Aspects of Biochemical Engineering

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Lecture – 09

Reaction Thermodynamics I

We will come back to my course Aspects of Biochemical Engineering. In the last lecture I tried to discuss the stoichiometry of bioprocess and stoichiometry of bioprocess basically deals with the intermolecular relationship of different component present in the reaction mixture. And also we can determine what is the theoretical limitation of this particular process. And in addition to that the stoichiometry gives two information one is the validity of the experimental results and another is that you know amount of heat evolved and in the biochemical process. As you know that most of the biochemical processes are usually operated and ambient temperature and atmospheric pressure and particularly since we are in the tropical country during summer the temperature rises to as high as 45 degree centigrade. So, since it is the exothermic reaction so we required a lot of cooling requirement to maintain that temperature close to 30-35 degree centigrade.

So, that is why we want to we can calculate how much heat evolved through this biochemical process. Now, today I have I want to discuss the very important topic that is reaction thermodynamics. And as you know the thermodynamics is a very important topic and it deals with, if you look at it deals with mostly the heat and temperature with the relation to energy and work.

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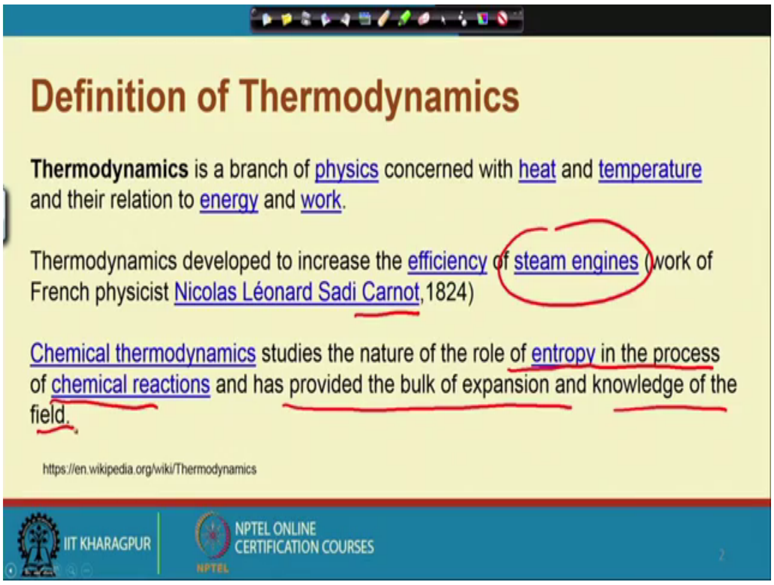

Definition of Thermodynamics

Thermodynamics is a branch of physics concerned with heat and temperature and their relation to energy and work.

Thermodynamics developed to increase the efficiency of steam engines (work of French physicist Nicolas Léonard Sadi Carnot,1824)

Chemical thermodynamics studies the nature of the role of entropy in the process of chemical reactions and has provided the bulk of expansion and knowledge of the field.

https://en.wikipedia.org/wiki/Thermodynamics

That now this thermodynamics that increases the efficiency of the steam engine we call it Carnot cycle, we know this is the Carnot this in the name of French physicist Nicolas Leonard Sadi Carnot in 1824 and he developed the thermodynamics how to increase the efficiency of the steam engines. Now, but chemical we are interested here mostly on chemical thermodynamics. Chemical thermodynamics studies the nature of the role of entropy in the process of the chemical reaction has provides the bulk expansion and knowledge of the field. So, we basically discussed that how entropy the ethics in the chemical reaction and also will discuss some kind of Gibbs free energy changes that affect the chemical reaction.

So, in this lecture I divided into two part chemical thermodynamics 1 and chemical thermodynamics 2. Chemical thermodynamics 1 mostly deal with the thermodynamics as whole how it is looks and chemical engineering thermodynamics 2 mostly I shall discuss on the thermodynamics of the chemical process.

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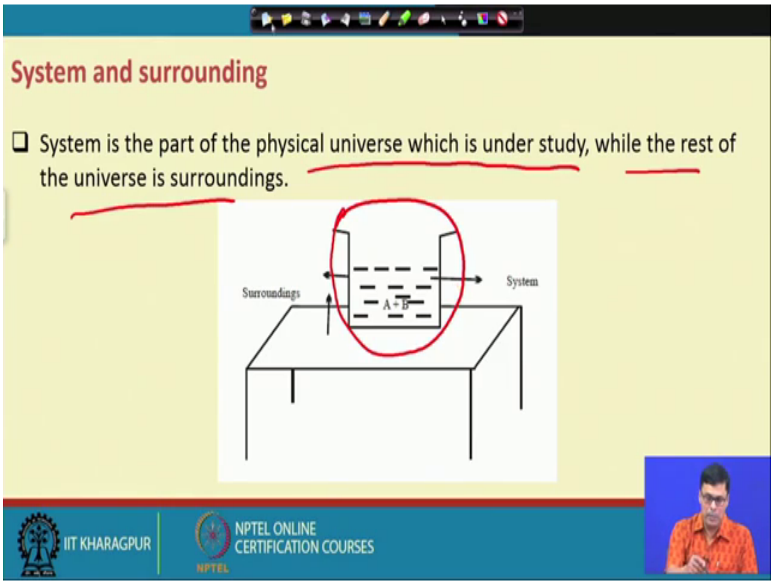

System and surrounding

- ❑ System is the part of the physical universe which is under study, while the rest of the universe is surroundings.

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Now, if you look at first let us try to find out what do what do you mean by system and surroundings. Now, system if you look at here that system is the part of the physical universe we understudy and while the rest of the universe is the surrounding. Now, suppose they beaker this is the I should the beaker and inside the beaker we have water and this is we considered a system, the system lying on a table and this is all the other than the beaker whatever we have that is we call it surroundings. So, there should be this is how system and surroundings can be defined.

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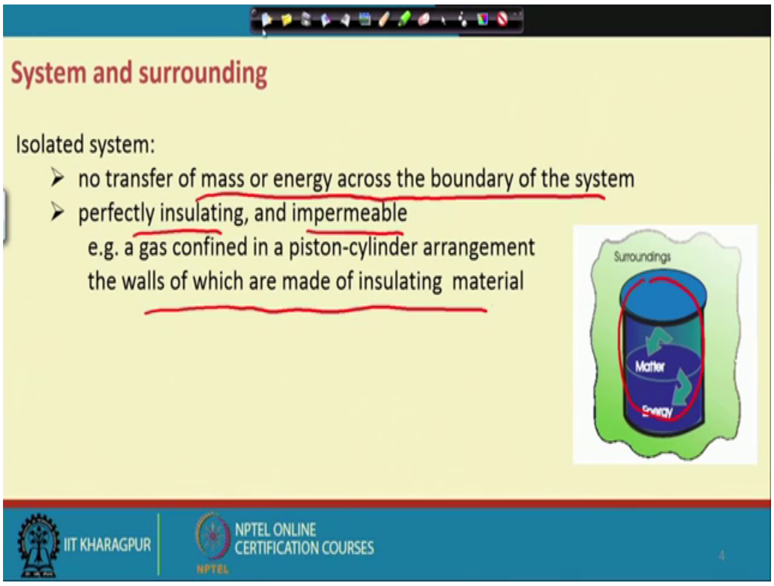

System and surrounding

Isolated system:

- ➢ no transfer of mass or energy across the boundary of the system
- ➢ perfectly insulating, and impermeable

  e.g. a gas confined in a piston-cylinder arrangement the walls of which are made of insulating material

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Now, if you look at again system and surroundings we have three different system like we have isolated system.

