Concepts of Chemistry for Engineering
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Lecture 54
Helmholtz and Gibbs Free Energies, Concept of Spontaneity

Hello, and welcome to the next segment of our discussion about thermodynamics. So, over here so far, we have discussed the first law and second law of thermodynamics, we understand the connection between the energy, work and heat, we have understood two important parameters enthalpy and entropy, we looked into the effect of entropy, how it can lead us to the spontaneity of a reaction and how entropy can also define the third law of thermodynamics. So, in this segment, we will talk about the free energies. So, let us start our discussion about that particular factor in thermodynamics.

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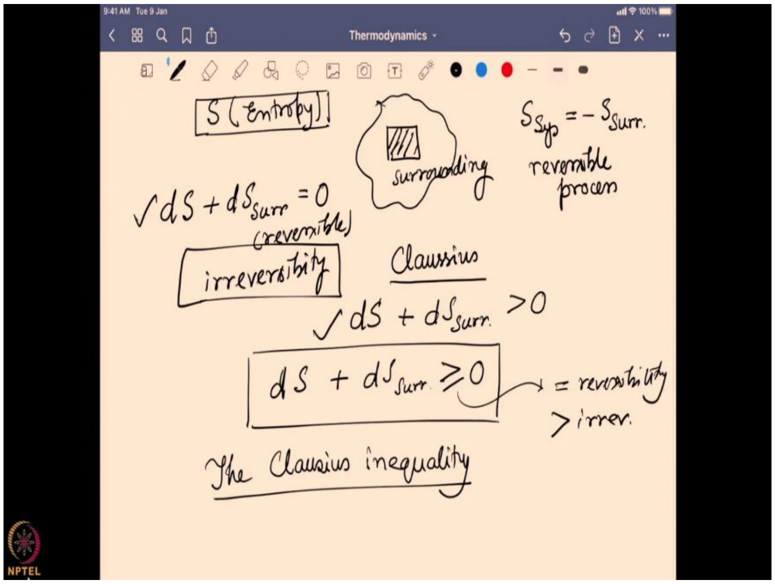

$\boxed{S\ (\text{Entropy})}$

$S_{Sys} = -S_{Surr.}$

reversible process

✓ $dS + dS_{surr} = 0$ (reversible)

$\boxed{\text{irreversibity}}$

Claussius

✓ $dS + dS_{surr.} > 0$

$$\boxed{dS + dS_{surr.} \geq 0}$$

= reversibility

> irrev.

The Clausius inequality

So, when we talk about the entropy, we say during a process this process is spontaneous when the entropy actually increases. Now, this system whose entropy is increasing it is present around the surrounding, now when we increase the entropy of a system at the same time the surrounding entropy is also decreasing to balance it out, because we are talking about a reversible process, and ideal reversible process this will always be true.

So, even if we looked at in a very minute scale, this will remain same. Say dS is the entropy change in minute amount on the system plus dS the entropy change on the surrounding will be equal to 0

$ds + ds_{surrounding} = 0$, if it is a reversible system. But what happens if we include the irreversibility, what happens if the system is not reversible? That was the question posed by the scientist Clausius whom we already discussed for the second law of thermodynamics statement.

So, what Clausius said that if it is an irreversible system and if this is happening, then the overall entropy will increase that means dS of the system plus dS of the surrounding will increase in the irreversible system. Now, if we compare and bound these things together, we can say entropy change in minute amount for a system plus entropy change in minute amount on the surrounding is always greater than 0 $ds + ds_{surrounding} \geq 0$.

Where the equal term defines the reversibility, whereas the greater than term talks about the irreversibility, and this particular equation is known as the famous the Clausius inequality. So, now we want to find out what is actually happening in terms of the heat exchange with this Clausius inequality.

