# Introduction to Chemical Thermodynamics and Kinetics
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## Lecture- 14
## Spontaneity and equilibrium – part 2

So, we discussed the properties of entropy, in the previous class. So, today we will continue along that direction and we will define the conditions for spontaneity and equilibrium.

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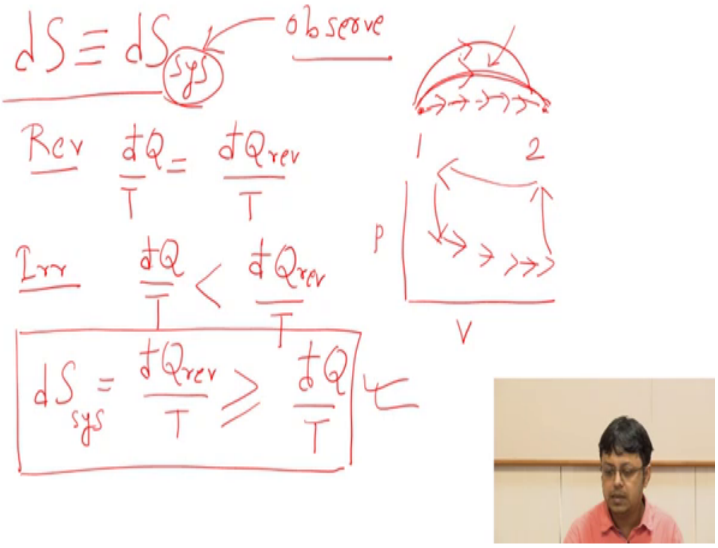

Now, remember that whenever I write d S or any differential change in entropy, from now onward we will consider these d S to be equal to the d S of the system only. We are not considering the d S of the universe; the reason is when you do an experiment, the focus is on the system not on the surrounding. We do some experiment in the surrounding so that, we make some changes in the system and we observe the system, as we make those changes. Now, also remember that for a reversible process, we will have d cross Q by T is nothing but d cross Q reversible by T, but if the process is irreversible, then the d cross Q by T associated with the system is actually less than d cross Q reversible by T.

So, by definition entropy d S, differential change in entropy, which is defined as the reversible heat change d Q reversible by T, must be greater than or equal to d cross Q by

T. Now, when I say d cross Q, it is the differential heat change associated with the process, if it is reversible, then d cross Q by T is nothing but d cross Q reversible by T, so that is equivalent to entropy.

However, if it is irreversible then, d cross Q by T is not equivalent to d cross Q reversible by T and what it means, we discussed that the reversible heat change between say, state 1 and state 2 can be brought in by many methods and if we consider an irreversible path, which is suppose this path, then the associated heat change is not equivalent to the reversible heat change. So, when you consider entropy, we have to consider an reversible path, which is associated between these 2 states. So, always keep that in mind that d cross d S is actually d cross Q reversible by T.

Now, this we proved starting from a discussion of how this, how basically we had a reversible path and then, if you remember from the previous class that we considered a cyclic process, which was just kind of reverse of our Carnot cycle and then from the argument we showed that these will always hold, that d S is always greater than equal to d cross Q by T and again remember that, we are now only talking about d S system, because, even if I do not write it that the d S will always mean that we are only looking at or observing the system.

Now, the question is, as I said that we have irreversible path which I have drawn here as a dotted line and then we have to consider a equivalent reversible path which is here, but there could be many reversible paths. Let us, try to understand this, but what it means is that for any reversible path, the value of d cross Q reversible by T has to be equal, because otherwise we will have a in consistency in the definition of entropy.

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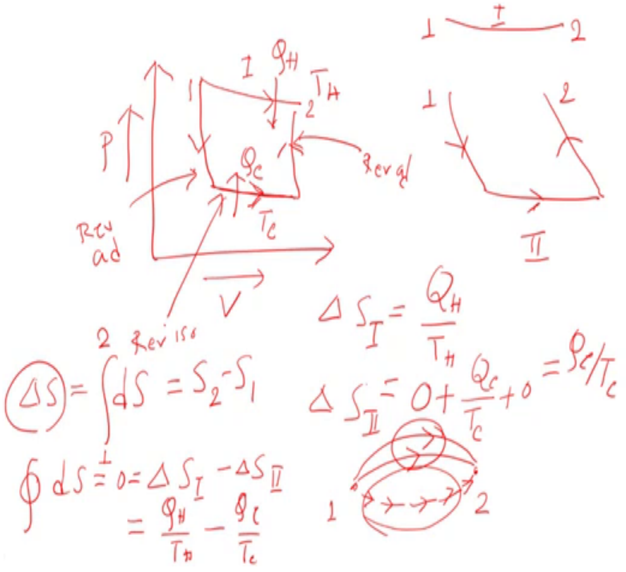

