

Chemical and Biological Thermodynamics: Principles to Applications
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Lecture - 10
Third Law of Thermodynamics

Today we will discuss third law of thermodynamics; it is very important law because it talks about the entropies at absolute 0. At T equal to 0 Kelvin the thermal motion of all pure crystals is quenched; that means, there is an absence of thermal motion and special disorder. This suggests that the entropy of perfectly crystalline substances at absolute 0 should be 0 and this also coincides with the statistical definition of entropy S is equal to $k \log w$ that if there is only one arrangement in which the crystal can be arranged at absolute 0 w is equal to 1. So, S is equal to $k \log 1$ equal to 0. So, is it that all the substances have entropy at absolute 0 equal to 0 or not, we will further discuss here in this lecture.


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Third Law of Thermodynamics

If the entropy of every element in its most stable state at $T = 0$ is taken as zero, then every substance has a positive entropy which at $T = 0$ may become zero, and which does become zero for all perfect crystalline substances, including compounds

Third-Law entropies: Entropies based on $S(0) = 0$ are called Third-Law entropies or often just entropies

Standard reaction entropies :
$$\Delta_r S^\circ = \sum_J \nu_J S_m^\circ(J)$$



MOOCs 2

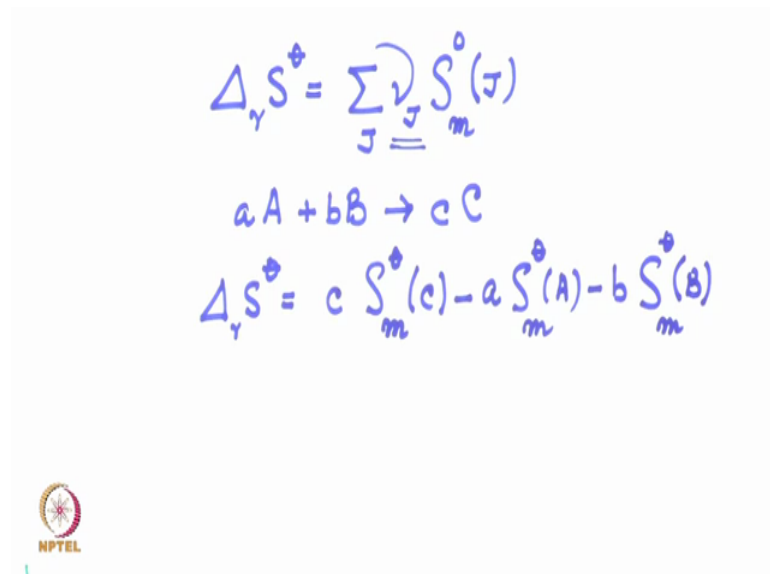
Let us look at the formal definition of third law of thermodynamics. It states that if the entropy of every element in its most stable state at T equal to 0 is taken as 0 then every substance has a positive entropy which at T equal to 0 may become 0 and which does become 0 for all perfect crystalline substances including compounds. And the entropies which are based upon $S(0) = 0$ or called third law entropies or we just often call

them entropies. Now you see by this definition we say that at absolute 0 all perfectly crystalline substances including compounds have entropy equal to 0.

In fact, the third law does not say that the entropy of all perfectly crystalline substances is equal to 0 at absolute 0 it should be interpreted in this way that the extent of order in all perfectly crystalline substances at absolute 0 is same, and by taking this value equal to 0 is just a matter of convenience. That is why for all the perfectly crystalline substances we set S_0 equal to 0 and in the previous lecture you remember that we discussed how to get the temperature dependence of entropies. And we also discussed that the entropy at any temperature can be calculated if we have the information on the value of S_0 and if we set S_0 is equal to 0 then the entropies based upon this are called third law entropies.