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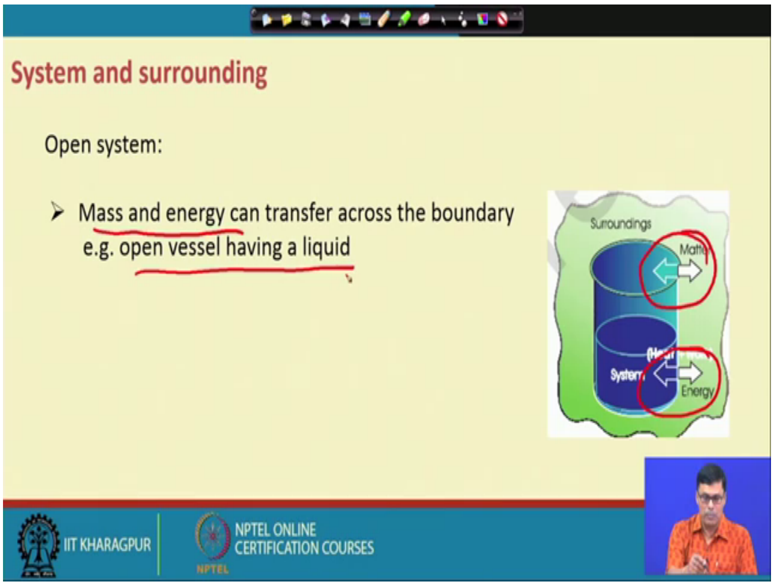

System and surrounding

Open system:

- Mass and energy can transfer across the boundary
  e.g. open vessel having a liquid

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Open system and the closed system.

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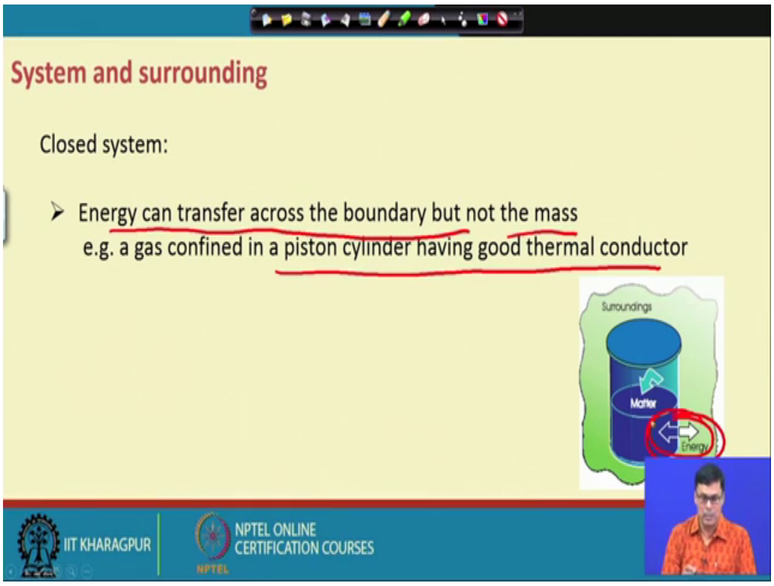

System and surrounding

Closed system:

- Energy can transfer across the boundary but not the mass
  e.g. a gas confined in a piston cylinder having good thermal conductor

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Now, let us see what do you mean by isolated system. Isolated system means that no transferred of mass, mass or energy across the boundary of the system. So, here this is the system and there is no energy and mass transfer take place and this since there is no energy and mass transfer take place across this boundary, we call it isolated system and it is perfectly insulated and impermeable.

A gas confined in a piston cylinder arrange the wall of which are made of insulated material. So, this is; now next is the open system open system what is happening both the mass and energy, energy can transferred you see the here the mass transfer it is the energy transferred that across this, that transfer take place between the system and the surroundings. Now, we call it the open vessel a having a liquid that is we can give the example of the system. Now, closed system what is happening in the closed system the energy can be transferred across the boundary, but not the mass. So, here the energy transfer takes place, but not much. A gas confined in a piston cylinder having good thermal conductor. So, the energy transfer take place, but due to a good conductivity of the material some kind of energy transmission take place, but not mass. If it is this we call it closed system.

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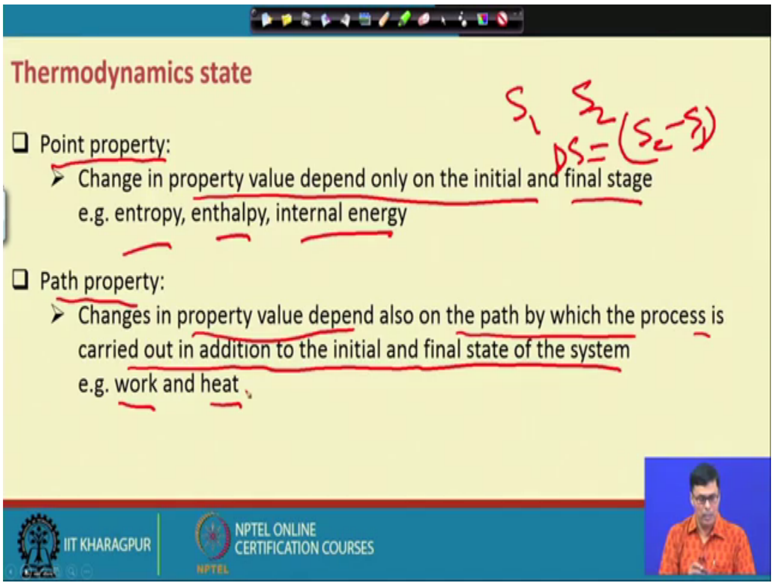

Thermodynamics state

❑ Point property:

➢ Change in property value depend only on the initial and final stage

e.g. entropy, enthalpy, internal energy

S_1 S_2 $\Delta S = (S_2 - S_1)$

❑ Path property:

➢ Changes in property value depend also on the path by which the process is carried out in addition to the initial and final state of the system

e.g. work and heat

Now, another very important term is there what is called thermodynamic states. Now, what do you mean by thermodynamics states we have two different property we have, one is called point property another is path property.

Point property means one point initial point and final point. Now, initial that change of property value depends on the initial and final state. So, suppose temperature is the entropy the initial entropy was this is 1 and final entropy is 2. So, change of entropy is S

2 minus S 1 this is we call it del S, this is the entropy change, enthalpy change and internal energy change and there is a point property. And what is the path property change your property value depends on the path by this the process carried out in addition to initial and final how this changes take place as for example, work and work and heat transferred, how will there take place in between the system. If you look at the Carnot cycle we have this has been done very nicely that how this path property can be done.

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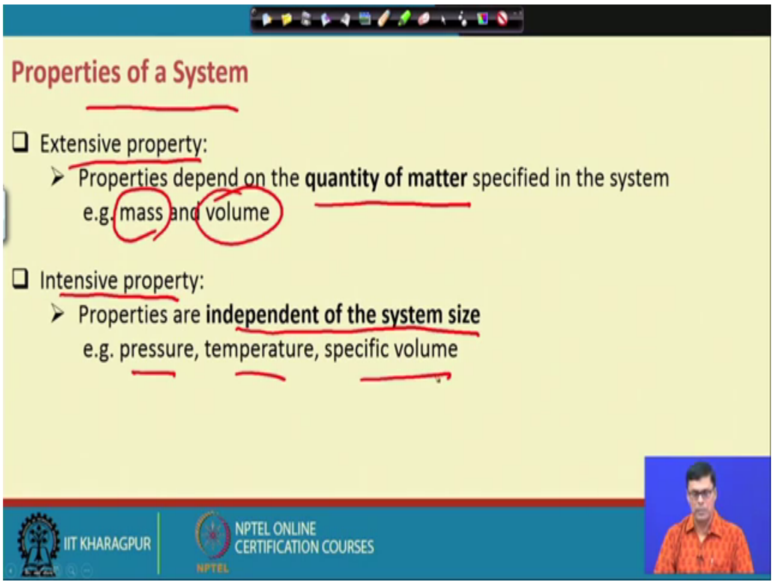

Properties of a System

❑ Extensive property:

- Properties depend on the **quantity of matter** specified in the system

  e.g. mass and volume

❑ Intensive property:

- Properties are **independent of the system size**

  e.g. pressure, temperature, specific volume

Now, another if you look at the properties of this of the system that we have two properties one is called the extensive property another there is the intensive property. The extensive property deals with the quantity of matter specified in the system. Now, as for example, we when we call it mass of the system, mass of the material volume of the material, then it is the kind of extensive property. Intensive property independent of the of the system size that is for example, pressure temperature specific volume. So, we have two properties as well thermodynamic system is concerned, one is called extensive property another is intensive property.

