Concepts of Chemistry for Engineering
Professor Arnab Dutta
Center for Distance Engineering Education Programme
Indian Institute of Technology, Bombay
Lecture 53
Second Law of Thermodynamics:
Entropy and Third law of Thermodynamics

Welcome to the next segment of our discussion of Thermodynamics. So, so far, we have discussed the first law of thermodynamics and find out one important parameter enthalpy, which is an intrinsic state function which defines the changes in the heat content or the bond energy during a chemical or physical process happening in a system. So, now we will go a little bit further and find out another important parameter entropy.

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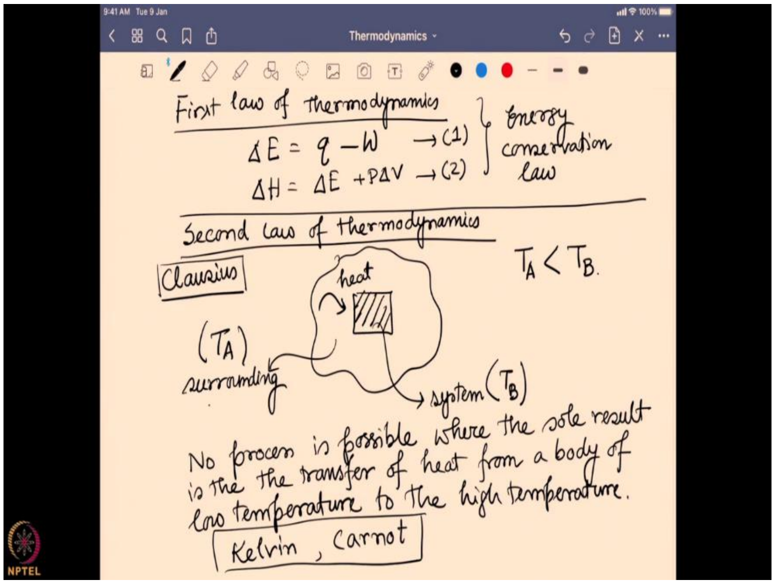

First law of thermodynamics

$\Delta E = q - W \rightarrow (1)$

$\Delta H = \Delta E + P\Delta V \rightarrow (2)$

Energy conservation law

Second law of thermodynamics

Clausius

$T_A < T_B.$

No process is possible where the sole result is the the transfer of heat from a body of low temperature to the high temperature.

Kelvin, Carnot

So, so far, we have discussed the first law of thermodynamics and in the first law of thermodynamics, what we actually find out that a change in the energy of a system is given by the heat is coming into the system and the work done by that particular system. And from there, we actually expanded it further and I find another important term ΔH, which is nothing but ΔE+pΔV, which is nothing but the enthalpy and it gives us about the heat content of the system.

Now, over here the first law of thermodynamics give us a very good idea how much heat or how much energy is actually exchanged, how much work can be done, but it never gives us an idea which side the reaction should occur, which side a particular process should go on, it gives us an idea what will be the overall change, but does not give us an idea which side is actually it favors, which side the reaction will be spontaneous.

To understand that, we have to look into the second law of thermodynamics where we get the idea of spontaneity. So, again reiterating back to the first law of thermodynamics, it is generally known as the energy conservation law, which actually says that none of the energy can be destroyed it will be end up with a mixture of heat plus work, but you cannot destroy the overall energy.

And in the second law of thermodynamics, it actually given by different scientists and actually explained in different ways, so I am just using one particular scientist version Clausius, how he explained the system, so he explained the system in the following way. He said we have a system and we have its surrounding and say the surrounding temperature is T_A, and system temperature is T_B. Now, say temperature of T_A is less than temperature of T_B, temperature of T_A is actually less than the temperature of T_B that means, surrounding has lower temperature compared to the temperature of the system.

The second law of thermodynamic says that no process is possible where the sole result is the transfer of heat from a body of low temperature to the high temperature. It seems quite obvious because we generally know that heat actually moves from the high temperature to the low temperature. But despite it is saying that it is not possible if there is the only thing happening or if we do not have anything happening from the outside to tune that process the heat cannot go from the low temperature to the high temperature.

