Chemical Engineering Thermodynamics
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Lecture-24
Equilibrium and Stability-I

Welcome back, in today's lecture, we are going to talk about Equilibrium and Stability. In the early stage of this lecture, we looked at the concept of the Entropy Maximum for defining an equilibrium condition.

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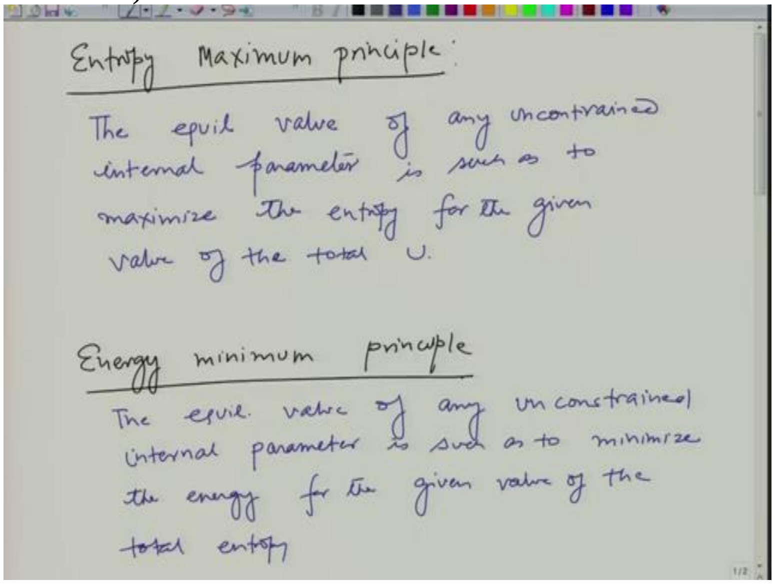

Entropy Maximum principle:

The equil value of any unconstrained internal parameter is such as to maximize the entropy for the given value of the total U.

Energy minimum principle

The equil. value of any unconstrained internal parameter is such as to minimize the energy for the given value of the total entropy

So, the earlier definition or what we have used was something called Entropy Maximum Principle. So, I am going to just write it down, this is something which we have used to obtain conditions such as temperature equality, pressure equality and chemical potential equality for an equilibrium system.

So, the definition is that 'the equilibrium value of any unconstrained internal parameter is such as to maximize the entropy for the given value of the total internal energy'. So, for given internal energy the system tends to maximize the entropy, okay in order to achieve the equilibrium condition.

So, that is what we used in the earlier stage of the course and we use the maximization of entropy to obtain various different conditions. Now, what we saying this particular concept or principle is equivalent to the Energy Minimum Principle okay, which says that the equilibrium value of any unconstrained internal parameters, so it says ‘the equilibrium value of any unconstrained internal parameters is such as to minimize the energy for the given value of the total entropy’.

So, it says that for fixed entropy, the energy is going to get minimized to achieve the equilibrium state, okay that is what is saying that, so these two statements or two principles are equivalent.

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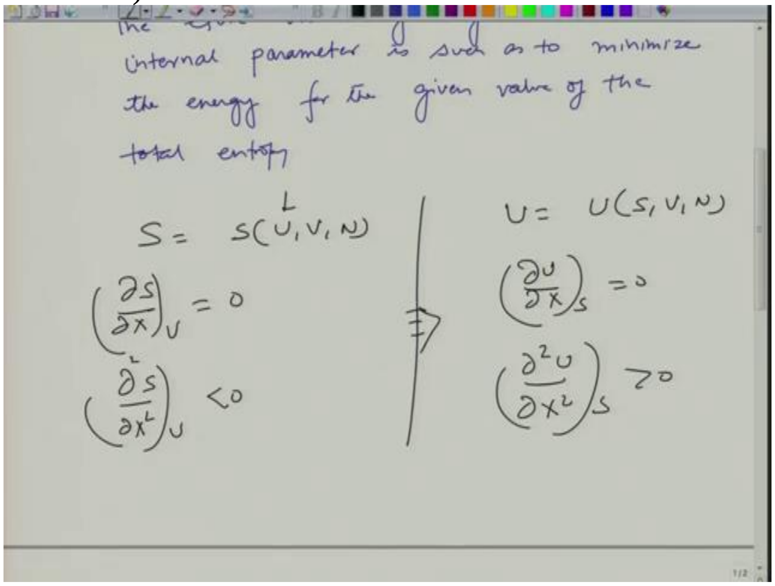

The

internal parameter is such as to minimize the energy for the given value of the total entropy

$$S = S(U,V,N) \qquad U = U(S,V,N)$$

$$\left(\frac{\partial S}{\partial X}\right)_V = 0 \quad \Rightarrow \quad \left(\frac{\partial U}{\partial X}\right)_S = 0$$

$$\left(\frac{\partial^2 S}{\partial X^2}\right)_U < 0 \qquad \left(\frac{\partial^2 U}{\partial X^2}\right)_S > 0$$

$$S = S(U, V, N)$$

$$\left(\frac{\partial S}{\partial X}\right)_V = 0$$

$$\left(\frac{\partial^2 S}{\partial X^2}\right)_U < 0$$

$$U = U(S, V, N)$$

$$\left(\frac{\partial U}{\partial X}\right)_S = 0$$

$$\left(\frac{\partial^2 U}{\partial X^2}\right)_S > 0$$

So, this is because this S has to be maximum. So, this is the definition of the maximum, the first and second derivatives should be zero and less than zero respectively. Now, this we are saying that this is equivalent or saying that if we consider U as a function of SV so, far given total S, so this is equivalent in some sense. So, let us try to get this proof of kind of equivalence.

