Thermal Physics
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Lecture - 49
Condition for Thermodynamic Equilibrium

Hello and welcome back to another lecture of this NPTEL lecture series on thermal physics. Now for today's lecture we will be revisiting this Maxwell's relations and free energy function. Specially to the aim that we want to have a mnemonic diagram so that we can remember those things very easily. And after that we will be discussing the general condition for thermodynamic equilibrium and we will see that under certain circumstances certain energy function has to be optimized.

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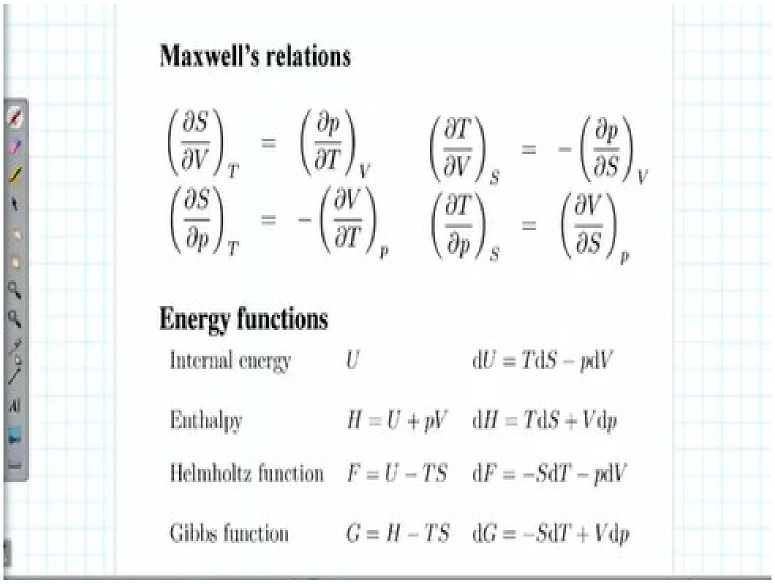

Maxwell's relations

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \qquad \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

Energy functions

Internal energy	U	$dU = TdS - pdV$
Enthalpy	$H = U + pV$	$dH = TdS + Vdp$
Helmholtz function	$F = U - TS$	$dF = -SdT - pdV$
Gibbs function	$G = H - TS$	$dG = -SdT + Vdp$

So, without further delay let us start with Maxwell's relation which we have already discussed many times for over last few classes. So, these are the four Maxwell's relation and these are the four energy functions with the definition of these energy functions are given and also the differential form of this energy function from which we can find out that U is the natural variable of entropy and volume H is a natural variable of entropy pressure.

F which is a Helmholtz function is a natural variable of temperature and volume and Gibbs function is a natural variable of temperature and pressure. So, let us first start with the mnemonic diagram for these four energy functions because U we all remember but H probably U plus p V we all remember but sometime we have problem remembering which one is Helmholtz function, which one is Gibbs function what is the exact form.

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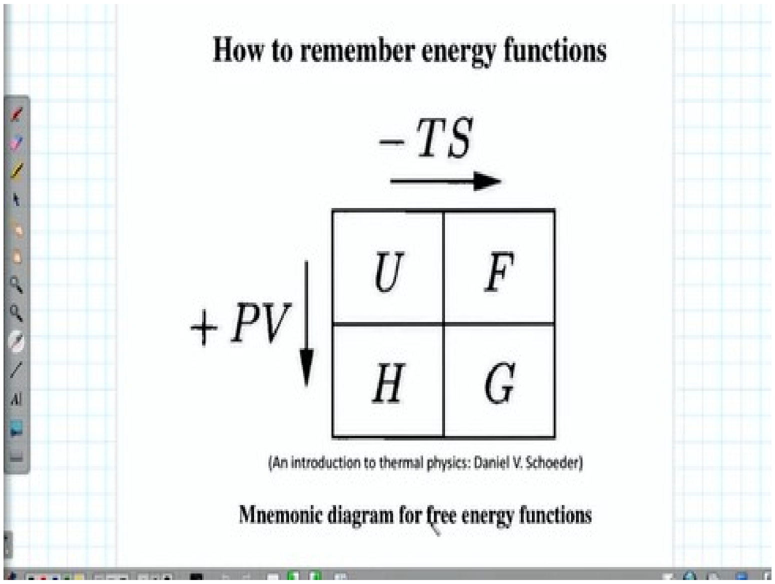

How to remember energy functions

(An introduction to thermal physics: Daniel V. Schoeder)

Mnemonic diagram for free energy functions

So, from this book of introduction to thermal physics by Daniel Schoeder this is a diagram if you just remember this square U all you have to remember is the left, I mean out of these four partitions the left corner top left partition has U the internal energy and then F G H and remembering this sequence F G H is very easy because it is alphabetical E F G H. So, instead of E you have U so U F G H and then you have minus TS plus PV.

So, if you can remember this, see U plus PV is equal to H, U - TS = F, U + PV - TS = G. So, this is a probably a bit better way of remembering this free energy function. Of course, if you can remember it, you can directly remember this relation. This itself is good enough but just in case you might need this.

