# Chemical and Biological Thermodynamics: Principles to Applications

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## Lecture – 11
## Discussion on Helmholtz energy

We have earlier discussed the criteria of spontaneity in terms of changes in the entropy of system entropy of surroundings, and then we have discussed the criteria for spontaneity in terms of changes in the properties of system alone. Along with that we have also discussed that in each case the second law of thermodynamics is obeyed.

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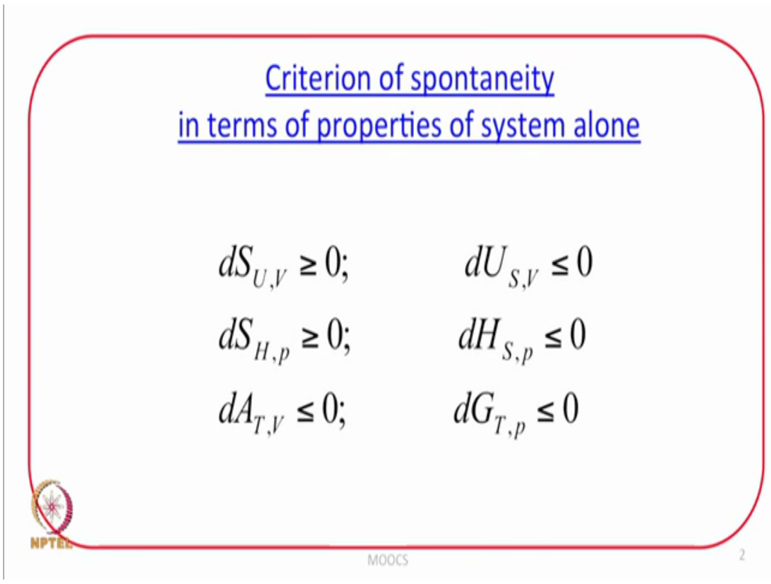

Criterion of spontaneity
in terms of properties of system alone

$dS_{U,V} \geq 0;$ $dU_{S,V} \leq 0$

$dS_{H,p} \geq 0;$ $dH_{S,p} \leq 0$

$dA_{T,V} \leq 0;$ $dG_{T,p} \leq 0$

Let us take a look at this slide these are the 6 criteria of spontaneity that we have discussed in terms of properties of system alone and each individual criteria of spontaneity obeys the second law of thermodynamics. Today we will pick up this d A at constant temperature and volume it should be less than or equal to 0 as one of the criteria of spontaneity; A: we have earlier introduced which is called Helmholtz energy.

And let us discuss further about Helmholtz energy and what information is available from the changes in Helmholtz energy.

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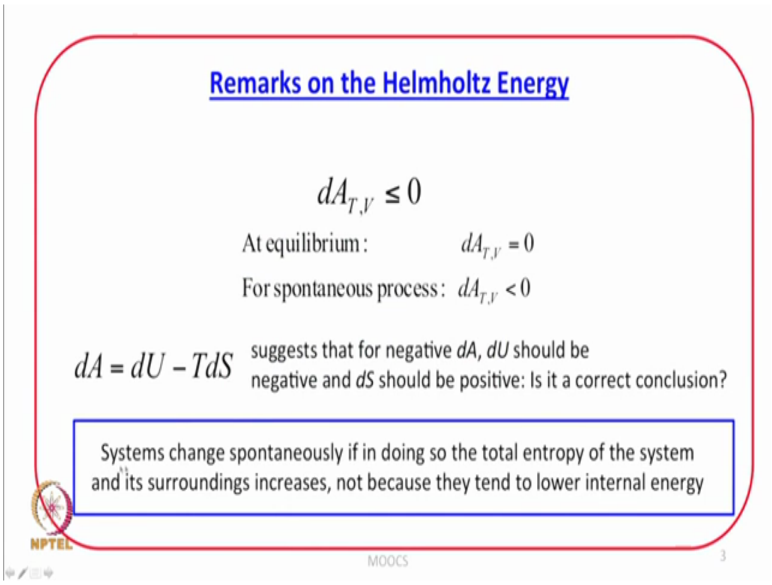

Remarks on the Helmholtz Energy

$$dA_{T,V} \le 0$$

At equilibrium: $dA_{T,V} = 0$

For spontaneous process: $dA_{T,V} < 0$

$dA = dU - TdS$ suggests that for negative *dA*, *dU* should be negative and *dS* should be positive: Is it a correct conclusion?

