Fundamentals of Statistical Thermodynamics

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Lecture: 44

Residual Entropy (continued)

Welcome back. We have been discussing residual entropy. The entropy which is still present in the system or disorder which is still present in the system when the temperature is absolute 0. We have also discussed that the residual entropy can arise because of the disorder and the disorder arises because of the magnitude of the molecular dipole moment. Basically, you want to understand how many minimum energy confirmations of a system can be present at absolute 0, and then by using S is equal to k log W one can get the value of residual entropy. This formula is valid at all temperatures.

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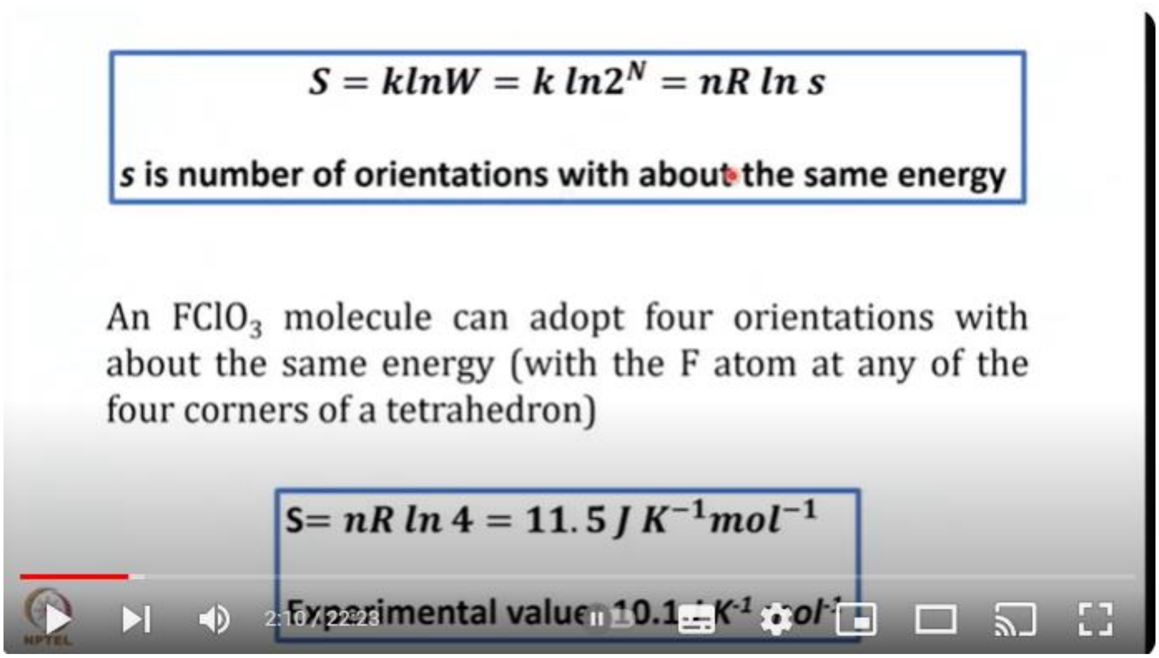

So, therefore, you can use it for S (0) also. So, we discussed that S is equal to k log W, and in the example of carbon monoxide or an example of a molecule like AB in which the dipole moment of AB is very very small. Then there are two possible orientations AB or BA for one molecule and for N molecules it will be W will be equal to 2 raise to the power N. You can bring N in the along with K say and then it becomes nR log S.

I am replacing 2 by S where S is the number of orientations with about the same energy. As a general formula to evaluate the residual entropy you can use S is equal to nR log S where S is the number of orientations with about the same energy. Take an example of $FClO_3$ molecule. This $FClO_3$ molecule can adopt four orientations with about the same energy with the fluorine atom at any of the four corners of a tetrahedron. So, four orientations that mean the value of S that you are going to use here is 4.

So, S is equal to nR log 4 and the molar if you put N equal to 1 the molar residual entropy turns out to be 11.5 joules per K per mole whereas, the experimental value is 10.1 joules per K per mole. There is a fair degree very good degree of agreement between the calculated value and the experimental value. So, I hope it is clear how to theoretically calculate the residual entropy you are going to use the formula nR log S where S is the number of orientations with about the same energy.

With this knowledge let us move ahead. Now, we are interested in understanding the residual entropy of water that means entropy of water at T equal to 0 or absolute 0. The question that we are going to address is that whether this residual entropy will be 0 or it will be non-zero. Non-zero means it has to be positive. For that you will have to go back to the structure of water and structure of water in different phases.

