Chemical Engineering Thermodynamics
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Lecture -26
Stability Criteria

Welcome back. In the last class we listed out some of the questions. These questions were, does thermodynamic place any restriction on the derivatives of the thermodynamic properties, which, can be written in terms of isothermal compressibility, heat capacity, and so forth

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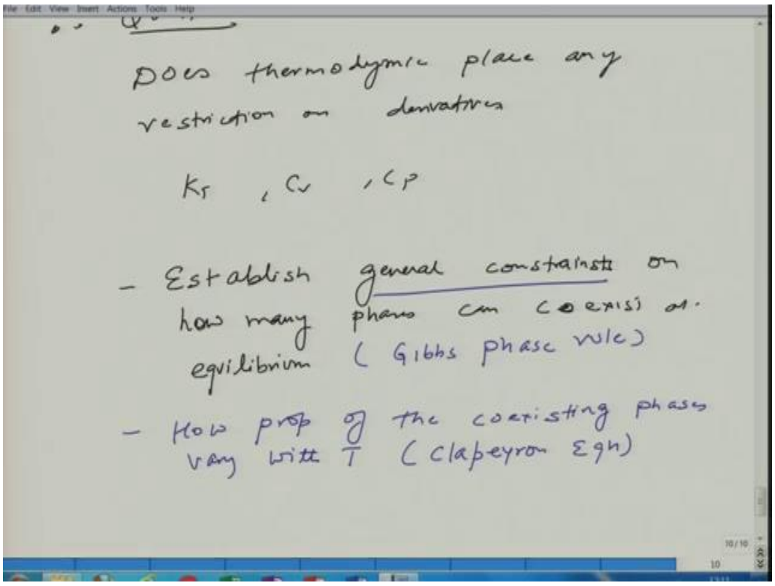

Does thermodymic place any restriction on derivatives

K_T, C_v, C_p

- Establish general constraints on how many phases can coexist at equilibrium (Gibbs phase rule)
- How prop of the coexisting phases vary with T (Clapeyron Eqn)

So, that was a first question which we will try to address in today's lecture. So, I will start with basic criteria for stability.

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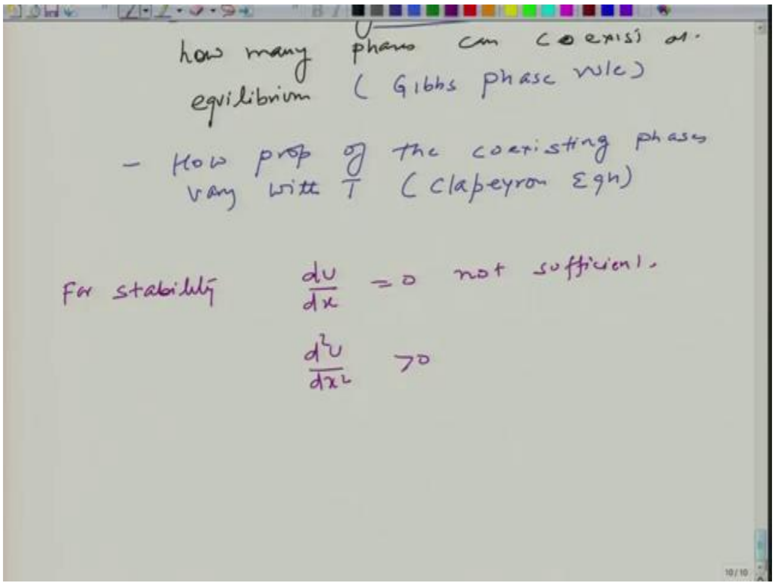

how many phases can coexist at equilibrium (Gibbs phase rule)

- How prop of the coexisting phases vary with T (Clapeyron Eqn)

For stability $\frac{dU}{dx} = 0$ not sufficient.

$\frac{d^2U}{dx^2} > 0$

So, for stability, we know that this is not sufficient and earlier we shown that we need to also look at the second derivative. In the case of internal energy, this must be greater than 0. Now, you can actually try to journalize this and look at different forms of potential energy surface occur in this two dimensional case. So, let us look at just two dimensional expect of it.

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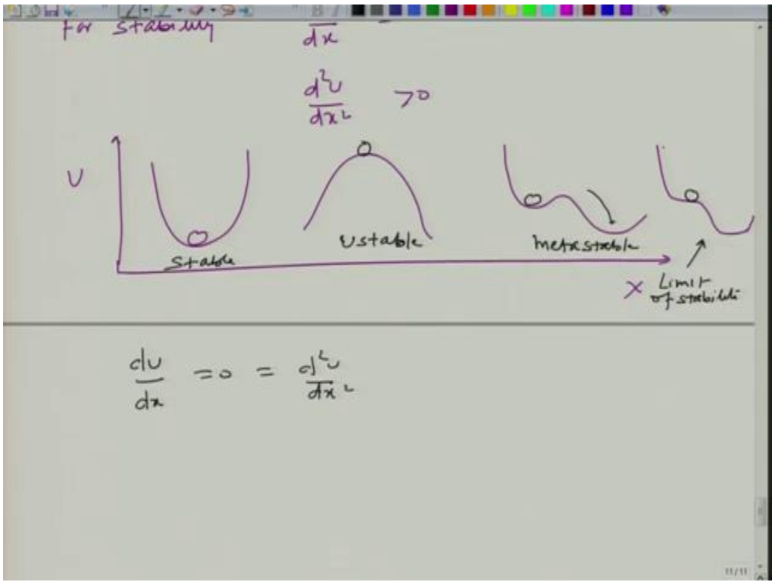

For stability $\frac{dU}{dx}$

$\frac{d^2U}{dx^2} > 0$

$\frac{dU}{dx} = 0 = \frac{d^2U}{dx^2}$

So, what I am drawing here is internal energy and some variable which a thermodynamic variable here could be volume, could be other kind of variables. But, in general this the kind of a plots are very generic in nature. So, you may get something like this or and finally Okay right. So, if you look at this plots, this is nothing but stable. Because, if you perturb the particles from here is going to be returning back to the original state. So, this is your stable and this would be something which is unstable. Because, if you perturb it, it is going to, go to the next possible state and hence, it is going to lose that initial position.

