Course on Phase Equilibrium Thermodynamics
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Lecture 07
Criteria Of Spontaneity

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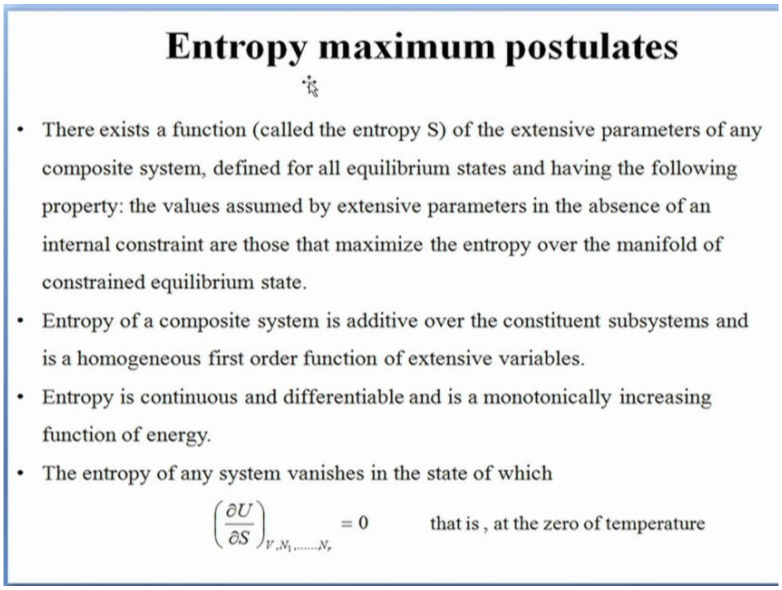

Entropy maximum postulates

- There exists a function (called the entropy S) of the extensive parameters of any composite system, defined for all equilibrium states and having the following property: the values assumed by extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium state.
- Entropy of a composite system is additive over the constituent subsystems and is a homogeneous first order function of extensive variables.
- Entropy is continuous and differentiable and is a monotonically increasing function of energy.
- The entropy of any system vanishes in the state of which

$$\left(\frac{\partial U}{\partial S}\right)_{V,N_1,\ldots\ldots,N_r} = 0 \qquad \text{that is , at the zero of temperature}$$

Well to continue with our discussion regarding the entropy the maximization principle, so in this particular slide I have noted down the entropy maximum postulates which states that entropy is one particular function which is a function of different extensive parameters of the system we can calculate the entropy just like we did in the last class.

You can calculate the entropy as a function of the different extensive parameters and then we find out the entropy we know that for different values of the extensive parameters we get different values of entropy and out of the values of entropy that we have got the state which corresponds to the maximum entropy is the stable state or it is the equilibrium state.

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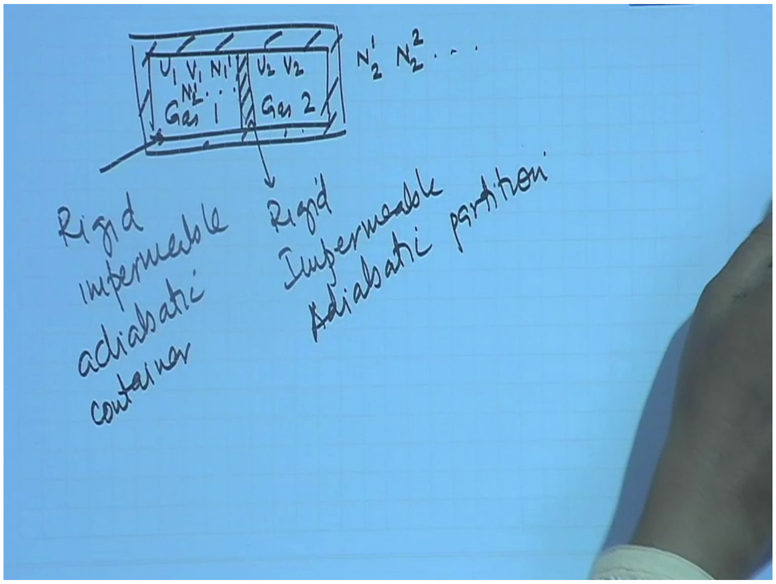

Now if we take a concrete example say for example suppose I have a very rigid insulated container and in this particular rigid insulated container there are 2 compartments which are again which are set here and there is a Gas1 here and there is a Gas2 here and this has a internal energy U1 say V1 and it contains a large number of moles of say N1, N2 and so on and here and in this particular case what we have is that we have U2, this container 2 it has a volume V2 and again there are number of moles of the gas say N1 component into N2 component into, here also it was N1 1 and N21, right?

So here we have N1, this is N2. So in this particular way for both these compartments we find that there is a Gas1 here there is a Gas2 here and the Gas1 it possesses a total internal energy of U1 and the total volume of V1 and it has got a number of components say 123 and the total number of moles are N1 of component 1, N2 of component 2 etc and in the compartment 2 we have the Gas2 whose total internal energy is U2 and total volume is V2 and it has the composition or rather the mole numbers of the different components as N21, N22 and so on and so forth.