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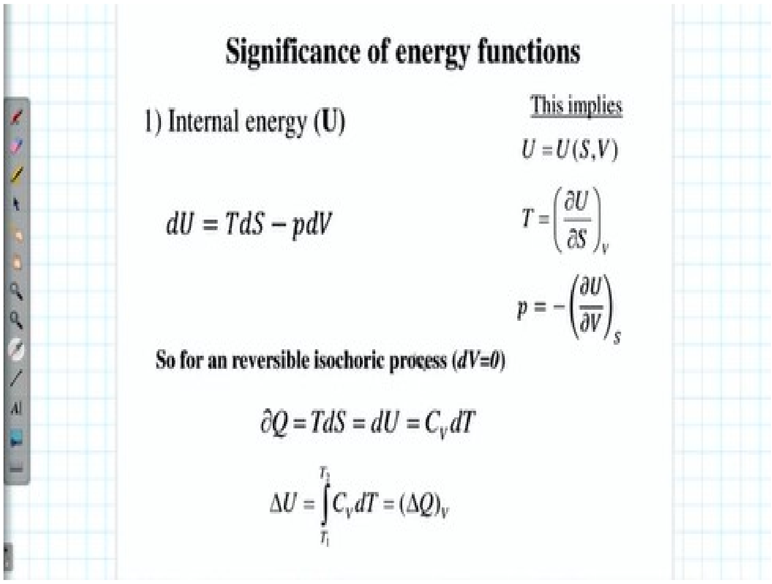

Significance of energy functions

1) Internal energy (**U**)

This implies

$U = U(S,V)$

$$dU = TdS - pdV$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V$$

$$p = -\left(\frac{\partial U}{\partial V}\right)_S$$

So for an reversible isochoric process (*dV=0*)

$$\partial Q = TdS = dU = C_V dT$$

$$\Delta U = \int_{T_1}^{T_2} C_V dT = (\Delta Q)_V$$

So, before we go into the further mnemonic diagrams so let us quickly revisit the significance of this energy functions, we have internal energy U which is dU = TdS - pdV then we can write temperature as del U del S v and pressure as minus del U del V s are two parameters two you know the what you call the two important parameters which can be the system parameters which can be derived directly if we know the full form of entropy full form of energy function in terms of entropy and volume.

Now and we have also seen that for a reversible isochoric process where dV is equal to 0. The total heat exchange is equal to the total change in internal energy. So, for a reversible isochoric process delta U is equal to delta Q.

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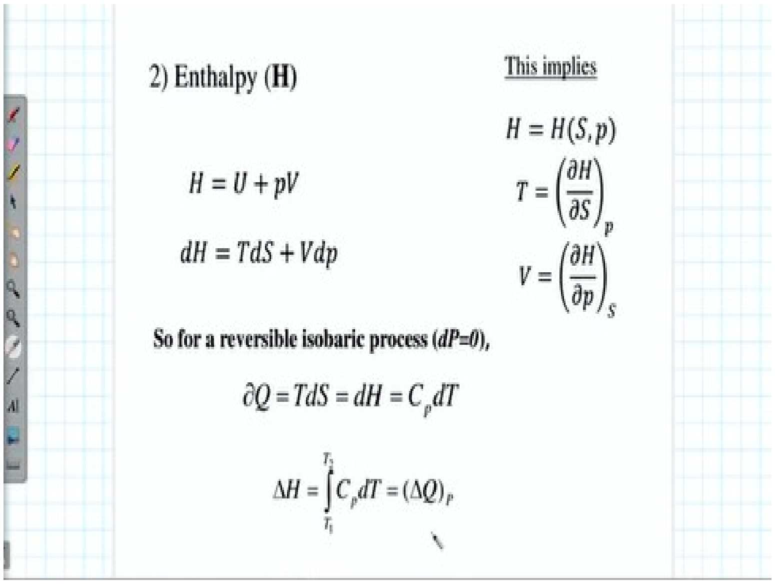

2) Enthalpy (**H**)

$$H = U + pV$$

$$dH = TdS + Vdp$$

<u>This implies</u>

$$H = H(S,p)$$

$$T = \left(\frac{\partial H}{\partial S}\right)_p$$

$$V = \left(\frac{\partial H}{\partial p}\right)_S$$

So for a reversible isobaric process (*dP=0*),

$$\partial Q = TdS = dH = C_p dT$$

$$\Delta H = \int_{T_1}^{T_2} C_p dT = (\Delta Q)_P$$

Similarly, we have enthalpy which is given as H = U + pV and dH is TdS + Vdp that tells you that enthalpy is a natural variable of entropy and pressure and we can write temperature and volume as the first derivative of these two free energy functions of this particular free energy function. Now for a reversible isobaric process we have dP is equal to 0 so this equation reduces to dH is equal to TdS, so we have delta H delta Q which is equal to C p dT becomes equal to dH.

So, that delta I mean capital delta H is equal to capital delta Q. So, in a reversible isobaric process where which takes place under constant pressure the total heat that enters or I mean that goes in or out of the system is equal to the enthalpy change of the process. Now this is a very important result because by this type of equality we can actually measure the change in enthalpy or internal energy of a system in during a particular process.

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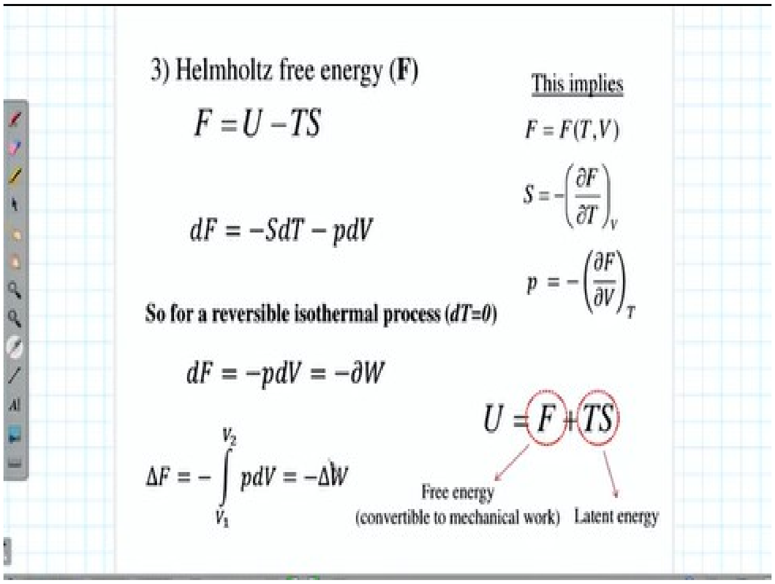

