Fundamentals of Statistical Thermodynamics

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Lecture: 43

Residual Entropy

Welcome back to the next lecture of Statistical Thermodynamics. Today, we are going to talk about residual entropy. Entropy is a very important thermodynamic quantity because the changes in entropy decide or contribute to the spontaneity of a process. The spontaneity of a process usually we talk in terms of changes in Gibbs free energy and we say that if delta G at constant temperature and pressure is negative, then the process is spontaneous and this delta G is a combination of delta H and a combination of T delta S. Therefore, the negative value of delta H and positive value of delta S, they contribute to the spontaneity of a process. The second component that is T delta S which is basically the change in entropy suggests that entropy is a very important thermodynamic quantity.

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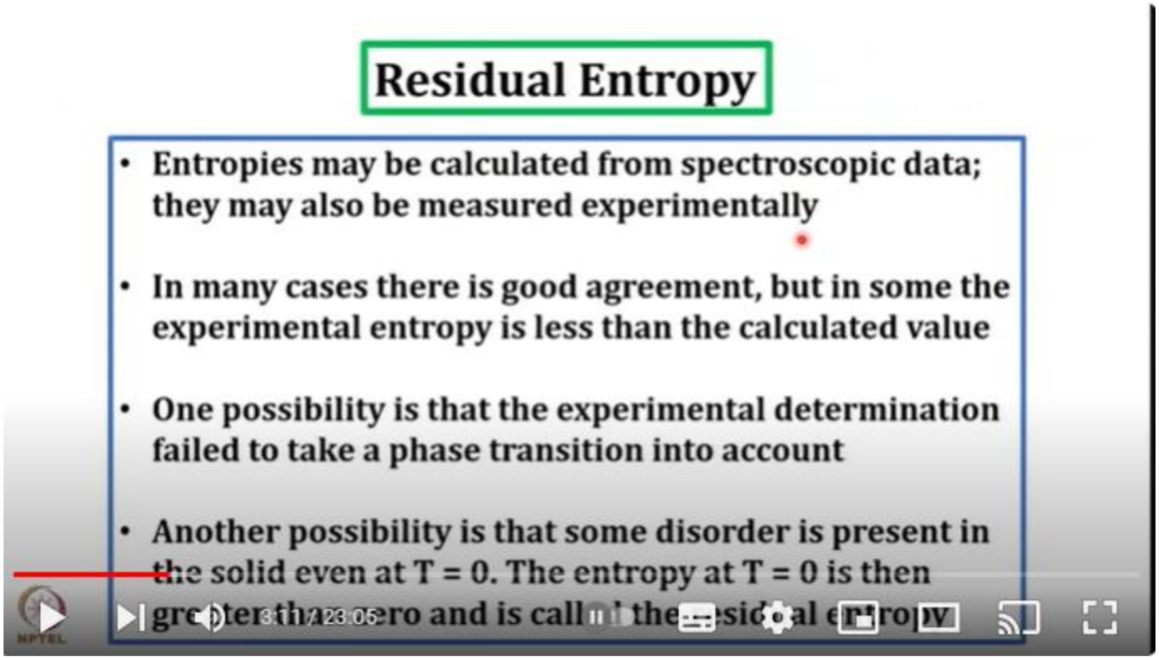

Residual Entropy

- Entropies may be calculated from spectroscopic data; they may also be measured experimentally
- In many cases there is good agreement, but in some the experimental entropy is less than the calculated value
- One possibility is that the experimental determination failed to take a phase transition into account
- Another possibility is that some disorder is present in the solid even at T = 0. The entropy at T = 0 is then greater than zero and is called the residual entropy

So obviously, the question comes that how to determine absolute entropy experimentally. Here we recall the third law of thermodynamics which suggests that entropy of every substance is positive, it may become 0, it may become 0 at absolute 0 and it does become 0 at absolute 0 for perfectly crystalline substances. The catch there is perfectly crystalline substances. What the third law says that the entropy of every substance is positive and it may become 0 at absolute 0, may.

That means it does not say that it is 0 at absolute 0. It says it may become 0 at absolute 0 and it does become 0 at absolute 0 for perfectly crystalline substances. That means if a substance is not perfectly crystalline, the entropy at absolute 0 may not become 0. Now, let us take a look at some of the comments. First comment is entropies may be calculated from spectroscopic data and they may also be measured experimentally.