So, once again we are showing most of the things in the pressure volume diagram. Suppose, I have reversible path, which is say going from here to here, say state 1 to state 2. Now, or better actually considered this path, which is a state 1 to 2 and then let us call this process as process 1 and also imagine that we took Q H amount of heat during this transformation and this is typically an isothermal reversible transformation. Now, the question is, there could be other reversible paths as we just start with what could be the other reversible path, going from the same initial state which is state 1 to the same final state which is the state 2.

Now, you can consider another path, which is like this. This part is also reversible, because there is a reversible adiabatic, then there is a reversible isotherm and again will have a reversible adiabatic, so this enter path which is just like this, let us, de notice as path 2. So, basically we said going from 1 to 2, we have either a path like this, which we called as path 1 or there is a path which is like this, which is a also reversible, but it consists of 3 different sub steps, but that is also a reversible path.

So, the question is, are the heat changers similar? It has to be, because by definition the delta S or the final change in entropy, which actually we can get by going from a finite change in the integrating over finite path that will be nothing but S 2 minus S 1. So, whatever path we take as long as it is reversible, the associated heat will be d Q reversible by T and since entropy is a state function which does not depend on path, the associated heat change should be equivalent.

Now, you can easily figure that out because we already discussed it in slightly different argument we provided, when we were discussing the Carnot cycle. Now, you remember that for the path 1, if you calculate this quantity delta S, which will be nothing but Q H at say T H, suppose the temperature was T H and again, just think about that the temperature for the sink or the heat sink was T c. Now, see here that we are doing a reversible expansion here.

So, unlike Carnot cycle there will be a heat absorption, suppose this is Q c, now for the second step then delta S 2, which has actually 3 sub steps. So the first sub step is adiabatic. So, the entropy change will be 0 because heat changes is 0. Second one is, heat withdrawn from the surrounding is Q c, that will be divided by T c and then we will have again 0. So, a together we are having something like Q c divided by T c. Now, we can always construct a cyclic process, where we can say that the delta is 1 and then if we consider the reverse of delta S 2, which will make again the entire process as a cyclic process.

So, then we can always argue that this step has to be 0 because entropy is a state function and for any cyclic process, for any state function the value of the, at the end of the cyclic process the state actually is regained, so which means the associated change of that particular quantity will be 0, just like internal energy or entropy. So, we can always argue that, will have Q H by T H minus Q c by T c, which is equal to 0.

Now, we there is no surprise that we got it, because we already considered the Carnot cycle and similar expressions also appeared there, but the logic we are discussing right now slightly different. So, what we got just now is the entropy change for the first state, is exactly equal to the entropy state, entropy change in the second path. So, path 1 or path 2 as long as we considered the reversible path it does not matter which reversible path you choose.

So, in a nutshell what we just said is that we have 2 states, state 1 and state 2 and if you consider an irreversible path and ask this question, what is this entropy change? You have to consider a reversible path, which reversible path it does not matter because as long as it is reversible all the d cross Q reversible by T for all these family of paths will be same and you have to take that value, to define entropy. However, the heat change associated with this path will always be less than d cross Q reversible by T, but that quantity d Q by T, d cross Q by T is not necessarily entropy. If it is reversible it is equal to entropy, if it is irreversible it is not equal to entropy.

