Chemical and Biological Thermodynamics: Principles to Applications

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Lecture - 07
Entropy

After having discussed the first law of thermodynamics, now it is time to move towards the second law of thermodynamics. And in this discussion, we will discuss about the driving force for the various processes, is it the energy or is it the dispersal of energy in some form, what is it that constitutes the driving force of a process. We are going to discuss the concept of entropy and build upon that.

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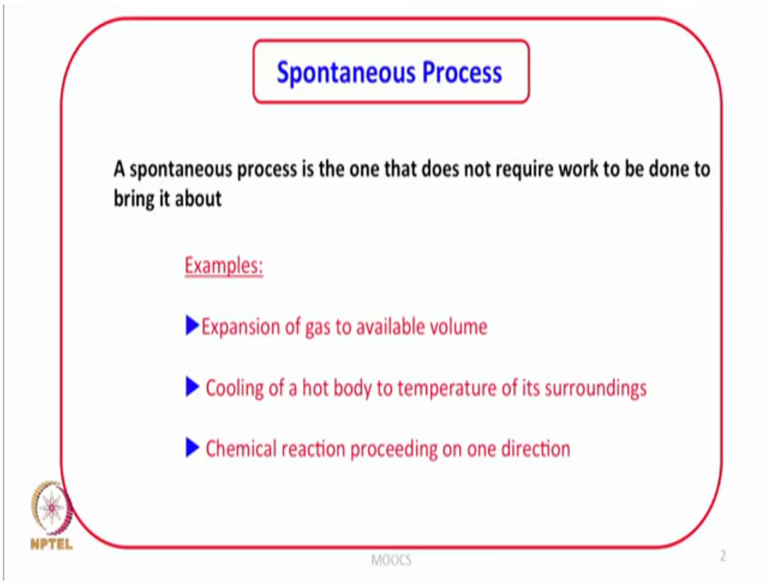

Spontaneous Process

A spontaneous process is the one that does not require work to be done to bring it about

Examples:

- Expansion of gas to available volume
- Cooling of a hot body to temperature of its surroundings
- Chemical reaction proceeding on one direction

However, before talking about entropy let us discuss what are spontaneous processes. As the name suggests spontaneous process is the one which does not require any work to be brought about, we do not have to do any work when the process happens spontaneously. There are various examples of spontaneous process. Let us check the first example expansion of gas to available volume. If we have a gas in a container and then we allow the lid of the container to be opened or raise the lid of a container, the gas will expand to whatever volume is available to it no work is required.

Another example can be cooling of a hot body to temperature of surroundings. An example, which we see every day is that you take a cup of tea, a hot cup of tea and keep it on the table after some time it will cool down. And nobody has to do any work cooling of a hot body to temperature of its surroundings is a spontaneous process. Third example that some chemical reactions proceed in one direction, those are spontaneous processes. If you talk about the reverse the compression of a gas, when you compress a gas the work has to be done, it is not spontaneous. When you need to warm up a cup of tea, it has to be put in a microwave oven or it has to be put on a stove it does not happen spontaneously work has to be done. And if the chemical reactions such as the electrolysis of water will not happen automatically, some work will have to be done. So, these are the examples of non spontaneous process.

What is the driving force for this spontaneous process? When we discussed the first law of thermodynamics, we said that the total energy of an isolated system remains constants. And if we now say that for a spontaneous process, the energy of the system decreases; then are we not violating the first law of thermodynamics. If we look at the overall in totality that the energy of the system may decrease, but at the same time this energy has to go somewhere that is energy of the surroundings will increase. If I take another example that the expansion of a perfect gas under isothermal conditions; we have earlier discussed that if the condition is isothermal, the internal energy does not change. If the internal energy does not change, but the gas is spontaneously expanding to available volume then what is the driving force. It is that driving force that we are going to discuss today.

