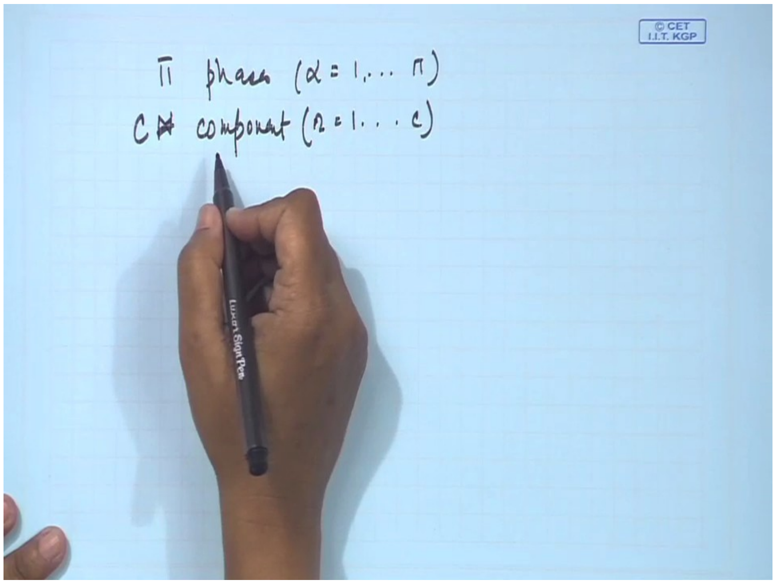
Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
Department of Chemical Engineering
Indian Institute of Technology Kharagpur
Lecture 24
Heterogeneous Closed Systems

Well, hello everybody so as I had discussed in the last class in this particular class we are going to deal with heterogeneous closed systems, right? So therefore what do we assume? We assume that there are large number of homogeneous systems. Just in the last class I had taken up to homogeneous open systems inside a closed system. It was one particular pure substance into 2 different phases.

(Refer Slide Time: 0:56)

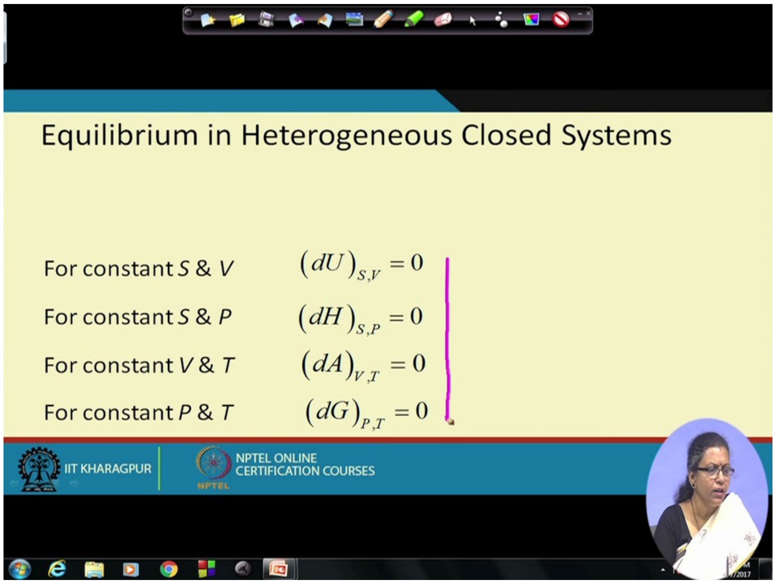


π phases $(\alpha = 1, \ldots \pi)$

C # component $(n = 1 \ldots c)$

So therefore in this case I would like to extend it slightly further and I would have say I have pi number of phases. Since the derivation is slightly involved it is very important that we keep all our nomenclatures in a proper form, okay. So therefore it has say pi phases and the phases has are numbered with alpha such that alpha varies from 1 to pi. And if we assume that there are N numbers of components where each or rather we can take it as C number of components where the components are numbered as n this is one to C and so long what we have done?

(Refer Slide Time: 1:59)



Equilibrium in Heterogeneous Closed Systems

For constant S & V $(dU)_{S,V} = 0$

For constant S & P $(dH)_{S,P} = 0$

For constant V & T $(dA)_{V,T} = 0$

For constant P & T $(dG)_{P,T} = 0$

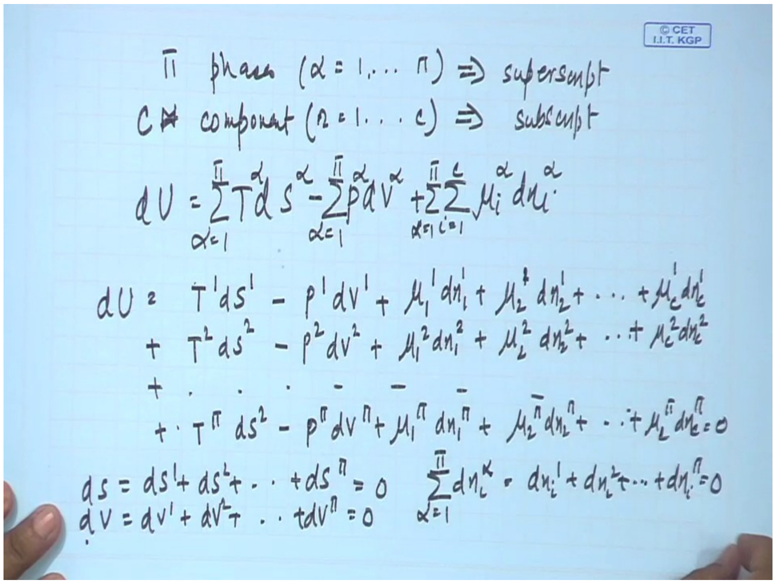
For these particular type of heterogeneous closed system we have already derived the situation we have already derived the condition of equilibrium for different type of interactions between the close system and the surroundings and we have derived the following equations that has been noted down here. As I have already mentioned the first equation is for constant S and V and then it is S and P then V and T and this is for constant P and T conditions.

So therefore in this case we already know the condition of equilibrium for heterogeneous closed systems but we know these in terms of thermodynamic potentials or we know these in terms of extensive parameters. Very frequently we would like to express them in terms of intensive parameters which can be easily measured or they can be easily estimated.

Now we already know the conditions we know that I had mentioned in the first-class that thermodynamic equilibrium is the simultaneous maintenance of thermal, mechanical and chemical equilibrium and that time I had also mentioned that thermal equilibrium implies equality of temperature, mechanical equilibrium implies equality of pressure and chemical equilibrium implies equality of chemical potential but just by the statement of someone it is not always good to get convinced.

So I would prove it from you I would start with the condition of equilibrium which we had already derived so long from one of these equations and I will arrive at the condition of equilibrium expressed in terms of intensive variants.