Now in this particular situation we find that this whole thing is contained in a rigid impermeable an adiabatic container, right? And the 2 compartments they are also separated by a partition which is again rigid, impermeable and adiabatic partition, right? Now this particular composite system this is an isolated system and each particular compartment that is also an isolated compartment, so now at this particular moment the gas in compartment1 is in a state of internal equilibrium the gas in compartment two is in a state of internal equilibrium and the entire composite system is also in a state of internal equilibrium.

Now suppose what I do is, I just try to make this particular partition slightly movable means I remove the attachments here such that the partition can move freely within the container what is going to happen? We find that the partition will move some way this way that way and finally settled down into a new position which is a new equilibrium position of the gases in compartment 1 and 2. So I have removed one internal constant and allow the partition not to be rigid but to be movable and we find that both the gases have settled down they can interact with one another and they have settled down to a new equilibrium state.

Next what I do? I remove the adiabatic covering from the partition such that each can flow from one compartment to the other. Again I find that in the 2 compartments a good amount of heat exchange takes place finally thermal equilibrium within the composite system is established and the gases in the 2 compartments settle down to a new particular temperature.

So one another internal constant got and we attain another internal another equilibrium state. Next what I do? I make a number of holes in this partition such that gases can diffuse from compartment 1 and 2 or vice versa. I find that the gases keep on diffusing between the 2 compartments and finally they settle down into a new equilibrium state where more or less there is uniform composition of the 2 gases in the 2 compartments, So in this process what I have done?

I have removed internal constants one by one and I have the gases have settled down to a new equilibrium states, right? And the point is just to find out which particular equilibrium state is going to be most stable we need to calculate the entropy change of the gases as each of the internal constants are removed and then we need to find out that particular value of entropy which is the maximum for any particular combination of the extensive variables U1, V1, N1, N2 etc.

So therefore we find that finally this particular isolated system is going to settle down in a new internal equilibrium state which can be decided by the entropy maximization principle where the entropy can be calculated as an objective function of the different extensive variables possible, so this is known as the entropy maximum postulate.

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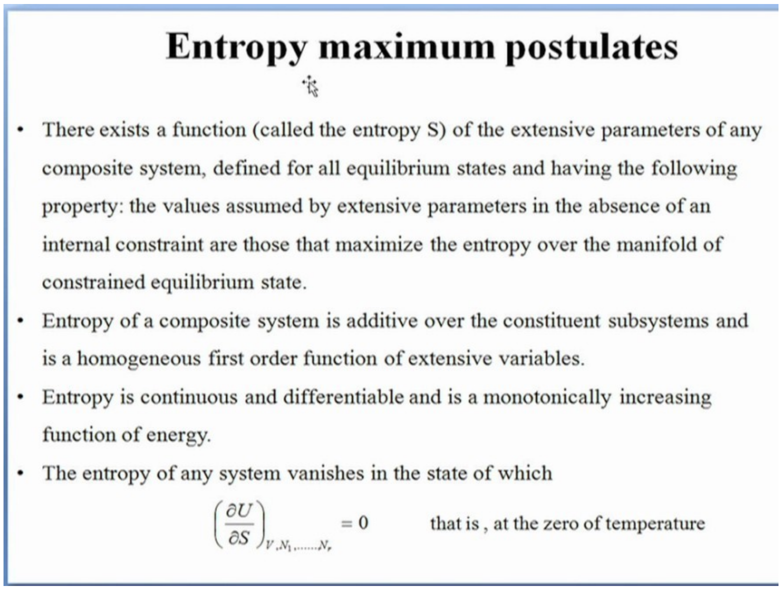

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And in order to calculate entropy I would like to remind you certain properties which entropy has first thing is entropy is an extensive quantity or it is additive.

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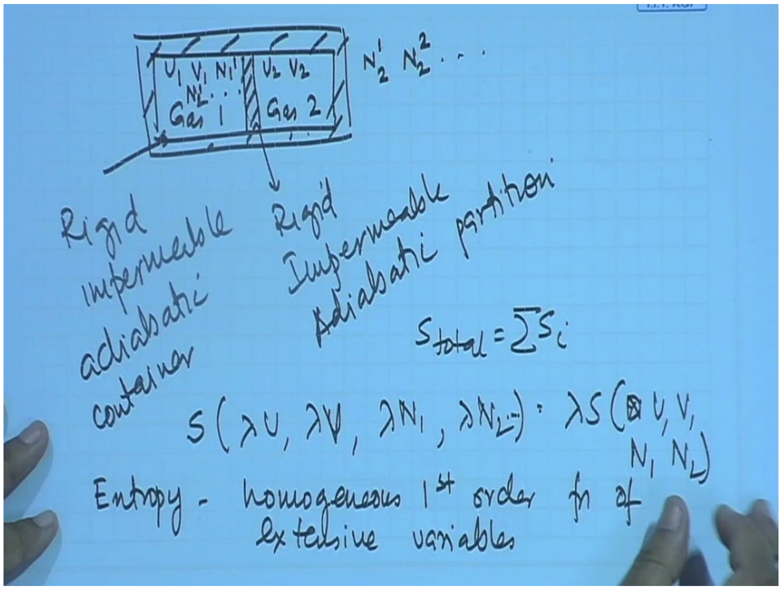

$$S_{total} = \sum S_i$$

$$S(\lambda U, \lambda V, \lambda N_1, \lambda N_2 \ldots) = \lambda S(U, V, N_1, N_2)$$

Entropy - homogeneous 1st order fn of extensive variables

So therefore the total entropy of this particular system S total it is simply a summation of the entropies of the subsystems. The next important thing is entropy it is a continuous differentiable and monotonically increasing function of energy or in other words entropy it is a first order function of energy. So therefore what does it imply? It implies the first order function implies that S, suppose I increase each V extensive parameter by an equal amount of lambda then in that case my entropy increases by the same amount lambda. So this is first thing we find that for a system entropy it is a homogeneous first-order function of extensive variables these facts help us to calculate entropy of the different systems.