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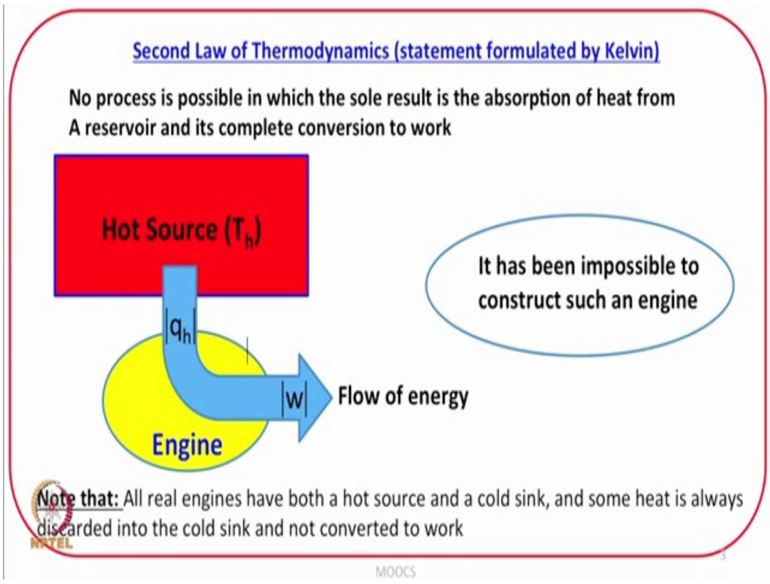

Second Law of Thermodynamics (statement formulated by Kelvin)

No process is possible in which the sole result is the absorption of heat from
A reservoir and its complete conversion to work

It has been impossible to construct such an engine

Note that: All real engines have both a hot source and a cold sink, and some heat is always discarded into the cold sink and not converted to work

Let us first discuss the second law of thermodynamics. The statement which is formulated by Kelvin, the spontaneous process or non spontaneous process form a content of this form of the second law; according to which no process is possible in which the sole result is the absorption of heat from a reservoir, and its complete conversion to work. As we see in this figure that it has been impossible to construct such an engine in which the heat is taken from a hot source, and there is a complete conversion into work, it has not been possible to construct certain engine. So, it must be noted that all real engines have both a hot source and a cold sink, and some heat is always discarded into cold sink and not converted to work.

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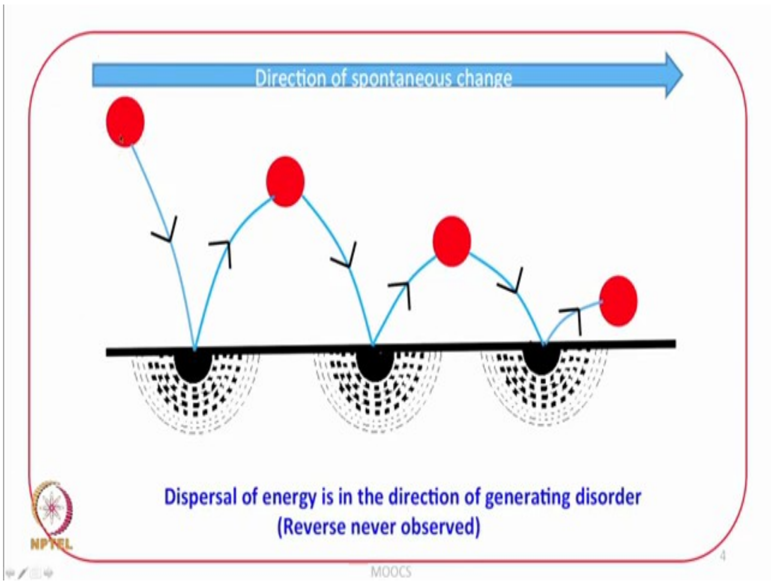

Dispersal of energy is in the direction of generating disorder
(Reverse never observed)

We will connect the second law of thermodynamics and spontaneity in the discussion ahead. What is the direction of spontaneous change is it in the direction of lowering of energy, but we cannot violate the first law of thermodynamics. Therefore, what is this spontaneous change direction connectivity? Let us take an example as shown in the figure that you take a ball and let this ball fall on the ground, it is a spontaneous process because when you are holding a ball, and you just throw it you just leave it you do not need any work to do the ball will automatically go.

Now, when this ball, let us take at this figure is bouncing is touching the ground, some of its energy is transferred to the infinite atoms of the flow. The thermal motion is induced, and since some of the energy is transferred, now the ball will rise to a lesser height. And once again when it bounces it touches the ground, again it will disperse some of its energy in the form of generating some thermal disorder or thermal motion in the infinite atoms of the floor. And then again the ball goes up, comes down and then what happens is again some of the energy is transferred, and then the ball rises with the lesser energy and eventually it comes to this.

The falling of a ball on the ground and then after taking few bounces it goes to raise this is a spontaneous process. But now try let us try to see what has happened in this spontaneous process, how the energy has been degraded or how the energy has been dispersed. Take a look at the figure what has happened to the atoms of the infinite floor, there has been generation of more disorder because the atoms of the infinite floor have been set into thermal motion. So, clearly we see the dispersal of energy is in the direction of generating more disorder. We have never seen the reverse; you have never seen that a ball which is resting on ground automatically starts bouncing that we have never seen. Because in order for the ball to be pushed up the infinite atoms of the floor have to concentrate energy at one place and then push the ball up that never happens that is not a spontaneous process. So, therefore, we can conclude that the dispersal of energy is in the direction of generating more disorder. We have connected the direction of spontaneous change towards generating more disorder.