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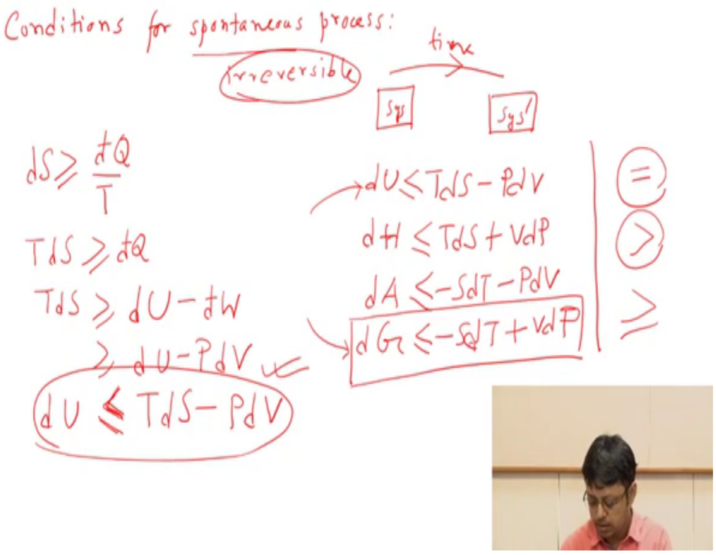

Conditions for spontaneous process:

irreversible

$dS \geq \frac{đQ}{T}$

$TdS \geq đQ$

$TdS \geq dU - đW$

$\geq dU - PdV$

$\boxed{dU \leq TdS - PdV}$

$dU \leq TdS - PdV$

$dH \leq TdS + VdP$

$dA \leq -SdT - PdV$

$\boxed{dG \leq -SdT + VdP}$

Now, let us move on and then try to understand, what are the possibilities or conditions for spontaneity or conditions for having spontaneous process. Now, spontaneous process means actually it is just spontaneous, it happens all by itself. So, there is no driving force required for that. Now, all spontaneous processes which means are must be irreversible in nature, which we discussed that by irreversibility we mean there is a arrow of time. So, at a earlier time the system was in some state and then the system is evolving as the time progresses to a new state and then this is irreversible in the sense that it cannot be reverse back because it is a and it happens spontaneously. So, spontaneous process by the definition is an irreversible process.

Now, let us understand what are the conditions for spontaneity, we already have it that this d S, remember it d S of the system must be greater than equal to d cross Q by T. Now, we can rewrite it, we already wrote it in different fashion. Like, you can write it in T d S is greater than equal to d cross Q. So, the greater than sign means it is a spontaneous process and equal to means it is a under equilibrium, which means it is a reversible process when the system is in equilibrium. Now, you can write that d cross Q as d U plus d cross W as before and we showed that, if you write it in that way T d S will be nothing but, remember that from the first law d U is d cross Q plus d cross W. So, d cross Q is nothing but d U minus d cross W.

So, we see that we can actually for a reversible process also further write the work as a pressure volume work and we can write it as a P d V for any process not only reversible or P opposing T V. Now, notice here that what do, the way you are writing is, if I move the d U on the left hand side, will have d U is less than equal to T d S minus P d V.

Now, if you remember we wrote series of equations, there are total 4 equations. One for U, one for H enthalpy, one was for A help of energy and one was for G, which is gives energy and we wrote equal sign. All these energies, when you write it in terms of equal sign that means, actually these are the conditions of equilibrium and similarly you can have, this conditions for spontaneity, where we will write it as the less than sign. So, this is basically the condition for spontaneity and equilibrium written together.

So, all these equations will be slightly modified in the sense that, you will have d U is less than equal to T d S minus P d V. So, all the equal sign you can discover later, how it comes. So, you have to just follow from this fundamental equation and then you can build up all other equations as we showed in the last class and d H will be nothing but T d S plus V d P, similarly d A will be nothing but minus S d T minus P d V and d G will be nothing but minus S d T plus V d P.

So, yesterday we wrote everything as equal sign, which is one stands for equilibrium and today this greater than sign stands for the spontaneous process, so just writing it together, the condition for spontaneity and equilibrium. Now we will examine one by one, particularly we will start with this one, but we will see that the most important equation is which is very important for chemist, is perhaps the equation for the Gibbs free energy and we will have a slightly more discussion on the Gibbs free energy. Now, let us start with the equation for d U.