3) Helmholtz free energy (**F**)

$$F = U - TS$$

$$dF = -SdT - pdV$$

So for a reversible isothermal process (*dT=0*)

$$dF = -pdV = -\partial W$$

$$\Delta F = -\int_{V_1}^{V_2} pdV = -\Delta W$$

This implies

$$F = F(T,V)$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$U = F + TS$$

Free energy (convertible to mechanical work)

Latent energy

Now next comes the Helmholtz free energy function F when we have F = U - TS so dF = - SdT – pdV. So, once again F can be expressed as a natural variable of temperature and volume and entropy and pressure becomes two you know two first derivatives of the Helmholtz free energy function. Now for a reversible isothermal process where dT is equal to 0 dF is equal to minus delta W so that means delta F is equal to minus delta W.

So, during a reversible isothermal process the total work done either by the system or on the system is equal to the negative of the change of Gibbs free energy. So, if we can compute the work done during an isothermal process, we can actually have an idea of the change in the internal and I mean it gives Helmholtz not gives Helmholtz free energy of the system. And also, if you rewrite this expression, we have U = F + TS.

And we see F is proportional I mean F is correlated to the work done either on the system or by the system. So, that is why U the internal energy can be written as a combination of a free energy function that is F and a latent energy which is TS.

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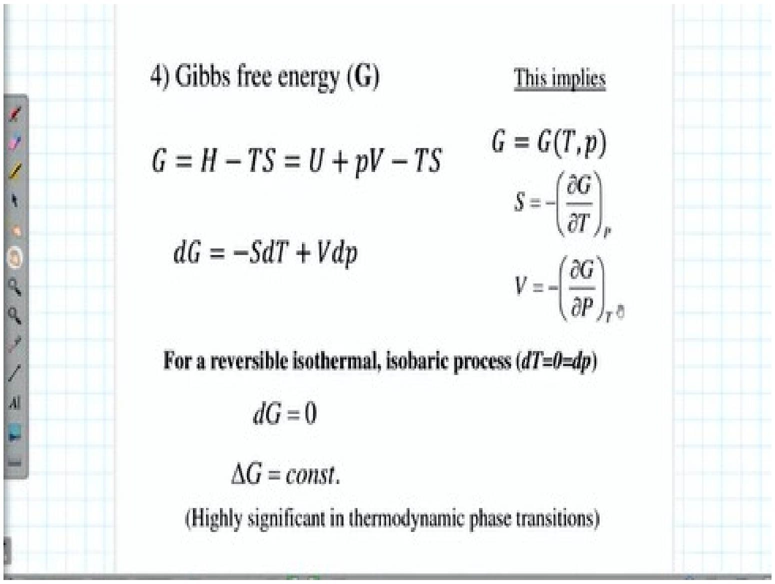

4) Gibbs free energy (G)

This implies

$$G = H - TS = U + pV - TS$$

$$G = G(T,p)$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_p$$

$$dG = -SdT + Vdp$$

$$V = -\left(\frac{\partial G}{\partial P}\right)_T$$

For a reversible isothermal, isobaric process ($dT=0=dp$)

$$dG = 0$$

$$\Delta G = const.$$

(Highly significant in thermodynamic phase transitions)

Finally, we have the Gibbs free energy which is G = U + pV - TS once again we can write the natural variable G as a natural variable of temperature and pressure because of this differential form and we can derive I mean we can express entropy and volume as the first derivative functions of the Gibbs free energy. Now for a reversible isothermal isobaric process when we have dT = 0 = dp we have dG is equal to 0 and delta G is equal to constant.

Now this result is of very high significance in thermodynamic phase transition and also as we will see in the next lecture that this is also very important when we are talking about chemical reaction. Because typically chemical reactions and phase transitions, they took they take place under isothermal isobaric condition. Now of course we these all these four relations that we have derived including this delta G is equal to constant these are all under reversible processes.

Now what happens in irreversible process we will see very soon when we will discuss about the general condition for equilibrium.

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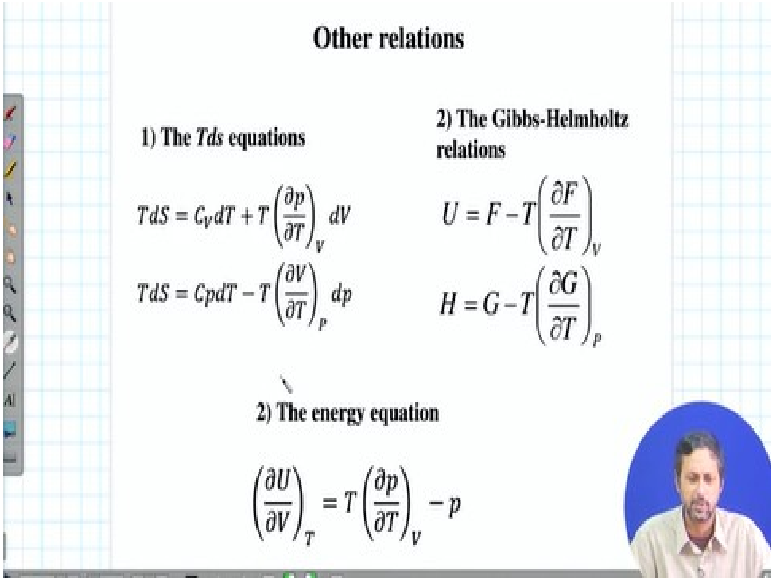

Other relations

1) The *Tds* equations

$$TdS = C_V dT + T\left(\frac{\partial p}{\partial T}\right)_V dV$$

$$TdS = CpdT - T\left(\frac{\partial V}{\partial T}\right)_p dp$$

2) The Gibbs-Helmholtz relations

$$U = F - T\left(\frac{\partial F}{\partial T}\right)_V$$

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_p$$

2) The energy equation

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

Now, apart from these four energy functions we have also had discussed about TdS equations the first and the second TdS equation. I have just given one form of it and if you recall this particular term can be further simplified or rather further modified to express in terms of the bulk modulus. Similarly, this one can also be expressed in terms of bulk modulus. So, we have different forms of the TdS equation.

