Basic Thermodynamics

Prof. S. K. Som
Department of Mechanical Engineering
Indian Institute of Technology, Kharagpur

Lecture - 31

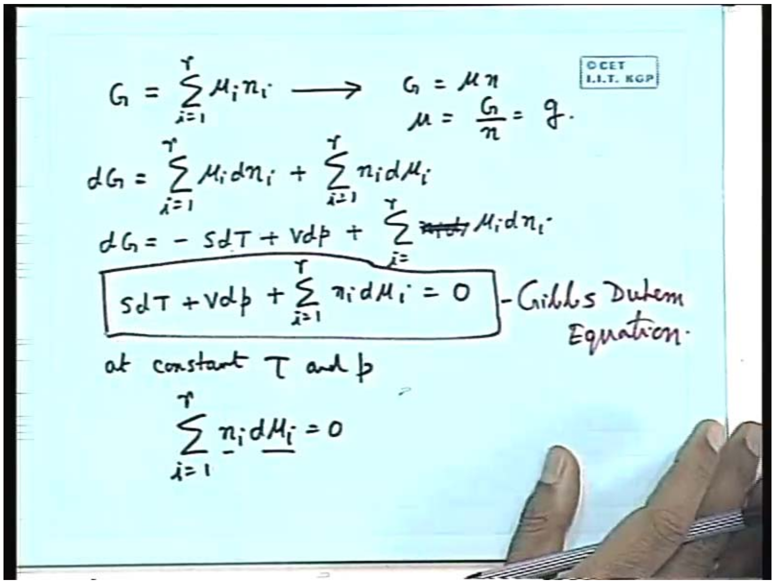
Thermodynamics of Multi Component System – II

Good morning. I welcome you to the session of thermodynamics. Before I start the class I should mention one thing today which I should have mentioned in the last class. Now we are discussing about the multi component systems but at the beginning of this course I have shown the course curriculum where this part was not included, this should be made clearly at this juncture. But, at a later period it was felt necessary that some fundamental thermodynamic principles are multi component systems and thermodynamic equilibrium and equilibrium of multi component multiple systems are essentially as a part of this course.

Therefore this has been included, that is why I am going to teach this but at this moment I am not going to tell you the detail syllabus of course curriculum for it. But I tell you in short that, this will include a brief discussion or basic thermodynamic principles of multi component system which we are discussing then I will discuss on thermodynamic equilibrium and the equilibrium of multi component and multiple system.

This was not shown earlier at the beginning of this course as a part of the course curriculum. Therefore I want to tell this before I start for today's lecture. Let us start as a continuation of our last class discussions where we ended in the last class probably if you recollect we ended here.

(Refer Slide Time: 02:44)



©CET I.I.T. KGP

$$G = \sum_{i=1}^{r} \mu_i n_i \longrightarrow G = \mu n$$

$$\mu = \frac{G}{n} = g.$$

$$dG = \sum_{i=1}^{r} \mu_i dn_i + \sum_{i=1}^{r} n_i d\mu_i$$

$$dG = - SdT + Vdp + \sum_{i=}^{r} \cancel{n_i d\mu_i} \mu_i dn_i.$$

$$\boxed{SdT + Vdp + \sum_{i=1}^{r} n_i d\mu_i = 0}$$ - Gibbs Duhem Equation.

at constant T and p

$$\sum_{i=1}^{r} n_i \underline{d\mu_i} = 0$$

G, the Gibbs function of a multi component system can be defined as m_i n_i, this was derived for r number of components with the help of the definition of thermodynamic potential the definition of Gibbs function and the Euler's theorem for homogeneous function.

We defined this relationship. If you recall the last class G as the sum of the m_i ni from which we derived an uniform conclusion that for a single component system G is m into n which means m the thermodynamic potential is the molar Gibbs function that means the Gibbs function per unit number of moles this we already discussed in the last class.

Today we start like this, if we differentiate this dG then we get $m_i dn_i$ first term i is equal to 1to r plus we get this n_i d m_i so these are all at constant pressure and temperature. This is at constant pressure and temperature always G at T and p that we get this relationship dG is m_i dn_i plus n_i d m_i.

Earlier, if you recall we had this relationship dG is equal to minus sdT when we defined the thermodynamic potential, where from we got this relationship $m_i dn_i$ i is equal to 1 to r. This we got by expressing G as a function of T and p and then by recognizing the fact that dG is minus sdT plus vdp for a single component pure substance.

dG is minus sdT plus vdp so this part is for the multi component system. If we express G as a function of T and p this we defined earlier. Now, if we compare these two then we can write sdT plus vdp, if we compare this two dG they are equal plus summation of $n_i dm_i$, this as i is equal to 1 to r is equal to 0. This equation is very important equation and is known as Gibbs Duhem equation in multi component system.

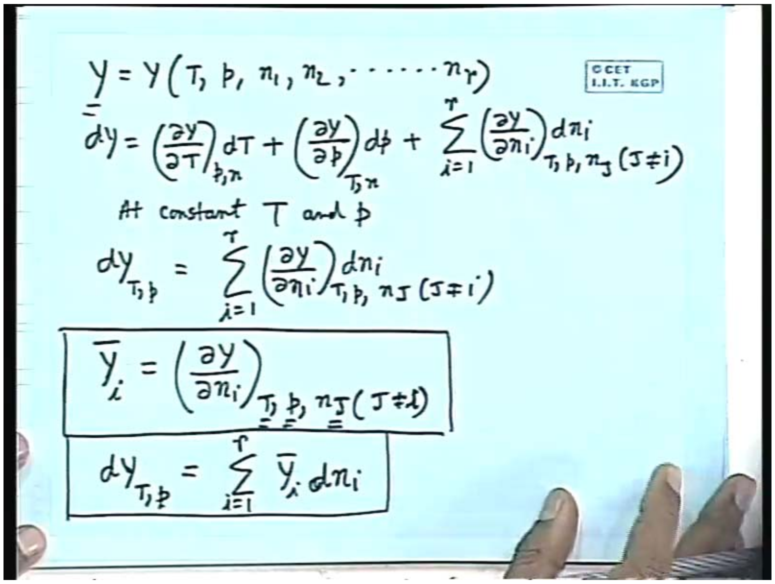
At constant pressure and temperature T and p Gibbs Duhem equation becomes $n_i dm_i$ is equal to 0 that means for r number of components at constant pressure and temperature summation of

$n_i dm_i$ is equal to 0. This is an important relationship between the change in thermodynamic potential and the number of moles.

Next, I will start a very important property which is known as partial molar property. In a multi component system which is very important. As we know for a single component system a molar property is the property per unit mole this molar property or the specific property are defined for extensive properties that means properties which are directly related to mass. The property per unit mass is the specific property. For example, specific internal energy specific enthalpy, specific Helmholtz function, specific Gibbs function, specific entropy.