When we say that entropies may be calculated from spectroscopic data, that means essentially here we are talking about the connection of entropy with partition function because partition functions can be determined from spectroscopic data. The second comment is they may also be measured experimentally. When I say they may be measured experimentally, then what I mean is we know this expression S at a final temperature is equal to S at initial temperature plus integration T i to T_f C_p by T dT. According to this expression, if I set the initial temperature to be 0, that means then I am talking about S (0). If my initial temperature is 0, then S (0), that means then at any general temperature I can write S (T) is equal to S (0) plus integration 0 to T C_p by T dT.

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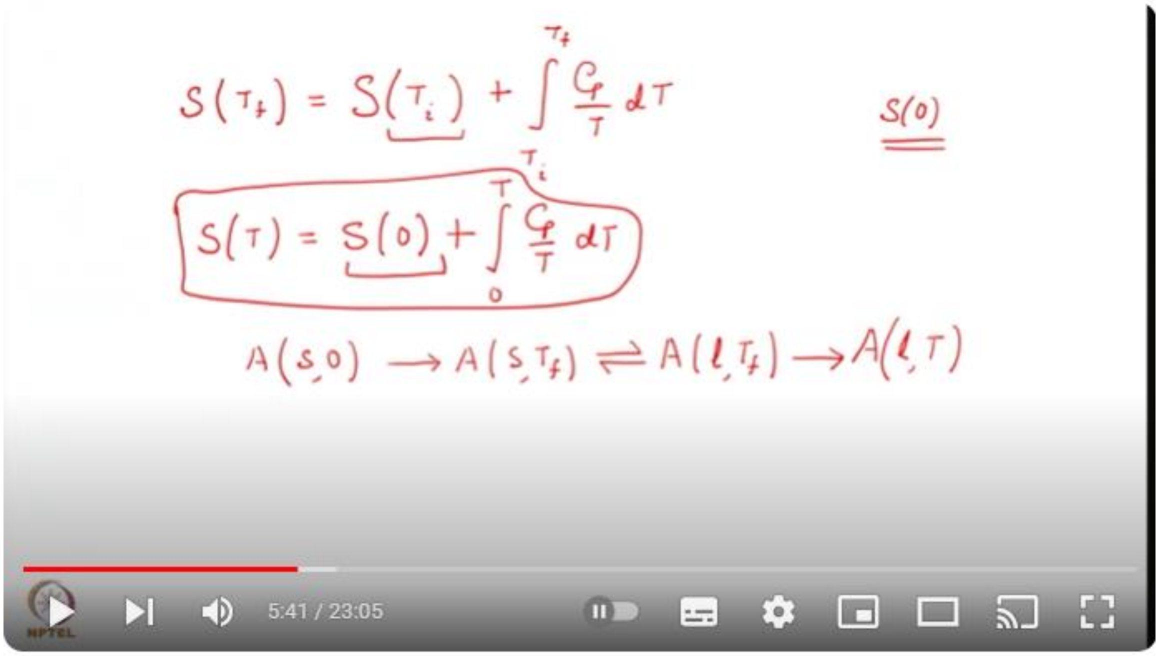

$$S(T_f) = \underbrace{S(T_i)} + \int_{T_i}^{T_f} \frac{C_p}{T}\, dT$$

$$\underline{\underline{S(0)}}$$

$$\boxed{S(T) = \underbrace{S(0)} + \int_{0}^{T} \frac{C_p}{T}\, dT}$$

$$A(s,0) \longrightarrow A(s,T_f) \rightleftharpoons A(l,T_f) \longrightarrow A(l,T)$$

So, from the knowledge of S (0), I can experimentally determine the value of entropy provided I know the heat capacity and heat capacities can be determined calorimetrically. So, this is the experimental determination of entropies. This is something which you have studied in classical thermodynamics. Calorimeters are required to measure heat capacities and once we know the temperature-dependent heat capacity, we can easily get the value of the entropy at any temperature T. This expression that I wrote may not be always true if there is a phase transition.

That means if I have, if I start from the solid form at 0 kelvin, then when I heat it, A will be solid up to its freezing point, then there is an equilibrium. So, A becomes liquid at the freezing point and then I can further heat it A, let's say I can have liquid and any general temperature. The point that I am going to make here is that the comment number 2 says that in many cases there is a good agreement, but in some cases, the experimental value is less than the calculated value. In general, there is a good agreement, but that is not necessary. Sometimes there can be discrepancies also.