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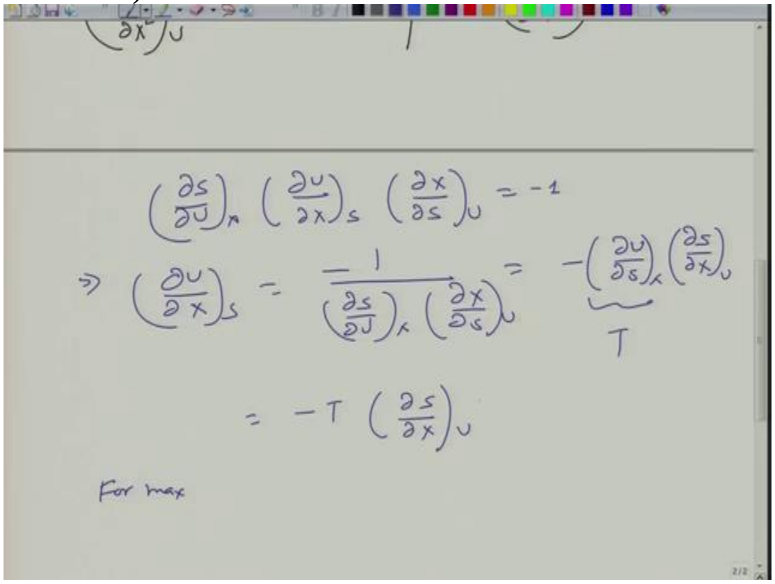

$$\left(\frac{\partial S}{\partial U}\right)_X \left(\frac{\partial U}{\partial X}\right)_S \left(\frac{\partial X}{\partial S}\right)_U = -1$$

$$\Rightarrow \left(\frac{\partial U}{\partial X}\right)_S = \frac{-1}{\left(\frac{\partial S}{\partial U}\right)_X \left(\frac{\partial X}{\partial S}\right)_U} = -\underbrace{\left(\frac{\partial U}{\partial S}\right)_X}_{T} \left(\frac{\partial S}{\partial X}\right)_U$$

$$= -T \left(\frac{\partial S}{\partial X}\right)_U$$

For max

So, for in order to get that let me just first consider the following, so the question is how do you prove this? So, let us consider the chain rule, okay where X could be anything here, this must be one okay, right, so you have SUX and that is what this relation we know.

$$\left(\frac{\partial S}{\partial U}\right)_X \left(\frac{\partial U}{\partial X}\right)_S \left(\frac{\partial X}{\partial S}\right)_U = -1$$

$$\left(\frac{\partial U}{\partial X}\right)_S = -\frac{1}{\left(\frac{\partial S}{\partial U}\right)_X \left(\frac{\partial X}{\partial S}\right)_U} = -\left(\frac{\partial U}{\partial S}\right)_X \left(\frac{\partial S}{\partial X}\right)_U = -T \left(\frac{\partial S}{\partial X}\right)_U$$

So, this at maximum X should be equal to zero,

$$\left(\frac{\partial U}{\partial X}\right)_S = 0$$

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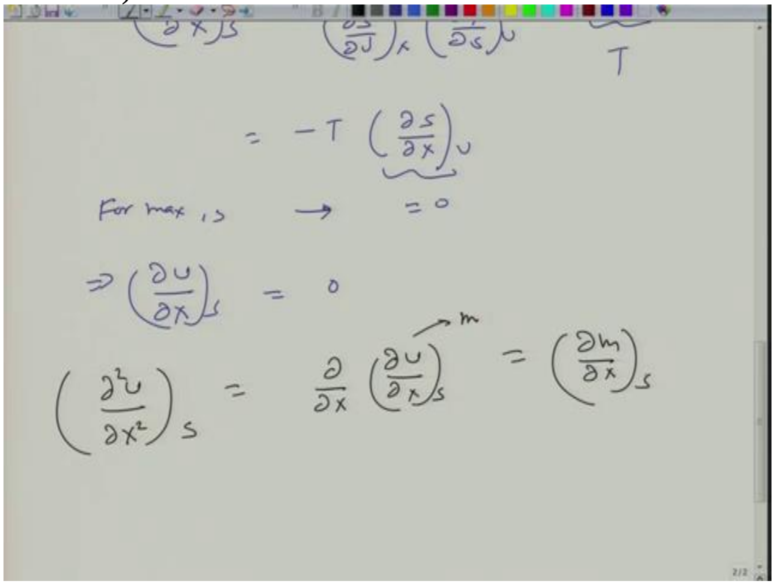

$$T$$

$$= -T \underbrace{\left(\frac{\partial S}{\partial X}\right)_U}$$

For max, S $\rightarrow$ $= 0$

$$\Rightarrow \left(\frac{\partial U}{\partial X}\right)_S = 0$$

$$\left(\frac{\partial^2 U}{\partial X^2}\right)_S = \frac{\partial}{\partial X}\overset{\rightarrow m}{\left(\frac{\partial U}{\partial X}\right)_S} = \left(\frac{\partial m}{\partial X}\right)_S$$

So, this we are trying to get the equivalence of these two different relations which we are saying that these are both equivalent. So, for a given S, U should be minimum or vice versa okay and we are talking about unconstrained at this point internal variables.

So, let me also get the second derivative, second derivative we have to prove for minimum U they should be negative, how do we do that? So, let us first start with the expression, okay we want this to be evaluated, so let me just break this again here Del U by Del X, okay. For the sake of simplicity we are saying this as a m.

$$\left(\frac{\partial^2 U}{\partial X^2}\right)_S = \frac{\partial}{\partial X}\left(\frac{\partial U}{\partial X}\right)_S = \left(\frac{\partial m}{\partial X}\right)_S$$

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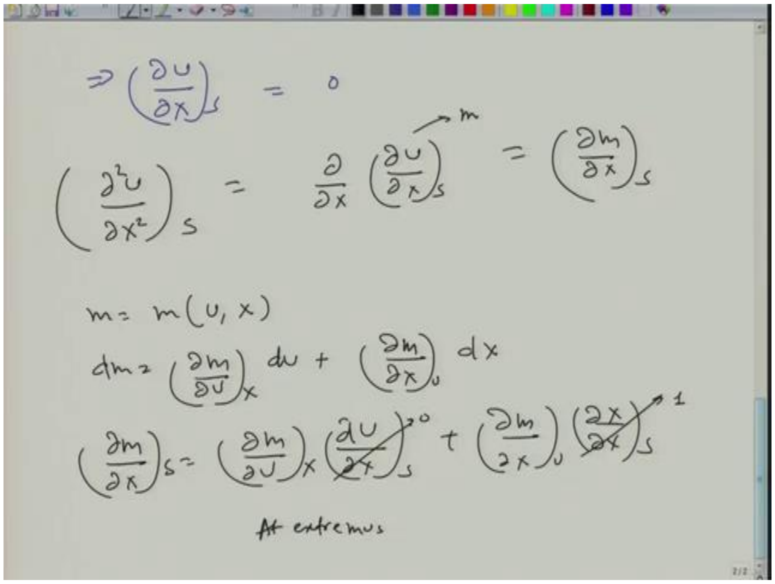

$$\Rightarrow \left(\frac{\partial U}{\partial X}\right)_S = 0$$

$$\left(\frac{\partial^2 U}{\partial X^2}\right)_S = \frac{\partial}{\partial X}\overset{\nearrow m}{\left(\frac{\partial U}{\partial X}\right)_S} = \left(\frac{\partial m}{\partial X}\right)_S$$

$$m = m(U, X)$$

$$dm = \left(\frac{\partial m}{\partial U}\right)_X dU + \left(\frac{\partial m}{\partial X}\right)_U dX$$

$$\left(\frac{\partial m}{\partial X}\right)_S = \left(\frac{\partial m}{\partial U}\right)_X \cancel{\left(\frac{\partial U}{\partial X}\right)_S}^{\,0} + \left(\frac{\partial m}{\partial X}\right)_U \cancel{\left(\frac{\partial X}{\partial X}\right)_S}^{\,1}$$