Similarly, if you consider moles as the unit of mass that indicating the amount of substance as we know earlier definition of mole. Then for a single component system this extensive property per unit mole is the molar property. For example, the molar internal energy, molar Gibbs function, molar enthalpy like this but in a multi component system when there are number of components, this molar property for a particular component existing with other components in the system are expressed in terms of partial molar property and we are going to discuss this partial molar property how they are defined in a multi component system.

(Refer Slide Time: 07:39)



©CET I.I.T. KGP

$$\underline{Y} = Y(T, p, n_1, n_2, \cdots\cdots n_r)$$

$$dY = \left(\frac{\partial Y}{\partial T}\right)_{p,n} dT + \left(\frac{\partial Y}{\partial p}\right)_{T,n} dp + \sum_{i=1}^{r}\left(\frac{\partial Y}{\partial n_i}\right)_{T,p,n_J\,(J\neq i)} dn_i$$

At constant T and p

$$dY_{T,p} = \sum_{i=1}^{r}\left(\frac{\partial Y}{\partial n_i}\right)_{T,p,\,n_J\,(J\neq i)} dn_i$$

$$\boxed{\bar{Y}_i = \left(\frac{\partial Y}{\partial n_i}\right)_{\underline{T},\,\underline{p},\,\underline{n_J}\,(J\neq i)}}$$

$$\boxed{dY_{T,p} = \sum_{i=1}^{r} \bar{Y}_i\, dn_i}$$

Let us start with partial molar properties. Let us consider Y, an extensive property as a function of temperature pressure and the number of moles. Let r number of components, r number of moles.

Now, as usual we can write del dy the change in y as del y del T at constant p and n dT plus del y del p at constant T and n dp plus obviously sum of all the derivatives with respect to number of moles for ith component where other moles are fixed. That is nj, J not is equal to i and this summation extends from i is equal to one.

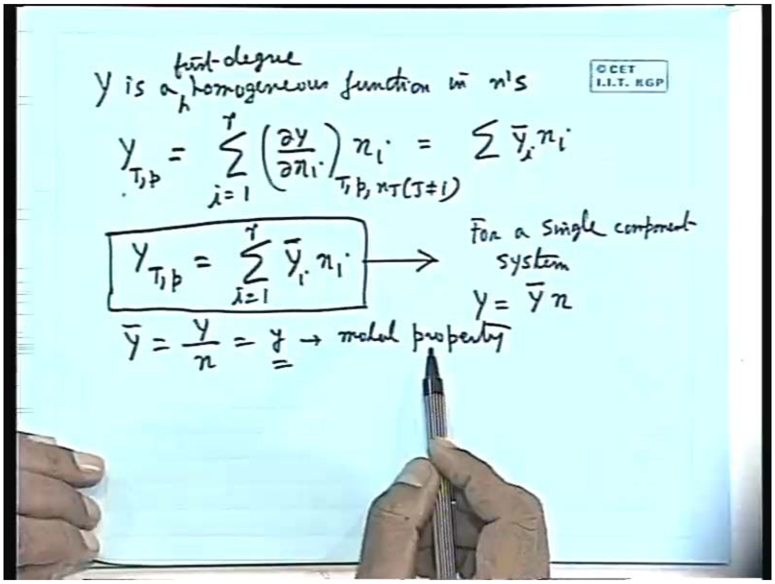
If temperature and pressures are constant at constant T and p, we can tell that change of this extensive property at constant T and p therefore responsible for this del y del n_i these terms T p n_j J not is equal to i.

After this mathematics we come to the definition of the partial molar property. Partial molar property for a component i is denoted as Y with a bar suffix i is defined as the rate of change of the extensive property of the system of r components with respect to the change in the number of moles of that component for which we are going to define the partial molar property at constant temperature, pressure and other constituents compositions of the J not is equal to i other constituents.

Again the physical definition comes from this is the partial molar property of a particular constituent i is the rate of change of that extensive property for which the partial molar property of the constituent is defined is the rate of change of that extensive property with respect to the number of moles of that constituent for which the partial molar property is defined when temperature pressure and the compositions of the other components remain fixed this is defined as the partial molar property . This is the basic definition of the partial molar property of a component in a multi component system.

With definition and the nomenclature for the partial molar property we can write the change of any extensive property in a multi component system at constant temperature and pressure is the sum of the partial properties. Here I have missed this term dn_i so Y bar dn_i therefore it is a very interesting relationship that the change in any extensive property Y at constant temperature and pressure of a multi component system consisting of r number of components equals to sum of the product of the partial molar property times the change in the number of moles of a particular component and this summation extends from one to r that is for all the number of components therefore this is a very important relationship.

(Refer Slide Time: 11:27)



©CET I.I.T. KGP

Y is a first-degree homogeneous function in n's

$$Y_{T,p} = \sum_{i=1}^{r} \left(\frac{\partial Y}{\partial n_i}\right)_{T,p,n_j(j\neq i)} n_i = \sum \bar{Y}_i n_i$$

$$\boxed{Y_{T,p} = \sum_{i=1}^{r} \bar{Y}_i n_i} \longrightarrow$$

For a single component system

$$Y = \bar{Y} n$$

$$\bar{Y} = \frac{Y}{n} = \underline{\underline{y}} \rightarrow \text{molal property}$$

If we consider that Y we get some more important relationship, you consider Y is a homogeneous function, now we exploit the Euler's theorem on homogeneous function so Y is a first degree homogeneous function in n’s.

Obviously Y is an extensive property it depends upon the number of moles and it has to be at a first degree homogeneous function of n. If n is increased by some factor…. if we consider dn_i at lambda n_i then Y will be increased by the same proportional factor lambda that means it is the first degree homogeneous function in s. Then by Euler's theorem we can write that the function $Y_{T,p}$ is sigma del y del n_i into n_i, this we have all ready seen. Earlier that is the Euler's function that $Y_{T,p}$ the constant temperature and pressure is equal to i 1 to r del y this is the first degree homogeneous function in n.

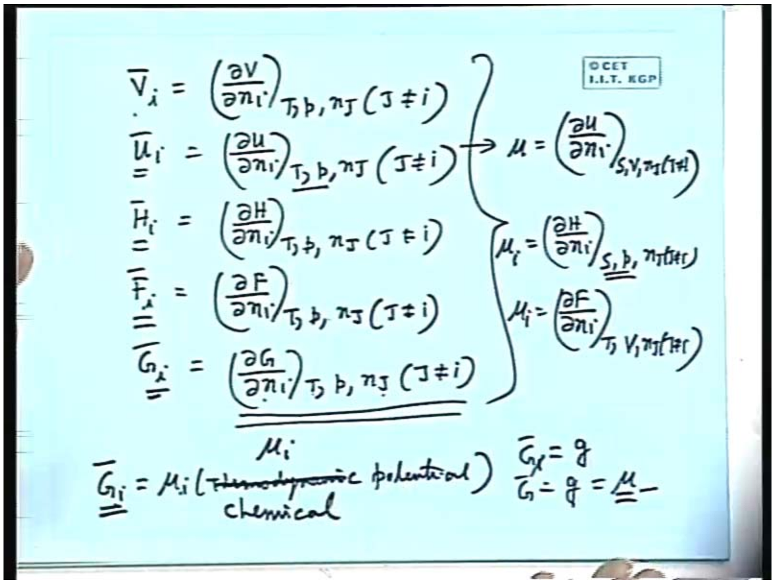
Therefore we can write this equal to del y del n_i. This del y del n_i at constant temperature and pressure n_J J not is equal to I. This is equal to Y bar i n_i so $Y_{T,p}$ is Y by r n_i therefore here also one important property comes or important conclusion comes that the extensive property of a multi component system at constant temperature and pressure is given by the sum of the partial molar properties times the number of moles.

