Basic Thermodynamics

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Lecture - 30

Thermodynamics of Multi Component System – I

Good morning. Welcome to the session of Thermodynamics. Today, I will start with thermodynamics of multi component system. While discussing thermodynamics of reactive systems, we have recognized some part of thermodynamics of multi component systems through the use of certain concepts and formulas. This is because a reaction involves number of species and components. As we have seen, in the reactants there is usually more than one component. Similarly in the products there are more than one component so we recognize some of the rules and information on thermodynamics of multi component system. Today, we will discuss it in detail.

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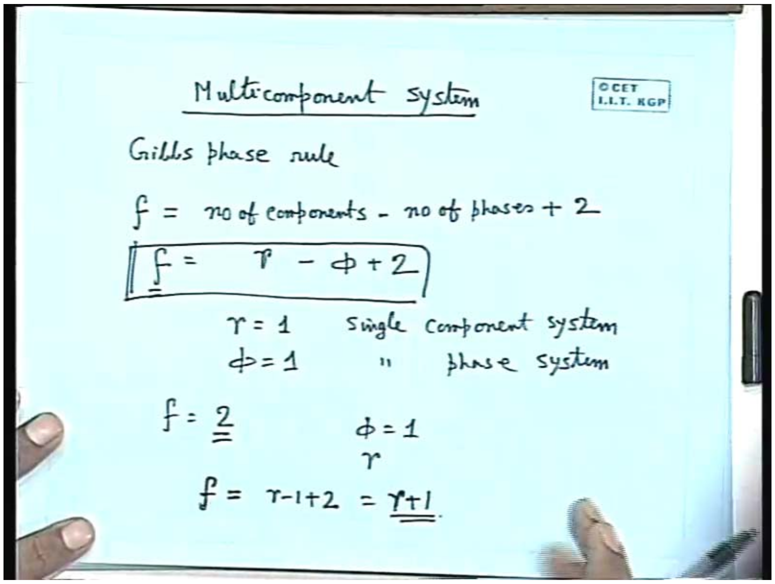

Multicomponent system

Gibbs phase rule

$f =$ no of components − no of phases + 2

$$\boxed{\underline{f} = r - \phi + 2}$$

$r = 1$ Single component system

$\phi = 1$ " phase system

$\underline{\underline{f = 2}}$ $\quad \phi = 1$

r

$f = r - 1 + 2 = \underline{\underline{r + 1}}$

At the outset, let us recall one thing, while we first discussed about the state variables. For a system at equilibrium, the properties are fixed and we require minimum number of properties as the independent variables or independent properties, so that if they are fixed other properties are fixed. This number of independent variables or independent properties required to fix the equilibrium state of a system, depends upon the number of components and the number of phases of the system. This is given by a formula known as Gibbs phase rule.

Gibbs phase rule gives the number of independent variables or properties to fix the equilibrium state of a system, where f is the number of independent properties and is equal to the number of components of a system minus number of phases plus 2. Let us denote the number of components as r and number of phases as phi. f determines the number of independent intensive properties that is required to fix the equilibrium state of the system.

Let us take an example, simple case which we had discussed so far. If this is a single component system $r = 1$ and a single phase system phi (φ) = 1. We get $f = 2$, that means there are a minimum of two properties are required and they are sufficient, which means two properties are required to fix the equilibrium state of a system, all other properties are automatically fixed. This comes from the Gibbs phase rule for a single component, single phase system. If, number of components and phases are more than one then, the minimum numbers of independent intensive properties are more according to this Gibbs phase rule.

For example, if we consider a single phase system with r components, then $f = r + 1$ that means, for a single phase system consisting of r components number of independent intensive properties required to fix the equilibrium state of the system is equal to $r + 1$. Thus, from the Gibbs phase rule, we can find out the number of independent intensive properties required to fix the state of the system.

Let us consider an extensive property. There are large numbers of extensive properties as we know whose specific values; that is, the extensive properties per unit must become intensive properties. For example, specific internal energy, specific enthalpy, internal energy enthalpy, Helmholtz function, Gibbs function volume, is the extensive property. Similarly, specific internal energy, specific volume, specific enthalpy, specific Helmholtz function, specific Gibbs function, are the intensive property. Let us start with such an extensive property.