(Refer Slide Time: 3:44)



π phases ($\alpha = 1, \dots \pi$) $\Rightarrow$ superscript

C component ($i = 1 \dots c$) $\Rightarrow$ subscript

$$dU = \sum_{\alpha=1}^{\pi} T^{\alpha} dS^{\alpha} - \sum_{\alpha=1}^{\pi} p^{\alpha} dV^{\alpha} + \sum_{\alpha=1}^{\pi}\sum_{i=1}^{c} \mu_i^{\alpha} dn_i^{\alpha}$$

$$\begin{aligned} dU = {} & T^1 dS^1 - p^1 dV^1 + \mu_1^1 dn_1^1 + \mu_2^1 dn_2^1 + \dots + \mu_c^1 dn_c^1 \\ & + T^2 dS^2 - p^2 dV^2 + \mu_1^2 dn_1^2 + \mu_2^2 dn_2^2 + \dots + \mu_c^2 dn_c^2 \\ & + \dots \\ & + T^{\pi} dS^2 - p^{\pi} dV^{\pi} + \mu_1^{\pi} dn_1^{\pi} + \mu_2^{\pi} dn_2^{\pi} + \dots + \mu_c^{\pi} dn_c^{\pi} = 0 \end{aligned}$$

$$dS = dS^1 + dS^2 + \dots + dS^{\pi} = 0 \qquad \sum_{\alpha=1}^{\pi} dn_i^{\alpha} = dn_i^1 + dn_i^2 + \dots + dn_i^{\pi} = 0$$

$$dV = dV^1 + dV^2 + \dots + dV^{\pi} = 0$$

Now here I would like to mention that is particular derivation it was for or this particular prove was first given by Gibbs and what he did? He used the first equation say dU equals to Tds minus Pdv plus Sigma I, mui, dni he used the equation for dU in order to do this derivation. The primary reason for using U as a starting point was possibly because of the symmetry of the equation if you observe.

We find that in the expression of U each differential on the right-hand side is a differential of an extensive property and the coefficient that we have that is an intensive property. Usually if you consider the other equations we find that the differential and the coefficients there are mixtures of intensive and extensive properties and just because this symmetry is there only in U.

So therefore Gibbs also started proving the condition of thermodynamic equilibrium from dU from the expression of dU and we will also be doing the same thing and this is and from here we are going to start and we are going to arrive at the uniformity of all intensive variables at equilibrium by considering just one function U.

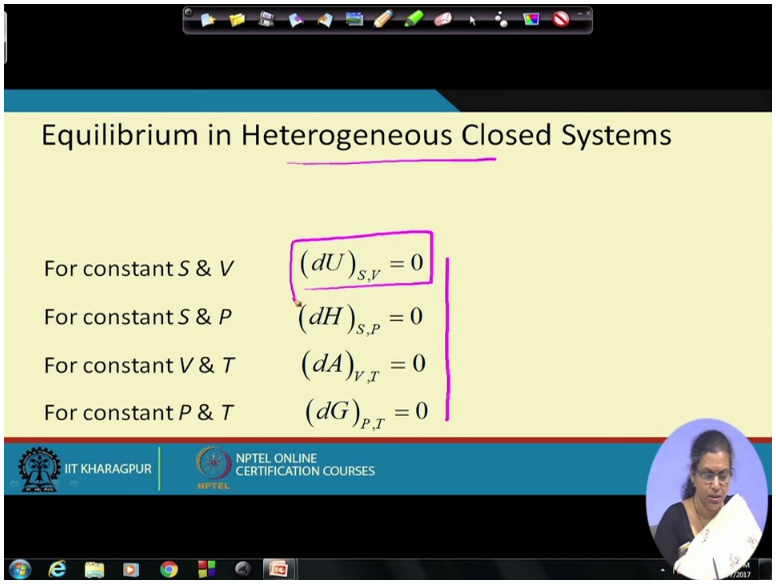
So therefore while we are considering this particular function the generalized expression this was written for just one phase. Now if we have pi's number of phases so naturally then in that case this generalized expression should be written in this particular form it should be T alpha dS alpha where Alpha equals to 1 to pi. Now here I would again like to mention I have taken up pi number of phases I have taken up C number of components and the phases are numbered with alpha the components are numbered with n and I denote the phase by means of a superscript I denote component by means of a subscript.

Since the derivation is slightly involved it is very important for us to remember the conventions that we are using. So therefore and if we consider this equation again we find that since there are more than one phase, so therefore this should be P alpha this should be dv alpha this also should be from Alpha equals to 1 to Pi. What about the last equation? In the last equation we find that here I should be equal to 1 to C and before that there should be alpha equals to 1 to pi, in that case as I have already mentioned my subscript refers to the component and my superscript will be referring to the phases.

So from here what do we get? From this particular situation, so we find that for all the phases I can write down this equation. Now if I slightly elaborate it and write, what do I get? If I just breakdown the sigma values it is basically T for phase 1 dS1 minus P1dV1 plus mu1 phase1 dn1 plus mu2 phase1 dn2 plus so on to muC dnC phase1 plus again for the second phase it is T2 dS2 minus P2 dV2 plus mu1 in phase 2 dn1.

Sorry I need to refer to the components here dn1 in phase 2 plus mu2 phase 2, dn2 phase 2 plus so on till we get muC2 dnC2 I can keep on continuing this for phase 3 phase 4 and finally for the Pith phase it is going to be P pi dV pi plus mu1 pi dn1pi, mu2 pi dn2 pi plus so on till mu Cpi dn Cpi, right? And we have to remember that we are dealing with a heterogeneous closed system as I have mentioned in here.

(Refer Slide Time: 8:43)



Equilibrium in Heterogeneous Closed Systems

For constant S & V $\boxed{(dU)_{S,V} = 0}$

For constant S & P $(dH)_{S,P} = 0$

For constant V & T $(dA)_{V,T} = 0$

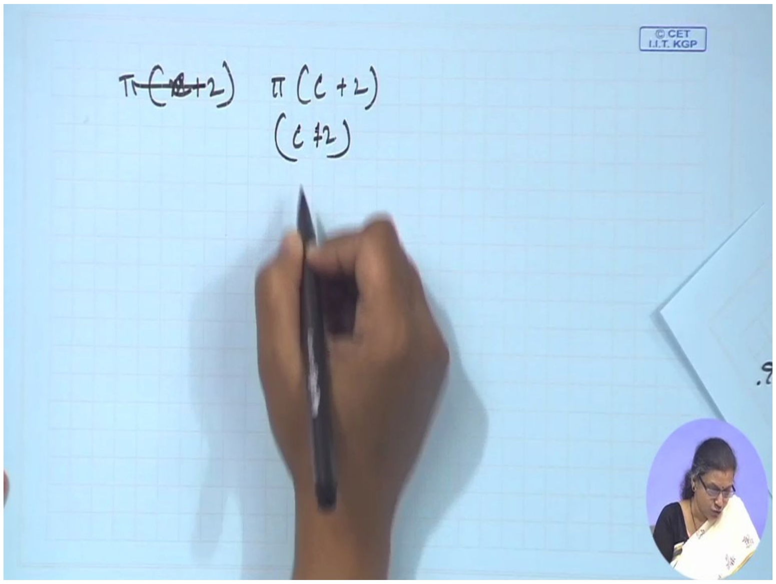
For constant P & T $(dG)_{P,T} = 0$

So when it is a heterogeneous closed system and I am dealing with dU, so therefore this equation should be supposed to hold, so therefore what do I mean to say is this whole thing should be equal to 0, right?

Now apart from this we also need to remember that there are also some additional constraints here, what are the additional constraints? The first thing is the individual variations of entropy the individual variations of volume and the individual variations of the total number of moles of each chemical species they can vary but subject to the condition that the total entropy, the total volume and the total number of moles remains constant or in other words ds which is equal to ds1 plus ds2 plus so on till ds pi this should be equal to 0 because after all it is a close heterogeneous closed system.

Same way dv1 plus dv2 plus so on till dv pi this should be equal to 0. In the same one for each and every individual component we can write down dni alpha this should be dni1 plus dni2 plus so on till dni pi this should be equal to 0. So therefore what do I get? I find that I have written down one particular equation in terms of how many variables?

