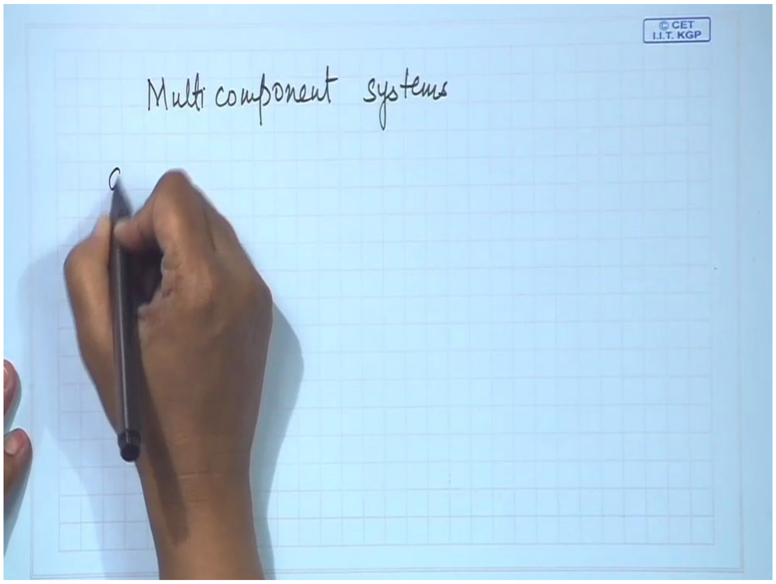
Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
Department of Chemical Engineering
Indian Institute of Technology Kharagpur
Lecture 21
Concept of Chemical Potential(Contd.)

(Refer Slide Time: 0:30)

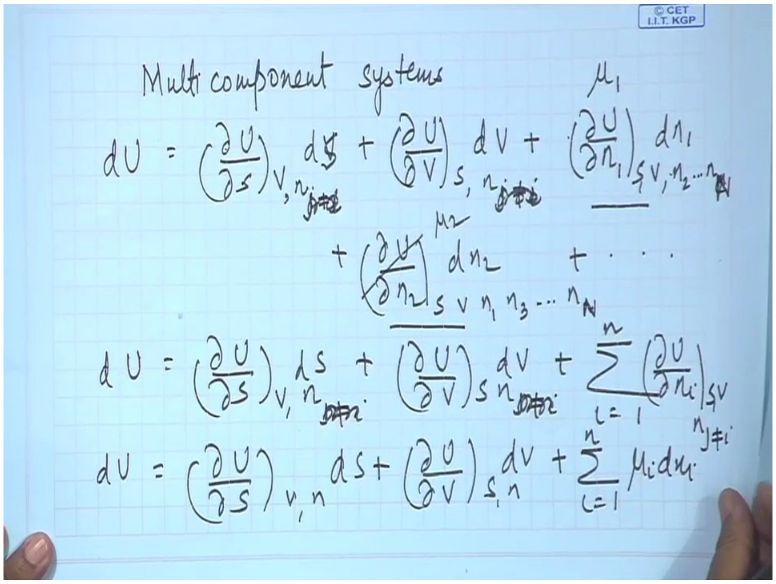


© CET I.I.T. KGP

Multi component systems

Now let us see what happens for multi-component systems, for multi-component systems if we take it up thus same equation with little with some more terms again I repeat we are going to deal with only PV type of work and I will be doing the entire derivation considering internal energy keeping in mind that the same derivation can be applied for other systems as well.

(Refer Slide Time: 0:46)



Multi component systems

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_{j\neq i}} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_{j\neq i}} dV + \underline{\overset{\mu_1}{\left(\frac{\partial U}{\partial n_1}\right)_{S V,n_2 \cdots n_N}}} dn_1$$

$$+ \underline{\overset{\mu_2}{\left(\frac{\partial U}{\partial n_2}\right)_{S V n_1 n_3 \cdots n_N}}} dn_2 + \cdots$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_{j\neq i}} dS + \left(\frac{\partial U}{\partial V}\right)_{S n_{j\neq i}} dV + \sum_{i=1}^{n} \left(\frac{\partial U}{\partial n_i}\right)_{S V n_{j\neq i}}$$

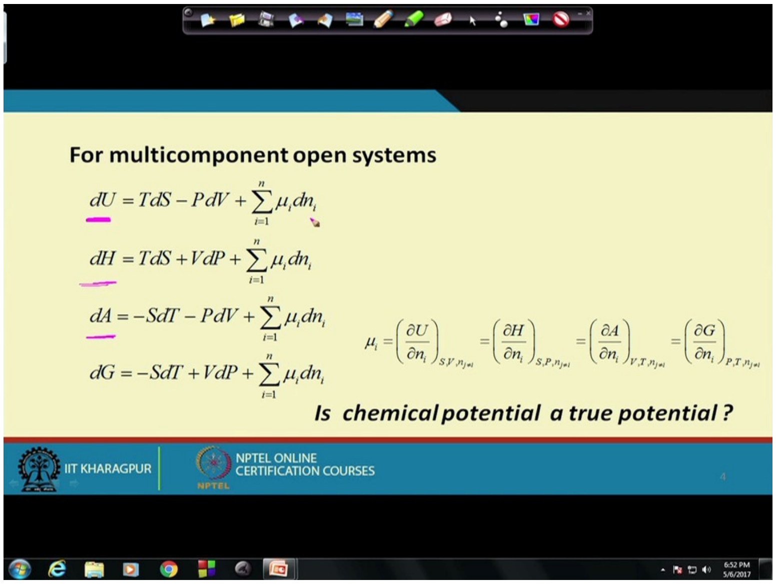
$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n} dV + \sum_{i=1}^{n} \mu_i dn_i$$

So in this particular case what did I write down initially? This was equal to del U del s at constant v dv for closed systems del U del V at constant s sorry this was dS this was dV. Now if if I have more than one component then what do I do? This is equals to ni not equal to j this is nj not equal to i, nj not equal to i where I varied the number of moles of the neth component. So therefore this is going to be del U say del n1 at constant s, v n2 to the final component nM of whatever number or say nC is the total number of components, okay.

