Chemical and Biological Thermodynamics: Principles to Applications

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Lecture – 08

Entropy and Second Law: Basics

So we have discussed the first and second law of thermodynamics. And while discussing the second law of thermodynamics, we talked about entropy, a very important concept. Because the driving force of a reaction is largely dependent upon the entropy. And we demonstrated last time that the direction of spontaneous process is in the direction of generation of more disorder. Today in this lecture we will extend the discussion on entropy. It is very important to understand entropy, entropy change in the system entropy change in the surroundings, because it is directly connected to the spontaneity to the feasibility of a process.

So, let us first discuss some basics, and then we will move on to some applications including some numerical problems.

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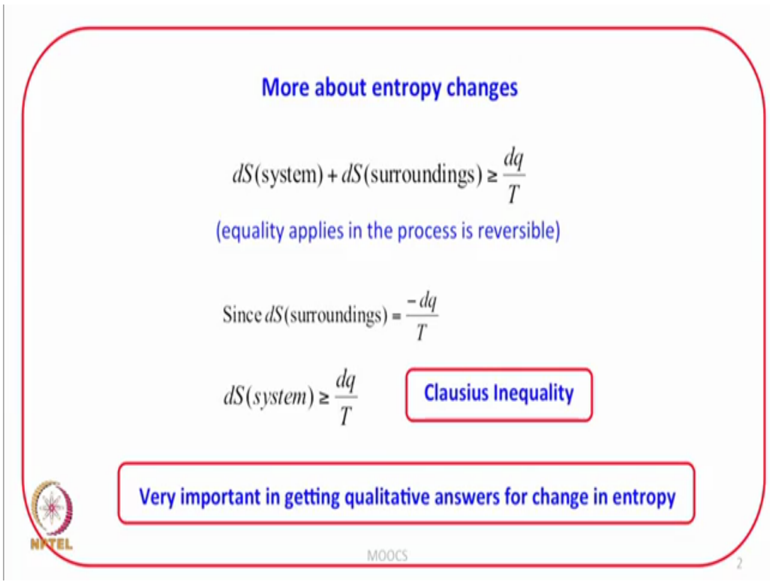

More about entropy changes

$$dS(\text{system}) + dS(\text{surroundings}) \ge \frac{dq}{T}$$

(equality applies in the process is reversible)

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

$$dS(system) \ge \frac{dq}{T}$$

Clausius Inequality

Very important in getting qualitative answers for change in entropy

The second law of thermodynamics says that the entropy of an isolated system increases during the course of a spontaneous process. That means, if we want to make a general statement that what should be the sign of entropy change in the system, plus entropy change in the surroundings so, if I combine these two.

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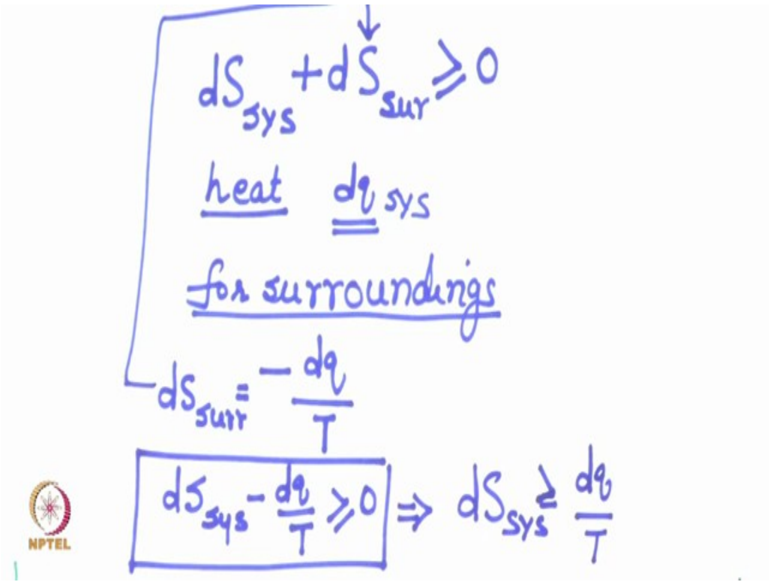

$dS_{sys} + dS_{sur} \geq 0$

heat dq_{sys}

for surroundings

$dS_{surr} = -\frac{dq}{T}$

$\boxed{dS_{sys} - \frac{dq}{T} \geq 0} \Rightarrow dS_{sys} \geq \frac{dq}{T}$

I will write these as entropy change in the system plus entropy change in the surroundings, I will write greater than or equal to 0. Why I am writing greater than or equal to 0? Because if the process is irreversible, is spontaneous then dS system plus dS surrounding has to be positive, by the second law of thermodynamics. And equality applies to reversibility, so whenever the process is reversible, we will use equal to sign and when the process is spontaneous or irreversible we will use greater than sign.