Now, this is a Meta stable, so you need to perturb in a large amount so that it can cross the barrier. But, still this is not the lowest energy and hence, when you perturb it is going to move to the lowest energy and such a case we call it Meta stable. And the last one is to reflect the limit of stability is inflection point and essentially at these conditions the derivatives are the first and second derivative are 0.

So, this is the basically the limit of stability. And, that state you have second and first derivative 0. So, this basically gives you mathematically the conditions of limit of stability. We further would like to explore this. So, what would be the typical, what would be the condition of stability, on the sign of the first and second order of derivatives. Particularly we are interested now in second order derivative. So, let me just swipe this down.

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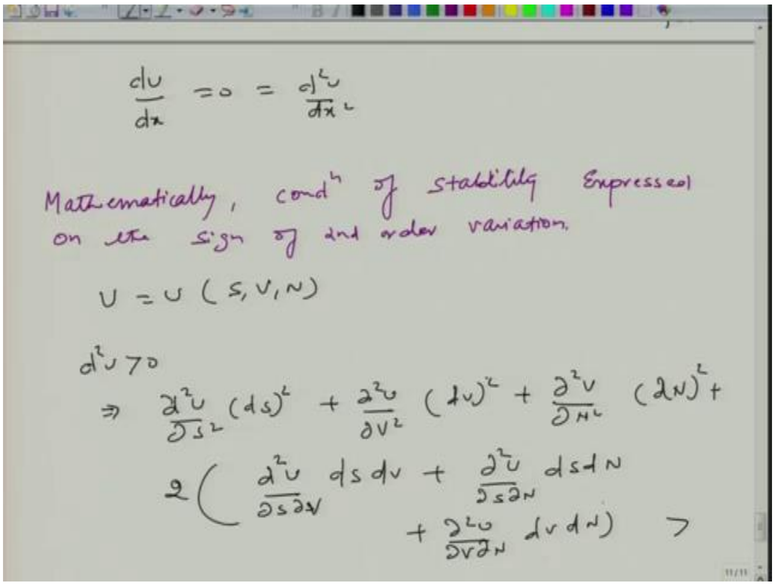

$$\frac{du}{dx} = 0 = \frac{d^2u}{dx^2}$$

Mathematically, condⁿ of stability Expressed on the sign of 2nd order variation.

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

$$d^2U > 0$$

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

So, mathematically what would be the condition of stability expressed on the sign of second order variation? So, let us look at again the energy U, which is a function of S, V, N that is a natural variable. So, if you look at the derivative here and of course we know we have just calculated earlier or derived earlier that the second derivative has to be greater than 0. This essentially can be written as in the following way. So, this without explicitly deriving this I am writing down these expressions.

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

$$d^2U > 0$$

$$or, \quad \frac{\partial^2 U}{\partial S^2}(dS)^2 + \frac{\partial^2 U}{\partial V^2}(dU)^2 + \frac{\partial^2 V}{\partial N^2}(dN)^2$$
$$+ 2\left(\frac{\partial^2 U}{\partial S \partial V} dSdV + \frac{\partial^2 U}{\partial S \partial N} dSdN + \frac{\partial^2 U}{\partial N \partial V} dNdV\right) > 0$$

So, this term essentially should be greater than 0. Now, considering the fact that S, V, N are independent we can consider variation in one in which one of this variable dS, dV and dN are non-zero. Because, they are independent so, we can consider one of the non-zero rest can be zero.

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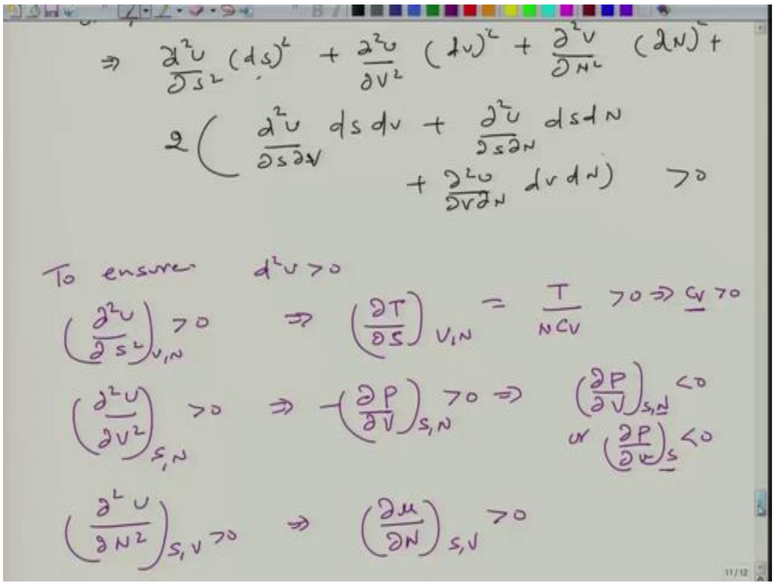

$$\Rightarrow \frac{\partial^2 U}{\partial S^2}(dS)^2 + \frac{\partial^2 U}{\partial V^2}(dV)^2 + \frac{\partial^2 V}{\partial N^2}(dN)^2 +$$
$$2\left(\frac{\partial^2 U}{\partial S \partial V} dSdV + \frac{\partial^2 U}{\partial S \partial N} dSdN + \frac{\partial^2 U}{\partial V \partial N} dVdN\right)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

To ensure $d^2U > 0$

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

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

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

$$To\ ensure, d^2U > 0,$$

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

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

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

Sometimes this is called ’Thermal Stability’ this refers to mechanical stability and this refers to chemical stability in some sense. Now, we can bring more kind of relations by analyzing other thermodynamic functions, so thermodynamic potentials. So, let us look at additional relation based on Helmholtz free energy.