If I know the partial molar properties of each and every component r for r number of components then the sum of the partial molar property times the number of moles of their respective component gives the total extensive property.

Here we again derive a very important conclusion that for a single component system, we get Y is equal to Y bar into n that means Y bar for a single component system is Y by n that means small y that is the molar property. For a single component system is the molar property molar Y so partial molar property is the molar Y. This is a very important relationship for a multi component system. We get this for a single component system.

Now with this as the definition of single compared with partial molar property. Now we just write the partial molar properties for different extensive properties.

(Refer Slide Time: 14:57)



© CET I.I.T. KGP

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_J\,(J \neq i)}$$

$$\underline{\underline{\bar{U}_i}} = \left(\frac{\partial U}{\partial n_i}\right)_{\underline{T,p},n_J\,(J \neq i)} \rightarrow \mu = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_J\,(J \neq i)}$$

$$\underline{\underline{\bar{H}_i}} = \left(\frac{\partial H}{\partial n_i}\right)_{T,p,n_J\,(J \neq i)} \qquad \mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{\underline{\underline{S,p}},n_J\,(J \neq i)}$$

$$\underline{\underline{\bar{F}_i}} = \left(\frac{\partial F}{\partial n_i}\right)_{T,p,n_J\,(J \neq i)} \qquad \mu_i = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_J\,(J \neq i)}$$

$$\underline{\underline{\bar{G}_i}} = \underbrace{\underline{\underline{\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_J\,(J \neq i)}}}}_{\mu_i}$$

$\underline{\underline{\bar{G}_i}} = \mu_i$ (~~thermodynamic~~ chemical potential)

$$\bar{G}_i = g$$

$$\bar{G} = g = \underline{\underline{\mu}}$$

For example, we start with the partial molar volume for an ith component, we can write del v del n_i at T p nJ J not is equal to i.

Similarly for u, we can write ui for an ith component, the similar way better we should write it this will develop your practice nJ J not is equal to i. If we have to define the partial molar enthalpy for ith component then we should write this del H del n_i at T p nJ J not is equal to i. Similarly, if we want to write the partial Helmholtz function for ith component then we write del F del ni at T p and nJ that is J not is equal to i.

Similarly, if we want to define the partial molar property for the Gibbs function of the ith component then we can write del G del n_i at T p and nJ J not equals to i. Therefore we can recollect this but one important thing that while we define the thermodynamic potential if you remember this was also the definition of thermodynamic potential mu i from there we can write the partial molar Gibbs function is the thermodynamic potential.

Thermodynamic potential was defined by many relations, if you remember that we had many definitions for thermodynamic and one of the definitions for thermodynamic potential was the del G del n_i T p nJ.

Now, it has to be made clear that the partial molar properties for other properties are not equal to thermodynamic potential. For example, if we express chemical potential with terms of u then you remember mu is equal to del u del n_i at s and v so for you remember s v nJ J not is equal to i. This is not at constant temperature and pressure very important. For ith H that means if you express chemical potential in terms of H it was del H del n_i at s and p nJ that means it is not T and p s and p for Fi it is the same differential del F del n_i but not at T and p rather T and v and of course nJ J not is equal to i.

It is only for Gibbs function, if you recollect the definition of thermodynamic potential you will see that it is only for the Gibbs function where we define the thermodynamic potential in terms of del G del n_i at constant temperature pressure and nj J not is equal to i. Therefore it is the partial molar Gibbs function which equals to thermodynamic potential very important. It is not partial molar Helmholtz function, not the partial molar enthalpy, not the partial molar internal energy, not the partial molar volume which becomes equal to the thermodynamic potential so G_i bar is thermodynamic potential.

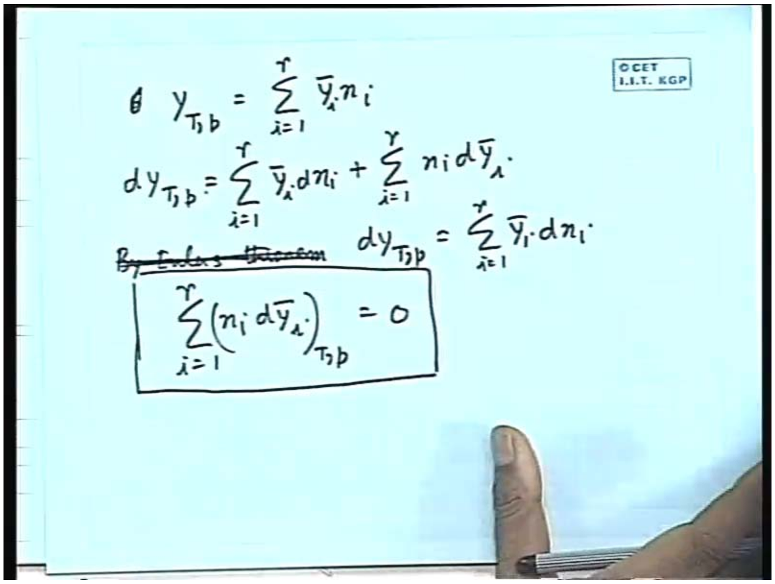
For a single component system, we know G_i bar is nothing but the molar Gibbs function just now we have seen that Y bar that is the partial molar property becomes for a single component is the molar property.

Therefore for a single component G bar is the molar Gibbs function and that becomes equal to chemical potential. For a single component system the chemical potential becomes equal to the molar Gibbs function for that single component system. Whereas for a multi component system chemical potential becomes equal to the partial molar Gibbs function.

Again I am telling for a single component system the chemical potential equals to the molar Gibbs function which is the partial molar property for a single component system. Why partial does not come there it is only the molar property molar Gibbs function but for a multi component system. Thermodynamic potential becomes equal to the partial molar Gibbs function. This is one very important relationship.

