Professor Jayant K. Singh
Department of Chemical Engineering,
Indian Institute of Technology, Kanpur
Lecture-25

Equilibrium and stability-II

Welcome back, in the last class we looked at the changes in the thermodynamic functions at equilibrium or the conditions of the equilibrium with respect to the thermodynamic functions. So the one which we have looked at is Helmholtz free energy for the parameters or the natural variables T, V, N.

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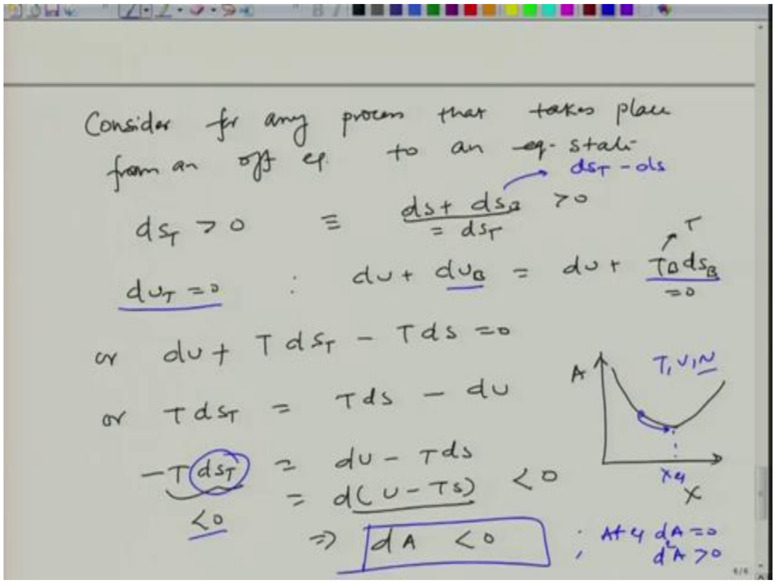

Consider for any process that takes place from an off eq. to an eq. state

$dS_T - dS$

$$dS_T > 0 \equiv \underbrace{dS + dS_B}_{= dS_T} > 0$$

$$\underline{dU_T = 0} \quad : \quad dU + \underline{dU_B} = dU + \underbrace{\overset{T}{T_B} dS_B}_{=0}$$

or $dU + TdS_T - TdS = 0$

or $TdS_T = TdS - dU$

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

$$\Rightarrow \boxed{dA < 0} \quad ; \quad \text{At eq } dA = 0, \; d^2A > 0$$

And what we have done is a simple analysis particularly for, in the last class we covered this (part) fact that if you are off equilibrium and going towards the equilibrium state, then in that case

$$dS_T > 0\,; \quad dS + dS_B = dS_T > 0$$

So the total energy has to be equal to zero. That means $dU_T = 0$; $dU + dU_B = dU + T_B dS_B = 0$. Because of the fact that we are considering in this case no change in the volume and hence dU is nothing but whatever the heat exchange associated with the bath which is TB dSB at the boundary. And since TB is equal to T because of the thermal equilibrium. We can rewrite this now in terms of this expression Or, $dU + TdS_T - TdS = 0$

So, rearranging this expression in this we can get this expression and where we know that for this process going from off equilibrium to equilibrium the entropy has to be, the change in the entropy has to be greater than zero. $TdS_T = TdS - dU$;
$dU - TdS_T = dU - TdS = d(U - TS) < 0$Or, $dA < 0$
this process we are going from off equilibrium to equilibrium. The free energy or Helmholtz free energy which is a natural thermodynamic potential for variables A, V, N, for variables T, V, N. This should approach towards minimum value. At equilibrium dA has to be equal to zero. We also showed that $(dA)^2 > 0$