So, in this case the heat cannot go from the surrounding to the system if nothing else is happening because the surrounding temperature is lower than the system temperature. So, this is how Clausius defined the second law of thermodynamics and you can find also the statement from Kelvin or Carnot and you can find they actually defined the similar statement in different ways. Our goal is not to distinguish between the different statement, but we are trying to understand the inherent understanding of the second law of thermodynamics.

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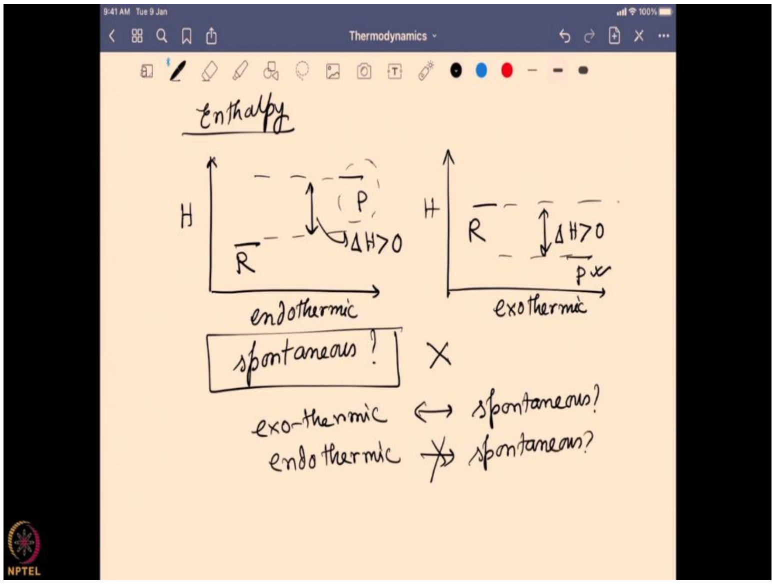

So, so far, we have talked about the enthalpy and we know if we have a system and if we measure with respect to enthalpy if this is my reactant, this is my product, this is a ΔH greater than 0 system where product enthalpy is higher than the reactant or it is known as an endothermic reaction. And in the other way I can have the opposite scenario where the product enthalpy is lower than the reactant and I can say I have a ΔH less than 0 system or exothermic process.

Now, this exothermic and endothermic process is saying how much heat will be released and whether it is coming out of this process or it is going inside the process, but it never talk anything about the spontaneity of the reaction, whether the reaction will be spontaneous or not, that question is unanswered till now, is it always that an exothermic reaction only occur spontaneously, because the product is a little bit stabilized with respect to enthalpy then the reactant does it means.

So, what is the relation between exothermic reaction and spontaneity? Is this spontaneous? Or endothermic reaction in that way, because the product has higher enthalpy, then the reactant it should never go through spontaneous reaction, is it does it what we mean? To understand that, we will take an example.

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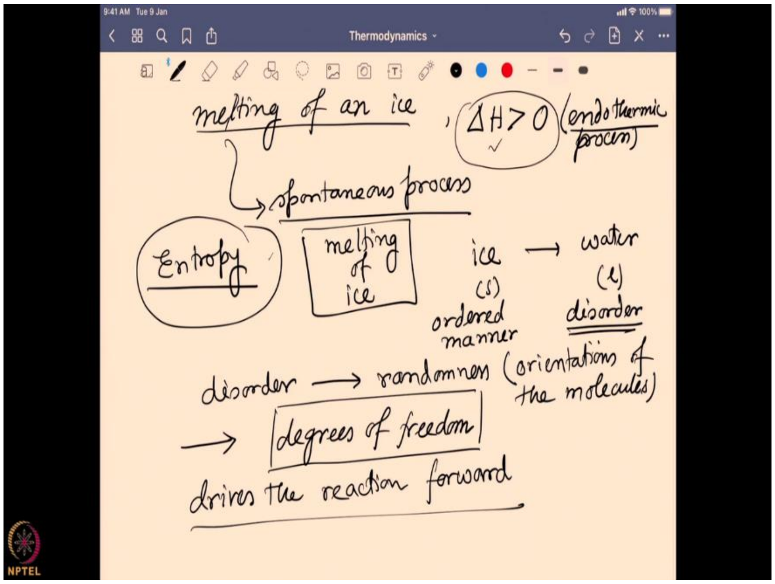