After this I will derive some other very important relationship

(Refer Slide Time: 20:35)



$$y_{T,p} = \sum_{i=1}^{r} \bar{y}_i n_i$$

$$dy_{T,p} = \sum_{i=1}^{r} \bar{y}_i dn_i + \sum_{i=1}^{r} n_i d\bar{y}_i$$

~~By Euler's theorem~~ $dy_{T,p} = \sum_{i=1}^{r} \bar{y}_i dn_i$

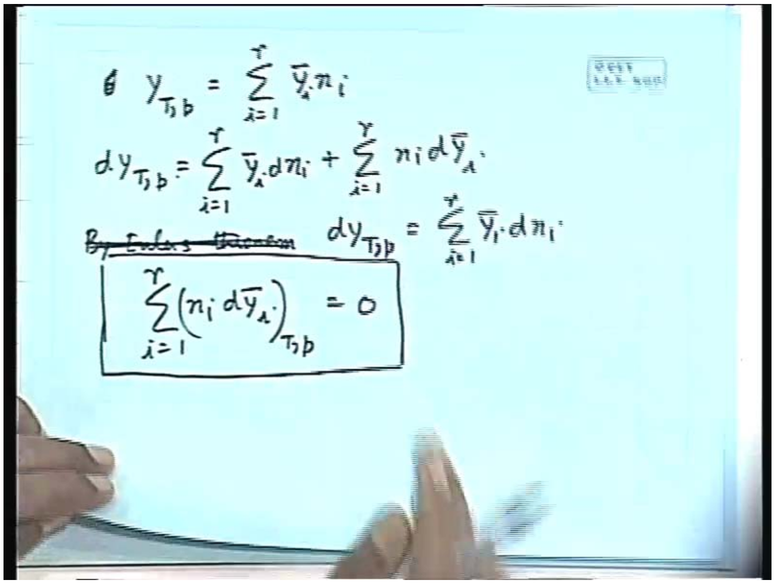
$$\boxed{\sum_{i=1}^{r} \left(n_i d\bar{y}_i\right)_{T,p} = 0}$$

If we write y at T and p we have seen is sum of the y bar n_i at constant temperature and pressure. Similarly, in the same way as we did earlier for the Gibbs function, if we make the differential at constant temperature and pressure then what we get?

y bar i dn_i plus n_i dy bar i, i 1 to r and i 1 to r so this is the relationship dy at constant temperature and pressure therefore we get that. Now $dy_{T,p}$ at the constant temperature and pressure is this one. By Euler's theorem we can write one very important thing before that we want to tell earlier we derived that $dy_{T,p}$ is sigma y_i dn_i at constant temperature.

Just now we have discussed that $dy_{T,p}$ is sigma y_i bar dn_i, i is equal to 1 to r. If you compare these two we get at constant temperature and pressure always this constant temperature and pressure thing is there, this is equal to 0. It is again one very important relationship. Just like n_i d mu_i is 0. Similarly n_i dy bar i is 0. It is very important relationship among the partial molar properties and the number of mole.

(Refer Slide Time: 22:56)



6 $y_{T,p} = \sum_{i=1}^{r} \bar{y}_i n_i$

$dy_{T,p} = \sum_{i=1}^{r} \bar{y}_i dn_i + \sum_{i=1}^{r} n_i d\bar{y}_i$

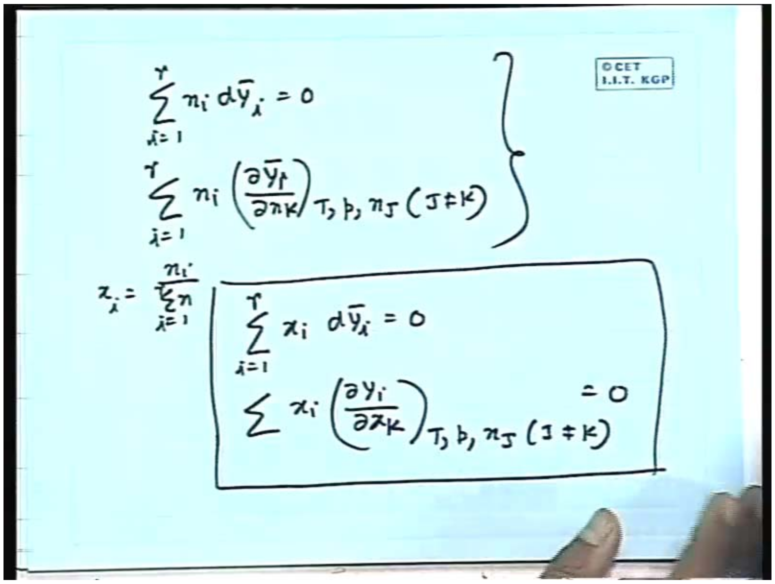
~~By Euler's theorem~~ $dy_{T,p} = \sum_{i=1}^{r} \bar{y}_i dn_i$

$$\boxed{\sum_{i=1}^{r} \left(n_i d\bar{y}_i\right)_{T,p} = 0}$$

Now I use the Euler's theorem on homogeneous function. Considering that y_i bar is a 0 degree function of n’s. Because y is a first degree homogeneous of n we know because y is an extensive property so y bar is del y del n for any particular component so from the dimension we see that if it is a first degree its differential is 0 degree so therefore partial molar property is a 0^0 homogeneous function of n so there if we put the Euler's theorem we get 0 is equal to sigma n_i del y bar del nk here we take n_k Tp and nJ J not is equal to k so this is one of the very important relationship n_k del y.

Another equation just now we have derived that sigma n_i. These two are very important relationship just now we have derived n_i dy_i bar at T and p is equal to 0. Again we write this two equations.

(Refer Slide Time: 24:44)



$$\sum_{i=1}^{r} n_i \, d\bar{y}_i = 0$$

$$\sum_{i=1}^{r} n_i \left(\frac{\partial \bar{y}_i}{\partial n_K}\right)_{T,p,n_J (J \neq K)}$$

$$x_i = \frac{n_i}{\sum_{i=1}^{r} n}$$

$$\sum_{i=1}^{r} x_i \, d\bar{y}_i = 0$$

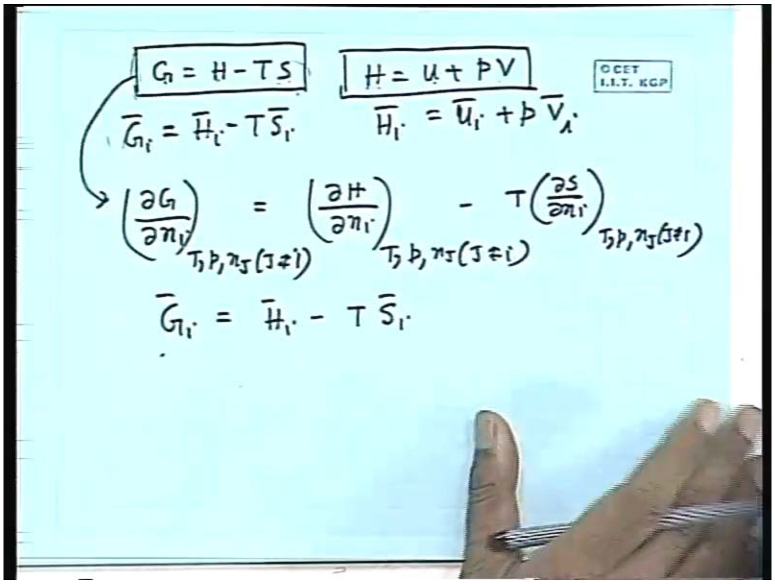
$$\sum x_i \left(\frac{\partial y_i}{\partial x_K}\right)_{T,p,n_J (J \neq K)} = 0$$

One is sigma n_i dy_i little bit mathematics is there so you will have to bear with it now in multi component thermodynamics little mathematics is there. del y bar del yi bar that is the partial molar property del nk it is from the Euler's theorem on homogeneous function considering the function y_i is a homogeneous of 0 degree in n.