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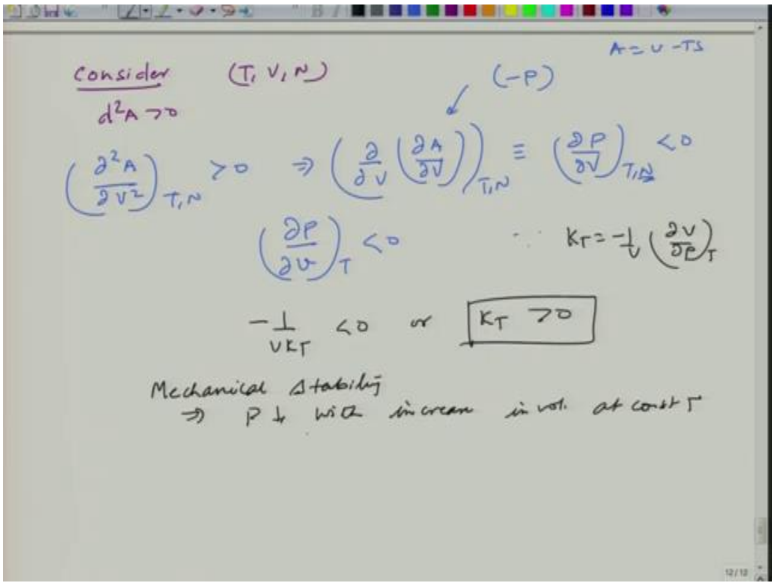

Consider (T, V, N) $A = U - TS$

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

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

$$\left(\frac{\partial P}{\partial v}\right)_T < 0 \quad \because \kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$$

$$-\frac{1}{v\kappa_T} < 0 \text{ or } \boxed{\kappa_T > 0}$$

Mechanical stability

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

$$Considering, \qquad (T, V, N)$$

$$d^2A > 0$$

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

$$\left(\frac{\partial P}{\partial v}\right)_T < 0 \quad since, \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$-\frac{1}{V\kappa_T} < 0 \;\; or, \;\; \kappa_T > 0$$

So, this again we are saying this to be mechanical stability.

It implies essentially that P decreases with increase in volume at constant temperature. It also means that the P decreases when you increase the volume at constant entropy. Of course that is more difficult to achieve when in the real state. But, this is something which would be occurring in the more commonly in the experiments and hence you can check whether the system is behaving in a manner which lead to the stability by looking at this variable.

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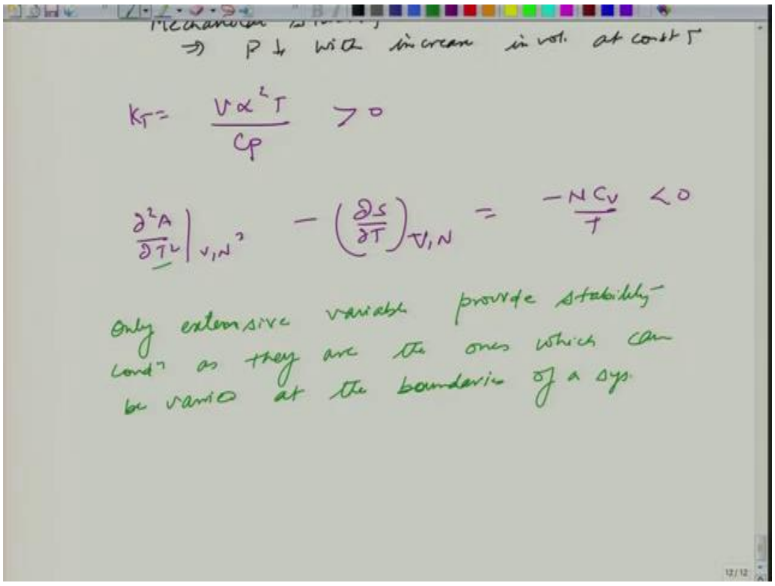

⇒ P ↓ with increase in vol. at const T

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

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

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

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

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

The other thing is that in you can also connect this thing, the definition you can show that this is nothing but V alpha square or BT square, this is expansivity and this divided by C P. So, V alpha square T C P alpha is basically expansivity. And this, it must be greater than 0. Now, we can show also that C V is greater than 0 or hence alpha has to be, alpha square is to be greater than 0. (Of course) Which means alpha basically can be positive or negative and that is one the reason that you observe water in some case alpha is negative.

Now, there is another important expect that, why we are looking at all the time the derivative of this thermodynamic potentials with respect to extensive variable. So, if you look at let us say del A del square A with respect second derivative A with respect to T, what you get? You will not get the clearly the positive sign and that is something which you can see here so, del square A by del T square V N this the minus del S by del T V of N this is minus of N C V by T. And of course C V is greater than 0 so, this has to be less than 0.

So, this term usually we try to avoid it, this kind of derivative, so only extensive variable provide the stability condition as or the major reason is that you can actually vary, the extensive variable at the boundary of the system. So, let me write down this that why do not we try to you make use this kind of derivative with respect to the intensive variable such as T or P. So, only extensive variable provide stability condition as they are the ones which can be varied. So, this is something which really comes out of it.