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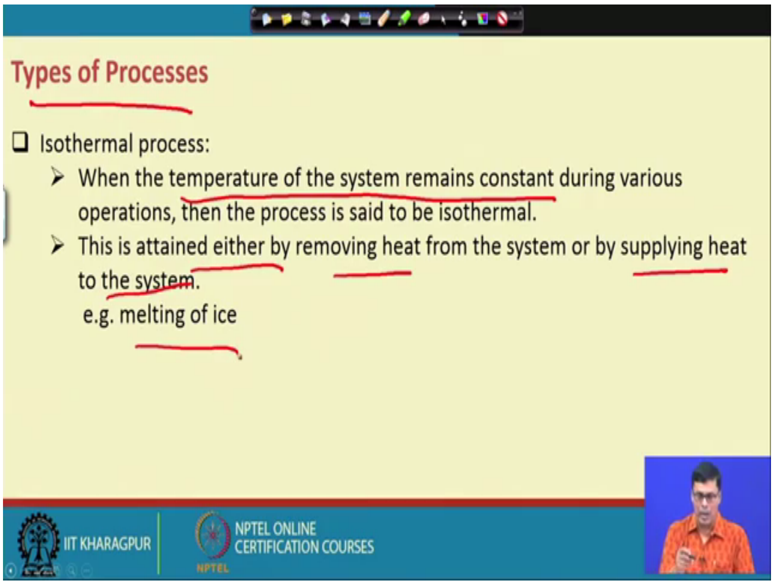

Types of Processes

❑ Isothermal process:

- When the temperature of the system remains constant during various operations, then the process is said to be isothermal.
- This is attained either by removing heat from the system or by supplying heat to the system.
  e.g. melting of ice

Now, if you look, if you come to the process we have two type of process one is called isothermal process and adiabatic process. Now, isothermal process basically the temperature of the system remains constant and adiabatic process the heat transfer remaining constant. There is no heat transfer take place, that is how this is defined.

Now, in case of isothermal process it attains that the temperature is constant either by removing heat or supplying the heat to the system, as for example, melting of ice.

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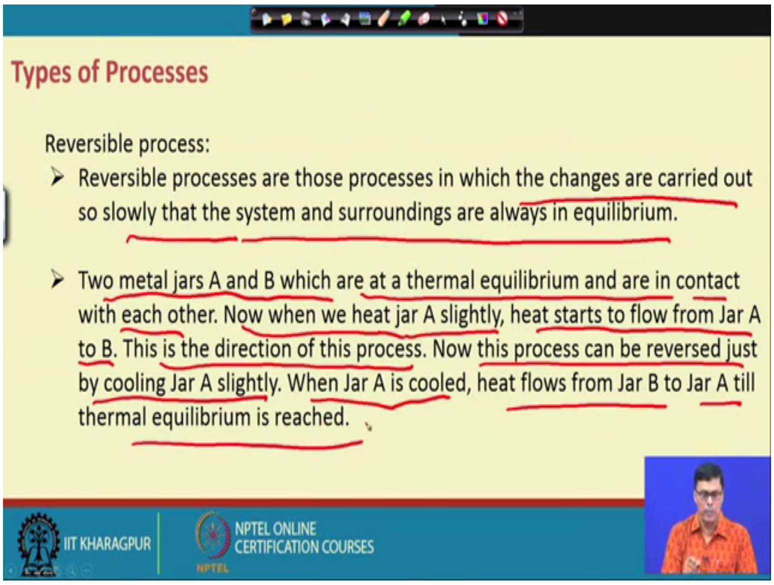

Types of Processes

Reversible process:

- Reversible processes are those processes in which the changes are carried out so slowly that the system and surroundings are always in equilibrium.
- Two metal jars A and B which are at a thermal equilibrium and are in contact with each other. Now when we heat jar A slightly, heat starts to flow from Jar A to B. This is the direction of this process. Now this process can be reversed just by cooling Jar A slightly. When Jar A is cooled, heat flows from Jar B to Jar A till thermal equilibrium is reached.

Now, another we have the reversible process. The reversible process are those processes in which the changes are carried out slowly and that the system and surrounding always are in equilibrium this is called a reversible process. Now, I can give a very typical example suppose there is a system comprises of A and B and they are in equilibrium now if we increase the temperature of A then what will happen, that heat will transferred from A to B the kind of, now if you cool the temperature of a then heat will flow from B to A. So, this is what is metal that two metals yard A B which are in thermal equilibrium or in contact with each other. Now, when the heat jar is the A is slightly heat jar A slightly heat starts flow from jar A to jar B and this is the direction of this process. Now, this process can be reversed just the cooling the jar slightly then when the jar is cooled heat flow from B to A till the thermal equilibrium reached.

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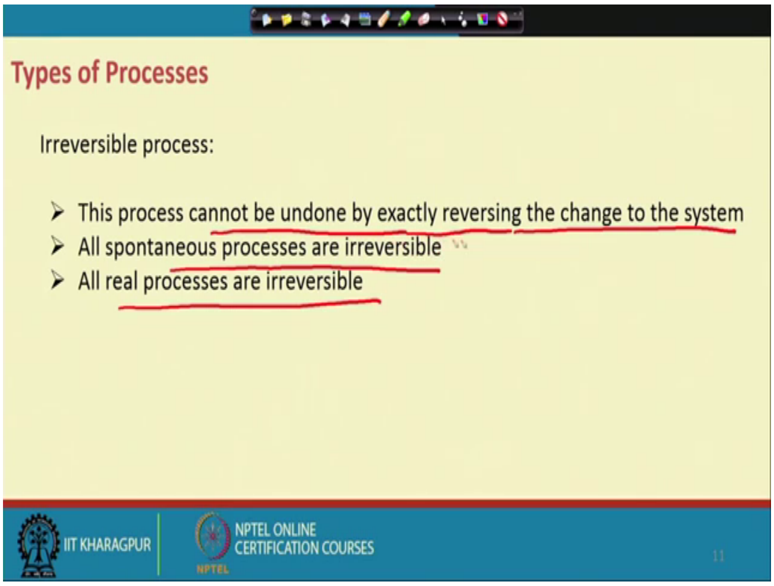

Types of Processes

Irreversible process:

- This process cannot be undone by exactly reversing the change to the system
- All spontaneous processes are irreversible
- All real processes are irreversible

Now, another process we have that is called a reversible process. Now, if you look at a reversible process that we have, this process cannot be done undone by exactly reversing the changes of the system. All spontaneous processes are irreversible. All real processes are irreversible, that is irreversible inside we want to mean the unidirectional and reversible means is the bidirectional. So, this process cannot be undone by exactly reversing the change of the system that is why we call it a reversible system.