melting of an ice, $\Delta H > 0$ ✓ (endothermic process)

↳ spontaneous process

Entropy

melting of ice

ice (s) ordered manner → water (l) disorder

disorder → randomness (orientations of the molecules)

→ degrees of freedom

drives the reaction forward

And we will take an example of a melting of ice, a melting of an ice piece, if we look into the change of the enthalpy, it is delta H greater than 0 that means it is a endothermic process, and if you keep a piece of ice at a particular temperature you can easily see the ice generally melts, so the melting of ice is generally a spontaneous process.

So, it has nothing to do with endothermic or exothermic reaction pattern but altogether there is some other factor is playing a role over here. So, we try to understand what is the role of this. So, why even the melting of ice is an endothermic process how it becomes spontaneous. To understand that, we look into the details of the melting of ice in a molecular level, and we found this another factor playing a huge role over there and that factor is known as entropy.

So, what is entropy? Let us, take a look into melting of ice. So, when the melting of ice is happening, there is a change from ice to water, so it is more of a solid to liquid form. So, in the solid ice all the water molecules are actually present in a very ordered way, because it is crystalline in nature, whereas in water it becomes liquid, so there is some disorder now present.

Previously, the water molecules have to be oriented in a particular way so that it can form the crystal, now once it becomes a liquid, it does not have that much of a pressure to be in a particular orientation, it can be in different orientation and that brings some disorder in the system. And this disorder in the system is actually coming from the randomness of the orientations of the molecules.

Now, can the molecule orient in every different way possible, it does, but it still follows some particular feature that actually controls how many different ways the molecule can move around a system and that is known as degrees of freedom, and that is actually depend how many atoms are actually present in a molecule what is their overall symmetry and all these things comes together and give you an idea that degrees of freedom.

So, once we go from a solid to liquid, the randomness or degrees of freedom or movement is actually improving, and this increase in the disorder, this increase in the randomness is the prime factor which actually drives the reaction forward. So, that randomness factor or known as entropy is the crucial factor over here which makes sure that the melting of ice is a spontaneous process, it is connected to the enthalpy but enthalpy is not the only factor, both this entropy and enthalpy coming together and the entropy factor overcomes the endothermic nature of the process and making it a spontaneous process. So, how we measure entropy?

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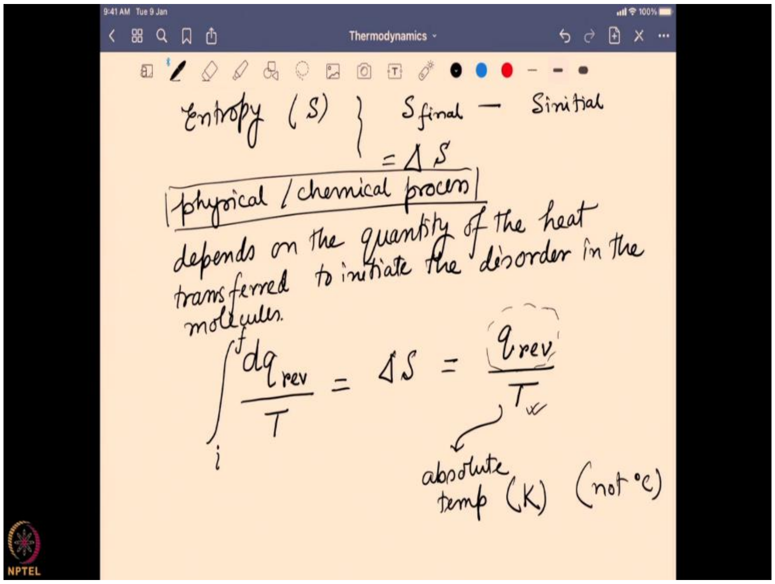