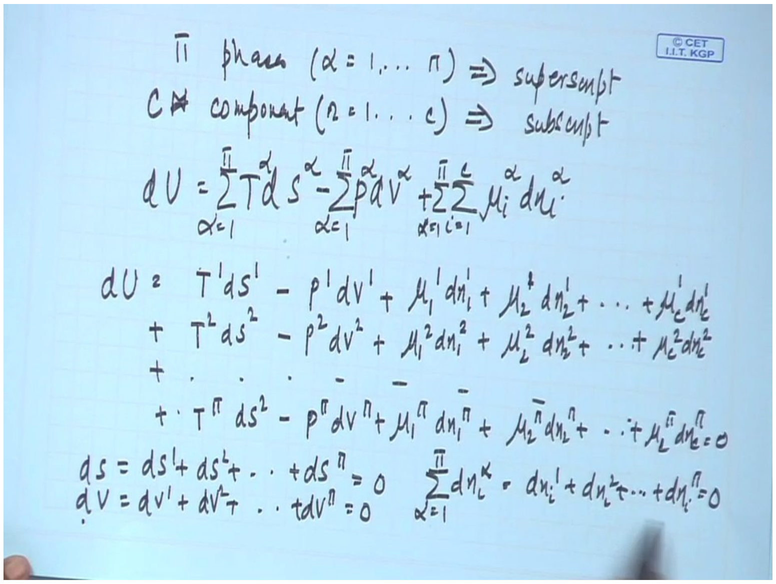
(Refer Slide Time: 11:00)



$\pi\cancel{(c+2)}$ $\pi(c+2)$

$(c+2)$

(Refer Slide Time: 10:43)



π phase $(\alpha = 1, \ldots \pi) \Rightarrow$ superscript

C ~~#~~ component $(i = 1 \ldots c) \Rightarrow$ subscript

$$dU = \sum_{\alpha=1}^{\pi} T^{\alpha} dS^{\alpha} - \sum_{\alpha=1}^{\pi} p^{\alpha} dV^{\alpha} + \sum_{\alpha=1}^{\pi}\sum_{i=1}^{c} \mu_i^{\alpha} dn_i^{\alpha}$$

$$\begin{aligned} dU = {} & T^1 dS^1 - p^1 dV^1 + \mu_1^1 dn_1^1 + \mu_2^1 dn_2^1 + \ldots + \mu_c^1 dn_c^1 \\ & + T^2 dS^2 - p^2 dV^2 + \mu_1^2 dn_1^2 + \mu_2^2 dn_2^2 + \ldots + \mu_c^2 dn_c^2 \\ & + \ . \quad . \quad . \quad - \quad - \quad - \\ & + T^{\pi} dS^2 - p^{\pi} dV^{\pi} + \mu_1^{\pi} dn_1^{\pi} + \mu_2^{\pi} dn_2^{\pi} + \ldots + \mu_c^{\pi} dn_c^{\pi} = 0 \end{aligned}$$

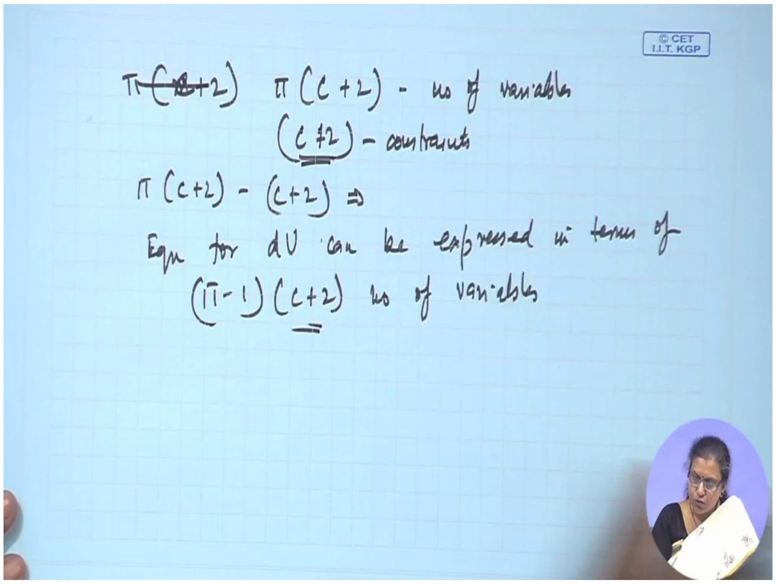
$$dS = dS^1 + dS^2 + \ldots + dS^{\pi} = 0 \qquad \sum_{\alpha=1}^{\pi} dn_i^{\alpha} = dn_i^1 + dn_i^2 + \ldots + dn_i^{\pi} = 0$$

$$dV = dV^1 + dV^2 + \ldots + dV^{\pi} = 0$$

I have written it down if there are pi numbers of phases then I have written down the whole equation in terms of pi into m plus 2 numbers of variables and out of that, how many constraints do I have? I have 2 constraints for sv and since there are C numbers of components I have constraints for all these C number of components.

So therefore many number of constants, sorry it is not m it is C because C is my number of components and how many constraints do I have? My numbers of constraints are C plus 2, so therefore it is always possible that I can eliminate a few of these variables.

(Refer Slide Time: 11:10)



$\pi\,\cancel{(C+2)}$ $\pi(C+2)$ - no of variables

$(\underline{C+2})$ - constraints

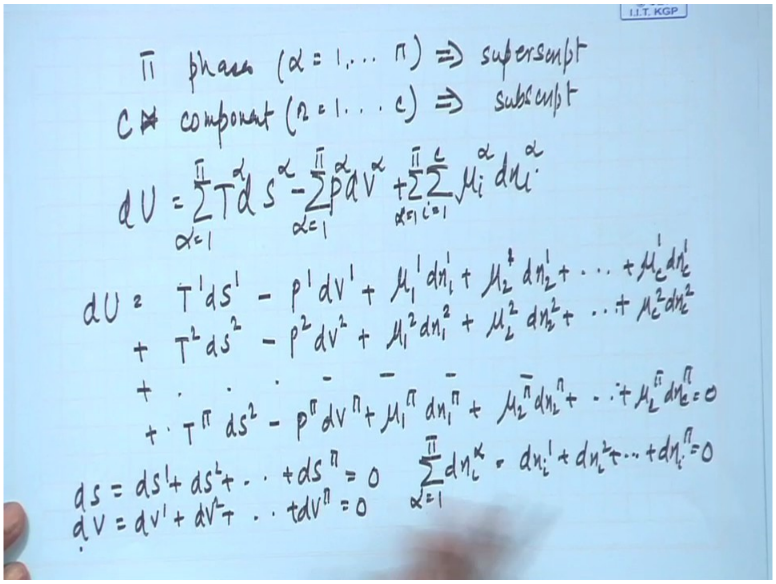
$\pi(C+2) - (C+2) \Rightarrow$

Eqn for dU can be expressed in terms of

$(\pi-1)(\underline{C+2})$ no of variables

And I should be able to write it down in terms of pi into C plus 2 minus C plus 2 number of variables or in other words this particular equation the equation for dU can be expressed in terms of pi minus1 into C plus 2 number of variables. Or in other words these number are the truly independent variables, since we have eliminated other variables using the C plus 2 number of constraints these are the number of constraints that we have, these are the number of variables that my system has.