Systems change spontaneously if in doing so the total entropy of the system and its surroundings increases, not because they tend to lower internal energy

This is the criteria of spontaneity which we have chosen now for further discussion, according to this criteria of spontaneity, the change in Helmholtz function of Helmholtz energy at constant temperature and volume should be less than or equal to 0. Let us recall that equal to sign is used for reversible process means we are talking about equilibrium at equilibrium d A at constant temperature and volume should be equal to 0 whereas, for spontaneous process we use less than sign. If the process is to be spontaneous the value of d A at constant temperature and volume should be negative.

So, now, if we take a look at d A is equal to d U minus T dS this comes from the definition of Helmholtz energy.

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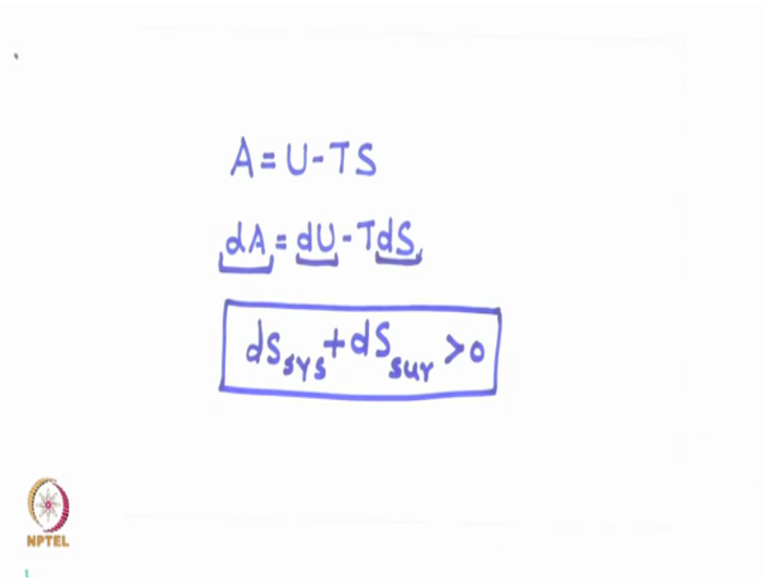

$$A = U - TS$$

$$\underbrace{dA} = \underbrace{dU} - T\underbrace{dS}$$

$$\boxed{dS_{sys} + dS_{sur} > 0}$$

Helmholtz energy or Helmholtz function A is equal to U minus TS. We have defined earlier d A is equal to d U minus T dS at a constant temperature s d t term goes away; and we are interested in the negative value of d A, the negative value of d A is in the direction of negative value of d U and positive value of ds. What I mean is if d U is negative dS is positive then that supports the negative value of d A. Let us go back to the slide and discuss further. So, they just discuss the d A is equal to d U minus T dS suggest that for negative d A, d U should be negative and dS should be positive is it a correct conclusion. D U is negative it means that the system should go towards lower energy, and dS is positive means the entropy of the system must increase.

By saying so, are we violating the first and second law of thermodynamics because the first law of thermodynamics says that the energy the total energy of an isolated system must remain constant so that means, this change in internal energy negative change must be doing something somewhere else. So, that the total energy of the isolated system remains constant and secondly, the dS is positive, what about the entropy change in the surroundings. This decrease in internal energy can be used up or it can enter a part of it can enter in the surroundings in the form of heat and generate enough disorder. So, that the dS system plus dS surrounding is greater than 0. Second law is obeyed and at the same time the first law is also obeyed, that is why these comment that systems change spontaneously if in doing so, the total entropy of the system and surroundings increases not because they tend to lower internal energy ok.

Now, let us move towards a discussion on the significance of Helmholtz energy. A: Helmholtz energy is sometimes called the maximum work, maximum work function or just work function what is the origin of this letter A? Actually Arbeit is German word for work.

