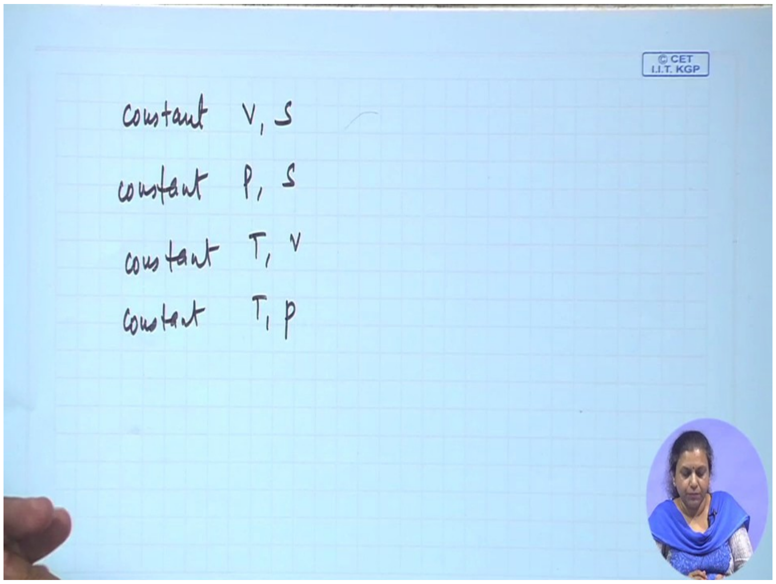
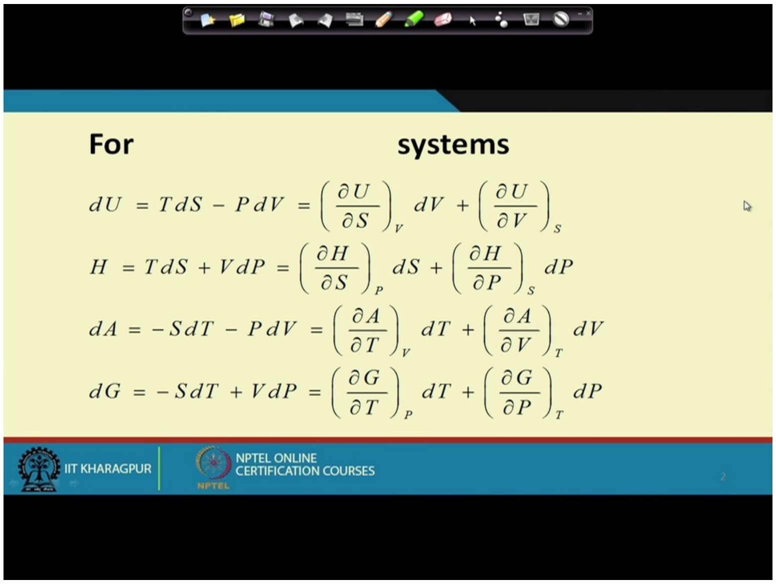
Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
Department of Chemical Engineering
Indian Institute of Technology Kharagpur
Lecture 20
Concept of Chemical Potential.

(Refer Slide Time: 0:45)


constant V, S
constant P, S
constant T, V
constant T, P

Hello everybody, so till now our discussion they were primarily confined to close systems, right? Close systems means those systems which have been interacting with the surroundings under different conditions of interest maybe say for example they were interacting with the surroundings under constant volume entropy they were also interacting under constant P, S, they are interacting under constant T,V and they were interacting under constant T, P but in all the cases we had kept in mind that we are dealing with closed systems where all the interactions did not concern mass changes of the system due to interaction with the surroundings even if there was a chemical reaction inside the system we ensure that the affect was primarily that of volume change while the composition and the total mass of the system were kept constant.

(Refer Slide Time: 1:25)



For systems

$$dU = TdS - PdV = \left(\frac{\partial U}{\partial S}\right)_V dV + \left(\frac{\partial U}{\partial V}\right)_S$$

$$H = TdS + VdP = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

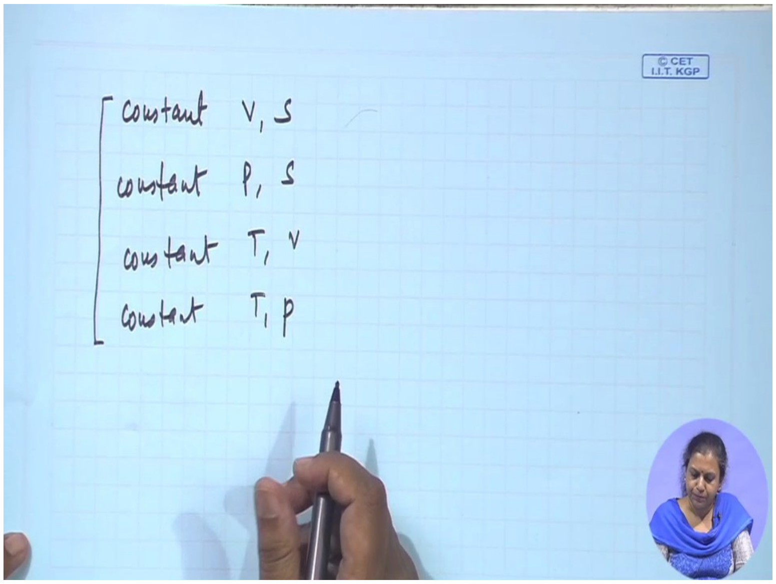
$$dA = -SdT - PdV = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$$

$$dG = -SdT + VdP = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

IIT KHARAGPUR

NPTEL ONLINE CERTIFICATION COURSES

(Refer Slide Time: 2:07)