So therefore it goes on continuously into dn1 plus del U del n2 dn2 again this is at constant s, v, n1, n3 till n and maybe a number of components N plus and so on we can keep on writing. So therefore this can be summarized and it can be written down as this is equal to del U del s constant nj not equal to i d s plus del U del V constant s nj not equal to i d v plus summation of i equals to 1 to n where n is the total number of components del U del ni constant s, v nj not equal to i.

I am sorry in this particular case I am extremely sorry it should have been total N. I am very sorry for this mistake it should have been total N, right? So therefore this is the final equation which we are going to get for multi-component systems and in this particular equation we find that each and every variation of U with the mole numbers each of them they correspond to the chemical potential of that particular component mu2.

(Refer Slide Time: 4:19)



For multicomponent open systems

$$dU = TdS - PdV + \sum_{i=1}^{n} \mu_i dn_i$$

$$dH = TdS + VdP + \sum_{i=1}^{n} \mu_i dn_i$$

$$dA = -SdT - PdV + \sum_{i=1}^{n} \mu_i dn_i$$

$$dG = -SdT + VdP + \sum_{i=1}^{n} \mu_i dn_i$$

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j\neq i}} = \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_{j\neq i}} = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}}$$

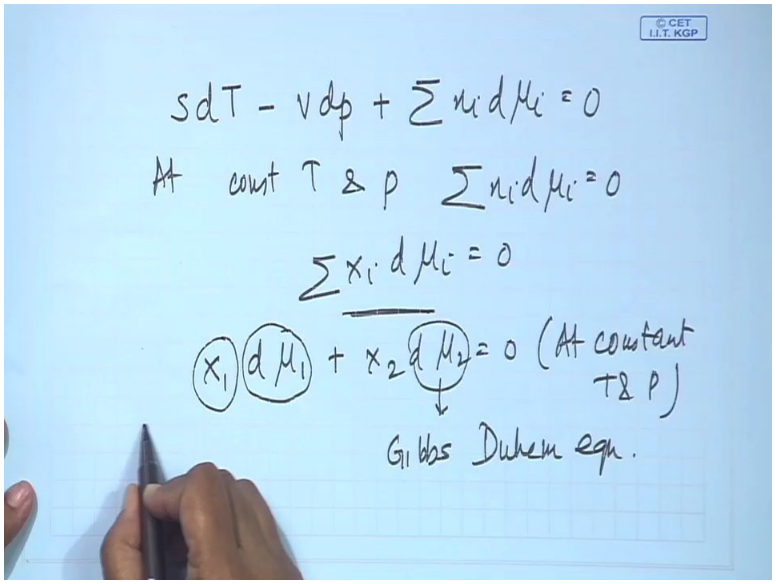
Is chemical potential a true potential?

So therefore this can also be written down as del U del S at constant v, n ds plus del U del V at constant s, n dv plus Sigma i equals to 1 to n mui dni, right? Where each mui it corresponds to del U del ni of the ith component where the number of total number of moles of all other components except the ith component is kept constant, I have written down the equations for the multi-component open systems in each case.

You can see and in each case again it can be proved that the property change due to the change in the number of moles of component i when the number of moles of all other components are kept constant is given by mui dni in each particular case where muis just like mu for single component systems.

In this particular case also we find that it corresponds to the molar internal energy or the molar thermodynamic potential subject to the respective constraints and in reality it is the molar isobaric isothermal potential when the number of moles of any 1 component is changed while the number of moles of the other components are kept constant and in this case also just like the previous case we can define the Gibbs Duhem equation in fact the Gibbs Duhem equation is much more convenient when we are defining it for multi-component systems.

(Refer Slide Time: 5:22)



$$sdT - vdp + \sum n_i d\mu_i = 0$$

At const T & p $\sum n_i d\mu_i = 0$

$$\sum x_i d\mu_i = 0$$

$$x_1 d\mu_1 + x_2 d\mu_2 = 0 \text{ (At constant T \& P)}$$

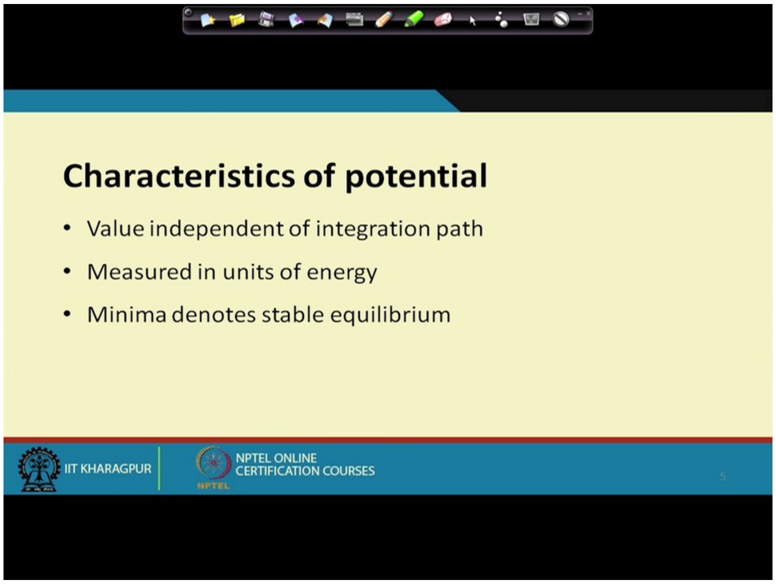
Gibbs Duhem eqn.

In this particular case the equation becomes sdT minus vdp plus Sigma ni d mui equals to 0 and at constant T and P this becomes Sigma ni d mui equals to 0 and if we divide it by the total number of moles it becomes Sigma xi d mui equals to 0. The importance of this equation can be immediately understood if we know the composition of the mixture and if we know the chemical potential of n minus one number of components we can use this particular equation to find the chemical potential of the neth component.

Say for example for a true-component system this just reduces to x1 dmu1 plus x2 dmu2 equals to 0 at constant T and P. So if we know x1 if we know the change of mu1 then by using this equation we can find out this particular quantity and there is where the importance of the Gibbs Duhem equation this is the Gibbs Duhem equation for multi-component system and we will find later that this is very important to test the thermodynamic consistency of the data that we use because we need to remember that most of the these data they are obtained from experiments. So therefore before using them for any particular calculation it is very important to test that this data are thermodynamically consistent and this particular equation is usually used to test the thermodynamic consistency of this data.