Now let us say that the heat change is dq for the system this is the infinitesimally small amount of heat, which is either given out or taken in by the system. And hence if there is a thermal equilibrium between system and surrounding, let us say at temperature T. Then the heat change for the surroundings, for surroundings the heat change is going to be minus dq because if this is for the system then the surrounding will be with a negative sign. And let us recall the discussion of the previous lecture, the heat change in the surrounding divided by the temperature is equal to the entropy change in the surroundings; that means, this is entropy change in the surrounding.

Now, let us take a look at the slide. As I mentioned that in general we can write dS system plus dS surrounding is greater than or equal to dq by T. And this equation comes by substituting dS surrounding in to this equation, according to this dS system minus dq by T is greater than or equal to 0. From this general equation that is by the second law of thermodynamics dS system plus dS surrounding is greater than or equal to 0, I am going towards deriving another equation. And now if I rearrange this equation then I get the equation dS system is greater than or equal to dq by T. This leads to the equation dS system is equal to greater than or equal to dq by T, that is what is mentioned on the slide and this is called clausius inequality. That is the entropy change in the system in general will be equal to or greater than dq by T. And here again equality applies to reversibility and greater than sign applies to irreversible or spontaneous process.

This clausius inequality is very important, because by using clausius inequality we can get qualitative answers to several questions. Qualitative in the sense that if I know the sign and magnitude of dq I can talk about how much will be or in which direction will be the entropy change of the system. So, that is why the conclusion written on the slide is that this clausius inequality is very important in getting qualitative answers for change in entropy.

So, what kind of qualitative answers we can expect from clausius inequality? Clausius inequality is dS if I am not writing surroundings that means.

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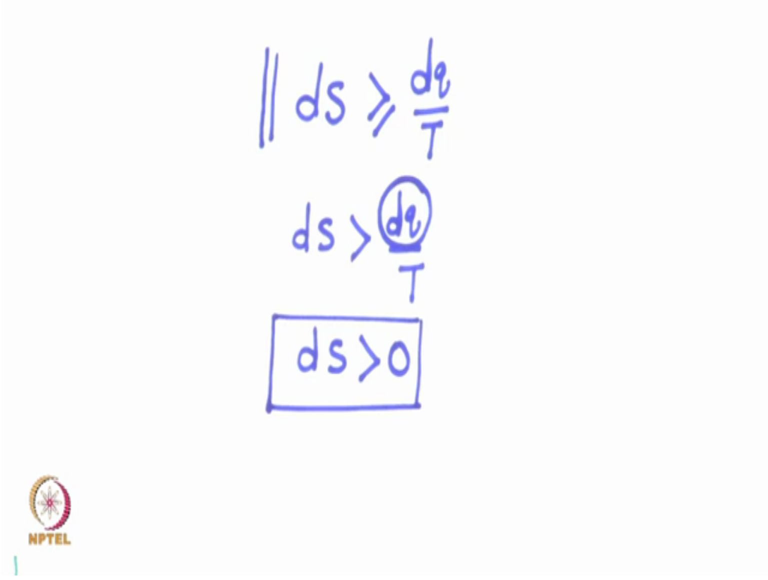

$$\| \; ds \geq \frac{dq}{T}$$

$$ds > \frac{dq}{T}$$

$$\boxed{ds > 0}$$

We should understand dS means entropy change in the system is greater than or equal to dq by T. The question is comment on the entropy changes.

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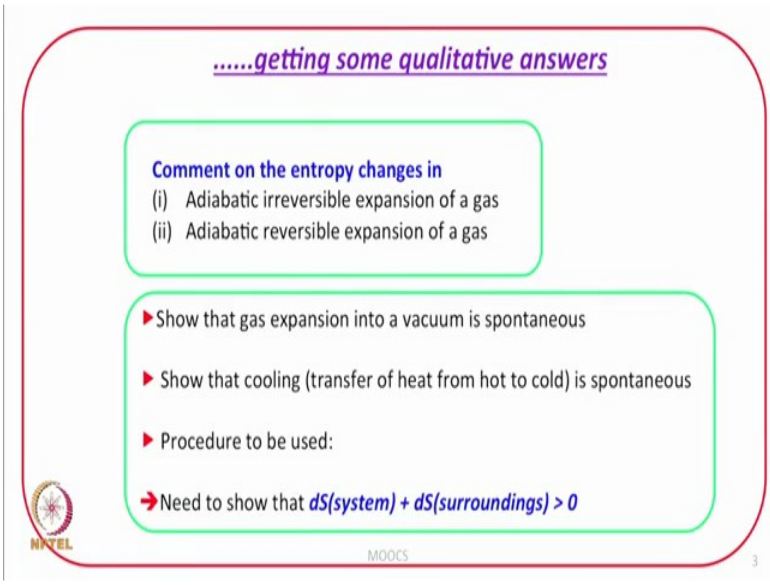