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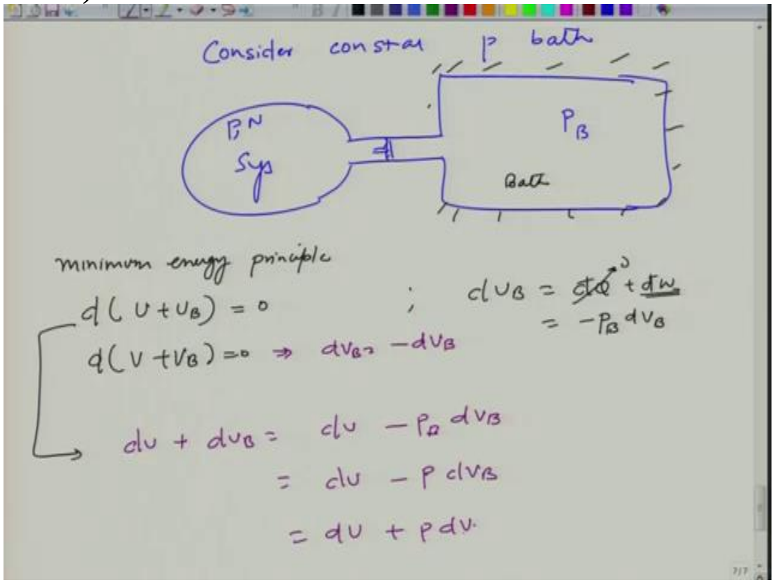

Consider constant P bath

minimum energy principle

$d(U + U_B) = 0$; $dU_B = \cancel{dQ}^{0} + \underline{dW}$
$= -P_B dV_B$

$d(V + V_B) = 0 \Rightarrow dV_B = -dV_B$

$dU + dU_B = dU - P_B dV_B$
$= dU - P dV_B$
$= dU + P dV$

Now, we can extend this kind of analysis for other cases. So just for completion of this understanding we also, I would also conduct this exercise, where we consider a constant pressure bath case system. So you have a system here and essentially we can consider this to be system and this is associated with some piston cylinder, some kind of a piston cylinder case and this effectively is also connected to the pressure bath.

So, this is our kind of overall system. So, you basically this system is at essentially P the pressure is going to be constant. And of course the number of moles are going to be constant here right. The volume is not constant. So what we have now is the conditions of the energy minimum. So, basically we are going to use minimum energy principle. So we start with again

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

The other condition is that the volume effectively for the system and the bath, that must be zero.$d(V + V_B) = 0$ So, let us also look at d of UB which is $dU_B = dQ + dW = -P_B dV_B$ And there is no heat, in this case we would be associating this making to be insulated . So, the only change is due to work. So I can write now this expression as

$$dU + dU_B = dU - P_B dV_B$$

So, at the equilibrium the pressure has to be equal. That I am not trying to prove it here . So, I am going to use this as , $dU + dU_B = dU - PdV_B = dU + PdV$

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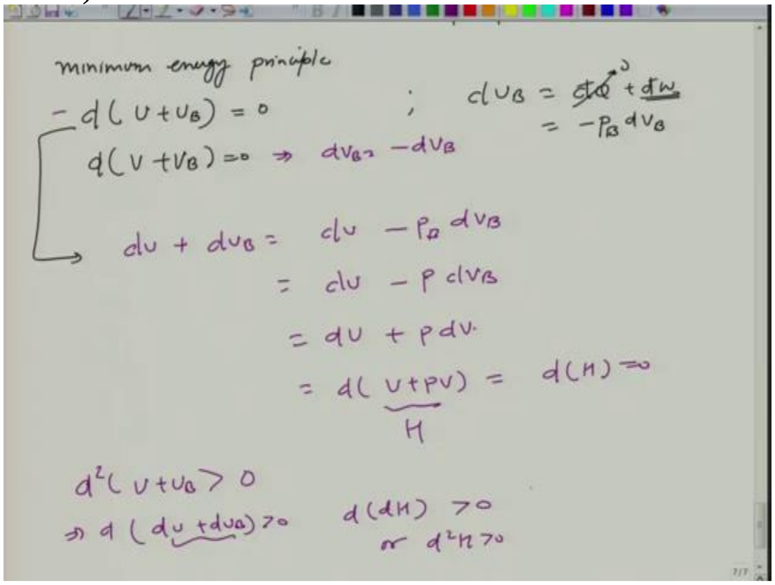

minimum energy principle

$- d(U + U_B) = 0$; $dU_B = \cancel{dQ}^{0} + \underline{dW}$

$= -P_B dV_B$

$d(V + V_B) = 0 \Rightarrow dV_B = -dV_B$

$du + dU_B = dU - P_B dV_B$

$= dU - P dV_B$

$= dU + PdV.$

$= d(\underbrace{U + PV}_{H}) = d(H) = 0$

$d^2(U + U_B > 0$

$\Rightarrow d(\underbrace{dU + dU_B}) > 0$ $d(dH) > 0$

or $d^2H > 0$

Now, since pressure is going to be a constant, we can write this as $d(U + PV)$ So this is nothing but H here. So, this is we can write this as $dU + dU_B = d(H) = 0$ (at equilibrium). You can also consider the second condition of minimum energy principle, that is

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

$$\text{Or, } d(dU + dU_B) > 0$$

$$d(dH) > 0$$

$$Or, d^2H > 0$$

So, if you can prove the above by doing this analysis.

