Chemical Engineering Thermodynamics
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Lecture-27
Intrinsic stability of the thermodynamic system

Welcome back. So, in the last lecture we were trying to look at the equilibrium and stability analysis of thermodynamic systems and in particular, we address the conditions or constraints on the thermodynamic variable as far as the signs are concerned.

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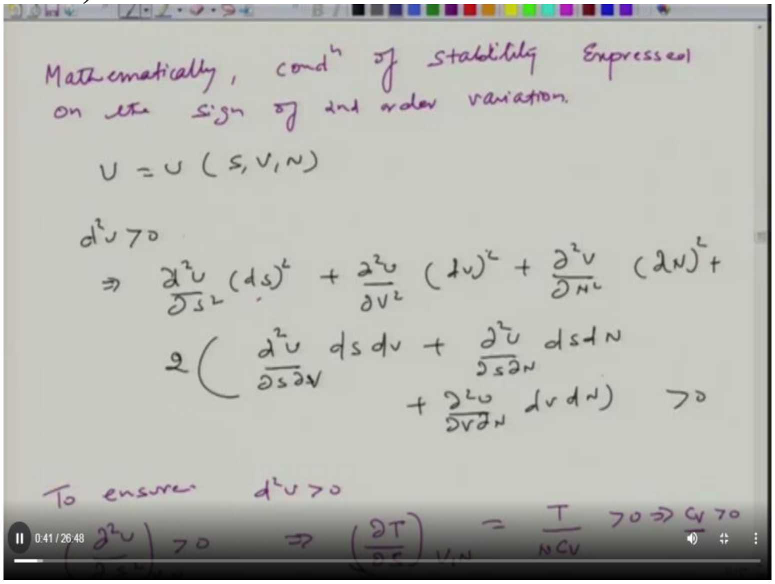


Mathematically, cond^n of stability expressed on the sign of 2nd order variation.

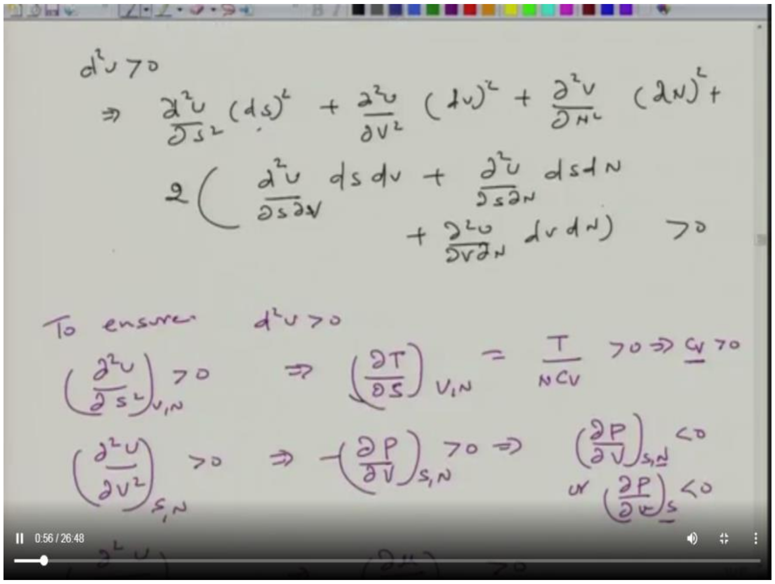
$$U = U(S, V, N)$$

$$d^2U > 0$$

$$\Rightarrow \frac{\partial^2 U}{\partial S^2}(dS)^2 + \frac{\partial^2 U}{\partial V^2}(dV)^2 + \frac{\partial^2 U}{\partial N^2}(dN)^2 + 2\left(\frac{\partial^2 U}{\partial S \partial V} dS\, dV + \frac{\partial^2 U}{\partial S \partial N} dS\, dN + \frac{\partial^2 U}{\partial V \partial N} dV\, dN\right) > 0$$

To ensure $d^2U > 0$

$$\left(\frac{\partial^2 U}{\partial S^2}\right) > 0 \Rightarrow \left(\frac{\partial T}{\partial S}\right)_{V,N} = \frac{T}{N C_V} > 0 \Rightarrow C_V > 0$$



$$d^2U > 0$$

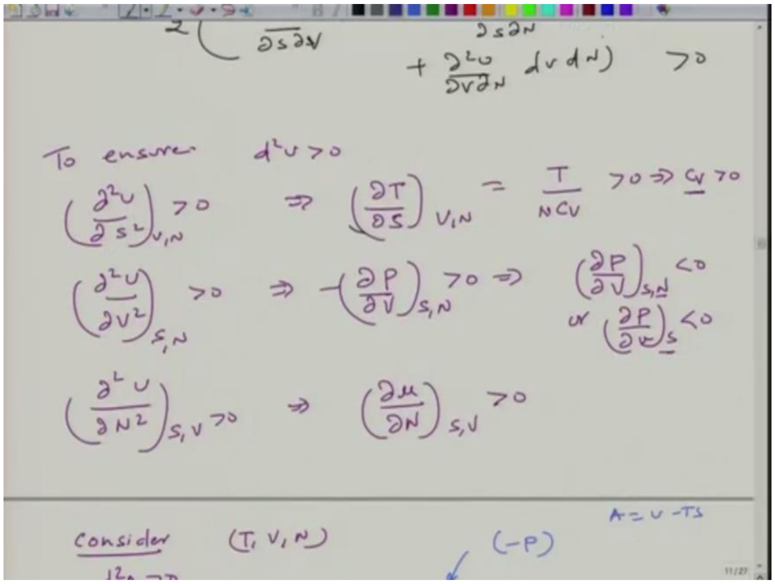
$$\Rightarrow \frac{\partial^2 U}{\partial S^2}(dS)^2 + \frac{\partial^2 U}{\partial V^2}(dV)^2 + \frac{\partial^2 U}{\partial N^2}(dN)^2 + 2\left(\frac{\partial^2 U}{\partial S \partial V} dS\, dV + \frac{\partial^2 U}{\partial S \partial N} dS\, dN + \frac{\partial^2 U}{\partial V \partial N} dV\, dN\right) > 0$$

To ensure $d^2U > 0$

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,N} > 0 \Rightarrow \left(\frac{\partial T}{\partial S}\right)_{V,N} = \frac{T}{N C_V} > 0 \Rightarrow \underline{C_V} > 0$$

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_{S,N} > 0 \Rightarrow -\left(\frac{\partial P}{\partial V}\right)_{S,N} > 0 \Rightarrow \left(\frac{\partial P}{\partial V}\right)_{S,N} < 0$$

$$\text{or } \left(\frac{\partial P}{\partial v}\right)_{s} < 0$$



$$2\Big(\frac{\partial^2 U}{\partial S\partial V} \quad \frac{\quad}{\partial S\partial N} + \frac{\partial^2 U}{\partial V\partial N}\,dV\,dN\Big) > 0$$

To ensure $d^2U > 0$

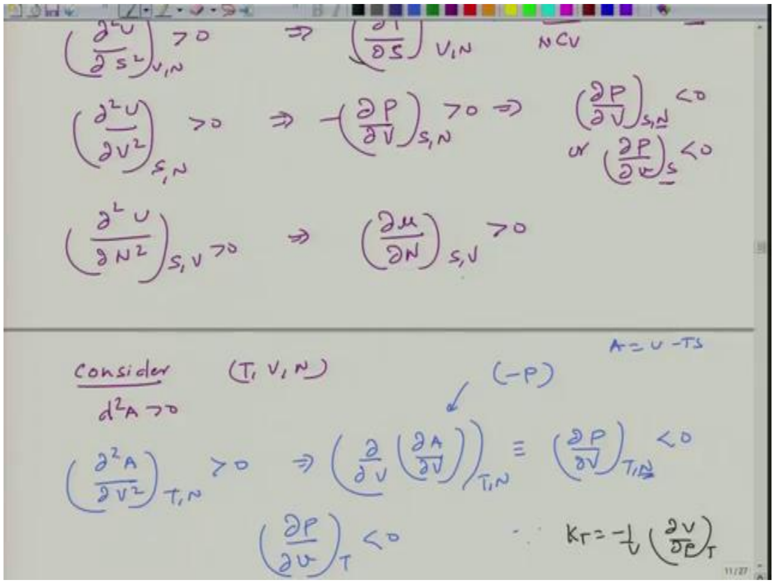
$$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,N} > 0 \Rightarrow \left(\frac{\partial T}{\partial S}\right)_{V,N} = \frac{T}{NC_V} > 0 \Rightarrow \underline{C_V} > 0$$

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_{S,N} > 0 \Rightarrow -\left(\frac{\partial P}{\partial V}\right)_{S,N} > 0 \Rightarrow \left(\frac{\partial P}{\partial V}\right)_{S,\underline{N}} < 0 \text{ or } \left(\frac{\partial P}{\partial V}\right)_{\underline{S}} < 0$$

$$\left(\frac{\partial^2 U}{\partial N^2}\right)_{S,V} > 0 \Rightarrow \left(\frac{\partial \mu}{\partial N}\right)_{S,V} > 0$$

$A = U - TS$

Consider (T, V, N) $(-P)$



$$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,N} > 0 \Rightarrow \left(\frac{\partial T}{\partial S}\right)_{V,N} \quad NC_V$$