(Refer Slide Time: 12:09)



π phases $(\alpha = 1, \ldots \pi)$ ⇒ superscript

C component $(i = 1 \ldots c)$ ⇒ subscript

$$dU = \sum_{\alpha=1}^{\pi} T^{\alpha} dS^{\alpha} - \sum_{\alpha=1}^{\pi} p^{\alpha} dV^{\alpha} + \sum_{\alpha=1}^{\pi}\sum_{i=1}^{c} \mu_i^{\alpha} dn_i^{\alpha}$$

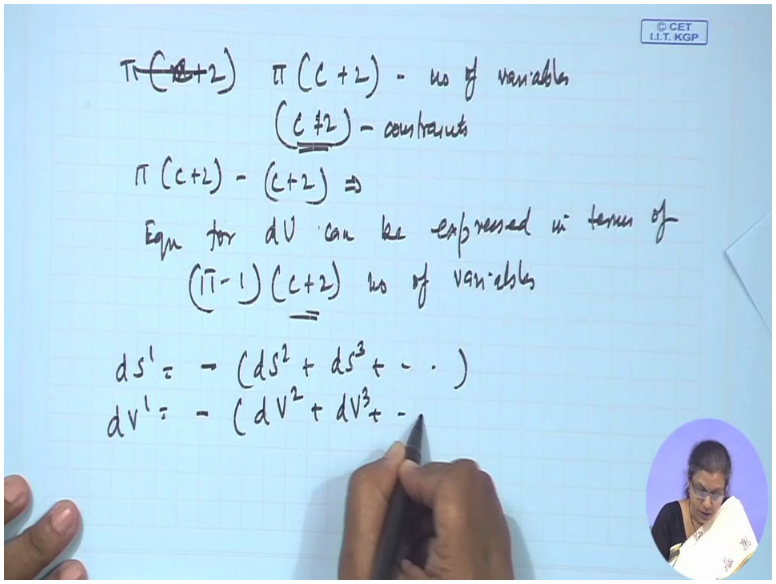
$$\begin{aligned} dU = {} & T^1 ds^1 - p^1 dv^1 + \mu_1^1 dn_1^1 + \mu_2^1 dn_2^1 + \ldots + \mu_c^1 dn_c^1 \\ & + T^2 ds^2 - p^2 dv^2 + \mu_1^2 dn_1^2 + \mu_2^2 dn_2^2 + \ldots + \mu_c^2 dn_c^2 \\ & + \; . \quad . \quad . \quad - \quad - \quad - \quad - \\ & + T^{\pi} ds^2 - p^{\pi} dv^{\pi} + \mu_1^{\pi} dn_1^{\pi} + \mu_2^{\pi} dn_2^{\pi} + \ldots + \mu_c^{\pi} dn_c^{\pi} = 0 \end{aligned}$$

$$ds = ds^1 + ds^2 + \ldots + ds^{\pi} = 0 \qquad \sum_{\alpha=1}^{\pi} dn_i^{\alpha} = dn_i^1 + dn_i^2 + \ldots + dn_i^{\pi} = 0$$

$$dV = dv^1 + dv^2 + \ldots + dv^{\pi} = 0$$

So therefore now I should be in a position to express the entire equation of dU in terms of lesser number of variables, here the number of variables as I have mentioned is pi into C plus 2. I should be in a position to eliminate C plus 2 variables from here. How can I do this? I know this particular equation, so instead of ds1 can I not substitute it with minus of ds2 plus so on to ds pi? Same thing can I not do it with dv and same thing can I not do it with dni alpha?

(Refer Slide Time: 12:55)



~~π (c+2)~~ $\pi(c+2)$ - no of variables

$(\underline{c+2})$ - constraints

$\pi(c+2) - (c+2) \Rightarrow$

Eqn for dU can be expressed in terms of

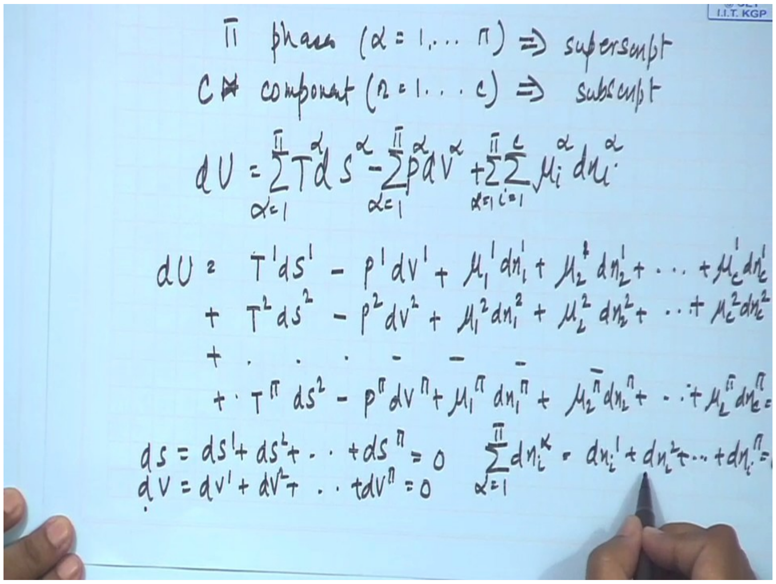
$(\pi - 1)(\underline{c+2})$ no of variables

$ds^1 = -(ds^2 + ds^3 + \dots)$

$dv^1 = -(dV^2 + dV^3 + \dots$

So what do I mean is instead of ds1 I can substitute it as minus ds2 plus ds3 plus so on instead of dv1 can I not substitute it with dv2 plus dv3 plus so on.

(Refer Slide Time: 13:04)



Π phase (α = 1, … Π) ⇒ superscript

C # component (i = 1 … c) ⇒ subscript

$$dU = \sum_{\alpha=1}^{\Pi} T^{\alpha} ds^{\alpha} - \sum_{\alpha=1}^{\Pi} p^{\alpha} dV^{\alpha} + \sum_{\alpha=1}^{\Pi}\sum_{i=1}^{c} \mu_i^{\alpha} dn_i^{\alpha}$$

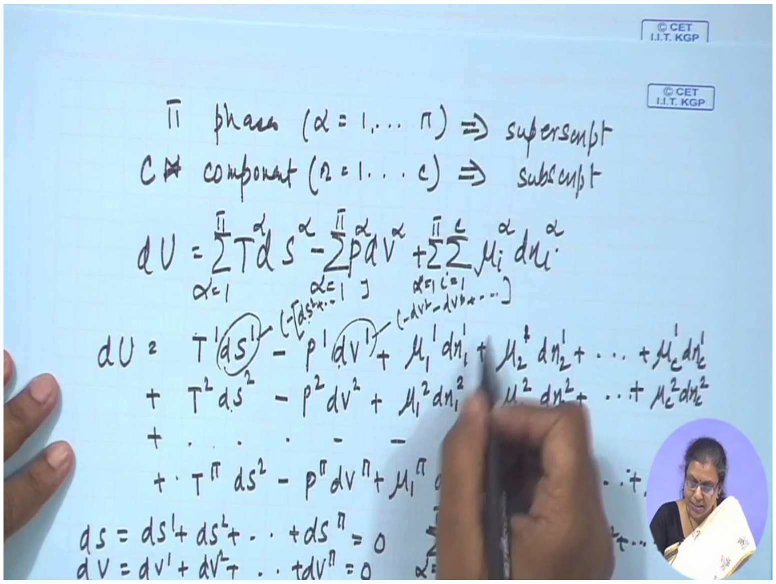
$$\begin{aligned} dU = {} & T^1 ds^1 - p^1 dv^1 + \mu_1^1 dn_1^1 + \mu_2^1 dn_2^1 + \dots + \mu_c^1 dn_c^1 \\ & + T^2 ds^2 - p^2 dv^2 + \mu_1^2 dn_1^2 + \mu_2^2 dn_2^2 + \dots + \mu_c^2 dn_c^2 \\ & + \;.\quad .\quad .\quad -\quad -\quad - \\ & + T^{\Pi} ds^2 - p^{\Pi} dv^{\Pi} + \mu_1^{\Pi} dn_1^{\Pi} + \mu_2^{\Pi} dn_2^{\Pi} + \dots + \mu_c^{\Pi} dn_c^{\Pi} = \end{aligned}$$