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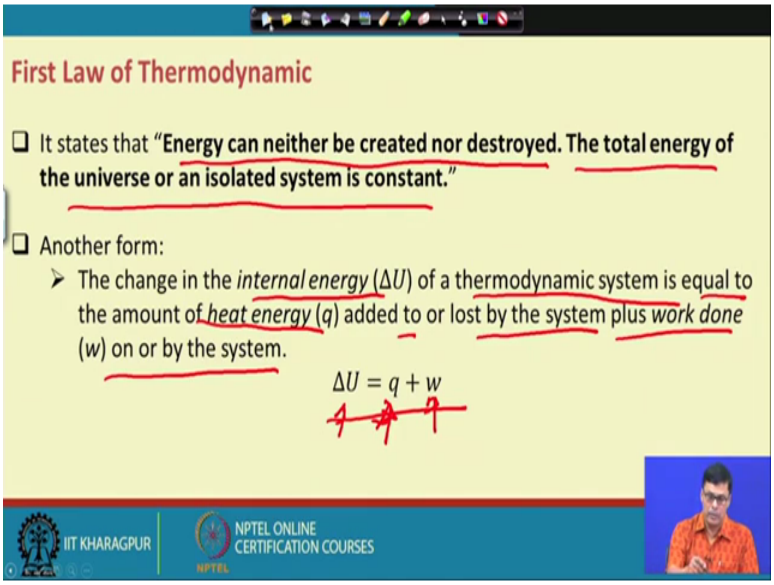

First Law of Thermodynamic

- ☐ It states that "**Energy can neither be created nor destroyed. The total energy of the universe or an isolated system is constant.**"
- ☐ Another form:
  - ➢ The change in the *internal energy* (ΔU) of a thermodynamic system is equal to the amount of *heat energy* (q) added to or lost by the system plus *work done* (w) on or by the system.

$$\Delta U = q + w$$

Now, let me discuss about the first law of thermodynamics. What is the first law of thermodynamics? It states that energy can neither be created nor destroyed. The total energy of the universe or isolated system is constant. So, this is the first law of thermodynamics.

Now, another form we can explain like this the change of internal energy of a thermodynamic system is equal to the heat energy added to or lost by the system plus work done or not by the system. This is, this can be mathematically or you know they express like this del U equal to q plus and w, where q we considered at the heat energy that change that take place and w is the work and del U is considered as the change of internal energy.

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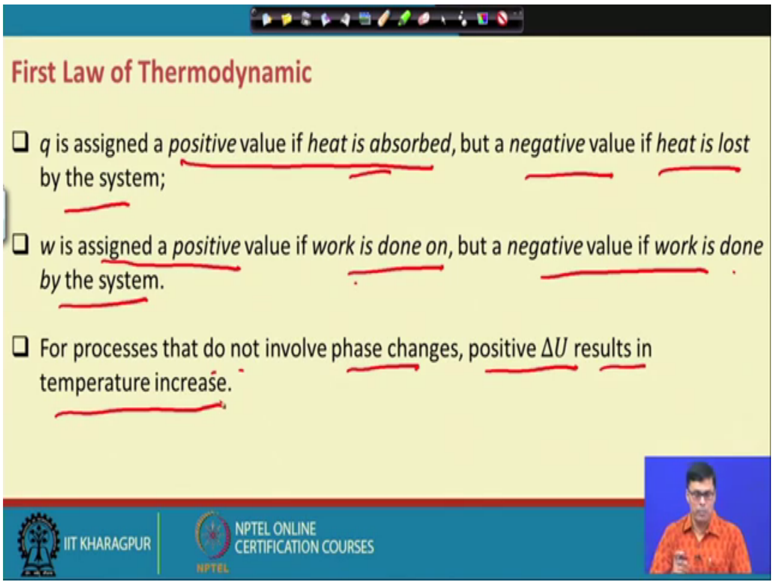

First Law of Thermodynamic

- q is assigned a *positive* value if *heat is absorbed*, but a *negative* value if *heat is lost* by the system;
- w is assigned a *positive* value if *work is done on*, but a *negative* value if *work is done by* the system.
- For processes that do not involve phase changes, positive ΔU results in temperature increase.

Now, q assigned to be positive, q is assigned to be positive value when heat is the absorbed, but it is negative when heat is loss by the system. So, one is the endothermic and there is the exothermic. So, w is assigned positive when its work is done on, but negative when work is done by the system. Now, for processes that do not involve the phase changes the positive value of internal energy results in temperature increase.

So, if we do not have any change of phases then change of internal energy positive that indicate temperature will rise in the process.

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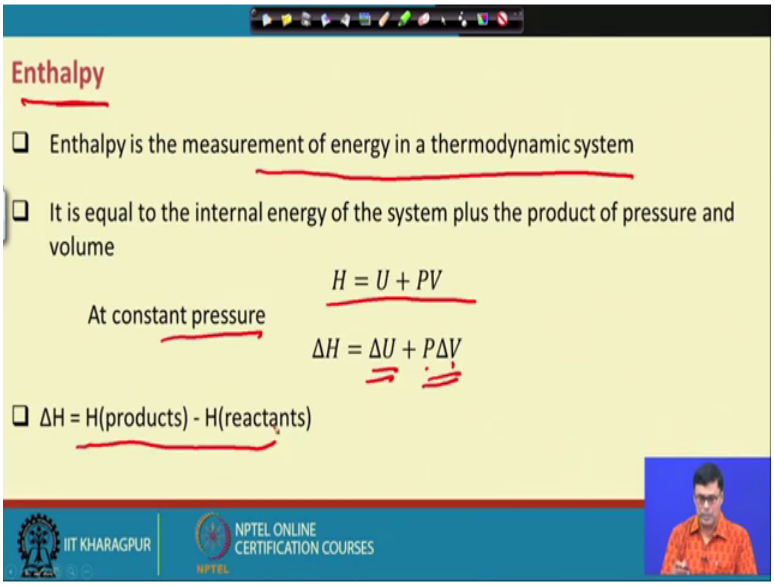

Enthalpy

- Enthalpy is the measurement of energy in a thermodynamic system
- It is equal to the internal energy of the system plus the product of pressure and volume

$$H = U + PV$$

At constant pressure

$$\Delta H = \Delta U + P\Delta V$$

- ΔH = H(products) - H(reactants)

Now, enthalpy there is another very important term what you call enthalpy. That enthalpy is the measurement of energy in a thermodynamic system. Now, how we can define? This is equal to internal energy plus P into V being the being the work done by the system this is internal energy plus P into P. Now, even at constant pressure then P into del V is the kind of work done and this is the internal energy. The change of internal energy is the H product minus the H reactant.

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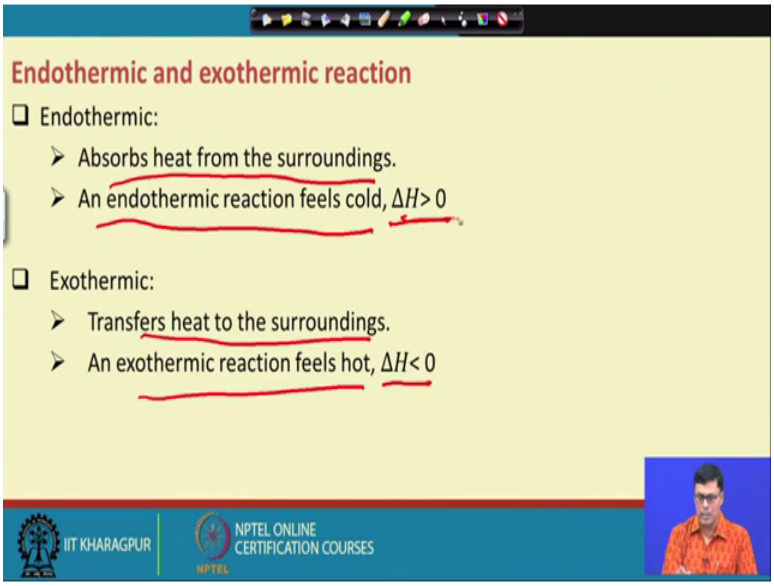

Endothermic and exothermic reaction

- ☐ Endothermic:
  - Absorbs heat from the surroundings.
  - An endothermic reaction feels cold, $\Delta H > 0$
- ☐ Exothermic:
  - Transfers heat to the surroundings.
  - An exothermic reaction feels hot, $\Delta H < 0$

Now, we have two type of reactions as you know one is called endothermic reaction another is exothermic reaction. Endothermic reaction means we mean that absorb the heat from the surroundings and endothermic reaction feel cold where del G is the always greater than greater than 0. I can give the example when glucose when we make a solution in the water then the temperature cools down that is the kind of example of the endothermic reactions.