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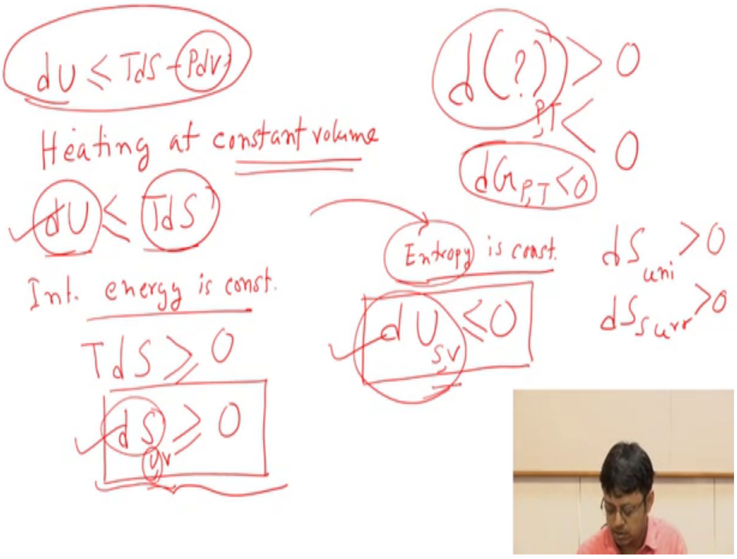

Now, as we see that, what we have is for the condition of spontaneity is d U is less than equal to T d S minus P d V. Now consider heating at constant volume. So, when you heat a substance, whichever substant it is, be it gas, liquid or some solid. So, what are the conditions that will happen, that will make the system or the transformation spontaneous? Of course, we know that the temperature of the system will increase. Now, if we consider constant volume and I am supplying heat, so the condition can be further reduced since the volume is constant d V will be 0.

So, this is the condition, now think about it. What is d S? d S we already know that for, this is basically the change in entropy. Now, think about one step further, if we have not only constant volume, we have also imposing that the internal energy is constant. So, if we make this condition energy or better to write it as internal energy is constant.

So then, we will have the condition that d U is 0, which means the condition for spontaneity will be d S greater than equal to 0 or d S is greater than equal to 0 because temperature is constant, for constant U because we already made 2 constraints, one is energy is constant and we had earlier, made another constant that volume is also constant.

So, this is one of the equations for our conditions for spontaneity, when both the energy and the volume are kept fixed. Similarly, you can also argue that if I kept the entropy fixed, entropy is constant then this term is 0 then the condition will be d U is less than equal to 0 under what condition constant entropy and constant further.

So, we will see that similar equations will be very necessary, where we are keeping the internal energy constant and volume constant. Now, this will be the conditions for this particular 2 constant, constant volume and energy, but usually when you make a transformation, you do not keep the internal energy or volume constant. Suppose, usually suppose we are doing a transformation at constant pressure and temperature.

So, this is an usual condition for chemist, like when you, for example, boil water and you keep the temperature constant because it is suppose being heated at 100 degree centigrade and the temperature does not change as long as water is water vaporizes and suppose we are doing it at 1 atmosphere, so the pressure is also not changing.

So, we have to make a condition of some quantity, we do not know it yet, which will be greater than or less than 0 and we need to find out these conditions at constant pressure temperature how the system behaves. Now, we have to define this quantity and we will figure out that actually, the conditions will be given by the Gibbs free energy at constant pressure and temperature should be equal to the less than 0 that will be the condition for spontaneity.

So, what I am trying to say here is that, the internal energy keeping it fixed and volume keeping it fix is not a natural choice for experiment. Whenever you do experiments, probably pressure and temperature are the 2 conditions that you can kept keep constant, but then if you keep pressure and temperature constant d S greater than equal to 0 is not a condition for spontaneity and equilibrium. You will, you have to have some other equation that we will discuss and will discover that Gibbs free energy is the condition. Now just like we had d S and d U for constant energy and volume and constant entropy and volume, we can also start with the equation for d H in the similar way like we started with the equation for d U and let us see what we get out of it.