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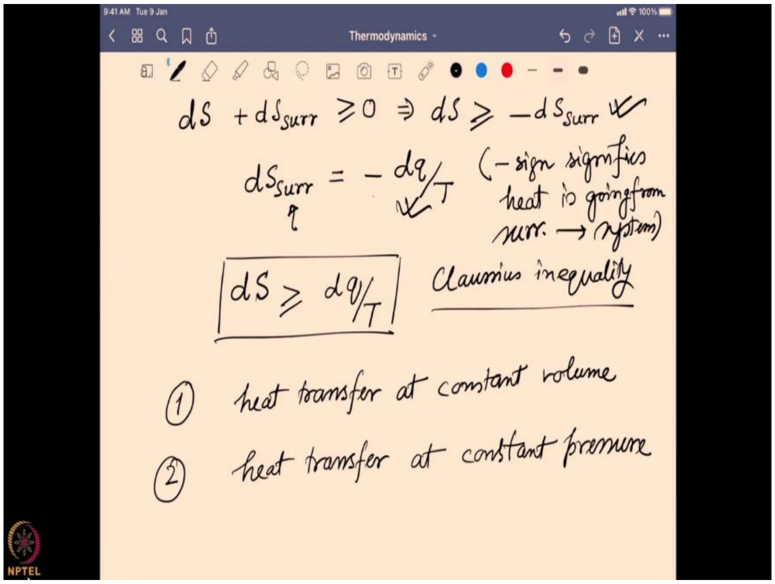

$dS + dS_{surr} \geq 0 \Rightarrow dS \geq -dS_{surr}$ ✓

$dS_{surr} = -dq/T$ (− sign signifies heat is going from surr. → system)

$\boxed{dS \geq dq/T}$ Clausius inequality

① heat transfer at constant volume

② heat transfer at constant pressure

So, you already know the Clausius inequality says $ds + ds_{surrounding} \geq 0$. So, we can just rearrange that and write, $ds \geq -ds_{surrounding}$. Now, over there with this equation, we know some heat exchange is happening, the heat is actually going to the system from the surrounding, so that means $dS_{surrounding}$ I can write it as -dq/T, again this minus sign signifies that heat is going from surrounding to the system.

And as we just know once the heat is actually coming to the system it is positive, but now we are talking with respect to the surrounding, now the surrounding we are talking about and surrounding is losing heat to the system. So, with respect to that we can say surrounding is actually losing heat, so that is why this negative term is coming over here.

Now, if we all put this together equation this equation this one, we can say dS the minute change in the entropy of the system is greater than equal to dq/T, because there two negative signs actually cancel each other out. And this is another way we can write the Clausius inequality. So, which says that the change in the entropy is always greater than or equal to the heat exchange during the experiment at that particular temperature.

And this is actually said the field for understanding the change in the free energy. Now, over here, this heat transfer can happen in two different scenarios, first scenario will be the heat transfer at a constant volume and the second one will happen heat transfer at constant pressure. So, these are the two scenarios we can play with and find out what is the effect of entropy change with respect to the heat and temperature. Let us take a look into them one by one.

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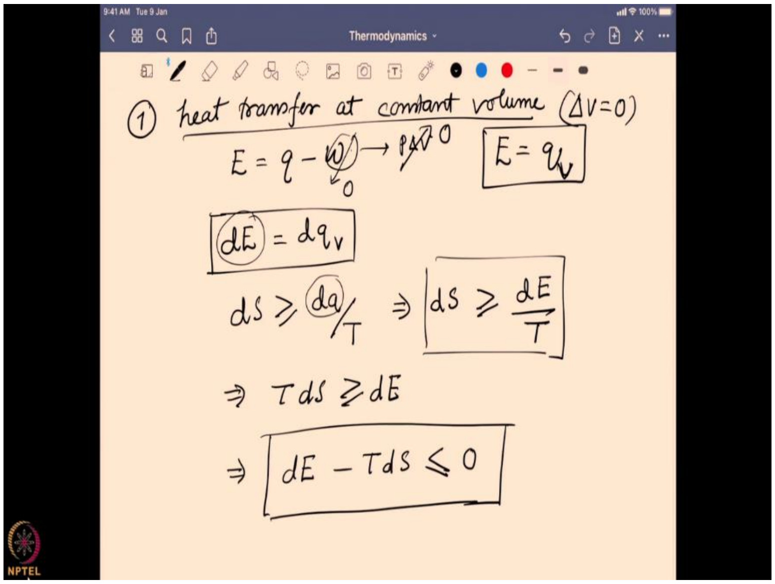