At extremus

$$m = m(U, X)$$

$$dm = \left(\frac{\partial m}{\partial U}\right)_X dU + \left(\frac{\partial m}{\partial X}\right)_U dX$$

$$\left(\frac{\partial m}{\partial X}\right)_S = \left(\frac{\partial m}{\partial U}\right)_X \left(\frac{\partial U}{\partial X}\right)_S + \left(\frac{\partial m}{\partial X}\right)_U \left(\frac{\partial X}{\partial X}\right)_S$$

So, we need to find out this. Now, M is basically a function of U and X okay, from the definition you can clearly see M is a function of U and X hence I can write D M as D del M by Del U constant X DU plus Del X constant U Del X okay. So, this is by simple, if you do take the differentiation.

Now, since we want Del M by Del X so, I take this, differentiate this with respect to X. So, Del M by the Del X; keeping S constant, so, this will be Del M by Del U X Del U by Del X keeping S constant plus okay, now this will be one and what about this at extremum. So, at extremum this should be zero as we have already defined it here.

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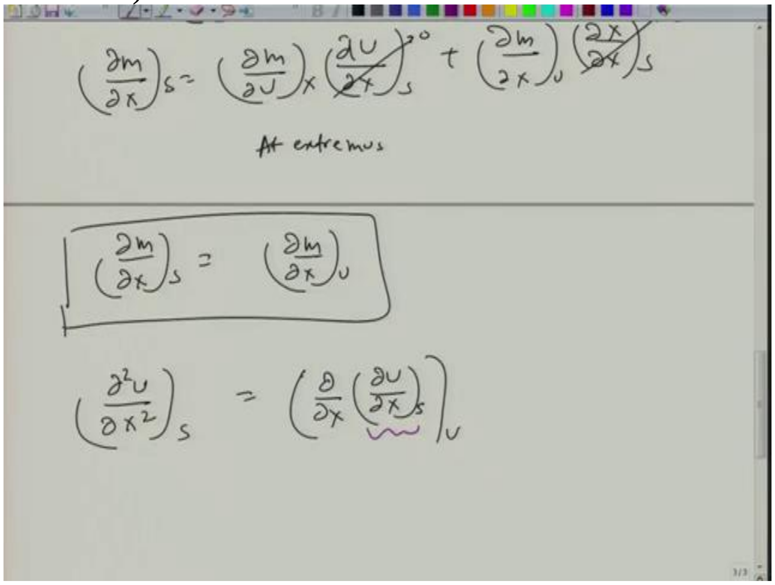

$$\left(\frac{\partial m}{\partial x}\right)_s = \left(\frac{\partial m}{\partial U}\right)_x \cancel{\left(\frac{\partial U}{\partial x}\right)_s}^{0} + \left(\frac{\partial m}{\partial x}\right)_U \cancel{\left(\frac{\partial x}{\partial x}\right)_s}$$

At extremus

$$\boxed{\left(\frac{\partial m}{\partial x}\right)_s = \left(\frac{\partial m}{\partial x}\right)_U}$$

$$\left(\frac{\partial^2 U}{\partial x^2}\right)_s = \left(\frac{\partial}{\partial x}\underbrace{\left(\frac{\partial U}{\partial x}\right)_s}\right)_U$$

So, this is what we can obtain from this derivation for the case of extremum okay.

$$\left(\frac{\partial m}{\partial X}\right)_S = \left(\frac{\partial m}{\partial X}\right)_U$$

So, now, we go back and put the variables here so,

$$\left(\frac{\partial^2 U}{\partial X^2}\right)_S = \left(\frac{\partial}{\partial X}\left(\frac{\partial U}{\partial X}\right)_S\right)_V$$

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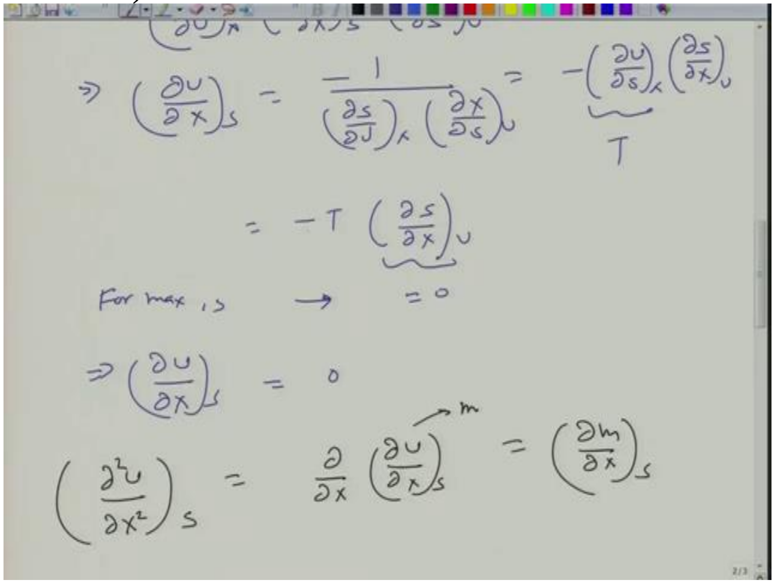