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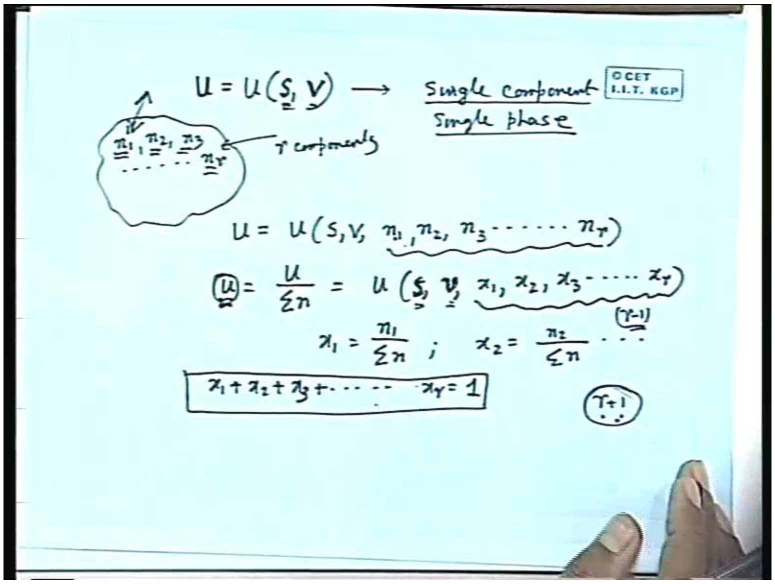

$U = U(\underline{\underline{S}}, \underline{\underline{V}}) \longrightarrow$ Single component / Single phase

$$U = U(S, V, \underbrace{n_1, n_2, n_3 \cdots\cdots n_r})$$

$$\underline{u} = \frac{U}{\Sigma n} = u(\underline{S}, \underline{V}, \underbrace{x_1, x_2, x_3 \cdots\cdots x_r}_{(r-1)})$$

$$x_1 = \frac{n_1}{\Sigma n}; \quad x_2 = \frac{n_2}{\Sigma n} \cdots$$

$$\boxed{x_1 + x_2 + x_3 + \cdots\cdots x_r = 1}$$

$r+1$

For example; U, the total internal energy which should be a function of any two other properties for a single phase single component system. Let them be expressed as a function of S and V. I will not consider a multi-phase system. Let us consider a single component system, where the extensive property U, the total energy is a function of S and V. S and V are the two independent properties to express the function of internal energy. S is the total entropy of an extensive property and V is the total volume which is also extensive properties.

If we consider a system consisting of r components and each component have number of moles as n_1, n_2, n_3… n_r; which means the system has r components. The system is an open system, which allows the material flux that means material can flow in and out. This is valid for all the components. The number of moles n_1, n_2, n_3,……n_r may vary as the system interacts with the surroundings, there is a change in the number of moles because of the material influx and efflux of the different constituents or components. Therefore, we consider a system of r components. In that case we can write U as a function of S V and all other number of moles. The composition of the constituents, which means that there are r number of components and depends upon the number of moles of the r constituents. This this is an extensive property.

If you write an intensive property for this system, if you divide it by the number of moles, U by sigma n, then you see U as a function of S V and n_1 by sigma n_i denote as x_1, this is the mole fractions. I check the Gibbs phase rule first. x_1 is n_1 by sigma n and x_2 is n_2 by sigma n. This mole fraction also satisfies the equation x_1+ x_2+ x_{3+}.... x_r is 1this is one constraining equation. Out of these r quantities, in terms of the mole fractions, they are all not independent; there are only r - 1 independent quantity, plus these two independent quantities.

Finally r + 1 number of independent quantities which is tally with the Gibbs phase rule. For r number of components in a single phase the intensive property U, this is a function of r + 1. This will be small s, this will be small v. We require r + 1 number of intensive properties to fix any properties. That means, any of the intensive properties can be expressed as a function of r + 1 number of intensive properties which are the independent parameters or independent variable. This is compatibility with the Gibbs phase rule.