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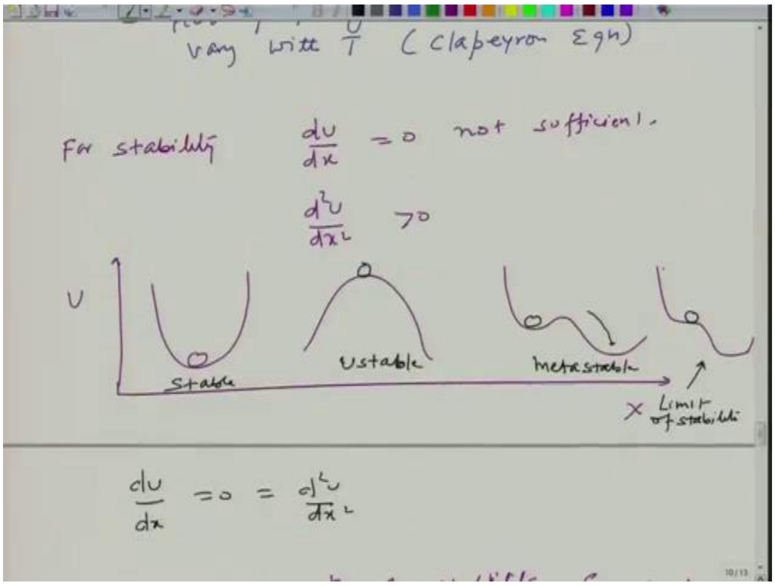

vary with $\frac{U}{T}$ (Clapeyron Eqn)

For stability $\frac{dU}{dx} = 0$ not sufficient.

$$\frac{d^2U}{dx^2} > 0$$

$$\frac{dU}{dx} = 0 = \frac{d^2U}{dx^2}$$

And we of course would like to consider single kind of nomenclature as far as the stability is concern because, we would like to have scenario such as this and which is only possible when you look at the second derivative greater than 0. So, we can actually do a bit of we can try different thermodynamic functions and that is look at the enthalpy now.

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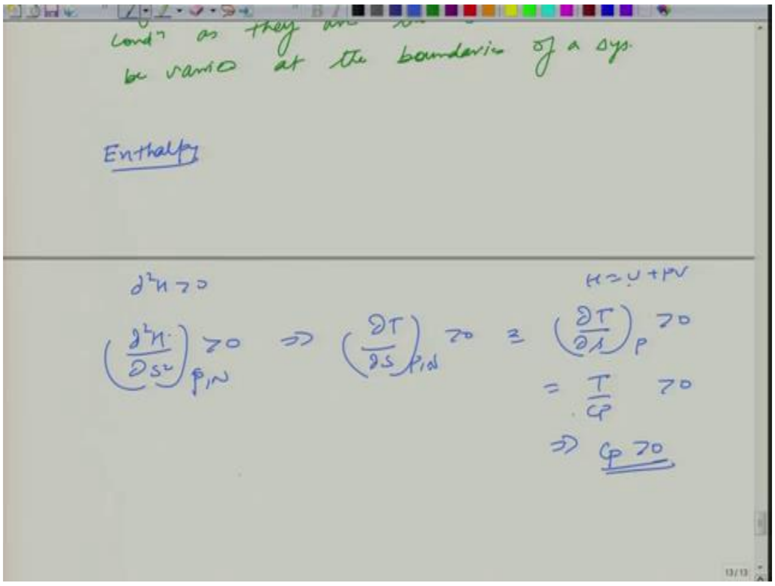

Cond^n as they

be varied at the boundaries of a sys.

Enthalpy

$d^2H > 0$

$H = U + PV$

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

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

$$\Rightarrow \underline{\underline{C_P > 0}}$$

We have got conditions of C V should be greater than 0. But, what about C P and is something which we can show also here by considering the second derivative of this. So, so, this you can show by considering the second derivative H with respect to S, this must be greater than 0. And we know (del S by) del H by del S is nothing but T. This must be greater than 0, remember that H is nothing but U plus P V. As far as the D H is concern you will still get the T, D, S. So, if you keep P N constant it must be del S by del S is nothing but, T.

So, this term, the derivative of entropy with respect to temperature is nothing but C P. So, if you divide by N, this can be written as del T by small del S at constant P and this is nothing but T by C P otherwise you have to bring the N here, if you keep this as a not a molar entropy. So, this term now, can be written as this and since this is greater than 0, this must be greater than 0, which implies that C P must be greater than 0.

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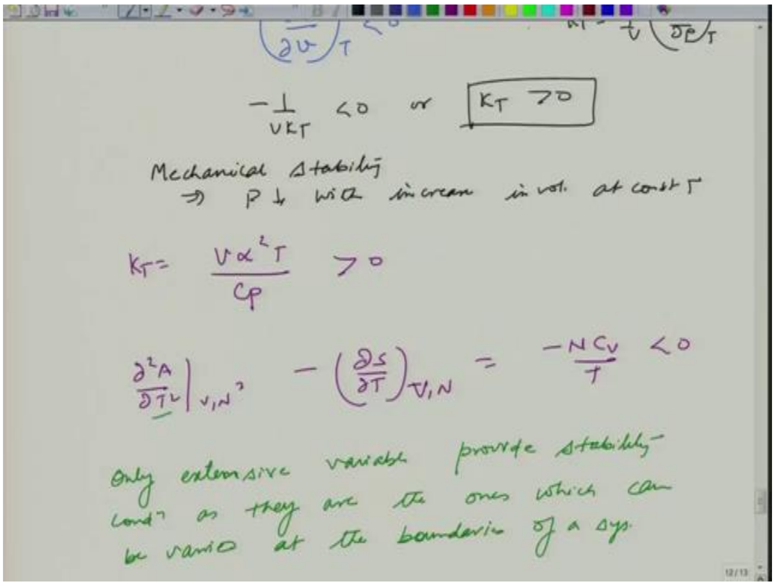

$-\frac{1}{VK_T} < 0$ or $\boxed{K_T > 0}$

Mechanical stability
⇒ 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.