© CET I.I.T. KGP

constant V, S

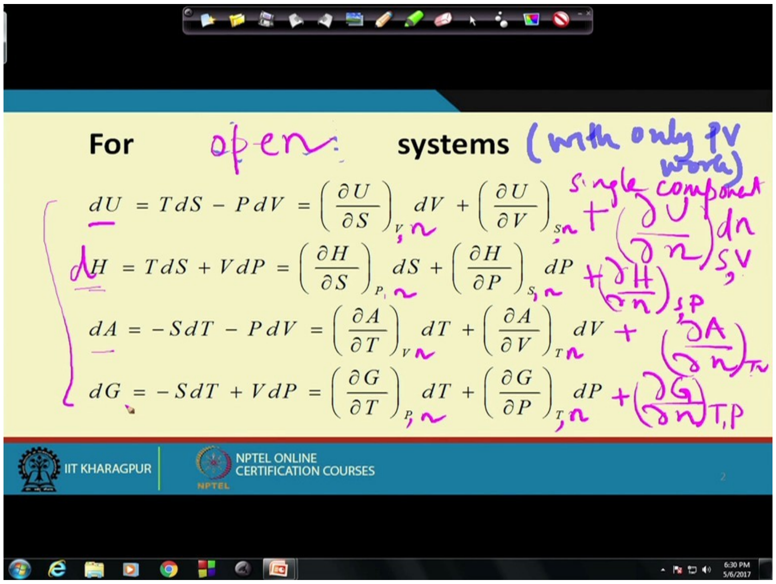
constant P, S

constant T, V

constant T, P

Now under that condition what did we observe? We found out for that particular condition we had defined different thermodynamic potentials or rather the changes of the different thermodynamics potentials under different conditions of interactions between the system and the surroundings and the changes between the different thermodynamic potentials they were related to changes in other properties when a system moves from one equilibrium state to the other equilibrium state while interacting with the surroundings under different particular conditions and these were the 4 conditions of interest which we were dealing with, right?

(Refer Slide Time: 2:17)



For open systems (with only PV work)

single component

$$dU = TdS - PdV = \left(\frac{\partial U}{\partial S}\right)_{V,n} dV + \left(\frac{\partial U}{\partial V}\right)_{S,n} + \left(\frac{\partial U}{\partial n}\right)_{S,V} dn$$

$$dH = TdS + VdP = \left(\frac{\partial H}{\partial S}\right)_{P,n} dS + \left(\frac{\partial H}{\partial P}\right)_{S,n} dP + \left(\frac{\partial H}{\partial n}\right)_{S,P}$$

$$dA = -SdT - PdV = \left(\frac{\partial A}{\partial T}\right)_{V,n} dT + \left(\frac{\partial A}{\partial V}\right)_{T,n} dV + \left(\frac{\partial A}{\partial n}\right)_{T,V}$$

$$dG = -SdT + VdP = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \left(\frac{\partial G}{\partial n}\right)_{T,P}$$

IIT KHARAGPUR

NPTEL ONLINE CERTIFICATION COURSES

Now suppose let me and one more thing I would like to remember that all the equations which I have written down here all this set of equations they are primarily concerned with only PV type of work of expansion and no other non-PV work involved. If there is a non-PV work then definitely we have a plus Fdr bar here that we have already discussed. We have discussed both the criteria of equilibrium both for PV type of work as well as for non-PV type of work. Now this entire thing this was for, the whole thing was suggested for close systems with only PV work.

Now suppose I try to deal with open systems when along with energy there is mass transfer between the system and the surroundings, what do you expect under this particular condition when we deal with open systems? Keeping in mind that even for open systems we shall be dealing with only PV type of work, now how have we defined the change of say if it is the first equation? How have we defined the change of du with change of S and V.

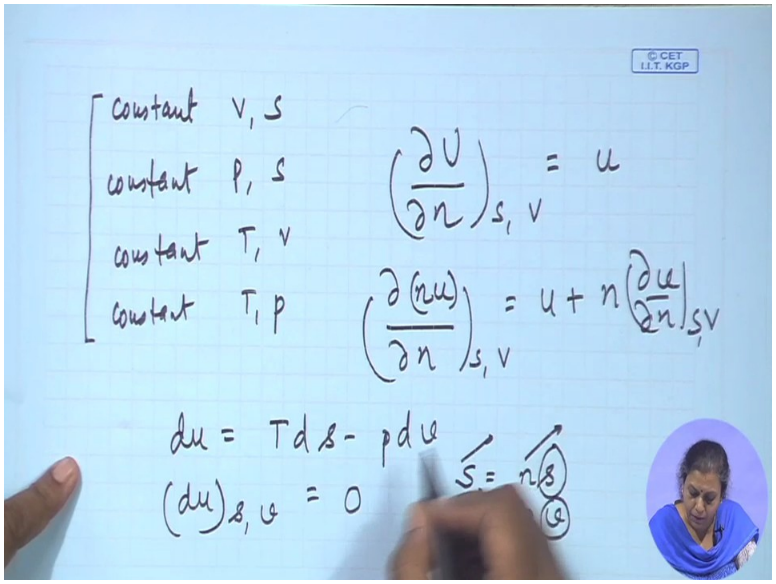
Remember another thing the equations which I have written down here, they are all for total properties or total extensive properties of the system and the importance of differentiating between the total and the molar or the mass specific properties will be very clear today itself in this class as I proceed further. Now in what way have I define the change of u? I have what changes in say total entropy and total volume. First I have defined del U del S at constant V times the dv and then I have defined del U del v at constant S.

Now suppose there is change in the number of moles, now for the time being again I mention that we are considering only PV type of work and single component systems these are the 2 things that we are going to consider for the time being. Now for these cases what do you expect which term is going to be added? Here we are going to have one term del U del n under conditions of constant s and v, right into dn and moment we add up one more variable, what are we required to do?

We are required to write Sn here we are required to write vn here. So therefore when dU changes as a result of change in total entropy, total volume and total number of moles of the system then the differential equation for dU comprises of 3 terms, the one term denoting the change of U with s when volume and the total number of moles are constant, the second term dealing with change of U with volume when entropy and total number of moles are constant and the third term deals with the change of U with n when total entropy and total volume of the system remains constant.

The same thing is applicable for each and every equation that we have written down for example here we are going to have something like del H del n at constant s and P and immediately we are supposed to put one n here and one n here. Same thing is going to apply to this case as well where we are going to write this down constant T and V both of them are capital and we have to write it down in this particular way. Here also we are we are supposed to write del G del n constant T, P here we are going to have a constant n, here we are going to have a constant n, right?So moment we shift from closed to open systems we find that initially we had 2 terms now we are having 3 terms in the entire differential equations.