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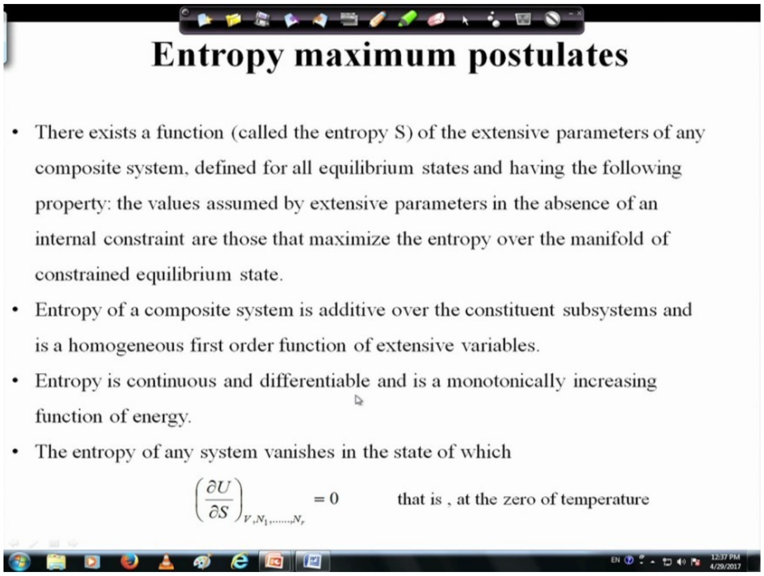

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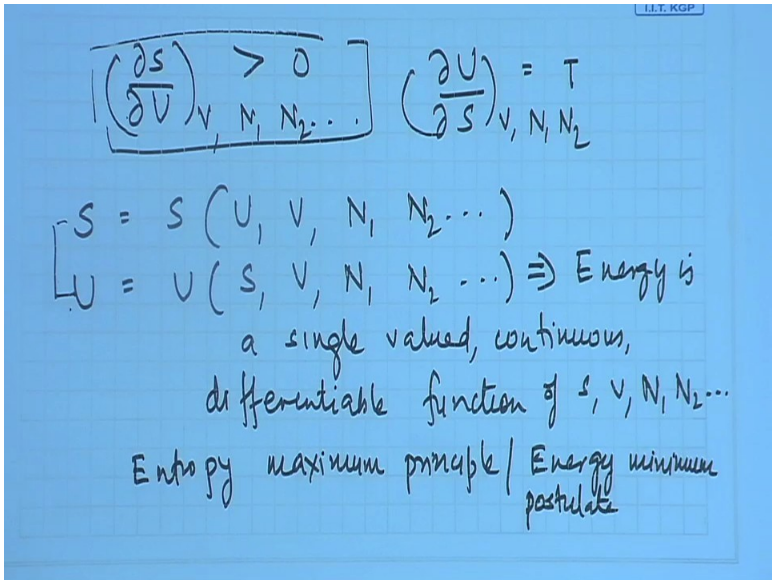

$$\boxed{\left(\frac{\partial S}{\partial U}\right)_{V, N_1, N_2 \ldots} > 0} \quad \left(\frac{\partial U}{\partial S}\right)_{V, N_1, N_2} = T$$

$$S = S(U, V, N_1, N_2 \ldots)$$

$$U = U(S, V, N_1, N_2 \ldots) \Rightarrow$$ Energy is a single valued, continuous, differentiable function of $S, V, N_1, N_2 \ldots$

Entropy maximum principle / Energy minimum postulate

What is the second thing? The second thing is that entropy of a system that entropy is continuous it is differentiable and it is a monotonically increasing function of energy, what does this imply? This monotonically increasing function of energy that implies that del S del U for constant V, N1,N2 etc is greater than 0 and you we will be seeing later that actually del U del S at constant V, N1, N2 etc that is equal to T which we will be seeing later.

Now from this particular equation we get something very important. We find out that since entropy it is a monotonically increasing function of energy and since we can express del S del U in this particular terms and we know that S it is a function of U, V, N1, N2 so on. So similarly we can write in terms of energy that U is also a function of S, V, N1, N2 etc which implies that energy is a single valued continuous differentiable function of S, V, N1, N2 and so on, what does it mean? It means that the entropy maximum principle also reduces to the energy minimum principle so therefore we find out that there can be systems where the entropy remains constant but the energy of the new state is the minimum.

And you will be recalling that in mechanics we find that the stable states correspond to the energy minimization principle I just wanted to show that the entropy maximum principle corresponds to the energy minimum principle and if we keep the energy to be constant than its entropy maximum which governs the stable equilibrium state and if we maintain the entropy of the system constant which we usually do in mechanical systems then it is the energy minimum principle which governs the stable equilibrium of the system.