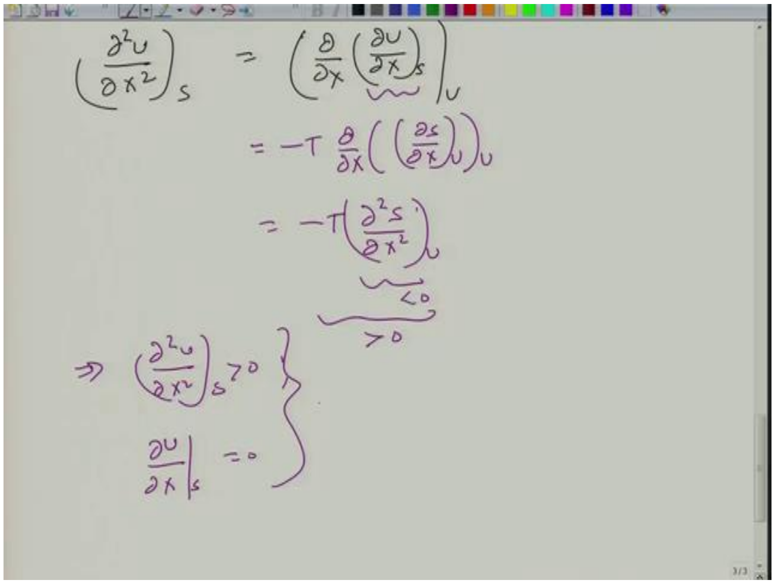
$$\Rightarrow \left(\frac{\partial U}{\partial x}\right)_s = \frac{-1}{\left(\frac{\partial s}{\partial U}\right)_x \left(\frac{\partial x}{\partial s}\right)_U} = -\underbrace{\left(\frac{\partial U}{\partial s}\right)_x}_{T}\left(\frac{\partial s}{\partial x}\right)_U$$

$$= -T\underbrace{\left(\frac{\partial s}{\partial x}\right)_U}$$

For max, s $\rightarrow$ $= 0$

$$\Rightarrow \left(\frac{\partial U}{\partial x}\right)_s = 0$$

$$\left(\frac{\partial^2 U}{\partial x^2}\right)_s = \frac{\partial}{\partial x}\overset{\to m}{\left(\frac{\partial U}{\partial x}\right)_s} = \left(\frac{\partial m}{\partial x}\right)_s$$



$$\left(\frac{\partial^2 U}{\partial X^2}\right)_S = \left(\frac{\partial}{\partial X}\underbrace{\left(\frac{\partial U}{\partial X}\right)_S}\right)_U$$

$$= -T\,\frac{\partial}{\partial X}\left(\left(\frac{\partial S}{\partial X}\right)_U\right)_U$$

$$= \underbrace{-T\underbrace{\left(\frac{\partial^2 S}{\partial X^2}\right)_U}_{<0}}_{>0}$$

$$\left.\begin{array}{l}\Rightarrow \left(\frac{\partial^2 U}{\partial X^2}\right)_S > 0 \\ \left.\frac{\partial U}{\partial X}\right|_S = 0\end{array}\right\}$$

$$\left(\frac{\partial^2 U}{\partial X^2}\right)_S = \left(\frac{\partial}{\partial X}\left(\frac{\partial U}{\partial X}\right)_S\right)_V$$

$$= -T\,\frac{\partial}{\partial X}\left(\left(\frac{\partial S}{\partial X}\right)_U\right)_U$$

$$= -T\left(\frac{\partial^2 S}{\partial X^2}\right)_U$$

Now, this we know at extremum if you look at the definition this must be less than zero okay. So, if this is less than zero that means, this is less than zero that means this is greater than zero. So, essentially this gives you the second condition.

$$\left(\frac{\partial^2 U}{\partial X^2}\right)_S > 0$$

$$\frac{\partial U}{\partial S}\Big|_S = 0$$

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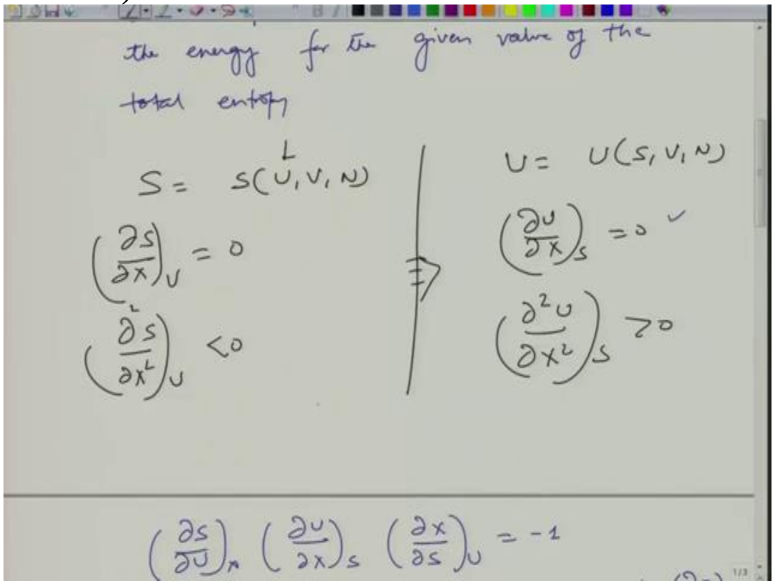

the energy for the given value of the total entropy

$$S = S(U, V, N) \qquad U = U(S, V, N)$$

$$\left(\frac{\partial S}{\partial X}\right)_U = 0 \quad \Rightarrow \quad \left(\frac{\partial U}{\partial X}\right)_S = 0 \checkmark$$

$$\left(\frac{\partial^2 S}{\partial X^2}\right)_U < 0 \qquad \left(\frac{\partial^2 U}{\partial X^2}\right)_S > 0$$

$$\left(\frac{\partial S}{\partial U}\right)_X \left(\frac{\partial U}{\partial X}\right)_S \left(\frac{\partial X}{\partial S}\right)_U = -1$$

So, this is something which we have derived and that means if you look at the original question was, that this principle was used to evaluate the equivalent conditions by maximizing the entropy for a given internal energy, okay this is equivalent to saying that U is minimum for a given entropy okay. So, that is an important aspect okay.