(Refer Slide Time: 6:57)



constant v, s

constant p, s

constant T, v

constant T, p

$$\left(\frac{\partial U}{\partial n}\right)_{s,v} = u$$

$$\left(\frac{\partial (nu)}{\partial n}\right)_{s,v} = u + n\left(\frac{\partial u}{\partial n}\right)_{s,v}$$

$$du = T\,ds - p\,dv$$

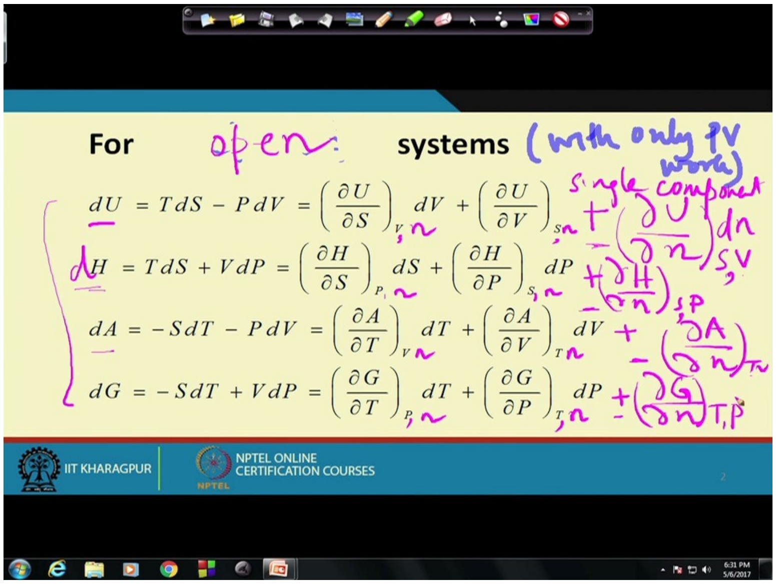
$$(du)_{s,v} = 0$$

$$S = n\,s$$

$$v$$

Well, so the next question which comes up is what are these particular terms that we have written down? What is this particular term? What is this particular term? What is this term and what is this term? Now just if you look closely at these terms, what is the term let me write it down here it is del U del n at constant s, v.

(Refer Slide Time: 7:35)



For open systems (with only PV work) single component

$$dU = TdS - PdV = \left(\frac{\partial U}{\partial S}\right)_{V,n} dV + \left(\frac{\partial U}{\partial V}\right)_{S,n} dV + \left(\frac{\partial U}{\partial n}\right)_{S,V} dn$$

$$dH = TdS + VdP = \left(\frac{\partial H}{\partial S}\right)_{P,n} dS + \left(\frac{\partial H}{\partial P}\right)_{S,n} dP + \left(\frac{\partial H}{\partial n}\right)_{S,P}$$

$$dA = -SdT - PdV = \left(\frac{\partial A}{\partial T}\right)_{V,n} dT + \left(\frac{\partial A}{\partial V}\right)_{T,n} dV + \left(\frac{\partial A}{\partial n}\right)_{T,n}$$

$$dG = -SdT + VdP = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \left(\frac{\partial G}{\partial n}\right)_{T,P}$$

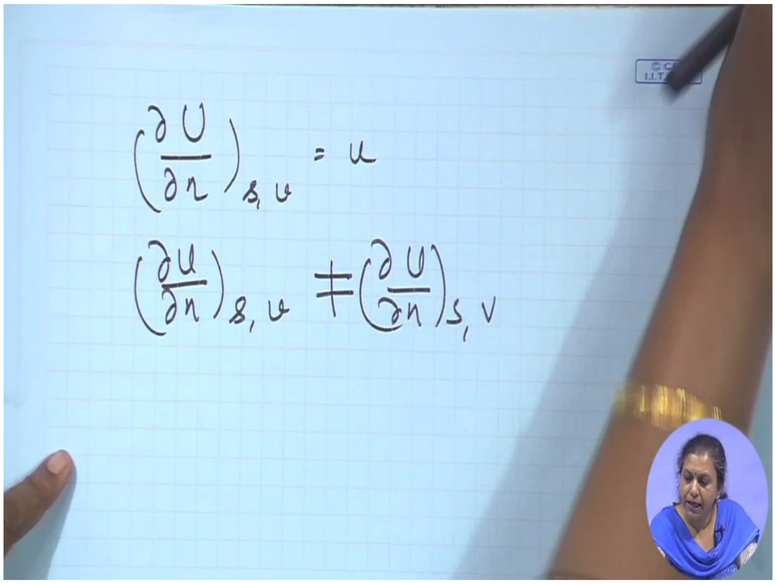
So therefore it is the change of internal energy with change in the number of moles, so at the first intuition it appears that this should be the molar internal energy of the system. Let us see if our initial intuition is correct or not and the same thing should apply to each and every case for example del H del n at constant SP this possibly then it should correspond to small h this should correspond to small a and this should correspond to small g.

Now let us see if our supposition is correct or not? What is Del U del n at constant capital s capital v? This is equal to u, now what is capital U? Capital U is nothing but n time's u. So therefore what is this particular term? This term is nothing but u plus n del u del n at constant capital S capital V, right? Now try to understand it very well, since this is the molar property so whatever equation I have written down for the total property the same equation should be applicable for the molar property when this equation is written in terms of molar quantities, right?

So therefore we know that du this is equal to Tds minus pdv, what does it imply? It implies that du at constant molar entropy molar volume is equal to 0, you get my point. So therefore if du at molar entropy, molar volume is equal to 0 so therefore and we know capital S is nothing but equal to ns we know capital V is equal to nv. So therefore if we are keeping this constant and we are varying this it's quite natural that this also has to be varied this cannot be kept constant.

The same way if we are keeping this constant and we want to vary this then this also has to vary this cannot be kept constant. So what I mean to say is you cannot keep total entropy and molar entropy constant at the same time when the total number of moles of a system is varied. The same thing is true for volume you cannot keep total volume and molar volume constant at the same time when the number of moles are varied.