So these 2 statements they are analogues to one another or in another words the stable state can be given by either the entropy maximum principle a postulate or it can be given by the energy minimum postulate and we will be seeing later that there are several other terms also or several other energy terms whose minimization also can give us the stable equilibrium states.

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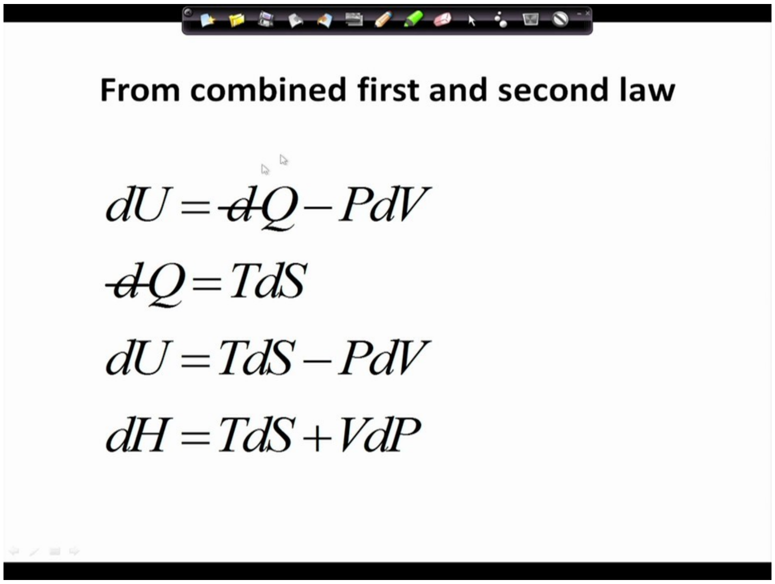

From combined first and second law

$$dU = \text{đ}Q - PdV$$

$$\text{đ}Q = TdS$$

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

And well the last part is, it just tells us that at the 0 of temperature the entropy of the system vanishes or in other words this gives rise to the third law of thermodynamics. So therefore with this what I meant to say is that we had derived the equation this was the equation which I had derived, this works from the combine first and second law we had derived this particular equation, right?

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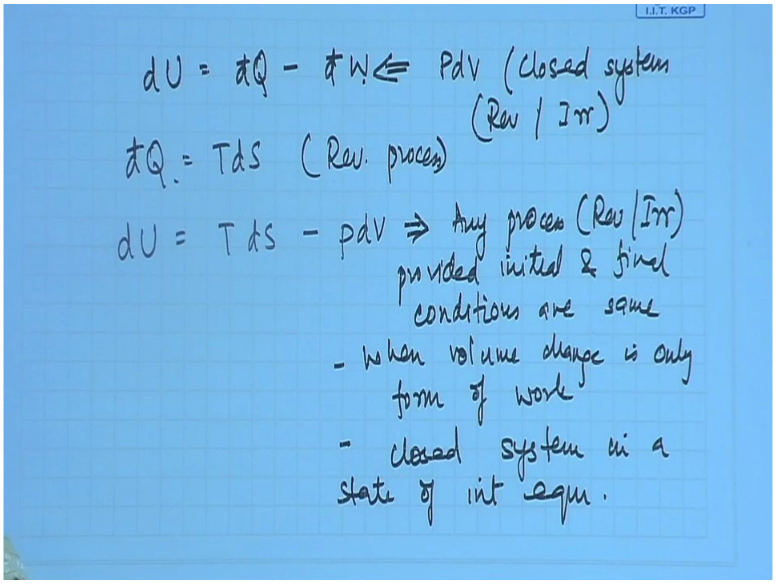

$dU = \text{đ}Q - \text{đ}W \Leftarrow PdV$ (Closed system (Rev / Irr)

$\text{đ}Q = TdS$ (Rev. process)

$dU = TdS - pdV \Rightarrow$ Any process (Rev/Irr) provided initial & final conditions are same

- when volume change is only form of work
- closed system in a state of int equm.

So therefore the equation was dU was equal to dQ minus dW, right? This was the equation when only pV work is concerned then dW can be replaced by PdV which has been done in this particular equation.

From second law what did I get? I got this particular equation but we need to remember that this equation is applicable only for a reversible process, isn't it? So therefore let us see that what happens in this particular case is, so in this particular case what do we see? Well, in this particular equation then what do we see? We find that when there is this from the first law this is applicable for closed systems the closed system we had derived this equation for both reversible as well as irreversible processes, isn't it?