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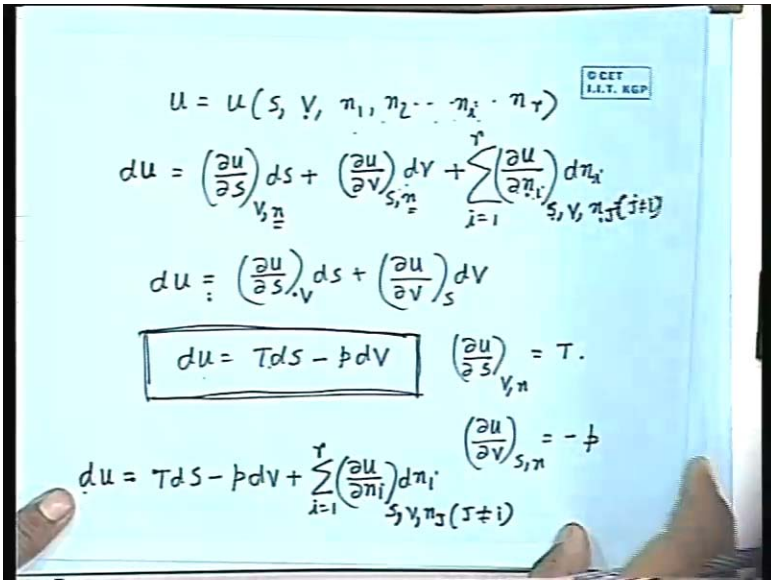

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$$u = u(s, v, n_1, n_2 \cdots n_i \cdot n_r)$$

$$du = \left(\frac{\partial u}{\partial s}\right)_{v,\underline{n}} ds + \left(\frac{\partial u}{\partial v}\right)_{s,\underline{n}} dv + \sum_{i=1}^{r}\left(\frac{\partial u}{\partial n_i}\right)_{s,v,n_j(j\neq i)} dn_i$$

$$du = \left(\frac{\partial u}{\partial s}\right)_{v} ds + \left(\frac{\partial u}{\partial v}\right)_{s} dV$$

$$\boxed{du = Tds - p\,dV} \qquad \left(\frac{\partial u}{\partial s}\right)_{v,n} = T.$$

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

$$du = TdS - p\,dv + \sum_{i=1}^{r}\left(\frac{\partial u}{\partial n_i}\right)_{s,v,n_j(j\neq i)} dn_i$$

U is a function of total internal energy, total entropy, total volume n_1, n_2….n_r. In a single component system, U is a function of S V, but in a multi component system consisting of r components, there will be n_1, n_2, $n_{3,}$…..n_r respective number of moles for the components. We can write, U as a function of S V and the number of moles. If we make the total differential, a small change in U can be written in terms of del U del s at constant v n ds. This is simply an expansion in the differential form. del U del v is an expansion, neglecting the higher order term.

This is elementary mathematics, where s n dv U is the function of s. If it could have been a function of sv, then it could have been sufficient and n would not be there.

Now, there are r number of n's so, there will be terms like this; del U del n_i where i is at i^{th} constituents sigma at constant s, constant v and constant number of moles nj, where j ≠ i. This is for dni and this has to be done for all the constituents. The sum of I is equal to 1 to r. We see an additional term, del U del ni dni at constant s, constant v and constant number of moles, except this one. When we take a differential with respect to the number of moles of the i^{th} constituent, then the composition of all other components remain the same. So, we can write this equation.

At the same time, we know that for a single component system, du is del U del s at v ds, where n is constant that means del U del v at s dv. We know the property relation du is Tds minus pdv. For a pure substance, the property relation du is Tds minus pdv. If you compare this equation with this one, or the first two terms of this, The first two terms are similar to this term as for a single component system; because here n remains constant.

When all n remains constant, it behaves as a single component system of a homogeneous composition. Therefore we can write the first term as T, and this term as minus v, that means we can write del U del s at constant v n at T. Similarly, we can write del U del v at s and n is minus v. By substituting this, I can write du is equal to Tds minus pdv plus del U del ni; the same terms as dni. This partial differential is at constant S V and the composition of all components except with which it is differentiated. Which means nj, where j ≠ i. Therefore, for a single component system this is the property relation.

If we have a multi component system, the same property relation can be written with an additional term in the right hand side; Tds minus pdv. When the composition does not change at all in a multi component system, it behaves like a single component system and these terms are 0. Sigma i is equal to 1to r, and then du becomes Tds minus pdv.