(Refer Slide Time: 9:54)

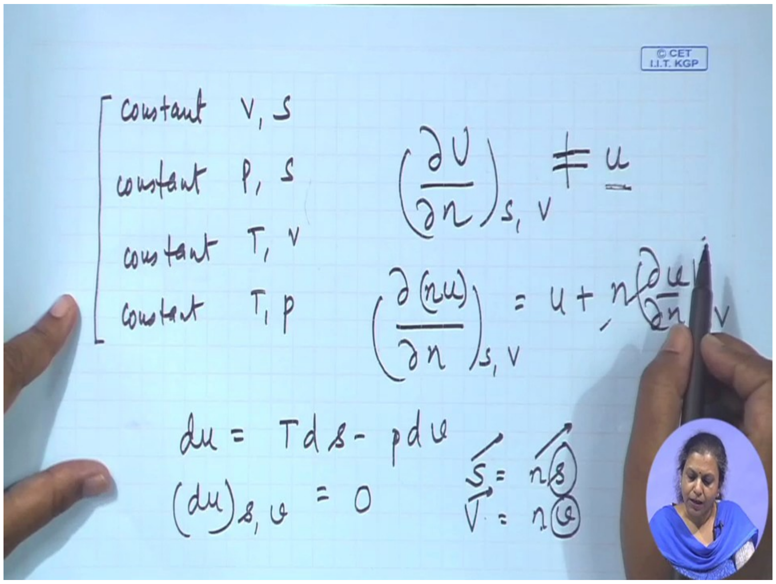


$$\left(\frac{\partial U}{\partial n}\right)_{s,v} = u$$

$$\left(\frac{\partial u}{\partial n}\right)_{s,v} \neq \left(\frac{\partial U}{\partial n}\right)_{S,V}$$

So therefore what I mean is that if your du at small s, v equals to 0 than definitely we can write this down as del capital U del n at small s, v this is equal to u, right? And we also can write this down as that del capital N del u for small s, v this cannot be equal to del U del n at capital S, capital V, right? Because you know that this and this cannot be kept constant at the same time when n is varying.

(Refer Slide Time: 10:32)



constant V, S
constant P, S
constant T, V
constant T, P

$$\left(\frac{\partial U}{\partial n}\right)_{S,V} \neq u$$

$$\left(\frac{\partial (nu)}{\partial n}\right)_{S,V} = u + n\left(\frac{\partial u}{\partial n}\right)_{S,V}$$

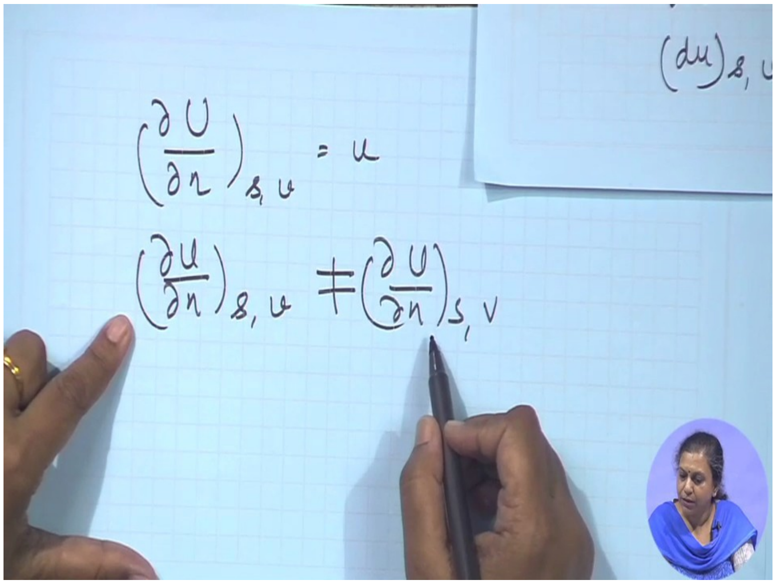
$$du = Tds - pdv$$

$$(du)_{s,v} = 0$$

$$S = n s$$

$$V = n v$$

(Refer Slide Time: 10:38)



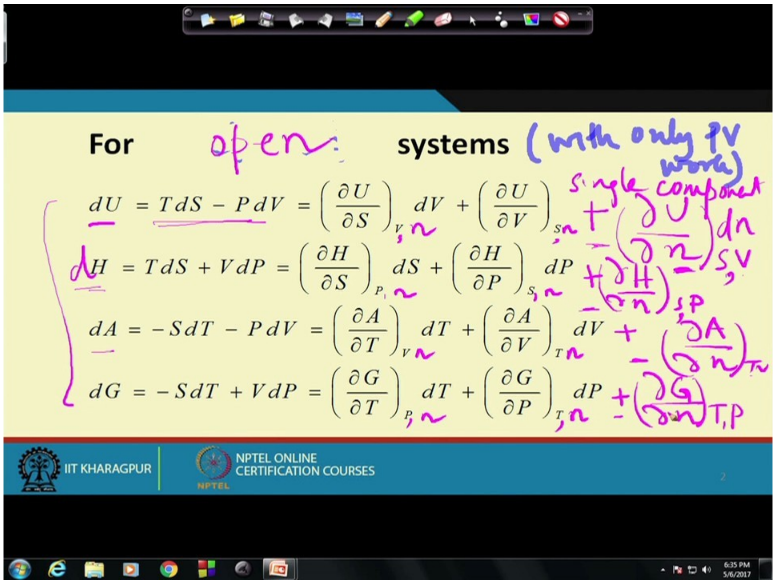
$$(du)_{s,}$$

$$\left(\frac{\partial U}{\partial n}\right)_{s,v} = u$$

$$\left(\frac{\partial u}{\partial n}\right)_{s,v} \neq \left(\frac{\partial U}{\partial n}\right)_{S,V}$$

Now if this equation has to be true then in that case this term has to vanish but we find that if this term vanishes then this term cannot vanish. So therefore it automatically implies that this is nonzero term as a result of which your del U del n at constant capital S, capital V is not equal to the molar internal energy of the system.

(Refer Slide Time: 11:21)



For open systems (with only PV work)

single component

$$dU = TdS - PdV = \left(\frac{\partial U}{\partial S}\right)_{V,n} dV + \left(\frac{\partial U}{\partial V}\right)_{S,n} + \left(\frac{\partial U}{\partial n}\right)_{S,V} dn$$

$$dH = TdS + VdP = \left(\frac{\partial H}{\partial S}\right)_{P,n} dS + \left(\frac{\partial H}{\partial P}\right)_{S,n} dP + \left(\frac{\partial H}{\partial n}\right)_{S,P}$$

$$dA = -SdT - PdV = \left(\frac{\partial A}{\partial T}\right)_{V,n} dT + \left(\frac{\partial A}{\partial V}\right)_{T,n} dV + \left(\frac{\partial A}{\partial n}\right)_{T,V}$$