In some cases where we use or different for the same TdS equation sometimes we use this particular form which where this term can be directly derived from the equation of state. And in some cases, we use the form where we have the second term in terms of the elastic modulus. Also, there are gives two Gibbs-Helmholtz relation which actually correlates the I mean it talks about the inter correlation between the free energy function.

And of course, the energy equation which gives you an estimate of free I mean which helps us to estimate the free energy of or rather the internal energy U of the system from starting from the equation of state this is given by this particular relation. We have already discussed those and we have taken numerous examples where these things have been calculated. So, we are not going into this is basically a recap of what we have done so far. Now next what we are going to discuss is the mnemonic diagram.

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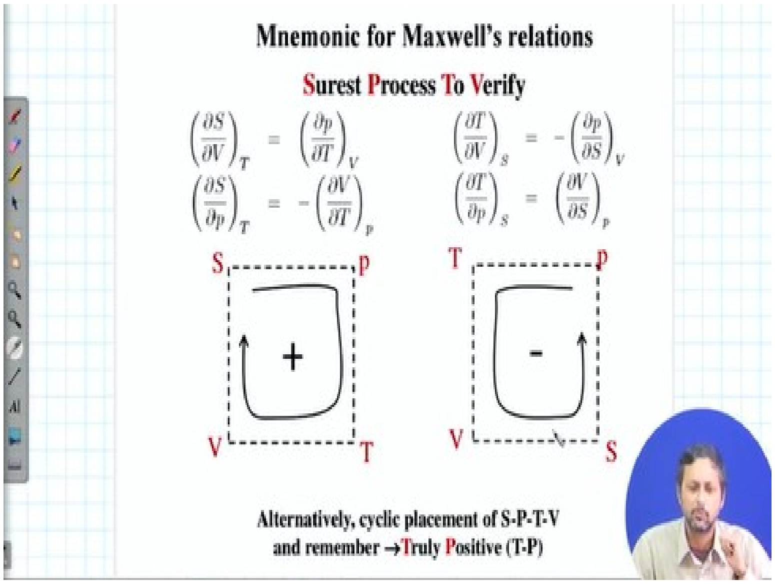

Mnemonic for Maxwell's relations

Surest Process To Verify

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \qquad \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

Alternatively, cyclic placement of S-P-T-V
and remember →Truly Positive (T-P)

Now what is the mnemonic diagram? A mnemonic diagram or mnemonic phrase is something that helps us to remember a complicated rather complicated relation. Or you know it could be a relation it could be some you know it could be some number there could be many different things where mnemonics are used. Now we in this lecture we will be discussing about two particular mnemonics; one is to remember the Maxwell's relation that is surest process to verify.

So, if we take the first letter of this phrase or I mean four words of this phrase we have S P T and V so basically these are the ingredients of the Maxwell's relation. So, how to get of course if we remember surest process to verify we know that Maxwell's relation has S P T and V but then how to reproduce this Maxwell's relation is there any hint inside that. So, apart from this surest process to verify we have to remember either we can just remember this diagram or we can remember this phrase truly positive.

So, both ways it is possible. So, let me briefly tell you how to use this particular diagram and how to use this particular phrase. So, first up let us examine this Maxwell's relation closely. We see every parameter appears twice in the numerator for example entropy numerator, numerator denominator, denominator similarly pressure numerator, numerator, denominator, denominator. So, every parameter out of so there are four equations there are 1, 2, 3, 4 four positions in each equation altogether there are 16 positions.

So, out of these four parameters every each parameter has arrived four times in this equation. So, basically once in every equation and twice it has arrived in the numerator twice it has arrived in the denominator. Now once we know that next, what we have to do is we need to learn how to arrange these parameters in order to get back to this Maxwell's equation. So, please remember S P T V is the sequence that we always have to maintain.

So, if we go to please remember now if we go clockwise, we get positive. If we go counter clockwise we get negative. So, just so there are two as I said there are two alternative ways. One way of this is remembering that going S P T V in a clockwise direction is positive and S P T V in a counter clockwise direction is negative. How? Let us have a look.

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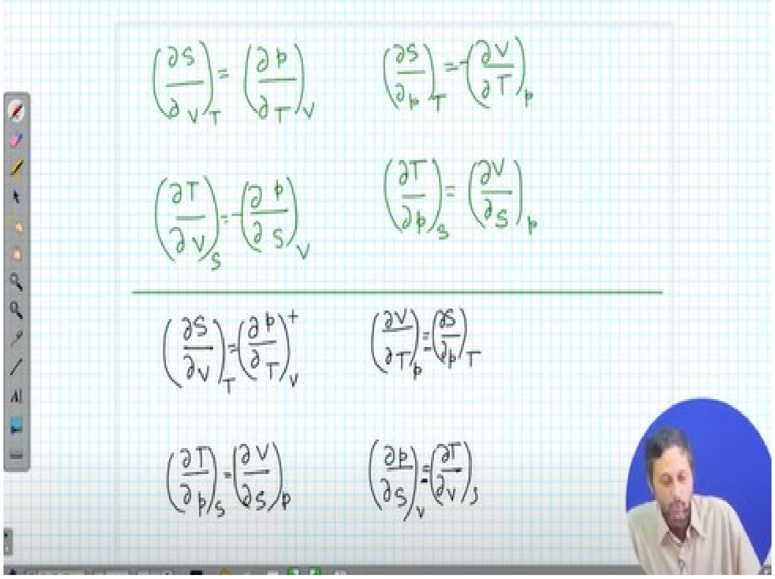

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \qquad \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V^{+} \qquad \left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \qquad \left(\frac{\partial p}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S$$

So, let us try this, so we have S P T V so this is given in clockwise direction and then we write S P T V in counter clockwise direction. Now next thing what do we do? We look at this diagram where we have S in the top left corner. In the second diagram, we have S in the bottom right corner. So, we once we write this twice once in clockwise once in anticlockwise direction keeping S in the top left corner.