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_{S,N} > 0 \Rightarrow -\left(\frac{\partial P}{\partial V}\right)_{S,N} > 0 \Rightarrow \left(\frac{\partial P}{\partial V}\right)_{S,\underline{N}} < 0 \text{ or } \left(\frac{\partial P}{\partial V}\right)_{\underline{S}} < 0$$

$$\left(\frac{\partial^2 U}{\partial N^2}\right)_{S,V} > 0 \Rightarrow \left(\frac{\partial \mu}{\partial N}\right)_{S,V} > 0$$

$A = U - TS$

Consider (T, V, N)

$d^2A > 0$ $(-P)$

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,N} > 0 \Rightarrow \left(\frac{\partial}{\partial V}\left(\frac{\partial A}{\partial V}\right)\right)_{T,N} \equiv \left(\frac{\partial P}{\partial V}\right)_{T,\underline{N}} < 0$$

$$\left(\frac{\partial P}{\partial V}\right)_T < 0 \quad \therefore K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

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

$$d^2U > 0$$

$$\frac{\partial^2 U}{\partial S^2}(dS)^2 + \frac{\partial^2 U}{\partial V^2}(dV)^2 + \frac{\partial^2 U}{\partial N^2}(2N)^2 + 2\left(\frac{\partial^2 U}{\partial S\partial V}dSdV + \frac{\partial^2 U}{\partial S\partial N}dSdN + \frac{\partial^2 U}{\partial V\partial N}dVdN\right) > 0$$

To ensure $d^2U > 0$

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,N} > 0 \quad Or, \quad \left(\frac{\partial T}{\partial S}\right)_{V,N} = \frac{T}{NC_V} > 0 \; Or, C_V > 0$$

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_{S,N} > 0 \quad Or, \quad -\left(\frac{\partial P}{\partial V}\right)_{S,N} > 0 \quad Or, \left(\frac{\partial P}{\partial V}\right)_{S,N} < 0 \; and \; \left(\frac{\partial P}{\partial V}\right)_{S} < 0$$

$$\left(\frac{\partial^2 U}{\partial N^2}\right)_{S,V} > 0 \quad Or, \quad \left(\frac{\partial \mu}{\partial N}\right)_{S,V} > 0$$

Consider (T,V,N) $A = U - TS$

$$d^2A > 0$$

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,N} > 0 \quad Or, \left(\frac{\partial\left(\frac{\partial A}{\partial V}\right)}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial V}\right)_{T,N} < 0$$

$$\left(\frac{\partial P}{\partial V}\right)_{T} < 0$$

So, we try to derive something like this where we showed that for the stability these variables such as isothermal compressibility and heat capacity must be greater than zero. This we analyzed using a simple fact that I know, using the simple nature of the curve as a function of some intensive variable or extensive variable that the second derivative must be greater than zero for the equilibrium conditions and this ensures that this derivative as is shown here, this must be greater than zero.

Now, note that this S here, these derivatives are with respect to the extensive variable S, V and N. Now, this leads to the condition such as C V must be greater than zero and the change in the pressure with respect to the volume at constant S must be less than zero and the change in the chemical potential with respect to change in the number of moles must be greater than 0.

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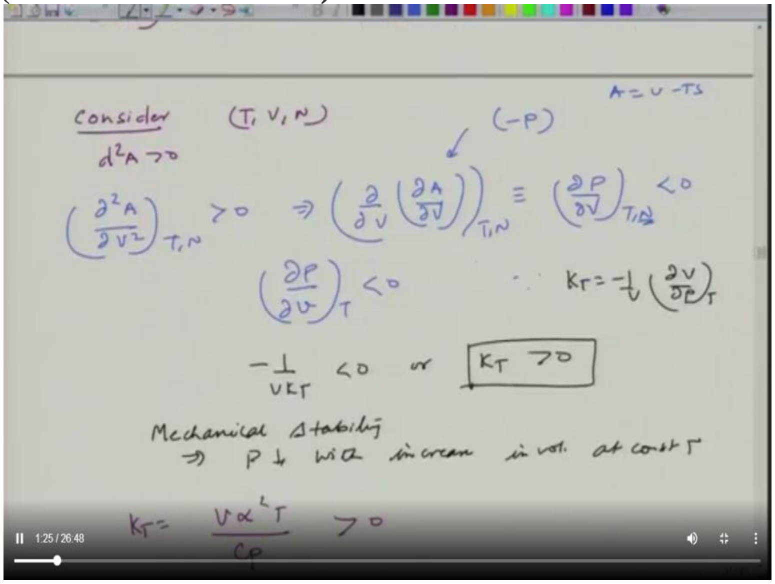


$A = U - TS$

Consider (T, V, N)

$d^2A > 0$

$(-P)$

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,N} > 0 \Rightarrow \left(\frac{\partial}{\partial V}\left(\frac{\partial A}{\partial V}\right)\right)_{T,N} \equiv \left(\frac{\partial P}{\partial V}\right)_{T,N} < 0$$

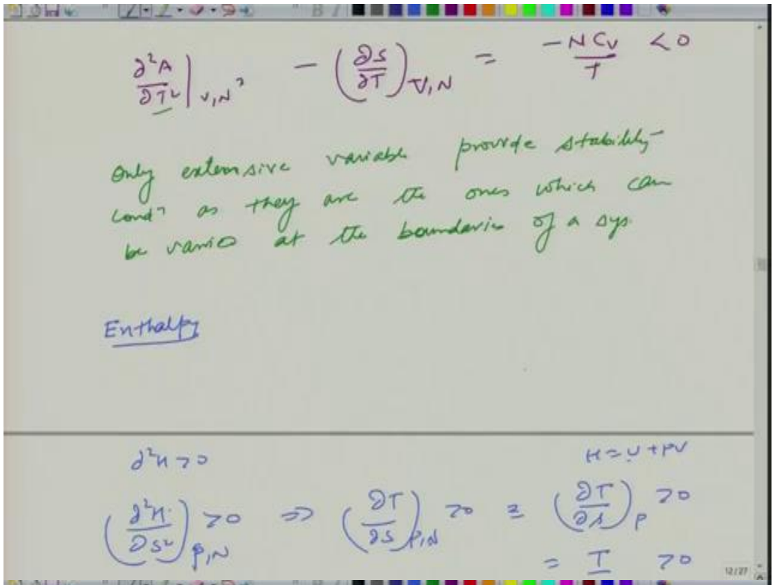
$$\left(\frac{\partial P}{\partial V}\right)_{T} < 0 \qquad \because K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$-\frac{1}{VK_T} < 0 \text{ or } \boxed{K_T > 0}$$

Mechanical stability

$\Rightarrow$ P ↓ with increase in vol. at const T

$$K_T = \frac{V\alpha^2 T}{C_P} > 0$$



$\frac{\partial^2 A}{\partial T^2}\Big|_{V,N}$? $-\left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{-NC_V}{T} < 0$

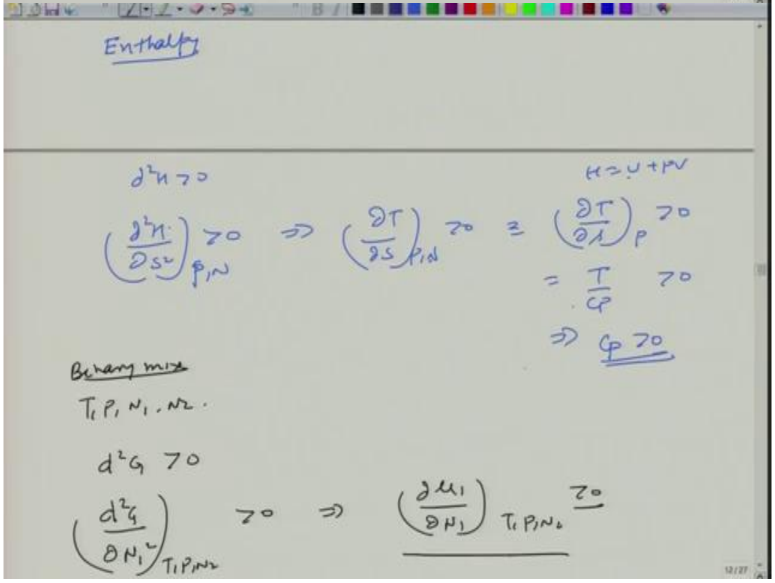
Only extensive variable provide stability cond^n as they are the ones which can be varied at the boundaries of a sys.