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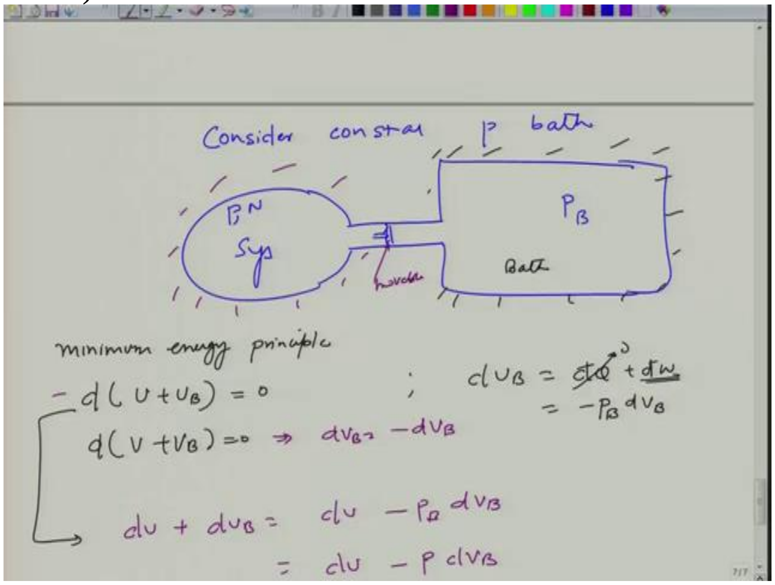

minimum energy principle

$- d(U+U_B) = 0$; $dU_B = \cancel{dQ}^{0} + \underline{dW}$

$= -P_B\, dV_B$

$d(V+V_B) = 0 \Rightarrow dV_B = -dV_B$

$dU + dU_B = dU - P_B\, dV_B$

$= dU - P\, dV_B$

So, that means in such a case where you have this kind of system insulated here only the pressure here and this is of course a movable one. Pressure is maintained here using a pressure bath. And you can apply this minimum energy principle. And of course here what we are trying to do is the total entropy is constant. So, essentially this would be of course insulated.

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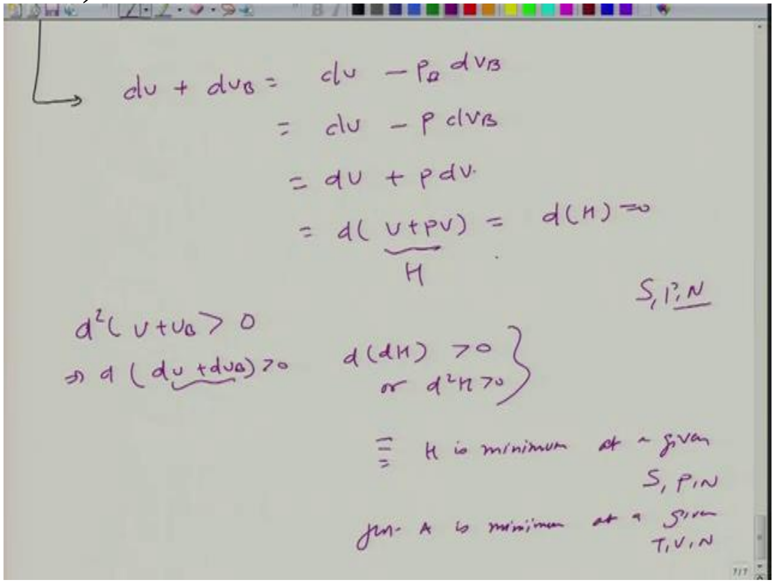

$dU + dU_B = dU - P_B\, dV_B$

$= dU - P\, dV_B$

$= dU + P\, dV$

$= d(\underbrace{U+PV}_{H}) = d(H) = 0$

$\underline{S, P, N}$

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

$\Rightarrow d(\underbrace{dU + dU_B}) > 0$

$\left.\begin{matrix} d(dH) > 0 \\ \text{or } d^2H > 0 \end{matrix}\right\}$

$\equiv$ H is minimum at a given S, P, N

sim. A is minimum at a given T, V, N

So, in that case when you are fixing the S, P, N. One can of course make use of the fact of that minimum energy principle that have been total internal energy will be minimum. But based on this we just derived that this minimum energy principle can be replaced simply by saying that H has to be minimum for such a condition.