That is what the comment is made over here that but in some cases the experimental entropy is lesser than the calculated value. Now, if it is less, then we have to assign a reason for that. What could be the possibility? Now look at the next comment. One possibility is that the experimental determination failed to take a phase transition into account. As I was trying to explain here that suppose if I miss this phase transition, then your experimental value of entropy will be lesser than the calculated value. Why? Let us see how to write it. For this, I will write S(T) is equal to S (0) plus integration 0 to T_f C_p of solid by T dT. I have covered this part. Now there is a phase transition and the phase transition is delta H fusion by the freezing point. This is the entropy of phase transition you have studied in classical thermodynamics and then when you further heat this liquid plus integration T_f to a general temperature T C_p of liquid by T dT.

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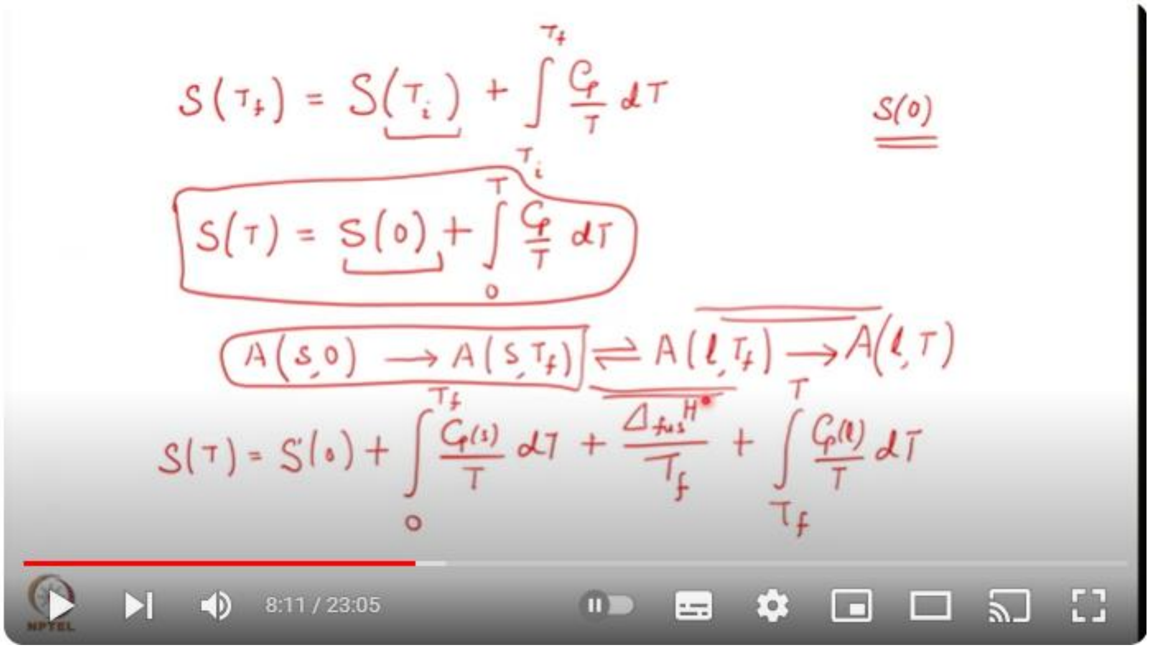

$$S(T_f) = \underbrace{S(T_i)} + \int_{T_i}^{T_f} \frac{C_p}{T}\, dT \qquad \underline{\underline{S(0)}}$$

$$\boxed{S(T) = \underbrace{S(0)} + \int_0^T \frac{C_p}{T}\, dT}$$

$$\boxed{A(s,0) \longrightarrow A(s,T_f)} \rightleftharpoons \overline{A(l,T_f) \longrightarrow A(l,T)}$$

$$S(T) = S(0) + \int_0^{T_f} \frac{C_p(s)}{T}\, dT + \frac{\Delta_{fus}H^\circ}{T_f} + \int_{T_f}^{T} \frac{C_p(l)}{T}\, dT$$

What this discussion suggests is that if by some chance you miss this phase transitions, then your experimental value will turn out to be lesser than the theoretical predicted. Remember that the phase transition does not necessarily have to involve the conversion of solid to liquid, liquid to gas, etcetera. There can be phase transitions within the solid itself. For example, sulfur orthorhombic monoclinic, carbon diamond form and graphite form both are solid forms. So, if there is a phase transition within a solid and if we somehow ignore that then our experimental value will be lesser than the theoretical value.