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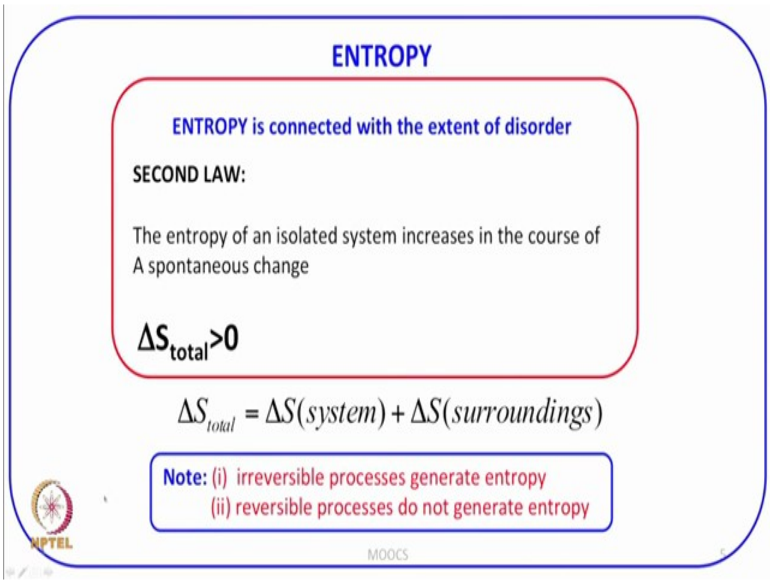

ENTROPY

ENTROPY is connected with the extent of disorder

SECOND LAW:

The entropy of an isolated system increases in the course of
A spontaneous change

$\Delta S_{total} > 0$

$$\Delta S_{total} = \Delta S(system) + \Delta S(surroundings)$$

Note: (i) irreversible processes generate entropy
(ii) reversible processes do not generate entropy

So, let us discuss more on entropy. What is entropy? Entropy is connected with the extent of disorder. If in a system there is a large amount of disorder, its entropy is more; and as the order increases, the entropy decreases. So, this can be formulated into another definition of second law of thermodynamic according to which the entropy of an isolated system increases in the course of its spontaneous change. When I talk about an isolated system over here that means, I am talking about global isolated system the system plus its immediate surrounding. So, in mathematical form, I can write the delta S total should be greater than 0 for a spontaneous change.

Many times we say the second law of thermodynamics in this form also that for a spontaneous change the entropy of the universe keeps on increasing and universe we divide into system plus surrounding. That means, if I want to connect the changes in entropy with the spontaneity then look at this figure look at the slide, I must calculate the entropy change in the system, I must calculate the entropy change in the surroundings add up the two. If it turns out to be positive that means, the process in that direction is going to be spontaneous; otherwise, it will not be spontaneous in that direction.

And as we just discussed that the entropy is connected with this order. So, two points to be noted here. One is that irreversible processes generate entropy; reversible processes do not generate entropy. All of a sudden expansion of a gas that is an irreversible process lot of entropy is generated, but if the process is carried out in infinitesimally small steps, and reversibility is maintained then the energy is not dispersed in a chaotic manner that is why the second statement that the reversible processes do not generate entropy. And these facts, these statements, we will be using in our next discussion.

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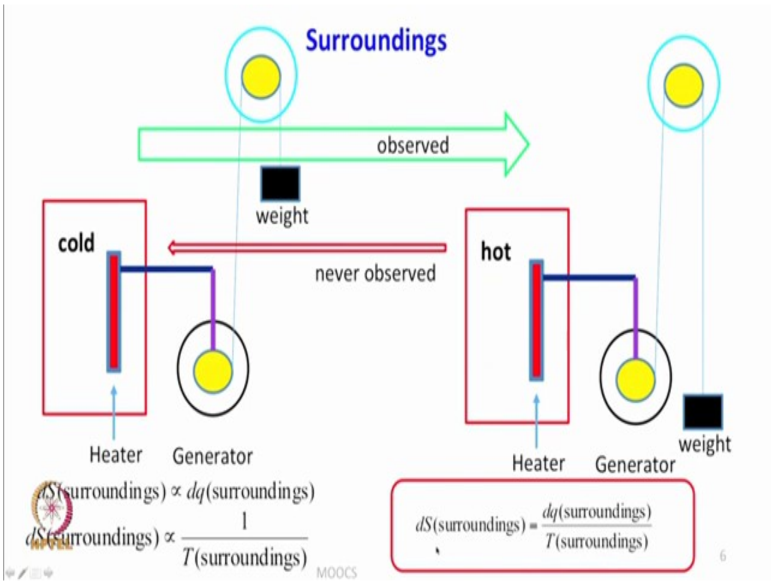