Next time we start from here and write S P T V which is once again counter clockwise and S P T V this is clockwise. Now these two will be positive we will see very soon see del S, now what do we have to do is? We have to put del S del V; I mean it is not very properly placed spaced but I think you understand del P del T. Now if V comes here in the differential this will be the constant, here if T comes here, it will be the constant here and put a equal sign.

And because it is clockwise starting from this left most left top corner this is positive. So, complete this S P once again T should be here, so this P is constant here T is constant here. This is counter clockwise so we put a negative sign del T del V del P del S once again it is counter clockwise, so we put a negative sign S will be constant here V will be constant here and del P del T del V del S here it is clockwise.

So, it will be positive S constant P constant that is how we get back this four Maxwell's relation. Alternatively, what we can do is so let me use another colour so that you all you have to remember once again this press here is process to verify and you have to remember another phrase truly positive. What is truly positive? When we have T and P participating in the same date differential then it will be positive as we see here T and P participates.

So, we have a positive sign T and P participates. We have a positive sign so, this is truly positive. So, in that case we do not have to you know follow any particular convention that two times right from the top left corner two times from the right bottom right corner instead we simply write S P T V and in cyclic permutation manner we write S P T V once again we write S P T V and S P T V.

The construction is the same you put rand differential here and here you put differential here and here. See here it is not truly positive because T and P is in a opposite differential, so you put a negative sign of course here P will be constant here T will be constant here. In a similar manner we put S constant V constant because this is also not truly positive, we should put a negative sign here, here also del V del S del P del T, S here P here this one is truly positive.

So, because T P is in the same differential. So, it remains that del S del V del P del T once again this is truly positive. So, we have T constant V constant, so that is how you can reproduce this four Maxwell's relation. Now this is one that is for the Maxwell's relation.

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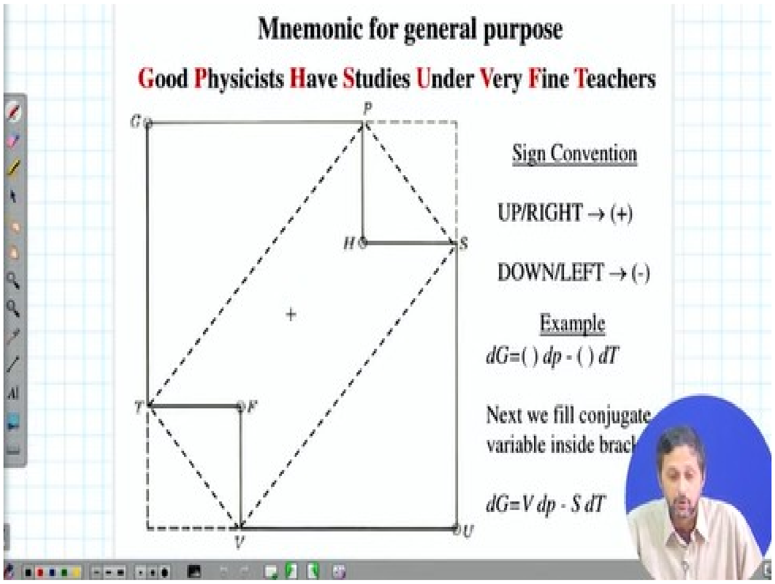

Mnemonic for general purpose

Good Physicists Have Studies Under Very Fine Teachers

Sign Convention

UP/RIGHT → (+)

DOWN/LEFT → (-)

Example

$dG = (\ )\, dp - (\ )\, dT$

Next we fill conjugate variable inside brac

$dG = V\, dp - S\, dT$

For the general property I mean for the general purpose we where we can remember all the Maxwell’s relation as well as the four-differential form of four free energy function. Actually, remembering free energy function is rather easy but differential of free energy function remembering that is slightly difficult. Because we see that free energy functions, we start with G = U + pV - TS but the final differential form is minus SdT plus Vdp it is not very intuitive.

So, that is why it is more difficult to remember this one rather than this one. So, now we learned how to remember this particular differential forms. We have to remember the phrase that good physicist have studied under very fine teacher. Actually, if we remember that this will also have this S P T V matrix inside S P T V block inside, we will come back to that. So, good physicist have studied under very fine teacher.

Take the first letters G that gives energy P pressure H enthalpy S entropy U internal energy V volume F Helmholtz free energy T temperature. Put it in the corners of this block where which is not a perfect square the perfect square would be this one, we have a chipping in this, corner chipping in this corner. Put G P H S U V F T in this particular sequence, you can immediately notice that there is a sub block which says S P which reads S P T and V.

So, you see this phrase heroes process to verify is also included. I mean or rather the sequence S P T V is also included here but that we have learned already. So, I am now let me tell you how to construct the free energy function. Start from any position if we go right or up you have a positive sign. So, let us say ok let us take the example for G so and if you go left or negative. So, for example from here to here or you know from here to here you have a negative sign.

So, let us what do we mean by positive and negative? G. What are the two nearest neighbours of G? P and T so we you write dG is equal to bracket dp minus bracket dT, why minus because T is below here and why plus because P is right to the value of G right to G. So, if you remember this block, you can always construct dp and minus dT. Now what do we put inside this bracket please remember this free energy functions have dimension of energy or all energy functions have the dimension of energy.