These two are very important relationship. If we define a mole fraction x for an ith component as n_i by sigma n, i is equal to 1 to r then what we can write from this that if we divided the all the terms by sigma n that means the total number of moles then this equation becomes x_i dy_i bar is 0 and this equation becomes i is equal to 1 to r and this equation becomes x_i del y_i del x_k T p nJ J not is equal to k is equal to 0.

These two are sometimes very much used in multi component system, where x_i is the mole fraction of the particular ith component. We will use this equation to derive some important relations.

(Refer Slide Time: 26:37)



$\boxed{G = H - TS}$ $\boxed{H = u + pV}$

$\bar{G}_i = \bar{H}_i - T\bar{S}_i$ $\bar{H}_i = \bar{u}_i + p\bar{V}_i$

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j(j\neq i)} = \left(\frac{\partial H}{\partial n_i}\right)_{T,p,n_j(j\neq i)} - T\left(\frac{\partial S}{\partial n_i}\right)_{T,p,n_j(j\neq i)}$$

$\bar{G}_i = \bar{H}_i - T\bar{S}_i$

Before that I will tell you another important thing that we know there are certain thermodynamic relations in terms of differentials or without any differential thing. For example, G is equal to H minus T, this is a thermodynamic relation which defines Gibbs function.

H = u + pV this is a thermodynamic relation which defines enthalpy. Now this is valid for single component and the multi component system. For a multi component system G is the Gibbs function of the system as a whole H is the enthalpy of the system as a whole, S is the entropy of the system as the whole, T is the temperature. Therefore H = u + pv is also like that for the system as a whole for a multi component system also for a single component system.

Now I will show you that the same relationship can be expressed for a multi component system in terms of the partial molar property of a particular component that means for a multi component system for the ith component we can write like this H_i that means the same relationship for which that means the partial molar Gibbs function is equal to the partial molar enthalpy minus T into partial molar enthalpy.

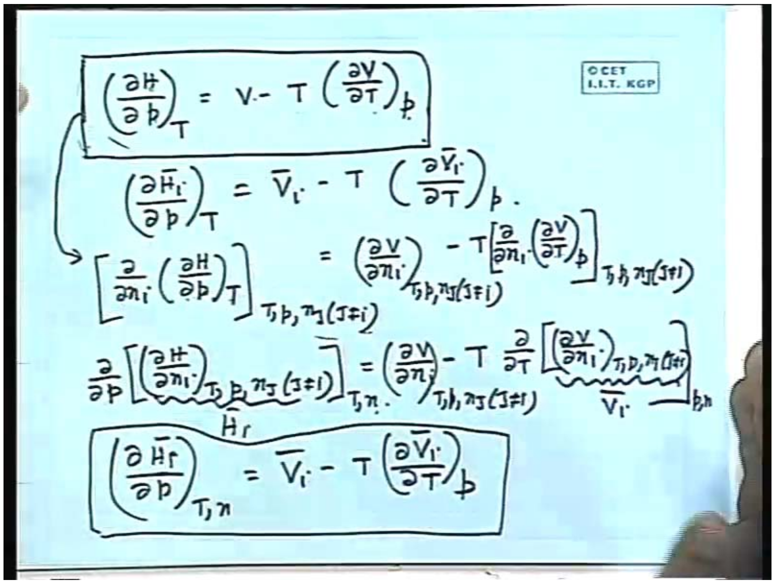
Similarly the partial molar enthalpy is partial molar internal energy plus p which means that relationship which holds good for the thermodynamic extensive property as a whole for the system holds for the partial molar property of the ith component also.

How can you prove it? Very simple you differentiate this function with respect to n_i. It is very simple at constant temperature pressure and n_J all other composition which not equals to i. Similarly this side also you do that because we have to do the same operations on both the side to maintains the equality with the same constant T p n_j J not is equal to i it is extremely simple. We are doing it at constant temperature and pressure so T is constant so therefore del s del n_i and T p n_J J not is equal to i.

By definition this is G_i bar and this is H_i bar and this becomes T S_i bar. Therefore we see that the same definition G is equal to H minus TS same relationship holds good for the partial molar component.

In the similar way we can also prove by ah taking the differentiation of H by taking the differentiation of u and V at constant p and T for both left hand and right hand side we derive the same thing.

(Refer Slide Time: 29:17)



$$\boxed{\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p}$$

$$\left(\frac{\partial \bar{H}_i}{\partial p}\right)_T = \bar{V}_i - T\left(\frac{\partial \bar{V}_i}{\partial T}\right)_p .$$

$$\left[\frac{\partial}{\partial n_i}\left(\frac{\partial H}{\partial p}\right)_T\right]_{T,p,n_J(J\neq i)} = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_J(J\neq i)} - T\left[\frac{\partial}{\partial n_i}\left(\frac{\partial V}{\partial T}\right)_p\right]_{T,p,n_J(J\neq i)}$$

$$\frac{\partial}{\partial p}\Bigg[\underbrace{\left(\frac{\partial H}{\partial n_i}\right)_{T,p,n_J(J\neq i)}}_{\bar{H}_i}\Bigg]_{T,n} = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_J(J\neq i)} - T\frac{\partial}{\partial T}\Bigg[\underbrace{\left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_J(J\neq i)}}_{\bar{V}_i}\Bigg]_{p,n}$$

$$\boxed{\left(\frac{\partial \bar{H}_i}{\partial p}\right)_{T,n} = \bar{V}_i - T\left(\frac{\partial \bar{V}_i}{\partial T}\right)_p}$$

Another thing is that this is true for the relationship in terms of differential. For example, you know a well known thermodynamic relationship del H del p at constant T is equal to v minus T del v del T at constant p so this is very important thermodynamic relationship in differential form. The earlier one was not in differential form here also we can show that del H what we are going to show that the same relationship in the differential form is also valid for the partial molar entropy of a particular component.

In case of multi component system these equation is valid as a whole for the system that means where H is the total enthalpy of the system, where v is the total volume of the system. For a single component system there is no point of any components where H is the enthalpy of the system v is the volume of the system. This is valid for a multi component system as a whole and the same relationship also like the earlier one in terms of differentiation also valid for the corresponding partial molar property of any component del v_i del T at constant p.

How to prove this thing?

This can be proved, first let us differentiate the left hand and right hand side with respect to ni that means what we do we take like this del n_i at constant T and p that means del n_i of this term del H del p at constant T that means this term we are differentiating with respect to n_i at constant T p and nJ J not is equal to i is equals to this side also we will differentiate del v del n_i with respect to ni at constant T p and nJ, J not is equal to i minus at constant T and p T remains constant del n_i of this term del v, del T at constant T p nJ J not is equal to i.