$$ds = ds^1 + ds^2 + \dots + ds^{\Pi} = 0 \qquad \sum_{\alpha=1}^{\Pi} dn_i^{\alpha} = dn_i^1 + dn_i^2 + \dots + dn_i^{\Pi} =$$

$$dV = dv^1 + dv^2 + \dots + dv^{\Pi} = 0$$

And in the similar way can I not substitute each and every ni1 with minus of ni2 plus ni3 etc. So once I make the substitution and I put it here, so instead of dS1 what am I going to have? Instead of this dS1 I am going to have minus of ds2 plus so on and so forth, isn't it? Instead of this dV1 also I should be having minus of dv2 minus of dv3 plus so on and so forth I can write it in this particular term.

(Refer Slide Time: 13:50)



π phase (α = 1, … π) ⇒ superscript

C # component (n = 1 … c) ⇒ subscript

$$dU = \sum_{\alpha=1}^{\pi} T^{\alpha} ds^{\alpha} - \sum_{\alpha=1}^{\pi} p^{\alpha} dv^{\alpha} + \sum_{\alpha=1}^{\pi}\sum_{i=1}^{c} \mu_i^{\alpha} dn_i^{\alpha}$$

$(-[ds^2 + \dots])$ $(-dv^2 - dv^3 - \dots])$

$$dU = T^1 ds^1 - p^1 dv^1 + \mu_1^1 dn_1^1 + \mu_2^1 dn_2^1 + \dots + \mu_c^1 dn_c^1$$

$$+\ T^2 ds^2 - p^2 dv^2 + \mu_1^2 dn_1^2 \quad \mu_2^2 dn_2^2 + \dots + \mu_c^2 dn_c^2$$

$$+\ \dots$$

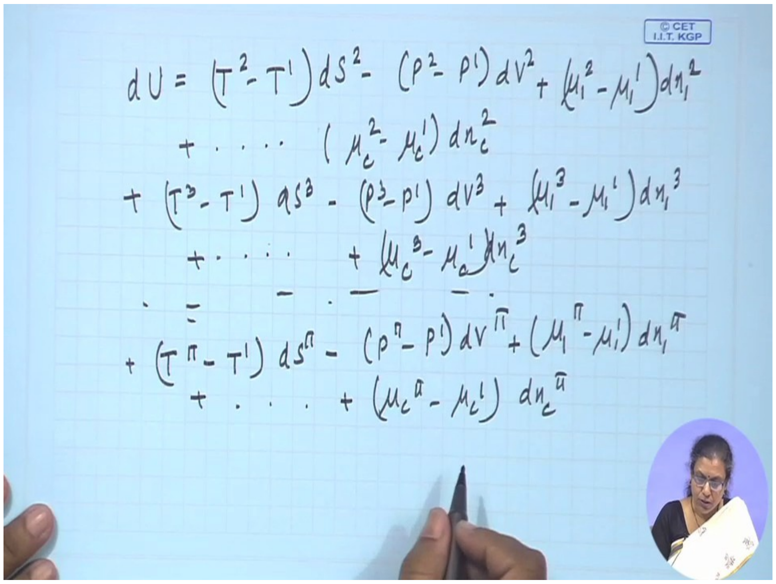
$$+\ T^{\pi} ds^2 - p^{\pi} dv^{\pi} + \mu_1^{\pi} \quad \dots +$$

$$ds = ds^1 + ds^2 + \dots + ds^{\pi} = 0$$

$$dv = dv^1 + dv^2 + \dots + dv^{\pi} = 0$$

So once I write it down in this particular term I find that there is a ds2 and there is a ds2 here, there is a dv2 there is a dv2 here as well. Same way there is a ds3 and there is a ds3 here.

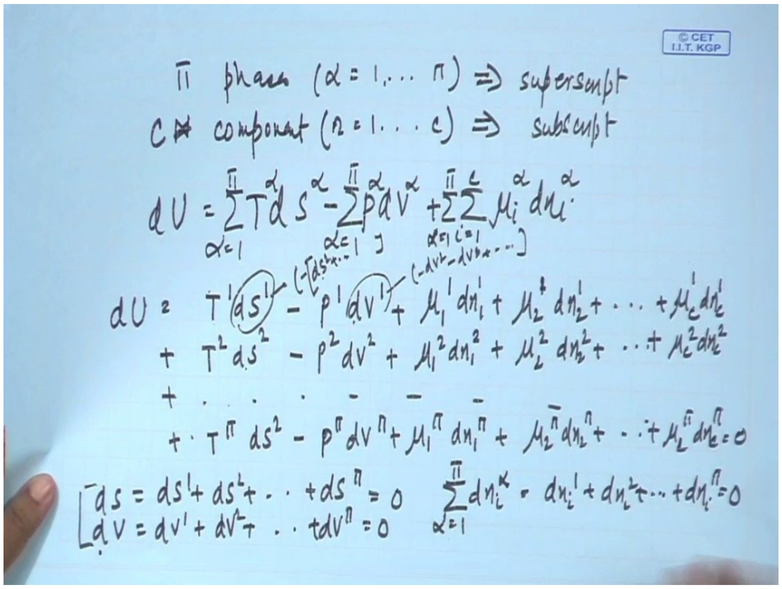
(Refer Slide Time: 14:04)



$$dU = (T^2 - T^1)\,dS^2 - (P^2 - P^1)\,dV^2 + (\mu_1^2 - \mu_1^1)\,dn_1^2$$
$$+ \cdot \cdot \cdot \cdot \; (\mu_c^2 - \mu_c^1)\,dn_c^2$$
$$+ (T^3 - T^1)\,dS^3 - (P^3 - P^1)\,dV^3 + (\mu_1^3 - \mu_1^1)\,dn_1^3$$
$$+ \cdot \cdot \cdot \cdot \; + (\mu_c^3 - \mu_c^1)\,dn_c^3$$
$$\cdot \quad = \quad - \quad \cdot \; - \quad - \; \cdot$$
$$+ (T^\pi - T^1)\,dS^\pi - (P^\pi - P^1)\,dV^\pi + (\mu_1^\pi - \mu_1^1)\,dn_1^\pi$$
$$+ \; \cdot \; \cdot \; \cdot \; + (\mu_c^\pi - \mu_c^1)\,dn_c^\pi$$

So once I start arranging it in this particular form what is the resulting expression that I get? The resulting expression which I get is T2 minus T1 into dS2 minus P2 minus P1 dV2 plus mu12 minus mu11 dn1 of 1 plus so on and so forth till muC2 minus muC1 dnC2 and in the same way I can write T3 minus T1 dS3 minus P3 minus P1 dv3 plus mu13 minus mu11 dn13 this was dn12 dn13 plus so on and so forth till muC3 minus muC1 into dnC3 and this we can keep on continuing till for the pith phase we can write T pi 1 minus T1 dS pi P pi minus P1 dV pi plus same way mu1 minus mu11 dn1pi continuing till mu Cpi minus muC1 dnC pi, right?