So, this is equivalently saying that H is minimum for a given at a given S, P, N. Just like A is minimum at a given T, V, N. So this is something which we just derived. You can extend this exercise and finally this will be our last exercise as far as this is concerned. But for the complete diathermal and volume and as well as the temperature reservoir.

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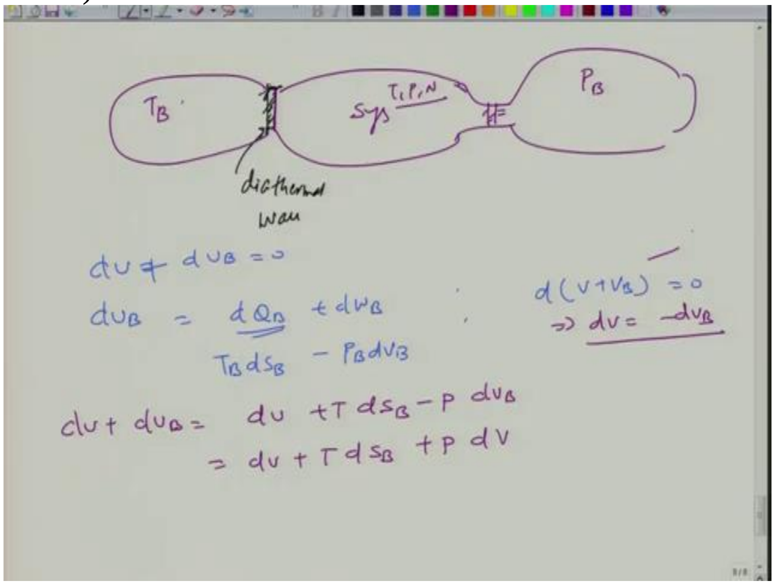

So, in this case, let us say we have a system and of course I can have this kind of piston here. And this is my bath, pressure bath. This is my temperature bath, so this wall I can have this kind of wall, which is rigid but diathermal wall. And this we have now TB and this is your system. So, if we consider such a system which essentially means the system will be at T, P, N. That is what we are trying to say that at equilibrium, the system is maintained at T, P, N.

So, in that case also we can try to extend this exercise of energy minimum principle for such a given (state) condition. And we can write $dU + dU_B = 0$. And dUB here has two components, the temperature bath is there and the pressure bath is there $dU_B = dQ_B + dW_B$. We can also write this expression as $dU_B = T_B dS_B - P_B dV_B$

And of course we have to write $d(V + V_B) = 0; Or\ dV = -dV_B$. Now, making use of the fact that the temperature will be equal pressure will be equal, I can write this

$$dU + dU_B = dU + TdS_B - PdV_B = dV + TdS_B + Pd$$

Because this is from the total volume is constant hence we can simply write in this way.

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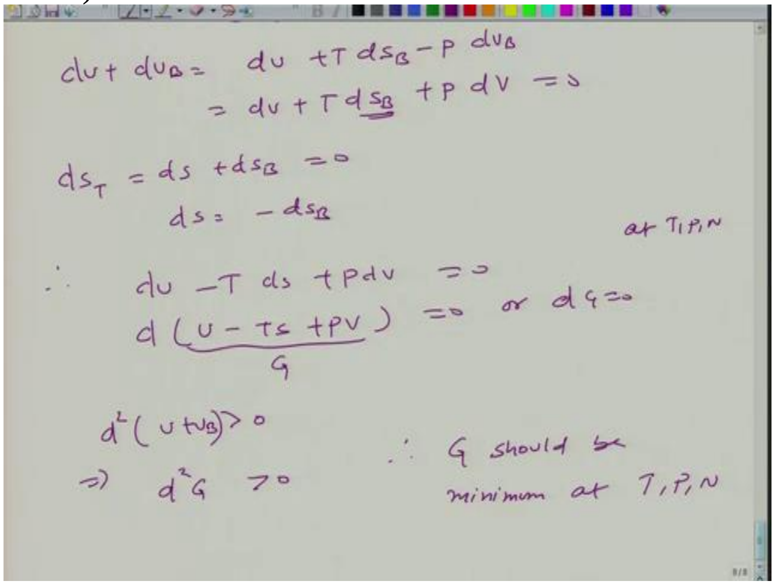