How do we get standard reaction entropies? Standard reaction entropies can be calculated from this expression that is $\Delta_r S^\ominus$ this r subscript signifies reaction. Sometimes you know many books write r many books do not write r. So, do not get confused. The reaction entropies or change in entropy during a reaction can be calculated from this expression $\sum_J \nu_J S_m^\ominus(J)$, where J is the species J and ν_J is the stoichiometric coefficient. How to interpret this?

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What we just discussed that the reaction entropies is equal to summation $\sum_J \nu_J S_m^\ominus(J)$ of species J. Suppose my reaction is a moles of A are reacting with b moles of B and producing c moles of C then according to this equation $\Delta_r S^\ominus$ will be equal

to, I expand this stoichiometric coefficient is positive for products and negative for reactants. So, c is a product which is therefore, it will be positive; that means, c times molar entropy of C and now I will use negative for the reactant - minus a times molar entropy of A minus b times molar entropy of B. This is how to interpret this or this is how to expand this summation.

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- ▶ World record low temperature is of the order of pico Kelvin
- ▶ Gases can be cooled by Joule Thomson expansion below their inversion temperature
- ▶ 4 K can easily be achieved (boiling point of He)
- ▶ 1 K can be achieved by pumping He through large temperature pipes
- ▶ Below this temperature, volatility of He is low and its superfluid phase begins to interfere with the cooling process
- ▶ The method used to reach very low temperature is Adiabatic Demagnetization

NPTEL MOOCs 3

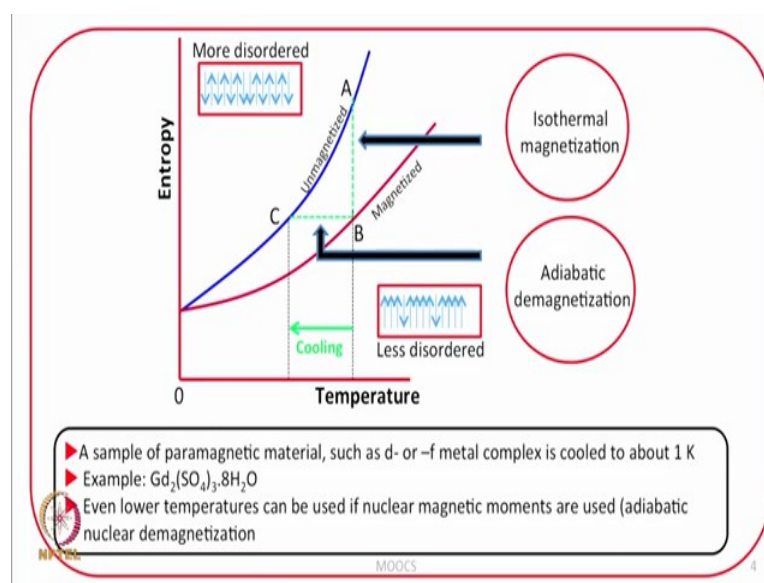
Now, let us discuss the technological applications of entropy. There are several technological applications of entropy and several applications of the information that is coming out from the change in entropy, but let us discuss first of all one example. Let me ask a question first what is the world, what is the value of the world record lower temperature ever achieved by anyone. The answer is that scientists have been able to achieve temperature as low as of the order of pico Kelvin, pico Kelvin means standard stood power minus 12 Kelvin. How does one achieve? Entropy has a large role to play here. So, let us discuss how to achieve this low temperature.

Gases can be cooled by Joule Thomson expansion below their inversion temperature that we know, helium can be used the boiling point of helium is 4 Kelvin therefore, by evaporating helium one can easily achieve temperature down to 4 Kelvin. Now if you evaporate helium by pumping through large diameter pipes then helium will absorb energy from the pipes whatever material is used and it will produce cooling. Temperature

down to one Kelvin can be produced by this method, by evaporating helium through or by pumping helium through large diameter pipes.