Therefore we see that first what we do? We differentiate the left hand and right hand side with respect to the number of moles n_i for a particular component i at T p constancy of the other number moles of the other components.

What we do? We interchange the order of differentiation this is possible provided this thermodynamic properties are continuous function. In a system the thermodynamic properties are continuous function so these are the properties they are the continuous function so therefore in this case the interchanging of order of differentiation is possible.

I just change it and I can write del del p of del H del n_i at constant T p n_J J not is equal to i so this term remains as it is del v del n_i minus T here also I change the order of the thing del del T that means I can write del del T of del v del n_i so del del p of this I can write at constant temperature and n because constant temperature was there so when I take del del p the differential constant temperature and n.

Similarly del del T i have taken del v del ni then changing the order of the differentiation del v del ni at T p nJ, J not is equal to i and this thing you just see like this at constant pressure and n number of moles.

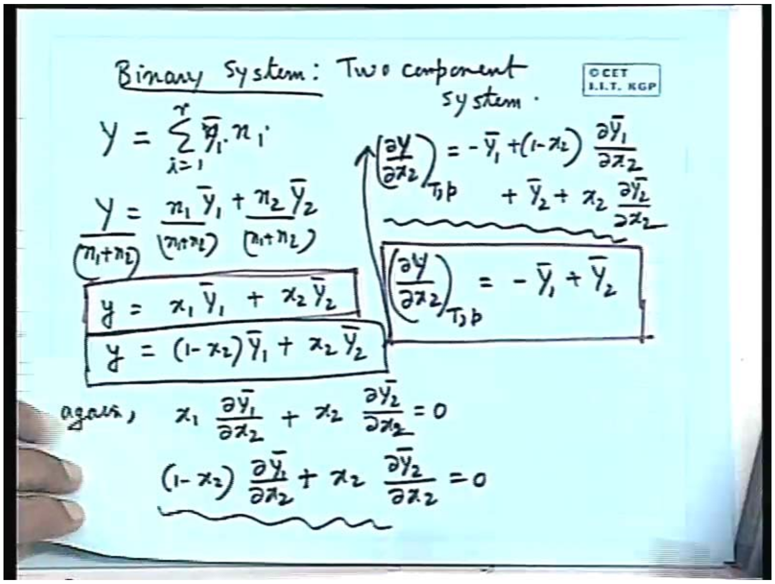
Therefore you see what is this del? This is H i bar so del H i bar del p at constant T and n is equal to this is what del v del n_i it is at constant T p n_J, J not is equal to i so this is the definition of partial molar volume minus T then this is also partial molar volume v_i so minus T del v_i bar del T at constant.

If you compare these two equations, we see that the equation is del H del p at constant temperature is equal to v minus T del v del T at constant that means thermodynamic relationship in differential form which is valid for the system as a whole a multi component system remains same if we express relation remains same. If we express this in terms of the partial molar property that means if this extensive properties of the system as a whole is replaced by the partial molar property of any component the same relationship can be used.

Therefore any thermodynamic relationship which is valid for the system as a whole is valid for the partial molar property of a component of the multi component system. Next, what I like to tell you that we all ready derived something which is very important derivation as you feel that this one so you remember this derivation that x_i dy_i bar y_i bar 0 x_i del y_i del x_k.

Now one very important thing for a binary system sometimes for the ease of working for a binary system few important equations can be made.

(Refer Slide Time: 36:00)



Binary System: Two component system.

©CET I.I.T. KGP

$$Y = \sum_{i=1}^{r} \bar{y}_i . n_i$$

$$\frac{Y}{(n_1+n_2)} = \frac{n_1}{(n_1+n_2)} \bar{y}_1 + \frac{n_2}{(n_1+n_2)} \bar{y}_2$$

$$\boxed{y = x_1 \bar{y}_1 + x_2 \bar{y}_2}$$

$$\boxed{y = (1-x_2) \bar{y}_1 + x_2 \bar{y}_2}$$

again, $$x_1 \frac{\partial \bar{y}_1}{\partial x_2} + x_2 \frac{\partial \bar{y}_2}{\partial x_2} = 0$$

$$(1-x_2) \frac{\partial \bar{y}_1}{\partial x_2} + x_2 \frac{\partial \bar{y}_2}{\partial x_2} = 0$$

$$\left(\frac{\partial y}{\partial x_2}\right)_{T,p} = -\bar{y}_1 + (1-x_2) \frac{\partial \bar{y}_1}{\partial x_2} + \bar{y}_2 + x_2 \frac{\partial \bar{y}_2}{\partial x_2}$$

$$\boxed{\left(\frac{\partial y}{\partial x_2}\right)_{T,p} = -\bar{y}_1 + \bar{y}_2}$$

Consider a binary system, binary system means two component system. Let we define component one and component two. Let Y is extensive property so we know that if Y is extensive property in a binary component system. We can write Y as we know Y is sigma n y_i bar n_i i is equal to 1 to r.

For a binary system we can write Y is n_1 y_1 bar plus n_2 y_2 bar and this we can write as, if we divided it by the total number of moles that means n_1 plus n_2 then it becomes small y that is the molar Y for the system as a whole it equal to x_1 that is the mole fraction of the component 1 and this is the mole fraction of the component 2 and x_1 we can write as 1 minus x_2 y_1 bar plus x_2 I replace or I express everything in terms of x_2.

Let us consider this equation as an important equation y is 1 minus x_2 y_1 bar plus x_2 y_2 bar. Again we can use this expression that from the Euler's theorem which we get x_i del y_i del x_k at T p n_j J not is equal to k_0 and this expression if you just remember this expression and use this for this multi component system.

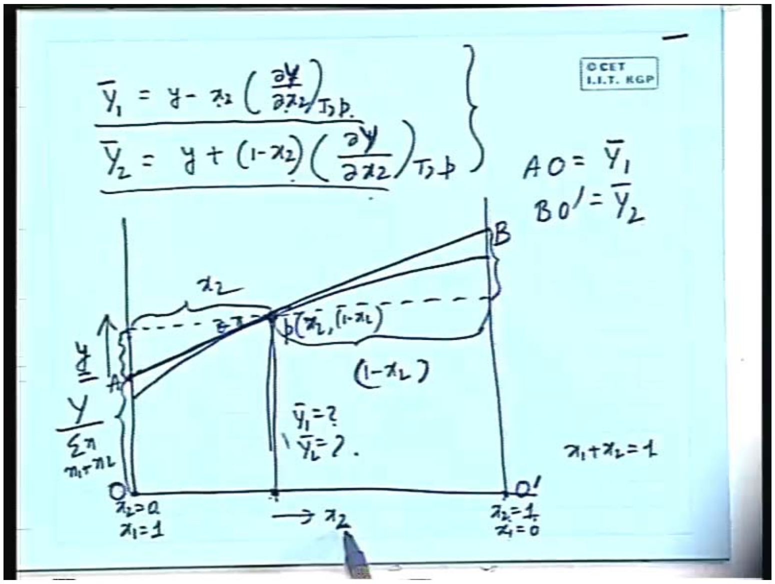
We can write x_1 del y_1 bar del x_2 where k is two we are using x_2 del y_2 bar del x_2 is 0 where what we have used. You have used this relationship x_i this is the sigma i is equal to 1 to r for a two component system it is x_1 del y_1 del $x_2$plus x_2 del y_2 del x_2. In place of x_1 I write 1 minus x_2 del y bar del x_2 plus x_2 del y_2 bar del x_2 is equal to 0. You differentiate this equation this 1 minus x_2. We differentiate this equation with respect to x_2.