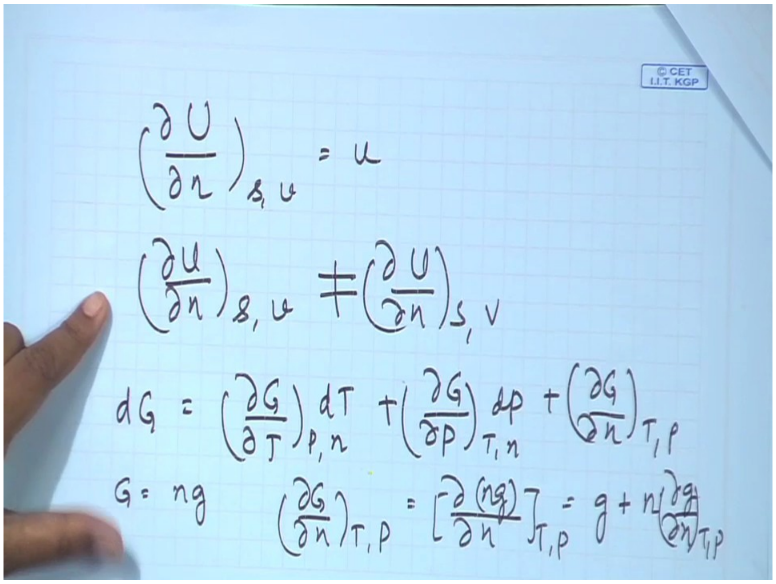
$$dG = -SdT + VdP = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \left(\frac{\partial G}{\partial n}\right)_{T,P}$$

IIT KHARAGPUR

NPTEL ONLINE CERTIFICATION COURSES

So therefore the first thing which we realized is that this particular term which has been written down this particular term is not equal to the molar internal energy. So the next question arises what is it? Then do we have to define it in terms of some other molar properties. Is that molar property different for each and every differential equation? Then we land up into a set of 4 additional molar properties which are not the true molar properties in that particular sense.

(Refer Slide Time: 11:52)



© CET I.I.T. KGP

$$\left(\frac{\partial U}{\partial n}\right)_{s,v} = u$$

$$\left(\frac{\partial u}{\partial n}\right)_{s,v} \neq \left(\frac{\partial U}{\partial n}\right)_{S,V}$$

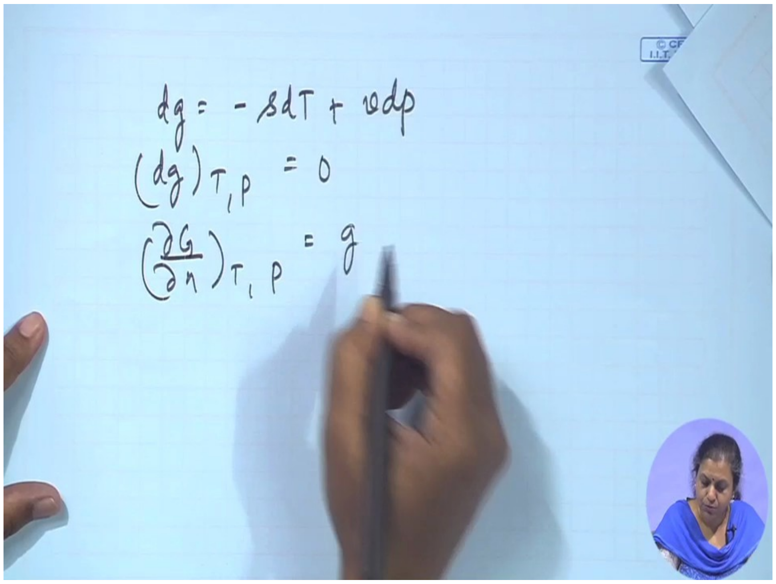
$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \left(\frac{\partial G}{\partial n}\right)_{T,P}$$

$$G = ng \qquad \left(\frac{\partial G}{\partial n}\right)_{T,P} = \left[\frac{\partial (ng)}{\partial n}\right]_{T,P} = g + n\left(\frac{\partial g}{\partial n}\right)_{T,P}$$

So the next, once it was realized that this quantities they do not correspond to the molar quantities at least for the first 3 cases. Let us see what the del G case what we get? For the del G case again we can write down dG it is equal to del G del T, I have already written the equation on the overhead slides yet I would like to repeat it once more.

Del G del P at constant T, n dP plus del G del n at constant T, P. I repeat again and again the same thing this equation is applicable only for a single component open system. Now in this case what is G equals to? Again proceeding in the similar way it is equal to ng. So therefore del G del n at constant T, P it is nothing but equals to ng del n at constant T, P which is nothing but equal to g plus n del g del n at constant T, P.

(Refer Slide Time: 13:17)

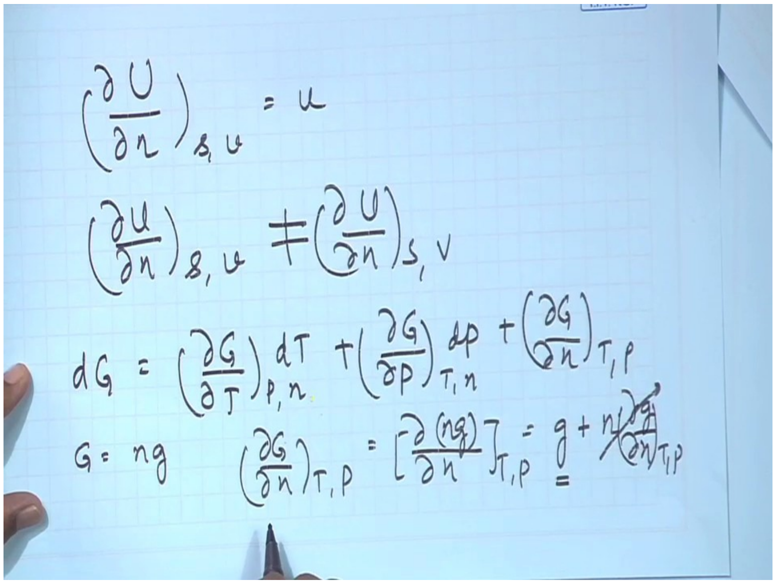


$$dg = -s\,dT + v\,dp$$

$$(dg)_{T,P} = 0$$

$$\left(\frac{\partial G}{\partial n}\right)_{T,P} = g$$

(Refer Slide Time: 13:35)