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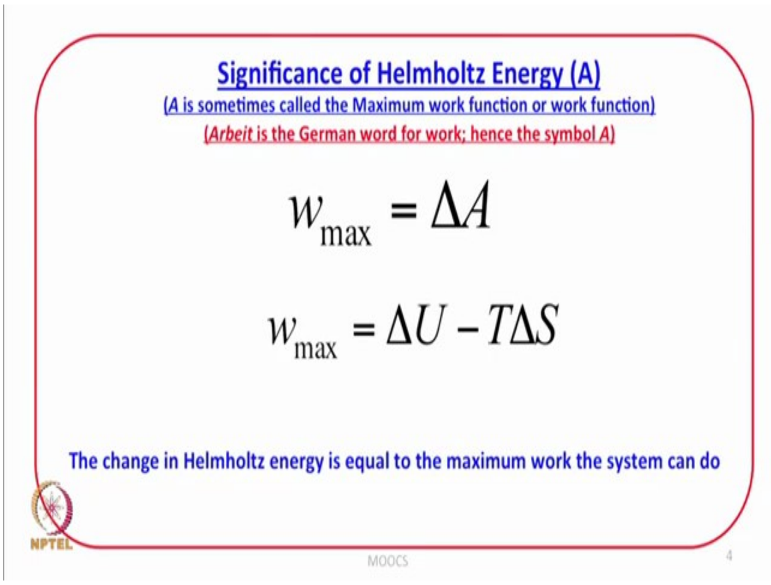

## Significance of Helmholtz Energy (A)

(A is sometimes called the Maximum work function or work function)

(*Arbeit* is the German word for work; hence the symbol *A*)

$$w_{\max} = \Delta A$$

$$w_{\max} = \Delta U - T\Delta S$$

The change in Helmholtz energy is equal to the maximum work the system can do

And from where the first letter A is chosen as a symbol for Helmholtz energy A. Since it is called the maximum work function or work function; that means, the changes in A must be connected to the maximum work which we can draw from a system and that is what we are going to prove now. That the maximum work available from a system is equal to changes in Helmholtz free energy or the change in Helmholtz free energy is a measure of maximum work that a system can do.

Let us prove that we will start with the clausius inequality according to which dS is greater than or equal to d q by T.

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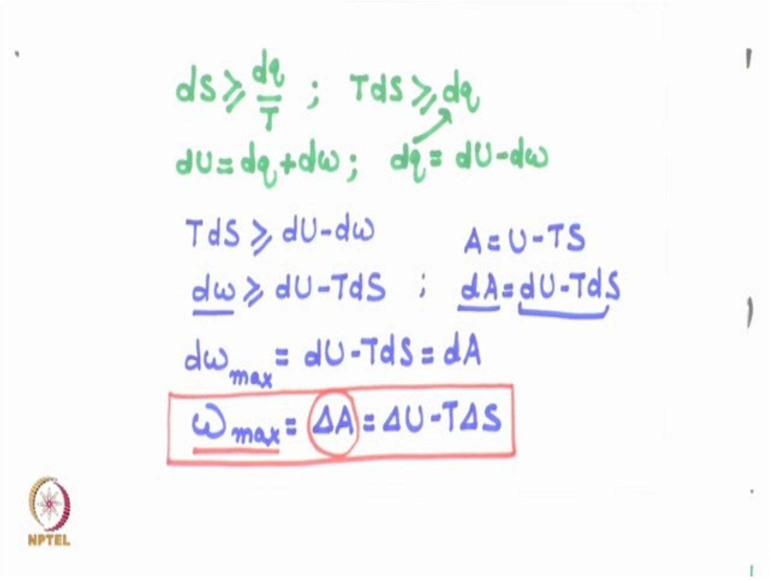

$$dS \geq \frac{dq}{T} \; ; \quad TdS \geq dq$$

$$dU = dq + d\omega \; ; \quad dq = dU - d\omega$$

$$TdS \geq dU - d\omega \qquad A = U - TS$$

$$\underline{d\omega} \geq dU - TdS \; ; \quad \underline{dA} = \underbrace{dU - TdS}$$

$$d\omega_{max} = dU - TdS = dA$$

$$\boxed{\underline{\omega_{max}} = \Delta A = \Delta U - T\Delta S}$$

From this equation I can write T dS is greater than or equal to d q fine; from the first law we know that d U is equal to d q plus d w. So, from this I can write d q is equal to d U minus d w, this d q I can substitute over here what do I get now? That means, I get T dS is greater than or equal to d U minus d w. Now rearranging this I get d w is greater than or equal to d U minus T Ds. Now let us remember we had defined A is equal to U minus TS this we have defined earlier therefore, at a constant temperature d A is equal to d U minus T d s.