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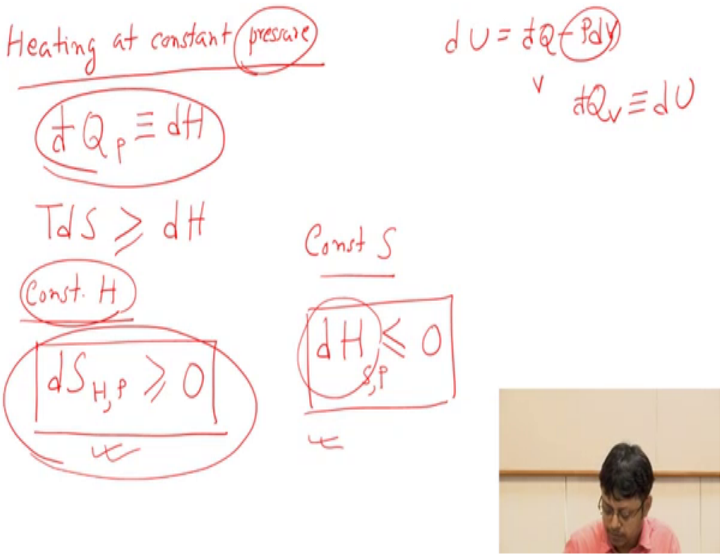

So, if you start with the d H equation, let us consider as before that we are heating a substance at constant pressure. Now, we started with the equation that d U is d cross Q minus P d V and we met the constant volume process to make this 0, but we could have just directly argued that at constant volume d cross Q at constant volume is nothing but d U. We already discussed it, when we discuss the processes like d U is c V d T plus del U del V T, d V when we discussed all those nice mathematical formulation, we discussed this one. Similarly, we know that if a constant pressure process happens, that d cross Q at constant pressure is nothing but enthalpy.

You can actually test it by using the same equation and then in the enthalpy equation d H you have a P d P term and you are just making the d P to be 0. So, that is the condition, but we are just making a direct argument here. Now, what it means is that, we have the same condition that T d S must be greater than equal to d H for a spontaneous or equilibrium process written together.

So, what we have again as before we can make the 1 constant same, say for example, we are saying that at constant entropy what happens or before that maybe we can first ask at constant enthalpy what happens. As before you can discover that for constant enthalpy as well as constant pressure because we have made 2 constant 1 is constant enthalpy, the other one is constant pressure.

So, what we see here is that, if we make those 2 conditions together, so the spontaneity or equilibrium is given by this equation and as before if we make it as or do the transformation at constant entropy then the condition for spontaneity and equilibrium are given by d H less than equal to 0, where the transformation were happening at constant entropy and pressure.

Now, let us try to understand, what does these quantities mean physically? Now, let us go back one step, we first said that this is a condition for equilibrium at constant energy and following. Now, this is not surprising. Suppose, you are heating a process, you are heating a substance in the process and you are doing this transformation at constant volume, what does it mean? So, if you keep the volume constant and if you supply heat, the temperature of the system will increase of course, and if you keep the internal energy also fixed then the entropy of the system must increase, so there is no surprising. Now, this one, when the entropy is constant and then we see that the d U is less than equal to 0 is the condition.

Now, for a spontaneous process, it means that the internal energy dropping down is a spontaneous process, which does not really make sense. Now, the explanation for this is just like that you are heating a substance and then you are not allowing the entropy of the system to drop down, then you know that the condition; the global condition for the spontaneity is delta S system must be greater than 0.

So, if the systems entropy is constant, sorry this for the global entropy we have the delta s universe must be greater than equal to 0. If we keep the systems entropy constant, that means the surroundings entropy must be greater than 0 and in order to make the surrounding entropy more, the system should supply energy to the surrounding, which means the energy of the system should drop down. So, that is the meaning of this process.

Similarly, if you ask this question if I have a constant enthalpy process at a constant pressure, it is not surprising that the spontaneity is given by d S greater than 0, the entropy of the system must increase and similarly if we keep the entropy of the system constant and ask about the spontaneity, then the surrounding entropy must increase. Then heat should flow from the system to the surrounding at constant pressure, which is nothing but the enthalpy and the enthalpy of the system should decrease.