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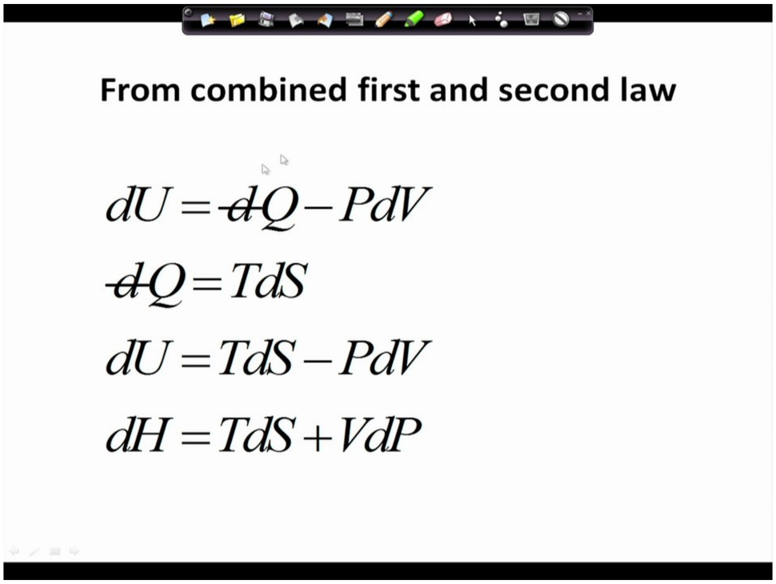

From combined first and second law

$$dU = \text{đ}Q - PdV$$

$$\text{đ}Q = TdS$$

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

Next from second law we have derived dQ was equal to TdS this was for a reversible process only, right? And then if we can replace this then we get dU equals to TdS minus PdV the equation which I have shown here. Now let us see for which condition this equation is applicable, this was applicable for a reversible process and a closed system this was applicable for a closed system and for any particular process.

Now if you observe this particular equation what do we find? We find that this equation gives us a relationship between internal energy, temperature, entropy pressure, volume all of these are properties of the system. So if all of these are properties of the system then they all of them should depend upon the initial and final states they should have nothing to do with the path which we follow, so therefore finally from these 2 equations we come across a equation which should be applicable for any process reversible or irreversible provided initial and final states or conditions are same.

We need to remember that for reversible processes TdS will be equal to dQ for irreversible processes TdS will not be equal to dQ in the same way PdV will not be equal to dW, so the difference between dQ and TdS will be equal to the difference between dW and PdV and accordingly we could derive this equation from this particular equation there are certain things which I need to mention about this particular equation. The first thing is this is applicable for any process but we have to remember that, two it is for any process but this is applicable when volume change is the only form of work that is only Pv is only form of work or in other words when the work done is just of the PdV type of work.

Next is it is applicable for a closed system in a state of internal equilibrium. So therefore this equation is applicable for a closed system in a state of internal equilibrium when volume change is the only form of work and more importantly we need to remember this can also be applicable when any particular system undergoes a internal chemical reaction as a result of which its composition changes but whatever be the case the composition change or the chemical reaction just affects the change in volume there is no other change within the system.

So therefore this can be applicable even when the system inside the close system that has some reaction going through into it but we need to remember that the affect of the reaction will be a change in volume and there will be no other work other than volume change occurring within this particular close system which is in a state of internal equilibrium. So under these conditions we find that the equation is applicable and if we replace this PdV with dpV minus VdP then we can just write down the internal energy equation in the form of enthalpy. So from the combined first and second law we have obtained these 2 generalized equations.

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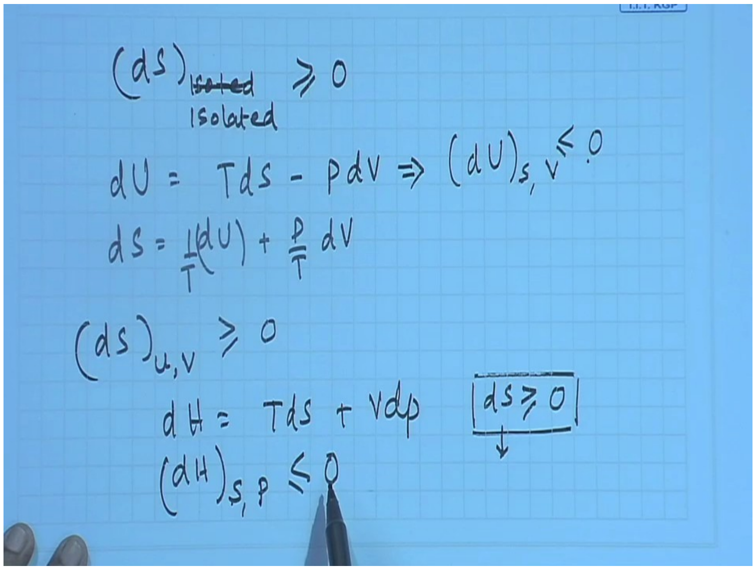

$$(ds)_{\cancel{\text{isoted}}} \geqslant 0$$

isolated

$$dU = Tds - pdV \Rightarrow (dU)_{s,v} \leqslant 0$$

$$ds = \frac{1}{T}(dU) + \frac{P}{T}dV$$

$$(ds)_{u,v} \geqslant 0$$

$$dH = Tds + Vdp \qquad \boxed{ds \geqslant 0} \downarrow$$

$$(dH)_{s,p} \leqslant 0$$

And the other thing which we have obtained from the combined first and second law is the criteria of spontaneity of a process but we need to remember that we could obtain the criteria of spontaneity just for an isolated system, what does this demand? This demands that in order to find out whether a process is feasible or not we need to find out the entropy change of the system and also the entropy change of the surroundings if the system is not isolated.

Here we need to remember that although finding the entropy change of a system is not very difficult finally the entropy change of the surroundings can often not be very easy and we would always like to concentrate our attention on the system we would like to calculate any change in state of the system in terms of the change of its properties this is much more straightforward than calculating the entropy change of the surroundings.