(Refer Slide Time: 15:52)



© CET I.I.T. KGP

Π phase ($\alpha = 1, \dots \Pi$) ⇒ superscript

C component ($i = 1 \dots c$) ⇒ subscript

$$dU = \sum_{\alpha=1}^{\Pi} T^{\alpha} dS^{\alpha} - \sum_{\alpha=1}^{\Pi} p^{\alpha} dV^{\alpha} + \sum_{\alpha=1}^{\Pi}\sum_{i=1}^{c} \mu_i^{\alpha} dn_i^{\alpha}$$

$(-[dS^2 + \dots])$ $\quad (-dV^2 - dV^3 \dots])$

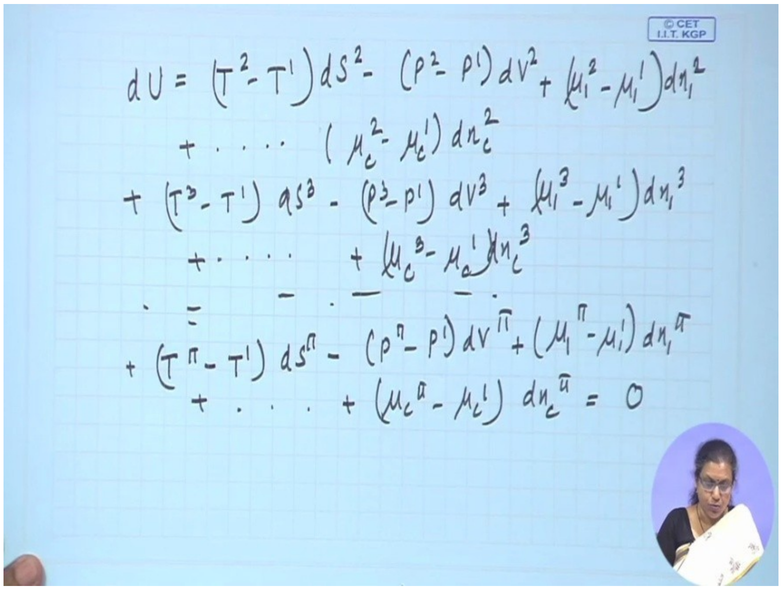
$$\begin{aligned} dU = {} & T^1 dS^1 - p^1 dV^1 + \mu_1^1 dn_1^1 + \mu_2^1 dn_2^1 + \dots + \mu_c^1 dn_c^1 \\ & + T^2 dS^2 - p^2 dV^2 + \mu_1^2 dn_1^2 + \mu_2^2 dn_2^2 + \dots + \mu_c^2 dn_c^2 \\ & + \dots \\ & + T^{\Pi} dS^2 - p^{\Pi} dV^{\Pi} + \mu_1^{\Pi} dn_1^{\Pi} + \mu_2^{\Pi} dn_2^{\Pi} + \dots + \mu_2^{\Pi} dn_c^{\Pi} = 0 \end{aligned}$$

$$dS = dS^1 + dS^2 + \dots + dS^{\Pi} = 0$$

$$dV = dV^1 + dV^2 + \dots + dV^{\Pi} = 0$$

$$\sum_{\alpha=1}^{\Pi} dn_i^{\alpha} = dn_i^1 + dn_i^2 + \dots + dn_i^{\Pi} = 0$$

(Refer Slide Time: 16:13)

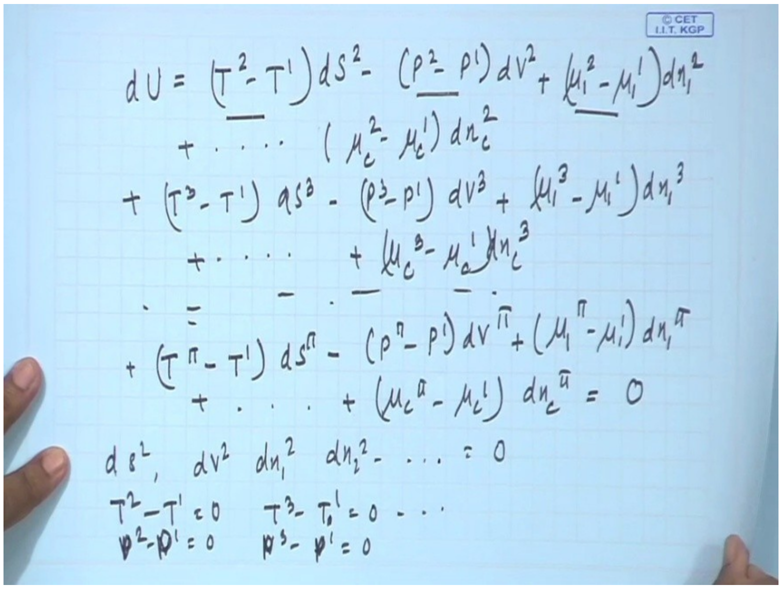


© CET I.I.T. KGP

$$\begin{aligned} dU = {} & (T^2 - T^1) dS^2 - (p^2 - p^1) dV^2 + (\mu_1^2 - \mu_1^1) dn_1^2 \\ & + \dots (\mu_c^2 - \mu_c^1) dn_c^2 \\ & + (T^3 - T^1) dS^3 - (p^3 - p^1) dV^3 + (\mu_1^3 - \mu_1^1) dn_1^3 \\ & + \dots + (\mu_c^3 - \mu_c^1) dn_c^3 \\ & \dots \\ & + (T^{\Pi} - T^1) dS^{\Pi} - (p^{\Pi} - p^1) dV^{\Pi} + (\mu_1^{\Pi} - \mu_1^1) dn_1^{\Pi} \\ & + \dots + (\mu_c^{\Pi} - \mu_c^1) dn_c^{\Pi} = 0 \end{aligned}$$

So therefore I had started with this particular equation I had minimized I had considered the constraints and then I could express this equation in lesser number of variables I could express it I had started with pi into C plus 2 variables I could express it in terms of pi minus 1 into C plus 2 variables and this is the final expression that I obtained and I know that for the closed heterogeneous closed systems this whole thing should be equal to 0.