If you differentiate with respect to x_2 then what we get del y del x2 at constant temperature and pressure what we get? We differentiate with respect to x_2 that means first term is minus y_1 bar second term is plus1 minus x_2 into del y_1 bar del x_2 plus y_2 bar plus x_2 del y_2 bar del x_2. Now, I am differentiating y with respect to x_2 and I get del y del x_2 is minus y_1 bar this one derivative x_2 minus 1 plus 1 minus x_2 del y_1 bar del x_2 plus y_2 bar plus x_2 del y_2 bar del x_2.

If I compare this equation with this equation now you see this plus this is 0 therefore I get is del Y del x_2 at T and p is equal to minus y_1 bar plus y_2 bar. I get these two equations one is this and another is this one y is x_1 y_1 bar plus x_2y_2 bar, remember these two equations.

If we solve these two equations for y_1 bar and y_2 bar this y_1 bar plus y_2 bar is del y del x_2 at T p and x_1 y_1 bar plus x_2 y_2 bar is y. If you solve these two equations then, what we get?

(Refer Slide Time: 41:30)



$$\bar{y}_1 = y - x_2\left(\frac{\partial y}{\partial x_2}\right)_{T,p}$$

$$\bar{y}_2 = y + (1-x_2)\left(\frac{\partial y}{\partial x_2}\right)_{T,p}$$

$AO = \bar{y}_1$

$BO' = \bar{y}_2$

If you solve these two equations then you get finally for y_1 bar you get y minus x_2 del Y del x_2 at T_2p. The small y is the molar property y for the system as a whole that means y divided by n_1 plus n2. I am solving this equation and this equation for y_1 bar and y_2 bar I get this.

Similarly I get Y_2 bar is equal to y plus 1 minus x_2 into del Y del x_2 at T and p. Now this equation has got a very good geometrical interpretation. How it is? That if I can plot this x_2 versus mole fraction of any of the components. Let us consider here the component two versus x_2. y versus x_2 that is the molar function that means Y by sigma n in this case it is n_1 plus n_2. That means the molar property if I just plot versus x_2 this y can be anything, this molar property can be partial molar volume then it will be molar volume, it maybe volume, it maybe Gibbs function, it maybe entropy, it maybe internal energy enthalpy anything .

If I denote this line or this point as $x_2=0$ and if I get that this is the line this point as $x_2=1$ now $x_2=0$ means x_1 is equal to 1 so $x_2=0$ means $x_1=1$and $x_2=1$ means here $x_1=0$ that is $x_2=1$ that means $x_1=0$ so here $x_2=0$ here $x_{2=}$ 1 here automatically $x_1=1$.

If I get a variation like this, for example, this is the variation that means this is the curve of y versus x_2 then at any point p, if I want to know any point on the curve p which has got a mole fraction x_2 and the corresponding x_1 will be 1 minus x_2. x_2 and 1 minus x_2 as the x_1 obviously because x_2 x_1 are related like this x_1 plus x_2 is equal to 1.

At this point, if I want to know what is the value of y_1 bar and y_2 bar this will follow this equation for a given value of x_2 that any $x_2$what is y_1 bar, given by this equation. What is y_2 bar, given by this equation. So at constant temperature and pressure if I have got the molar property y for different x_2 and if I can plot it then it is very simple graphically that if I draw a tangent at this point. Let this tangent is drawn at this point let this point is p and let the tangent is drawn at this point and which cuts here at A and here at B.

If I define this point as O and this point as O dash then I can write AO that means the intercept of the tangent on this ordinate where x_2 is 0 that is AO equal to Y_1 bar and the intercept of this tangent on this ordinate where x_2 is equal to 1 which is O dash B or BO dash. BO dash is equal to Y_2 bar. Now what is AO dash?

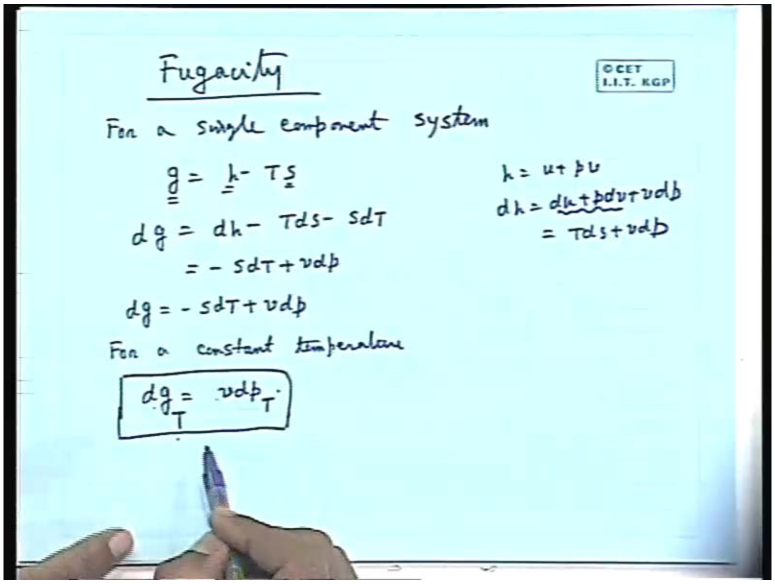
AO dash is y geometrically if you see that this is the y. This is the y minus this one and this is equal to x_2 del y del x_2 T p. del y del x_2 is slope of this line. del y del x_2 that is tan theta. If this is theta tan theta therefore this amount is x_2 del y del x_2 at T p. Therefore this minus this that means the length of this intercept AO is Y_1bar and similarly BO dash is the Y_2 bar that means this is the

Y_2 bar this can be proved that like this that this is the Y at this point. So this part is added, so this part is 1 minus x2 del y del x2 bar because if this is the x2 obviously this is 1 minus x2 that means this length is 1 minus x2 whereas this length is x_2.

Therefore, we can draw a tangent and sometimes geometrically these problems are solved that at any point on this curve y versus x_2, if we draw a tangent this cuts or the two ordinates where x_2 is 0 and x_2 1and this intercepts OA and OB. They can be taken as the partial molar properties y_1 bar and y_2 bar and this is valid for any partial molar property.

I will start a new property that is fugacity. What is fugacity?