So, if we have dp here we must put V if we have dT here we must put S. So, that is how we construct dG is equal to V dp minus S dT. Similarly, dU will be what will be dU it will be something times dS minus something times dV. Now it will be TdS minus pdV. So, this is how we can construct.

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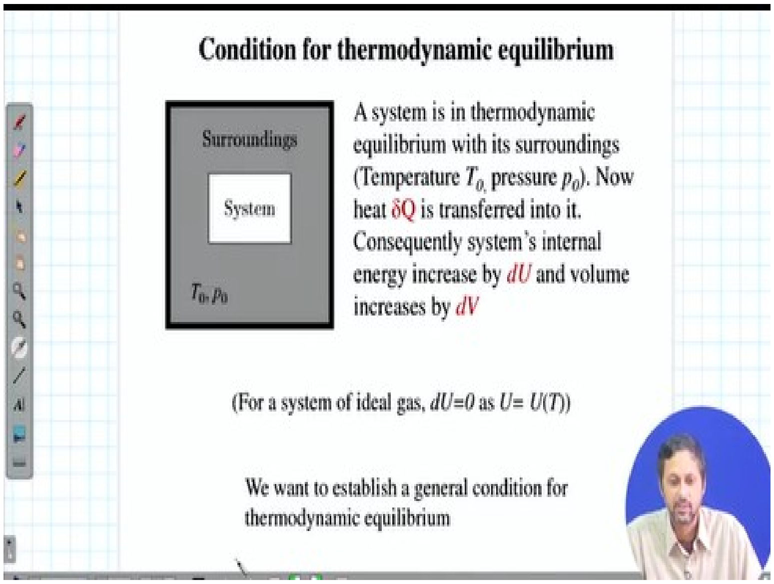

Condition for thermodynamic equilibrium

A system is in thermodynamic equilibrium with its surroundings (Temperature T_0, pressure p_0). Now heat δQ is transferred into it. Consequently system's internal energy increase by dU and volume increases by dV

(For a system of ideal gas, $dU=0$ as $U= U(T)$)

We want to establish a general condition for thermodynamic equilibrium

Now once we go through this mnemonic diagram let us focus on the final discussion of today's lecture which is the condition for general condition for thermodynamic equilibrium. So, far we have discussed about reversible processes and in reversible process we have seen that the free energy function does not change I mean we have dG is equal to 0, dF is equal to 0 but what happens in a norm I mean in a natural in a naturally occurring process in which the entropy always increases.

So, let us consider this we have a system and a surrounding. So, the surrounding temperature is p 0 and T 0s which remains constant. Now a small amount of heat delta Q is transferred into the system from the surrounding consequently systems internal energy increases by dU and volume increases by dV. So, pressure and temperature is not changing because the system is in mechanical and thermal equilibrium with the system or rather in thermodynamic equilibrium.

Because it is not exchanging any particle either. So, we are not including I mean it is not an open system, so it is a that is why we are not including any particle exchange also. So, it is in total thermodynamic equilibrium but so if the system in question is an ideal gas, then dU will not change because of a change in dV, why? Because for a system of ideal gas dU U is a function of 0 only so dV will not you know cause any change in dU and because U is a function of temperature.

But we are talking about real systems here, real system of real gases or something else where U and V are correlated. So, now we want to establish a general condition for thermodynamic equilibrium.

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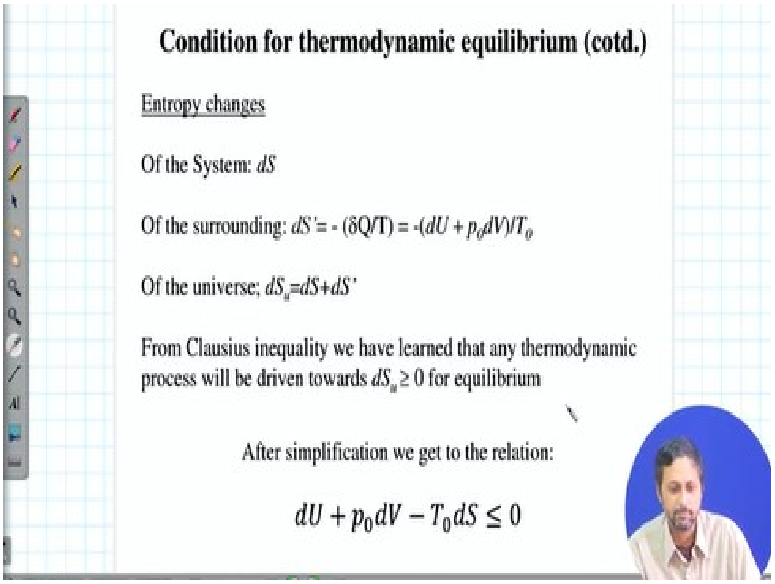

Condition for thermodynamic equilibrium (cotd.)

Entropy changes

Of the System: dS

Of the surrounding: $dS' = -(\delta Q/T) = -(dU + p_0 dV)/T_0$

Of the universe; $dS_u = dS + dS'$

From Clausius inequality we have learned that any thermodynamic process will be driven towards $dS_u \geq 0$ for equilibrium

After simplification we get to the relation:

$$dU + p_0 dV - T_0 dS \leq 0$$

Let us say the entropy change for the system is dS. Now entropy change for the surrounding which is dS prime is equal to minus dQ by T which will be equal to minus dU plus p 0 dV divided by T 0. Now because the system temperature and the surrounding temperature both pressure and temperature both are T 0 and p 0 and they are not changing we can write delta Q of that of the system is equal to delta U plus p 0 dV.