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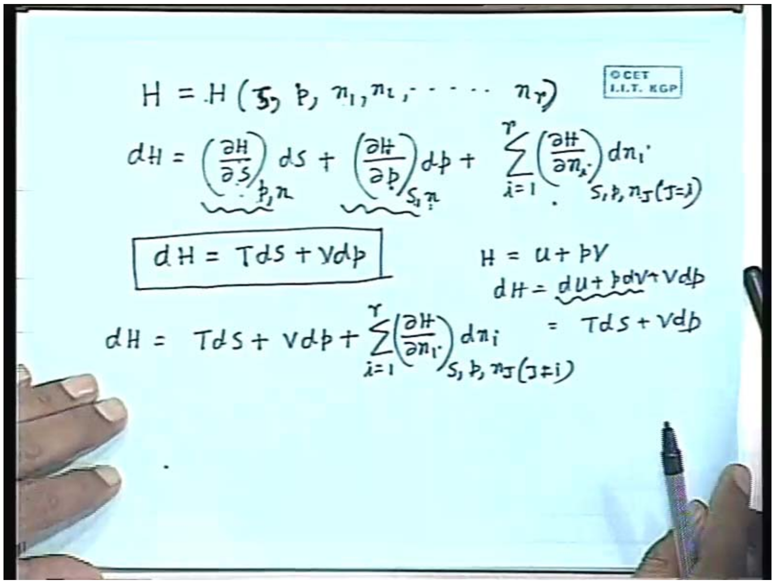

$$H = H(s, p, n_1, n_2, \cdots\cdots n_r)$$

$$dH = \underbrace{\left(\frac{\partial H}{\partial s}\right)_{p,n}} ds + \underbrace{\left(\frac{\partial H}{\partial p}\right)_{s,n}} dp + \sum_{i=1}^{r}\left(\frac{\partial H}{\partial n_i}\right)_{s,p,n_j(j=i)} dn_i$$

$$\boxed{dH = Tds + Vdp}$$

$$H = U + pV$$

$$dH = \underbrace{dU + pdV} + Vdp$$

$$= Tds + Vdp$$

$$dH = Tds + Vdp + \sum_{i=1}^{r}\left(\frac{\partial H}{\partial n_i}\right)_{s,p,n_j(j\neq i)} dn_i$$

Let us find a similar relation. If we start with H, the enthalpy of the same multi component system comprises r constituents as a function of s, p and number of moles. The implications of these will be clear from the concept that why we are expressing U as a function of s and v and the number of moles.

Why you are express H as a function of s and p?

By definition, U is always the internal energy. But we expressed it in terms of entropy and volume. In a closed system, volume remains constant; then we can take this change in U an indication of certain energy potential. Here this volume is not constant, but there is a concept for which U is expressed in terms of s and v; H is expressed in terms of s and p.

Let us first follow a routine manner, as if we can do it because, by mathematics we can express these in terms of any two properties. H can be expressed in terms of s and p. Now, dH is equal to del H by del s at p and n ds plus del H del p, because p is the variable as the pressure at constant s and n dp plus summation of all the differentials with respect to the number of moles del H del ni; where s p and nj are the number of moles of all the constituents, except the constituents whose moles is differentiated. That means $j \neq i$ dn_i and this is the summation of i_1 to r.

For a single component system these are the two terms. Again we can write, dH from property relations as Tds. dH is du + pdv + vdp and du + pdv is Tds + vdp. You can recall it like this. You do not have to remember the property relation. You have to remember the definition of H is U + pv. Therefore, it comes automatically as, du + pdv + vdp. du + pdv is Tds. This property relation tells that, if H is expressed in terms of s and p, then T is del H del s at p and n, and v is del H del p at s and n, where n is constant.

In a single component system, n remains constant. In a multi component system, all n's are held constant then this part is 0 and behaves as a single component system. You can replace this as T and this as v. Therefore, dH is Tds plus vdp plus i is equal to 1 to r del H del ni s p nj, where j not is equal to i dn_i. This is another important equation.