Since, we are interested in ice therefore, we will talk about the structure of ice. What is the structure of ice? It is a regular tetrahedral network of hydrogen bonded structure. As a result of this hydrogen bonding, the volume of the system increases and the density decreases. Therefore, ice is lighter than liquid water. Let us try to understand the arrangement of oxygen and hydrogens around each other in ice.

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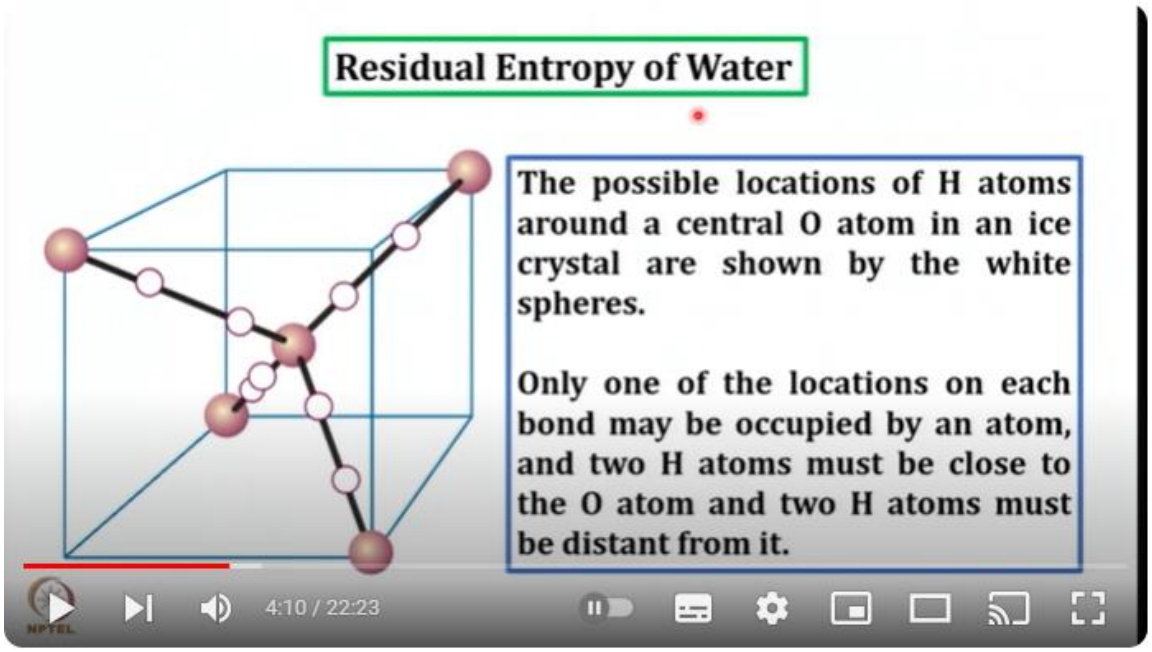

Look at this figure shown over here. These pink spheres treat these as oxygens. One oxygen is surrounded by 1, 2, 3, 4 other oxygen in a tetrahedral, regular tetrahedral manner. In between these two oxygens you have hydrogens. We have shown two possibilities of hydrogens.

What are those two possibilities? One of these is going to be a hydrogen bond and one of these is going to be a covalent bond. Because when you talk about water molecule H, O, H you have lone pair. This is a covalent bond and if some hydrogen bond is found over here that will be a hydrogen bond. So that is what is shown over here. There are two possibilities.

The covalent bond will be closer to this and if it is a hydrogen bond this will be far away from this. Now let us read the comments. This figure shows the possible locations of hydrogen atoms around a central oxygen atom. This is the central oxygen atom. In an ice crystal are shown by a white sphere.

These are hydrogen atoms which are shown in white spheres. Only one of the locations on each bond may be occupied by an atom and two hydrogen atoms must be close to the oxygen atom and two hydrogen atoms must be distant from it. As I said this one oxygen is surrounded by four oxygens and in between oxygens there are hydrogens. There are two types of bondings you will encounter here. One is hydrogen bonding; the other is covalent bonding.

Covalent bond will be shorter, hydrogen bond will be relatively lengthier. That is why it is written two hydrogen bonds must be close to the oxygen atom and two hydrogen bonds must be distant from it. Let us discuss further. Now we will consider n water molecules. Let us talk about there are n water molecules.