So, this d A d U minus T dS here I can replace by d A and another thing is since we are interested in the negative value of d w, because when the work is to be extracted from the system work is to be obtained from the system, in that case the value of d w has to be negative. According to this inequality the maximum negative value of d w is possible when we use equal to sign because if we use greater than sign, then the negative value of d w will be reduced and therefore, I will write d w max is equal to d U minus T dS and this is same as d A of course, at constant temperature. In other words for a finite change maximum work can be obtained from delta A which is equal to delta U minus T delta S.

Therefore delta A is a measure of maximum work that a system can do. Another point very important point which comes out of this discussion is that since we are using equal to sign and equality applies to reversibility therefore, the conclusion is that the maximum work is available from the system when it is operating under reversible conditions. Now you recall our discussion on the pressure volume work at that time from the plot of p versus v for an isotherm, we said that we made a conclusion that the maximum work is done by the gas when the gas is expanded under reversible conditions. And here we are we have come up with a conclusion which is true for all the systems, that maximum work is obtained from a system under reversible condition because the equality only applies for reversibility, and then in order to calculate maximum work we should act upon the change in Helmholtz free energy.

So, W max can be calculated from the changes in delta U and the changes in delta S. The change in Helmholtz energy is equal to maximum work the system can do let me stress upon this point that.

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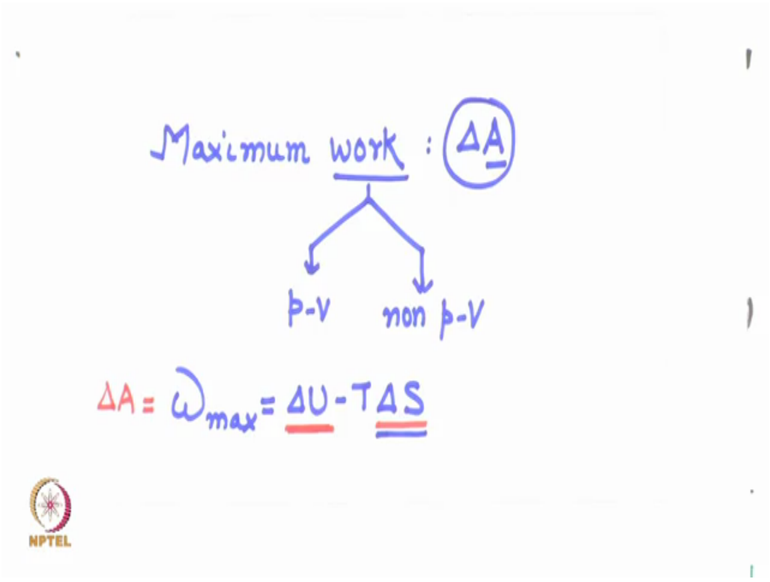

Maximum $\underline{\text{work}}$ : $\boxed{\Delta \underline{A}}$

p-V

non p-V

$$\Delta A = \omega_{max} = \underline{\Delta U} - T\underline{\underline{\Delta S}}$$

When we are interested in calculating maximum work we have to act upon delta A we have to act upon A and calculate it is change, because maximum work when I say work which is inclusive of pressure volume work and non-pressure volume work; that means, if we are to calculate to find out how much maximum work is obtainable from the system which is inclusive of both pressure volume and non-pressure volume work, we need to calculate the value of delta A, that is what the comment is mentioned here in the slide that the change in Helmholtz energy is equal to the maximum work the system can do. So that means, W max is equal to delta U minus T delta S. There are two components in this one is the change in internal energy, the other is the change in entropy. Whenever a system does work this is done at the cost of what work is done by the system at the cost of internal energy, when the system is doing work its own energy if the capacity to do work you know further work that is the internal energy decreases delta U has to be negative.