Surroundings

$dS(\text{surroundings}) \propto dq(\text{surroundings})$

$dS(\text{surroundings}) \propto \dfrac{1}{T(\text{surroundings})}$

$dS(\text{surroundings}) = \dfrac{dq(\text{surroundings})}{T(\text{surroundings})}$

Let us first talk about the surroundings. Now, we will start developing equations, which can be used to calculate the values of changes in entropy. We want to derive equations for calculating the change in entropy of the system and change in entropy of the surrounding. And it is a good idea to first start with surroundings and then go towards the system. Now, let us consider the surroundings. Let us consider the surroundings in the form of this reservoir. This is like a water bath, you know in which we have a heater, which can be used to maintain the temperature of this water bath; and there is no system we just consider surrounding at some temperature.

And let us say when the weight falls, the potential energy can be converted into heat energy, not through a generator which can pass some electric current through the heater and it can transfer heat energy to the molecules of the surrounding or atoms of the surrounding. If it is a water bath then the heat will be transferred to the water molecules. And once the heat is transferred to the water molecule, these molecules will be set into thermal motion. The setting up of thermal motion means there is creation of or generation of this order.

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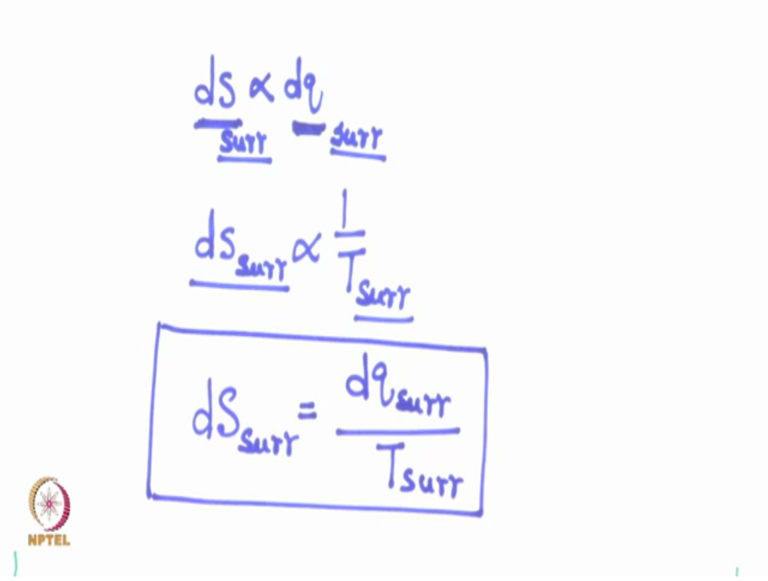

$$dS_{surr} \propto dq_{surr}$$

$$dS_{surr} \propto \frac{1}{T_{surr}}$$

$$\boxed{dS_{surr} = \frac{dq_{surr}}{T_{surr}}}$$

dS if I write as the change in entropy as a result of this disorder it is directly proportional to the amount of heat transfer. And at present, we are talking about surrounding; we are not talking about the system. Let us take a look at the figure. When the weight is fallen, the potential energy is converted here by the means shown in the figure to the heat and there is a generation of more disorder. So, this transfer of potential energy into electrical energy or a hence heat is observed reverse is not observed because the weight itself will not go up by itself. So, the change in entropy of the surroundings is equal to or is proportional to at directly proportional to the amount of heat transferred, because more is the current pass or more is the heat transferred, more is the generation of the disorder in terms of thermal motion of the molecules.

Now, the next is temperature dependence. How it is dependent on the temperature of the surrounding. This is you know a bit interesting discussion. Let us consider the transfer of heat to a cold body and the transfer of heat to a hot body. In which case, it is going to generate more disorder; obviously, it is going to generate more disorder when the heat is transferred to a cold body rather than when the heat is transferred to a hot body. The energy is degraded more completely when the heat is transferred from a hot body to a cold body rather than from a hot body to a hotter body. Another way of describing this is that if I sneeze in an empty hall, I will be heard very, very clearly, but if I sneeze in a hall which is full of people I may not be even heard.