① heat transfer at constant volume $(\Delta V = 0)$

$$E = q - \underset{0}{\cancel{w}} \rightarrow \cancel{p\Delta V} \; 0 \qquad \boxed{E = q_v}$$

$$\boxed{dE = dq_v}$$

$$dS \geq \frac{dq}{T} \Rightarrow \boxed{dS \geq \frac{dE}{T}}$$

$$\Rightarrow T dS \geq dE$$

$$\Rightarrow \boxed{dE - T dS \leq 0}$$

First, take a look into that heat transfer at constant volume. So, which means ΔV is equal to 0. So, there is no other what is going to happen, because everything is happening with respect to the change of the energy and heat and if we look into the first law of thermodynamics, it says E=q-w and over here w is nothing but pΔV and our pΔV is equal to 0. So, this w becomes 0.

So, we can over here write energy is equal to q and we are writing q_v to say that it is happening at a constant volume. Now, if you look into a minute amount of that smaller value of that we can say $dE=dq_V$. Now, we already know $dS \geq dq/T$, and we are doing this at constant volume where this dq becomes dE.

So, from there, we can create further and write $dS \geq dE/T$. So, just exchanging the dq with dE over here, and all these things this equation if I just rearrange it, I can write $TdS \geq dE$, or I am bringing the dE to the left hand side $dE - Tds$ and putting a minus 1 multiplication all together ≤ 0.

So, that is the function I am getting at this moment. So, change in energy minus temperature into the change in entropy will always be less than and equal to 0, equal to 0 when is reversible process, less than equal to 0 when it is irreversible process. So, that is what we got from the heat transfer at a constant volume. We will come into that in a while.

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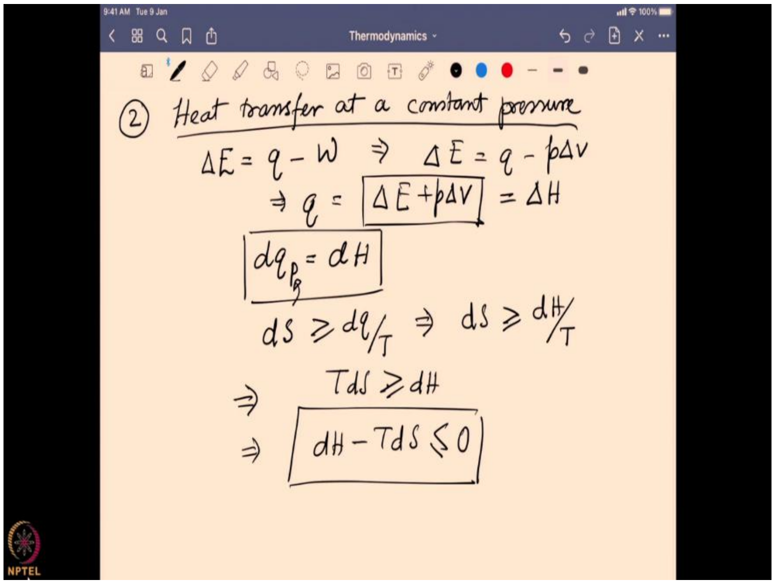