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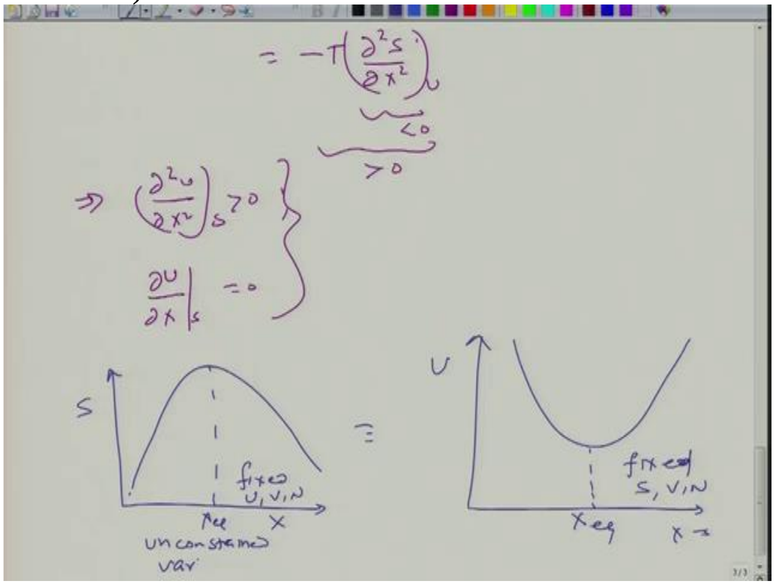

$$= -T\underbrace{\underbrace{\left(\frac{\partial^2 S}{\partial X^2}\right)_U}_{<0}}_{>0}$$

$$\Rightarrow \left.\begin{aligned} &\left(\frac{\partial^2 U}{\partial X^2}\right)_S > 0 \\ &\left.\frac{\partial U}{\partial X}\right|_S = 0 \end{aligned}\right\}$$

So, this essentially can be drawn also. So, one can come up with this kind of diagrammatic explanation of this that for S as a function of X which is unconstrained variable, okay this reaches a maximum for a fixed U, V, N and this is equivalent to saying that U or yeah some kind of this U as a function of again X unconstrained variable and this is something which we get a X equilibrium. So, this is X, okay for a fixed S, V, N okay. So, this is something which is equivalent, that is something which we have just derived.

So, using this concept of minimum energy we can actually try to again evaluate the conditions of equilibrium such as thermal equilibrium and so forth. So, for the sake of illustration, I am going to just do one example okay. So, this would be just establishment of thermal equilibrium and similarly you can do that for pressure and chemical potential.

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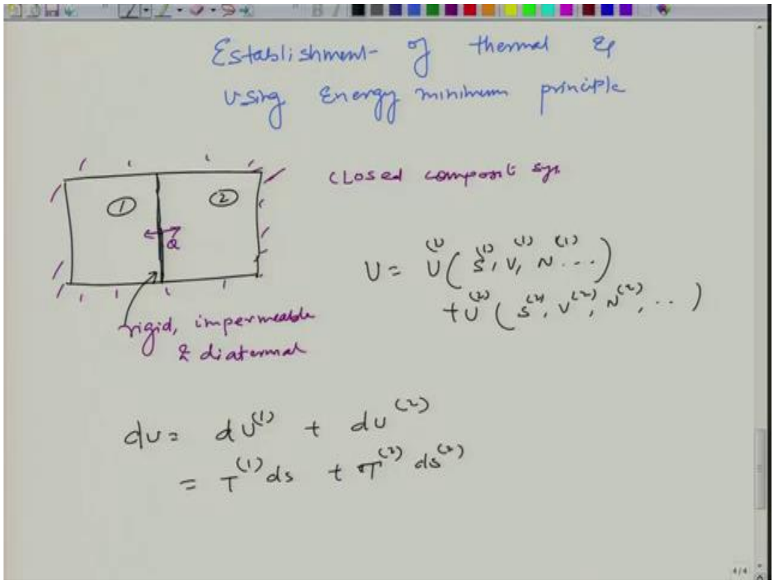

Establishment of thermal eq
using Energy minimum principle

Closed composite sys

$$U = U^{(1)}(S^{(1)}, V^{(1)}, N^{(1)} \ldots) + U^{(2)}(S^{(2)}, V^{(2)}, N^{(2)}, \ldots)$$

$$dU = dU^{(1)} + dU^{(2)}$$
$$= T^{(1)} dS + T^{(2)} dS^{(2)}$$

So, establishment of thermal equilibrium using Energy Minimum Principle, okay. So, consider the closed composite system, okay with a rigid, so we can draw it like this let us say okay. So, this is rigid, impermeable and diathermal. So, essentially the heat can exchange back and forth okay. But it is a closed system okay and is a composite, so, it is a closed composite system.

So, what is the total energy of this overall system? We can write it as:

$$U = U^1(S^1, V^1, N^1 \ldots) + U^2(S^2, V^2, N^2, \ldots)$$

So, what we know is that total volume and number of these are constant and known. So, total energy is fixed okay, and in the initial stage SN1 and S2 can change because of the heat exchange okay.

So, we can write:

$$dU = dU^1 + dU^2 = T^1 dS + T^2 dS^2$$

And since there we are saying that you know, the only contribution is through the heat. So, the change in the internal energy for one and two are caused by into the heat and we can write it there considering is an equilibrium processor slow process, we can write this directly as this, okay. So, this is something which we can write now, this has to be zero because total energy is constant okay.

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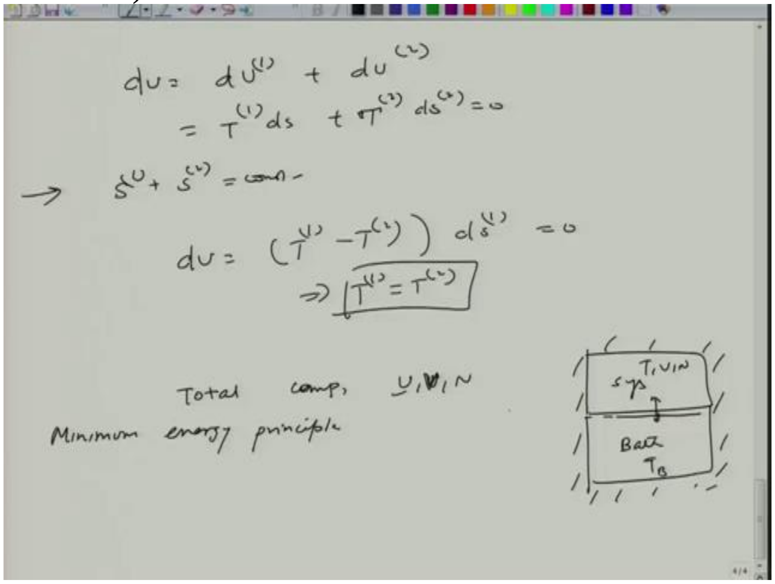

$$dU = dU^{(1)} + dU^{(2)}$$
$$= T^{(1)} ds + T^{(2)} ds^{(2)} = 0$$
$$\rightarrow \quad S^{(1)} + S^{(2)} = \text{const.}$$
$$dU = (T^{(1)} - T^{(2)})\, ds^{(1)} = 0$$
$$\Rightarrow \boxed{T^{(1)} = T^{(2)}}$$