Below this temperature that is below one Kelvin the volatility of helium is very low and its super fluid phase begins to interfere with the cooling process and therefore, you cannot achieve a temperature below 1 Kelvin by pumping helium through large diameter pipes. Therefore, what method is used? The method which is used to achieve very low temperature is called adiabatic demagnetization process. Let us discuss what is adiabatic demagnetization process. We just discussed that every substance has positive entropy; the entropy surely will depend upon the temperature because if the temperature is increased the extent of disorder will also increase. So, usually when the temperature is increased the entropy also increases.

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Let us take a look at a blue line in this figure. As the temperature increases, so this is a plot of entropy versus temperature. So, with increase in temperature the entropy is increasing in a non-linear fashion. So, what is done is a substance which has large number of unpaired electrons which is also called a paramagnetic substance is taken the example of such a substance is gadolinium sulfate octa hydrate or one can usually take sample which is paramagnetic materials usually will be from d or f block metal complex and we just discussed that how to achieve a temperature of about 1 Kelvin.

So, let us say we take this sample like gadolinium sulfate octa hydrate and plot its entropy against temperature this is the behavior this is the variation. And there are large number of unpaired electrons, so paramagnetic substance. When this substance is subjected to magnetic field what is the effect of magnetic field on paramagnetic substances. More electrons will align in the direction of the magnetic field. So, if by the application of magnetic field more electrons get aligned along the field, more alignment, more alignment means what? More alignment means the order is increasing if the order increases the entropy decreases; that means, for a magnetized sample this will be the behavior of entropy the redline, the entropy is lower than the unmagnetized sample at any point. This curve is for a magnet as unmagnetized sample and this curve is for a magnetized sample.

So, what is done is the substance is cooled to about 1 Kelvin let us say we start with the point a from the point A and then let the substance be surrounded by helium gas which will act as a thermal contact between the sample and the cold sink. Under isothermal conditions turn on the magnetic field, isothermal condition means which the temperature has to be constant you see here the temperature should remain constant and when you turn on the magnetic field the corresponding point on the magnetized curve you know or the curve corresponding to magnetized sample is B. Initially the entropy was corresponding to point a where the magnetic field is turned on the entropy decreases and the corresponding point on the magnetized sample entropy temperature curve is B, and this vertical line means temperature is remaining constant and then temperature is kept constant by means of having helium gas surrounding the sample which I just said is acting as a thermal contact with the cold reservoir.

The second step B to C means you turn off the magnetic field very slowly in a reversible manner, I repeat switch off the magnetic field very slowly in a reversible manner under adiabatic conditions that is what is called adiabatic demagnetization. You recall the clausius inequality dS is greater than or equal to dq by T .

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The image shows three handwritten equations in red ink. The first equation is $dS \geq \frac{dq}{T}$. The second equation is $dS = \frac{dq_{rev}}{T}$, with a red arrow pointing from the dq_{rev} term to the dq term in the first equation. The third equation is $\underline{\underline{dS = 0}}$. In the bottom left corner of the slide, there is a small circular logo with a star and the text 'NPTEL' below it.

Now, if I under adiabatic demagnetization if the process is reversible then I will have to use equal to sign it is dq reversible by T process is reversible and since the process is adiabatic the value of dq is equal to 0. That means, the entropy of the system should not change, there is no change in entropy of the system. So, if there is no change in an entropy then it should be horizontal here, the dependence should be horizontal, B C corresponds to no change in entropy.