② Heat transfer at a constant pressure

$$\Delta E = q - W \Rightarrow \Delta E = q - p\Delta V$$

$$\Rightarrow q = \boxed{\Delta E + p\Delta V} = \Delta H$$

$$\boxed{dq_p = dH}$$

$$dS \geq dq/T \Rightarrow dS \geq dH/T$$

$$\Rightarrow TdS \geq dH$$

$$\Rightarrow \boxed{dH - TdS \leq 0}$$

Let us go to the next part, where we are going to talk about heat transfer at a constant pressure. So, over here we can say from the first law of thermodynamics E=q-w, because over here it is constant pressure that means I can still change the volume. So, that means it becomes $\Delta E= q-p\Delta V$ or $q= \Delta E+p\Delta V$ and we all remember, $\Delta E+p\Delta V$ is nothing but a change in enthalpy ΔH.

So, over here the word heat change at constant pressure is nothing but the enthalpy change. So, we can write dq_p, p defines that it is happening at a constant pressure is nothing but dH again going to the Clausius inequality, $dS \geq dq/T$. So, from there we can write dS is $\geq dH/T$.

Again, if I rearrange that, we can write $TdS \geq dH$ or $dH - TdS \leq 0$. So, that is the function we found, so it is the change in enthalpy minus temperature into change into the entropy is less than equal to 0, equal to when it is reversible less than when it is irreversible.

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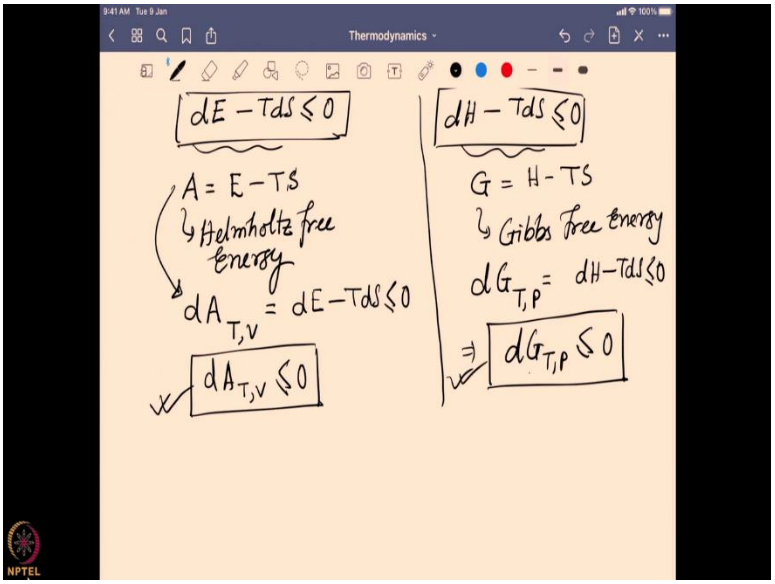

$$\boxed{dE - TdS \leq 0}$$

$$A = E - TS$$

↳ Helmholtz free energy

$$dA_{T,V} = dE - TdS \leq 0$$

$$\boxed{dA_{T,V} \leq 0}$$

$$\boxed{dH - TdS \leq 0}$$

$$G = H - TS$$

↳ Gibbs free energy

$$dG_{T,P} = dH - TdS \leq 0$$

$$\Rightarrow \boxed{dG_{T,P} \leq 0}$$

Now, if we draw all those two factors together $dE - TdS \leq 0$ it is happening at a constant volume and $dH - TdS \leq 0$ when it is happening at constant pressure. So, these things are actually giving me an idea when a reaction will be thermodynamically more spontaneous, especially when it is irreversible less than equals 0.

However, we need to define these two terms separately and that has been done by using these two functions. First function is known as A is defined as E- TS, which is known as Helmholtz free energy and over there it has been done at a constant temperature because from this equation you can write dA at constant temperature and constant volume ($dA_{T,V}$) = $dE - TdS \leq 0$. So, $dA_{T,V} \leq 0$. So, it is giving me an idea when a reaction will be spontaneous.