......getting some qualitative answers

Comment on the entropy changes in
(i) Adiabatic irreversible expansion of a gas
(ii) Adiabatic reversible expansion of a gas

- Show that gas expansion into a vacuum is spontaneous
- Show that cooling (transfer of heat from hot to cold) is spontaneous
- Procedure to be used:

→Need to show that ***dS(system) + dS(surroundings) > 0***

In number one, adiabatic irreversible expansion of a gas. Adiabatic irreversible means, I will use greater than sign. So, then I will write dS is greater than dq by T. Because the process is reversible I am using greater than sign. And since the process is also adiabatic process means dq has to be 0 no exchange of heat between system and surroundings. So, the answer is dS is greater than 0, because dq is 0. You know this is a common mistake which many times I have seen while discussing with several students, that whenever we say adiabatic process generally one tends to consider that since there is no exchange of heat between system and surrounding therefore, in each case the entropy change should be 0. No, call clausius inequality this 1 clausius inequality gives qualitative answers. You see here the process is irreversible.

So therefore, I use greater than sign and since the process is adiabatic I put dq equal to 0. So, dS is greater than 0, and this is the driving force for the process. This is a different question that how to calculate this change in entropy, we will deal with it with it separately. Now let us take a look at the second comment, adiabatic reversible expansion of a gas. Now let us consider the reversible case.

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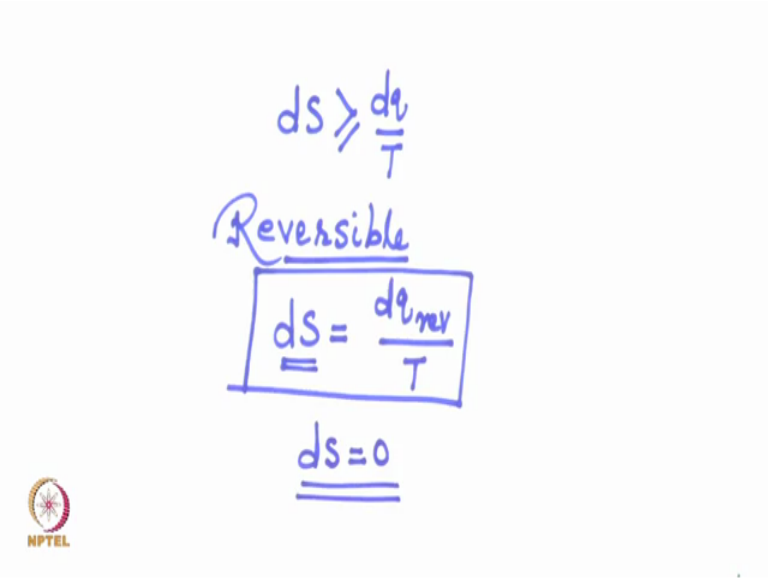

$$dS \geq \frac{dq}{T}$$

Reversible

$$\boxed{\underline{dS} = \frac{dq_{rev}}{T}}$$

$$\underline{\underline{dS = 0}}$$

Once again I will start with the clausius inequality dS is greater than or equal to dq by T, and if the process is reversible; that means, I will use equality sign. So, dS is equal to dq reversible by T. See this is the same equation that we derived last time, that in order to calculate the change in entropy we must connect the path by a irreversible manner. And since the process is adiabatic there is no heat exchange between system and surrounding.

So, I have to substitute dq equal to zero; that means, if the process is reversible there will be no change in the entropy. Irreversible process the entropy change was positive reversible process, you see the entropy change in the system is equal to 0 under adiabatic conditions. So, that is what I meant by saying that the clausius inequality quickly gives us qualitative answers to several questions. Let us move ahead and prove again by clausius inequality that the gas expansion into vacuum is spontaneous. How do we approach that?

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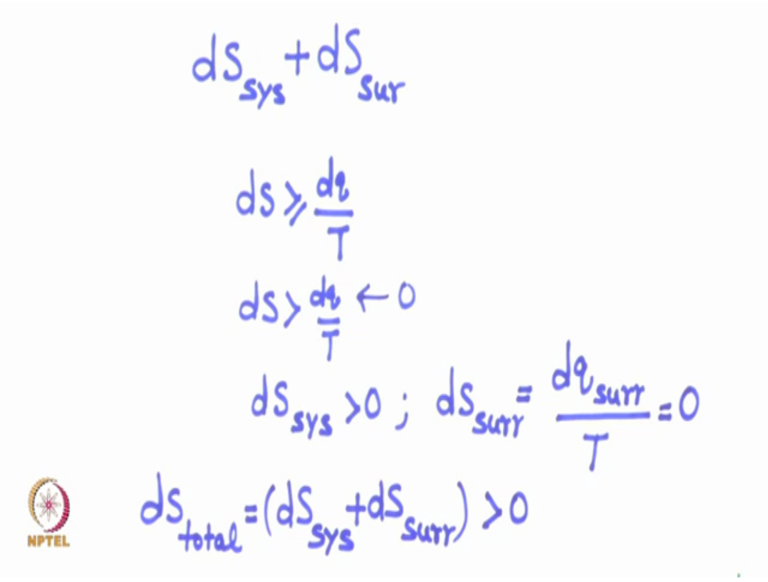