Now this is exactly equal to or rather that is this quantity is equal to delta Q so we can write delta S prime is equal to minus delta Q by T equal to this. Now for the universe the total change will be delta S plus delta S prime which will be greater than equal to 0 for equilibrium. That is Clausius inequality that we have already established so we are not going into the details of this one. Now if we use this condition from these two relations.

So, we take dS plus so basically dS minus dU plus p 0 dV by T 0 and apply that and put a greater than equal to 0 sign. After some modification we get back this relation that dU plus p 0 dV minus T 0 dS is less than equal to 0.

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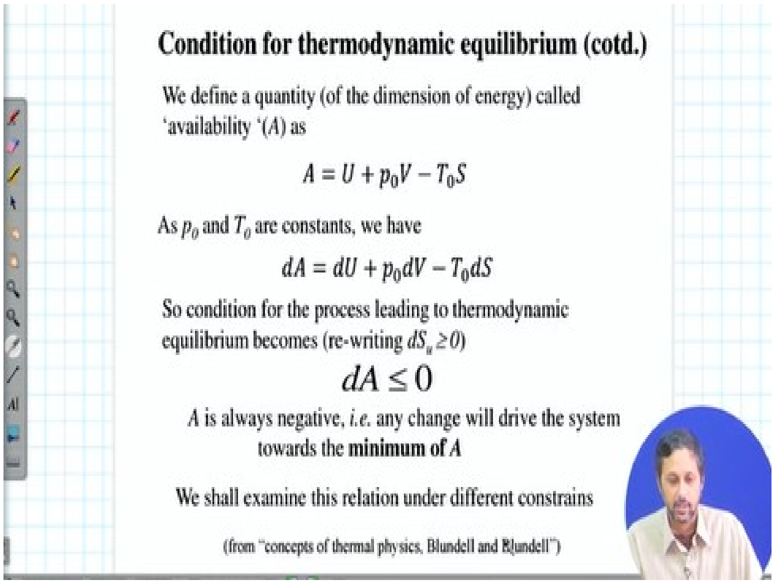

Condition for thermodynamic equilibrium (cotd.)

We define a quantity (of the dimension of energy) called 'availability '(A) as

$$A = U + p_0 V - T_0 S$$

As p_0 and T_0 are constants, we have

$$dA = dU + p_0 dV - T_0 dS$$

So condition for the process leading to thermodynamic equilibrium becomes (re-writing $dS_u \geq 0$)

$$dA \leq 0$$

A is always negative, *i.e.* any change will drive the system towards the **minimum of A**

We shall examine this relation under different constrains

(from "concepts of thermal physics, Blundell and Blundell")

Now we define a quantity called availability A which is U + p 0 V - T 0 S and as p 0 and T 0 are constant we can write dA = dU + p 0 dV - T 0 dS. Now the general condition this is nothing but this one so the general condition for thermodynamic equilibrium becomes dA is less than equal to 0. Please remember this is not a new physics, we are just writing the Clausius inequality in this particular form. So, that means the equal sign is for any reversible change.

And as we are talking about the irreversible processes any change which is in a naturally or any naturally occurring change will push dA to a negative value which means basically it will drive towards the minimum of A. So, now we shall examine the relation under different constraint. By the way this treatment is given in the concept of physics by Blundell and Blundell. If you are interested you, should you must read this chapter relevant chapter then you will understand it better.

So, basically what we have established so far that driving towards equilibrium is like driving to the minimum value of this A which is given here. Now you can identify A as something similar to the you know Gibbs energy function. So, it is somehow somewhat similar to the Gibbs energy function but we will see what comes out of it.

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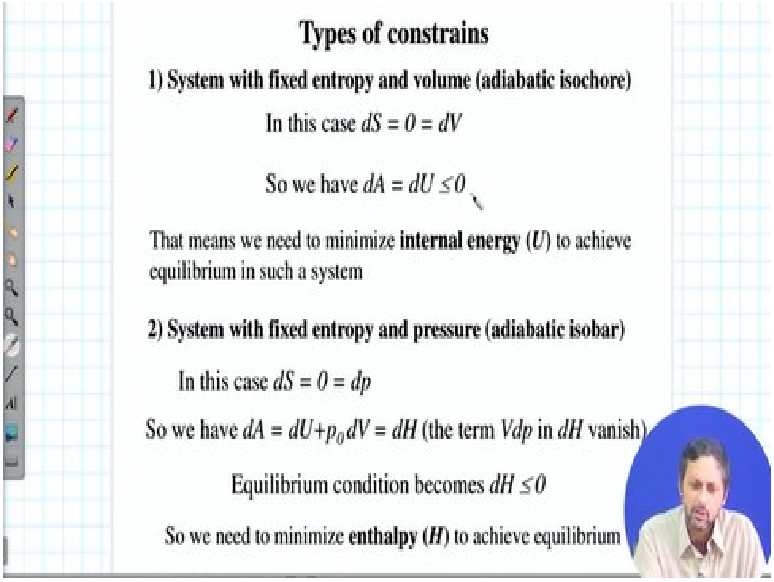

Types of constrains

1) System with fixed entropy and volume (adiabatic isochore)

In this case $dS = 0 = dV$

So we have $dA = dU \le 0$

That means we need to minimize **internal energy** (U) to achieve equilibrium in such a system

2) System with fixed entropy and pressure (adiabatic isobar)

In this case $dS = 0 = dp$

So we have $dA = dU+p_0dV = dH$ (the term Vdp in dH vanish)

Equilibrium condition becomes $dH \le 0$

So we need to minimize **enthalpy** (H) to achieve equilibrium

Now if we are talking about a system with fixed entropy and volume so basically, we are talking about adiabatic isochoric process then in this case dS = 0 = dV. So, we have dU or dA = dU so with these two quantity will go to 0 and so if we have an adiabatic isochoric process internal energy has to be minimized in order to achieve equilibrium for such a system. Similarly, if we have a adiabatic isobaric process that means a system with fixed entropy and pressure where dS = 0 = dp.