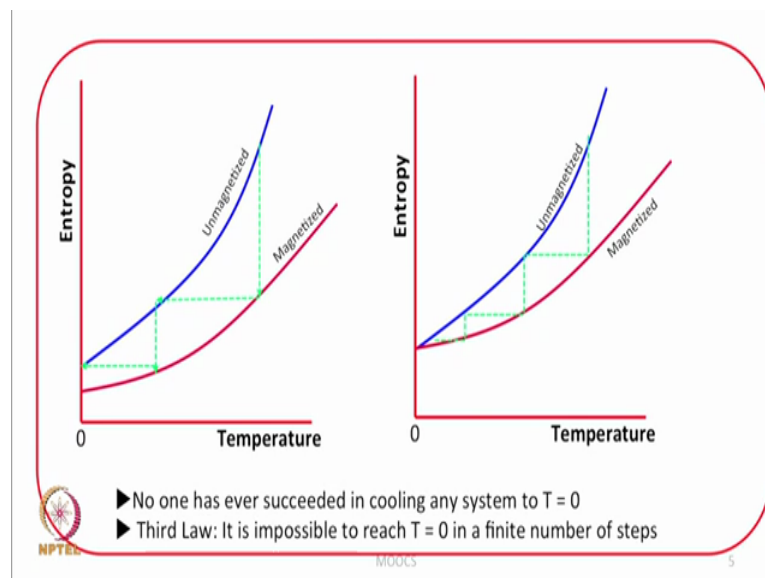
The corresponding point now on the unmagnetized sample curve is C. A to B was isothermal magnetization process, and B to C is reversible adiabatic demagnetization process and since there is no entropy change the path followed will be from B to C. Now if you carefully examine what has happened from B to C it has led to cooling the temperature has changed towards lower temperature. So, you see this one cycle of A to B and B to C has led to lowering of the temperature. And if we repeat this cycles we will keep on moving towards lower and lower temperature, this is how the adiabatic demagnetization process is used to achieve low temperature.

Remember that the kind of temperature low temperatures that I talked about the pico Kelvin is actually achieved by using the nuclear magnetic moments rather than the electronic magnetic moments. So, that is why the comment mentioned here is that even lower temperature can be obtained if nuclear magnetic moments are used that is process

then will be called adiabatic nuclear demagnetization process that is instead of the using the magnetic movements of electrons we use that of the nuclear.

So, a natural question that can arise from this discussion, let us again look at this figure that if you repeat this kind of A to B, B to C kind of processes we will keep on going towards lower and lower temperature will we be ever able to achieve 0 Kelvin by repeating this isothermal magnetization and then followed by adiabatic demagnetization process. Let us take a look at.

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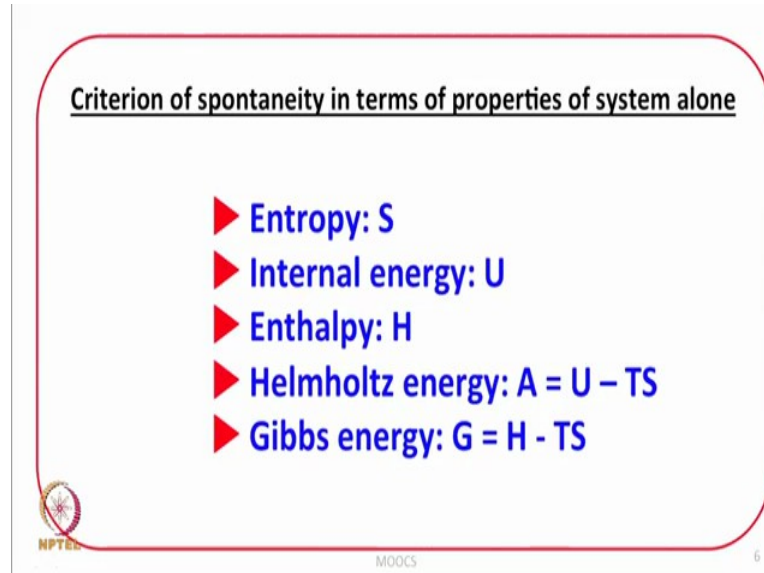


First let us take a look at the figure on the left hand side. According to this figure you see the cycles isothermal magnetization adiabatic demagnetization, isothermal magnetization adiabatic demagnetization. Yes we should be able to achieve absolute 0 provided the temperature entropy versus temperature curves are like this which do not coincide at absolute 0, but this is a violation of the third law of thermodynamics.