So therefore what we would like to do is, we would like to concentrate on this system and we would like to find out whether any criteria of spontaneity can be obtained by just considering the system without bothering about the surroundings for a closed system. For the time being we concentrate on systems where only Pv work is being performed, later on we are going to see what happens when even non-Pv work is involved in this particular case, right?

So before I start I would just like to you remind you something which I said a little time back what I meant to say is that when I say dS isolated equals to 0 and when I consider this particular equation what do I get? I get dU equals to TdS minus PdV or in other words what I get is dS equals to 1 by T dU plus P by T dV, right?

And from isolated system what does it imply? Isolated system implies that system has a constant internal energy and the system has a constant volume such that the system which means that the system does not perform any Pv type of work there is no change in internal energy of the system automatically which implies that the system has no interaction with the surroundings in the form of heat and work and for such a system we know that dS is greater than equal to 0.

Can this not just be reverted and written? If you observe this equation can I not write down that dU at constant S, V should be less than equal to 0, does this equation not imply this? It is almost equivalent to say that a circle is an enclosed surface which has a minimum area for a given parameter or a maximum perimeter for a given area, both the statements are the same. In the same way this statement and this statement they are equivalent to one another and we find that for constant entropy constant volume condition dU less than equal to 0 should be the criteria of spontaneity, right? Where U is the internal energy change of the system, mind it.

Similarly if we take up the other equation which is dH equals to TdS plus VdP from this equation we know that dS is greater than equal to 0 is the criteria of spontaneity does it not imply dH at constant S, P is less than equal to 0. So therefore from these 4 equations or rather from the last 3 equations what do we get?

We find out that for an isolated system dS U,V is greater than equal to 0, from here we automatically see that if the entropy of the system is kept constant then for this isentropic process the system has to interact with the surrounding such that the volume is also kept constant for such a system we can have dU is less than equal to 0 in the similar way that if this entropy and the pressure is constant then it implies that dH S,P should be less than equal to 0.

What I mean to say is that again I will repeat the same thing entropy maximum principle also corresponds to the energy minimization principle which you are so familiar with in your mechanics class. Now as I repeat that we would be more interested to find out the condition of equilibrium or the condition of spontaneity by just observing the system when the system undergoes some particular interactions with the surroundings.

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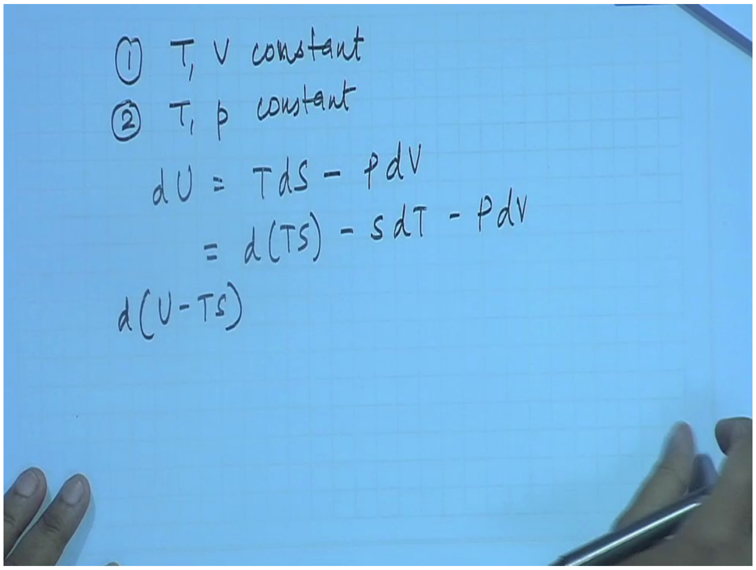

① T, V constant

② T, p constant

$$dU = TdS - pdV$$

$$= d(TS) - SdT - pdV$$

$$d(U - TS)$$

The 2 most common type of interactions which we are mostly interested or which we encountered in our practical applications are firstly system surrounding interacting under constant temperature volume conditions and second thing the more common work the more common phenomena is under constant temperature and pressure, now when such a thing happens let us see that if by looking at the system only we can find out the criteria of spontaneity.

Again we go back to the same equation and let us see dU equals to TdS minus PdV using the Legendre transform can we write down this equation as, in this particular form? I believe we can do this, so therefore what does it give you? Does it give you d of U minus TS. Well, I would just change this a little and I will write that will be better.

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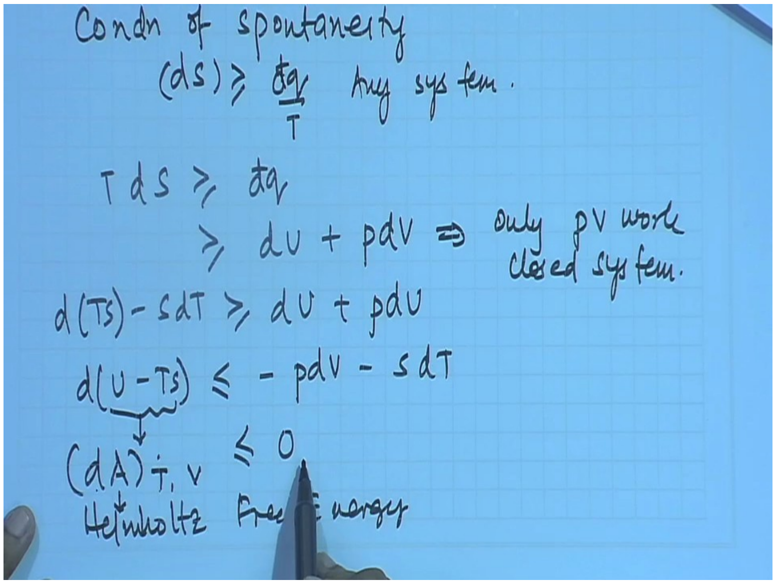

Condn of spontaneity

$(dS) \geq \frac{dq}{T}$ Any system.