And this is what also the indicative if K T is greater than 0. From here also you can clearly see that C P has to be greater than 0.

$$d^2H > 0$$

$$\left(\frac{\partial^2 H}{\partial S^2}\right)_{P,V} > 0 \;\; or \;\; \left(\frac{\partial T}{\partial S}\right)_{P,V} > 0 \;\; or, \left(\frac{\partial T}{\partial S}\right)_P > 0 \; or, \frac{T}{C_P} > 0 \;\; or, C_P > 0$$

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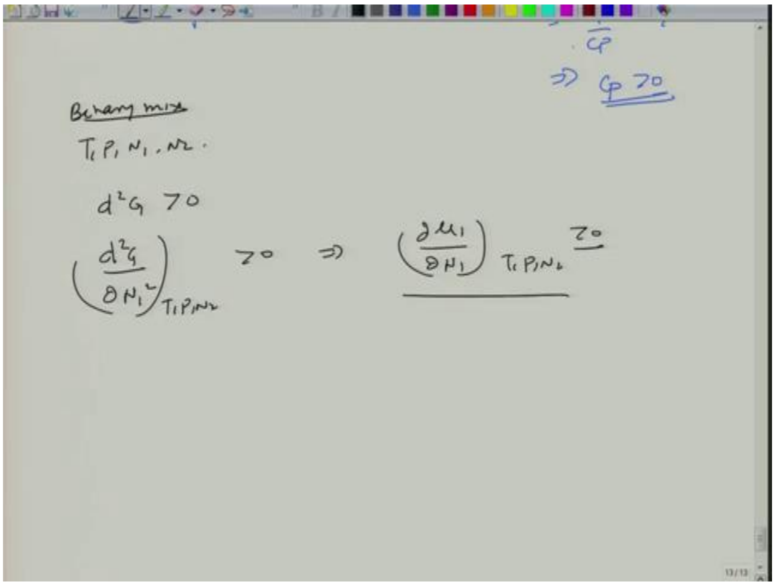

$\overline{C_P}$

$\Rightarrow \underline{\underline{C_P > 0}}$

Binary mix

T, P, N1, N2.

$d^2G > 0$

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

So, now the last part which remains is looking at the chemical potential part. So, we can consider the binary mixture.

$$Binary\ mixture\colon\ \ we\ consider\ T, P, N_1, N_2$$

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

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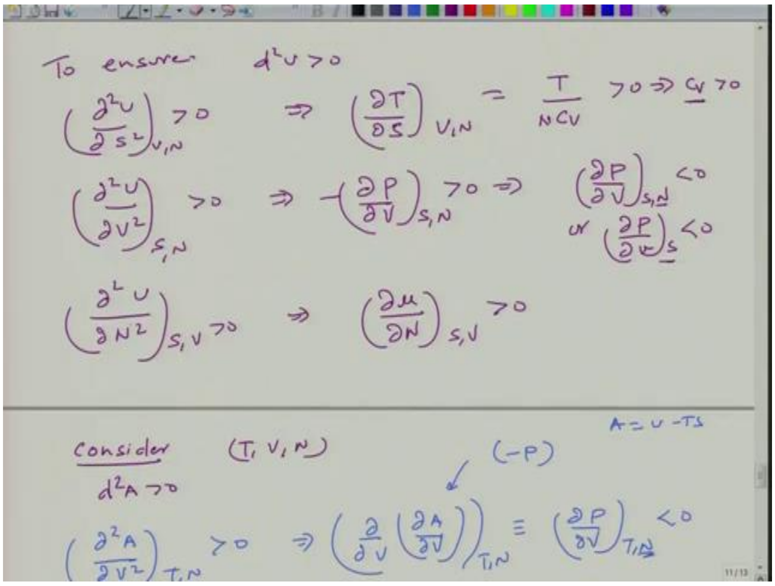


To ensure $d^2U > 0$

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

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

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

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

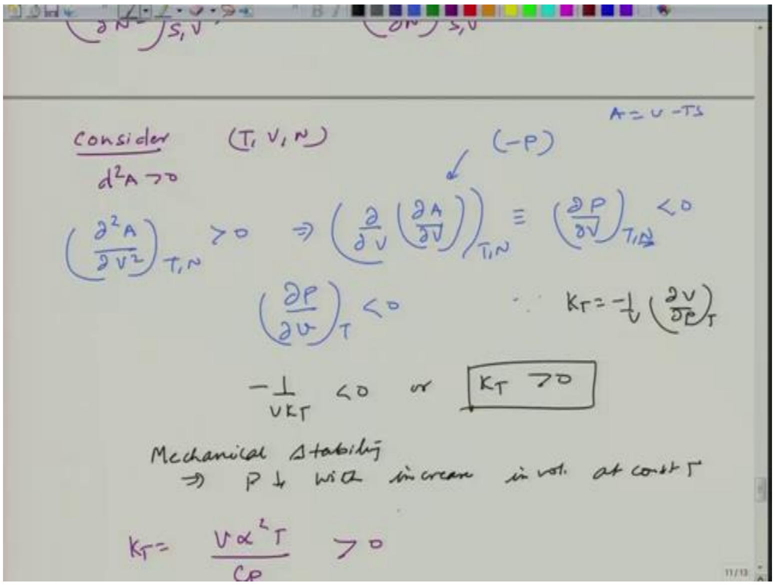
$A = U - TS$

Consider (T, V, N)

$d^2A > 0$

$(-P)$

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



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Consider (T, V, N)

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

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

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

Mechanical stability

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

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

So, earlier we mention above the third variable as far as U is concern here and we did mention that, you know this is nothing but the change in the chemical potential with respect to the number of moles keeping S and V constant. But, you can extend this thing further natural variable, certain natural variables, potentials which, in this case we consider this.

And for that the corresponding free energy is G and if you look into the second derivative, you will see this expression which is nothing but the same as per the meaning is concerned, that you know if you increased the mole of a species 1 the chemical potential must increase in a way it which is positive.

So, this gives you a clear stability as far as the chemical aspects of the system is concern. So, we obtain a very important criteria now for the stability. Particularly, this becomes a extremely important for the stability of the mixtures, if this does not happen for example, if this is not valid it means, that it would like to have some kind of phase separation or it will have some kind of immiscibility and this is something which we are going to focus more in the later part of the course.