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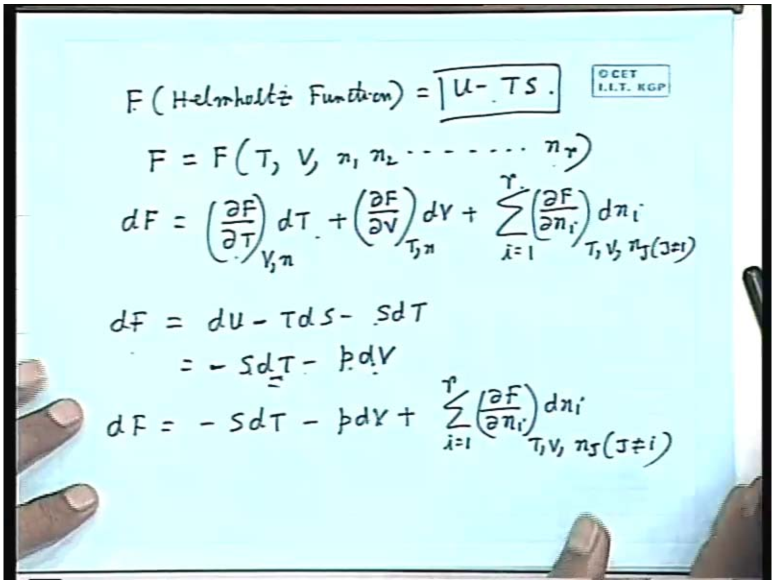

$$F\ (\text{Helmholtz Function}) = \boxed{U - TS.}$$

$$F = F(T, V, n_1, n_2 \cdots\cdots n_r)$$

$$dF = \left(\frac{\partial F}{\partial T}\right)_{V,n} dT + \left(\frac{\partial F}{\partial V}\right)_{T,n} dV + \sum_{i=1}^{r} \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_J(J\neq i)} dn_i$$

$$dF = dU - TdS - SdT$$

$$= -SdT - pdV$$

$$dF = -SdT - pdV + \sum_{i=1}^{r} \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_J(J\neq i)} dn_i$$

In the similar way Helmholtz function was defined as; F = U – Ts. If Helmholtz function is an extensive property of the system and let us consider T V at the variables. Implication of these two particular properties T V will be made clear. If the number of moles of the r components constitutes the system, then we can follow in the same similar manner of dF is del F del T at constant v n, dT + del F del V at constant T n, dv plus; again the same thing, the sum of del F del ni; that means the mole of the i^{th} component and it is for T V and nj, where j ≠ i dni and this summation is for all the components one to r.

From this relationship, we can express the differential, dF in terms of dT and dv. If we differentiate dF, you can also differentiate du - Tds – sdT. Tds is du + pdv, then du, du cancels. plus pdv, so it will be -sdT – pdv. Therefore, we can express F in terms of dT and dv for a single component system. For a single component system; dF is minus sdT minus pdv. We will stop here for a multi component system.

If ni, then there will not be any variation in all the moles of the constituting components, but here, it is not so. Therefore, we will substitute this as s and p; and this as minus p, as we did earlier and we get; sTd - pdv + the additional term. So, always we see the additional term comes as, del F del n_i dn_i and this partial derivative T V nj where j ≠ i. The summation i = 1 to r. Similarly, I can derive another extensive property. There are four very important extensive properties.

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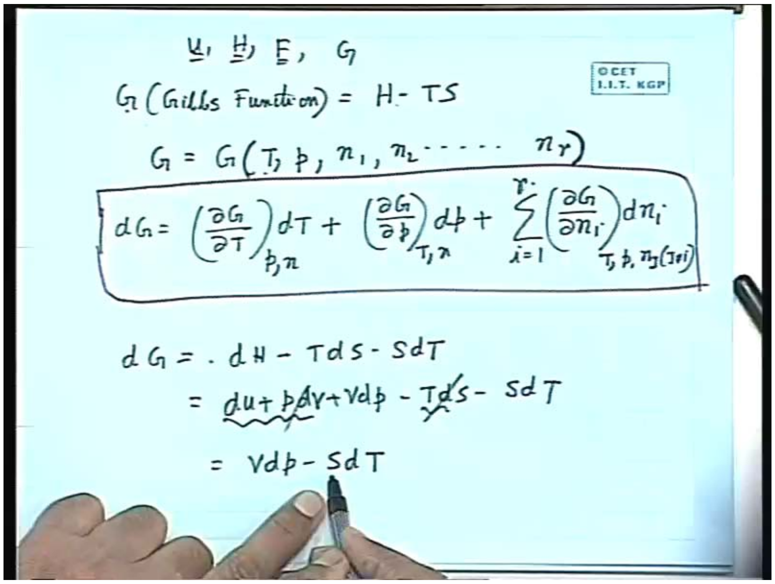

$\underline{U}, \underline{H}, \underline{F}, G$

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$G\,(\text{Gibbs Function}) = H - TS$