So, whatever is the change in delta U is all that change available for doing work whatever is the change in internal energy is all that available for doing work let us discuss that. You know that will depend upon two factors because the change in entropy can be positive and the change in entropy can be negative; and we will see now we will discuss now that how much a work is the maximum work we can draw from the system is it more than delta U or less than delta U when delta S is positive or delta S is negative let us take a look at them

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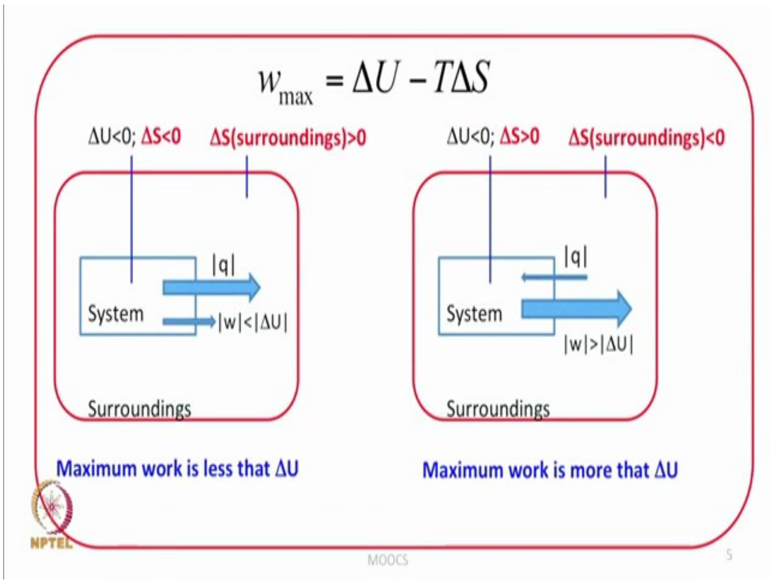

$$w_{\max} = \Delta U - T\Delta S$$

Maximum work is less that ΔU

Maximum work is more that ΔU

Let us take a look at the left hand side figure of course, delta U has to be negative. Case one when the change in entropy of the system is negative the entropy of the system is going down entropy is becoming more I mean the system is becoming more order.

The systems entropy decreases according to the second law of thermodynamics, the surroundings entropy must go up because the second law has to be obeyed. So, how will this entropy of the surrounding increase? Whatever is the negative change in delta U a part of that change in internal energy can enter the surroundings in the form of heat and generate enough disorder that is what is described in this figure, that in case delta S is negative some of the change in internal energy must enter the surroundings in the form of heat, so that enough disorder is generated to increase the entropic of surrounding delta S of surroundings should be positive because overall what you need is delta S system plus delta S surrounding to be positive for a spontaneous change.

Now, since part of the change in internal energy has been used up in doing in heating the surroundings therefore, all the change in internal energy is not available for getting work for doing the work. So, the maximum work available let us look at now the slide back that if delta S is negative, the maximum work available from the system is less than the change in internal energy, maximum work is less than delta U. This leads us to another important conclusion, since all the change in internal energy is not available for doing work part of change in internal energy has been used up in the form of heat to increase the entropy of the surrounding; that means, the nature is putting some tax on it all the change in internal energy is not available for doing work and let me now put delta A; we say delta A is a measure of maximum work the system can do, and A is called the Helmholtz free energy.

Why the term free you know many times this question comes to mind Gibbs free energy Helmholtz free energy why it is called free what is free in it. Here lies the answer that all the change in internal energy is not freely available, part of it has been used in the form of heat to increase the entropy of surrounding therefore, only a part of change in delta U is freely available for doing work that is the origin of the work free energy. It is like you know taking an example of our own salary we are not allowed to use all our salary because the government will deduct some tax on it is putting some tax on it. So, therefore, it is only after tax deduction we are able to use the remaining salary the free salary, we are use we are allowed freely allowed to use the salary only after tax deduction and that is why the term free enters into the Helmholtz free energy or Gibbs free energy as we will discuss later on.