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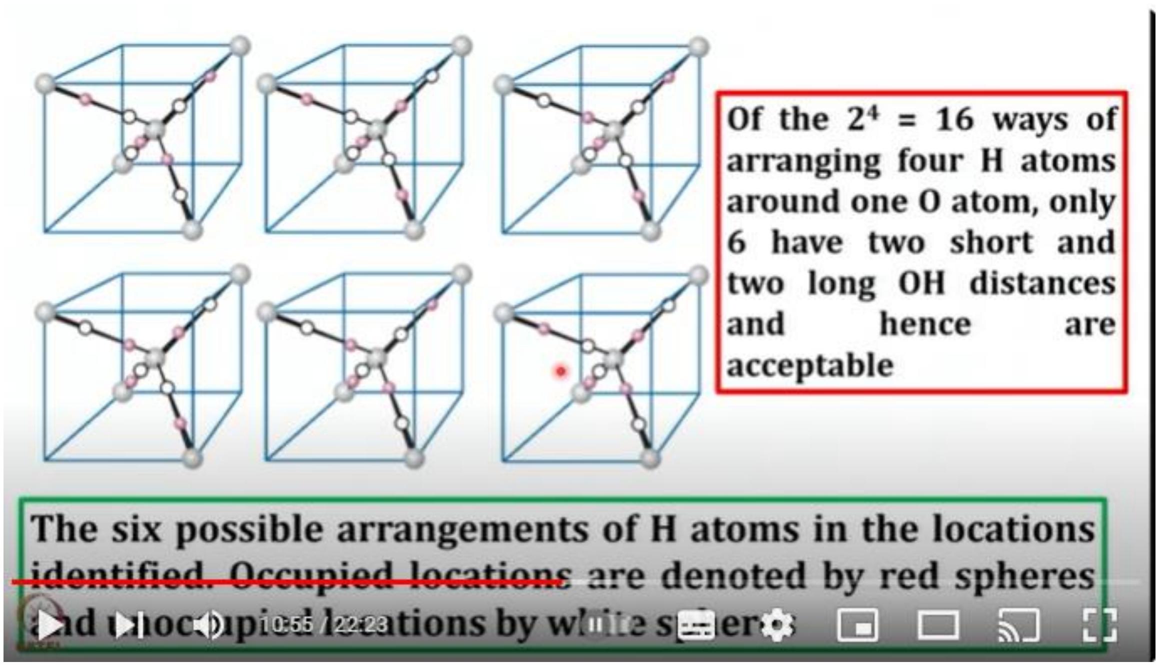

We already discussed that each oxygen atom is surrounded tetrahedrally 1, 2, 3, 4 by four hydrogen atoms, two of which are attached by short sigma bonds and other two by long hydrogen bonds. N water molecules mean there are 2^n hydrogen atoms. These 2^n hydrogen atoms can be in one of the two positions either close or far. I repeat n water molecule means 2^n hydrogen atoms and 2^n hydrogen atoms have two possibilities. One is the close means covalent bond, the other is away that is the hydrogen bond.

So, there are how many possible arrangements? 2 raised to the power 2n depending upon the number of molecules, n is the number of water molecules. There are 2 raised to the power 2n possible arrangements. This is a possibility, but there may be some constraints.

In the past also, we have talked about constraints. You remember when we derived the Boltzmann formula, we had to bring in the total number of molecules constraint, we had to bring the total energy constraint.

And what is the constraint here? The constraint here is that out of all the possible hydrogen atoms placed around, some are forming shorter covalent bond with oxygen and some are forming longer hydrogen bonds with the oxygen. 2 raised to the power 2n possible arrangements, but all these arrangements are not acceptable because all the hydrogen bonds around oxygen cannot be of one type, cannot be either covalent or hydrogen bonding. It has to be mixed, 2 covalent, 2 hydrogen bonding or 2 covalent whatever 2 raised to the power n possible arrangements are there. So, of the 2 raised to the power 4 that is 16 ways of arranging 4 hydrogen atoms on one oxygen 1, 2, 3, 4 and each hydrogen can be either covalently bound or it can be hydrogen bonded. So, therefore, 2 possibilities for 4 hydrogens, there are 16 ways of arranging 4 hydrogen atoms around 1 oxygen atom.