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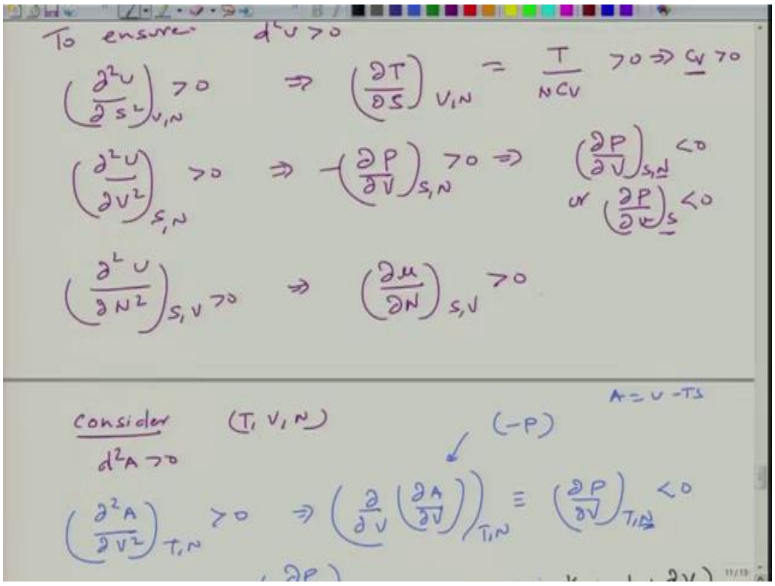

To ensure $d^2U > 0$

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

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

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

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

$A = U - TS$

Consider (T, V, N)

$d^2A > 0$

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

We have obtain the couple of conditions for the stability. One is of course this. This is one condition of the stability and other is this okay. So, the question is, are these conditions of stability are equivalent or (what) can we prove this equivalence of this stability criteria? So, if we talk about the stability criteria, you can have this three terms but, are they equivalent? So, that is something which we can now little bit focus on it and show that if one goes let say to 0 the others will also be 0.

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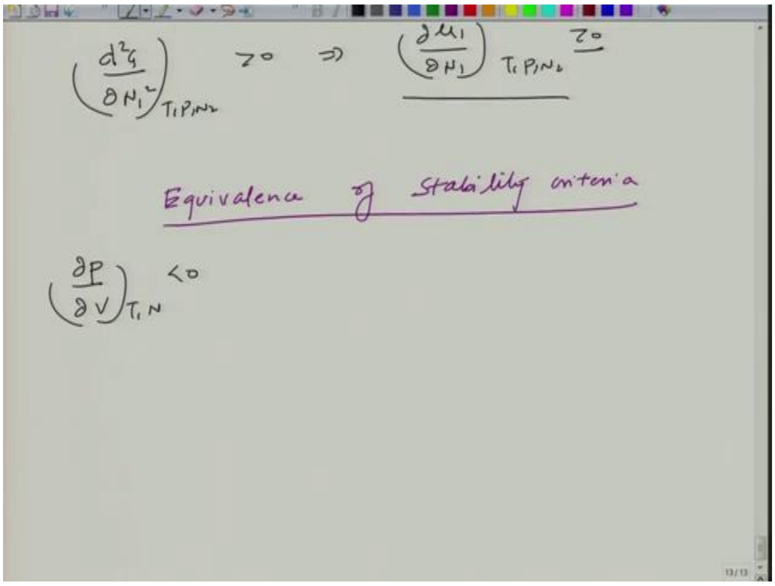

$$\left(\frac{d^2 G}{\partial N_1^2}\right)_{T,P,N_2} > 0 \Rightarrow \underline{\left(\frac{\partial \mu_1}{\partial N_1}\right)_{T,P,N_2} \underline{>0}}$$

Equivalence of Stability criteria

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

So, this would be your equivalent or equivalence or stability criteria. So, we will take 2 particular expressions which we obtain, one is the pressure derivative with respect to the volume keeping T, N constant. So, instead of the case of the entropy, we will take the other case.

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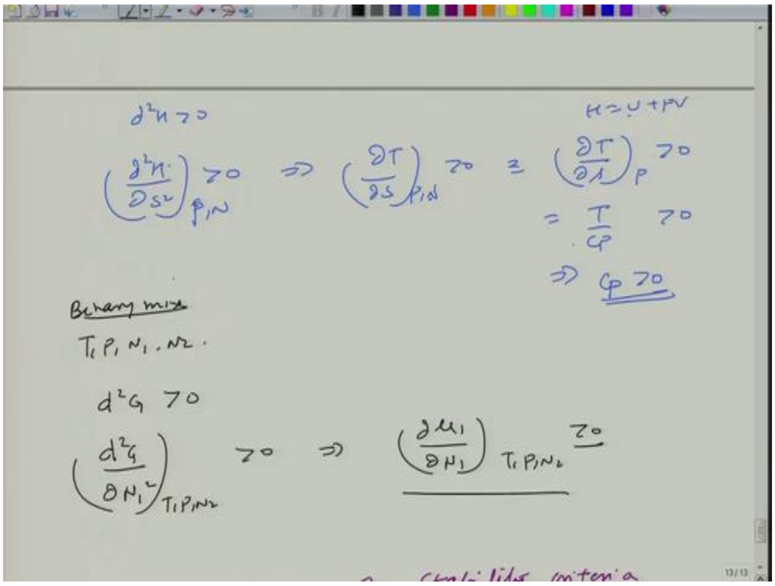