So, all these arguments suggest that the change in entropy which is inversely proportional to temperature. So, dS surroundings is inversely proportional to the temperature of surroundings by the arguments that I just described, that if you transfer heat from a higher temperature to lower temperature, you will see more generation of disorder rather than if you transfer from a certain temperature to a higher temperature. Now, when you combine these two then I can write dS surroundings is equal to dq surrounding divided by temperature of surrounding and proportionality constant I am consuming in this equality. And that is what we see in this slide that dS surrounding is equal to d q surrounding by T surroundings. So, this is the formula to be used if we want to calculate the change in entropy of the surrounding. We need to actually know the amount of heat transfer to the surrounding and the temperature of the surrounding.

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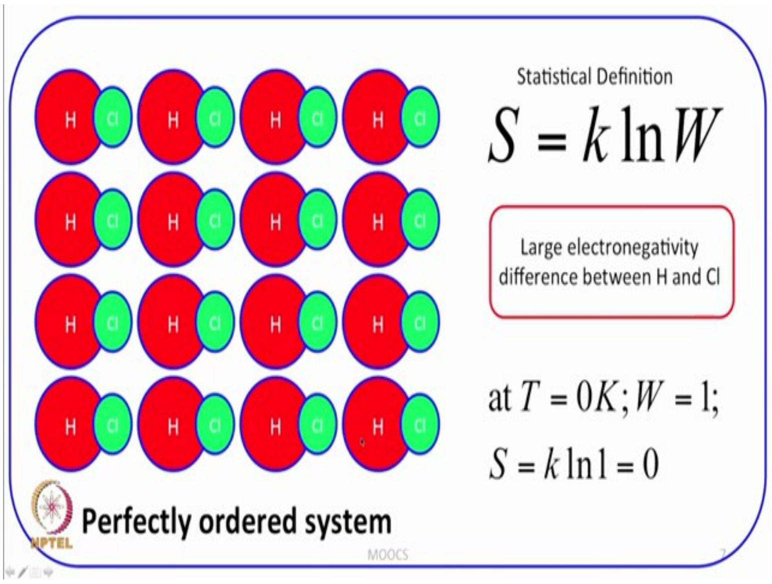

Statistical Definition

$$S = k \ln W$$

Large electronegativity difference between H and Cl

$$\text{at } T = 0K; W = 1;$$

$$S = k \ln 1 = 0$$

Perfectly ordered system

Since, I discussed entropy in terms of order or disorder let us take a look at this example of HCL at 0 Kelvin thermal motion is quenched. And all HCL molecules are arranged in this form H Cl, H Cl, H Cl and it is a perfectly ordered system. If a system is perfectly ordered, we take it as a reference system and assign a value of entropy equal to 0, else it will be shown later on that the statistical definition of entropy is S is equal to k log w where K is Boltzmann constant, and w is the statistical weight of the system corresponding to most probable configurations. At 0 Kelvin, there is only one way of arranging the HCL molecule to get the minimum energy and that is when HCL are arranged in a perfectly ordered way that H is on the left hand side and Cl is on the right hand side in all the molecules. There is only one way one way means the value of w the way of the configuration is 1. And then if you substitute W equal to 1 s is equal to 0.

So, therefore, the entropy of this system for HCL at t equal to 0, when the system is in perfectly ordered shape, the value of entropy is equal to 0. The point to be noted here is that there is large electronegativity difference between H and C l and that is why you know the HCL has to be arranged only in one configuration, one particular configuration to get the minimum energy of the crystal. This will become more clearer in the next example of carbon monoxide.

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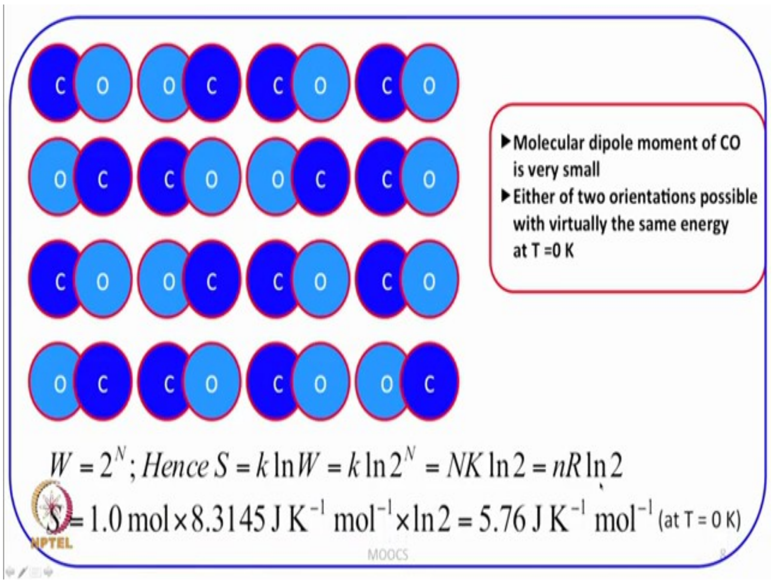