Now before we go further it is very important to understand that why is this so very important term? The molar Gibbs free energy given a special name and that took the name as chemical potential. Is it really a potential in the true sense just like u, h, a and g. Now in order to understand this we have to recall the properties of a thermodynamic potential which I had already discussed when I was discussing when I was trying to explain why u, h, a and g are thermodynamic potentials.

(Refer Slide Time: 8:01)

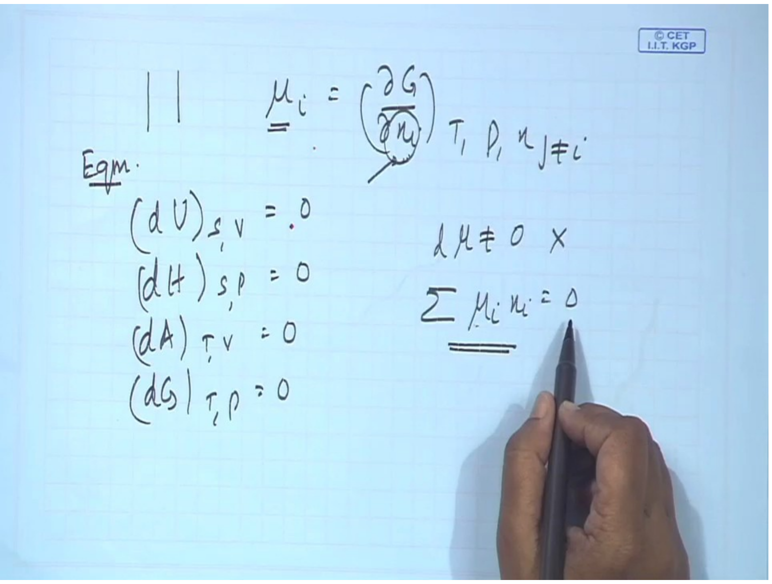


Characteristics of potential

- Value independent of integration path
- Measured in units of energy
- Minima denotes stable equilibrium

What are the properties of thermodynamic potentials if we recollect? What are the properties of thermodynamic potentials are? If you remember first is the value has to be independent of the integration part. What does it signify? It signifies that these particular property or rather these particular potentials they have to be properties of the system. Definitely chemical potential is a property of the system we know that. So in this case we do not have any problems, the other thing which we found out was that all these potentials they must be units of energy, right? Here also definitely chemical potential it is measured in the unit of energy but that is primarily accidental, why?

(Refer Slide Time: 8:35)



|| $\underline{\underline{\mu_i}} = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_{j \neq i}}$

Eqm.

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

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

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

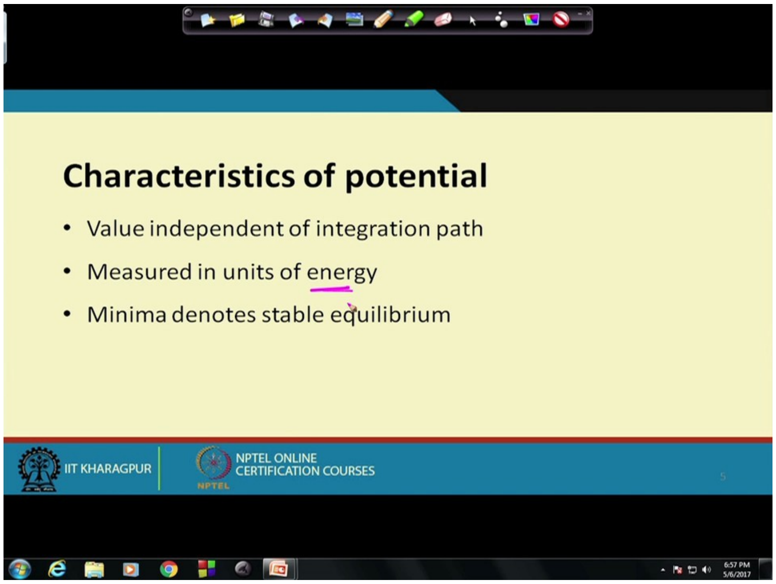
$(dG)_{T,P} = 0$

$d\mu \neq 0$ ×

$\underline{\underline{\sum \mu_i n_i = 0}}$

Because the chemical potential mui it is nothing but equal to del G del ni at constant T, P nj not equal to i and this particular number of moles it is basically a number, have I expressed in terms of concentration then this would have been a energy concentration instead of an energy unit. So therefore since mui is defined in terms of ni so therefore it has the units of energy but that is primarily accidental and what does the third condition of potential imply?

(Refer Slide Time: 9:12)

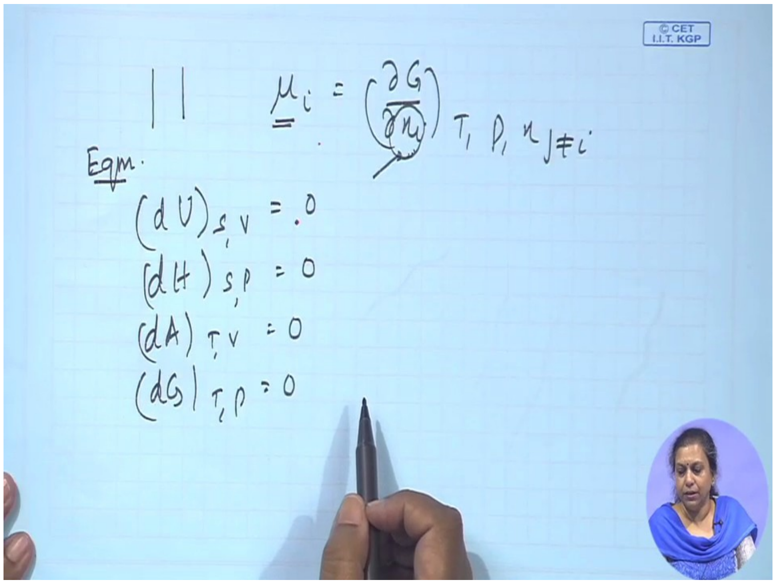


Characteristics of potential

- Value independent of integration path
- Measured in units of energy
- Minima denotes stable equilibrium

It implies that the minima denote stable equilibrium which we already know while we were discussing equilibrium under different conditions what did we find?

(Refer Slide Time: 9:28)



||

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_{j \neq i}}$$

Eqm.