Entropy (S) } $S_{final} - S_{initial} = \Delta S$

|physical / chemical process|

depends on the quantity of the heat transferred to initiate the disorder in the molecules.

$$\int_i^f \frac{dq_{rev}}{T} = \Delta S = \frac{q_{rev}}{T}$$

absolute temp (K) (not °C)

So, entropy is written with this symbol S, it is nothing but a randomness measurement or disorderness measurement, and we measured that in the final state, we measured that in the initial state and if we subtract that we get the overall entropy change. So, that is the mathematical system. Now, if you go a little bit details of that, so during a physical or chemical process the randomness of the system is changing and that is we are trying to measure.

And this particular entropy change during a physical or chemical process depends on the quantity of the heat transferred to initiate the disorder in the molecules. Now, over there, when this is happening, if we want to measure that very carefully, we measured it in such a way that it is happening almost very closely lying final an initial state, where the difference is very small and they are reversible in nature, that means they can go back and forth very easily.

And during that process, if the change in the heat is dq, and I am writing dq_{rev} reversible to mention that we are looking into reversible process and if I divide that by the temperature exactly what it is happening, because it is reversible process we are doing in such a way there is not much difference in the temperature, temperature remains identical, and there is a certain change only in the disorderedness of the molecule and then we find it out and find it out of all the process all such processes happening from the initial to final state, and if we integrate all of them together, then we figure it out that is nothing but ΔS.

And altogether we write it as q_{rev}/T for such process where the temperature does not change at all, for an example of a phase change, which is actually a reversible reaction in a way and over there the change in the heat during that phase change and the temperature remained constant, if we use this particular equation, we find that it is going to be the entropy change.

And over there one important thing this T or temperature has to be written in the form of absolute temperature, that means we have to write that in the Kelvin unit not in degree centigrade unit. So, the absolute temperature has to be used for finding out the entropy change during a process. Now, why it is very important the entropy? Because the entropy actually redefines the second law of thermodynamics.

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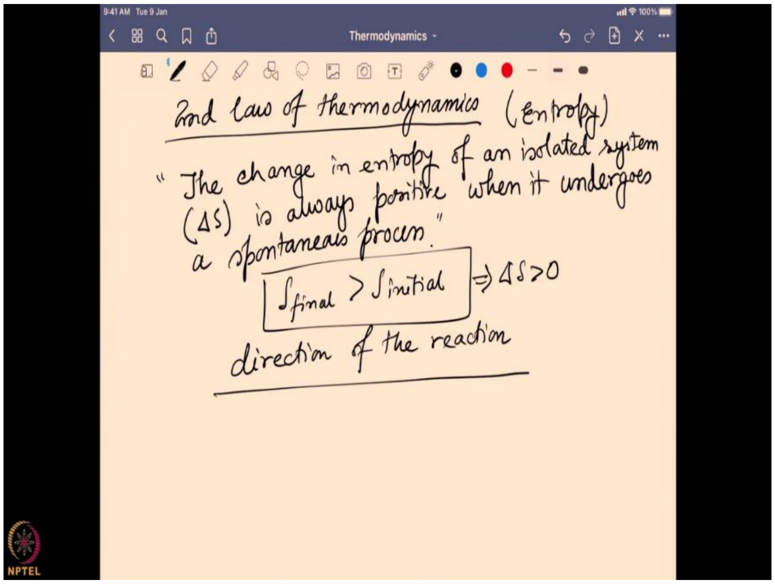

2nd law of thermodynamics (Entropy)

" The change in entropy of an isolated system (ΔS) is always positive when it undergoes a spontaneous process."