$$\left(\frac{\partial U}{\partial n}\right)_{s,v} = u$$

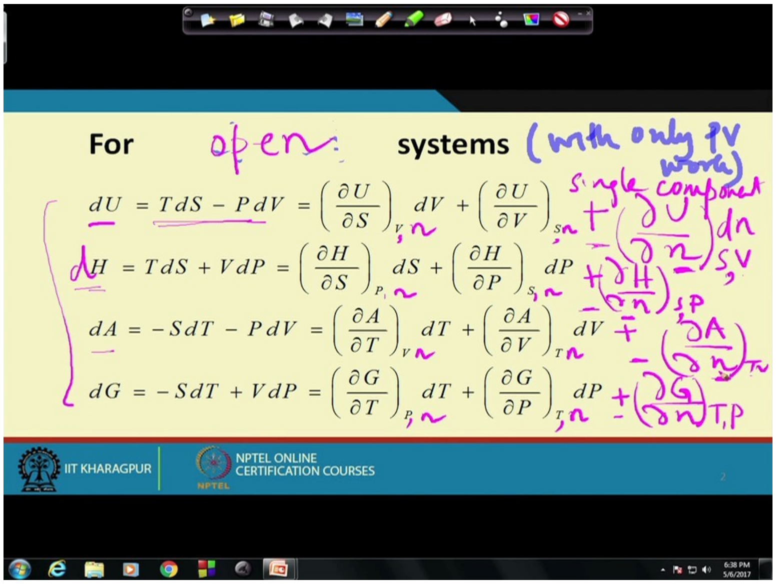
$$\left(\frac{\partial u}{\partial n}\right)_{s,v} \neq \left(\frac{\partial U}{\partial n}\right)_{s,v}$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial p}\right)_{T,n} dp + \left(\frac{\partial G}{\partial n}\right)_{T,P}$$

$$G = ng \qquad \left(\frac{\partial G}{\partial n}\right)_{T,P} = \left[\frac{\partial (ng)}{\partial n}\right]_{T,P} = \underline{\underline{g}} + n\cancel{\left(\frac{\partial g}{\partial n}\right)_{T,P}}$$

Here also I write down the same thing, I can write it down as dg equals to minus sdT plus vdp, right? So therefore dg at constant T, P equals to 0. So therefore del G del n at constant T, P this is equal to g. So therefore we find that in this particular case this part dg at constant T, P equals to 0. So therefore this part cancels out and we know del G del n at constant T, P is nothing but equal to the molar Gibbs free energy of the system.

(Refer Slide Time: 14:24)



For open systems (with only PV work) single component

$$dU = TdS - PdV = \left(\frac{\partial U}{\partial S}\right)_{V,n} dV + \left(\frac{\partial U}{\partial V}\right)_{S,n} + \left(\frac{\partial U}{\partial n}\right)_{S,V} dn$$

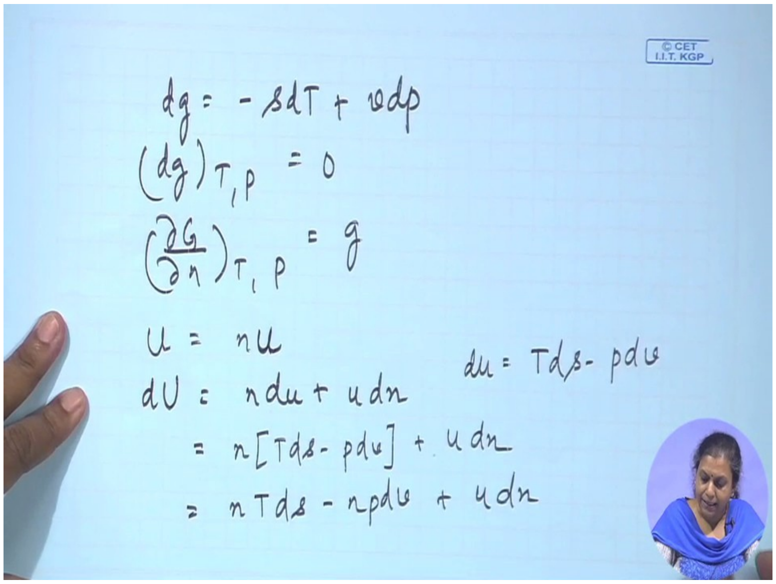
$$dH = TdS + VdP = \left(\frac{\partial H}{\partial S}\right)_{P,n} dS + \left(\frac{\partial H}{\partial P}\right)_{S,n} dP + \left(\frac{\partial H}{\partial n}\right)_{S,P}$$

$$dA = -SdT - PdV = \left(\frac{\partial A}{\partial T}\right)_{V,n} dT + \left(\frac{\partial A}{\partial V}\right)_{T,n} dV + \left(\frac{\partial A}{\partial n}\right)_{T,V}$$

$$dG = -SdT + VdP = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \left(\frac{\partial G}{\partial n}\right)_{T,P}$$

So therefore what we deduce is that although the previous molar quantities did not or rather the previous quantities the third terms which I have written do not correspond to the molar properties but del G del n at constant T, P corresponds to the molar Gibbs free energy. Now let us see what these terms corresponding to? I will be doing the derivations just with del U del n at constant s, v and please note that the same derivation is going to be applicable for this term same derivation is going to be applicable for this term I leave it as an home assignment to repeat the derivations which I have done and to find out the corresponding expression for del H del n and del A del n subject to the respective constraints.

(Refer Slide Time: 14:35)



$$dg = -s\,dT + v\,dp$$

$$(dg)_{T,p} = 0$$

$$\left(\frac{\partial G}{\partial n}\right)_{T,p} = g$$

$$U = nu \qquad du = T\,ds - p\,dv$$

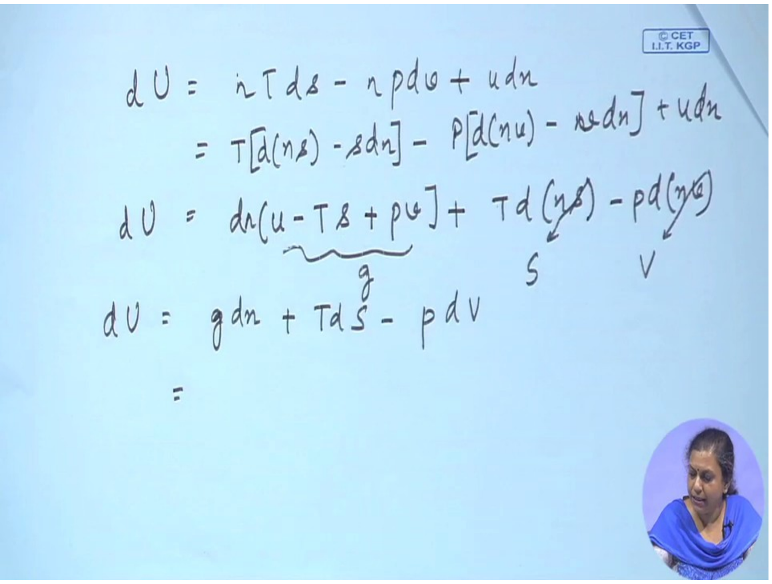
$$dU = n\,du + u\,dn$$

$$= n[T\,ds - p\,dv] + u\,dn$$

$$= nT\,ds - np\,dv + u\,dn$$

Let us see what it is? Now again I repeat U is nothing but equals to nu, right? This I know so therefore I can write it down as dU is nothing but equals to ndu plus udn I can definitely write it in this particular way. Now what is du equals to? du several times you must have learned by heart by this time write it down in this particular form therefore this can be written down as Tds minus Pdv since their properties I can play with them in any particular way it hardly matters provided initial and final states are constant and I can write it down in this particular way. So therefore this can be written down as nTds minus npdv plus udn, right?