Enthalpy

$\partial^2 H > 0$ $H = U + PV$

$\left(\frac{\partial^2 H}{\partial S^2}\right)_{P,N} > 0 \Rightarrow \left(\frac{\partial T}{\partial S}\right)_{P,N} > 0 \equiv \left(\frac{\partial T}{\partial S}\right)_{P} > 0$

$= \frac{T}{} > 0$



Enthalpy

$\partial^2 H > 0$ $H = U + PV$

$\left(\frac{\partial^2 H}{\partial S^2}\right)_{P,N} > 0 \Rightarrow \left(\frac{\partial T}{\partial S}\right)_{P,N} > 0 \equiv \left(\frac{\partial T}{\partial S}\right)_{P} > 0$

$= \frac{T}{C_P} > 0$

$\Rightarrow C_P > 0$

Binary mix

$T, P, N_1, N_2.$

$d^2G > 0$

$\left(\frac{d^2G}{\partial N_1^2}\right)_{T,P,N_2} > 0 \Rightarrow \left(\frac{\partial \mu_1}{\partial N_1}\right)_{T,P,N_2} > 0$

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$-\frac{1}{VK_T} < 0 \quad Or, \quad K_T > 0$$

$$K_T = \frac{V\alpha^2 T}{C_P} > 0$$

$$\frac{\partial^2 A}{\partial T^2}|_{V,N} - \left(\frac{\partial S}{\partial T}\right)_{V,N} = -\frac{NC_V}{T} < 0 \quad Or, C_V > 0$$

$$\partial^2 H > 0$$

$$\left(\frac{\partial^2 H}{\partial S^2}\right)_{P,N} > 0 \quad Or, \quad \left(\frac{\partial T}{\partial S}\right)_{P,N} > 0 = \left(\frac{\partial T}{\partial S}\right)_P > 0 = \frac{T}{C_P} > 0$$

$$Or, C_P > 0$$

$$d^2G > 0$$

$$\left(\frac{\partial^2 G}{\partial N_1^2}\right)_{T,P,N_2} > 0 \quad Or, \quad \left(\frac{\partial \mu_1}{\partial N_1}\right)_{T,P,N_2} > 0$$

Now, this is the further, if you do the analysis particularly with the Helmholtz free energy, this gives you the condition that KT must be greater than 0 and similarly other analysis we showed that a CV has to be greater than 0 and C P has to be greater than zero.

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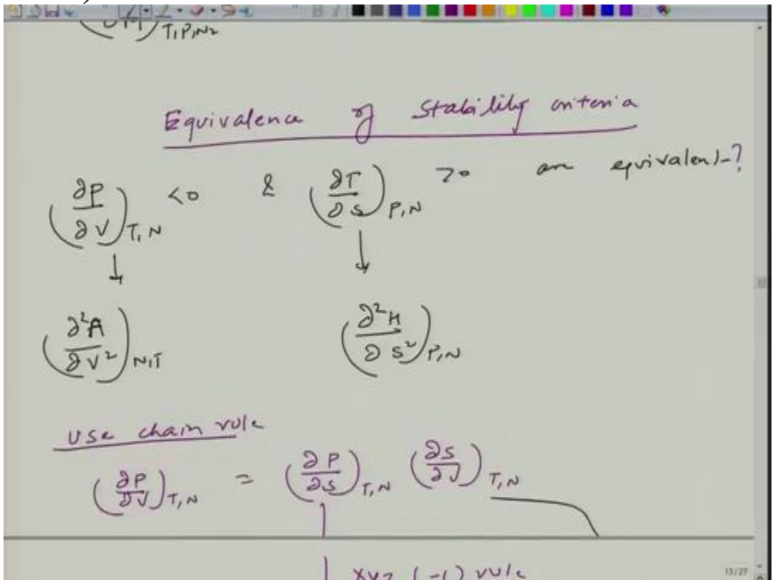


$)_{T,P,N_2}$

Equivalence of Stability criteria

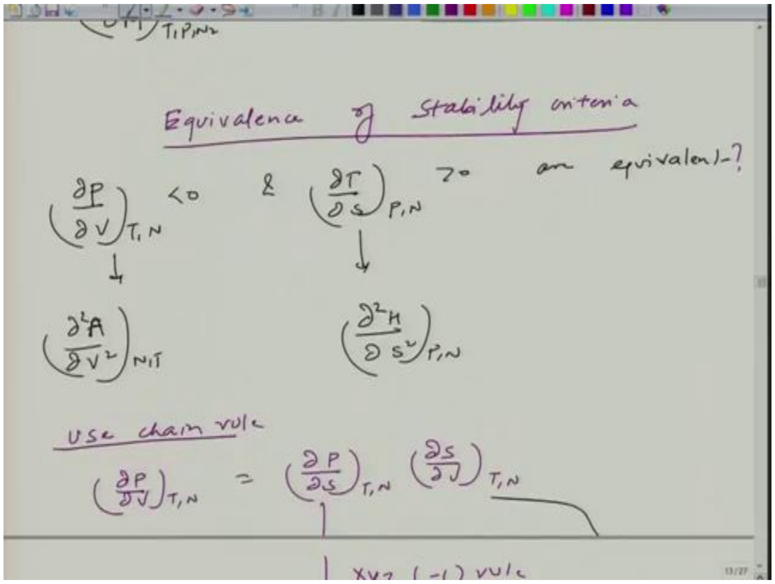
$\left(\frac{\partial P}{\partial V}\right)_{T,N} < 0$ & $\left(\frac{\partial T}{\partial S}\right)_{P,N} > 0$ are equivalent?

$$\left(\frac{\partial P}{\partial V}\right)_{T,N} \downarrow \left(\frac{\partial^2 A}{\partial V^2}\right)_{N,T} \qquad \left(\frac{\partial T}{\partial S}\right)_{P,N} \downarrow \left(\frac{\partial^2 H}{\partial S^2}\right)_{P,N}$$

use chain rule

$$\left(\frac{\partial P}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial S}\right)_{T,N} \left(\frac{\partial S}{\partial V}\right)_{T,N}$$

xyz (-1) rule



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use chain rule

$$\left(\frac{\partial P}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial S}\right)_{T,N} \left(\frac{\partial S}{\partial V}\right)_{T,N}$$

xyz (-1) rule

$$\left(\frac{\partial P}{\partial V}\right)_{T,N} < 0 \rightarrow \left(\frac{\partial^2 A}{\partial V^2}\right)_{N,T} \qquad and \qquad \left(\frac{\partial T}{\partial S}\right)_{P,N} > 0 \rightarrow \left(\frac{\partial^2 H}{\partial S^2}\right)_{P,N}$$

$$\left(\frac{\partial P}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial S}\right)_{T,N}\left(\frac{\partial S}{\partial V}\right)_{T,N}$$

So, we have analyzed this constraints on this thermodynamic properties which are nothing but the properties which you can evaluate in the experiment and hence you can find it out to whether the system you are working on are stable or not.

So, I will now extend this exercise and specifically look at the intrinsic ability of thermodynamic system where we would like to little bit differentiate between what is the local stability and global stability.

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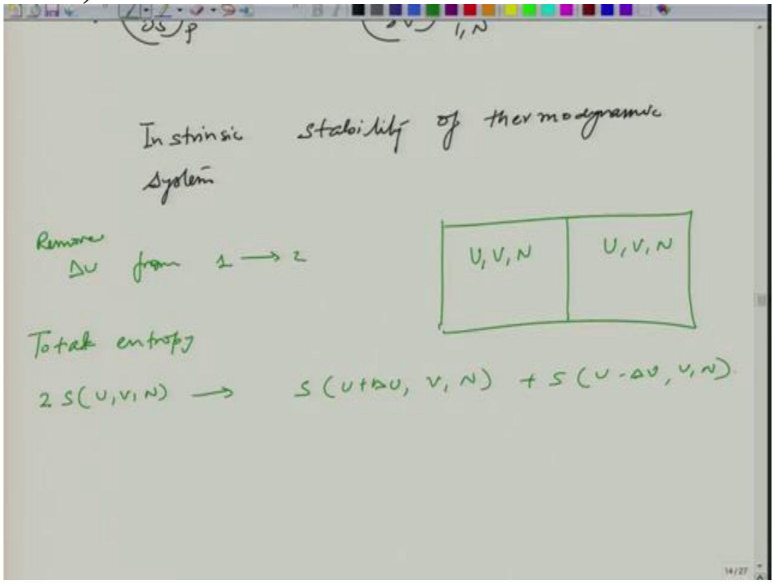

Instrinsic stability of thermodynamic System

Remove ΔU from $1 \longrightarrow 2$

Total entropy

$2S(U,V,N) \longrightarrow S(U+\Delta U, V, N) + S(U-\Delta U, V, N)$

So, in today's class I will try to address the remaining questions which we have listed down in the last class. But before that let me first finish the stability analysis aspect, where we did not address the global stability aspects and something which in today's class, it probably should become clear.

