Hello students, I am Ms. Shivta Tushar Mhamal from St. Xavier's College, Mapusa- Goa.

In today's session we are going to deal with the paper CHC 102 and the title of the paper is physical chemistry and organic chemistry. In this paper we are going to study Unit 1 and the name of the unit is chemical energetics.

I'm going to deal with the module number 8 and the name of the module is statement of third law of thermodynamics and calculation of absolute entropy of substances.

In this chapter we are going to study the various statements of the third law of thermodynamics.

Also, we are going to study the application of this third law of thermodynamics in calculating the absolute entropies of a substance.

At the end of the module, students will be able to understand an explain the third law of thermodynamics student will also be able to understand the importance of third law of thermodynamics in calculating the absolute entropies of the substances.

So what is third law of thermodynamics?

Third law thermodynamics deals with perfect crystalline solids. So in case of a perfect crystalline solid at absolute zero that is 0 Kelvin. What happens is the entropy of such crystalline solid is 0.

So when you have a perfect crystalline solid, a perfect crystalline solid will be a solid without any defect. So if we measure the entropy of a perfect crystalline solid at 0 Kelvin, it would mean that the entropy of the perfect crystalline solid is 0.

If the entropy of the solid is not equal to 0 at absolute temperature, it would mean that the solid is not a perfect crystalline solid. It has some defects.

So third law thermodynamics deals with the perfect crystalline solids whose entropy is supposed to be 0 at Absolute Zero. These are various statements for third law of thermodynamics.

The first statement given by Planck's says that at the absolute zero temperature entropy of every substance may become zero, and it does become zero in case of perfectly crystalline solid.
There is another form of third law of thermodynamics given by Lewis and Randall.

It says that every substance has a finite positive entropy, but at absolute zero of temperature, the entropy may become zero and it does become zero in case of a perfectly crystalline solid.

Let us understand the application of third law of thermodynamics.

We know the third law of thermodynamics tells us that at absolute zero temperature, the entropy of a perfectly crystalline solid is equal to 0. So. We're going to apply this law.

We know that internal energy is a state function and we cannot find out the absolute value of internal energy. But we can always find out the change in internal energy. So also enthalpy is a state function. In case of enthalpy also we cannot find out the absolute value of entropy but we can find out the change in enthalpy.

But we have this function that is entropy. It's a state function, but we can find out the absolute value of the state function. That is entropy with the help of third law of thermodynamics.

So let us understand how we determine the absolute entropy of the substances using the third law of thermodynamics.

So if you want to find out the absolute entropy of a substance, say at a temperature T Kelvin, We have to compare the entropy of this substance with its entropy at 0 Kelvin.

So we know at 0 Kelvin the entropy of a perfect crystalline substance is supposed to be 0,

so when we find out the absolute entropy of the substance at any temperature T by comparing it with the entropy of the substance at absolute zero, we can write the change in entropy as.

Entropy of the substance at temperature,T kelvin, minus the entropy of the system at absolute zero.

We know at absolute zero according to the third law of thermodynamic entropy of these substances 0.

So we get Delta S is equal to entropy of the substance at temperature T kelvin minus zero.
So hence we have Delta is is equal to entropy of the substance at any temperature,
so. If you want to find out the entropy of a substance at any temperature, we can find it out by comparing its entropy with the entropy of the substance at absolute temperature.
There is a derivation to derive. So let us begin in detail how we determine the absolute entropies of the substance.

We know from the definition of heat capacity, Cp is equal to dH by dT at constant pressure,
so this can be written as Cp is equal to dq by dT at constant temperature.

From the definition of entropy, we know the change in entropy, dS is equal to dq by T.

Therefore, in place of dq here we substitute TdS.

So we get Cp is equal toTdS by dT at constant P.
Rearranging this equation we get there for the change in entropy dS is equal to Cp dT by T.

This is equation #1.

Integrating equation number one from the temperature absolute zero to any temperature T we get integral from zero to T dS is equal to integral from zero to T Cp dT by T.

Integral of the Left hand term we get S T -- S zero. Which is equal to integral from zero to T Cp dT by T. This is equation #2.