$\boxed{S_{final} > S_{initial}} \Rightarrow \Delta S > 0$

direction of the reaction

Now, if we go back and take a look into the second law of thermodynamics one more time and we have already defined it as Clausius actually explained it before, but now we want to explain that with the entropy factor, and how does it matter? Because it says the change in entropy of an isolated system, we have defined isolated system earlier where neither the mass nor the energy can be exchanged between the system and surrounding.

The change in the entropy of an isolated system that means ΔS is always positive when it undergoes a spontaneous process. So, there is a change in the entropy positive means S_{final} is greater than $S_{initial}$ that means the randomness is higher in the final state then the initial state that means by ΔS positive and this increase in the randomness actually drives the reaction faster and that makes the overall reaction spontaneous.

So, now the second law of thermodynamics is giving me an idea on the direction of the reaction as we discussed earlier the first law of thermodynamics give me an idea how much energy will be used, how much work can be done, how much heat can be exchanged, so it is actually combining all those things and giving the idea like okay everything will be conserved energy will be conserved, but that does not say about the direction and the spontaneity of the reaction.

Second Law of Thermodynamics in the presence of the term entropy is introducing that factor and that is bringing up the spontaneity and also the direction of the reaction. Now, if we want to take a look of entropy of different processes, how does it looks like?

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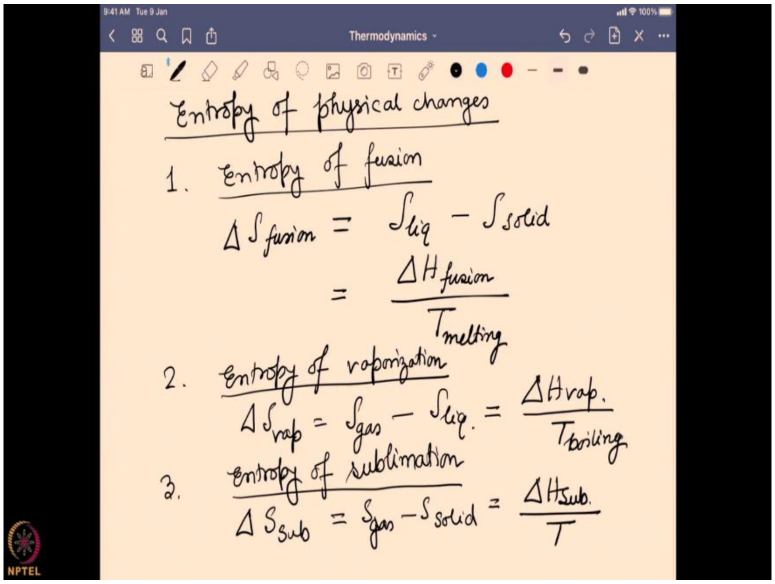

Entropy of physical changes

1. Entropy of fusion

$$\Delta S_{fusion} = S_{liq} - S_{solid} = \frac{\Delta H_{fusion}}{T_{melting}}$$

2. Entropy of vaporization

$$\Delta S_{vap} = S_{gas} - S_{liq.} = \frac{\Delta H_{vap.}}{T_{boiling}}$$

3. entropy of sublimation

$$\Delta S_{sub} = S_{gas} - S_{solid} = \frac{\Delta H_{sub.}}{T}$$

So, we want to look into entropy of different physical changes. So, for an example we start with entropy of fusion that means a melting process, ice to water such thing like that. So, during this process, the fusion will be such that the entropy change during this fusion process will be entropy of the liquid state minus entropy of this solid state ($\Delta S_{fusion}= S_{liq}-S_{solid}$), and that can be given by the heat exchange during this melting process, which is nothing but the enthalpy change in this fusion process divided by the melting point $\Delta H_{fusion}/T_{melting}$.

So, if we put this together, we will easily found the entropy change during a fusion process. And as you already know ΔH fusion is already positive for ice melting, that is also showing that ΔS fusion is also positive. Now, take the second one entropy of vaporization, where I am going from a liquid to a gaseous state.