Similarly, when you are doing that at a constant pressure this function is given by this function G, is defined at H -TS and G is known as Gibbs free energy. And what does it define? It define change in G at a constant temperature and pressure $dG_{T,P}$, then it becomes dH-TdS which is less than equals 0 or $dG_{T,P} \leq 0$, so it defines when a reaction will be spontaneous at a constant temperature pressure its Gibbs free energy goes to lower energy. So, that is the mathematical functions that we have derived but what is the physical significance of both this Helmholtz energy and Gibbs free energy that we want to discuss it further.

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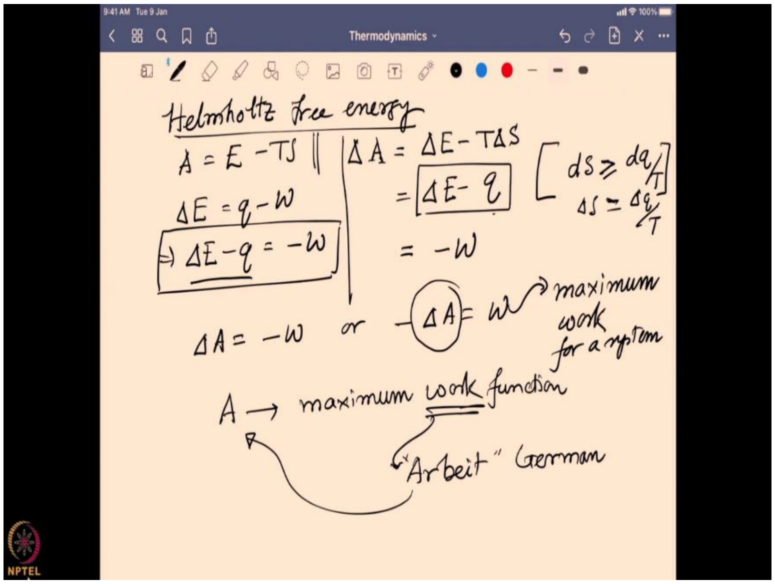

Helmholtz free energy

$A = E - TS$

$\Delta E = q - w$

$\Rightarrow \boxed{\Delta E - q = -w}$

$\Delta A = \Delta E - T\Delta S$

$= \boxed{\Delta E - q}$

$= -w$

$\left[dS \geq dq/T \right]$

$\Delta S = \Delta q/T$

$\Delta A = -w$ or $-\Delta A = w \rightarrow$ maximum work for a system

A → maximum work function

"Arbeit" German

First take a look into Helmholtz free energy, what does it actually means? So, as we know we have defined A = E - TS, now if we want to find out the differences in change in the Helmholtz free energy from initial to final for a process we can write this ΔA = ΔE - TΔS, it is happening at a constant temperature so that is why T remains constant.

Over there once we write it, we know ΔE = q - w, so ΔE - q we can write is nothing but - w. So, that we keep in our mind. Now, for a reversible process what happens over here ΔA = ΔE - TΔS for reversible process this is nothing but ΔE - q, why? Because as you remember dS ≥ dq /T. So, for reversible process dS = dq/T or ΔS = Δq/T.

So, that is the Δq is nothing but the heat exchange. So, we write it as only q and that is becoming this, so TΔS is nothing but q, so that we have included over there. And over here we just find out ΔE-q is nothing but - w, that the work can be done by the system. So, you can write it is nothing but -w.

So, what you can write that ΔA = -w or -ΔA = w which is nothing but the maximum work possible for a system during a process is actually given by this term ΔA. So, that is the maximum work possible and that is why A is known as maximum work function and the German term for work is Arbeit and that is why the term A actually is denoted over here for this Helmholtz free energy.

So, Helmholtz free energy is nothing but giving you an idea, how much work can be possible in the maximum if you are using this function, and as you know it is greater than or equal to, so that is the maximum work possible. So, you can have less than work but the maximum will be when it is a reversible system and that is what is defined by this Helmholtz free energy, nothing but the maximum work possible for a particular system. What happens for the Gibbs free energy?