So, the intrinsic stability of thermodynamic system, so to illustrate that let me consider a two compartments separated by this partition and initially you have those systems equivalent such that this is, both are same. Now, what we are trying to do is we let say we remove Delta U from system 1 and transfer it to 2. Now, in that case, the total entropy could be something like

$$2S(U,V,N) \rightarrow S(U+\Delta U,V,N) + S(U\Delta U,V,N)$$

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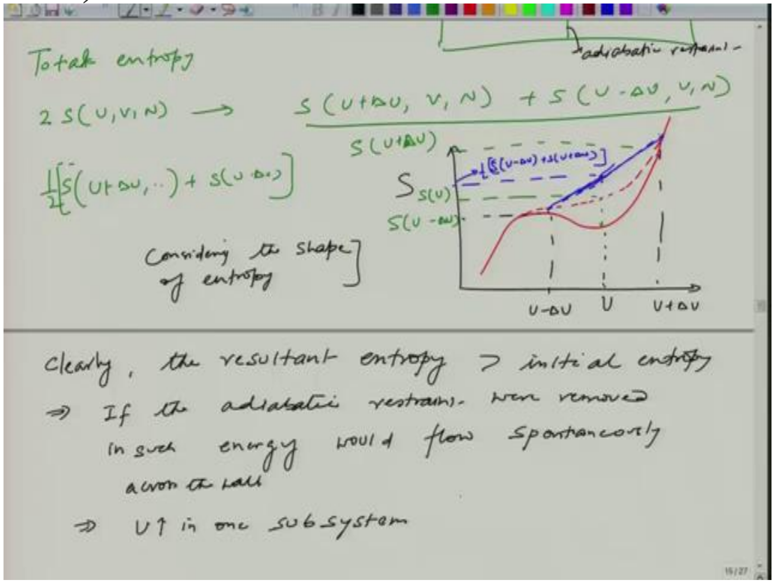

adiabatic restraint

Total entropy

$2S(U,V,N) \rightarrow \underline{S(U+\Delta U, V, N) + S(U-\Delta U, V, N)}$

$\frac{1}{2}\left[S(U+\Delta U, \ldots) + S(U-\Delta U)\right]$

[Considering the shape of entropy]

Clearly, the resultant entropy > initial entropy

⇒ If the adiabatic restraints were removed in such energy would flow spontaneously across the wall

⇒ U↑ in one sub-system

Now, assuming that entropy as a function of internal energy has this shape. So, let us assume this, so we consider the following shape and here at this point let us assume that this is U and then the change which we have considered is U minus Delta U and the corresponding change for the other compartments be U plus Delta U and here this is U S, U minus Delta U and this is your S U plus Delta U. We can consider this to be something like this. In that case S would be somewhere here U.

Now, if you consider this final perturbed version and if you look at the total or specifically if you just consider the half of this, so this may turn out to be somewhere which if you connect this two points here. I will make and I can draw a solid line instead. So, somewhere in the middle, this will be half of S U minus Delta U plus S U plus Delta U.

Now, clearly this means that entropy at the final state, if you have this kind of process where you remove Delta U from one end to another end or one compartment to another compartment, in that case the final state is going to be having more entropy compared to the original one.

Now, this can happen here. In this kind of a situation if you have transfer, so this means that if you take out the constraint then clearly the system will move in such a way to have this high entropy, but then the point is that this is not a physical system because the shape tells you that it undergoes this kind of thing whether you consider the solid one or whether you consider the dashed line and this kind of situation would yield phase separation such that it separate into this point another phase will come out to be this part. So, this kind of shape yields separation because there is no real phase space or the data point in this case. So, let me just write down the observation in such a case.

So, clearly the resultant entropy is greater than initial entropy. Now, this means that if this wall was adiabatic restraint initially, so if you remove if the adiabatic restraint is removed, were removed. In such a system, then in such a system which essentially means that you expecting, you assuming that this is a shape so, you can say considering the shape of entropy, where you do have this (convex) convexity in the intermediate region. So, if you consider this then the resultant entropy would be greater than the initial entropy.

If you transfer a small amount of let us say internal energy from one compartment to another the compartment and this would indicate that if you remove the adiabatic restraint then energy should flow spontaneously across the wall. So, if you remove the adiabatic restraint, that means we make it a thermal, then the energy would transfer from one compartment to another compartment across the wall. So, this means U will increase in one subsystem in that case, of course the temperature would be also increasing.

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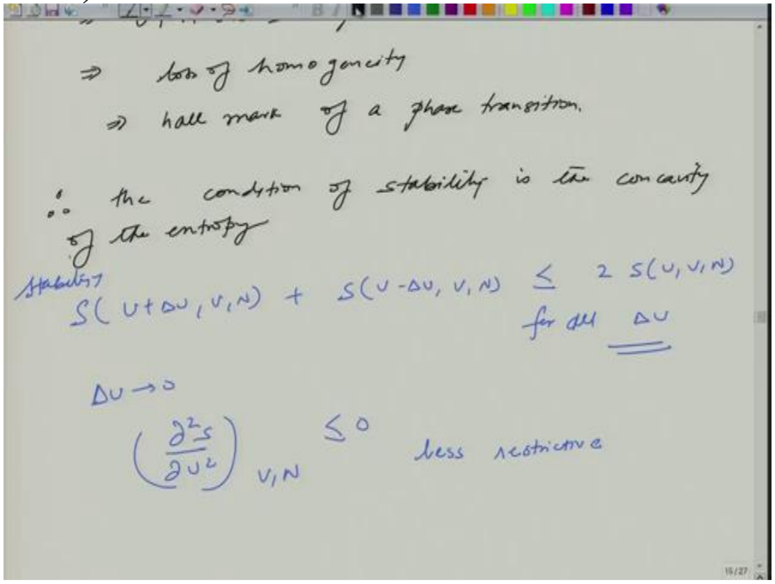

⇒ loss of homogeneity

⇒ hall mark of a phase transition.

∴ the condition of stability is the concavity of the entropy

stability

$S(U+\Delta U, V, N) + S(U-\Delta U, V, N) \leq 2S(U, V, N)$

for all $\underline{\underline{\Delta U}}$

$\Delta U \to 0$

$\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N} \leq 0$ less restrictive

Now, this also indicates that there could be you know, there would be loss of homogeneity, if you remove completely the adiabatic wall, then essentially this will face separate leading to two systems which are stable system. And that is what the statement is loss of homogeneity and this is the Classic Hallmark of Phase Separation.

Now, clearly it tells you that this occurred because there is a convexity in the intermediate and the phase separation will have two phases which are in this region somewhere here where is a concave and this also tells you or gives you an indication that the condition or stability is the concavity of the entropy.

Now, which means: $S(U+\Delta U, V, N) + S(U-\Delta U, V < N) \leq 2S(U, V, N)$ for all changes in Delta U, all changes in U. So, this is for stability. In the case, where is unstable it was opposite and that is why it would lead to phase transition in such a case, which is basically due to the convexity of the entropy shape of this curve.

So, now if you consider, $\Delta U \to 0$; $\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N} \leq 0$. Now, this is more strong condition. This is something which is also would lead to a global kind of condition. This is less restrictive as, this is valid for Delta U for very small change in U.

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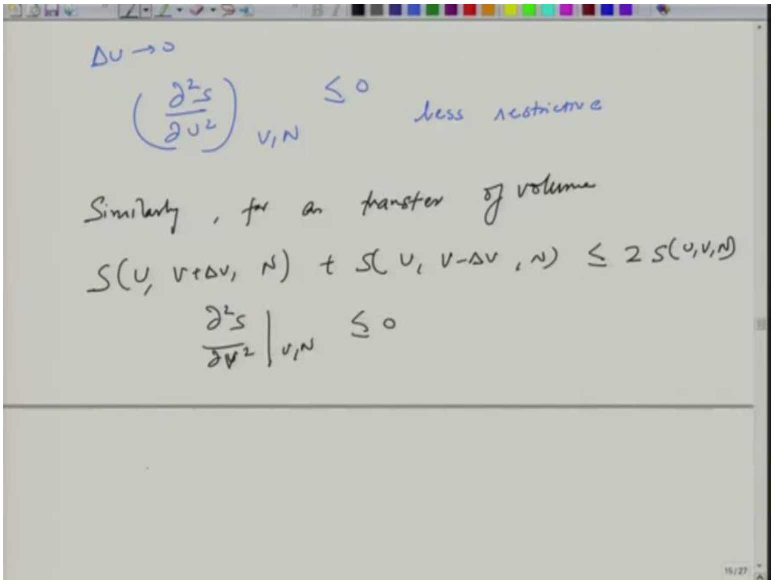

ΔU → 0

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N} \le 0 \quad \text{less restrictive}$$

Similarly, for an transfer of volume

$$S(U, V+\Delta V, N) + S(U, V-\Delta V, N) \le 2S(U,V,N)$$

$$\left.\frac{\partial^2 S}{\partial V^2}\right|_{V,N} \le 0$$

Now, similar exercises or similar exercise you can do for change in volume. So, similarly you can show that, similarly for transfer of volume :

$$S(U, V + \Delta V, N) + S(U, V - \Delta V, N) \le 2S(U, V, N).$$

So, this is when you transfer the volume from one compartment to another compartment and this would give us the following condition for Delta V tending towards 0. So, this is for the case of transfer of volume.

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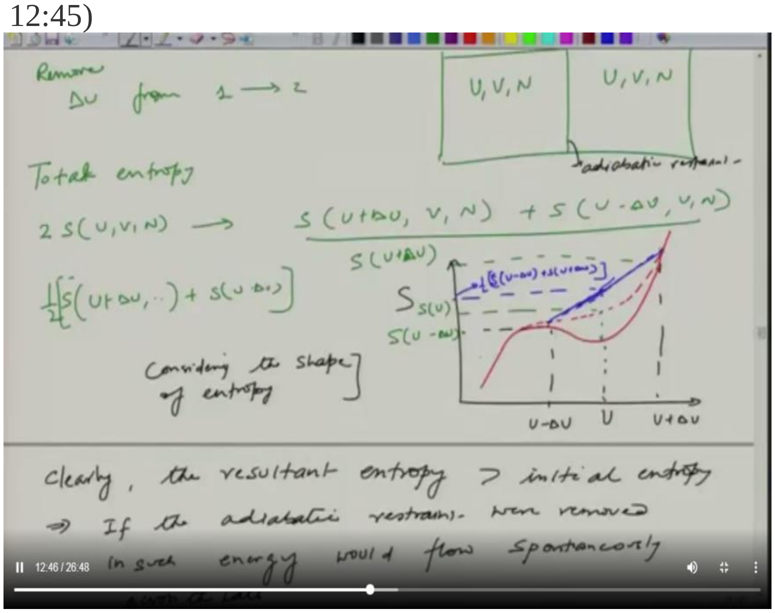

Remove ΔU from 1 → 2

Total entropy

$2S(U,V,N) \rightarrow S(U+\Delta U, V, N) + S(U-\Delta U, V, N)$

$\frac{1}{2}\left[S(U+\Delta U, \ldots) + S(U-\Delta U)\right]$

[Considering the shape of entropy]

Clearly, the resultant entropy > initial entropy

⇒ If the adiabatic restraint were removed

in such energy would flow spontaneously

Now, if you look at little carefully, this curve then essentially you can consider the tangent and look at the tangents which are below the curve or above the curve and then quantify the stability condition.