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

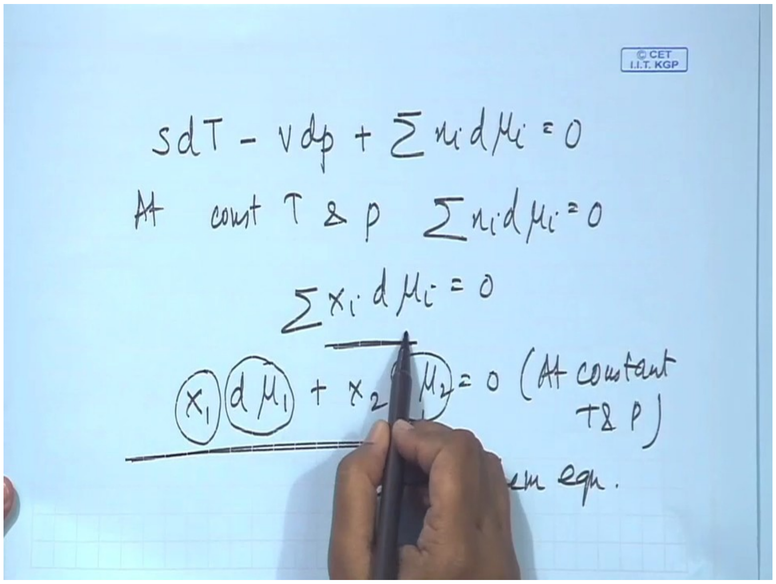
$$(dH)_{S,P} = 0$$

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

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

We found that dU s, v was equal to 0 the conditions of equilibrium work then dH S, P was equal to 0 then dA T, V was equal to 0 and dG T,P was equal to 0, right? So therefore we find that for each and every case the differential quantities are equal to 0.

(Refer Slide Time: 9:49)



$sdT - vdp + \sum n_i d\mu_i = 0$

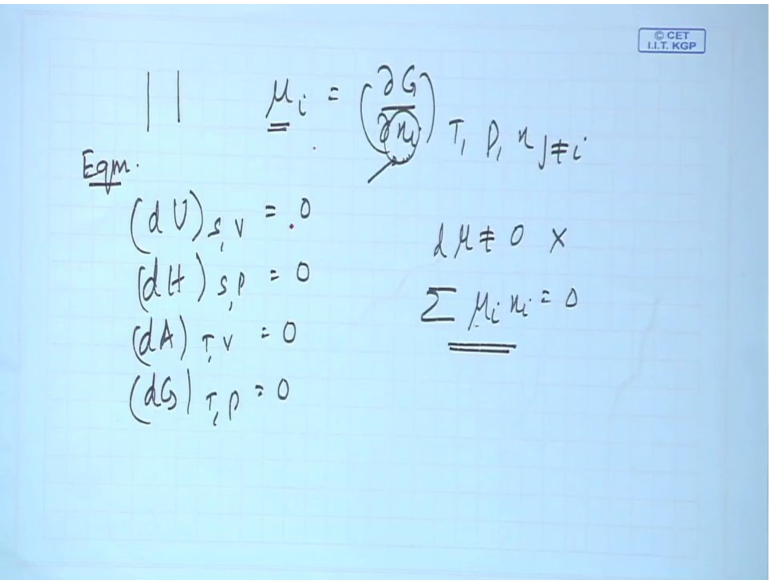
At const T & p $\sum n_i d\mu_i = 0$

$\sum x_i d\mu_i = 0$

$x_1 d\mu_1 + x_2 d\mu_2 = 0$ (At constant T & p)

um eqn.

(Refer Slide Time: 10:32)



$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, p, n_{j \neq i}}$

Eqm.

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

$(dH)_{S,p} = 0$

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

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

$d\mu \neq 0$ ×

$\sum \mu_i n_i = 0$

But in the case of chemical potential if you observe this particular equation and this particular equation it immediately appears to you it is not that the dmu is equal to 0, this does not happen on the contrary Sigma mui ni this is equal to 0. So therefore if you observe this that the summation of chemical potential for any particular reaction or for any particular process equals to 0 than it appears that it has been better if it would have been called by the name of the force because we find that this particular characteristic combines with or rather this particular characteristic it corresponds to a fourth quantity.

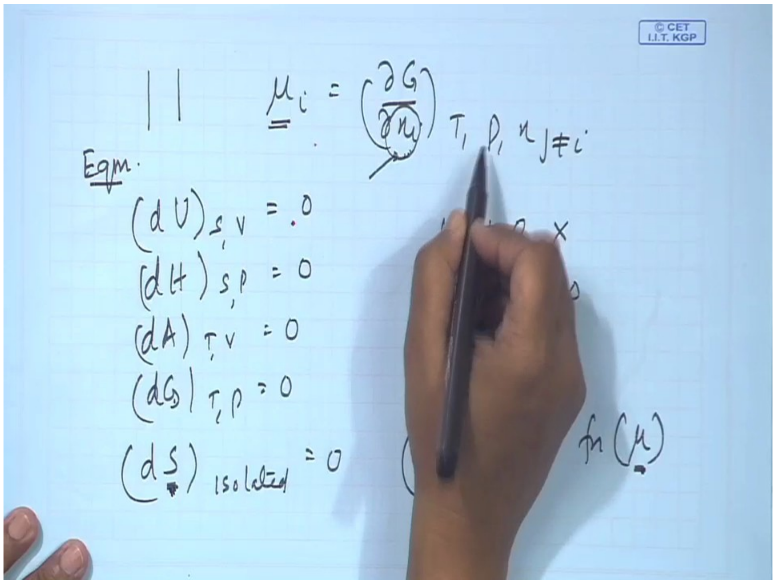
But again then we found out that if we name it by the force then we find that we have a force which has the unit of energy that is not something very convenient and the next thing which we observed was that very frequently we find that for non-equilibrium condition the driving force for current they can be identified with the gradient of chemical potential because very frequently we find that when we are dealing with non-PV type of work then we are dealing with electrical work and under that condition the current it is usually defined as the gradient of potential energy.

So therefore under that condition we find that it is a force being a derivative of a force that is also not a very comfortable feeling. So therefore what I mean to say is chemical potential is something very unique which combines some of the characteristics of potential but it cannot be consider a thermodynamic potential in the true sense.