$$dS_{Sys} + dS_{Sur}$$

$$dS \geqslant \frac{dq}{T}$$

$$dS > \frac{dq}{T} \leftarrow 0$$

$$dS_{sys} > 0 \; ; \; dS_{surr} = \frac{dq_{surr}}{T} = 0$$

$$dS_{total} = (dS_{sys} + dS_{surr}) > 0$$

Spontaneity In terms of entropy will be commented upon based on the entropy change in the system, plus entropy change in the surrounding. If we want to comment on the spontaneity of a process in terms of second law of thermodynamics, we must calculate the entropy change in the system and we must calculate the entropy change in the surrounding. And if that turns out to be positive then the process is spontaneous.

So, here the question is to show that gas expansion into vacuum is spontaneous. The first thing is we need to calculate the entropy change in the system. So, let me go back to the clausius inequality dS is greater than dq by T. Expansion in to vacuum means, expansion against p external equal to 0 is a spontaneous is an irreversible process. So, I will use dS is greater than dq by T, and if you remember we also demonstrated last time that when a gas expands in vacuum it is simultaneously both isothermal as well as adiabatic. I repeat when a gas expands in vacuum it is simultaneously both isothermal as well as adiabatic.

Now, if it is adiabatic I will immediately put dq equal to 0 so; that means, dS now let me write system is greater than 0. At the same time dS surrounding which is always defined as dq surrounding by T the actual amount of heat transferred to the surroundings. And since there is no exchange of heat between system and surroundings in adiabatic process this has to be equal to 0. So, dS total will be equal to dS system plus dS surrounding this is greater than 0 this is zero; that means, overall this is greater than 0, and by the second law of thermodynamics if the entropy change in the system plus entropy change in the surrounding turns out to be positive, then the process will be spontaneous in that direction.

So, hence we prove that the gas expansion into vacuum is a spontaneous process. The next question is show that cooling which is transfer of heat from hot to cold is spontaneous. So, here also we need to show that the entropy change in the system plus entropy change in the surrounding is positive.

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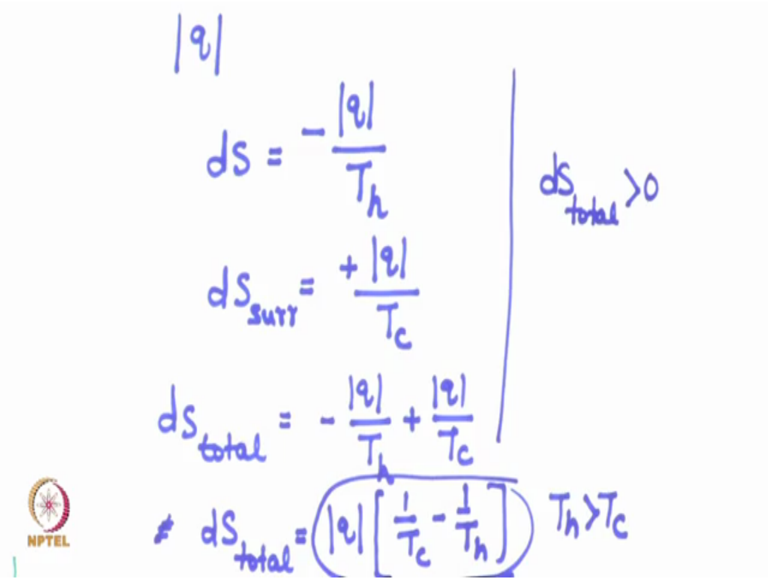

$|q|$

$$dS = -\frac{|q|}{T_h}$$

$$dS_{surr} = +\frac{|q|}{T_c}$$

$$dS_{total} = -\frac{|q|}{T_h} + \frac{|q|}{T_c}$$

$$\therefore dS_{total} = \boxed{|q|\left[\frac{1}{T_c} - \frac{1}{T_h}\right]} \quad T_h > T_c$$

$$dS_{total} > 0$$

So, let me consider that the hot body is the system and cold body is the surroundings. And the amount of heat transferred is let me take the magnitude is q. And when there is a transfer of heat from a hot body it is losing heat, right. So therefore, entropy change will be equal to it is losing minus this much amount of heat divided by T h, T H is the temperature of the hot body. And if I consider the cold you know wherever the heat is going to that as the surrounding then it will be plus because heat is being received there divided by T c, T c is the temperature of the cold body.