So, going back to the comments, one possibility is that the experimental determination failed to take a phase transition into account. So, what is another possibility? Another possibility is that some disorder is present in the solid even at T equal to 0. By the third law, I repeat the entropy of all perfectly crystalline substances is 0 at absolute 0, but that is only for perfectly crystalline substances. If the substance is not perfectly crystalline there may be still some disorder present in the solid at T equal to 0. That means, then at absolute 0 temperature the entropy will be greater than 0 and that entropy is called residual entropy.

The entropy which is still present in a system at absolute 0 is called the residual entropy. Hope this is clear. What is the origin and magnitude of residual entropy? Let us consider a crystal which is made up of AB. I will talk about AB solid and how this AB is formed? It is formed from atoms A and B. In a crystal lattice, how these A and B are arranged? Let us take one very simple arrangement of A and B atoms in the crystal lattice.

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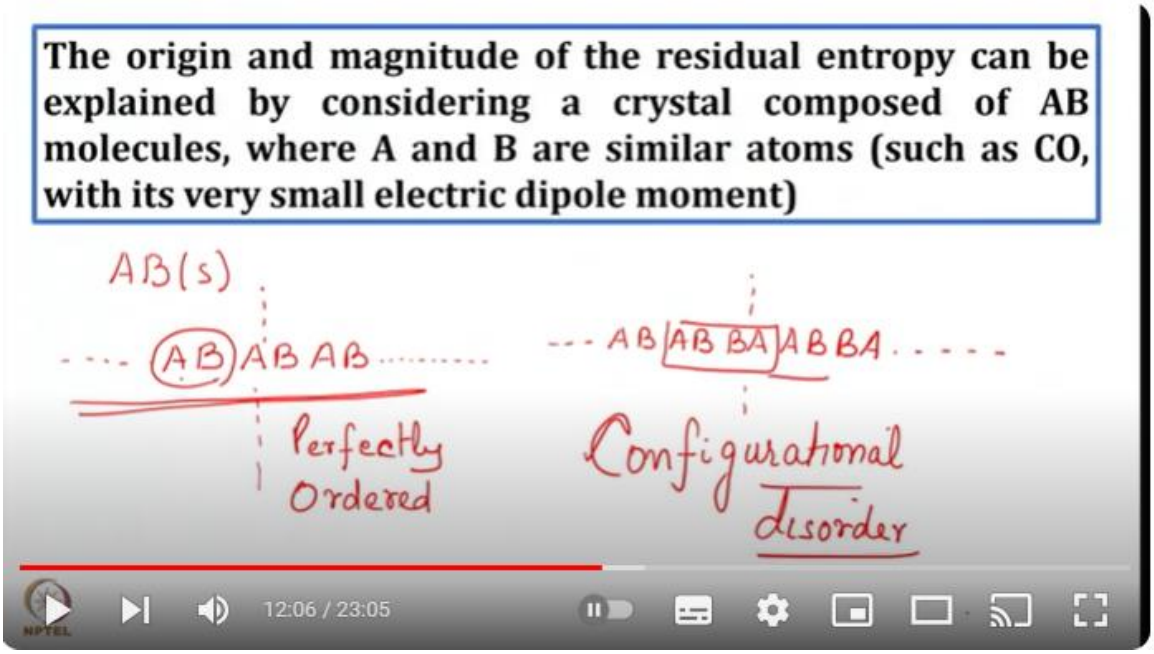

The origin and magnitude of the residual entropy can be explained by considering a crystal composed of AB molecules, where A and B are similar atoms (such as CO, with its very small electric dipole moment)

Let us say this one the compound AB is in the lattice arranged or in the crystal or in the solids arranged like AB, AB, AB, etcetera. It keeps on going in all possible directions. Suppose A and B are very similar atoms and the overall electric dipole moment of AB is negligible. I repeat consider A and B to be very similar atoms such that the dipole moment of AB is negligible. That means in this solid form if the arrangement is like you know AB, AB and somehow it is reverse BA then AB then BA and let us repeat in all directions.