$$du + du_B = du + T\,ds_B - P\,dv_B$$

$$= du + T\,d\underline{s_B} + P\,dV = 0$$

$$ds_T = ds + ds_B = 0$$

$$ds = -ds_B$$

at T, P, N

$$\therefore \quad du - T\,ds + P\,dv = 0$$

$$d\underbrace{(U - TS + PV)}_{G} = 0 \quad \text{or} \quad dG = 0$$

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

$$\Rightarrow \quad d^2G > 0$$

$\therefore$ G should be minimum at T, P, N

We have to make use of the fact $dS_T = dS + dS_B = 0\ (consider)$. And dS is for a given total entropy, S is equal to dSB. Therefore, I can write this $dU - TdS + PdV = 0$ because this is the minimum energy principle. So, this must be equal to zero given temperature and their pressure constant, I can write this as $(U - TS + PV) = 0\ or\ dG = 0$ at T, P, N at a given temperature, pressure, N.

So, you can also show that $d^2(U + U_B) > 0\ or, d^2G > 0$. This will give you the condition. The second derivative of G should be greater than equal to zero or in other word G should be minimum at a given temperature, pressure, N. So, with this exercise we can now summarise our understanding as far as the equilibrium state is concerned for different independent variables.

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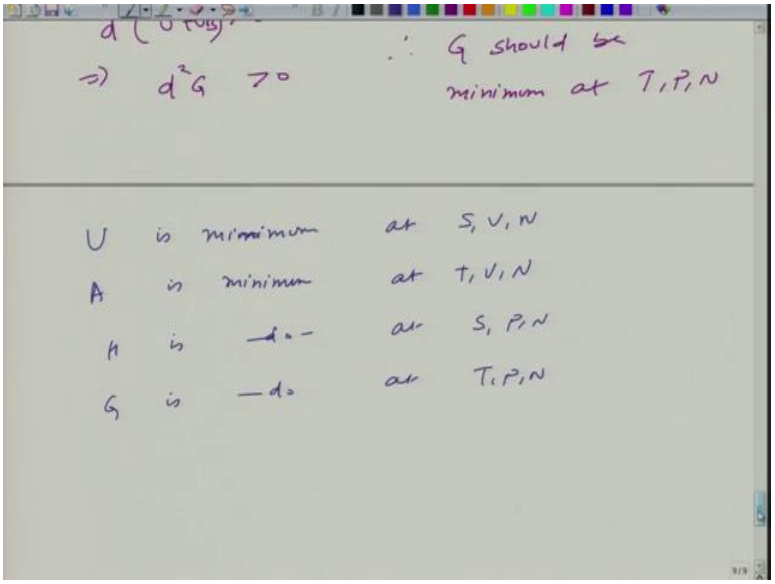

$\Rightarrow d^2G > 0$

∴ G should be minimum at T, P, N

U is minimum at S, V, N

A is minimum at T, V, N

H is —do— at S, P, N

G is —do— at T, P, N

So, let me just write it down, this now we have derived it earlier (we) probably have stated that. So, U is (minimum) minimum at S, V, N. For given total entropy, A is minimum at T, V, N. H is minimum at S, P, N. And G is minimum at T, P, N. So, that is something which now we can summarise based on our exercise.

Now, we can further extend this, so instead of just looking at the thermodynamic functions which of course provides the idea of how and what are the conditions of the system at particular equilibrium or if the process is driving towards the equilibrium, what would be the appropriate behaviour of the free energies or the thermodynamic functions. But in addition to that we can also look at the specific variables or thermodynamic properties which would be useful to examine the conditions of stability of the system. So, now we will be extend this analysis for stability.