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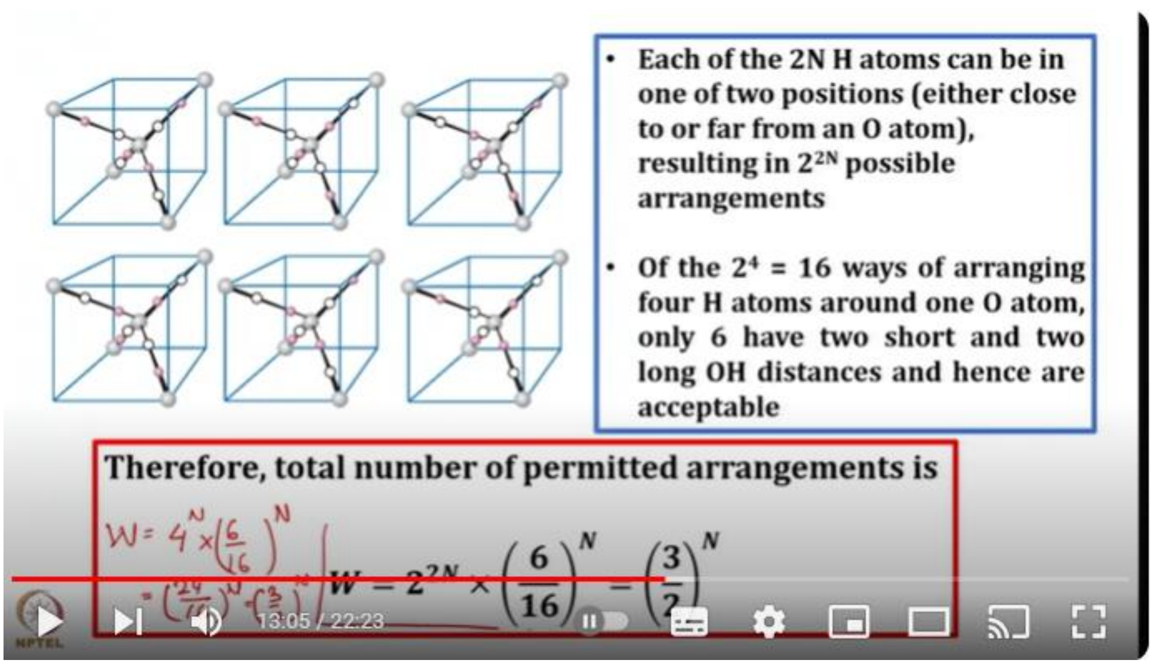

Out of 16, not all the meet arrangement, only 6 have 2 short and 2 long OH distances and hence are acceptable. That means out of the 16 ways of arranging 4 hydrogen atoms here discussed, only 6 are acceptable, all are not acceptable because there are some arrangements in which this restriction of 2 short and 2 long cannot be fulfilled and what are those 6 orientations can be seen in this and here different color coding has been given.

These are the 6, 1, 2, 3, 4, 5, 6, 6 possible arrangements of hydrogen atoms in the locations have been identified in these 6 figures. The occupied locations are denoted by red spheres and unoccupied locations are denoted by white spheres. That occupied means either it will be hydrogen bonded or it will be covalently bonded.

We know the formula S is equal to k log W that is the formula to be unambiguously used, S is equal to klog W. And our focus has to be on W, what will be the expression for W? What did we discuss? That there are 2n possible arrangements, this is the total 2n possible arrangements, all are not acceptable, only 6 out of 16 ways of arranging 4 hydrogen atoms around 1 oxygen atom are acceptable. So therefore, what should be the value of W? 2 raised to the power 2n possible arrangements and then we have to worry about arranging 4 hydrogen atoms around 1 oxygen atom. You can see 4 hydrogen atoms around 1 oxygen atom and out of the total number of arrangements 16 ways of arranging only 6 are possible and there are n water molecules. This is for 1 water molecule, for n water molecule this is n, overall weight of a configuration is the product of 2.