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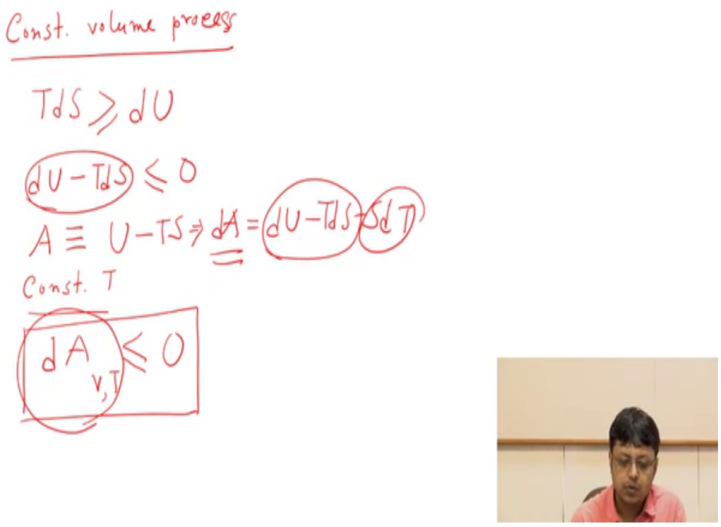

Const. volume process

$TdS \geq dU$

$dU - TdS \leq 0$

$A \equiv U - TS \Rightarrow dA = dU - TdS - SdT$

Const. T

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

Now, let us consider the 2 other situations, where we have to write something based on the Helmholtz energy and the Gibbs energy. If you look at the equations for Helmholtz energy and Gibbs energy, the natural condition for the first one, which is the Helmholtz free energy, is that we have to keep the volume constant. Now, if you consider our constant volume process, then we naturally see that the condition for spontaneity and equilibrium written together is this or d U minus T d S, is less than equal to 0 or now if we remember that A of the Helmholtz energy, was defined as U minus T S.

So, we can just write at say constant temperature or basically here will have d A is nothing but d U minus T d S minus S d T or we can make this term to be 0 at constant temperature. So, this term d U minus T d S is nothing but d A. So, you can write that d A is less than equal to 0, if the process happens at constant volume and constant temperature. Now, constant volume and temperature are 2 natural choices. So, in many cases we will keep the volume to be constant and then keep the temperature also constant and suppose we can heat up a system or do something else, where the relevant quantity to look at for spontaneity will be d A, just keep that in mind and similarly we could also get another equation for constant pressure process.

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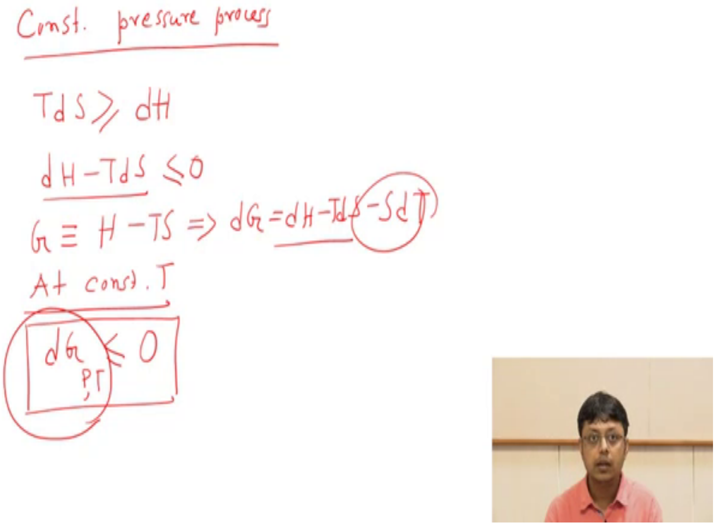

Const. pressure process

$TdS \geq dH$

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

$G \equiv H - TS \Rightarrow dG = \underline{dH - TdS}\,\boxed{-SdT}$

At const. T

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

Where we can actually right away use these other equation, where we wrote that constant pressure means, remembered it will be greater equal to d H because Q P is nothing but a d cross Q P is nothing but d H and then d H minus T d S is less than equal to 0. Now, as before we can write G as H minus T S that was the definition of Gibbs free energy, which will give us d G is nothing but d H minus T d S minus S d T following the chain rule, again we can make this term to be 0, you are further assuming at constant temperature this term is 0. So, d H minus T d S, this term which is d G is less than equal to 0 for constant pressure and temperature.

So, these 2 equations one is d A is less than equal to 0, d A at constant volume temperature less than equal to 0 and d G at constant pressure temperature less than equal to 0 are more natural choices for describing spontaneity. Now, if you try to remember all this thing, if you go back one step and remember that we had all these 4 equations.