It has some characteristic of a thermodynamic force but it cannot be considered a thermodynamic force in the true sense it has the unit of energy it is an intensive property of the system but the summation it corresponds to equilibrium and it’s Minima does not correspond to a stable equilibrium.

So all these things suggest that chemical potential has a unique place of its own and since it combines a large number of characteristics just because the way it has been defined, so therefore it has got a multifaceted aspect and since in the absence of any better name we would like to prefer to follow conventions and we would like to continue calling it as a potential but not a thermodynamic potential but a chemical potential keeping in mind that it is not a true thermodynamic potential.

(Refer Slide Time: 12:45)



$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j \neq i}}$$

Eqm.

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

$$(dH)_{S,p} = 0$$

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

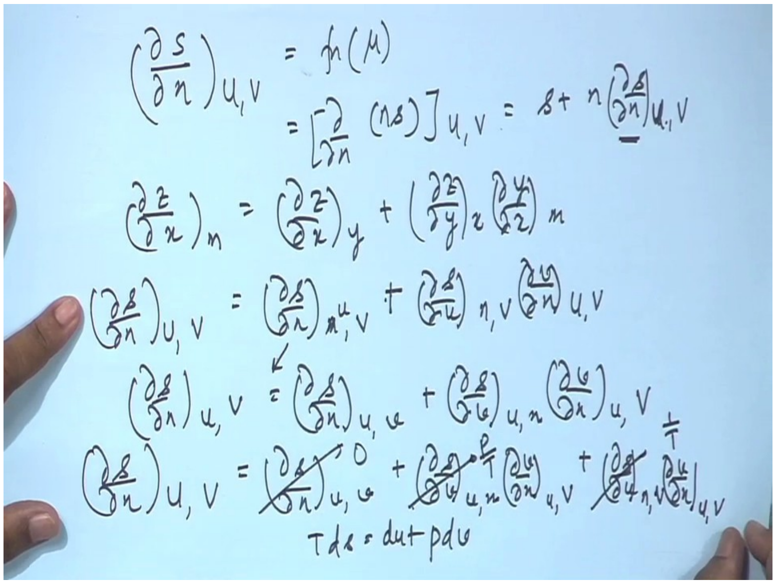
$$(dG)_{T,p} = 0$$

$$(dS)_{isolated} = 0$$

The next thing again which I would again I would like to say that what have we done in this particular case? For this particular case we have found out or rather we have related each and every thermodynamic potential with the chemical potential term. Now it would be interesting for us to find out that if we notice that for an isolated system what is the criterion of equilibrium?

For this particular case it is dS isolated equals to 0 where we know that S is not a thermodynamic potential. So therefore in this particular place it will be interesting to find out how this particular term del S del n at constant u, v in what way is it related to the chemical potential? Now this particle derivation it is slightly involved but we can go through it and we can try to appreciate keeping in mind that although it is not a thermodynamic potential it is often used in order to find out the criteria of equilibrium for an isolated system and it has got a very interesting relationship with chemical potential where the relationship is not of this particular form.

(Refer Slide Time: 14:14)



$$\left(\frac{\partial S}{\partial n}\right)_{U,V} = fn(\mu)$$

$$= \left[\frac{\partial}{\partial n}(ns)\right]_{U,V} = s + n\underline{\left(\frac{\partial s}{\partial n}\right)_{U,V}}$$

$$\left(\frac{\partial z}{\partial x}\right)_m = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_m$$

$$\left(\frac{\partial s}{\partial n}\right)_{U,V} = \left(\frac{\partial s}{\partial n}\right)_{\overset{u}{\cancel{n}},V} + \left(\frac{\partial s}{\partial u}\right)_{n,V}\left(\frac{\partial u}{\partial n}\right)_{U,V}$$

$$\swarrow$$

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

$$\left(\frac{\partial s}{\partial n}\right)_{U,V} = \cancel{\left(\frac{\partial s}{\partial n}\right)_{u,v}}^{0} + \cancel{\left(\frac{\partial s}{\partial v}\right)_{u,n}}^{\frac{p}{T}}\left(\frac{\partial v}{\partial n}\right)_{u,V} + \cancel{\left(\frac{\partial s}{\partial u}\right)_{n,v}}^{\frac{1}{T}}\left(\frac{\partial u}{\partial n}\right)_{U,V}$$

$$Tds = du + pdv$$

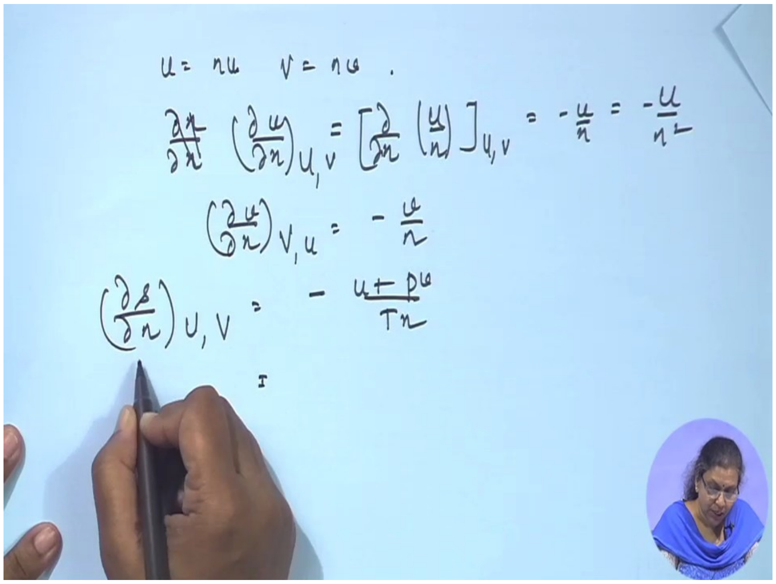
Let us see this particular relationship before we proceed further, now this particular case can we not write it down in this particular form dS equals to we can write it down as say del S del n at capital UV, right? We would like to find how this is related to mu? Now this particular equation you can definitely write it down as ns at constant UV which is nothing but equal to just like we are being doing for all cases del s del n at constant capital UV.