So, what do we get? dA will be dU plus p 0 dV which is nothing but dH for this particular system. So, this term so the equilibrium condition means enthalpy H has to be minimum and please remember we there is always a equal sign for any reversible process there is no net change in enthalpy but for any reversible process enthalpy will achieve a new minimum.

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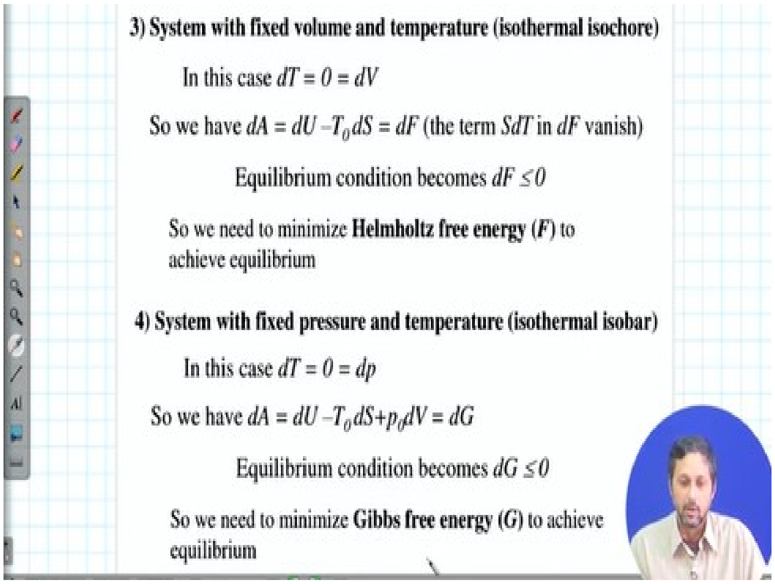

3) System with fixed volume and temperature (isothermal isochore)

In this case $dT = 0 = dV$

So we have $dA = dU - T_0 dS = dF$ (the term SdT in dF vanish)

Equilibrium condition becomes $dF \leq 0$

So we need to minimize **Helmholtz free energy (F)** to achieve equilibrium

4) System with fixed pressure and temperature (isothermal isobar)

In this case $dT = 0 = dp$

So we have $dA = dU - T_0 dS + p_0 dV = dG$

Equilibrium condition becomes $dG \leq 0$

So we need to minimize **Gibbs free energy (G)** to achieve equilibrium

Similarly, for isothermal isochoric process where dT = 0 = dV dA is dU - T 0 dS which is equal to dF which is that means for an isothermal isochoric process we need to minimize Helmholtz free energy to achieve equilibrium and for an isothermal isobaric process where we have dT = 0 = dp we have dA = U 0 - T 0 dS + p 0 dp which is dG which is equal to dG. So, that means equilibrium condition equilibrium is achieved when Gibbs free energy is minimized.

So, we got four different conditions in one. Let us start from the end. We have a fixed pressure and temperature system there Gibbs free energy will be minimized to achieve equilibrium. We have a system with fixed volume and temperature their Helmholtz energy free energy will be minimized to achieve equilibrium. We have a adiabatic system isolated system with fixed pressure their enthalpy will be minimized to reach equilibrium.

And we have an isolated system with fixed volume their internal energy is to be minimized in order to achieve equilibrium.

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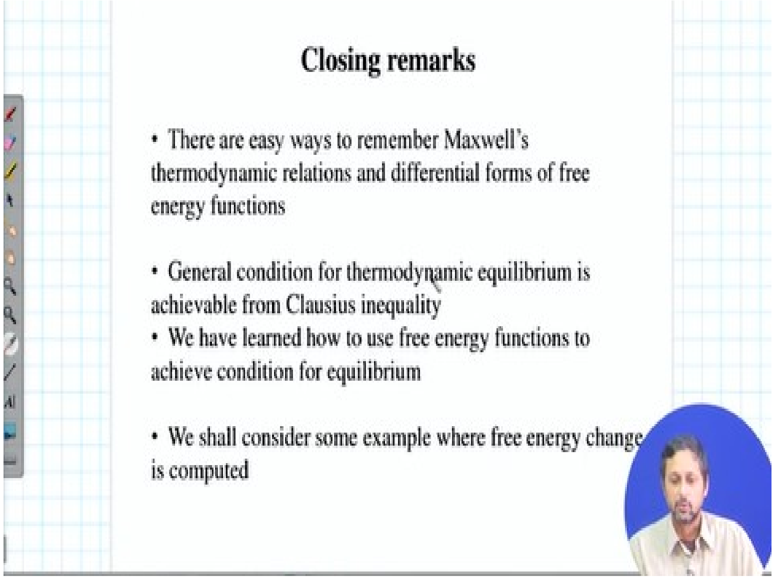

Closing remarks

- There are easy ways to remember Maxwell's thermodynamic relations and differential forms of free energy functions
- General condition for thermodynamic equilibrium is achievable from Clausius inequality
- We have learned how to use free energy functions to achieve condition for equilibrium
- We shall consider some example where free energy change is computed

So, in summary there are easy ways or to remember Maxwell's thermodynamic relations and different forms of differential form of the free energy function. The general condition for thermodynamic equilibrium is available from Clausius inequality once again this delta A, dA less than equal to 0 is nothing but Clausius inequality we are not going away from it we are just using it in a slightly different way.

And we have learned which under which condition which free energy function has to be optimized in order to get equilibrium. And next we shall consider some examples where the change in free energy is computed. We will also take examples of chemical reaction which is a very important part of thermodynamic systems. So, that is all for this lecture, see you again in the next lecture. Bye.