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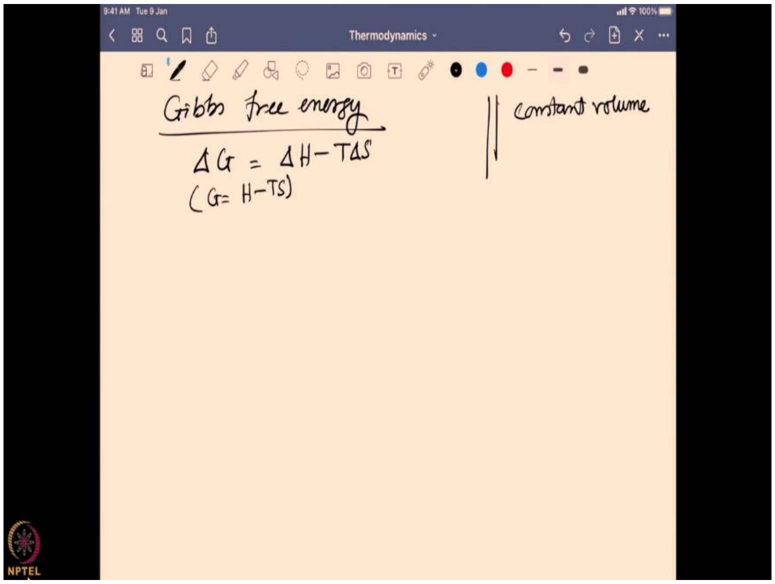
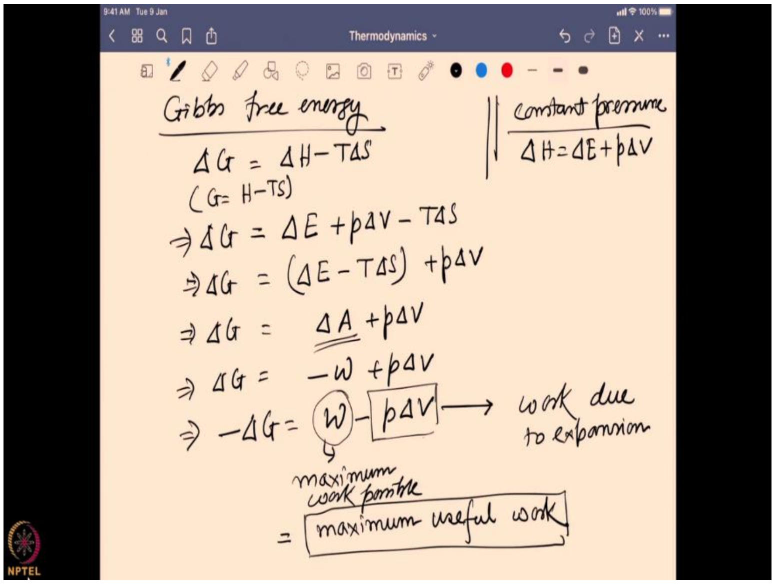


Gibbs free energy

$\Delta G = \Delta H - T\Delta S$

$(G = H - TS)$

constant volume



Gibbs free energy

$\Delta G = \Delta H - T\Delta S$

$(G = H - TS)$

constant pressure

$\Delta H = \Delta E + p\Delta V$

$$\Rightarrow \Delta G = \Delta E + p\Delta V - T\Delta S$$
$$\Rightarrow \Delta G = (\Delta E - T\Delta S) + p\Delta V$$
$$\Rightarrow \Delta G = \underline{\Delta A} + p\Delta V$$
$$\Rightarrow \Delta G = -W + p\Delta V$$
$$\Rightarrow -\Delta G = \underbrace{W}_{\text{maximum work possible}} - \boxed{p\Delta V} \longrightarrow \text{work due to expansion}$$
$$= \boxed{\text{maximum useful work}}$$

For a Gibbs free energy, we can do similar calculations and find out ΔG = ΔH - TΔS that is again from this equation G =H - TS and if you are doing that at a constant temperature ΔG = ΔH - TΔS, now as we know at a constant pressure, we know ΔH = ΔE + pΔV. So, if we include that in this equation, we go to ΔG = ΔE + pΔV - TΔS, a little bit of reorganization bringing E and TS together ΔE – TΔS+pΔV.