The third law of thermodynamics says that for the pure crystalline substances we should get coinciding entropy temperature curve at absolute 0. In such a case you can never achieve absolute 0 in a finite number of steps and this is formulated, in the form of another law, this is formulated in the form of an alternate form of third law which says that it is impossible to reach absolute 0 in a finite number of steps. In other words we can say that no one has ever succeeded in cooling any system to absolute 0. So, the third law can be expressed in terms of entropies that entropy at absolute 0 is equal to 0, as we just

discussed for perfectly crystalline substances in an alternate form this which is also sometimes use that it is impossible to reach absolute 0 in a finite number of steps.

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Criterion of spontaneity in terms of properties of system alone

- ▶ Entropy: S
- ▶ Internal energy: U
- ▶ Enthalpy: H
- ▶ Helmholtz energy: $A = U - TS$
- ▶ Gibbs energy: $G = H - TS$

NPTES MOOCs 6

So, we have now discussed a lot about the entropy. We discussed that the criteria of spontaneity in terms of second law of thermodynamics is that the entropy change in the system plus entropy change in the surrounding should be greater than 0. So, if we strictly follow the second law to understand the spontaneity of a process we will have to calculate the entropy change in the system, we will have to calculate the entropy change in the surrounding add up the two and then see the outcome. But can we derive criteria of spontaneity in terms of properties of system alone where we do not have to worry about calculations in the surroundings. Surroundings will be connected or will be inbuilt in our calculations anyway, but let us discuss the criteria of spontaneity in terms of properties of system alone and at the same time we will also defend those criteria of spontaneity in terms of the second law of thermodynamics also and prove that yes those criteria of spontaneity also obey the second law of thermodynamics. Let us move towards that.

We will derive criteria of spontaneity in terms of entropy alone entropy of the system alone we will not worry about entropy of the surrounding. We will also derive in terms of internal energy enthalpy. Let me introduce another term it is called Helmholtz energy defined by or designated by the symbol A letter A this is equal to U minus TS and the Gibbs energy G this is the symbol used or letter use for Gibbs energy G is equal to H

minus $T S$. You know many times we ask this question that can you define Helmholtz energy, how do you define Gibbs free energy. There should be no confusion in the definition.

The definitions of Helmholtz energy or Gibbs energy are simply for Helmholtz energy A is equal to U minus $T S$ and G is equal to H minus $T S$. U , T , S are all the thermodynamic properties of the system. G , H , T , S are all the thermodynamic properties of the system right. So, therefore, if someone asked that can be define Gibbs free energy or Gibbs energy the answer should be G is equal to H minus $T S$. Now let us derive the criteria of spontaneity it is very easy.

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The image shows handwritten mathematical derivations in red ink on a white background. At the bottom left, there is a small circular logo with a star and the text 'NPTEL' below it.

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

$$T ds \geq dq$$

$$T ds \geq dU \dots \text{Const. } V$$

$$\underbrace{(ds)_{U,V} \geq 0} ; \quad \underbrace{(dU)_{S,V} \leq 0}$$

I will start by the clausius inequality which says that dS is greater than or equal to dq by T . Let me rewrite this in this form $T dS$ is greater than or equal to dq . If I keep the volume constant then you know that heat supplied at constant volume is equal to dU we have discussed it earlier. Now this inequality gives rise to two criteria of spontaneity. The first criteria of spontaneity will be dS at constant U and V will be greater than or equal to 0 , if you fix internal energy dU is equal to 0 right, constant U and constant V if I fix U and V then dS should be greater than or equal to 0 .

The second criteria of spontaneity is dU , now I fix the entropy if I fix the entropy dS will be 0 . So, entropy and volume anyway we have held constant should be less than or equal to 0 . You see we have derived two criteria of spontaneity from here one is dS is constant

U and V should be greater than or equal to 0 and the second one is dU at constant S and V should be less than or equal to 0. Please note that here we are only talking about the system we have nowhere talked about the surroundings, that is why we call these as the criteria of spontaneity in terms of the properties of system alone. But you know any criteria has to also obey the second law of thermodynamics. Do these derived criteria obey the second law of thermodynamics let us see.