The exothermic reaction is the transferred of heat to the surroundings. I can give the very simple example heating of wood or in heating of coal where the temperature increases. The exothermic reaction feel hot where del G is greater than it less than 0 that del G always should be negative and here del H, here del H is negative and here del H would be positive.

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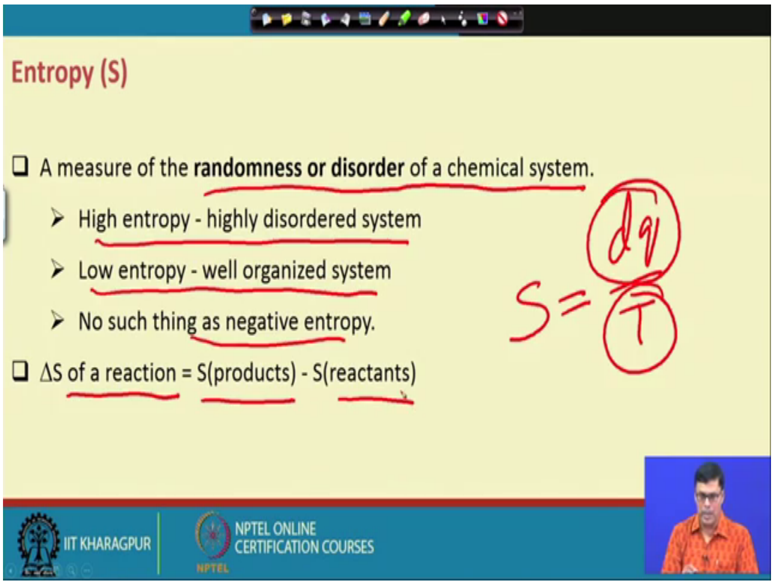

Entropy (S)

- ☐ A measure of the **randomness or disorder** of a chemical system.
  - High entropy - highly disordered system
  - Low entropy - well organized system
  - No such thing as negative entropy.
- ☐ ΔS of a reaction = S(products) - S(reactants)

$S = \frac{dq}{T}$

Now, let me come to the entropy because which is very important property of thermodynamics and it is a measure of randomness or disorder of the chemical system. If we have high entropy her question come how you define entropy. Entropy is the S is the this is equal to dq by T, dq is the heat change that take place and T is the temperature that we have. So, now the high entropy change is the highly disordered system and low entropy change; that means, well organized system no such thing as negative entropy. Now, del S of a chemical reaction we can always express as entropy of the product minus entropy of the reacted.

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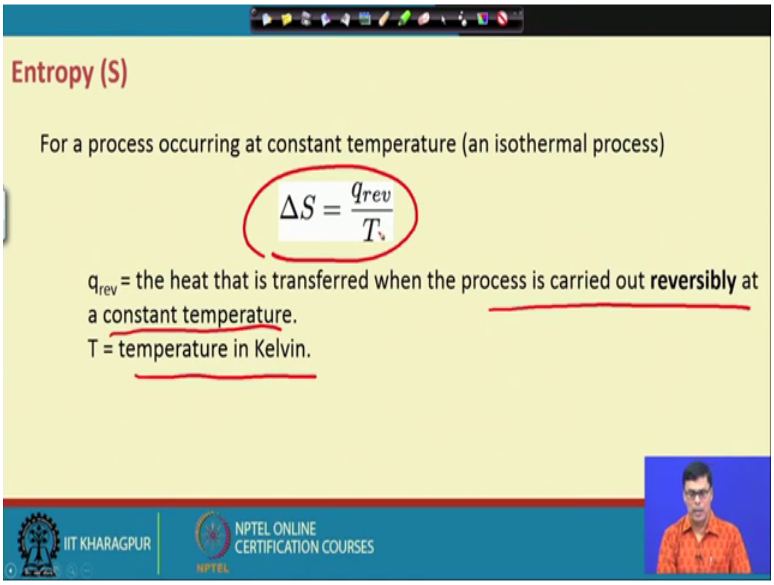

Entropy (S)

For a process occurring at constant temperature (an isothermal process)

$$\boxed{\Delta S = \frac{q_{rev}}{T}}$$

q_{rev} = the heat that is transferred when the process is carried out **reversibly** at a constant temperature.

T = temperature in Kelvin.

As I explained that as I had a constant temperature the entropy change, change of entropy can be explained like this. This is how we can we can explain where the q rev is the heat that is transferred when the process is carried out reversibly at a constant temperature and T is the temperature in Kelvin. So, capital T always we indicate has the Kelvin.

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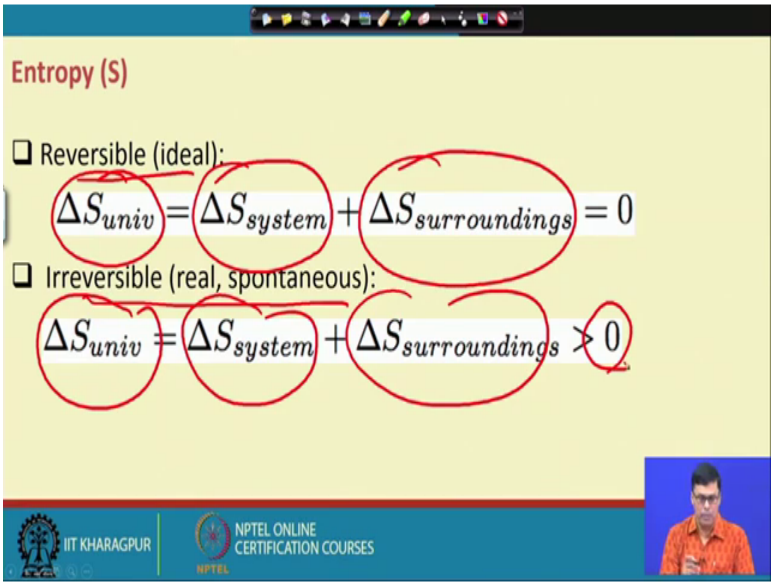

Entropy (S)

- ❑ Reversible (ideal):

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} = 0$$

- ❑ Irreversible (real, spontaneous):

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

Now, if you look at the reversible system ideally that ideal reversible system that change of entropy of the universe that is equal to that, the change of entropy of the system plus change of entropy in the sounding that should be equal to 0. Now, in case of irreversible process what we called real and spontaneous the change of entropy in the universe equal to change of entropy of the system plus surrounding that should be always greater than 0 that is one case of spontaneous system or less the entropy will be a higher value that we have.

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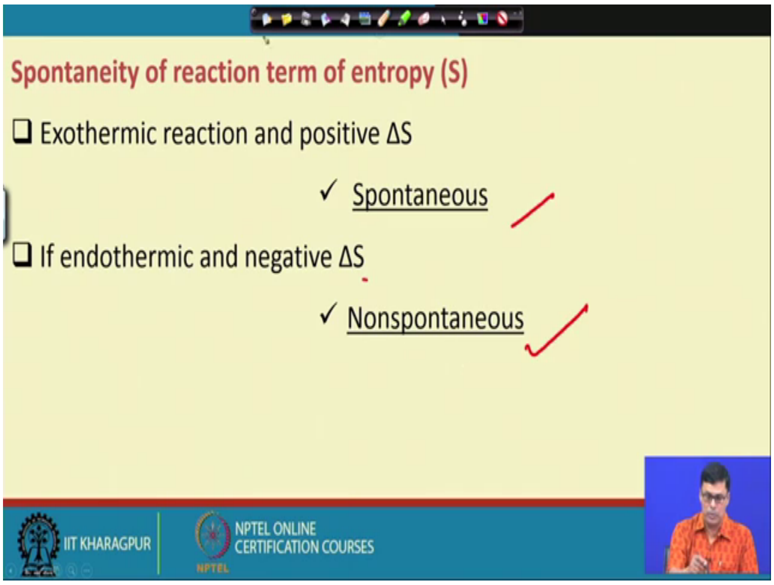

Spontaneity of reaction term of entropy (S)

☐ Exothermic reaction and positive ΔS

✓ Spontaneous

☐ If endothermic and negative ΔS

✓ Nonspontaneous

Now, exothermic reaction and positive enthalpy, as I told you this is called spontaneous and in case of endothermic reaction and negative del S we call non spontaneous. So, this is the two type of reaction that we have and on the basis of change of entropy we can easily find out what is the nature of the reaction, may be whether it is spontaneous or whether it is non spontaneous.