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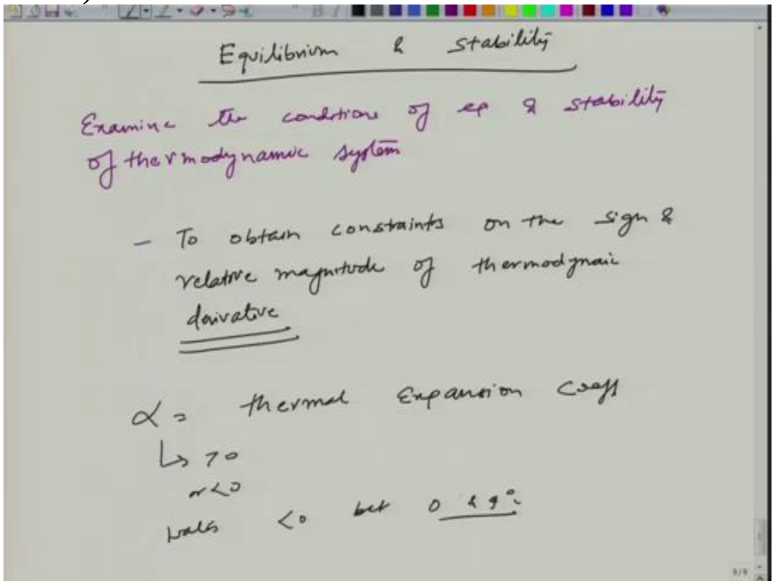

Equilibrium & stability

Examine the condition of eq & stability of thermodynamic system

- To obtain constraints on the sign & relative magnitude of thermodynamic derivative

α = thermal Expansion coeff

↳ > 0

or < 0

water < 0 bet 0 & 4°C

So, let us specifically say that this is what we are looking at. We are looking at Equilibrium and Stability. So, the goal is to examine the condition of Equilibrium and Stability of thermodynamic system. So, one of the important thing is that the signs of the thermodynamic derivative or derivative of the thermodynamic properties, variables plays extremely important role in identifying the stability of the system. So something which we are going to pay attention to.

So, that means one of the aim which we have is to obtain constraints on the sign and relative magnitude of the thermodynamic function. But mainly the derivatives. So, the derivatives plays the big role here. For example, just take an example of alpha which sometimes we call it as Thermal Expansivity. This can be positive or negative. For water is negative between 0 and 4. So, it tells you a specific behaviour of the properties and also can identify some expected stability.

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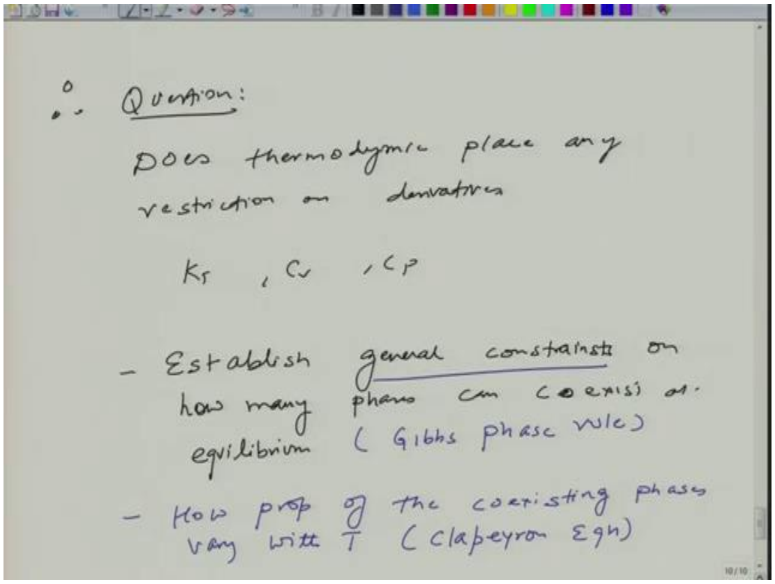

Question:

Does thermodynmic 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, we will look into that, but the major question is the following. So, the key questions which we have to worry about is, does thermodynamic place any constraint or restriction on the derivatives, on derivatives. So the derivatives which we are talking about, let us say it is KT or Cv or Cp.

Does thermodynamics place any restriction, can it be a negative, can it be positive for stability? For real system to have, do you think that a Cv (has) can be negative? That is another question. So, these are the questions which bring clarity in the way we deal with the phases and what we expect in reality. So, that is one part of it. The other thing is, do we have some kind of a rule which gives you a constraint for many phases to coexist? Or in other word do we, can we establish general constraints on how many phases can coexist at equilibrium?