Total comp, U, V, N

Minimum energy principle

Now, we also can consider that at equilibrium of course, at equilibrium what is the conditions of this temperature? So, at equilibrium of course, we are considering that will, the total energy will be fixed here and thus, we can write:

$$S^1 + S^2 = constant$$

$$dU = (T^1 - T^2) dS^1 = 0$$

$$T^1 = T^2$$

So, we are not making use of that at this point. But of course, we can clearly see here we made use of the total entropy is constant, okay, that from the different perspective here, okay, so you can do the similar exercises for the pressure equality and chemical potential equality, okay. So what we are going to do is we are going to change these conditions now, we will be using the Energy Minimum Principle to find out what is the thermodynamic variable which we should look at if we change the natural variable.

So, as of now, the natural variables are S, V, N for the internal energy, but since we have now developed thermodynamic functions for different changes, different conditions of the natural variables for the case of T, V, N it is harness free energy for the case of you know T, P, N is a Gibb's free energy.

So, considering those changes, what is this natural variables or changes in the natural variables or the corresponding thermodynamic functions. Considering different constraints, what would be the conditions on the thermodynamic functions if there is a change in the equilibrium state? Total let us say composite system at U, V, N we still can consider that but our systems or the system which we are interested in is at T, V, N, by making sure that you have a diathermal rigid wall, but heat, heat is being exchange with a bath which is at temperature T okay. So, this could be a T, B okay.

So, with this bath essentially the system temperature will reach at T and so, we can consider this to be all isolated. So, total composite could be total energy U, V, and N okay. Now, with this we can apply Minimum Energy Principle, okay and find out what is the appropriate variables which would give the indication of equilibrium condition or in another word what would be the conditions of the thermodynamic functions associated with T, V, N, okay will it be positive, will it be negative, so, that is something which we would like to lead to that kind of conclusion.

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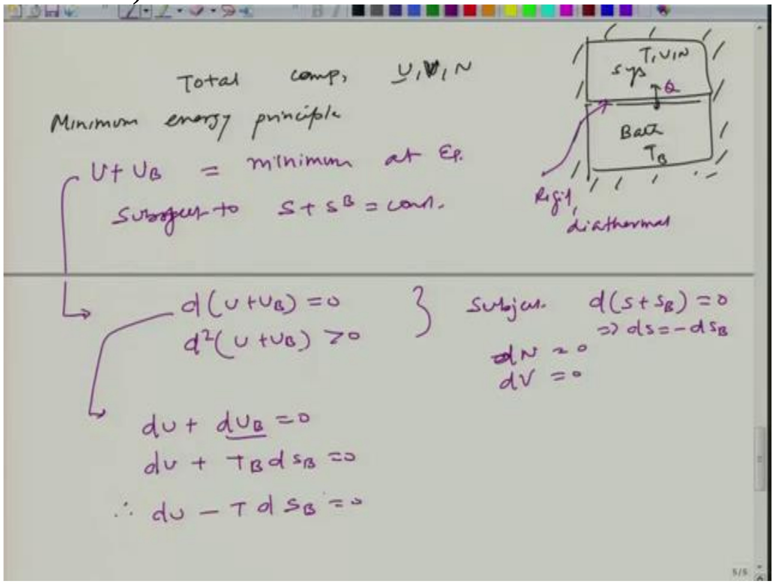

Total comp, U, V, N

Minimum energy principle

$U + U_B$ = minimum at Ep.

Subject to $S + S^B$ = const.

$d(U+U_B) = 0$

$d^2(U+U_B) > 0$

subject $d(S+S_B) = 0$

$\Rightarrow dS = -dS_B$

$dN = 0$

$dV = 0$

$dU + \underline{dU_B} = 0$

$dU + T_B dS_B = 0$

$\therefore dU - T dS_B = 0$

$$U + U_B = minimum\ at\ equilibrium\ \ subject\ to\ S + S_B = constant$$

$$d(U + U_B) = 0 \qquad subject\ to, d(S + S_B) = 0$$

$$d^2(U + U_B) > 0 \qquad or, dS = -dS_B$$

$$dU + dU_B = 0 \qquad dN = 0$$

$$dU + T_B dS_B = 0 \qquad dV = 0$$

$$Therefore, dU - TdS_B = 0$$

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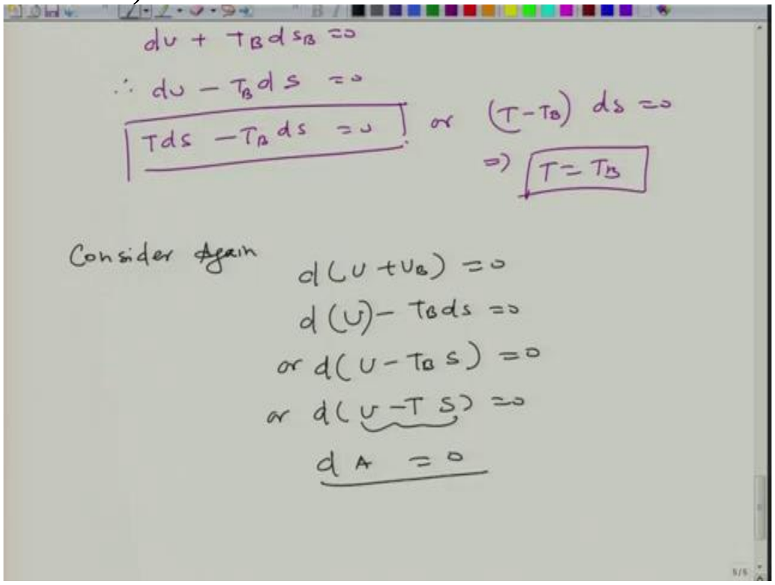

$dU + T_B dS_B = 0$

$\therefore dU - T_B dS = 0$

$\boxed{T dS - T_B dS = 0}$ or $(T - T_B)\, dS = 0$

$\Rightarrow \boxed{T = T_B}$

Consider Again

$d(U + U_B) = 0$

$d(U) - T_B dS = 0$

or $d(U - T_B S) = 0$

or $d(\underbrace{U - TS}) = 0$

$\underline{dA = 0}$

$$d(U + U_B) = 0$$

$$d(U) - T_B dS = 0$$

$$or, d(U - TS) = 0$$

$$dA = 0$$

So, that means, one of the condition is of course, that dA should be equal to zero, for such a system here okay, where we maintaining the temperature volume and number of moles.