- Molecular dipole moment of CO is very small
- Either of two orientations possible with virtually the same energy at T =0 K

$$W = 2^N; \text{Hence } S = k \ln W = k \ln 2^N = NK \ln 2 = nR \ln 2$$

$$S = 1.0\,\text{mol} \times 8.3145\,\text{J K}^{-1}\,\text{mol}^{-1} \times \ln 2 = 5.76\,\text{J K}^{-1}\,\text{mol}^{-1} \text{ (at T = 0 K)}$$

Now, if you look at the arrangement here you have carbon oxygen then oxygen and carbon if instead of co the molecule is arranged in the form of o c at absolute 0. Then c o c o and somewhere if you see in this arrangement, see instead of c o you have o c. And here the point to be noted is that molecular dipole moment of carbon monoxide is very small because of small electronegativity difference between carbon and oxygen. So, therefore, when whether it is c o or it is o c, either of the two orientations will virtually have the same energy at T equal to 0.

So, therefore, you can have the same energy of the crystal when this molecule can be arranged in two orientations either in c o or in o c. So, one molecule can be arranged in two orientations to get the same energy of the crystal at absolute 0. If two orientations are possible for one molecule, and if there are n molecules, then the total number of orientations possible are 2 raised to the power n. And for W, if you substitute 2 raised to the power n, then n comes down you have n k log 2.

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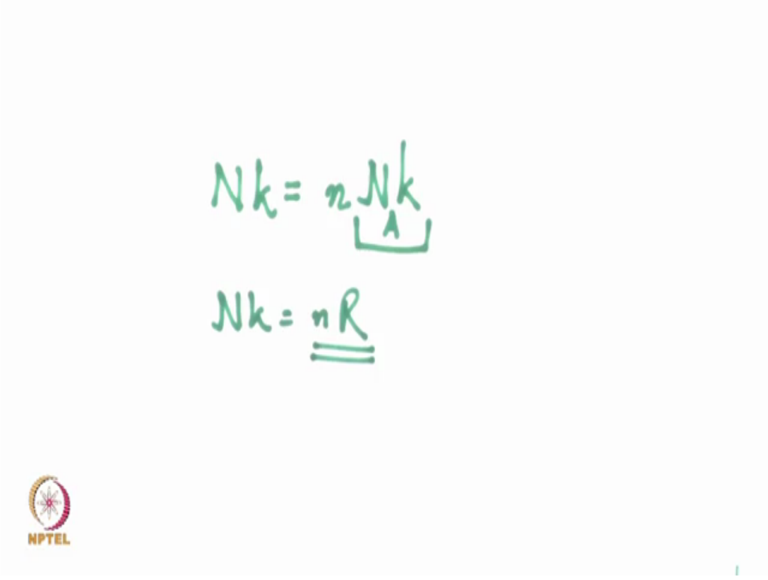

$$Nk = n\,\underbrace{N_A k}$$

$$Nk = \underline{\underline{nR}}$$

And then n k n is the total number of molecules k is the Boltzmann constant, n is equal to number of moles into Avogadro constant and Boltzmann constant. Boltzmann constant into Avogadro constant is equal to gas constant. So, I can substitute over here now let us go back to the slide instead of n k, I use n R this is n R log 2. And once we will substitute the numbers the entropy comes out be 5.76 joules per Kelvin per mol. So, the point to be noted here is that in this case the entropy at absolute zero is not zero there is some value of entropy which is 5.76 joules per Kelvin per mol that means there is a configurational disorder here and later on we will discuss that this configurational disorder forms the residual entropy of the system.

We have discussed how to calculate the entropy change in the surrounding. We have also discussed what we understand by entropy that it is connected with the disorder. By taking the example of HCL and c o we shown that if the system is perfectly ordered that entropy is equal to 0; and if there is a small disorder due to whatever reason, the entropy is not equal to 0.