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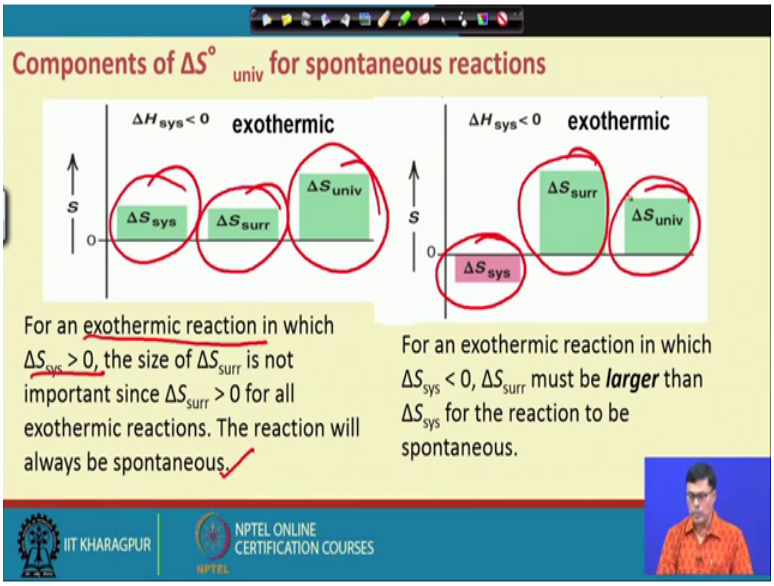

Components of ΔS°_{univ} for spontaneous reactions

For an exothermic reaction in which $\Delta S_{sys} > 0$, the size of ΔS_{surr} is not important since $\Delta S_{surr} > 0$ for all exothermic reactions. The reaction will always be spontaneous.

For an exothermic reaction in which $\Delta S_{sys} < 0$, ΔS_{surr} must be ***larger*** than ΔS_{sys} for the reaction to be spontaneous.

Now, this is very interesting that if we how we can monitor the exothermic reaction, how the system and sounding influence the entropy change of the system. Now, here the all are the examples of the exothermic reaction and the 100 volt circumstances we have the exothermic reaction.

Now, let us take the first instance. For a exothermic reaction in which the change of entropy of the system this is the change of entropy of the system is positive and change of the entropy of the surroundings is positive then in a change of entropy of the universe this should be positive the reaction will be always spontaneous. Now, in case of the change of that entropy is negative, but if the change of entropy of the surroundings is more than change of entropy of the system then this entropy of the universe will be positive.

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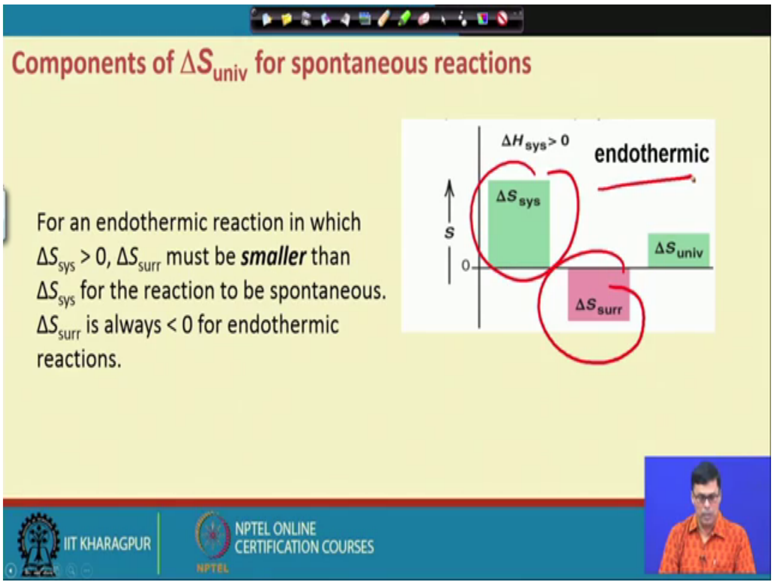

Components of ΔS_{univ} for spontaneous reactions

For an endothermic reaction in which $\Delta S_{sys} > 0$, ΔS_{surr} must be ***smaller*** than ΔS_{sys} for the reaction to be spontaneous. ΔS_{surr} is always < 0 for endothermic reactions.

Another instance we have for a, endothermic reaction in which the change of system is positive and change of entropy in the system is positive, but change of surroundings also smaller than that of the change of entropy of the system then surroundings will be also positive. And this is also example of the endothermic reaction.

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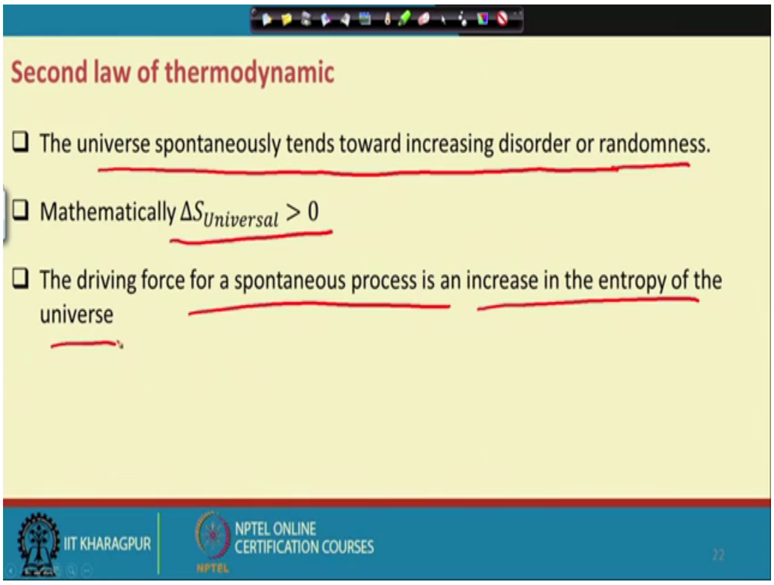

Second law of thermodynamic

- ☐ The universe spontaneously tends toward increasing disorder or randomness.
- ☐ Mathematically $\Delta S_{Universal} > 0$
- ☐ The driving force for a spontaneous process is an increase in the entropy of the universe

So, in second law of thermodynamics is that the universe spontaneously tends towards the increasing the disorder or randomness. This is the nature of the system that we have with always tends to increasing the disorder or randomness and mathematically the change of entropy the universal that will be always greater than 0. Driving force of the spontaneous process is an increase in the entropy of the universe as I told you this is the real system that we have that always is the entropy should be positive.