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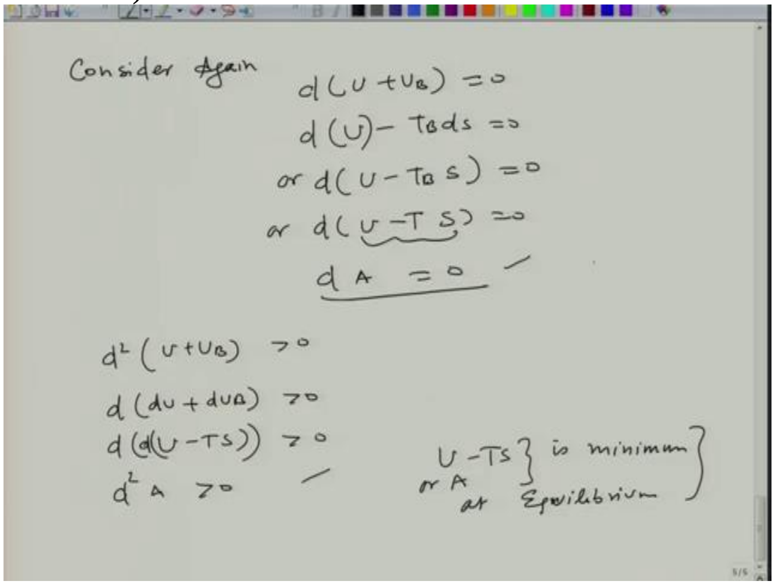

Consider Again

$$d(U + U_B) = 0$$

$$d(U) - T_B ds = 0$$

$$or \ d(U - T_B S) = 0$$

$$or \ d(\underbrace{U - T S}) = 0$$

$$\underline{dA = 0} \ ✓$$

$$d^2(U + U_B) > 0$$

$$d(dU + dU_B) > 0$$

$$d(d(U - TS)) > 0$$

$$d^2 A > 0 \ ✓$$

$$\left.\begin{matrix} U - TS \\ or \ A \end{matrix}\right\} \text{is minimum at Equilibrium}$$

Now, let us look at the second derivative.

$$d^2(U + U_B) > 0$$

$$d(dU + dU_B) > 0$$

$$d\big(d(U - TS)\big) > 0$$

$$d^2A > 0 \qquad U - TS \ or \ A \ is \ minimum \ at \ equilibrium$$

So, this indicates that both this condition indicates that for the case of such a system, where you maintaining temperature, volume and and N your U minus TS must be minimum. So U minus TS or A is minimum at equilibrium. So something which we have derived, okay other thing which we have derived from this is of course, the temperature equality.

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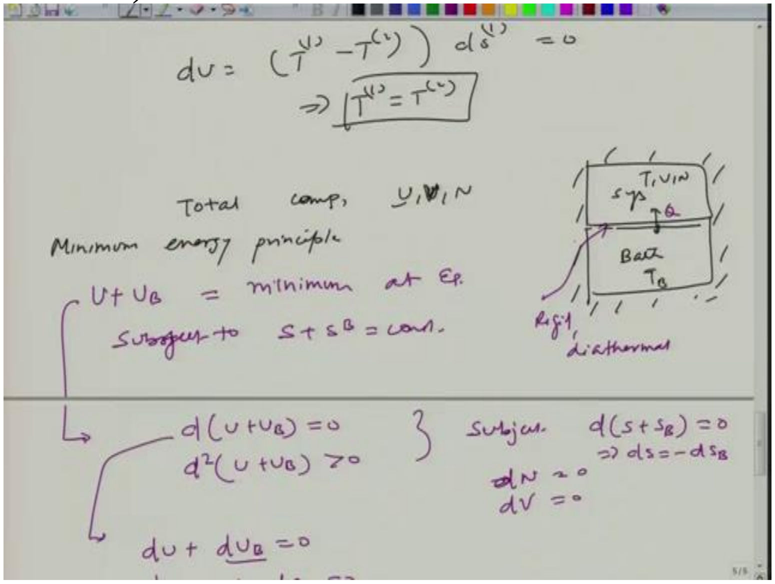

$dU = (T^{(1)} - T^{(2)})\, dS^{(1)} = 0$

$\Rightarrow \boxed{T^{(1)} = T^{(2)}}$

Total comp, U, V, N

Minimum energy principle

$U + U_B$ = minimum at Eq.

subject to $S + S^B$ = const.

$d(U+U_B) = 0$

$d^2(U+U_B) > 0$ } subject $d(S+S_B) = 0$

$\Rightarrow dS = -dS_B$

$dN = 0$

$dV = 0$

$dU + \underline{dU_B} = 0$

Because, so that was for this constraint where we put temperature of course, you can extend this understanding and analysis for more difficult conditions. Now, what we have done is all this derivation was at an equilibrium.

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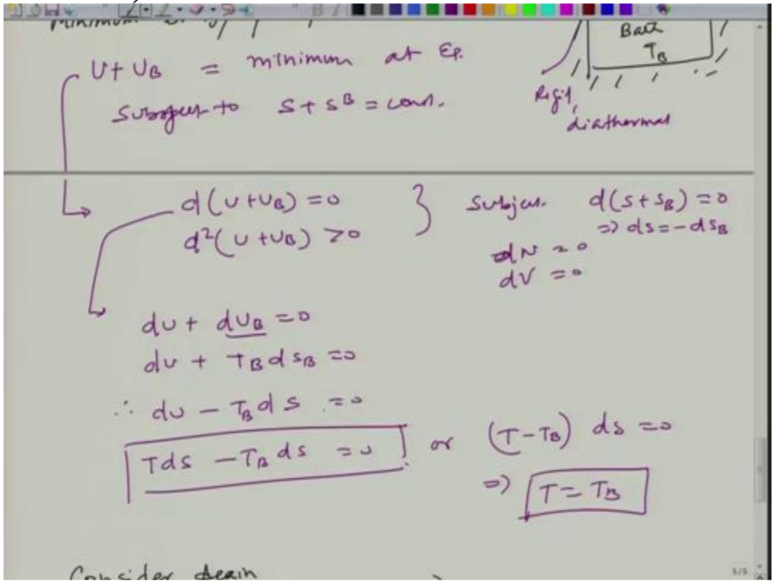


$U + U_B$ = minimum at Eq.

subject to $S + S^B$ = const.