(Refer Slide Time: 15:48)



$$dU = nTds - npdv + udn$$

$$= T[d(ns) - sdn] - P[d(nv) - vdn] + udn$$

$$dU = dn(\underbrace{u - Ts + pv}_{g}] + Td(\underset{\overset{\swarrow}{S}}{ns}) - pd(\underset{\overset{\swarrow}{V}}{nv})$$

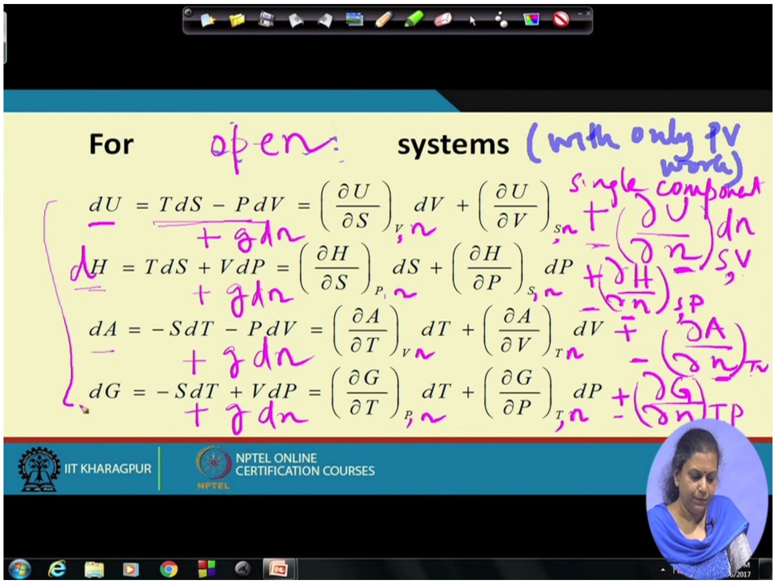
$$dU = gdn + TdS - pdV$$

$$=$$

Now can I write this particular equation as I will just write it down once more to maintain continuity nTds minus npdv plus udn, right? Can I write it down as T dns minus sdn from Legendre transform I can very well do this. Similar way I can also write this down as P dnv minus vdn plus udn. Now you look very carefully what I have got?

I have got dU equals to dn of u minus Ts plus pv, spu all of them are small case alphabets minus Td ns minus pd nv, what is this term? This is capital S this is capital V, so what do I get? I get and what is this term? U plus pv minus Ts, it is nothing but the molar Gibbs free energy. So what do I get? dU is nothing but equals to gdn minus Tds, sorry this is plus Tds minus pdv.

(Refer Slide Time: 18:01)



For open systems (with only PV work)

single component

$$dU = TdS - PdV + gdn = \left(\frac{\partial U}{\partial S}\right)_{V,n} dV + \left(\frac{\partial U}{\partial V}\right)_{S,n} + \left(\frac{\partial U}{\partial n}\right)_{S,V} dn$$

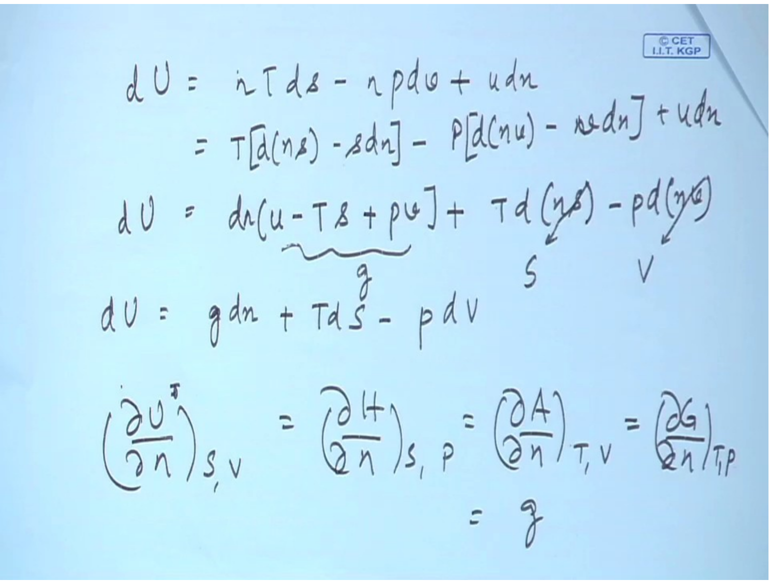
$$dH = TdS + VdP + gdn = \left(\frac{\partial H}{\partial S}\right)_{P,n} dS + \left(\frac{\partial H}{\partial P}\right)_{S,n} dP + \left(\frac{\partial H}{\partial n}\right)_{S,P}$$

$$dA = -SdT - PdV + gdn = \left(\frac{\partial A}{\partial T}\right)_{V,n} dT + \left(\frac{\partial A}{\partial V}\right)_{T,n} dV + \left(\frac{\partial A}{\partial n}\right)_{T,V}$$

$$dG = -SdT + VdP + gdn = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \left(\frac{\partial G}{\partial n}\right)_{T,P}$$

So therefore what do I find? That my initial equation which I had written down for closed systems along with that I need one more term gdn here in order to extend the closed system equation to open systems. If we repeat the derivations for dH dA etc we find that for each case we can incorporate a term gdn and the equation becomes applicable for open systems and even this gd in term is applicable for the fourth equation as well. So therefore for all the equations I find that for open systems we find that this particular term it corresponds to the molar Gibbs free energy.