So, that is another question. That can we, do we have some kind of constraints that for a given set of temperature and pressure only a certain number of phases can coexist? Or for that matter you can have only one phase for let us say one particular condition for three phases to be coexist on and so forth.

So, the question is, is there any general rule for that? That this is something which we call it Gibbs Phase rule. The other thing is that, how property of the coexistence phases, the phases which are at equilibrium with each other such as liquid vapour solid liquid. So, how property of the coexistence phases vary with temperature? So, this we call Clapeyron Equation. Something which we learn.

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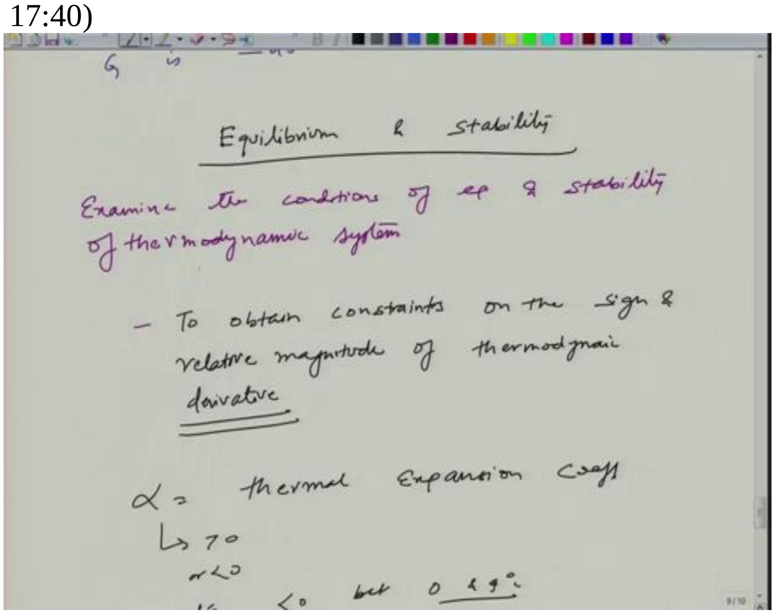

G is

Equilibrium & stability

Examine the conditions of eq & stability of thermodynamic system

- To obtain constraints on the sign & relative magnitude of thermodynamic derivative

$\alpha =$ thermal Expansion coeff

$\hookrightarrow > 0$

$\alpha < 0$

< 0 bet 0 & 4°C

So, these are the questions which we would like to elaborate more and and we will spend some time to understand this the conditions of the equilibrium, particularly with respect to the stability that means, how the stability criteria brings its constraints on the signs of the derivatives of the properties, that is number one.

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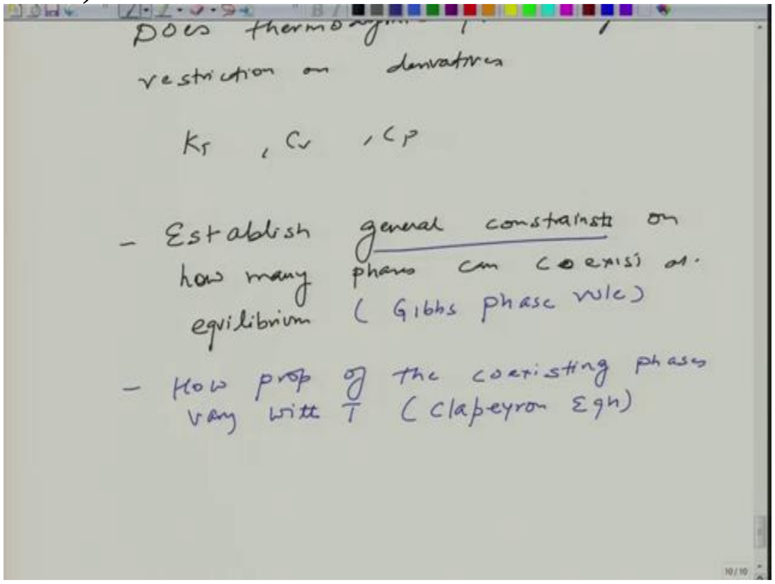

Does thermodynamic

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)

The (second) the other two questions is basically to come up with the constraints which defines how many phases can coexist. And the third is that how the coexistence phase vary with temperature. So, these are the three things which we have to now elaborate on it.

So, at this point I will stop and in the next lecture I will start with the stability criteria and bring this at least address the first part of this questions, which we have listed. So, I will see you in the next class.