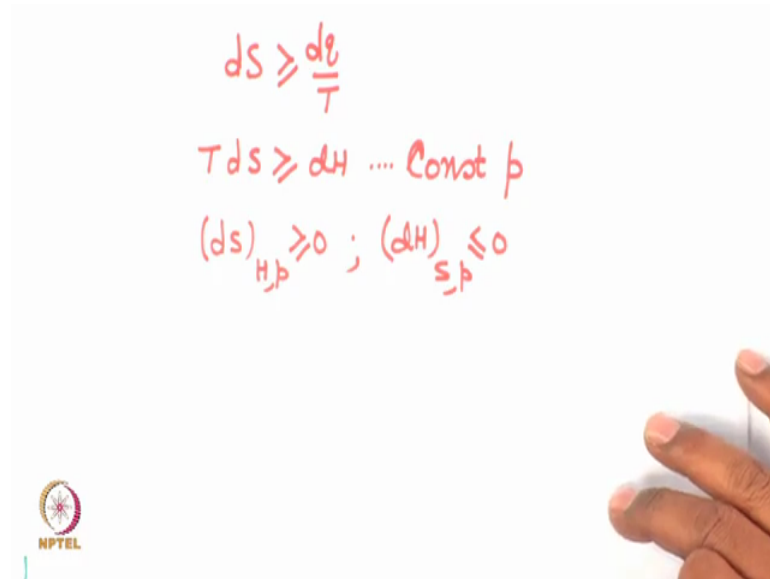
Let us now take a look at this criteria of spontaneity. According to this criteria of spontaneity you fix the internal energy, you fix the volume the entropy of the system must increase during a spontaneous process. See equal to sign is applicable for reversible process and if as the process is spontaneous we use greater than sign. So, according to this the entropy of the system must increase during its spontaneous process which is actually the content of the second law of thermodynamics. So, it does obey the second law of thermodynamics.

On the other hand for this criteria of spontaneity according to this if the entropy of the system is held fixed and the volume is held fixed then the internal energy of the system must decrease. I repeat if the entropy is held fixed then the internal energy of the system must decrease, according to this criteria if ΔS system is 0 if the entropy of the system is held fixed means ΔS for the system is 0, then according to second law the ΔS of surrounding must increase and that is what is seen in this criteria of spontaneity.

The decrease in internal energy will enter the surrounding in the form of heat and will generate more disorder in the surrounding. So, this criteria of spontaneity is to be viewed as the entropy of the system is remaining constant therefore, for the process to be spontaneous the entropy of the surrounding must increase. How it will increase? Some of the internal energy must decrease in the form of heat to enter the surrounding and hence generate some disorder there. So, you see that although we are writing these criteria of spontaneity in terms of properties of system alone, it is automatically connected with the surrounding and these criteria of spontaneity are obeying the second law of thermodynamics.

Let us derive few more criteria of spontaneity.

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$$dS \geq \frac{dq}{T}$$
$$T dS \geq dq \dots \text{Const } p$$
$$(dS)_{H,p} \geq 0 ; (dq)_{S,p} \leq 0$$

The image shows a whiteboard with handwritten equations in red ink. The equations are: $dS \geq \frac{dq}{T}$, $T dS \geq dq \dots \text{Const } p$, and $(dS)_{H,p} \geq 0 ; (dq)_{S,p} \leq 0$. In the bottom left corner, there is a circular logo with a star and the text 'NPTEL'. A hand is visible on the right side of the whiteboard, pointing towards the equations.

Once again I start with the same definition dS is greater than or equal to dq by T , and $T dS$ is greater than or equal to dH here I will put the pressure constant because dq at constant pressure is equal to dH and here the criteria of spontaneity will be dS at constant H and p should be greater than or equal to 0 and dH at constant S and p should be less than or equal to 0 by the same arguments that we discussed earlier. And the interpretation is also similar that here according to this criteria if you fix the enthalpy the entropy of the system must increase that is the content of the second law, and here in the second criteria here if I fix entropy some of the enthalpy must decrease, the enthalpy of the system must decrease and enters the surrounding in the form of heat to generate enough disorder. So, that $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$ is positive.