$TdS \geq dq$

$\geq dU + pdV \Rightarrow$ only pV work closed system.

$d(TS) - SdT \geq dU + pdU$

$\underbrace{d(U-TS)}_{\downarrow} \leq -pdV - SdT$

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

$\downarrow$ Helmholtz Free Energy

Sorry, if it's a condition of spontaneity that I want to find out, the condition of spontaneity which gives you dS is greater than equal to dq by T or TdS is greater than equal to dq which is greater than equal to dU plus PdV provided only Pv work happens and the system is a closed system.

So therefore for this particular thing using the Legendre transform I can write it down as or in other words can I not write it down as d of U minus TS is less than equal to minus pdv minus SdT and what is this U minus TS? This is nothing but the Helmholtz free energy it is nothing but the Helmholtz free energy which we find that under conditions of constant temperature and constant volume this is less than equal to 0.

So what I have deduced? From the condition of spontaneity for any system we know that the condition of spontaneity is dS greater than equal to this from here I have deduced that for any system when the temperature and the volume remains constant the Helmholtz free energy is less than equal to 0. In the same way suppose we would like to find out the condition of spontaneity under constant temperature pressure conditions.

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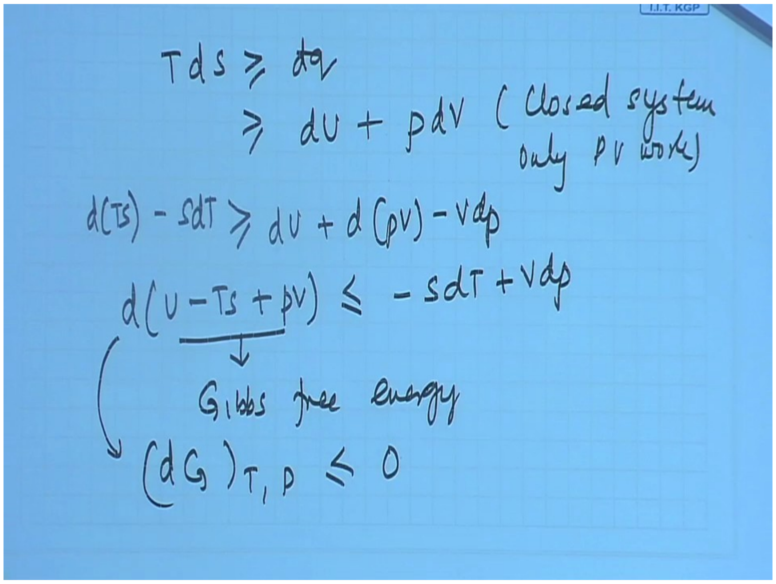

$$Tds \geq dq$$

$$\geq dU + pdV \quad (\text{Closed system only PV work})$$

$$d(Ts) - SdT \geq dU + d(pV) - Vdp$$

$$d(\underbrace{U - Ts + pV}_{\downarrow}) \leq -SdT + Vdp$$

Gibbs free energy

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

We start from the same thing TdS is greater than equals to dq which is greater than equal to dU plus pdV we need to remember that we are just working again with closed system only PV work So therefore this will be greater than equal to dU plus d Pv minus vdp this can be written down as TdS minus SdT, so therefore what we get? We get U minus TS plus pv this is less than equals to minus SdT and plus Vdp or in other words as we all know this is nothing but the Gibbs free energy and this equation implies dG at constant temperature pressure conditions is less than equal to 0.

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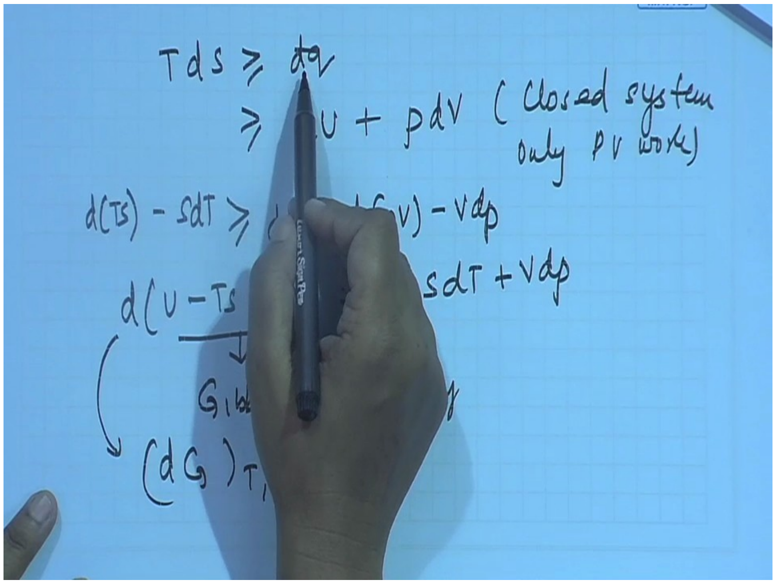