(Refer Slide Time: 16:37)



$$
\begin{aligned}
dU = {} & (\underline{T^2} - T^1)\,ds^2 - (\underline{P^2} - P^1)\,dV^2 + (\underline{\mu_1^2} - \mu_1^1)\,dn_1^2 \\
& + \cdots (\mu_c^2 - \mu_c^1)\,dn_c^2 \\
& + (T^3 - T^1)\,ds^3 - (P^3 - P^1)\,dV^3 + (\mu_1^3 - \mu_1^1)\,dn_1^3 \\
& + \cdots + (\mu_c^3 - \mu_c^1)\,dn_c^3 \\
& \vdots \\
& + (T^\pi - T^1)\,ds^\pi - (P^\pi - P^1)\,dV^\pi + (\mu_1^\pi - \mu_1^1)\,dn_1^\pi \\
& + \cdots + (\mu_c^\pi - \mu_c^1)\,dn_c^\pi = 0
\end{aligned}
$$

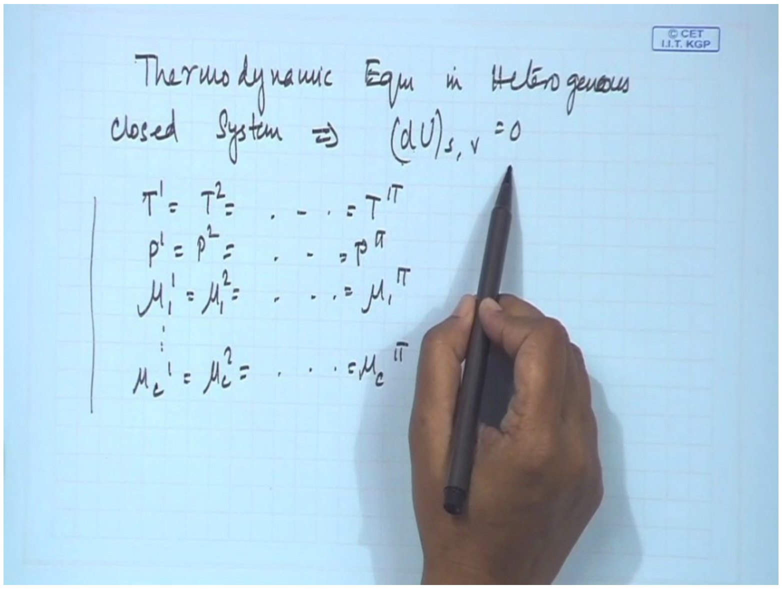
$$ds^2,\ dV^2\ dn_1^2\ dn_2^2 - \ldots = 0$$

$$T^2 - T^1 = 0 \qquad T^3 - T^1 = 0 \ldots$$

$$P^2 - P^1 = 0 \qquad P^3 - P^1 = 0$$

Now if this has to hold if you observe the individual terms we find that in order for the entire expression to be 0 the individual variations or the individual coefficients of ds2 dv2 dn12 dn22 etc all the individual coefficients of each and every differential they should be individually be equal to 0 if the entire composite dU has to be equal to 0. And what does it imply? It automatically implies that each of these terms they will be individually 0 provided T2 minus T1 equals to 0 again T3 minus T1 equals to 0 and so on. The same way I can write V2 minus V1 equals to 0 V3 minus V1 equals to 0. So in general sorry not v very sorry P2 T3 minus P1 very sorry.

(Refer Slide Time: 18:55)



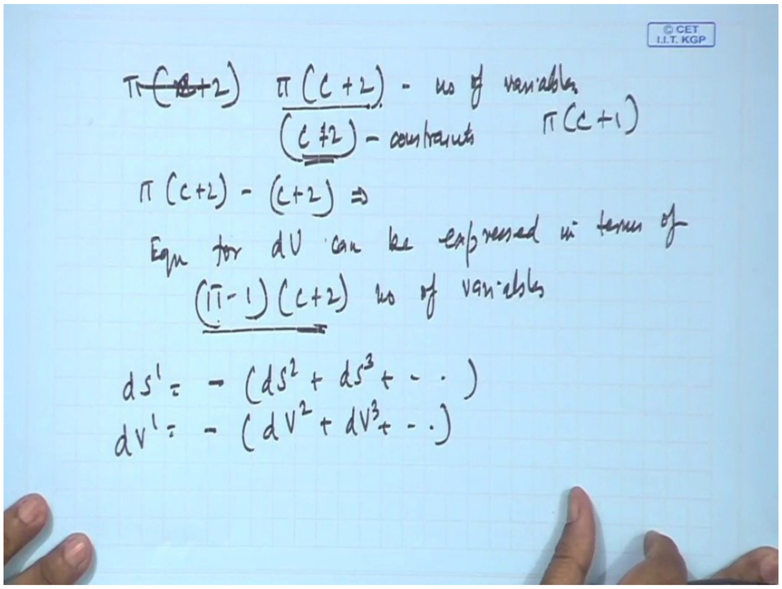
Thermodynamic Eqm in Heterogeneous closed System $\Rightarrow (dU)_{s,v} = 0$

$$T^1 = T^2 = \dots = T^{\pi}$$
$$P^1 = P^2 = \dots = P^{\pi}$$
$$\mu_1^1 = \mu_1^2 = \dots = \mu_1^{\pi}$$
$$\vdots$$
$$\mu_c^1 = \mu_c^2 = \dots = \mu_c^{\pi}$$

So in general from here what do I deduce? I deduce that for thermodynamic equilibrium in a heterogeneous closed system starting from dU s,v equals to 0 I have arrived at a condition that T1 equals to T2 equals to Tpi, P1 equals to P2 equals to P pi, Mu1 of component1 equals to mu1 component 2 to mu1pi. In the same way we can continue to use C1 equals to mu C2 equals to mu Cpi and therefore what have I arrived at the end?

At the end I find that the thermodynamic equilibrium express in terms of the thermodynamic potential reduces to the condition of equality of temperature, equality of pressure and equality of all the chemical potentials of each and every component present in the mixture and therefore we can express thermodynamic equilibrium either in terms of the extensive properties or we can express it in terms of the intensive properties it is all the same.

(Refer Slide Time: 19:13)



$\pi \cancel{(C+2)}$ $\quad \pi(C+2)$ - no of variables

$(C+2)$ - constraints $\quad \pi(C+1)$

$\pi(C+2) - (C+2) \Rightarrow$

Eqn for dU can be expressed in terms of

$(\pi - 1)(C+2)$ no of variables

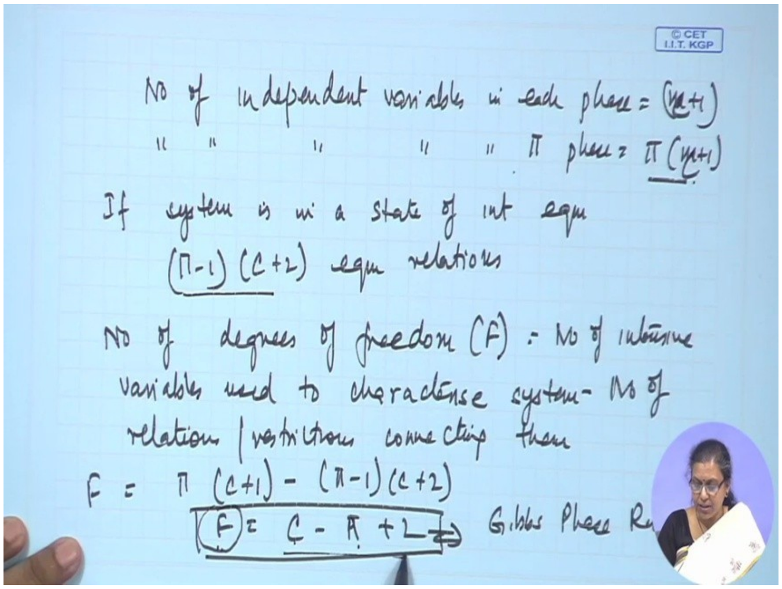
$$dS^1 = -(dS^2 + dS^3 + \dots)$$

$$dV^1 = -(dV^2 + dV^3 + \dots)$$

And very importantly from here I have come across another very important observation, what did I observe? We observe that I had started initially with pi into C plus 2 numbers of variables. Now this entire pi into C plus 2 numbers of variables are not independent, why? Yesterday we had derived Gibbs Duhem equation and while deriving the Gibbs Duhem equation we found out that for each and every phase the S,T and all the compositions are not independent if suppose it is a single component then S,T and Mu cannot be varied independently if 2 are fixed the other automatically gets fixed.