Now, let us take a look at the second case the right hand side figure, this is an example of the change in entropy is positive. Now the situation is interesting here the change in entropy of the system is positive; we can still afford a slight reduction in entropy of the surrounding that is let some of the energy flow in into the system in the form of heat and add up to doing work, I repeat let some of the energy flow into the system and add up to doing work; however, in doing so, the entropy of surroundings will decrease.

But as long as the entropy change in the system plus entropy change in the surroundings is positive, it is the process can be spontaneous; that means, when delta S is positive some of the heat can enter into the system and add up to doing work so that the maximum work available from the system is now more than the changes in internal energy maximum work is more than delta U. So, I hope the situation is clear here that if the entropy change in the system is negative, in that case the maximum work is less than that of delta U and if entropy change in the system is positive the maximum work is more than the change in internal energy.

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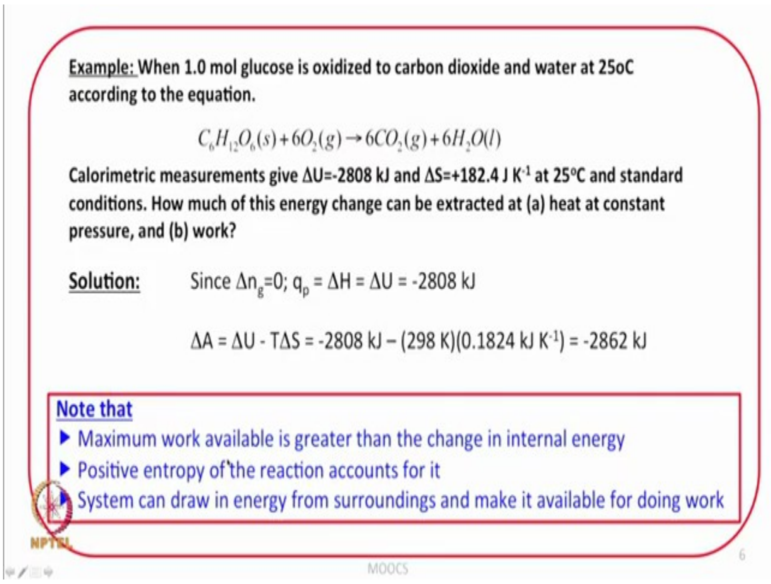

**Example:** When 1.0 mol glucose is oxidized to carbon dioxide and water at 25oC according to the equation.

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

Calorimetric measurements give $\Delta U = -2808$ kJ and $\Delta S = +182.4$ J $K^{-1}$ at 25°C and standard conditions. How much of this energy change can be extracted at (a) heat at constant pressure, and (b) work?

**Solution:** Since $\Delta n_g = 0$; $q_p = \Delta H = \Delta U = -2808$ kJ

$\Delta A = \Delta U - T\Delta S = -2808\ \text{kJ} - (298\ \text{K})(0.1824\ \text{kJ K}^{-1}) = -2862\ \text{kJ}$

Note that
- Maximum work available is greater than the change in internal energy
- Positive entropy of the reaction accounts for it
- System can draw in energy from surroundings and make it available for doing work

Let us now discuss an example, the question is when one mole of glucose is oxidized to carbon dioxide and water at 25 degree Celsius according to the equation, glucose plus 6 oxygen forming 6 carbon dioxide plus 6 water, calorimetric measurements gave delta U equal to minus 2808 kilo joules and delta S equal to plus 182.4 joules per kelvin at 25 degree Celsius and standard conditions.

How much of this energy can be extracted as a heat at constant pressure and b work; the first part of the question heat at constant pressure.