$d^2H > 0$

$H = U + PV$

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

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

$$\Rightarrow \underline{\underline{C_P > 0}}$$

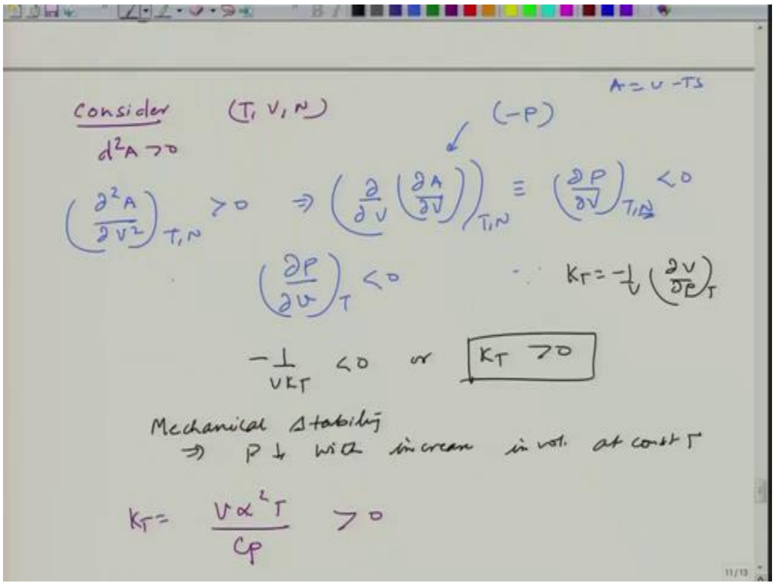
Binary mix

$T, P, N_1, N_2.$

$d^2G > 0$

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

stability criteria



Consider (T, V, N)

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

$(-P)$

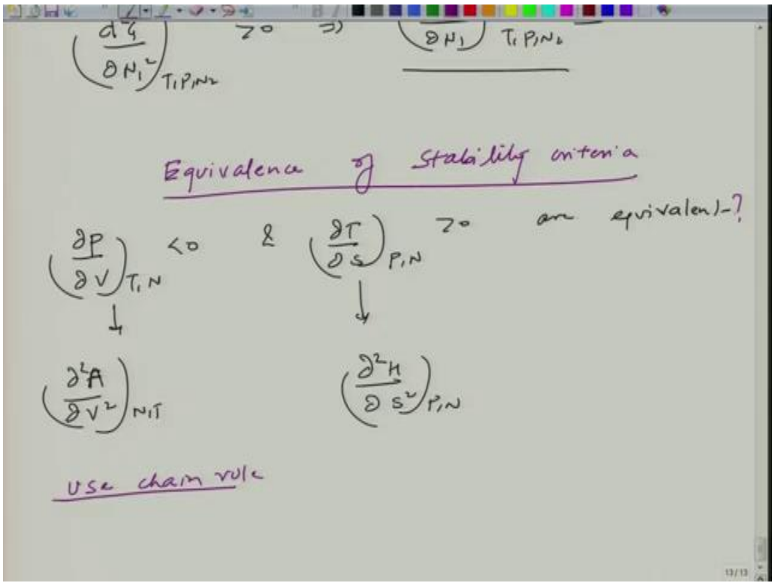
$$\left(\frac{\partial P}{\partial V}\right)_T < 0 \qquad \because K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

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

Mechanical stability

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

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



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

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?

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

Use chain rule

$$Equivalence\ of\ stability\ criteria$$

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

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

So, we will try to now use not just this specifically 2 but, let us say from the Helmholtz free energy analysis and from the enthalpy analysis we will consider this so are equivalent. So, we are just trying to listed this, that I mean of course you can come up with the different combination. The important thing is that we will show that if one goes to 0, others goes to also 0.

So, let me take this this particular part or this comes directly from or this is nothing but (del F) del A by del V square keeping anti constant and this comes from the fact that this is nothing but, del H square del S square P of N. So, these are 2 different thermodynamic functions which we have considered. Both are second derivative with respect to its natural variable. So, A is basically the appropriate thermodynamic functions for the natural variable and N, V, T. H is thermodynamic function for the natural variable S, P, N. So, basically both of them are the secondary, with respect to its natural variables.

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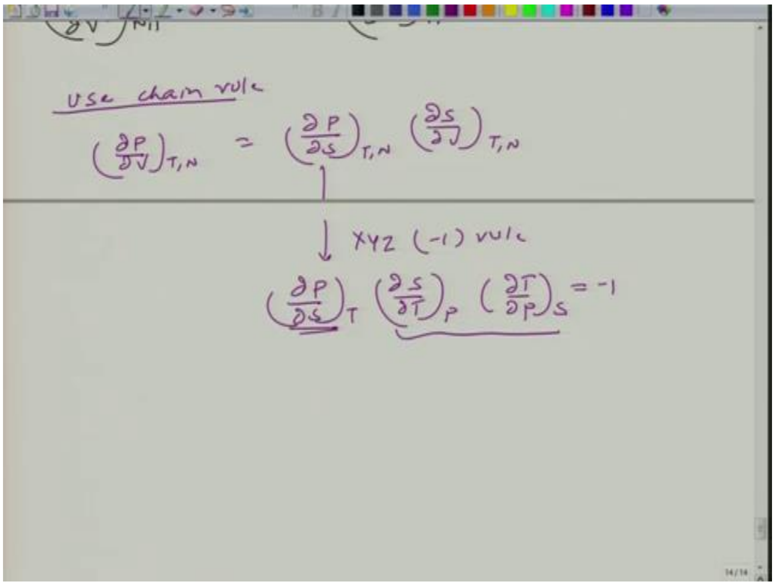

use chain rule

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

xyz (-1) rule

$$\left(\frac{\partial P}{\partial S}\right)_{T}\underbrace{\left(\frac{\partial S}{\partial T}\right)_{P}\left(\frac{\partial T}{\partial P}\right)_{S}} = -1$$

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

$$or, \qquad \left(\frac{\partial P}{\partial S}\right)_{T}\left(\frac{\partial S}{\partial T}\right)_{P}\left(\frac{\partial T}{\partial P}\right)_{S} = -1$$

Now, what we have do is we have to express now in terms of each other. Let me make use of the chain rule. So, the question is, are they equivalent? So, this can be replaced by this.