Look at the switch over. Here it is perfectly crystalline substances. This is perfectly ordered. We are talking about the scenario at 0 Kelvin perfectly ordered. Here the arrangement is not perfectly ordered. There is a configurational disorder. Why this configurational disorder arises is that AB has a negligible dipole moment. That means whether in the crystal you have AB, AB, AB, AB, AB kind of arrangement or you have AB, AB, BA, BA, AB, BA kind of arrangement also.

So that is a disorder and this disorder leads to residual entropy. There is still some entropy due to this configurational disorder at absolute 0 that is called the residual entropy. So, I hope the origin and magnitude of residual entropy are clear to you. We will take an example. Let us take the example of carbon monoxide in the solid form at absolute 0.

Carbon and oxygen atoms do not have a very large electronegativity difference. In other words, the dipole moment of carbon monoxide is negligible and in this if you look at the arrangements you have CO and OC, CO, CO, OC, CO, OC it is not perfectly crystalline at absolute 0 because there is some configurational disorder, but this configurational disorder does not change the energy of the crystal. That means, at absolute 0 the minimum energy conformation can have either carbon monoxide arranged like CO or like OC it does not make any difference. Two possible orientations of carbon monoxide which give rise to the same minimum energy in the crystal.

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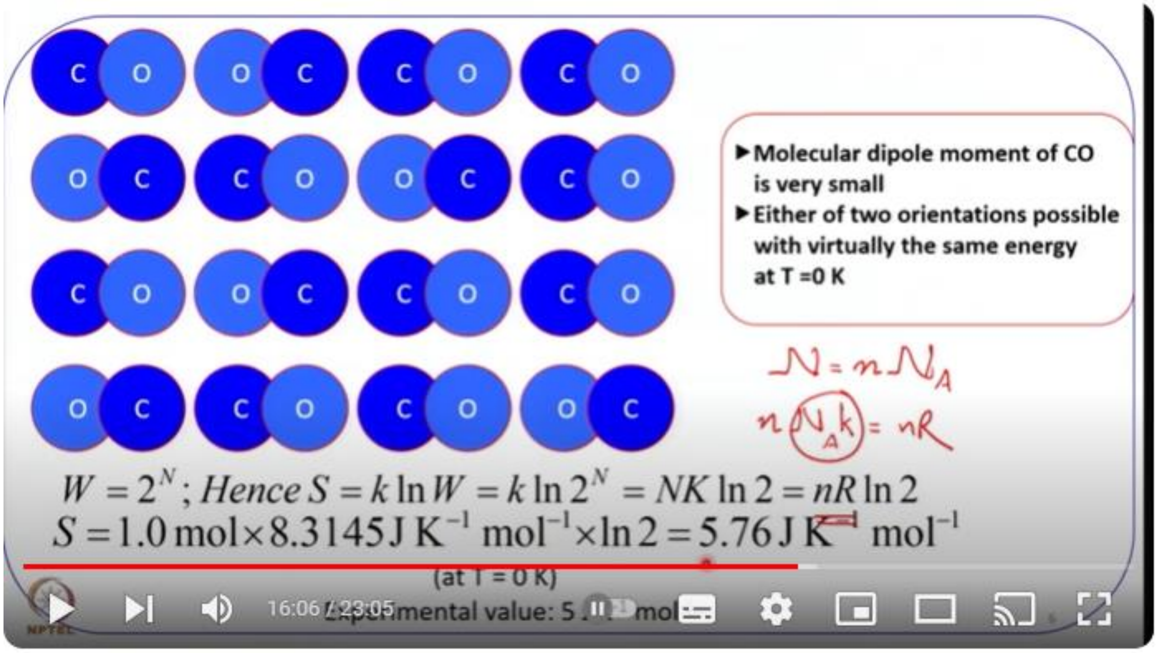

- Molecular dipole moment of CO is very small
- Either of two orientations possible with virtually the same energy at T =0 K

$N = nN_A$

$n\boxed{N_A k} = nR$

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

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

(at T = 0 K)

Experimental value: 5 [illegible] mol

Look at the comments now. The molecular dipole moment of carbon monoxide is very small. We just discussed either of two orientations possible with virtually the same energy at absolute 0. So, therefore, W is equal to 2 for one molecule of carbon monoxide and if there are N molecules then W is equal to 2 raised to the power N. Once you substitute W is equal to 2 raised to the power N which is substituted here it becomes N k log 2 and N k log 2 is nR log 2 because capital N is equal to small n number of moles into Avogadro constant and then N times N_A times k is equal to k times N_A is equal to R nR. So, that is why you have Nr log 2 over here.