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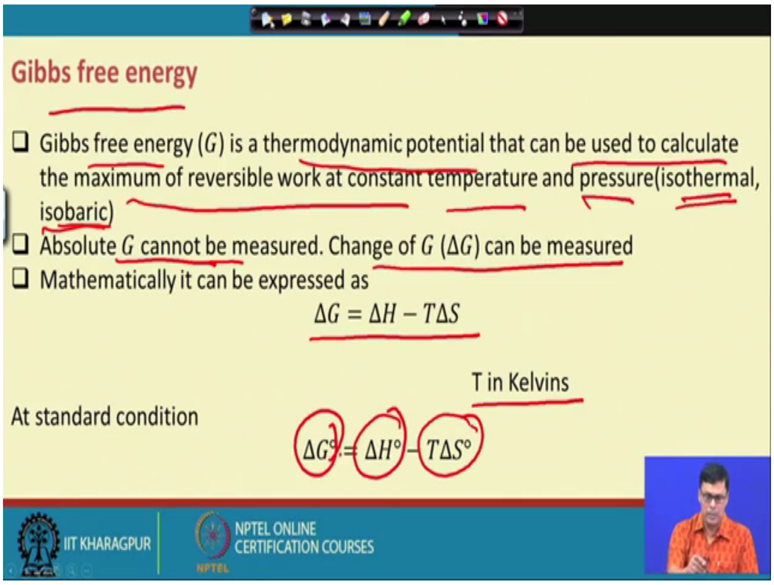

Gibbs free energy

- ☐ Gibbs free energy (G) is a thermodynamic potential that can be used to calculate the maximum of reversible work at constant temperature and pressure(isothermal, isobaric)
- ☐ Absolute G cannot be measured. Change of G (ΔG) can be measured
- ☐ Mathematically it can be expressed as

$$\Delta G = \Delta H - T\Delta S$$

T in Kelvins

At standard condition

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

Another very interesting term that we have as where thermodynamics concerned what do you call Gibbs free energy change.

Now, Gibbs free energy change is the thermodynamics potential that can be used to calculate the maximum reversible work at constant temperature and pressure that is the isothermal or isobaric. Isothermal means where temperature is the remaining constant, isobaric means where the pressure remaining constant. The absolute value of G or free energy, the free energy cannot be measured, but change of free energy can be measured the mathematically it can be expressed like this change of free energy equal to del H minus T into del S, T is the Kelvin a measure in Kelvin and as standard conditions, standard free energy change equal to standard change of enthalpy plus T into standard change of that entropy of the system. So, this is the equation we should remember for calculating the free energy change.

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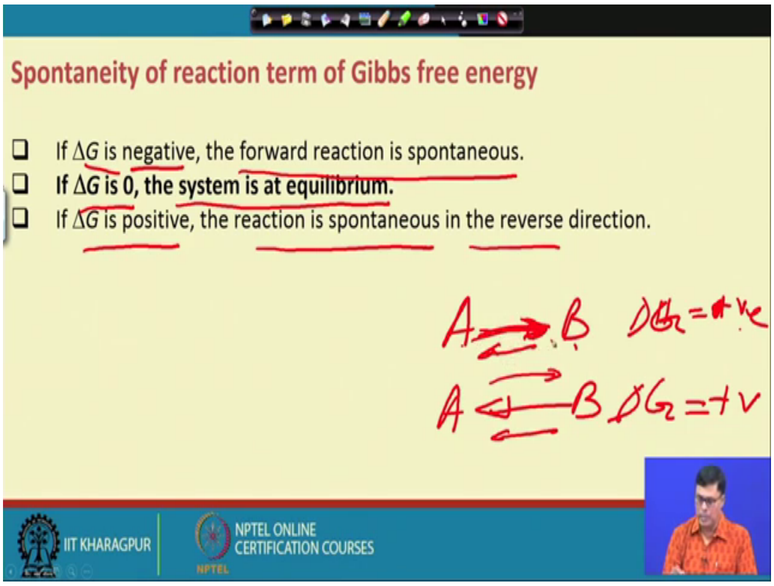

Spontaneity of reaction term of Gibbs free energy

- ☐ If ΔG is negative, the forward reaction is spontaneous.
- ☐ **If ΔG is 0, the system is at equilibrium.**
- ☐ If ΔG is positive, the reaction is spontaneous in the reverse direction.

Now, if you look at the del G, if del G is negative free energy change is negative the forward reaction is spontaneous and if del G is 0 then this is the in equilibrium and del G is positive the reaction is spontaneous in the reverse direction. Reverse direction means I want to mean that is A to B this is the reaction that we have if this, the direction is there then del G should be positive then del G would be positive. But if we have this A to in the reverse direction then del G and sorry this is negative, this is if del G is negative then it is spontaneous A to B, but if del G is positive, this is positive then if the reverse direction it will be spontaneous.

But there is direction it is non spontaneous, but at the equilibrium condition that equilibrium condition what will happen, del G the change of internal energy there should be equal to 0.

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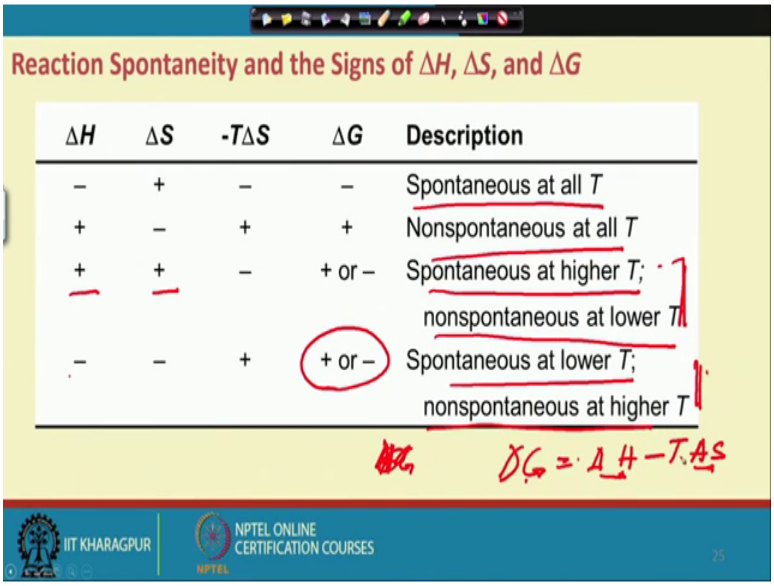

Reaction Spontaneity and the Signs of ΔH, ΔS, and ΔG

ΔH	ΔS	$-T\Delta S$	ΔG	Description
–	+	–	–	Spontaneous at all T
+	–	+	+	Nonspontaneous at all T
+	+	–	+ or –	Spontaneous at higher T; nonspontaneous at lower T
–	–	+	+ or –	Spontaneous at lower T; nonspontaneous at higher T

$\Delta G = \Delta H - T\Delta S$

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Now, this is the reaction spontaneity and the sign of del H, del S and del G. So, this is if we here if del H is for negative. And now if you look at previous, so we have this equation that we shall have to remember this equation del H equal to del H minus T del S. Now, if you see it, you have I can write like this del G equal to we can del G equal to del H minus T into del S, am I right.

Now, we can compare here. If del H is positive and del S is positive then this is negative and del S is negative and then del H is negative and if this is negative and this is negative then this will be negative. So, this will be spontaneous at all temperature. Now, if del H is positive and del S is negative then this will be T into del S will be positive then del H will be positive. There is non spontaneous at all temperature.

Now, here if del H is positive del S is positive, del H is positive where del S is positive means this is negative and this may be plus or minus. So, it may be at spontaneous at high temperature non spontaneous low temperature. Now, if del H is negative and del S is pos negative then this will be positive now again that the change of free energy it may be plus or minus, the spontaneous has lower temperature this is the reversible of this if you whatever we have and whatever we have just reversible of this and non spontaneous at high temperature.

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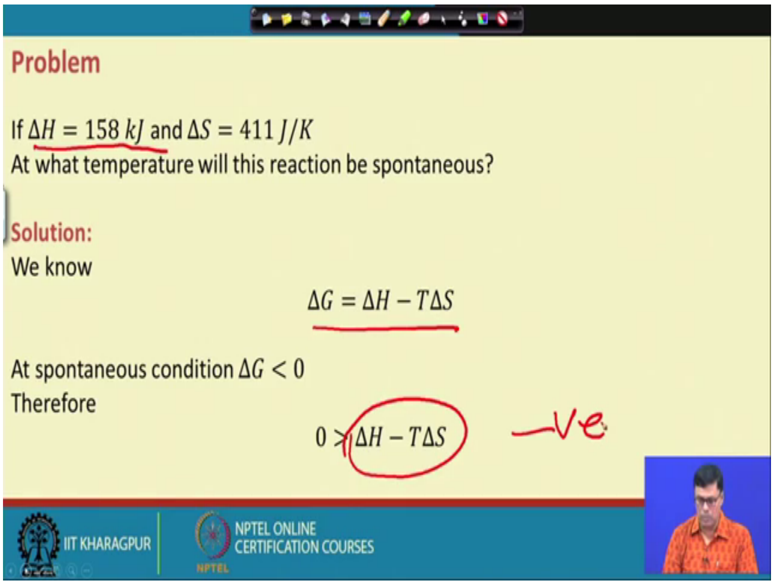

Problem

If $\Delta H = 158\ kJ$ and $\Delta S = 411\ J/K$
At what temperature will this reaction be spontaneous?