So, overall now if I say dS total this plus this will be equal to minus q by T H plus q by T c or what we get is dS total is equal to let us take q out an inside we have one over T c minus one over T H and; obviously, from here you see since T H is greater than T c then; that means, this whole quantity is greater than 0. So, we show here that dS total is greater than 0 because T H is greater than T c. And again by the arguments of the second law of thermodynamics here we again demonstrate that the cooling transfer of heat from a hot body to a cold body spontaneous. So, once again emphasizing on how to prove that a given process is spontaneous in terms of second law of thermodynamics, we need to show that entropy change in the system plus entropy change in the surrounding is greater than 0.

We will need to calculate the entropy change in the system and we will need to calculate entropy change in the surroundings add up the both, if it turns out to be positive then the process is spontaneous in that direction. Now let us look at some specialized cases, isothermal expansion of perfect gas.

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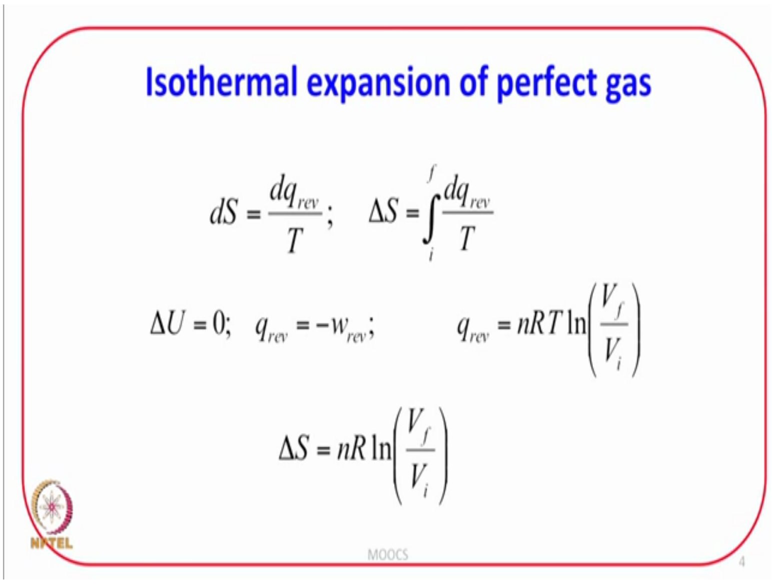

Isothermal expansion of perfect gas

$$dS = \frac{dq_{rev}}{T}; \quad \Delta S = \int_i^f \frac{dq_{rev}}{T}$$

$$\Delta U = 0; \quad q_{rev} = -w_{rev}; \qquad q_{rev} = nRT\ln\left(\frac{V_f}{V_i}\right)$$

$$\Delta S = nR\ln\left(\frac{V_f}{V_i}\right)$$

We want to derive an equation to calculate entropy change when there is an isothermal pressure volume change for a perfect gas.

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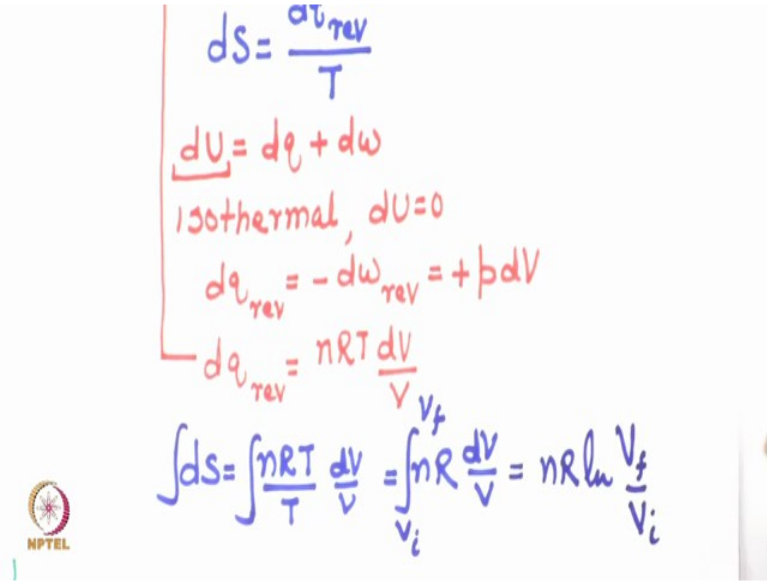

$$dS = \frac{dq_{rev}}{T}$$

$$\underbrace{dU}= dq + dw$$

isothermal, $dU=0$

$$dq_{rev} = -dw_{rev} = +pdV$$

$$dq_{rev} = nRT\frac{dV}{V}$$

$$\int dS = \int \frac{nRT}{T}\frac{dV}{V} = \int_{V_i}^{V_f} nR\frac{dV}{V} = nR\ln\frac{V_f}{V_i}$$

So, what we will do is we will start with the definition of change in entropy dS is equal to dq, remember that we always have to put subscript reversible divided by the temperature. This is the general expression.