Now I would like to remind you of a very important rule of differentiation which is given as del z del x at constant n is nothing but del z del x at constant y plus del z del y at constant x into del y del x at constant M. So if we apply this particular equation here, what do we get? We get del s del n at constant capital U capital V is nothing but del s del n at u v plus del s del u at n, v into del v del n at u, v we can write it down in this particular terms.

Then this particular term can also be expanded in the similar way. We can again write this term as del s del n at small u small v plus del s del v, u n into del v del n, u capital V, right? And then we can substitute this equation there. Once you substitute what do we get? We get del s del n at capital U capital V this is nothing but equal to del s del n small u small v plus del s del v small u small n into del v del n uv plus del s del u nv, del u del n capital U capital V, we can write it down in this particular way.

Or if you observe this equation what do you find? The first thing is this particular term del s del n at small u, v this term this term this becomes equal to 0, what about this term? Here I would like to remind you that Tds equals to du plus pdv, right? So from there what is this term equal to can you tell me? This term then becomes equal to P by T, what about this particular term? This term becomes equal to 1 by T.

(Refer Slide Time: 17:39)



$U = nu \quad V = nv$.

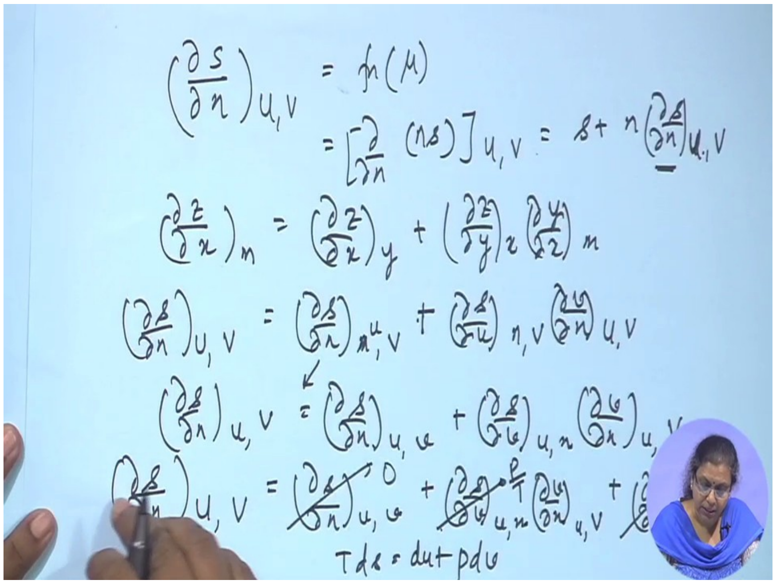
$$\left(\frac{\partial u}{\partial n}\right)_{U,V} = \left[\frac{\partial}{\partial n}\left(\frac{U}{n}\right)\right]_{U,V} = -\frac{u}{n} = -\frac{U}{n^2}$$

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

$$\left(\frac{\partial s}{\partial n}\right)_{U,V} = -\frac{u+Pv}{Tn}$$

So therefore and we have to keep in mind that capital U is nothing but equal to nu capital V is equals to nv. So therefore from there what do we get? We get del u del n capital U, v this is nothing but equals to del del n of u by n U, v which is nothing but equals to minus u by n or in other words this is equal to minus capital U by n square. Same way we can write it down as del v del n capital V, u is nothing but equals to minus v by n. So therefore from there what do we get? del s del n at capital UV it is nothing but equals to minus of u plus Pv by Tn from there what do we get?

(Refer Slide Time: 18:45)



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

$$= \left[\frac{\partial}{\partial n}(ns)\right]_{u,v} = s + n\underline{\left(\frac{\partial s}{\partial n}\right)}_{u,v}$$

$$\left(\frac{\partial z}{\partial x}\right)_m = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x\left(\frac{\partial y}{\partial x}\right)_m$$

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

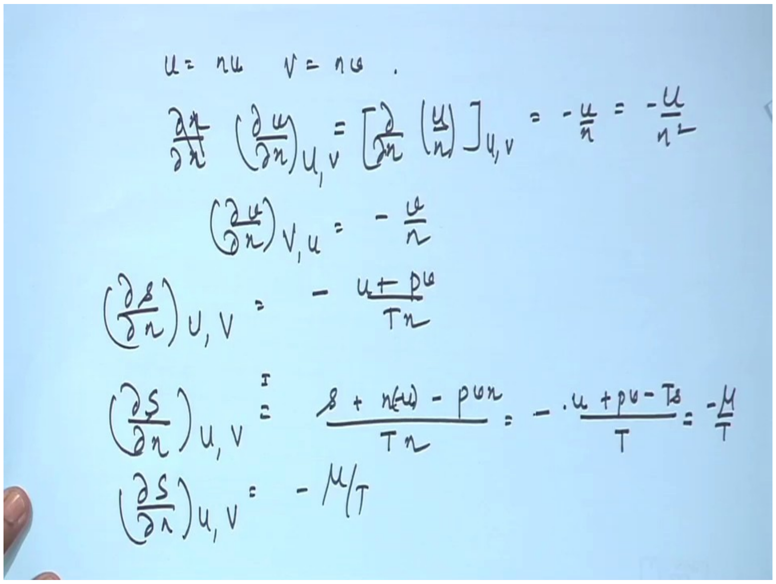
$$\left(\frac{\partial s}{\partial n}\right)_{u,v} \swarrow = \left(\frac{\partial s}{\partial n}\right)_{u,v} + \left(\frac{\partial s}{\partial v}\right)_{u,n}\left(\frac{\partial v}{\partial n}\right)_{u,v}$$

$$\left(\frac{\partial s}{\partial n}\right)_{u,v} = \cancel{\left(\frac{\partial s}{\partial n}\right)_{u,v}}^{\,0} + \cancel{\left(\frac{\partial s}{\partial v}\right)_{u,n}}^{\,p/T}\left(\frac{\partial v}{\partial n}\right)_{u,v} +$$

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

We get that then this becomes equal to and if we substitute this particular term in the first equation that we have, then finally what do we arrive at?