So therefore we find out of this pi into C plus 2 numbers of variables that we have the actual number of variables are pi into C plus one because there is a Gibbs Duhem equation relating the different number of variables in each of the phases that we are considering. So therefore from here what do we find?

(Refer Slide Time: 20:37)



© CET I.I.T. KGP

No of independent variables in each phase = $(\cancel{m}C+1)$

" " " " " π phase = $\underline{\pi}(\cancel{m}C+1)$

If system is in a state of int eqm

$\underline{(\pi-1)}(C+2)$ eqm relations

No of degrees of freedom (F) = No of intensive variables used to characterise system − No of relation / restrictions connecting them

$F = \pi(C+1) - (\pi-1)(C+2)$

$\boxed{F = C - \pi + 2} \Rightarrow$ Gibbs Phase Ru

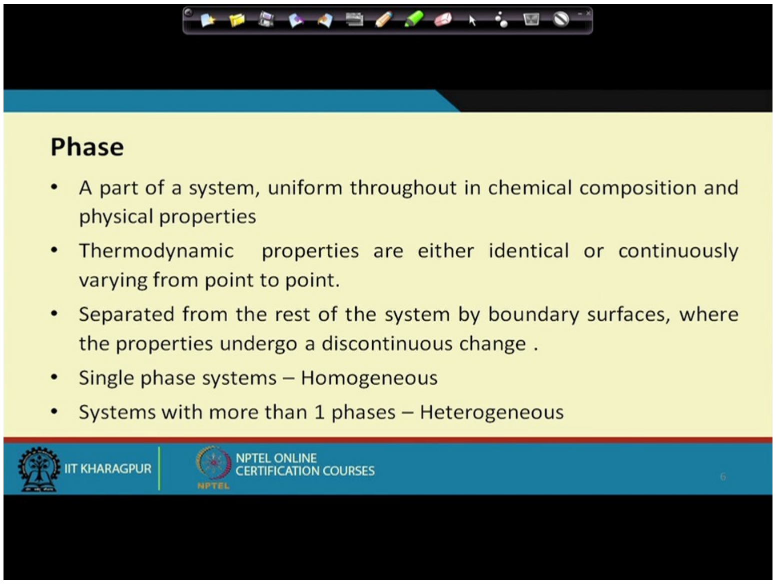
We find that in this particular case the actual number of independent variables the number of independent variable in each phase is m plus 1 since the Gibbs Duhem equation relates or rather relates the meth variable with the m plus 1 variable. So therefore the number of independent variables in pi number of phases should be equal to pi into m plus 1, right? And if the system is in a state of internal equilibrium then in that case we find that as we have just now found that there are pi minus 1 sorry all of these are C, I am extremely sorry. There are pi minus 1 into C plus 2 equilibrium relations connecting them this we have just now we have found this out.

So therefore we find that if there are number of variables are pi into C plus one then for a state to be in a state of internal equilibrium there are pi minus 1 into C plus 2 equilibrium relations. So from there what do we deduce? We deduce that the number of degrees of freedom which we had defined earlier as F, which is nothing but the number of intensive variables if you recollect they were dealing with intensive variables used to characterize a system minus the number of relations or restrictions connecting them, what is this equal to?

This is going to be equal to Pi into C plus one minus this particular equation, so therefore F is nothing but equal to pi into C plus one minus pi minus 1 into C plus 2 which is nothing but equal to C minus pi plus 2 and if you recollect this is the Gibbs phase rule that I have stated without proving and this is a proof which is available which shows us that for any particular system in a state of internal equilibrium be it homogeneous be it heterogeneous be it a pure substance be it a mixture of substances whatever it is, the number of intensive properties that are needed to characterize the system depends upon the number of components and the number of phases and the relation is expressed by the Gibbs phase rule.

Now well, I end here but before I end I would just like to mention that I have written down the definitions of the number of phases and the definition of phase and definition of component and the number of degrees of freedom or variance because very frequently I find that there are quite number of confusions regarding these things.

(Refer Slide Time: 23:37)

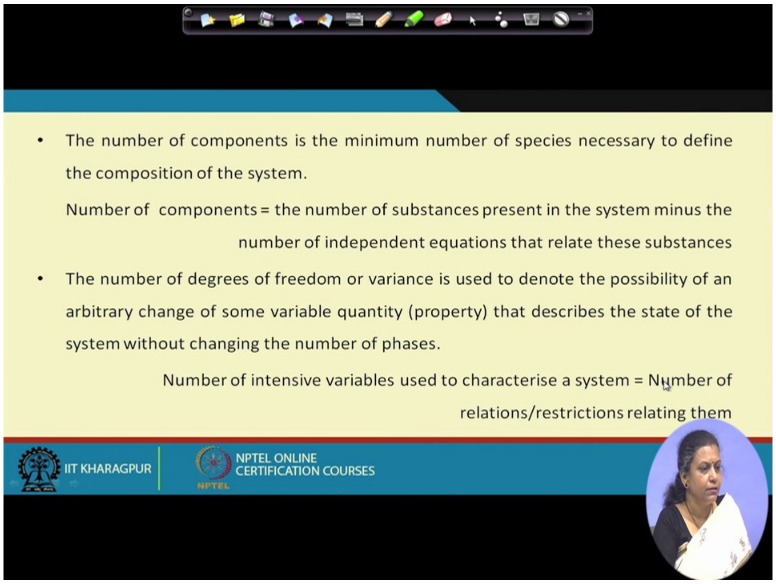


Phase

- A part of a system, uniform throughout in chemical composition and physical properties
- Thermodynamic properties are either identical or continuously varying from point to point.
- Separated from the rest of the system by boundary surfaces, where the properties undergo a discontinuous change .
- Single phase systems – Homogeneous
- Systems with more than 1 phases – Heterogeneous

So therefore you can go through these particular definitions which states that the phase is nothing but a part of the system uniform throughout in chemical composition and physical properties and each particular phase is separated from the rest of the system by means of boundary surfaces when we have single phase systems they are homogeneous when we have more than one phases then they are known as heterogeneous systems.

(Refer Slide Time: 24:06)



- The number of components is the minimum number of species necessary to define the composition of the system.

  Number of components = the number of substances present in the system minus the number of independent equations that relate these substances

- The number of degrees of freedom or variance is used to denote the possibility of an arbitrary change of some variable quantity (property) that describes the state of the system without changing the number of phases.

  Number of intensive variables used to characterise a system = Number of relations/restrictions relating them

And the number of components is nothing but the minimum number of species which are necessary to define the composition of the system. For example if we have an acetic acid water mixture then in that particular solution there will be acetate ions, hydrogen ions, hydroxyl ions and so on and so forth but the number of components are 2 its acetic acid and its water since they are soluble.

So therefore the number of phases is 1 in this case and according with number of degrees of freedom or the variance that I have already written down. So therefore in this particular class I have dealt with closed heterogeneous or rather heterogeneous closed systems and I have derived the criteria of thermodynamic equilibrium with respect to intensive variables and from there I have also deduced the Gibbs phase rule which you will be using very frequently henceforth.

In the next class we continue with our discussions on the physical interpretations and the means of determining the chemical potential on mu which we have already come to realize is quite an important parameter as far as phase equilibrium thermodynamics is concerned, thank you very much.