Now let me use the first law d u is equal to dq plus d w. And since we are dealing with isothermal expansion, isothermal case the internal energy does not change. Isothermal means d u is equal to 0. So therefore, what I have is dq according to this equation, if I put reversible sign is equal to minus dW, let me again use reversible and dW is minus pdV. So, it becomes plus pdV. In other words dq reversible is equal to here p use the ideal gas equation p V is equal to nRT. So, p is equal to nRT dV by V, this is what we get. And this I will now substitute over here. And let us see what do we get. What we get is dS is equal to nRT by T dV by V which is equal to nRT V by V. And now we are ready to calculate the entropy changes. Since dS is equal to dq reversible by T, here we will see and for a finite change delta S will be integration of dq reversible by T. And as we just showed that q reversible is equal to nRT. And what we show here is now I integrate here and I integrate from V I to V f. So, what we get is the equation or I can write here is equal to nR log V final over V initial.

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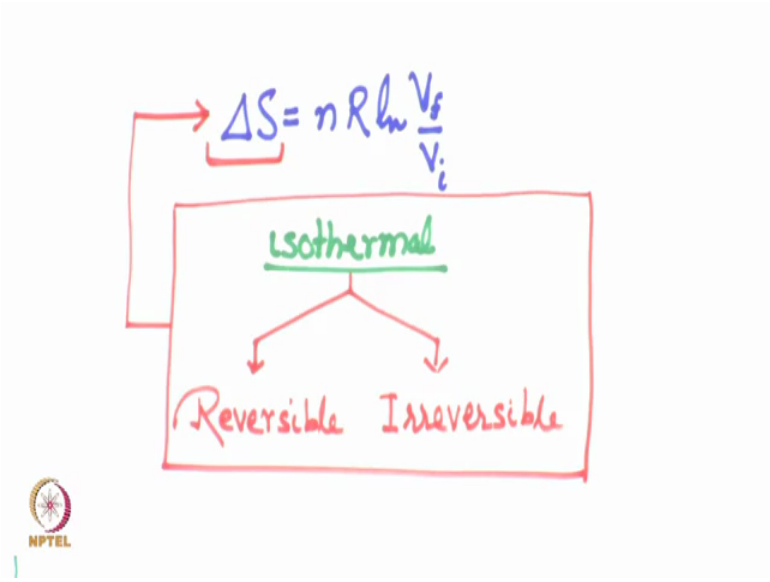

$$\Delta S = nR\ln\frac{V_f}{V_i}$$

So, what we have derived now? Is let me write on a fresh page, is that delta S is equal to nR log V final over V initial. This is the expression or equation to be used for calculating the entropy change in the system when the gas expands under isothermal conditions. There is also point to be noted that there is no temperature appearing. Although we are saying it is an equation to be used for calculation of entropy change and isothermal conditions, but actually in the expression there is no temperature appearing. And if V final expansion means V final is greater than V initial; that means, logarithmic term is positive. So, during expansion delta S is positive and entropy will increase. Therefore, according to this equation the increase in entropy does not depend upon the temperature, but it will depend upon the values of V f and V I.

Another point to be noticed here is that, since entropy is a state function therefore, delta S is going to be same. As long as the process is isothermal whether it is reversible or it is irreversible. So, as long as the process is isothermal it does not matter whether it is reversible or irreversible, we are going to use the same equation to calculate the entropy change when the gas expands from a 5 initial volume of V I to a final volume of V f.

Now, let us take another special case of entropy of phase transitions. What is a phase transition?

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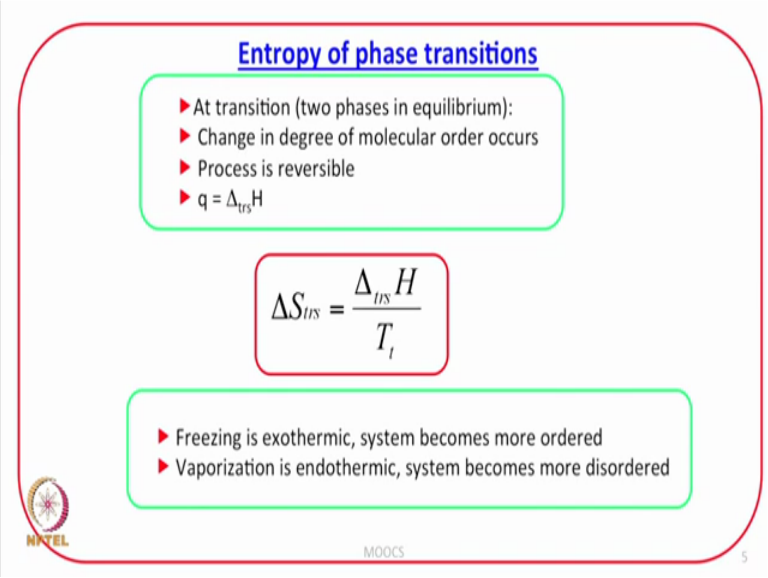

Entropy of phase transitions

- At transition (two phases in equilibrium):
- Change in degree of molecular order occurs
- Process is reversible
- $q = \Delta_{trs}H$

$$\Delta S_{trs} = \frac{\Delta_{trs}H}{T_t}$$

- Freezing is exothermic, system becomes more ordered
- Vaporization is endothermic, system becomes more disordered

MOOCS

A phase transition is a transition at which the phase of a system changes, the state of a system changes from one phase to another phase. An example of phase transition can be, melting of ice where water changes from if from ice to liquid water. And as we can see in the slide that at transition the 2 phases are in equilibrium that means.