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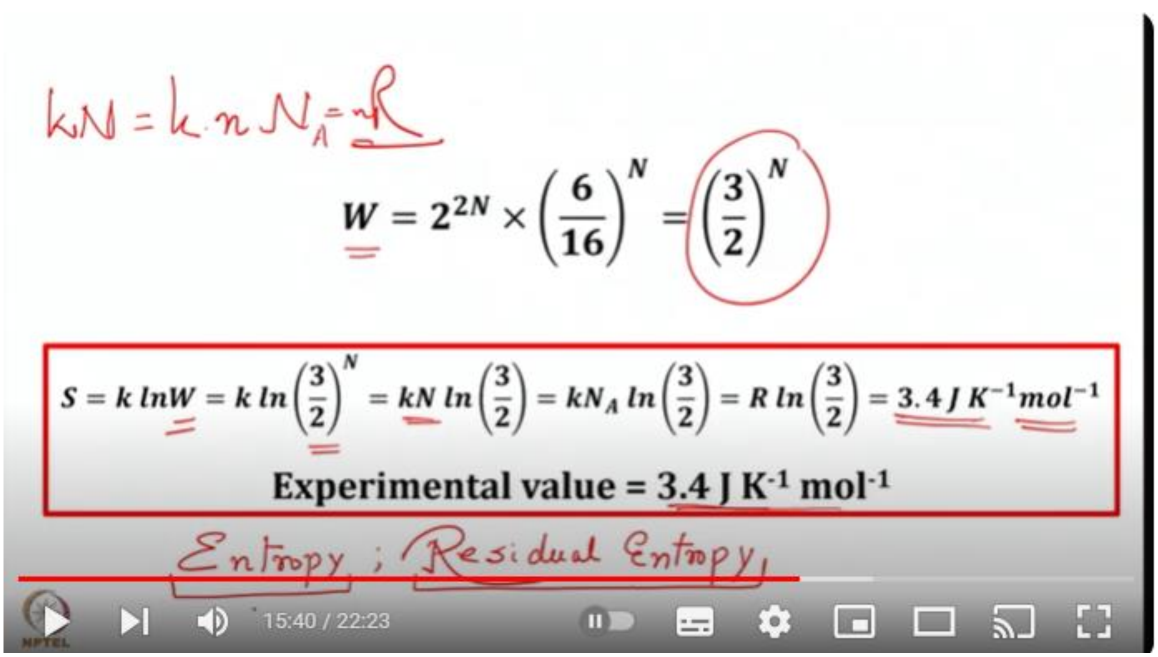

What you have is W here is equal to 2 raised to the power 2n, I will write 4 raised to the power n into 6 by 16 raised to the power n, which is equal to 4 into 6, 24 by 16 raised to the power n, which is equal to 3 by 2 raised to the power n. So therefore, W is equal to 3 by 2 raised to the power n. Once we have an expression for W, the next step is S is equal to k log W. S is equal to k log W, W we know is 3 by 2n, put 3 by 2 raised to the power n, n comes here and k times n is equal to k times small n into n a, K times n is K small n times N_A, which is equal to n R. I can consume this n and make it molar; I can write this molar you see per mole when you substitute n equal to 1.

From this value of statistical weight, you have S is equal to k log W and substitution here gives you a residual entropy of water as 3.4 joules per kelvin per mole. Incidentally the experimental value is also 3.4 joules per kelvin per mole. So here what we see that the entropy of ice at absolute 0 is not 0.

There is some value and whatever is that value we call that as residual entropy, which in the case of water it turns out to be 3.4 joules per kelvin per mole. So now our terminology, so now our terminologies that we have discussed, one is entropy, we have also discussed residual entropy. This entropy can be determined spectroscopically, it can also be determined experimentally. We have now discussed a method where you can calculate the value of residual entropy.

Residual entropy measurements require calorimeters, calculation of residual entropy requires knowledge of various confirmations which can give rise to the same energy at absolute 0. So, in that the molecular dipole moment plays a big role. We also discussed the origin, origin of residual entropy. We discussed that the origin of residual entropy is the prevalence of disorder at absolute 0. The concept of entropy is extremely important.

We are interested in changes in entropy. In chemical thermodynamics you have come across various relations which connect Δ S with other thermodynamic parameters for solid gas liquid. Delta S can also be calculated from the knowledge of absolute molar entropies and we should have a means of either calculating or experimentally determining the value of molar entropy. In the second law of thermodynamics, what the second law says during the course of a spontaneous process the entropy of an isolated system increases. What the third law says that entropy of all the perfectly crystalline substances is 0 at absolute 0.

We do have some residual entropy and we discussed that this residual entropy depends upon the molecular properties. Therefore, we should not blindly say that entropy at absolute 0 is equal to 0. That entropy at absolute 0 is equal to 0 only for perfectly crystalline substances. Therefore, when you use this expression S at T is equal to S (0) plus integration 0 to T C_p by T dt and you might have seen that many textbooks towards the end provide a table which contains the third law entropies. What is that third law entropy? Let me write that also a term here third law entropy.