Now from the third law of thermodynamics we know that entropy of a perfectly crystalline solid at absolute zero is equal to 0.

So applying this third law of thermodynamics to equation #2 we get ST is equal to integral from zero to T Cp dT by T ST is the absolute temperature of the substance under study at temperature T.

In this equation in the above equation, we know that dT by T is equal to dlnT

Or if you convert this natural log to the base ten, we get dT by T is equal to 2.303 d log to the base 10 T.

So now equation becomes.The absolute entropy ST is equal to integral from zero to T Cp dT, which is equal to integral from zero to T Cp dlnT, which is equal to 2.303 integral from zero to T Cp d log to the base 10 T.

Now the entropy of the substance at any temperature T can be calculated by finding out the heat capacities and by calculating heat capacities at a number of temperatures between zero to T Kelvin.

We have this equation three now.

We can plot a graph of Cp against temperature in Kelvin, or we can plot a graph of Cp against log T we will get. Plots like this, as shown in the figure.

The integral in this equation, equation #3 can be calculated or can be evaluated by plotting the graph of Cp against log T or maybe Cp against temperature in Kelvin, the area under the curve gives us the value of this integral. So, if we know what is the area under the curve,we get the value of the integral and from there from the value of the integral we get the absolute entropy of this substance at any temperature T,
but then.
It is very difficult,
but then heat capacities cannot be measured with accuracy.

Because we cannot find out the heat capacities below 15

below temperature of 15 Kelvin.
So the curve is extrapolated with the help of the equation called the Debye T-cubed law. It says that Cp is equal to a T cube ,where a is a constant and it is determined from the value of Cp at some lower temperature.

So say for example.

The one is the temperature above which heat capacity can be measured.

So this corresponds to the temperature T at which the entropy of the substance is to be determined.

So from the figure, If you want to determine point so this integral can now be split as ST is equal to integral from zero to T 1C,TYT plus integral from T1 to T3.

So this integral can be split as St is equal to integral from zero to T1

CPD TYT plus integral from T1 to TCPDTYT.

Remember here T one is the temperature. Upto which heat capacities can be measured.

So to calculate this first integral we make use of the Debye T-cubed law.

This is at CPS equal to 80 Q, so using that for this.

For the first part of the integral we get integral from zero to T 180,

^3 et by T is equal to integral

from zero to T 180 squared.

This T&ST cancels out a T squared DT.

So either constant an after integrating

this T squared DT we get one by.

We get. One by three A into T1Q.

Now 81 Q.

Since we know CP is equal to 80 Q,

we read the situation as one by TCP ACK T1.

For the second integral in that inequation, in the second integral can be evaluated by finding out the area under the curve BC, and Hence the entropy of the solid between temperature 0 Kelvin to
T Kelvin is given by equation.

#7ST is equal to 1 by T.

St is equal to 1 by three CP at temperature

T1 plus integral from T1 to TCPDLNT.

so the entropy of transition, that is delta HT upon TT has to be added in this equation.
So we get this equation with the help of this equation, we can calculate the absolute entropy of solid.
In case of liquids and gases, to find out the absolute entropy of liquids and gases, the total absolute entropy of the substance at a given temperature will be the total of all entropy changes with the substance undergoes.

In order to reach that particular state starting from the crystalline solid at zero degrees. At Absolute 0, have to be considered.
So if you want to find out the absolute entropy of a substance at 25 degrees C.

We have to compare it with the absolute entropy at 0 Kelvin and then we have to consider all the processes which the substance undergoes to get converted from the solid at absolute zero to the solid or two. To the substance at 25 degrees C.

So this is how you have to calculate the absolute entropy of the liquid.

We have to consider the entropy of heating or the crystalline solid from zero to T to the Melting point of the solid.

Then we also have to consider the phase change. We have to also add the entropy of heating from the boiling from the melting point to the boiling point.

We have to consider the entropy of vaporization that takes place.

We also have to consider the entropy of heating from the melting point from the boiling .225 degrees C.
so this expression. Helps us to calculate the entropy of our system at temperature T.

Thank you.