So, ΔS vaporization will be difference between $S_{gaseous}$ state – S_{liq} state and that is nothing but enthalpy of vaporization, enthalpy change in the vaporization divided by the boiling point $\Delta H_{vap}/T$, and can you can imagine this is also going to be positive factor because from a liquid to gaseous I am actually expanding the overall volume of the system so that will increase the overall entropy of a system when it is going from a liquid to the gaseous state.

Similarly, the other physical change remains entropy of sublimation where its solid straight directly go to the vaporization state, $\Delta S_{sub}=S_{gaseous}-S_{solid}$ and that is given by $\Delta H_{sublimation}/T$, the temperature where the sublimation is happening. So, over here you can find it out that the entropy change of different physical processes can be easily find out by the enthalpy change of that particular process and divided by the temperature where it is actually happening which generally a constant temperature.

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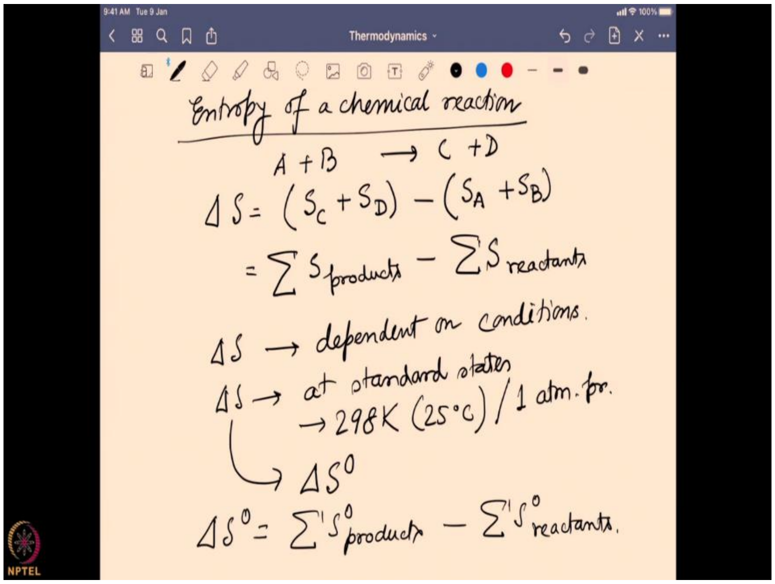

Entropy of a chemical reaction

$A + B \rightarrow C + D$

$\Delta S = (S_C + S_D) - (S_A + S_B)$

$= \sum S_{products} - \sum S_{reactants}$

$\Delta S \rightarrow$ dependent on conditions.

$\Delta S \rightarrow$ at standard states

$\rightarrow 298K\ (25°C) / 1$ atm. pr.

$\hookrightarrow \Delta S^0$

$\Delta S^0 = \sum' S^0_{products} - \sum' S^0_{reactants}$.

Now, how about measuring the entropy of a chemical reaction? Now, very similar to the enthalpy change, entropy change can be also connected. So, over here I am doing this reaction A+B going to C+D and over there I want to find out what is the entropy change for this process. So, what I need to do I have to find out what is the entropy for the products, so it is entropy of C (S_c) + entropy of D (S_D) and subtract that of the initial entropy of the reactant and that means entropy of A (S_A) and entropy of B (S_B).

So, which is nothing but very similar to Hess's law what we actually discussed earlier, but it is enthalpy and this is in the terms of entropy, it is the entropy of the products to add it all together and subtract that from the sum of the entropy of the reactants altogether. And from there, you can actually get the overall entropy change.

Now, entropy change is actually dependent upon the condition at which condition I am doing the change, if I am doing that a different temperature different pressure, the entropy change will vary. So, that is why we want to standardize it, and we can standardize it by doing the entropy change measurement at standard states. What do you mean by standard state? That means at 298 Kelvin or 25 degree centigrade temperature, 1 atmospheric pressure of any gas solid state is already in the standard state, and all together if I measure all the system in this particular condition, my entropy change becomes delta S_0 or entropy change in the standard state.