Now, the conditions for spontaneity if you want to impose, if you use the first equation remember that I have to get d S constant and d V constant then only I will get d U less than equal to 0, it directly follows from this equation. Similarly, for d H less than equal to 0, I have to keep d S and d P constant, but usually those are not natural choice that you had in experiment. Natural choices in experiment are pressure temperature volume those you can keep constant, you can either keep temperature and pressure constant or you can keep temperature and volume to be constant.

If you keep the temperature and volume to be constant, then your condition is d A is less than equal to 0 and if you keep the temperature and pressure to be constant, then your condition for spontaneity is d G less than equal to 0. When I say less than equal to and say spontaneity, it means that it is spontaneity and equilibrium together, if you consider only spontaneity it will be less then.

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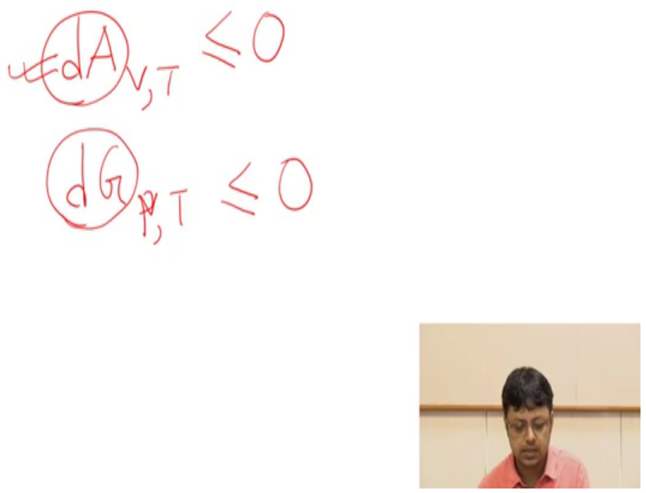

$$(dA)_{V,T} \leq 0$$

$$(dG)_{P,T} \leq 0$$

So, now we have 2 useful relations, one is d A at constant volume and temperature less than equal to 0 and the other one is d G at constant pressure and temperature should be equal to 0. So, whenever we are considering or whenever we will consider constant volume temperature process we will look at what is the associated change in Helmholtz free energy, whenever we look at a constant pressure temperature process we will look at what is the associated change in Gibbs free energy.

Now, let us move on and try to understand what these Gibbs free energy and Helmholtz free energy is all about. Now to understand that, let us try to understand first what is d A? What is the physical significance of d A? What is, what does it mean?

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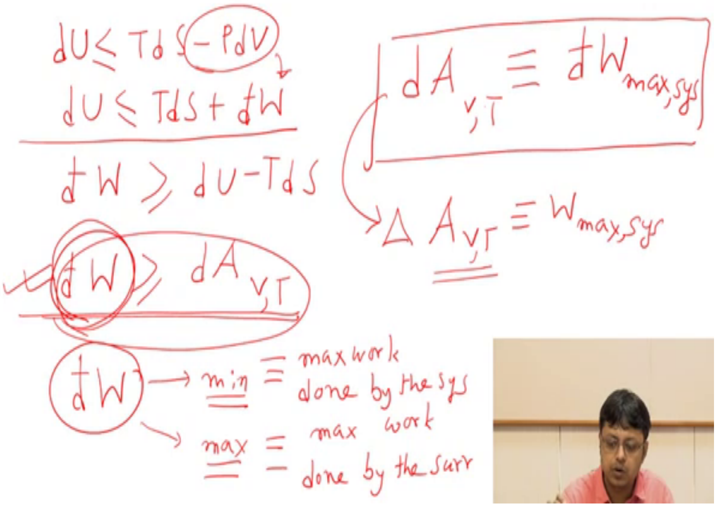

Now, you can easily get a very nice equation for that. We can again start from d U is less than T d S minus P d V, but instead of writing it P d V you can always write it as the original equation, which was T d S plus d cross W, where d cross W is some kind of work and the we know what is this work, it is a pressure volume work.

So, we could write that d cross W as greater than equal to d U minus T d S, but we know that this d U minus T d S is nothing but d A at constant volume and temperature and of course, this will be applicable for any change, but we will consider only the equality sign right now, because we are just considering the maximum or minimum amount of work.