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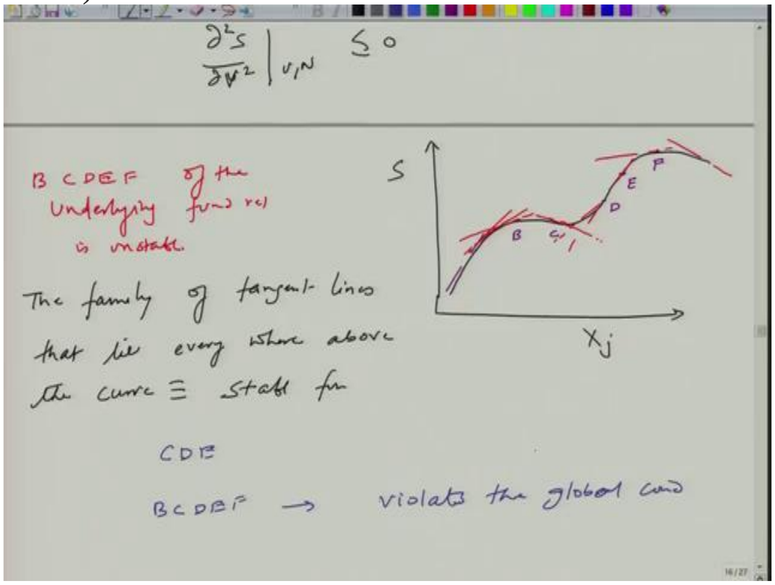


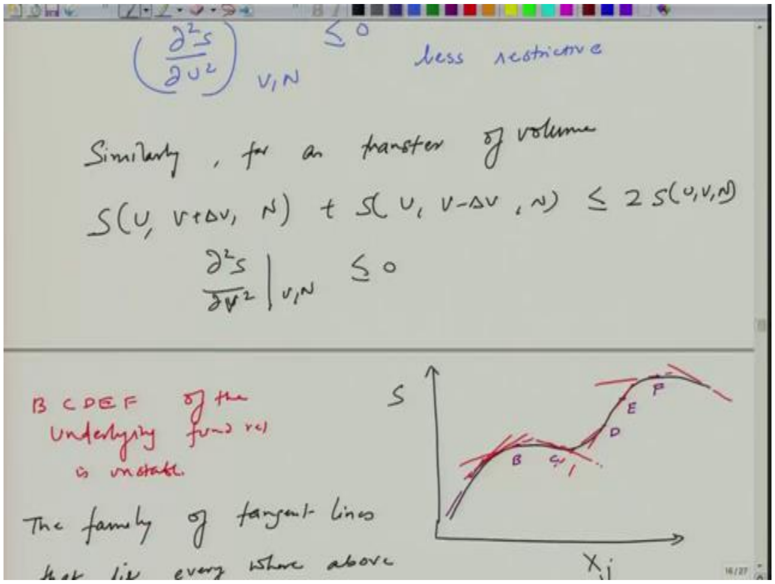
$$\left.\frac{\partial^2 S}{\partial V^2}\right|_{U,N} \leq 0$$

BCDEF of the underlying fund rel is unstable.

The family of tangent lines that lie every where above the curve ≡ stable for

CDE

BCDEF → violates the global cond



$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N} \leq 0 \quad \text{less restrictive}$$

Similarly, for an transfer of volume

$$S(U, V+\Delta V, N) + S(U, V-\Delta V, N) \leq 2S(U,V,N)$$

$$\left.\frac{\partial^2 S}{\partial V^2}\right|_{U,N} \leq 0$$

BCDEF of the underlying fund rel is unstable.

The family of tangent lines that lie every where above

So, let me try to elaborate this again by drawing this pictorial aspect of this shape extensive variable here and let me just draw. So, this is the curve which we have, alright. So, here if you look at it, this is your B. Let us say this is your somewhere and C this is again D. This is your F as somewhere this is your E where this, this basically the dot points are related to the kind of a slope. If you can draw these slopes at each point, so you can have slopes like this. Let me use the other color, so you can slope here, slope here.

So, these are above the curve and here this is slope which goes below the curve and then again it comes above the curve. So, if you look at the convexity then this is the range here which tells you this is a convex from B to F, which essentially will tell you B, C, D, E, F is basically unstable. So, all these points along this curve will be unstable.

So, B, C, D, F of the underlying fundamental relation is unstable or it means because if you look at from the slope point of view, all the slopes are crossing it is going below the curve. So, from the slope point of view the family of tangent line that lie everywhere above the curve can be said as stable. Now, you little, little bit carefully you see, one is C, D, E. So C, D, E if you look at it, these are C, D and then you have this B, C, D, E, F. Now, B, C, D, E, F is something which is, is unstable or violates the global condition, Global form or Global condition of stability, which is the case this, but if you look at the C, D, E, this violates the local conditions.

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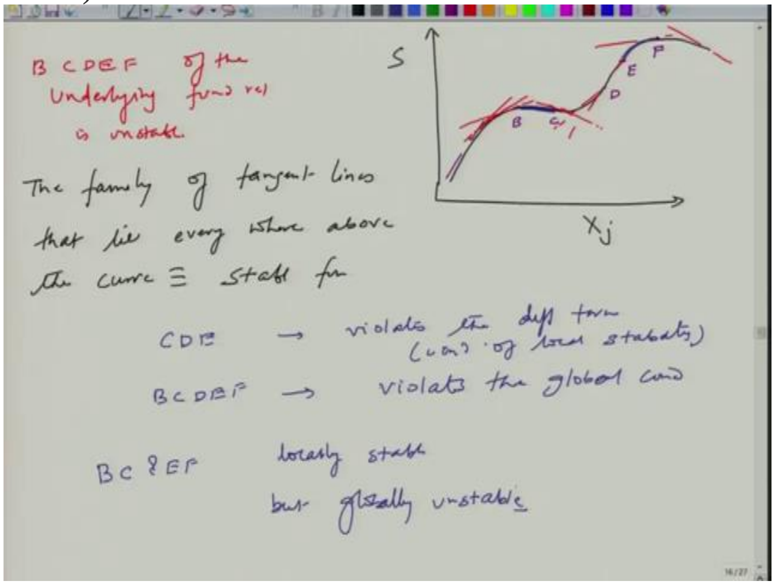


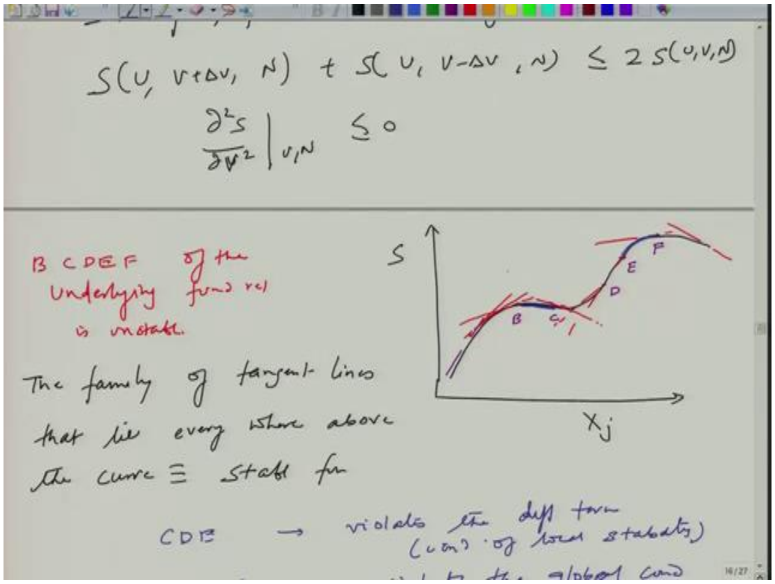
BCDEF of the Underlying fund rel is unstable.

The family of tangent lines that lie every where above the curve ≡ stable fn

CDE → violates the diff form (cond of local stability)

BCDEF → violates the global cond

BC & EF locally stable but globally unstable



$$S(U, V+\Delta V, N) + S(U, V-\Delta V, N) \le 2S(U,V,N)$$

$$\left.\frac{\partial^2 S}{\partial V^2}\right|_{U,N} \le 0$$

B CDEF of the underlying fund rel is unstable.

The family of tangent lines that lie every where above the curve ≡ stable fn

CDE → violates the diff form (cond. of local stability)

The second derivative differential form or condition of local stability, so it violates the local stability. So, B and C in that case this particular case. So, C, D, E is anyway is unstable. But B and C and E and F these are the range here and here the second derivative will be also second derivative in this case is so this B and C will not violate this derivative form but still is going to be unstable. So, that is what we say B, C and E, F are locally stable but globally unstable. So, this is something which we can make use of the basic analysis.