(Refer Slide Time: 18:58)



$U = nu \quad V = nv$.

$$\cancel{\frac{\partial n}{\partial n}} \left(\frac{\partial u}{\partial n}\right)_{U,V} = \left[\frac{\partial}{\partial n}\left(\frac{U}{n}\right)\right]_{U,V} = -\frac{u}{n} = -\frac{U}{n^2}$$

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

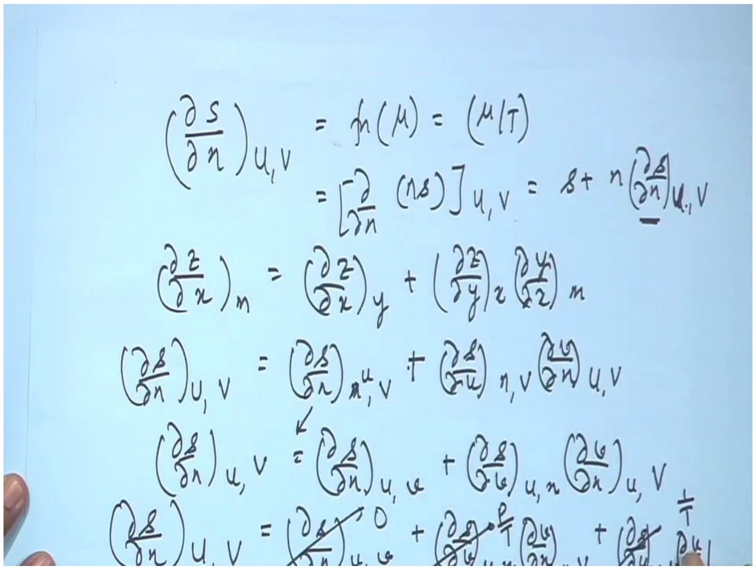
$$\left(\frac{\partial s}{\partial n}\right)_{U,V} = -\frac{u+pv}{Tn}$$

$$\left(\frac{\partial S}{\partial n}\right)_{U,V} = \frac{s + n(-u) - pvn}{Tn} = -\frac{u+pv-Ts}{T} = -\frac{\mu}{T}$$

$$\left(\frac{\partial S}{\partial n}\right)_{U,V} = -\mu/T$$

We arrive at a condition that del S del n capital U, V is nothing but equal to s plus nu minus pvn by Tn from there what do we get? We get minus of, so we get minus of u plus pv minus Ts by T which is nothing but equals to minus mu by T. So therefore what do we get? We get that del S del n at capital U, V is nothing but equals to minus mu by T.

(Refer Slide Time: 19:47)



$$\left(\frac{\partial S}{\partial n}\right)_{U,V} = fn(\mu) = (\mu/T)$$

$$= \left[\frac{\partial}{\partial n}(ns)\right]_{U,V} = s + n\underline{\left(\frac{\partial s}{\partial n}\right)}_{U,V}$$

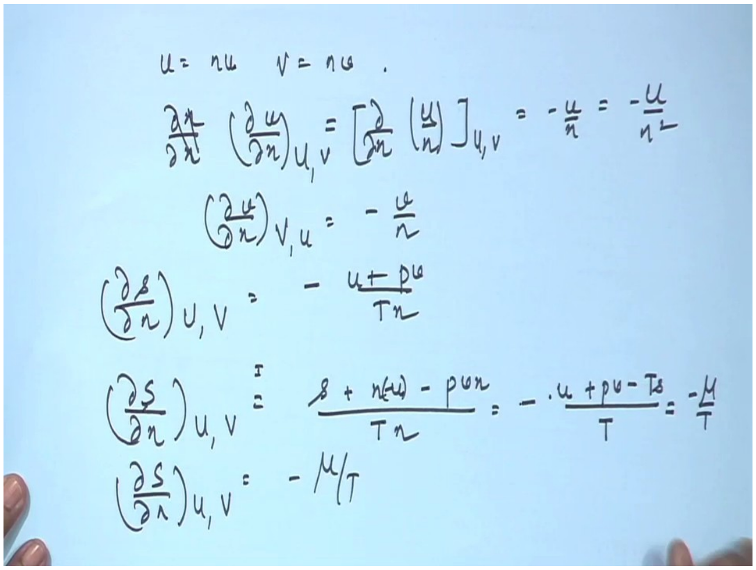
$$\left(\frac{\partial z}{\partial x}\right)_m = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_m$$

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

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

$$\left(\frac{\partial s}{\partial n}\right)_{U,V} = \overset{0}{\cancel{\left(\frac{\partial s}{\partial n}\right)_{u,v}}} + \overset{p/T}{\cancel{\left(\frac{\partial s}{\partial v}\right)_{u,n}}} \left(\frac{\partial v}{\partial n}\right)_{V} + \overset{1/T}{\cancel{\left(\frac{\partial s}{\partial u}\right)}} \frac{\partial u}{}$$

(Refer Slide Time: 19:49)



$U = nu \quad V = nv$.

$$\cancel{\frac{\partial n}{\partial n}} \left(\frac{\partial u}{\partial n}\right)_{U,V} = \left[\frac{\partial}{\partial n}\left(\frac{U}{n}\right)\right]_{U,V} = -\frac{u}{n} = -\frac{U}{n^2}$$

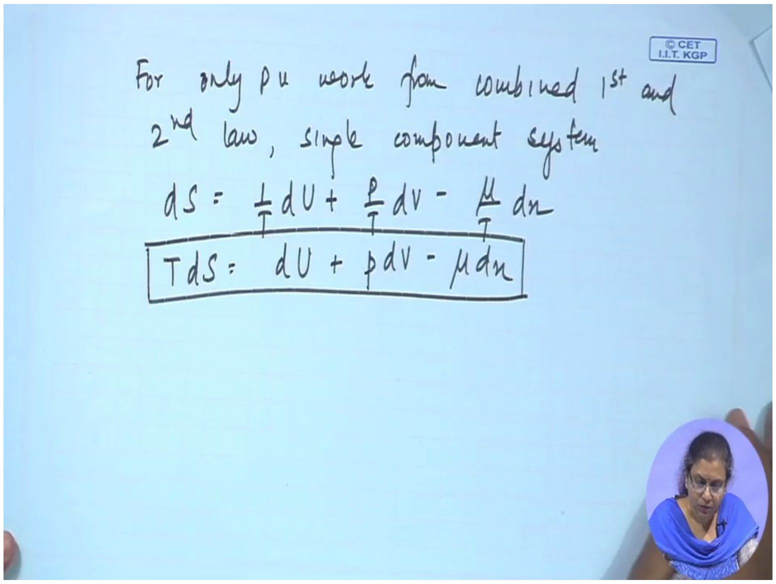
$$\left(\frac{\partial v}{\partial n}\right)_{V,U} = -\frac{v}{n}$$

$$\left(\frac{\partial s}{\partial n}\right)_{U,V} = -\frac{u + pv}{Tn}$$

$$\left(\frac{\partial S}{\partial n}\right)_{U,V} \overset{I}{=} \frac{s + n(-u) - pvn}{Tn} = - \cdot \frac{u + pv - Ts}{T} = -\frac{\mu}{T}$$

$$\left(\frac{\partial S}{\partial n}\right)_{U,V} = -\mu/T$$

(Refer Slide Time: 20:47)