$d(U+U_B) = 0$

$d^2(U+U_B) > 0$ } subject $d(S+S_B) = 0$

$\Rightarrow dS = -dS_B$

$dN = 0$

$dV = 0$

$dU + \underline{dU_B} = 0$

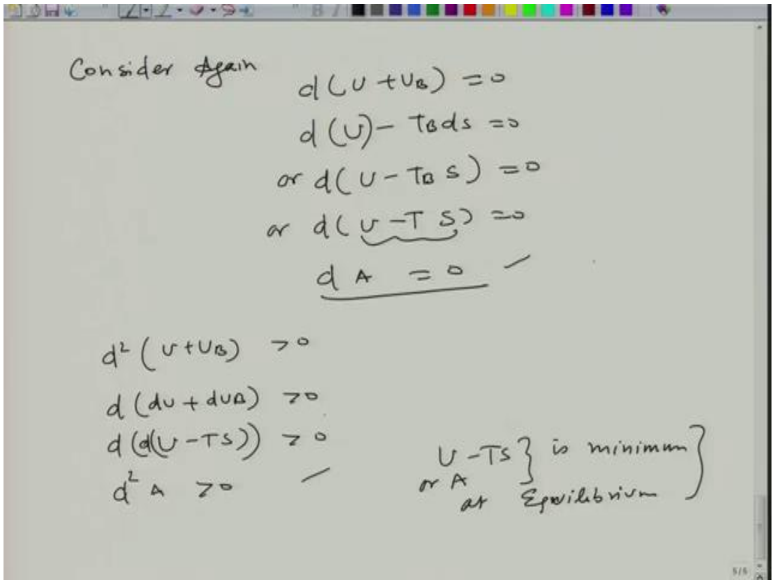
$dU + T_B\, dS_B = 0$

$\therefore dU - T_B\, dS = 0$

$\boxed{T dS - T_B dS = 0}$ or $(T - T_B)\, dS = 0$

$\Rightarrow \boxed{T = T_B}$

Consider again



Consider Again

$$d(U + U_B) = 0$$
$$d(U) - T_B\,dS = 0$$
$$\text{or } d(U - T_B S) = 0$$
$$\text{or } d(\underbrace{U - TS}) = 0$$
$$\underline{dA = 0} \;\checkmark$$

$$d^2(U + U_B) > 0$$
$$d(dU + dU_B) > 0$$
$$d(d(U - TS)) > 0$$
$$d^2A > 0 \;\checkmark$$

$U - TS$ or A } is minimum at Equilibrium

So, but you can also consider the case where you a little bit off equilibrium in that case your entropy is not going to be constant, is going to be greater than zero, total entropy. So, how do you do that? What would be the appropriate variables which you are going to get as far as this Helmholtz energy is concerned. So, let us look at it, okay because in your case, you can clearly see the DA is equal to zero, the first derivative and second derivative is greater than zero that means A is to be minimum for such a condition.

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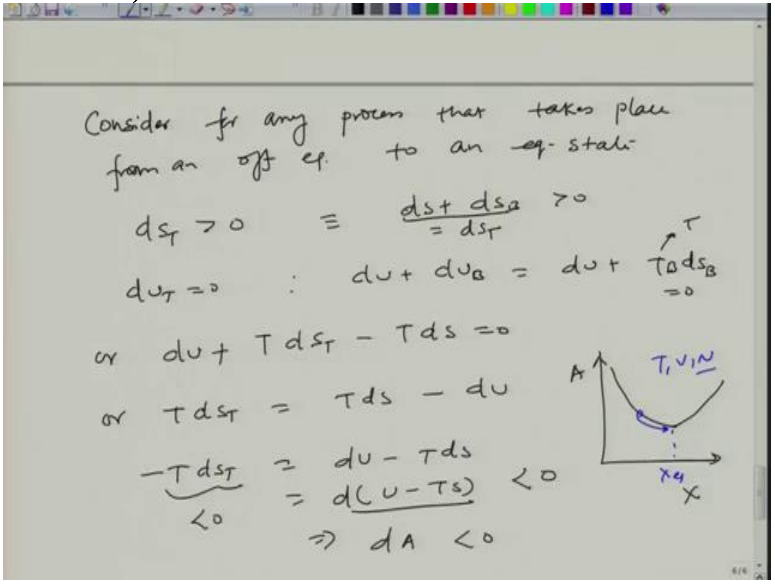

Consider for any process that takes place from an off eq. to an eq. state

$$dS_T > 0 \quad \equiv \quad \underset{= dS_T}{\underline{dS + dS_B}} > 0$$

$$dU_T = 0 \quad : \quad dU + dU_B = dU + \underset{=0}{\overset{T}{T_B}\,dS_B}$$

$$\text{or} \quad dU + T\,dS_T - T\,dS = 0$$

$$\text{or} \quad T\,dS_T = T\,dS - dU$$

$$\underbrace{-T\,dS_T}_{<0} = dU - T\,dS = \underline{d(U - TS)} < 0$$

$$\Rightarrow dA < 0$$

So, now let us little bit extend it so, that we can understand the complete picture here. So, consider for any process that takes place from an off equilibrium to an equilibrium state, okay. So, we are considering a process which takes from an off equilibrium and going towards an equilibrium space, in such case your total entropy should be greater than zero, total energy still remains zero.

$$dS_T > 0 \quad or, dS + dS_B > 0$$

$$dU_T = 0 \quad or, \qquad dU + dU_B = dU + T_B dS_B = 0$$

$$dU + TdS_T - TdS = 0$$

$$TdS_T = TdS - dU$$

$$-TdS_T = dU - TdS = d(U - TS) < 0 \; or, dA = 0$$

So what we are, what we do by doing this simple exercise is when you have a process that takes place from an off equilibrium to an equilibrium state, the free energy tends to reduce and eventually at equilibrium the dA is going to be zero.

So, it will reduce until the point equilibrium reaches. So you can draw this like this, so you have A and some X is unconstrained variables. So it is going to be like this of your like here, then if you are like off process going towards the minimum then essentially the DA has to be less than zero, okay.

Similarly, for the case of whether it is off equilibrium here, so this is your X equilibrium for a given T okay. So you can, you can do these exercises for other cases as well. But for now, I think we can stop and we will take this further in the next class, okay, so see you in the next class.