$Tds \geq \bar{d}q$

$\geq \quad U + pdV$ (Closed system only PV work)

$d(TS) - SdT \geq \quad v) - vdp$

$d(U - TS \quad SdT + Vdp$

Gib

$(dG)_{T,}$

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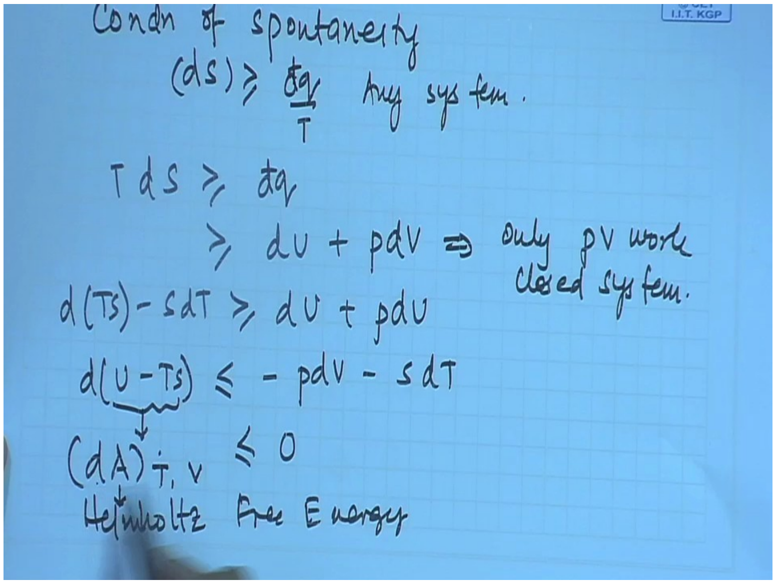

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$TdS \geq \bar{d}q$

$\geq dU + pdV \Rightarrow$ only pV work closed system.

$d(TS) - SdT \geq dU + pdU$

$d(\underbrace{U - TS}) \leq -pdV - SdT$

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

Helmholtz Free Energy

So therefore from the condition of spontaneity we found out that if you really want to find out the condition of spontaneity when the system and the surroundings are interacting under constant temperature volume conditions than the actual conditions rather whether the process is spontaneous or not can be found out by calculating the Helmholtz free energy if it is less than equal to 0 the process is spontaneous and if the system and the surrounding interacting under isobaric isothermal conditions we need to calculate the Gibbs free energy. If the total Gibbs free energy of the system is less than or equal to 0 the process is spontaneous.

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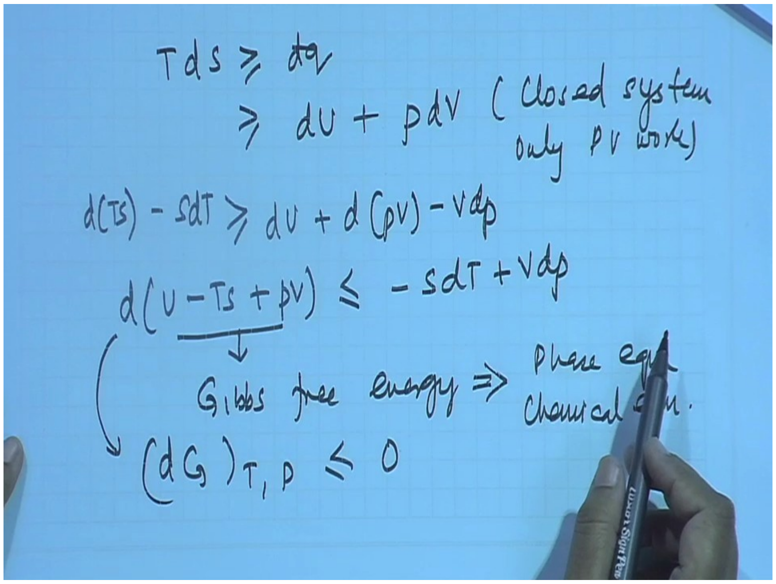

$$Tds \geqslant dq$$

$$\geqslant dU + pdV \quad (\text{Closed system only PV work})$$

$$d(TS) - SdT \geqslant dU + d(pV) - Vdp$$

$$d(\underbrace{U - TS + pV}_{\text{Gibbs free energy}}) \leqslant -SdT + Vdp$$

Gibbs free energy ⇒ Phase eqm. Chemical eqm.

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

So therefore we have once more deduced 2 other important properties the Helmholtz free energy and the Gibbs free energy and I would like to remind you that since we are mostly dealing with constant temperature constant pressure conditions this Gibbs free energy is going to be very important for all phase equilibrium and chemical equilibrium problem and this is going to stay with us for the remaining portion of our phase equilibrium thermodynamics class. So we continue with these discussions on Gibbs free energy Helmholtz free energy in our next class, thank you very much.