So, now over here this ΔE – TΔS is nothing but the Helmholtz free energy function, ΔA+pΔV, and I already know the ΔA is nothing but -w, the maximum work possible. So, with respect to that we can write -ΔG= w- pΔV where w is the maximum work possible, whereas, pΔV is nothing but work done by the system due to the expansion, because at a constant pressure we can still change the volume, so it is expansion process and there I am losing some work done by the system. This is over work possible and this is the work I am losing by this expansion work.

So, what is remaining is the maximum useful work possible, is the maximum useful work doable other than the expansion work. So, Helmholtz function gives me the overall work possible, it does not define what is the mechanical work what is actual work, whereas Gibbs free energy gives me the difference between the actual work minus the mechanical or the expansion work.

So, actual useful work that can be used during a process from a system is given by ΔG. So, that is why ΔG or Gibbs free energy becomes a very unique quantity a unique parameter because that defines us how we can find what is the overall maximum work, we can use without doing the mechanical or extension work for a system. So, that is the important, importance of the Gibbs free energy.

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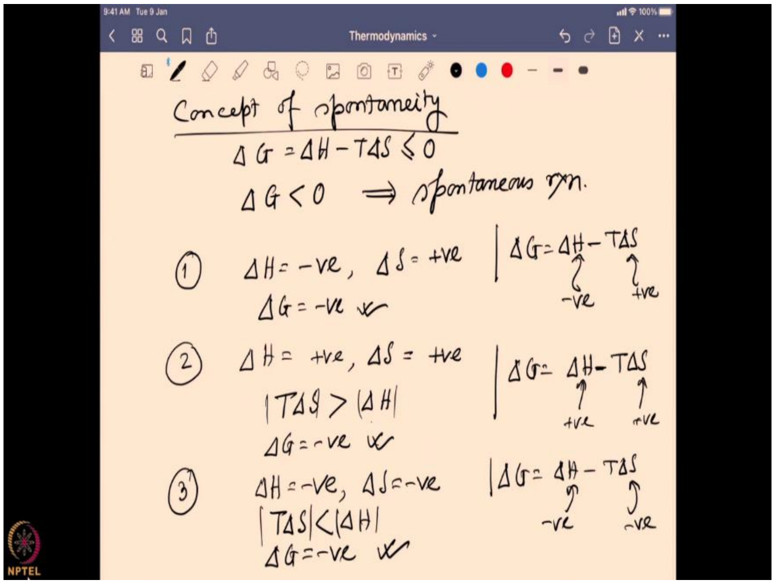

Concept of spontaneity

$\Delta G = \Delta H - T\Delta S \lessgtr 0$

$\Delta G < 0 \Rightarrow$ spontaneous rxn.

① $\Delta H = -ve,\ \Delta S = +ve$ | $\Delta G = \underset{-ve}{\underset{\uparrow}{\Delta H}} - \underset{+ve}{\underset{\uparrow}{T\Delta S}}$

$\Delta G = -ve$ ✓

② $\Delta H = +ve,\ \Delta S = +ve$ | $\Delta G = \underset{+ve}{\underset{\uparrow}{\Delta H}} - \underset{+ve}{\underset{\uparrow}{T\Delta S}}$

$|T\Delta S| > |\Delta H|$

$\Delta G = -ve$ ✓

③ $\Delta H = -ve,\ \Delta S = -ve$ | $\Delta G = \underset{-ve}{\underset{\uparrow}{\Delta H}} - \underset{-ve}{\underset{\uparrow}{T\Delta S}}$

$|T\Delta S| < |\Delta H|$

$\Delta G = -ve$ ✓

Now, with respect to that we come into the system the concept of spontaneity. So, now we have discussed over here that the $\Delta G = \Delta H - T\Delta S$ and it can be less than equals 0, and for irreversible process it is less than 0. So, over there the entropy is actually increasing and according to second law of thermodynamics, that is where my spontaneous reaction would be.