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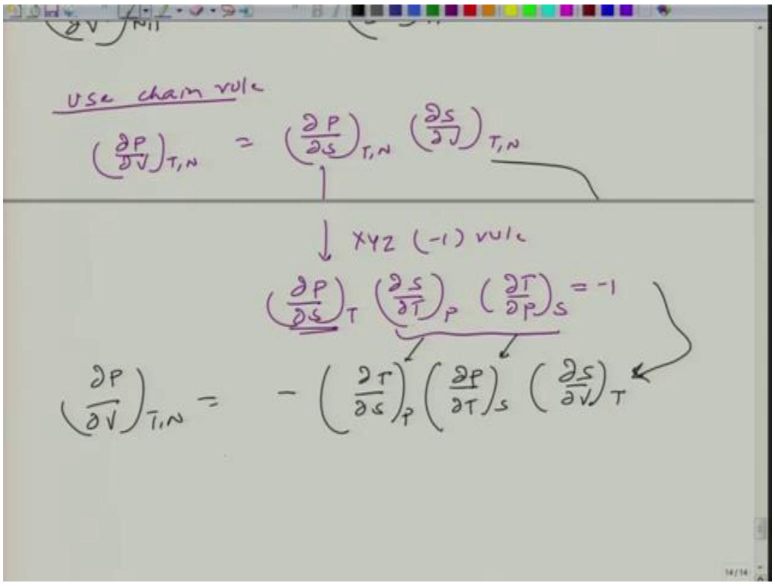

use chain rule

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

xyz (-1) rule

$$\left(\frac{\partial P}{\partial S}\right)_{T}\underbrace{\left(\frac{\partial S}{\partial T}\right)_{P}\left(\frac{\partial T}{\partial P}\right)_{S}} = -1$$

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

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

So, now this is expression so now, we can look at if how they are equivalent.

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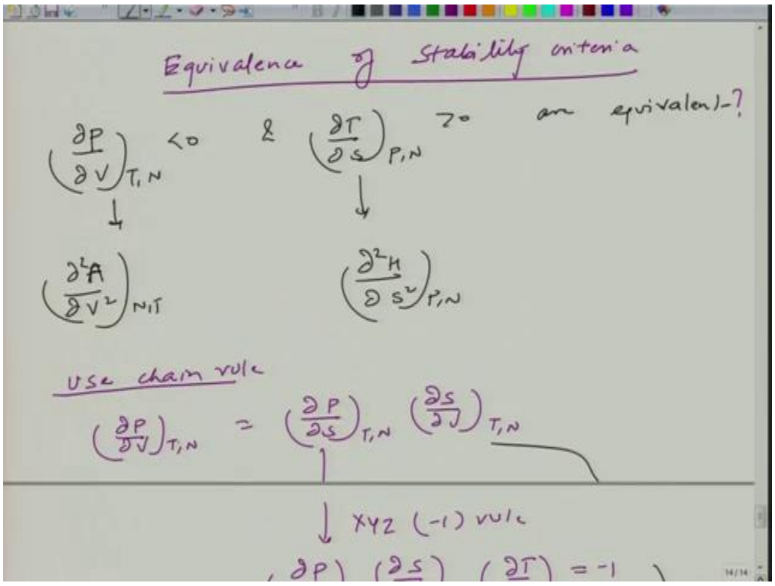


Equivalence of Stability criteria

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

$$\downarrow \qquad \downarrow$$

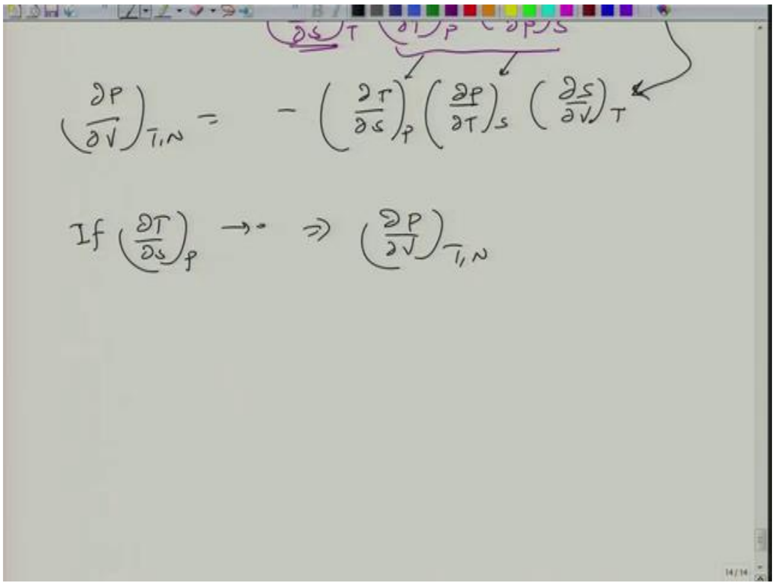
$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{N,T} \qquad \left(\frac{\partial^2 H}{\partial S^2}\right)_{P,N}$$

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

$$\left(\frac{\partial P}{\partial S}\right)_{T} \left(\frac{\partial S}{\partial T}\right)_{P} \left(\frac{\partial T}{\partial P}\right)_{S} = -1$$



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

If $\left(\frac{\partial T}{\partial S}\right)_{P} \to 0 \Rightarrow \left(\frac{\partial P}{\partial V}\right)_{T,N}$

So, let us see that this is a 2 term which we wanted. So, essentially what you can see that if del T by del S at P if this goes to 0, essentially this imply del P by del V T and N. That something which we can clearly see. So, this essentially is the way we to convince ourselves that these are equivalent as far as the stability analysis are concern and remember that the signs are different here.

That, something which you can clearly see because the signs are also different here. So, I think that is something which as far as we wanted to talk in today's lecture. And then in the next lecture what I am going to do is, I am going to look at the intrinsic stability of the thermodynamic system, where basically we will try to bring more understanding of the curvature effect of the thermodynamic functions.

And, essentially what are the mathematical expressions, which are related to such such kind of functions. And, we will bring that more clarity, as far as the local stability and the global stability expects of the thermodynamic functions. So, with this I will stop in today’s lecture and I will see you in the next lecture.