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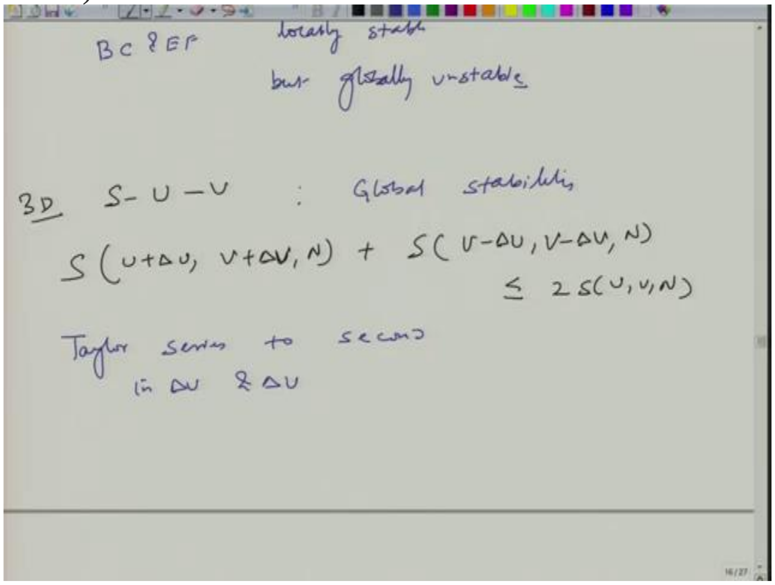

BC & EF locally stable but globally unstable

3D S-U-V : Global stability

$$S(U+\Delta U, V+\Delta V, N) + S(U-\Delta U, V-\Delta V, N) \le 2S(U,V,N)$$

Taylor series to second in ΔV & ΔU

Now, if we can extend this to arbitrary change in S, arbitrary change in U and V by considering this S, U, V subspace or three dimensional things then essentially I can write for the composite system completely I can write the following:

$$S(U + \Delta U, V + \Delta V, N) + S(U - \Delta U, V - \Delta V, N) \leq 2S(U, V, N)$$

Now, this must be less than 2 S U V N for the stability criteria because essentially the initial one should be more should have more entropy and that is why it should be stable. So, if you consider these three dimensional S, U, V, the global condition, the global stability criteria would be the following.

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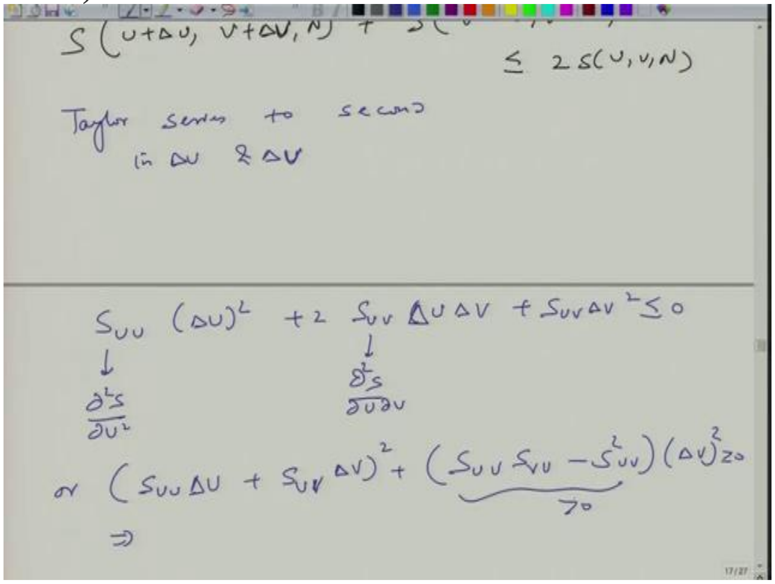


$S(U+\Delta U, V+\Delta V, N) + S($

$\leq 2S(U, V, N)$

Taylor series to second in ΔU & ΔV

$$\underset{\frac{\partial^2 S}{\partial U^2}}{\underset{\downarrow}{S_{UU}}} (\Delta U)^2 + 2 \underset{\frac{\partial^2 S}{\partial U \partial V}}{\underset{\downarrow}{S_{UV}}} \Delta U \Delta V + S_{UV} \Delta V^2 \leq 0$$

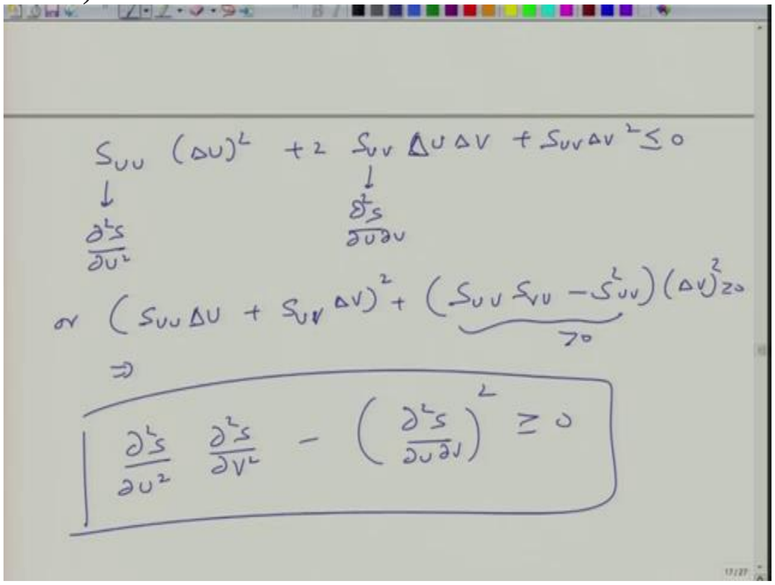
$$\text{or } (S_{UU}\Delta U + S_{UV}\Delta V)^2 + (\underbrace{S_{UU}S_{VU} - S_{UV}^2}_{>0})(\Delta V)^2 \geq 0$$

$\Rightarrow$

$$S_{UU}(\Delta U)^2 + 2S_{UV}\Delta U\Delta V + S_{UV}\Delta V^2 \leq 0$$
$$Or, (S_{UU}\Delta U + S_{UV}\Delta V)^2 + (S_{UU}S_{VU} - S_{UU}^2)(\Delta V)^2 \geq 0$$

Now, if you consider the Taylor series, to the second order in Delta U and Delta V one can derive the following without I am not illustrating the derivation, where the subscript indicate that this is the second derivative with respect to U square. This indicates, this is Del U, Del V and so forth. Now, this can be further rearranged in the following way. Now, this indicates because this is a positive, so this must be also positive.

(Refer Slide Time: 19:22)



$$S_{UU}(\Delta U)^2 + 2 S_{UV}\Delta U \Delta V + S_{UV}\Delta V^2 \leq 0$$

$$S_{UU} \downarrow \frac{\partial^2 S}{\partial U^2} \qquad S_{UV} \downarrow \frac{\partial^2 S}{\partial U \partial V}$$

$$\text{or } (S_{UU}\Delta U + S_{UV}\Delta V)^2 + (\underbrace{S_{UU}S_{VU} - S_{UV}^2}_{>0})(\Delta V)^2 \geq 0$$

$$\Rightarrow$$

$$\boxed{\frac{\partial^2 S}{\partial U^2}\frac{\partial^2 S}{\partial V^2} - \left(\frac{\partial^2 S}{\partial U \partial V}\right)^2 \geq 0}$$

Now, this particular condition, which I can now write like this : $\frac{\partial^2 S}{\partial U^2}\frac{\partial^2 S}{\partial V^2} - \left(\frac{\partial^2 S}{\partial U \partial V}\right)^2 \geq 0.$ This becomes a global stability criteria, which you can now which I can generalize is because now this is for the both U and V. So, this exercise which we have done is for only for entropy.

Now, entropy it is very clear that concavity is a criteria for stability. That means anything is a convex would indicate locally and or globally unstable. But if you are interested to derive the similar exercise for the case of internal energy then without actually going into details because of the nature of a entropy and internal energy is opposite.

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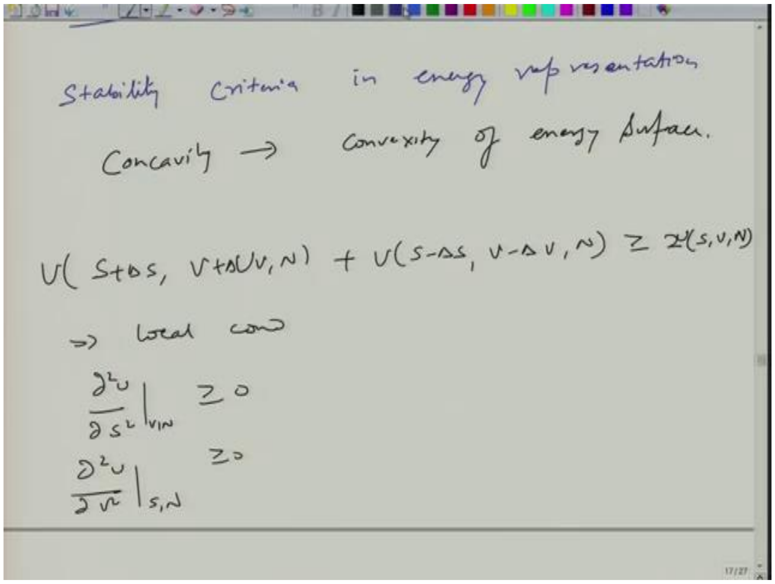

Stability criteria in energy representation

Concavity → convexity of energy surface.