What is the third law entropy? The entropies which are determined they based upon S (0) equal to 0 are called third law entropies. I repeat entropies which are based upon the values of S (0) equal to 0 are third law entropies. That means you are assuming the system to be perfectly crystalline and we have discussed that for perfectly crystalline substances the entropy is 0 at absolute 0. At absolute 0 there is no thermal motion so things are frozen and in that frozen state if there is a configurational disorder that gives rise to the residual entropy. As the first law is very important, the second law is also very important, the third law is very important understanding of entropy requires a little more effort because the entropies can be connected with the partition function, entropies can be connected with heat capacity and there are many other relations which you can establish for the entropy.

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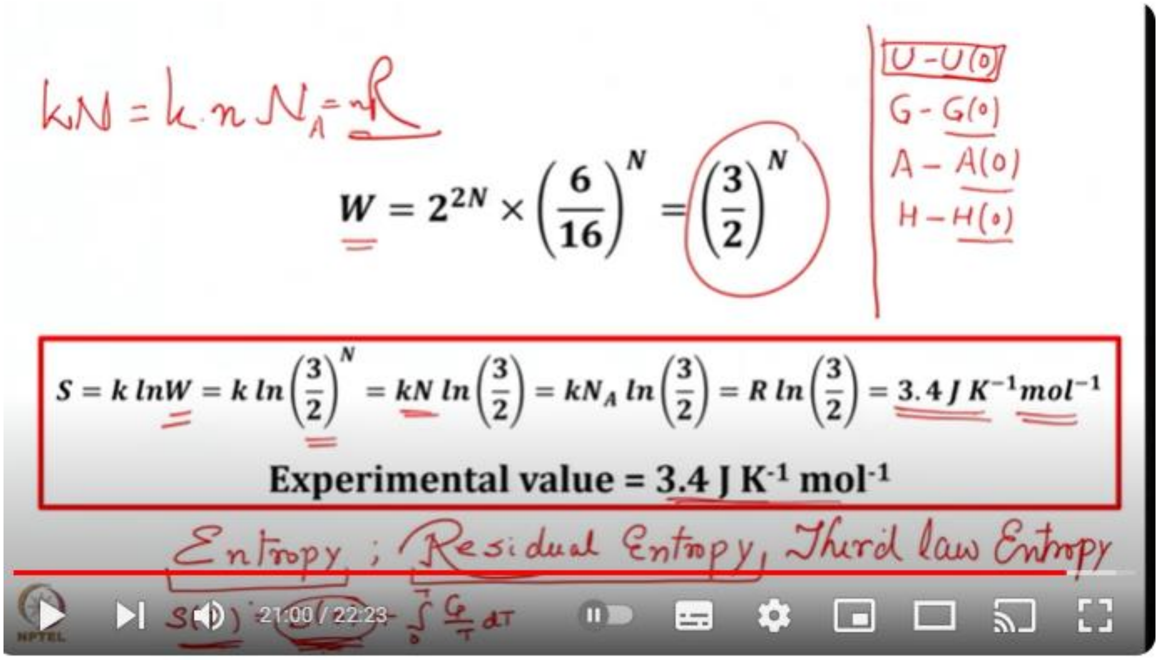

To address the question can we experimentally determine the absolute value of enthalpy or the absolute value of Gibbs free energy and then generally we give an answer that we are not interested in knowing the absolute values. Taking our discussion, a little further we have talked wherever we derived some expressions for example, I talked about internal energy, we talked about U minus U (0), Gibbs energy, we talked about G minus G (0), Helmert's energy we talked about A minus A (0), H minus H (0). Each expression was with reference to some A (0) H (0) G (0) U (0) and similarly here we are saying with reference to S (0). In a sense U minus U (0) is actually a difference because although we have derived some expressions by assuming U (0) is equal to 0, but the oscillators do have some 0-point vibrational energy which has to be accounted for. So, everything is relative to some reference.

Here also the third law entropy is also relative to some reference S (0) and if S (0) is not equal to 0 there is residual entropy that the topic that we have discussed today in details. By now we have connected molecular partition function with all thermodynamic quantities except one which is remaining which connects the changes in Gibbs free energy with the equilibrium constant of a reaction very important discussion. How to connect equilibrium constant with the molecular partition function, but that discussion will require knowledge of expression of Gibbs free energy in terms of molecular partition function and then for the changes in Gibbs free energy because it is ΔG° which is connected to k that we will be discussing soon in the coming up lectures. Thank you very much. 2