$G = G(T, p, n_1, n_2 \cdots\cdots n_r)$

$$\boxed{dG = \left(\frac{\partial G}{\partial T}\right)_{p,n} dT + \left(\frac{\partial G}{\partial p}\right)_{T,n} dp + \sum_{i=1}^{r} \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j(j\neq i)} dn_i}$$

$$\begin{aligned} dG &= dH - Tds - SdT \\ &= \cancel{du + p\,dv} + Vdp - \cancel{Tds} - SdT \\ &= Vdp - SdT \end{aligned}$$

U, internal energy, enthalpy H, and Helmholtz function. Now, we will go to Gibbs function, G. This property is defined as H – Ts. If there will be an implication with G as a function of T and p. F was expressed as a function of T and V. Here it is T and p. and n1, n2…. You could appreciate these implications while we discussed the energy. We have seen the implication of G. When temperature and pressure remains constant it is the change in the Gibbs function which gives the availability of the maximum useful work. The temperature and pressure is same as that of the surrounding, when the system interacts with the surrounding.

I can write this in the similar fashion as, del G del T this is again a routine matter; p n dT plus del G del p at T n dp, plus del G del n_i $dn_{i,}$ where T p and nj, j ≠ i are held constant. This summation is taken from i = to one to r.

Now, we have got four equations. U is one du, we get this equation, then for H we got these equations, for F we got this equation, and lastly for G we have got this equation. I will write all these four equations in the same place for better understanding.

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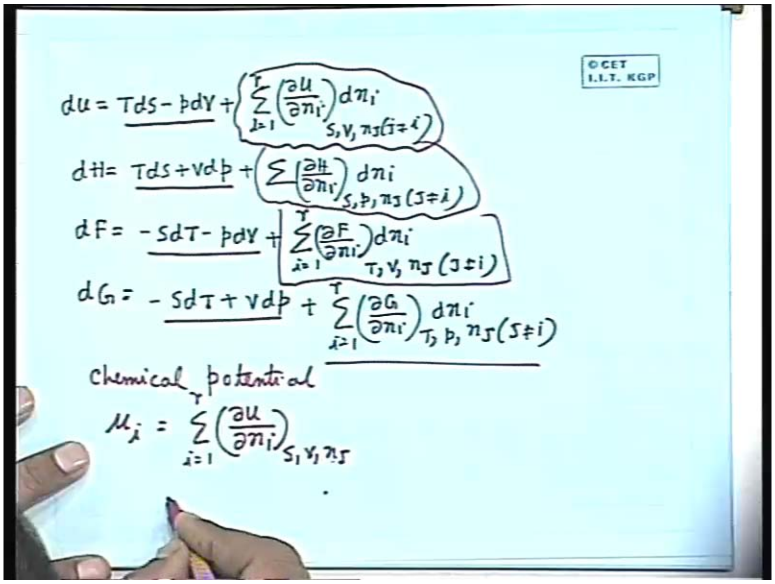

$$du = \underline{Tds - pdv} + \sum_{i=1}^{r}\left(\frac{\partial u}{\partial n_i}\right)_{s,v,n_j(j\neq i)} dn_i$$

$$dH = \underline{Tds + vdp} + \sum\left(\frac{\partial H}{\partial n_i}\right)_{s,p,n_j(j\neq i)} dn_i$$

$$dF = \underline{-sdT - pdv} + \sum_{i=1}^{r}\left(\frac{\partial F}{\partial n_i}\right)_{T,v,n_j(j\neq i)} dn_i$$

$$dG = \underline{-sdT + vdp} + \underline{\sum_{i=1}^{r}\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j(j\neq i)} dn_i}$$

Chemical potential

$$\mu_i = \sum_{i=1}^{r}\left(\frac{\partial u}{\partial n_i}\right)_{s,v,n_j}$$

Let us first write U here; dU = Tds - pdv + sigma i is equal to one to r del U del n_i dn_i,S where s v and v and nj J ≠ i. Similarly, for H; dH = Tds + vdp + sigma del H del n_i s p and nj j ≠ i dni. For Helmholtz function, dF is the basic first two terms and same for the single component dF is the property relation - sdT – pdv + sigma del F del ni. dni, T V and nj j ≠ i, therefore, i = 1 to i.