$U(S+\Delta S, V+\Delta V, N) + U(S-\Delta S, V-\Delta V, N) \geq 2U(S,V,N)$

⇒ local cond

$\frac{\partial^2 U}{\partial S^2}\Big|_{V,N} \geq 0$

$\frac{\partial^2 U}{\partial V^2}\Big|_{S,N} \geq 0$

So, whatever the condition which we have mentioned for the case of stability, so, you can just reverse that if you are using the energy representation. So, I can now have this criteria in energy representation, where concavity condition will be replaced by convexity of energy surface. So, in other word the following would be the case.

$$U(S+\Delta S, V+\Delta V, N) + U(S-\Delta S, V-\Delta V, N) \geq 2U(S,V,N)$$

$$\frac{\partial^2 U}{\partial S^2}|_{V,N} \geq 0$$

$$\frac{\partial^2 U}{\partial V^2}|_{S,N} \geq 0$$

That U has to be minimum and hence any perturbation in the original system leading to total energy such as U plus U S minus Delta S for the same two compartment system that must be greater than equal to the original two times the original energy. And this would lead to a local conditions which without I am deriving this we can write this as square greater than equal to 0 Del square U Del V square S and N, V and N greater than equal to 0.

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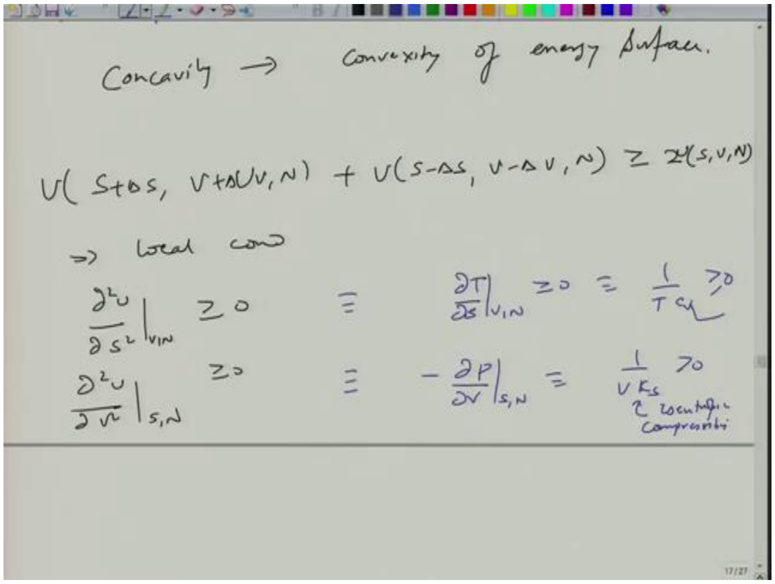

Concavity → Convexity of energy surface.

$$U(S+\Delta S, V+\Delta V, N) + U(S-\Delta S, V-\Delta V, N) \geq 2U(S,V,N)$$

⇒ local cond

$$\left.\frac{\partial^2 U}{\partial S^2}\right|_{V,N} \geq 0 \equiv \left.\frac{\partial T}{\partial S}\right|_{V,N} \geq 0 \equiv \frac{1}{TC_V} > 0$$

$$\left.\frac{\partial^2 U}{\partial V^2}\right|_{S,N} \geq 0 \equiv -\left.\frac{\partial P}{\partial V}\right|_{S,N} \equiv \frac{1}{VK_S} > 0$$

isentropic compressibi

Now, this we can further simplify by bringing the other information. For example

$$\frac{\partial T}{\partial S}|_{V,N} \geq 0$$

So, if you bring N here this becomes molar entropy and then you can write it like this

$$\frac{1}{TC_V} \geq 0 .$$

Similarly,

$$-\frac{\partial P}{\partial V}|_{S,N} \geq 0.$$

This will give us:

$$\frac{1}{VK_S} > 0$$

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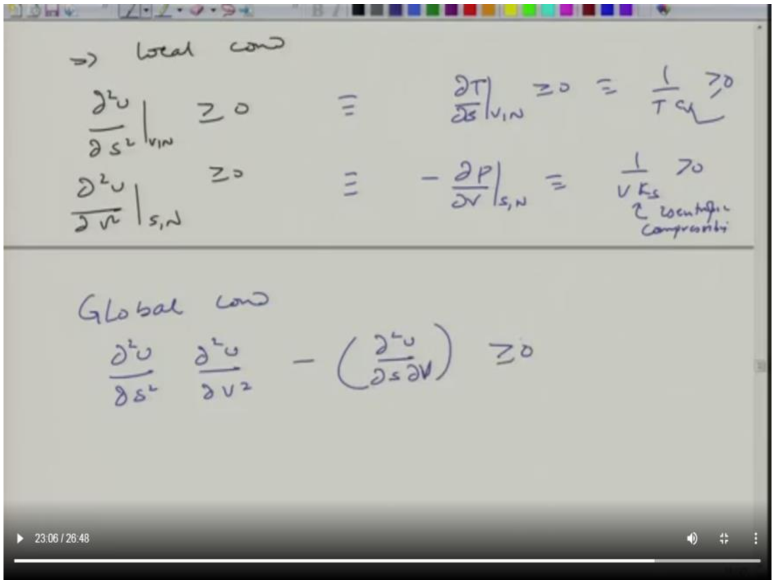

⇒ Local cond

$$\left.\frac{\partial^2 U}{\partial S^2}\right|_{V,N} \geq 0 \equiv \left.\frac{\partial T}{\partial S}\right|_{V,N} \geq 0 \equiv \frac{1}{T C_V} \geq 0$$

$$\left.\frac{\partial^2 U}{\partial V^2}\right|_{S,N} \geq 0 \equiv -\left.\frac{\partial P}{\partial V}\right|_{S,N} \equiv \frac{1}{V \kappa_S} \geq 0$$

κ_S isentropic compressibility

Global cond

$$\frac{\partial^2 U}{\partial S^2}\frac{\partial^2 U}{\partial V^2} - \left(\frac{\partial^2 U}{\partial S \partial V}\right) \geq 0$$

Now, similar to the case of the entropy I can also write the global condition for this. So, Global condition would be the same as we have done in a similar spirit, but now the only thing is different is, we are taking the derivative of U with respect to the other intensive variables. And this must be greater than equal to 0.

$$\frac{\partial^2 U}{\partial s^2}\frac{\partial^2 U}{\partial V^2} - \left(\frac{\partial^2 U}{\partial S \partial V}\right) \geq 0$$

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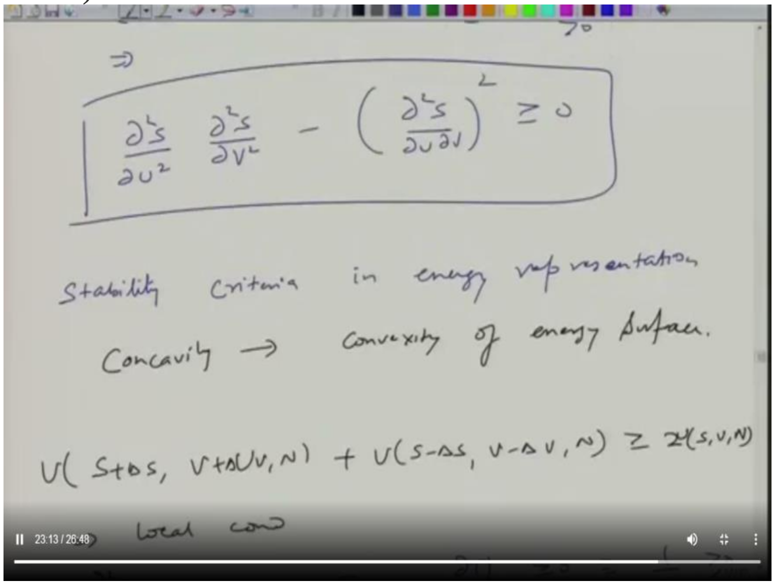


⇒

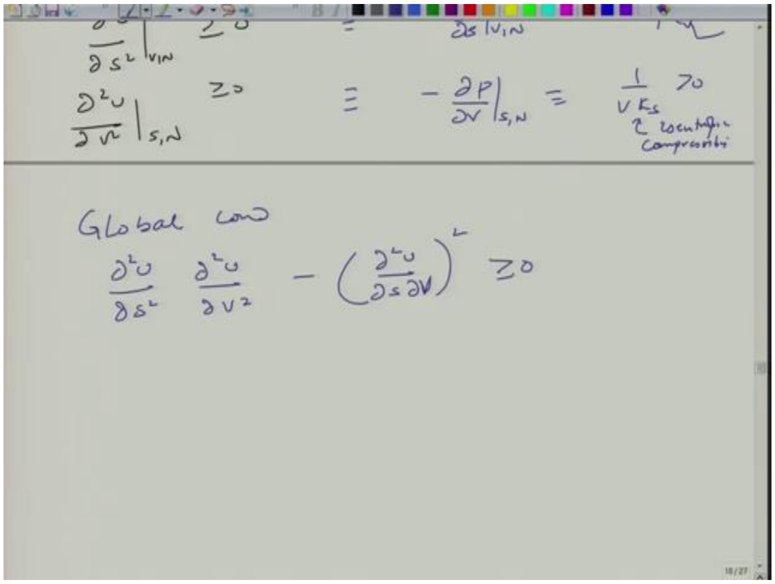
$$\boxed{\frac{\partial^2 S}{\partial U^2}\frac{\partial^2 S}{\partial V^2} - \left(\frac{\partial^2 S}{\partial U \partial V}\right)^2 \geq 0}$$