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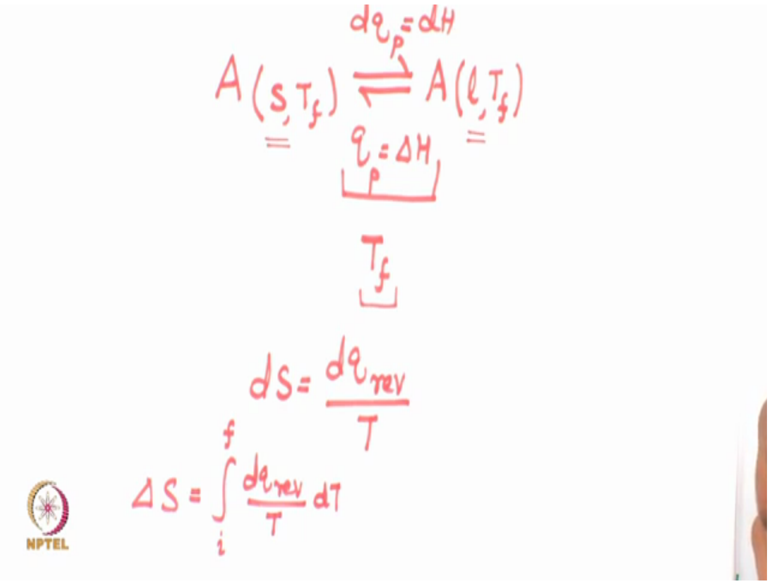

$$A(s, T_f) \underset{q_p = \Delta H}{\overset{dq_p = dH}{\rightleftharpoons}} A(l, T_f)$$

$$T_f$$

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

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

If I talk about any substance a, and this is at in the solid form at any temperature let us say at it is freezing temperature. And it melts a goes to liquid form at freezing temperature this is a phase transition. And phase transition is a reversible process, but what is happening here is, it is only the molecular order changing. Going from solid to liquid the order is decreasing. If it is reversed going from liquid to solid the order is increasing. So, there is a change in the degree of molecular order.

Since the process is reversible occurring at constant pressure. So, whatever is the change in heat since it is at a constant pressure this is equal to dH or I will say q p is equal to delta h, which is at a temperature T f another property of phase transition is, that whatever heat is supplied that is used to change the phase of the system. In changing from solid to liquid it does not change the temperature, you know that the transition takes place at a single temperature unique temperature that is, whatever is the phase transition temperature. So therefore, if I now write dS is equal to dq reversible by T or if I write delta S as integration from initial to final dq reversible by T, d T.

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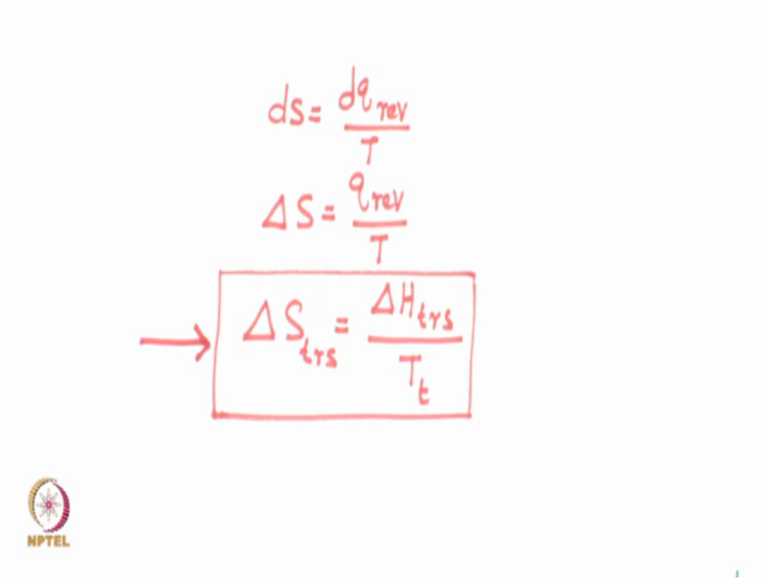

$$dS = \frac{dq_{rev}}{T}$$

$$\Delta S = \frac{q_{rev}}{T}$$

$$\longrightarrow \boxed{\Delta S_{trs} = \frac{\Delta H_{trs}}{T_t}}$$

So, once I have dS is equal to dq reversible by T then delta S is equal to q reversible by T. And at phase transition I will write delta S of transition this is equal to delta H of transition q p is equal to delta H divided by the transition temperature. This is how you calculate the entropy change in the phase transition. And by looking at this equation the sin of delta H we will decide whether the entropy change will be positive or negative. For example, freezing is exothermic, exothermic is delta H is less than 0 is negative. So, freezing means delta S should be negative it makes a sense, because in freezing the molecules become more ordered. So therefore, the entropy change will be negative.