And that is going to be constant because the entropy change for any reaction of the products minus entropy change of any set of reactants, they are going to be constant, because the entropy of one particular system at a particular temperature and condition especially at the standard state is constant. So, that is why a standard entropy change is going to be an important parameter that we can use to look into a reaction at a time and find out what will be the overall change of the entropy for this particular system.

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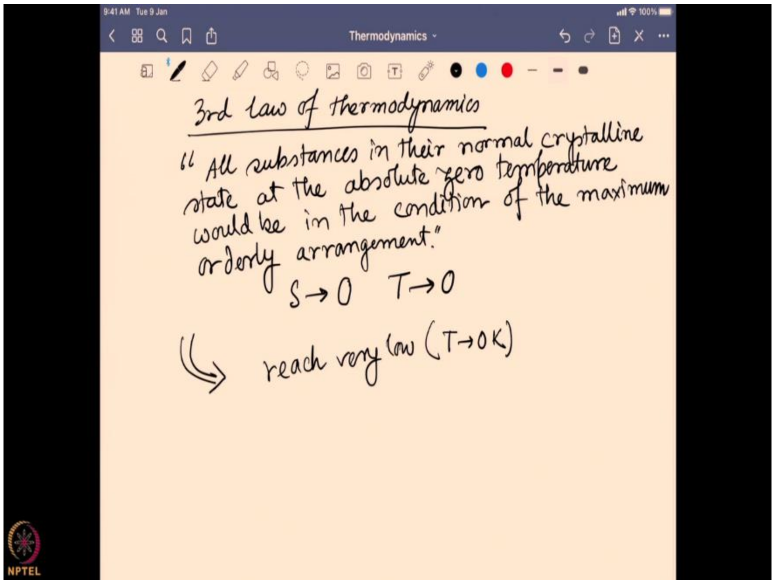

3rd law of thermodynamics

" All substances in their normal crystalline state at the absolute zero temperature would be in the condition of the maximum orderly arrangement."

$S \to 0 \quad T \to 0$

reach very low $(T \to 0\,K)$

So, now, this entropy change is also giving us an extension to a very unique third law of thermodynamics. So, already we have defined the second law of thermodynamics with respect to the entropy where it says that spontaneous process will be that which has an isolated system the entropy change is positive. But it also says that how low I can go with respect to the entropy.

So, if I want to go very low in the entropy, I have to go to the most ordered state of a particular system, and now we know that when we are actually putting up a temperature, there will be a disorder in a system, there will be some randomness in the molecule, and if I want to get rid of all the randomness, all the disorder I have to get rid of this temperature induced randomness.

So, that means I have to go to 0 temperature absolute 0 temperature, 0 Kelvin and that is actually where we come to the factor of the third law of thermodynamics which says all the substances in their normal crystalline state at the absolute zero temperature would be in the condition of the maximum orderly arrangement that means that will be the perfect orderly arrangement, no disorder at all and it can be only achieved at absolute 0 temperature, which actually can be written in this form, if we want to go entropy close to 0, we have to go temperature as close as to 0.

And this is actually important factor because this particular third law of thermodynamics derived from the entropy factor give us an idea how we can reach very low almost close to 0 Kelvin temperature with respect to that, so that is an important factor of third law of thermodynamics. So, in this particular segment, we discussed about the spontaneity of a reaction and we find out the second law of thermodynamics can explain which side of the reaction will be spontaneous.

But for that, we need another important factor the entropy, entropy is nothing but the randomness or the disorder present in a particular molecule. And this entropy factor defines which side the reaction would go. And at the same time, we also find out the entropy can be defined as the change in the heat for a particular physical or chemical change happening at a particular temperature where the temperature is represented as an absolute temperature.

So, with respect to that will conclude this particular segment of the thermodynamics discussion and we look forward to match you again in the next segment of the thermodynamic discussions. Thank you.