For only pv work from combined 1st and 2nd law, single component system

$$dS = \frac{1}{T}dU + \frac{p}{T}dv - \frac{\mu}{T}dn$$

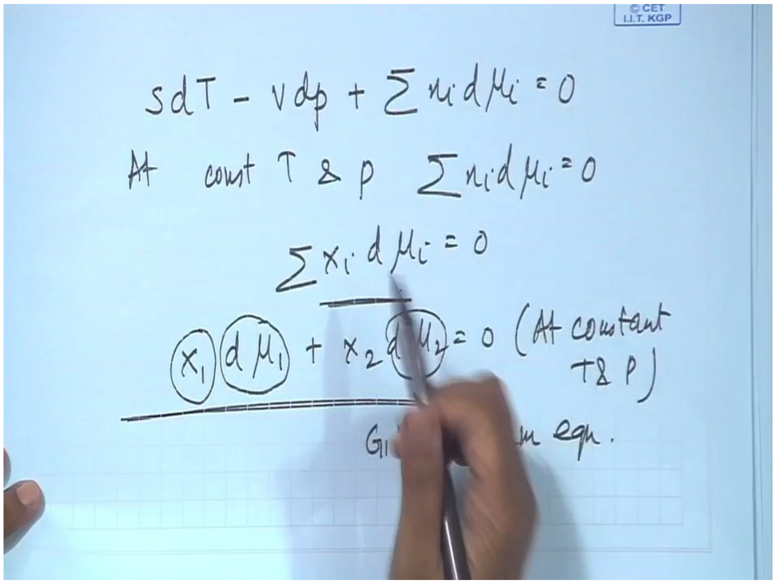
$$\boxed{TdS = dU + pdv - \mu dn}$$

So therefore we were trying to find this relationship we know now that this is equals to mu by T. So therefore we combine first and second law for open systems for only Pv work from combined first and second law and single component system for all these conditions, what do we get? We get dS is nothing but equals to 1 by T dU plus P by T dv minus mu by T dn or in other words Tds equals to dU plus pdv minus mu dn. So this is the equation which we derive derivation was slightly involved with large number of capital and small case alphabets involved.

But by this particular discussion what I wanted to impress upon you is the importance of identifying the total and molar properties and I would like you to remember that we are not dealing with mass specific properties at the moment, same equations will be applicable for mass specific properties as well.

And from here what we came to know is when we have to deal with open systems when the system interacts with the surroundings not only by energy interaction but also by changes in the number of moles or by mass interaction then we find that we had to introduce a new chemical property which was actually not new it is basically the molar Gibbs free energy but we had called it by a new name the chemical potential.

(Refer Slide Time: 22:02)



$$s\,dT - v\,dp + \sum n_i\, d\mu_i = 0$$

At const T & p $\sum n_i\, d\mu_i = 0$

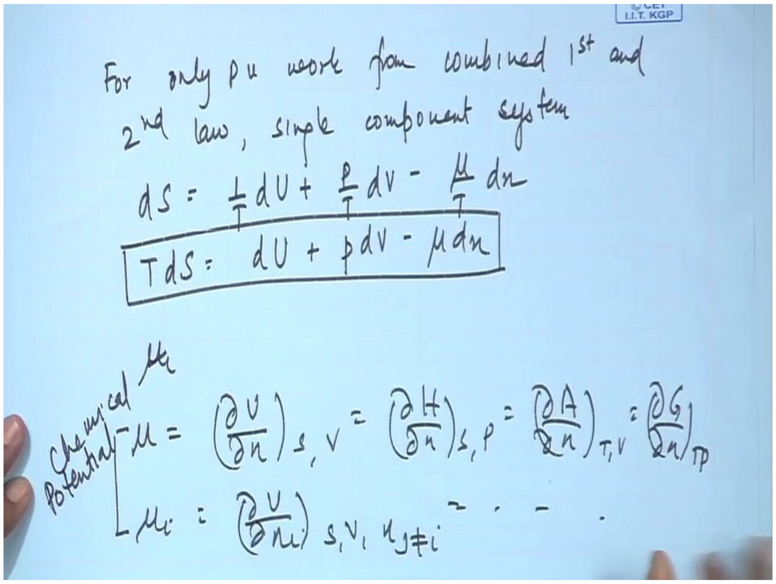
$$\underline{\sum x_i\, d\mu_i = 0}$$

$$\boxed{x_1}\,\boxed{d\mu_1} + x_2\, d\boxed{\mu_2} = 0 \quad \text{(At constant T \& P)}$$

Gi [illegible] m eqn.

Why did we have to put a new name to it? Because we found out that for single property system it was the molar Gibbs free energy but moment we are dealing with multi-component systems we find that this particular property it becomes equal to mui in this particular case, right?

So therefore just in order to combine both single component and multi-component systems we had defined or rather we have defined the Gibbs molar Gibbs free energy for single component systems as chemical potential.



For only pv work from combined 1st and 2nd law, simple component system

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dn$$

$$\boxed{TdS = dU + pdV - \mu dn}$$

Chemical Potential

$$\mu_i$$

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

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}} = \cdots$$

And we keep in mind for single component systems chemical potential is equal to this particular expression which for a multi-component system it becomes del U del ni s, v, nj not equals to i and so on and so forth and both these terms they are referred by the same name it is known as the chemical potential and we will remember that the chemical potential is not a true thermodynamic potential but it has a number of characteristics of a thermodynamic potential.

So in the next class we shall be going to deal with open systems, first we are going to deal with single component open systems and then we are going to extend it for multi-component open systems.