Solution:
We know

$$\Delta G = \Delta H - T\Delta S$$

At spontaneous condition $\Delta G < 0$
Therefore

$$0 > \Delta H - T\Delta S \quad -ve$$

Now, this is the problem that we also try to walk out that how this we can use for calculating the temperature required for any kind of reaction, chemical reaction. Now, let us assume that del H of the reaction is the 158 kilo joule and del S is 411 joule per Kelvin.

Now, this is the rico equation we have and, so in case of spontaneous reaction that delta T should be less than this value this is equal del G this will be this value should be less than 0, that mean it should be negative then and only then it should be it should be spontaneous.

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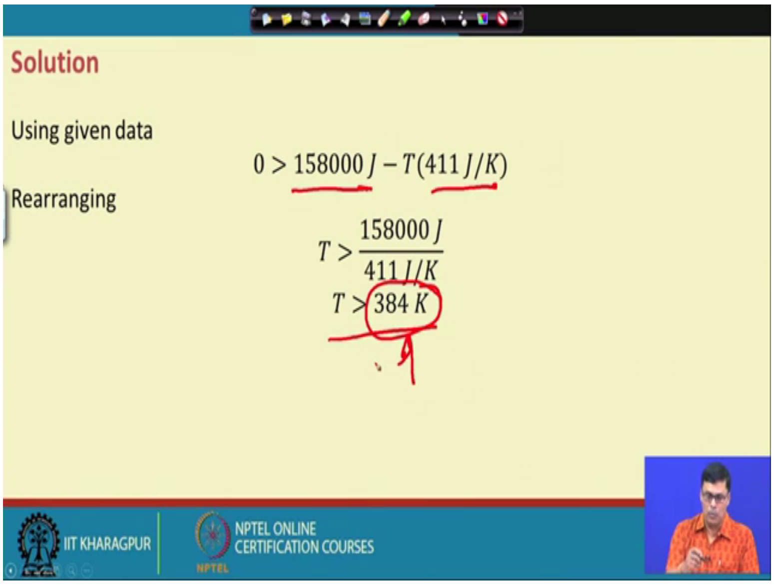

Solution

Using given data

$$0 > \underline{158000\,J} - T(\underline{411\,J/K})$$

Rearranging

$$T > \frac{158000\,J}{411\,J/K}$$

$$T > \boxed{384\,K}$$

Now, what we can write? We can put these values here, we can put the value here that that value of H and value of S we can put and then we can interchange you can find p is greater than 384 Kelvin. That means, if we wanted to have the spontaneity of the reaction we shall have to maintain the temperature at 384 degree centigrade. So, this is a very interesting problem how we can determine that is spontaneous of the direction at a different temperature. But this is suppose we want to because we whenever we carry out any kind of chemical reaction we are interested to make it spontaneous to get more product. So, initially that, so question comes that under what circumstances it can give the more product. So, this is one very interesting thing that we have.

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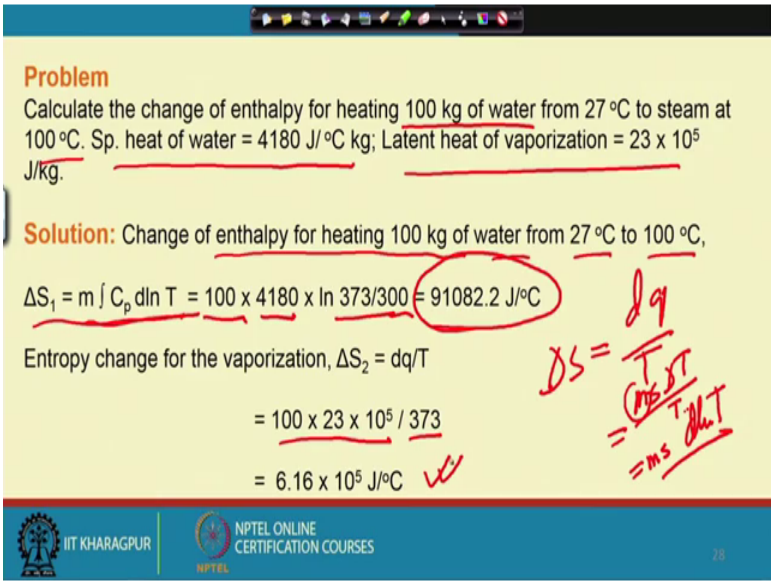

Problem

Calculate the change of enthalpy for heating 100 kg of water from 27 °C to steam at 100 °C. Sp. heat of water = 4180 J/ °C kg; Latent heat of vaporization = 23 x 10^5 J/kg.

Solution: Change of enthalpy for heating 100 kg of water from 27 °C to 100 °C,

$\Delta S_1 = m \int C_p d\ln T = 100 \times 4180 \times \ln 373/300 = 91082.2$ J/°C

Entropy change for the vaporization, $\Delta S_2 = dq/T$

$= 100 \times 23 \times 10^5 / 373$

$= 6.16 \times 10^5$ J/°C ✓

$$\delta S = \frac{dq}{T} = \frac{ms\,\delta T}{T} = ms\, d\ln T$$

Next problem that I have that is calculate the change of entropy by heating 100 kg of water from 27 degrees centigrade to steam at the 100 degree centigrade. Specific heat of water is this much and latent heat of vaporization of this also we can we can calculate very easily.

As you know the change of entropy therefore, heating 100 kg of water from 27 degree to 200 degree centigrade we can calculate at m C p into the dln T. So, I have already told you that del S equal to what; del S equal to dq by T am I right. So, when you heat of water what is happening what is the ms into del T, the del T by del T. So, this is equal to m S this is dln T that we have. So, we can have similar type of expression here. So, mass is 100 kg that is given there this is the specific heat of water and this is the ln, this is the 3, this is the temperature this is the 100 degree centigrade and this is 27 degree centigrade. So, this is the change of enthalpy that we have if we heat the water from 27 to 100 degree centigrade. Now, if you do the vaporization the equation will be different the reason is that vaporization take place is 100 degree centigrade it is kind of his change from the liquid to vapor and latent heat vaporization is this 23 into into10 to the power 5 joules per kg then we can then 100 into if we calculate that we can find it very easily that the 100 into this equal to heat and this is the temperature that we required. So, this is how we can calculate the change of entropy for the evaporation.

So, we can calculate this entropy of the system very easily. So, what will learn in this that we want to find out that what do you mean by thermodynamics. Thermodynamic basically it is deals with the temperature and it basically it deals with the mass and temperature also how it related with the energy. And then we try to find out the, define the system and surroundings how this affects the system and how the how we can define the spontaneous system and non spontaneous system. And spontaneous system and non spontaneous system can be explained, with respect to entropy, with respect to free energy change. Now, when you when talk about the entropy in case of spontaneous system the entropy keep on increasing, but in case of a reversible system the change of entropy should be equal to 0.

Now, in case of free energy change we find out that in case of exothermic reaction or a spontaneous reaction change of entropy should be negative and in case of non spontaneous reaction it will be positive, but if you do the reverse reaction then it should be we can convert it to the spontaneous. But, I hope in the next lecture this will be clearer when we deal with other different type of reaction.

Thank you.