Now look at this equation, what does it mean? So, we wrote that d cross W, which is the work done is greater than or equal to that change in Helmholtz free energy at constant volume temperature. Now, what it exactly means is that I can have some work done and by definition the work done means here the work done by the system will be negative and work done by the surrounding will be positive.

So, if the work done can be it is saying this equation like the magnitude of the work done can be equal to d A or it can be more. So, what it means is that the minimum amount of work that we can get is d A. Now, what is the minimum amount of work? Minimum amount of work means this change.

Now, we have to consider the work done by the system, because remember for system it is a negative work, if the system works. So, if the system works in a maximum way d cross W will be, minimum, because it is a negative work. If the surrounding does maximum work, so then d cross W will be maximum. So, from system perspective this is equivalent to maximum work done by the system and this is nothing but the maximum work done by the surroundings.

So, since, from this equation we get the minimum value of d cross W, we can argue that this d cross W is nothing but or if I write it in the other way that ds d A at constant volume temperature will be equivalent to the maximum work done by the system. So, what we just discovered that this Helmholtz free energy at the differential change in the Helmholtz free energy is equivalent to the work done, by the differential work done by the system at the maximum differential work done by the system.

We could also use just remove the differential notation and we could just write that this Helmholtz free energy is nothing but the maximum work done by the system. Remember, it is always we are saying that it is by the system.

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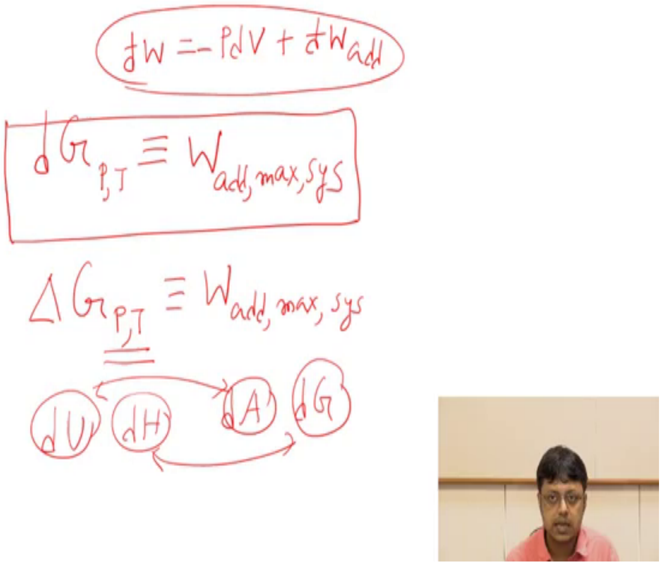

So, similarly you can figure out that these other differential which is d G, just like here we had the maximum work done, but remember this work is, what kind of work? It is the pressure volume work because instead of minus P d V we wrote d cross W, but there could be other non P V work, which is known as non pressure volume work. For example, suppose electrons are flowing in a circuit. So, that will cause electricity and that involves and a finite amount of work. So, that work will be the non pressure volume work and you can write these d cross W as some P d V term, which is always negative P d V because of our convention plus some additional work, which I am writing as d cross W additional and then you can easily show if we just write the total work done as like this and if you start from the same equation which we started with d U is T d S plus d cross W and use the fact that H is G minus d S and write it in terms of the differential notation.

Then, you will discover that this d G at constant pressure temperature, remember that when you write as A, the natural choices are constant volume temperature, but when you write anything in terms of say, the Gibbs free energy, the natural choices are constant pressure temperature and that will be nothing but the maximum additional work done by the system.

So, that is kind of physical interpretation that we have, that the Gibbs free energy, corresponds to the maximum additional work, but the non P V work that the system can do. So, again I refine my statement, the maximum non P V work done by the system will be equivalent to the Gibbs free energy at constant pressure temperature because this is very important. Similarly, the maximum P V work which is done by the system is can be related to the Helmholtz free energy at constant volume and temperature.

Now, usually when this notation stands for we have to use a delta sign here because we are considering a finite chain and we do not use any delta sign here because it is a inexact differential. Similarly, we can use actually at delta G sign here, because it is also an exact differential. Now, why it is exact and inexact differential? You can easily figure that out because we wrote that they are all connected to d U and d H, which were actually all exact differentials and similarly you can also argue from the connection of d U and d H, that d A and d G are also exact differentials.