Now you substitute the numbers N is equal to 1, R is equal to 8.3145 joules per kelvin per mole and log 2 whatever the value is when you solve it comes out to 5.76 joules per kelvin per mole that is even when the temperature is absolute 0. This is the residual entropy. This is an example of residual entropy where even at absolute 0 there is still some disorder.

The experimental value is 5 joules per kelvin per mole. So, there is a good agreement between the experimental value and the calculated value. I hope with this example the meaning of residual entropy is relatively clear. Now let us take an example of another molecule HCl, hydrogen and chlorine. The electronegativity difference between hydrogen and chlorine is a highly polar molecule.

Dipole moment is high that means in the crystal if I have this HCl, HCl, HCl and then I have HCl, ClH, HCl this arrangement will have a different energy than this arrangement because of a bigger electronegativity difference between the constituent atoms. Therefore, there is only one minimum energy confirmation possible. Only one I repeatedly say only one minimum energy confirmation possible and that is shown over here. If at all HCl transforms or rotates in ClH then that arrangement will give different minimum energy, different energy because the interaction energy will be different between within the adjacent molecules. So, this is perfectly ordered systems.

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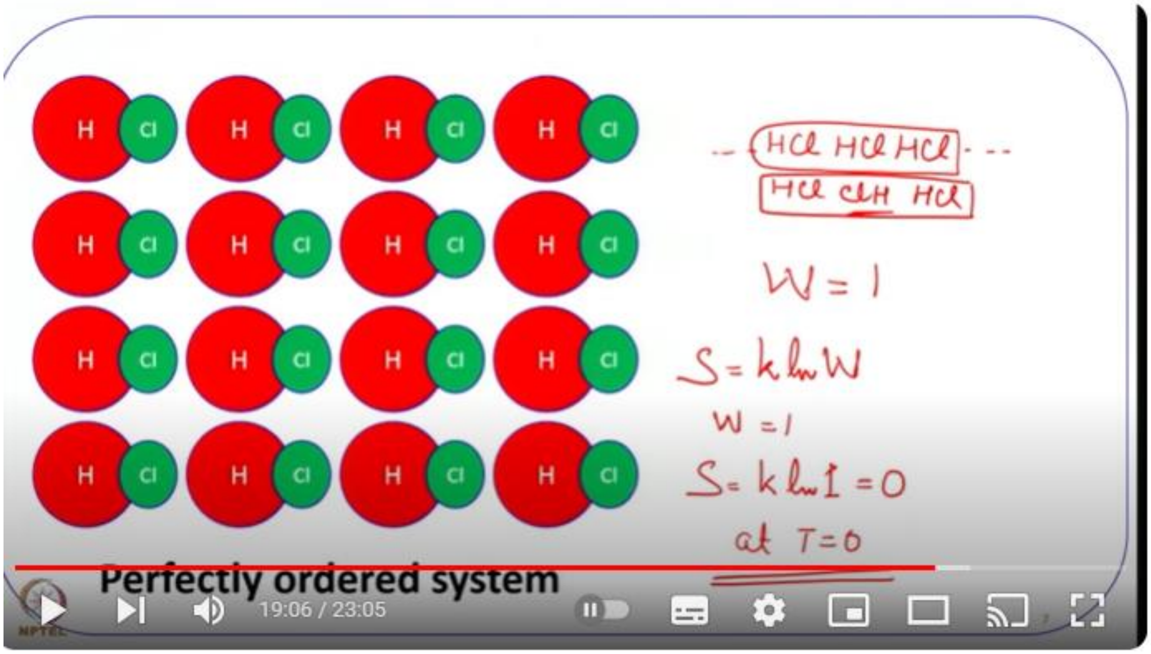

Perfectly ordered system

-- HCl HCl HCl --

HCl ClH HCl

$W = 1$

$S = k \ln W$

$W = 1$

$S = k \ln 1 = 0$

at $T = 0$

What does that mean? When I say perfectly ordered system that means the weight of a configuration is equal to 1. There is only one way you can arrange HCl to get the minimum energy confirmation. Then our usual S is equal to K log W. If W is equal to 1 then S is equal to K log 1 this is equal to 0. What we have is for the perfectly ordered systems there is no residual entropy.