(Refer Slide Time: 47:34)



Fugacity

©CET
I.I.T. KGP

For a single component system

$$\underline{\underline{g}} = \underline{\underline{h}} - T\underline{\underline{s}}$$

$$h = u + pv$$

$$dh = \underline{du + pdv} + vdp$$

$$= Tds + vdp$$

$$dg = dh - Tds - sdT$$

$$= -sdT + vdp$$

$$dg = -sdT + vdp$$

For a constant temperature

$$\boxed{dg_T = vdp_T}$$

First of all I tell you this concept of fugacity will be given not with respect to a multi component system but I will first tell you, what is fugacity for a single component system?

The concept of fugacity holds good for a single component system. For any single component system which does not behave as ideal gas I will tell what fugacity is because this concept of fugacity will be required to understand the dilute and ideal solutions.

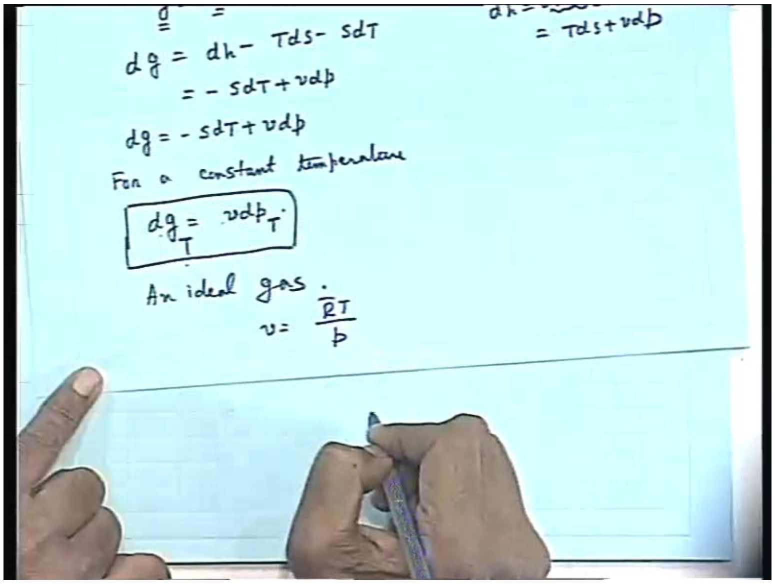
When there is a mixture of different components whether they behave as dilute solutions or ideal solutions, for that we require the concept of fugacity that is why we will first start fugacity. We know for a single component system that g = h - TS that is the molar Gibbs function molar enthalpy and if we take dg = dh - Tds – sdT. We just recapitulate this thing again and dh is du plus pdv and Tds and sdT so obviously dh is vdp minus Tds, as usual you can write dh is vdp plus Tds therefore this becomes sdT plus vdp because h is u plus pv.

If you take dh is du plus pdv plus vdp again the recapitulation of the earlier thing the basic things du plus pdv is Tds plus vdp therefore if we just substitute this dh we get dg is equal to minus sdT so this will be sdT plus vdp.

Now, for a constant temperature when temperature remains constant we can write dg is equal to vdp at constant temperature vdp at constant temperature. This is a very important relationship in thermodynamic that is the molar Gibbs function for a single component pure substance dgT is vdp$_T$ at constant temperature dg is vdp.

If we consider the system as an ideal gas, then we can write v as R bar T by p, where R bar is the universal gas constant. Then we can write this dg$_T$ vdp is like this.

(Refer Slide Time: 50:31)



$= Tds + vdp$

$dg = dh - Tds - sdT$

$= -sdT + vdp$

$dg = -sdT + vdp$

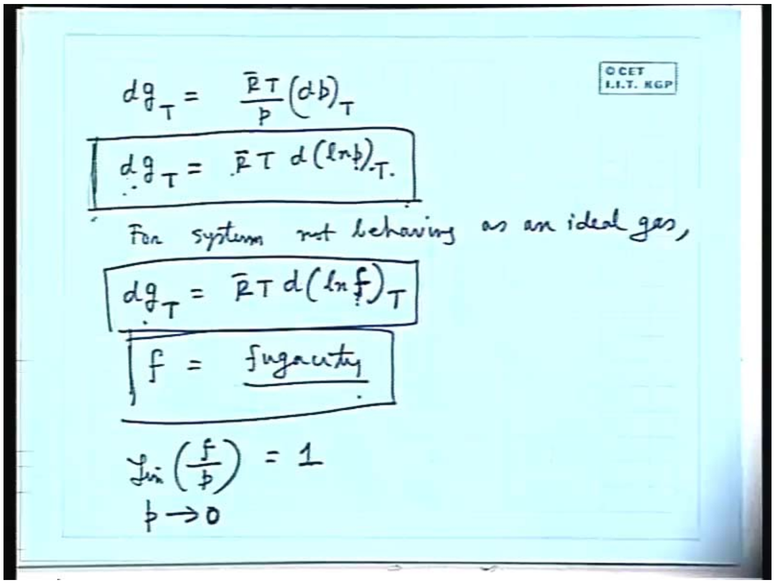
For a constant temperature

$\boxed{dg_T = vdp_T}$

An ideal gas

$v = \frac{\bar{R}T}{p}$

(Refer Slide Time: 50:55)



$$dg_T = \frac{\bar{R}T}{p}(dp)_T$$

$$\boxed{dg_T = \bar{R}T\, d(\ln p)_T}$$

For system not behaving as an ideal gas,

$$\boxed{dg_T = \bar{R}T\, d(\ln f)_T}$$

$$\boxed{f = \underline{\text{fugacity}}}$$

$$\lim_{p \to 0}\left(\frac{f}{p}\right) = 1$$

dg_T is R bar T by p dp, this is at constant dp so dp by T we can write as dg_T as R bar T d of lnp at constant T because dp by p is lnp. This is the relationship which holds good for an ideal gas so it has to be a single component system and for an ideal gas if the system behaves like an ideal gas then this dg at constant temperature becomes equal to R bar T into d lnp T.

It has been seen that in many thermodynamic relationships with multiple component system, it is very important to retain this function. This functional form is very useful and it has been shown that this functional form has to be retained in many applications for multi component system.

Even if the system does not behave as an idea gas, If we want to retain this type of functional relationship in terms of this ln to express the molar Gibbs function as this it is very useful then what we can do we cannot use p we can define a function f as a property which makes the same relationship for dg that means the change in the molar Gibbs function at constant T for an ideal gas that means instead of p we defined a function f for non ideal gas systems so that, for same functional relationship for dg at constant temperature can be expressed then this f is known as fugacity.

Fugacity of a system is same as that of a pressure in an ideal gas, its unit is same and its sense is also same and you can tell this way that fugacity of a system does the same thing as the pressure of an ideal gas does with respect to the change in the molar Gibbs function so this is the basic definition of fugacity.

From this it is clear that the limit of f by p, f is not p but f tends to p when p tends to 0 why? because at very low pressure any gas behaves as an ideal gas but if the pressure is increased the deviation is there so that the fugacity is not equal to pressure.

Today I will end here, next class I will discuss it in detail.

Thank you.