So, that is why we define ΔG should be less than 0, if I want to have a spontaneous reaction. Now, how the ΔH and ΔS factors into here? So, now there are three conditions, first say ΔH is negative and ΔS is positive and ΔG is a summation of $\Delta H - T\Delta S$, and if ΔH is already negative, ΔS is positive, and it is multiplied by -T, so the overall ΔG value will be negative. So, the reaction will be spontaneous.

So, if enthalpy is actually less than 0 for exothermic reactions and entropy is increasing it is going to be a spontaneous reaction. What happened ΔH is positive, ΔS is also positive, but in such a way that $T\Delta S$ is actually larger than ΔH, if that is the case, now imagine ΔH is positive, ΔS is also positive, but ΔS into -T is a huge negative term and magnitude wise $T\Delta S$ is greater than ΔH, so the overall term becomes negative.

So, ΔG still remains negative and the reaction will be spontaneous, that is actually what is happening during the melting of ice that we have discussed earlier that enthalpically it is endothermic reaction ΔH is positive, but ΔS is so positive that at that temperature of melting it is giving a value of $T\Delta S$ as such that it is overcoming the ΔH and it becomes a spontaneous process.

How else we can actually achieve spontaneity? Say ΔH is negative, ΔS is also negative, so in the case $\Delta G= \Delta H - T\Delta S$, so ΔH is negative, ΔS is also negative, so $T\Delta S$ is going to give me a positive value - $T\Delta S$, but in such a way that the magnitude of T delta S is actually less than the magnitude of delta H.

In that case what will happen? The ΔH negative will overcome the positive term given by $T\Delta S$ and ΔG will still remain negative and the reaction will be spontaneous. So, over here we can find that it is a combination of both entropy change and enthalpy change coming to the picture and then it actually defines whether the reaction will be spontaneous or not.

It does not matter whether it is an endothermic or exothermic reaction and if we can play with the entropy term such that the overall ΔG is negative, then the reaction will be spontaneous. Similarly, a ΔS is positive, always go for a spontaneous reaction, but a ΔS is negative that means a change in the disorder such that disorder is decreasing that always does not mean the reaction will not be spontaneous.

If the enthalpy factor can cover up the difference of $T\Delta S$, we can still get a ΔG negative value and it can still support us with a system which can be spontaneous. So, with respect to that, we will try to conclude this particular section where we will discuss in this particular section, we have discussed the Clausius inequality and we talk about two different important free energy function, one is the Helmholtz free energy function, one is the Gibbs free energy function, Helmholtz free energy function is given as energy minus TS factor, Gibbs free energy is given us H minus TS factor.

Helmholtz free energy function has been developed from a constant volume calculation and the Gibbs free energy is actually derived from a constant pressure calculation. The Gibbs free energy gives us the actual work that can be found from a system removing the expansion work, whereas the Helmholtz function gives us the idea of the overall work possible to get from a particular system during a process.

So, that is why ΔG and ΔA value always give us an idea, which side the reaction is going, we generally follow the Gibbs free energy because it gives us mostly the work that can be done by a system without the expansion work or the mechanical work. So, that is why Gibbs free energy is widely used, and that becomes very famous to us that the ΔG negative value means a spontaneous reaction. We have also discussed how ΔG is connected with ΔH and ΔS and what are the different combinations are possible to get a ΔG negative with respect to the ΔH and ΔS. Thank you.