(Refer Slide Time: 18:45)



$$dU = nT\,ds - np\,dv + u\,dn$$

$$= T[d(ns) - s\,dn] - P[d(nu) - v\,dn] + u\,dn$$

$$dU = dn(u \underbrace{- Ts + pv}_{g}] + T\,d\underset{\swarrow\ S}{(ns)} - p\,d\underset{\swarrow\ V}{(nv)}$$

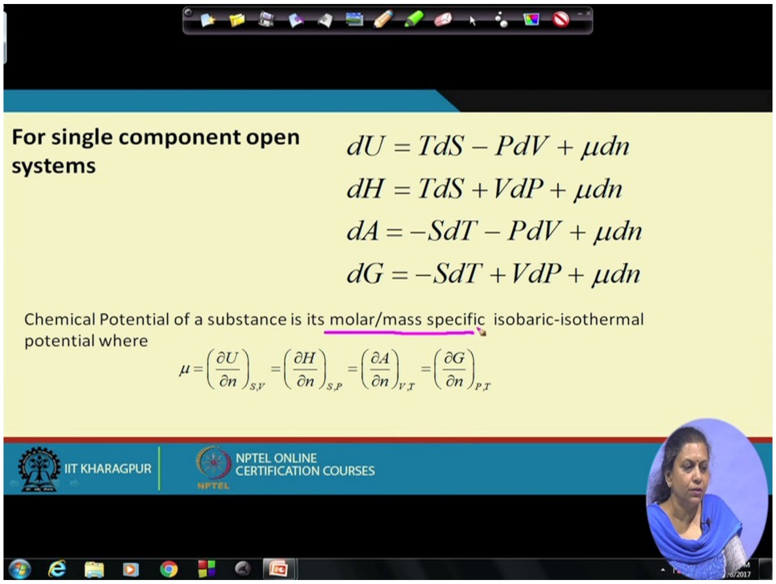
$$dU = g\,dn + T\,dS - p\,dV$$

$$\left(\frac{\partial U}{\partial n}\right)_{S,V} = \left(\frac{\partial H}{\partial n}\right)_{S,P} = \left(\frac{\partial A}{\partial n}\right)_{T,V} = \left(\frac{\partial G}{\partial n}\right)_{T,P}$$

$$= g$$

So therefore we can write it down as del U del n at constant S,v this is equal to del H del n constant S, P, del A del n at constant T, V this is equal to del G del n at constant T, P which is nothing but equal to g.

(Refer Slide Time: 19:42)



For single component open systems

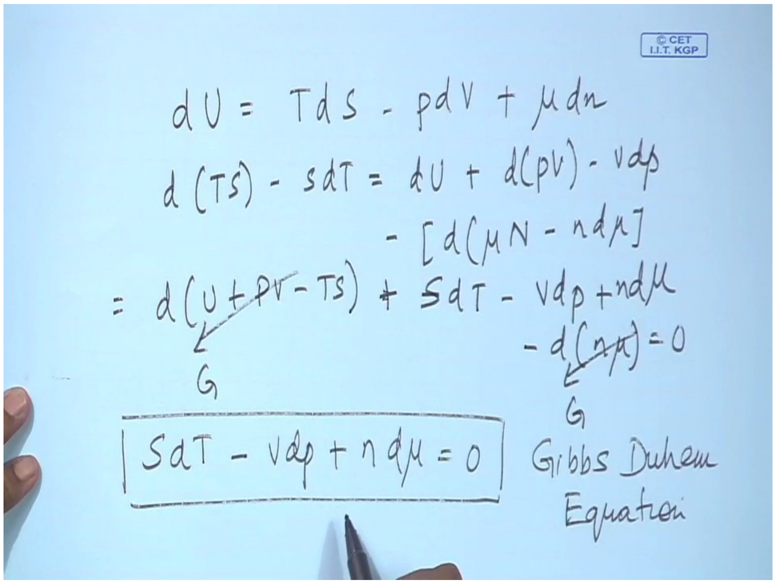
$$dU = TdS - PdV + \mu dn$$
$$dH = TdS + VdP + \mu dn$$
$$dA = -SdT - PdV + \mu dn$$
$$dG = -SdT + VdP + \mu dn$$

Chemical Potential of a substance is its molar/mass specific isobaric-isothermal potential where

$$\mu = \left(\frac{\partial U}{\partial n}\right)_{S,V} = \left(\frac{\partial H}{\partial n}\right)_{S,P} = \left(\frac{\partial A}{\partial n}\right)_{V,T} = \left(\frac{\partial G}{\partial n}\right)_{P,T}$$

Now therefore from here it is quite evident that this particular term the molar Gibbs free energy that is quite important and since it is quite important, so therefore this assumes a very important role in phase equilibrium thermodynamics and it is often called chemical potential of a substance and where chemical potential of a substance is nothing but it is molar isobaric-isothermal potential or it can be if mass specific isobaric isothermal potential it all depends upon the way we have defined the mole numbers or the mass numbers, right? Now this was for a single component system and from these particular equations we can arrive at another very important relationship.

(Refer Slide Time: 20:07)



$$dU = TdS - pdV + \mu dn$$

$$d(TS) - SdT = dU + d(pV) - Vdp$$

$$- [d(\mu N - nd\mu]$$

$$= d(\underbrace{U + pV - TS}_{G}) + SdT - Vdp + nd\mu$$

$$- d(\underbrace{n\mu}_{G}) = 0$$

$$\boxed{SdT - Vdp + nd\mu = 0}$$

Gibbs Duhem Equation

Let us see this particular relationship which I have written down. This particular relationship from there we can write it down as dU equals to Tds minus pdv plus since molar Gibbs free energy is often called chemical potential I can define it in terms of chemical potential. Now again applying Legendre transform we can write this equation as equals to dU plus d pv minus vdp minus of d of uN minus ndu, right?

So again from here we can write d of U plus Pv minus Ts this will be equal to plus SdT minus vdp plus ndu minus dnu equals to 0 where this we know is nothing but G, this part we know is nothing but G. So therefore this part and this part cancels out giving us a very important equation which is very useful for phase equilibrium thermodynamics and this particular equation is known as the Gibbs Duhem equation.

What does this particular equation suggest? It tells us that for a single component open system we cannot vary T, p and u at the same time. If we fix up mui and p, T automatically gets fixed up and it is true for all the other systems. So therefore all of them cannot be varied at the same time if one of them or rather both of them are varied the third one automatically gets fixed. Now this particular equation has got a greater applicability when we go for multi-component open systems which we will be discussing in the next lecture, thank you very much.