This is the value at absolute 0. Now we come back to our original definition of the third law of thermodynamics. It said that entropy of each substance is positive which may become 0 at absolute 0 and it does become 0 at absolute 0 for perfectly crystalline substances. And here is the example of perfectly crystalline substances. This is the example of perfectly crystalline substances. So, the comments which are there in the background here are the same that I discussed that it is the large electronegativity difference between H and Cl which accounts for this observation for which accounts for this fact. So, at T equal to 0 Kelvin then W is equal to 1. So S is equal to K log 1 which is equal to 0 that means the residual entropy of perfectly crystalline substances is equal to 0. Now if we want to use this formula S is equal to K log W if I want to use this formula then I need to know the weight of a configuration most probable configuration. And when we set the temperature equal to 0 when we move towards 0 that means we are moving towards the alignment of the atoms of the molecule or alignment of the molecules in a sort of ordered manner. This order may or may not be perfect because as we just discussed the case of carbon monoxide and HCl in some cases different orientation may not change the energy and in some cases different orientation changes the energy and therefore, there can be more than one minimum energy confirmations or only one minimum energy confirmation.

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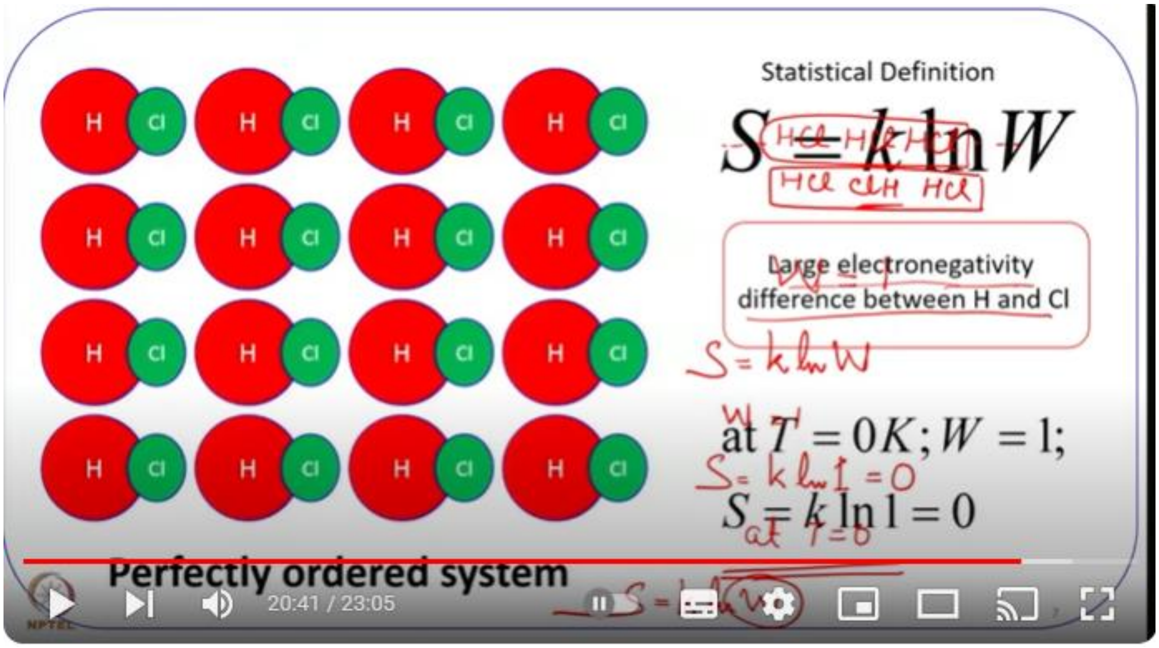

Statistical Definition

$$S = k \ln W$$

Large electronegativity difference between H and Cl

$$S = k \ln W$$

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

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

Perfectly ordered system

If there is only one minimum energy confirmation at absolute 0 then W is equal to 1 then S (0) is equal to 0. To theoretically calculate the value of residual entropy therefore, you need to know how many minimum energy confirmations are possible at absolute 0. We will take some examples and discuss ahead that how this entropy residual entropy depends upon the minimum energy confirmations and how to also calculate the weight of the configuration which is in the most probable form. But the take home lesson from this lecture is the residual entropy is the entropy of a system which is still present at absolute 0 and that entropy can come by virtue of configurational disorder. We will move ahead by taking more examples, but that will be done in the next lecture. Thank you very much. Thank you.