So, this is criteria number three, this is criteria number four. We will derive two more criteria of spontaneity.

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$$A = U - TS$$
$$dA = dU - TdS - SdT$$
$$\begin{cases} dA = dU - TdS \dots \text{Const } T \\ TdS \geq dU \dots \text{const } V \end{cases}$$
$$\boxed{(dA)_{T,V} \leq 0}$$


First let us talk in terms of A, A is equal to U minus TS. A is Helmholtz function or Helmholtz free energy, U is internal energy, T and S have their other usual meanings. Let there be some advancement. So, dA is equal to dU minus T dS minus S d T. Rewriting this dA is equal to dU minus T dS at constant temperature.

And we have earlier derived, you remember that we talked about that T dS is greater than or equal to dU at constant volume we have already discussed this. Now if I combine these two dU minus T dS should be less than or equal to 0, at constant volume once again dU minus T dS should be less than or equal to 0 at constant volume which if I substitute in this I get dA at constant temperature and volume should be less than or equal to 0 this is another criteria spontaneity. That is for a process which is carried out at constant temperature and fixed volume the Helmholtz free energy must decrease, is it a very useful criteria of spontaneity to be used for processes it is one of the criteria. But you know the difficulty in this is that this will only be applicable if the volume is held constant.

Let us now discuss the most widely used criteria of spontaneity in chemistry and that is in terms of the Gibbs free energy - G is equal to H minus TS.

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$$G = H - TS$$
$$dG = dH - TdS - SdT$$
$$\left\{ \begin{array}{l} dG = dH - TdS \dots \text{const } T \\ TdS \geq dH \dots \text{const } p \end{array} \right.$$
$$\boxed{(dG)_{T,P} \leq 0} \leftarrow$$


So, dG is equal to dH minus TdS minus SdT . Now I can write dG is equal to dH minus TdS at constant temperature. And by our earlier discussion TdS is greater than or equal to dH at constant pressure. So, from this dH minus TdS at constant pressure should be less than or equal to 0, I combined the two and come up with this criteria spontaneity dG at constant temperature and pressure should be less than or equal to 0. This criteria of spontaneity is most widely used criteria of spontaneity in chemistry or chemical engineering or wherever we want to use; the definition of G in defining the criteria of spontaneity.

See most of the time we say a process is spontaneous if ΔG is negative and this criteria of spontaneity is exactly the same that for a finite process ΔF should be negative for a spontaneous process, but we should also assign these constraints when we are talking that ΔG is negative. ΔG is negative under constant temperature and pressure conditions this is how we define the criteria of spontaneity.

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Criterion of spontaneity
in terms of properties of system alone

$$dS_{U,V} \geq 0; \quad dU_{S,V} \leq 0$$
$$dS_{H,p} \geq 0; \quad dH_{S,p} \leq 0$$
$$dA_{T,V} \leq 0; \quad dG_{T,p} \leq 0$$


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So, the criteria of spontaneity in terms of properties of system alone there are 6 criteria of spontaneity in terms of entropy, internal energy, enthalpy, Helmholtz free energy or Gibbs free energy and this one dG at constant temperature and pressure is less than or equal to 0 is the most widely used criteria of spontaneity because it is very easy to carry out the processes at constant pressure rather than fixing the volume. And we also discussed that all these criteria of spontaneity which are defined in terms of properties of system only also obey the second law of thermodynamics.

So, so far we have discussed a lot about entropy and as we will see later on that the changes in entropy provide a lot of information and the second law of thermodynamics is obeyed in all conditions. Today we also discussed the criteria of spontaneity which will be very useful in predicting whether the process will be feasible at a given condition or not.

Thank you very much.