Vaporization is endothermic vapors you know, liquid form goes to vapor and molecules have more degrees of freedom. And delta H is positive they are saying therefore, delta f is also positive; that means, the disorder increases upon vaporization. So, delta S is positive.

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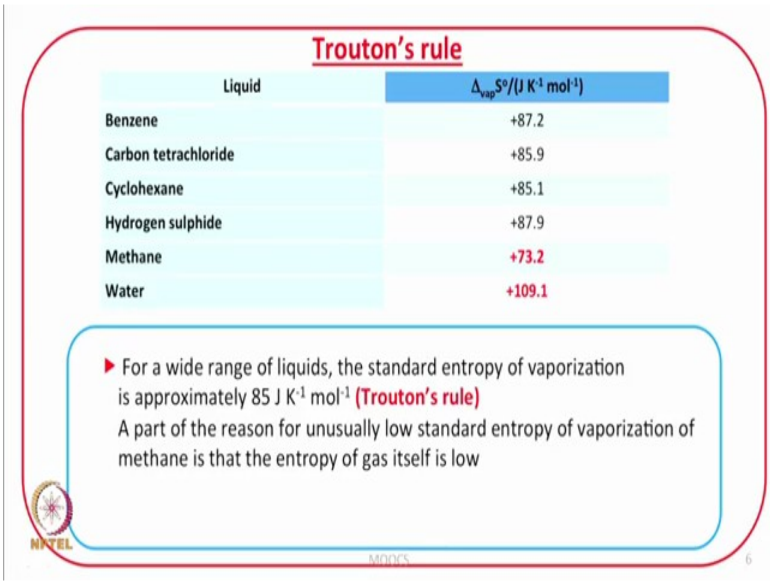

Trouton's rule

Liquid	$\Delta_{vap}S^{\circ}/(J\,K^{-1}\,mol^{-1})$
Benzene	+87.2
Carbon tetrachloride	+85.9
Cyclohexane	+85.1
Hydrogen sulphide	+87.9
Methane	**+73.2**
Water	**+109.1**

- For a wide range of liquids, the standard entropy of vaporization is approximately 85 $J\,K^{-1}\,mol^{-1}$ **(Trouton's rule)**
  A part of the reason for unusually low standard entropy of vaporization of methane is that the entropy of gas itself is low

Let us take a look at this table. In this table the values of entropy of vaporization for several liquids is given. And if we notice in the first 4 rows the value is approximately near 85 joules per Kelvin per mole. For a variety of liquids this value is about 85 joules per Kelvin per. And this observation for a wide range of liquids the standard entropy of vaporization is approximately 85 joules per Kelvin per mole if troutons rule. The reason for this is that for a variety of liquids when these are vaporized the same almost the same amount of disorder is generated. Whereas, if we take a look at the value of 4 water you see water value is about one 109.1 joules per Kelvin. This is much higher than 85. And the reason for this is that in water there is in liquid water there is an extensive amount of hydrogen bonded network.

And therefore, when water liquid is converted to water vapors that hydrogen bonding is broken and a large amount of disorder is generated, that is why for water the value is 109 it is much more than what is predicted by the troutons rule. Another deviation here is methane value is plus 73.2. And the value for methane is low a part of reason is the low standard and entropy of vaporization assigned to the low value of the entropy of the gas itself, that is the gas itself has a small amount of entropy, that is low entropy. And this is connected with moment of inertia these you will study later on.

We have already discussed for water the value is high because of a large amount of generated disorder as a result of breakage of extensive hydrogen bonded network. The entropy change for phase transitions. This is very important, not only in discussing the phase changes in solid liquid vapor etcetera. The phase change can be in within the solids also, for example, carbon graphite converting to carbon diamond that is the phase change. When we talk about even biological system a protein from it is native structure goes to an unfolded structure. That is also a change which is like a phase change a nucleic acid unfolds, that is also like a change, which can be treated as a phase change. So, in those cases we will later on demonstrate through several applications and several numerical problems that it is possible to calculate the value of entropy of phase transition. And then this value can be used to connect various thermodynamic parameters which are very, very important in predicting the feasibility spontaneity of a process under the given conditions of temperature and pressure.

We will continue our discussion on entropy further and connect these various basic principles that we have discussed with applications.

Thank you.