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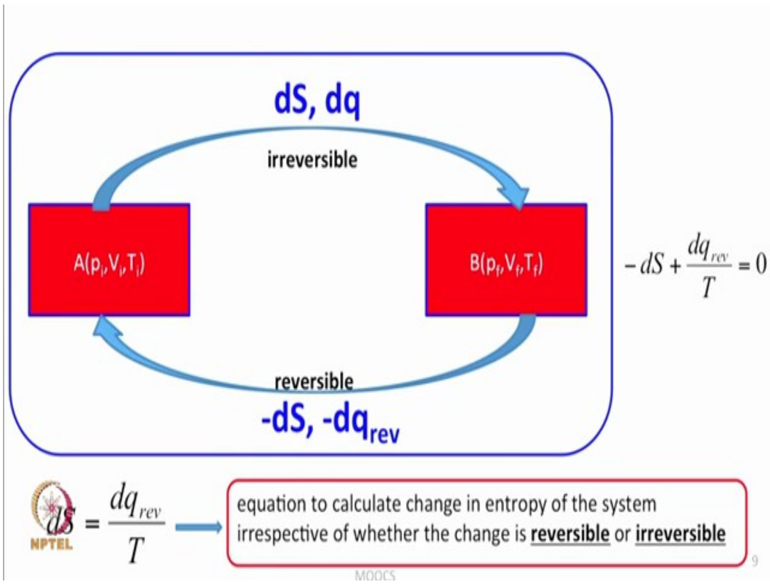

$$-dS + \frac{dq_{rev}}{T} = 0$$

$$dS = \frac{dq_{rev}}{T} \longrightarrow$$

equation to calculate change in entropy of the system irrespective of whether the change is **reversible** or **irreversible**

Now, we will discuss how to calculate the entropy change of the system. And please pay special attention to this because calculation of entropy change in the system is very important because the same formula will be used whether the process is reversible or irreversible since entropy is a state function. Let us take a look at this figure. We change the state of a system from A to B, A is at some p i, V i, T i; B is at p f, V f, T f. Now, for the time being let us considered consider that T i is equal to t f, and this system is isothermal. And we talk about isothermal change and let us say we go by this path and this path let it be reversible let us not care about reversibility the entropy change in the system is going to be dS and let us say in general the amount of heat transferred is equal to dq

Now, when I go back from B to A, remember that I am saying T i is equal to T f that is isothermal condition. When I go from B to A, and let me ensure that the path is reversible. Since, entropy is a state function, therefore, T s instead of dS, now it will be minus dS, because it is going back. So, it has to be with a negative sign and the heat change will also a minus dq, but let me now put a subscript reversible because the path is reversible. I do not need to mention with dS, because when you go from A to B or B to A, dS will remain same one in one case positive in another case negative because entropy is a state function. But heat is a path function; therefore I need to label it by a subscript reversible.

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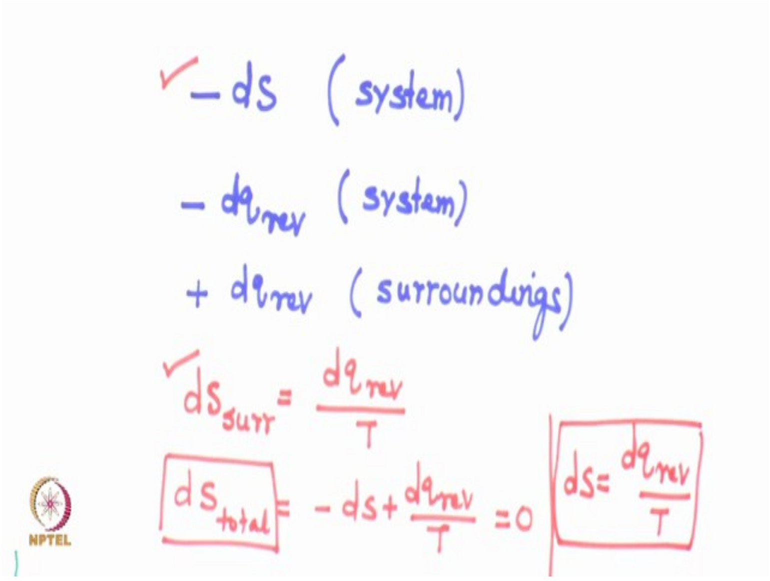

✓ $-dS$ (system)

$-dq_{rev}$ (system)

$+dq_{rev}$ (surroundings)