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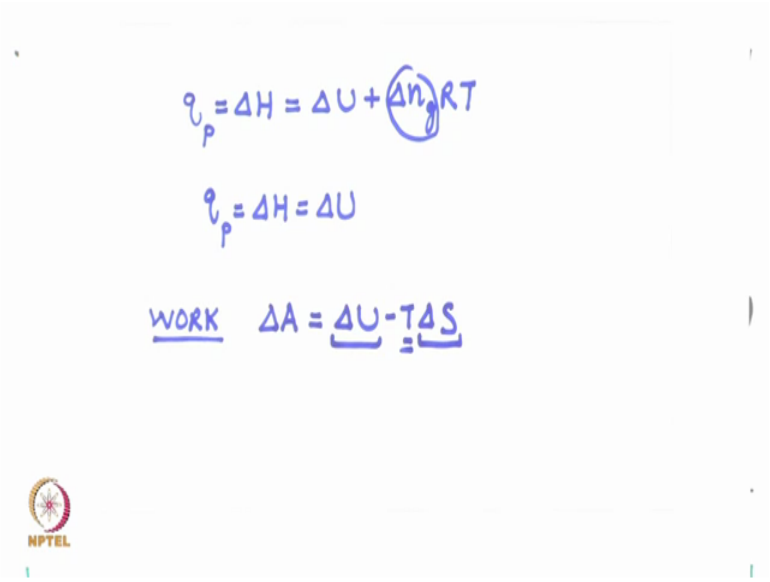

$$q_p = \Delta H = \Delta U + \boxed{\Delta n_g} RT$$

$$q_p = \Delta H = \Delta U$$

$$\underline{\text{WORK}} \quad \Delta A = \underbrace{\Delta U} - \underline{\underline{T}}\underbrace{\Delta S}$$

We have discussed several times now, that heat at constant pressure is equal to delta H and delta H can be calculated from delta U plus delta n g R T for a process which involves the changes in gaseous number of moles of the gaseous reactants and products. Let us take a look at the equation given to us relation given to us in this 6 moles of oxygen produce 6 moles of carbon dioxide. So, delta n g is equal to 0 since delta n g is equal to 0 q p is same as delta H and it is same as delta U.

Let us take a look at the slide since delta n g is equal to 0 therefore, the heat at constant pressure is equal to minus 2808 kilo joules that is the value of delta U which is given to us. Next is work and the question does not specify you calculate pressure volume work or you calculate non pressure volume work it is asking us to calculate work. When we have to calculate work inclusive of both pressure volume and non-pressure volume we have to act on a we have to calculate delta A, and delta A is equal to delta U minus t delta S at a constant temperature, since we know the value of delta U we know the value of delta S we know the value of temperature we can calculate the value of delta A immediately.

So, delta A will be equal to minus 2808 kilo joules minus substitute for temperature and substitute for the entropy change in kilo joules per kelvin, and the overall value we get is minus 2862 kilo joules. Now let us highlight an interesting observation here, the change in internal energy is minus 2808 kilo joule; however, the work maximum work which the system can do is minus 2862 kilo joules, 2862 is higher than 2808. So, this increased work comes because of the positive change in entropy, we have just discussed that if delta S is positive the maximum work available from system is greater than the value of delta U and that is what exactly you see over here and these are summarized into these conclusions that maximum work available is greater than the change in internal energy minus 2862 is greater than minus 2808, and what is the reason for this? The reason is the positive change in entropy that accounts for it and as we just discussed that if delta S is positive the system can draw in energy from surroundings in the form of heat and that heat can add up to the work.

So, the system can draw in energy from surroundings and make it available for doing work, and that is what is exactly seen in this numerical problem. So, what we have discussed in this lecture is discussion on Helmholtz free energy Helmholtz function which is also called the maximum work function or work function, we also discussed that what is the origin of using the term free and then we further discussed that the maximum work obtainable from the system can be greater than the changes in internal energy or it can be less than the changes in internal energy, depending upon whether the delta S for the system is positive or negative.

Thus the Helmholtz free energy helps a much more meaning than just a mathematical equation, first is the criteria of spontaneity d A at constant temperature and volume should be less than or equal to 0 and second the maximum work available from the system can be calculated from the changes in Helmholtz free energy that is delta A. We will further now discuss in the next lecture about the Gibbs free energy Helmholtz free energy and Gibbs free energy differ a little bit in their definition and the criteria of spontaneity also differs a little bit in the sense that when we discuss Gibbs free energy there the temperature and pressure are to be held fixed and those are the conditions which are much more widely used.

Thank you.