Stability criteria in energy representation

Concavity → Convexity of energy surface.

$$U(S+\Delta S, V+\Delta V, N) + U(S-\Delta S, V-\Delta V, N) \geq 2U(S,V,N)$$

Local cond



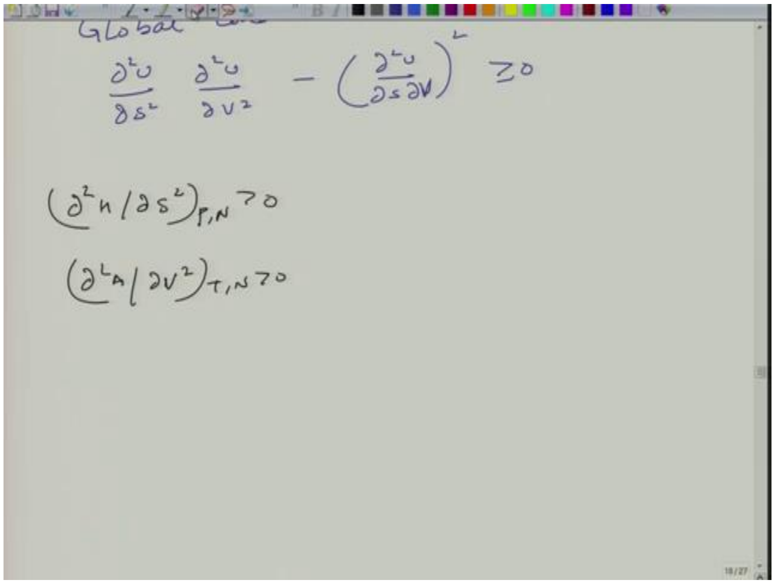
$$\frac{\partial^2 U}{\partial S^2}\Big|_{V,N} \geq 0 \qquad = \qquad \partial S\Big|_{V,N}$$

$$\frac{\partial^2 U}{\partial V^2}\Big|_{S,N} \geq 0 \qquad \equiv \qquad -\frac{\partial P}{\partial V}\Big|_{S,N} = \frac{1}{V\kappa_S} > 0$$

κ_S isentropic compressibi

Global con

$$\frac{\partial^2 U}{\partial S^2}\frac{\partial^2 U}{\partial V^2} - \left(\frac{\partial^2 U}{\partial S \partial V}\right)^2 \geq 0$$



Global con

$$\frac{\partial^2 U}{\partial S^2}\frac{\partial^2 U}{\partial V^2} - \left(\frac{\partial^2 U}{\partial S \partial V}\right)^2 \geq 0$$

$$\left(\partial^2 H / \partial S^2\right)_{P,N} > 0$$

$$\left(\partial^2 A / \partial V^2\right)_{T,N} > 0$$

So look at this, this was the case here and this is the case here. So, this must be square. Now, we have done only for entropy and enthalpy the exercises, but now I am going to summarize if you had done similar exercises for enthalpy, Helmholtz free energy or Gibbs free energy that if you can just summarize then the following can be written:

$$\left(\frac{\partial^2 H}{\partial S^2}\right)_{P,N} > 0$$

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,N} > 0$$

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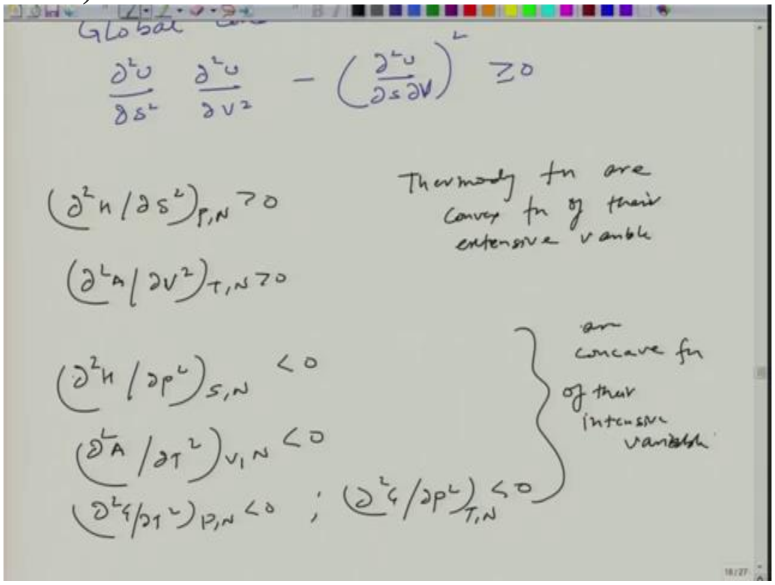

Global

$$\frac{\partial^2 U}{\partial S^2}\frac{\partial^2 U}{\partial V^2} - \left(\frac{\partial^2 U}{\partial S \partial V}\right)^2 \geq 0$$

$$\left(\partial^2 H/\partial S^2\right)_{P,N} > 0$$

$$\left(\partial^2 A/\partial V^2\right)_{T,N} > 0$$

Thermody fn are Convex fn of their extensive variable

$$\left(\partial^2 H/\partial P^2\right)_{S,N} < 0$$

$$\left(\partial^2 A/\partial T^2\right)_{V,N} < 0$$

$$\left(\partial^2 G/\partial T^2\right)_{P,N} < 0 \; ; \; \left(\partial^2 G/\partial P^2\right)_{T,N} < 0$$

are concave fn of their intensive variable

Now, if you notice the following that all this second derivatives or thermodynamic functions, convex function of their extensive variable. So, this is something which you can clearly see H here the A here and U also.

Now, if you consider the derivatives with respect to the intensive variable, the following can be written here.

$$\left(\frac{\partial^2 H}{\partial P^2}\right)_{S,N} < 0$$

$$\left(\frac{\partial^2 A}{\partial T^2}\right)_{V,N} < 0$$

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N} < 0$$

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N} < 0$$

So, it tells you this also that the thermodynamic functions are concave function of their intensive variable. And when we talk about the stability, we always prefer the extensive variable because of the sign here and we usually do not look at the intensive variables in this case. So, most of this analysis if you have seen is with respect to the extensive variable.

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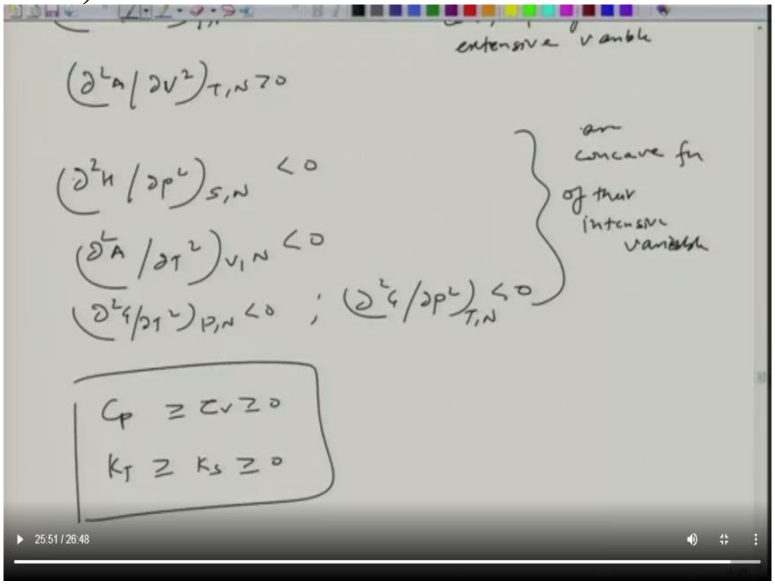

extensive variable

$$\left(\partial^2 A / \partial V^2\right)_{T,N} > 0$$

$$\left.\begin{array}{l} \left(\partial^2 H / \partial P^2\right)_{S,N} < 0 \\ \left(\partial^2 A / \partial T^2\right)_{V,N} < 0 \\ \left(\partial^2 G / \partial T^2\right)_{P,N} < 0 \quad ; \quad \left(\partial^2 G / \partial P^2\right)_{T,N} < 0 \end{array}\right\}$$

are concave fn of their intensive variable

$$\boxed{\begin{array}{l} C_P \geq C_V \geq 0 \\ K_T \geq K_S \geq 0 \end{array}}$$

So, let me summarize again. So, what we have done is we have shown

$$C_P \geq C_V \geq 0 \ and \ K_T \geq K_S \geq 0.$$

So, these are the final conclusion of this exercise.

So, what I am going to do now is I will take a break and I will start with another set of lecture in the next class, particularly on the phase transitions and I will look address the other questions which we left particularly the phase rules and the Clapeyron-Clausius Equation. So, I will see you in the next class.