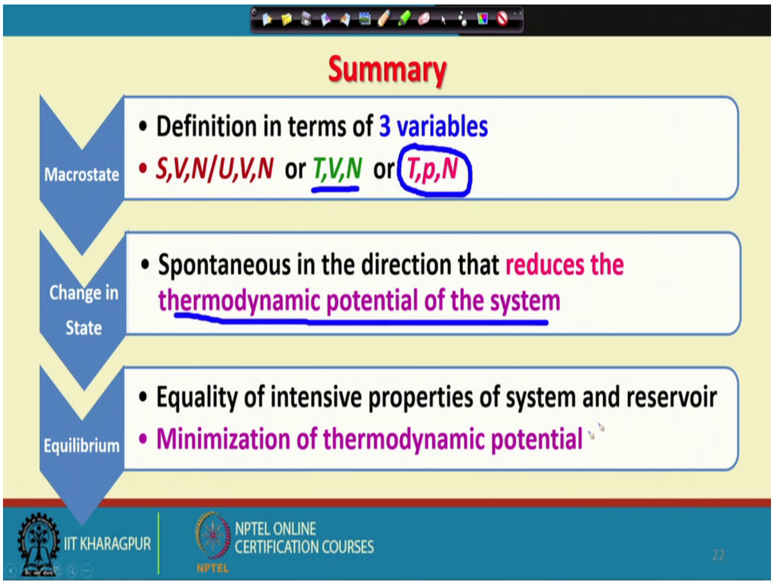
IIT KHARAGPUR

NPTEL ONLINE CERTIFICATION COURSES

Finally, when you have a system and thermostat; the thermodynamic potential is F and the condition of equilibrium entirely in terms of system properties is given by the minimization of F; under the condition that the temperature of the system is equal to the temperature of the reservoir. And similarly, we can extend the same consideration which I have not proved here; that if the system is in equilibrium with the thermostat and the barostat, then you define the macro state of the system by defining the temperature pressure and the number of particles.

And then it is a minimization of the Gibbs free energy that defines the condition of equilibrium under the situation, where the system temperature is equal to the reservoir temperature and the system pressure is equal to the reservoir pressure.

(Refer Slide Time: 35:20)



Summary

Macrostate
- Definition in terms of 3 variables
- S,V,N/U,V,N or T,V,N or T,p,N

Change in State
- Spontaneous in the direction that reduces the thermodynamic potential of the system

Equilibrium
- Equality of intensive properties of system and reservoir
- Minimization of thermodynamic potential

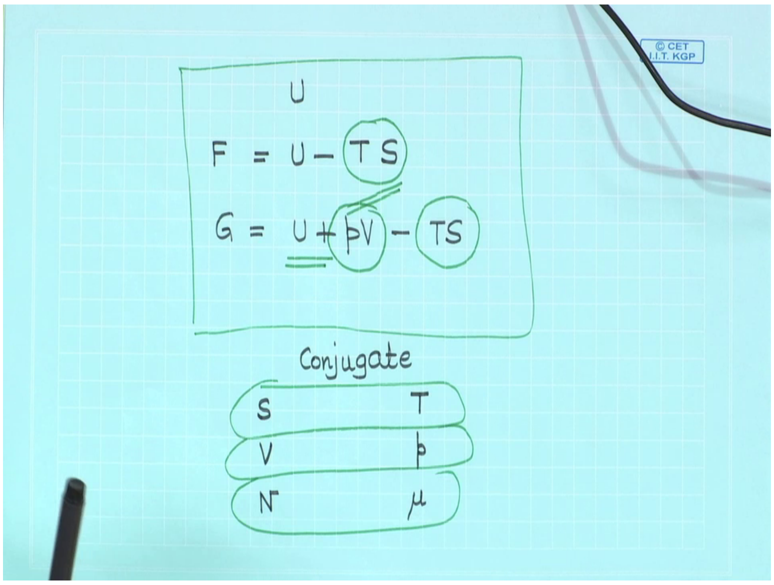
IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES

So, finally, this is the summary of what we have achieved while discussing the principles of thermodynamics. We have learnt that any thermodynamic system can be completely defined in an equilibrium state; in terms of three variables. And these three variables will very much depend on; the kind of system you are looking at, whether it is an isolated system or it is a system in contact with a thermal reservoir or you are talking in terms of a system that is being maintained at a constant temperature, constant pressure and it is a closed system.

We also understood that energy can be harnessed when the system is undergoing a change in state. And this change in state is spontaneous in the direction that reduces the thermodynamic potential of the system. So, you see that respective of which experimental condition you are looking at; you basically have one generalized principle for the direction of a spontaneous change in state.

And finally, when the equilibrium is reached you find that there will be a minimization of the thermodynamic potential; under the condition that some intensive property of the system is equal to that corresponding property of the reservoir. I would like to end my lecture today by showing you something that is very interesting.

(Refer Slide Time: 36:56)



U

$F = U - \textcircled{TS}$

$G = \underline{\underline{U}} + \textcircled{pV} - \textcircled{TS}$

Conjugate

S	T
V	p
N	μ

We started off with the internal energy, now we have the internal energy minus T into S and this is F. So, when you are allowing the system to maintain itself at a constant temperature; you see that a part of the internal energy is becoming unavailable, why is that so? This is the amount that this system is going to require; to maintain itself at the constant temperature T. And therefore, it is unavailable for doing external work.

If you are having this temperature constant pressure condition, in that case G is equal to U plus p V minus T S. So, while maintaining itself at a constant pressure; there is an additional amount of energy available to the system, which adds up to U, but again you lose a part of it.

Since the system is trying to maintain itself in at the condition of constant temperature. And that is simply the reason why there are so many energy functions when you deal with thermodynamics. And I hope now you understand that given an experimental situation, how you will choose the different independent variables to describe its equilibrium state? And finally, will you be using pressure and volume together? No, that is because we now have a concept of conjugate variables.

So, what do I mean by conjugate variables? As you have seen that I either use entropy or use T; I either use V or use p. Similarly, if you have an open system; you either have N or you have mu representing the independent variables describing the equilibrium state of the system. And therefore, S and T are conjugate variables; V and P are conjugate variables and N and mu are conjugate variables and either one of the pair is used to describe the equilibrium state of the system.

Thank you.