✓ $dS_{surr} = \frac{dq_{rev}}{T}$

$\boxed{dS_{total}} = -dS + \frac{dq_{rev}}{T} = 0 \quad \boxed{dS = \frac{dq_{rev}}{T}}$

Now, let us discuss further. Entropy change in the system is minus dS that is there entropy change in the system. How much is the heat change minus dq reversible. This is gain heat change for the system. And if there is a thermal equilibrium between system and surrounding then plus dq reversible will be the heat change for the surroundings. Now, the entropy change in the surroundings, remember we just discussed today, it is the actual amount of heat transferred the actual amount of heat transferred here is dq reversible divided by the temperature. This is the entropy change in the system; this is the entropy change in the surrounding. The total entropy change dS total will be this plus this which is minus dS plus dq reversible by T. And since the process is reversible, we discussed that the reversible processes do not generate entropy, this has to be equal to 0.

Now, when you rearrange this what you get is dS is equal to d q reversible by T. So, very important formula dS is equal to d q reversible by T, let us take a look at the slide. And this is the formula or equation to be used to calculate change in entropy of the system irrespective of whether the change is reversible or irreversible. Remember that entropy is a state function. Therefore, whether the process is reversible or irreversible as long as we maintain the temperature constant, it does not matter, the same formula is to be used.

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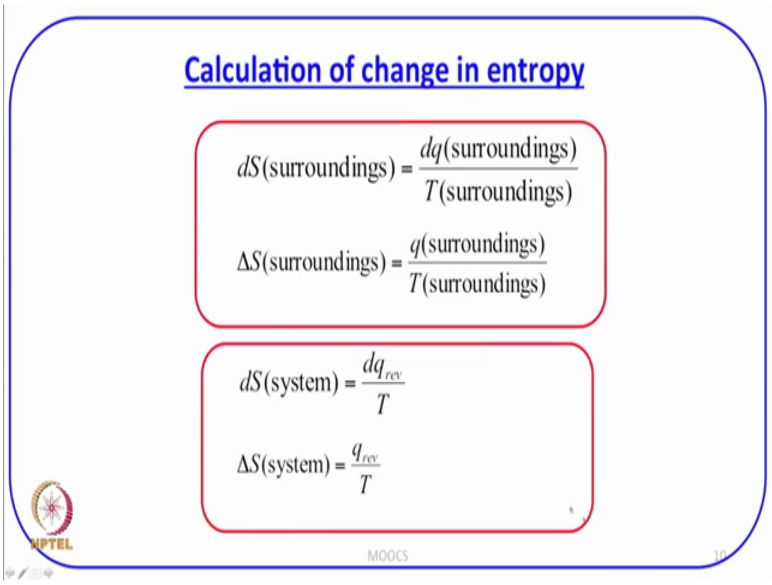

Calculation of change in entropy

$$dS(\text{surroundings}) = \frac{dq(\text{surroundings})}{T(\text{surroundings})}$$

$$\Delta S(\text{surroundings}) = \frac{q(\text{surroundings})}{T(\text{surroundings})}$$

$$dS(\text{system}) = \frac{dq_{rev}}{T}$$

$$\Delta S(\text{system}) = \frac{q_{rev}}{T}$$

So, therefore, how to calculate the change in entropy if we are interested in calculating the change in entropy of the surroundings then this is the formula to be used. For infinitesimally small changes dS surrounding is equal to dq surroundings by the temperature of the surrounding. For a finite change delta S will be equal to the actual amount of heat transferred to the surroundings divided by the temperature of the surroundings. However, when we are interested in calculating the changes of entropy in the system, we must use this formula; dS system is equal dq reversible by T. And remember even if the process is irreversible, we must find out a reversible path and get the information on dq reversible and use this formula dq reversible by T.

I once again emphasize on this that even if the process is irreversible, we must find out a reversible path to get the value of dq reversible and use this formula to calculate the change in entropy of the system. And for a finite change, we can use the integrated form which is q reversible by T. And then later on we will connect this q’s with the delta h for the exothermic and endothermic processes. And we will also solve a lot of numerical problems for different cases to calculate the values of changes in entropy. The changes in entropy, the number and the sign are very very important because this spontaneity of a process is associated with it, and the entropy is connected with disorder. And the disorder will also depend upon the nature of intermolecular interactions. It will also depend upon the strength of a system, and it will also depend upon how the system responds to the temperature. All these things we will discuss both qualitatively and quantitatively later on connecting with the chemical system and biological systems. If there are questions, queries, please note down for discussion in the help section.

Thank you very much.