Similarly, if I write dG, the Gibbs function becomes equal to….. Before that, we have to write dG. To make the differential G, from this so this we have learnt earlier, again Tds – sdT; and dH is du + pdv + vdp. So, du + pdv and Tds cancel. dG is vdp – sdT, that means, s becomes equal to del G del T at constant p and n, if G could have been expressed in terms of p and T. dG becomes this into dp, this into dT, means this is del G del T; that means in place of del G del T we put minus s and in place of del G del p we will put v. We are not separately putting it here we state we will put it here that - sdT + vdp. That means in this equation, I' am putting s instead of this and v instead of this plus this term sigma del G del ni well T P nj j ≠ i dni and this summation is from i.

In these four equations carefully, first two parts are similar to the single component system, but this additional part is there for multi component system comprising of r components. This is defined as the chemical potential. Chemical potential is defined for a particular constituent or a component that means each component has got different chemical potential. So for a chemical potential of ith component; mu_i is defined as any one of these derivatives, that means it is defined either as del U del ni that means the derivative i = 1 to r s v nj.

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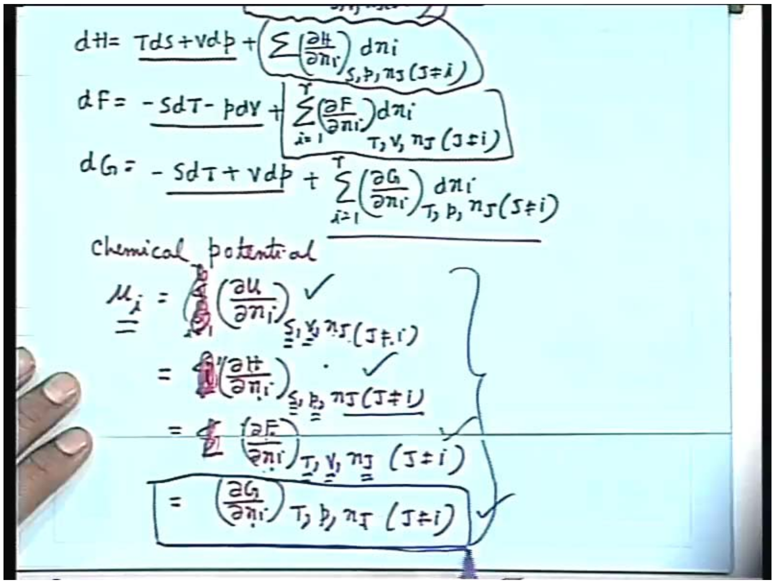

$$dH = \underline{Tds + vdp} + \left(\sum \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_J(J\neq i)} dn_i\right)$$

$$dF = \underline{-SdT - pdV} + \sum_{i=1}^{r} \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_J(J\neq i)} dn_i$$

$$dG = \underline{-SdT + Vdp} + \underline{\sum_{i=1}^{r} \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_J(J\neq i)} dn_i}$$

Chemical potential

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_J(J\neq i)} \checkmark$$

$$= \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_J(J\neq i)} \checkmark$$

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

$$\boxed{= \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_J(J\neq i)}} \checkmark$$

The chemical potential may be define by; del H any one of these can be the definition of the chemical potential depending upon the cases; nj j not equal to i. del F del n_i at T V nj j not equal to i or equals to any one of these, del G del ni at T p nj, j not equal to i. This gives the definition of a chemical potential of the i^{th} component, del U del n. Chemical potential, can give a physical definition by mathematical statement.

Chemical potential can be defined either as rate of change of internal energy with respect to the number of moles of that component, when entropy, volume and composition of the other components remains same; or it can be defined as, the rate of change of enthalpy with respect to the number of moles of that particular component for which the chemical potential is defined when the entropy pressure and the number of moles of other components are fixed.

Similarly, it can be defined as the rate of change of Helmholtz function, with respect to the number of moles of the component for which the chemical potential is defined when temperature volume and the number of moles of other components are fixed for the system. Similarly it can defined as, the rates of change of Gibbs function with respect to the number of moles when temperature pressure and the number of moles of other components are fixed. Any one of these four can be defined, but conventionally this is defined as the chemical potential of a multi component system del G del n_i.

From these four equations, the chemical potential is an indication of a change of certain energy quantity with respect to the number of moles, when a constant is placed on the process executed by the system. When we consider U as that energy quantity, then s v is constant. H, then s p is constant, F then T and v are constant, if G, T and p constant. For example, if we take this definition, then we can tell physically that, chemical potential of a system is like this. If there is a system of r component with constant temperature and pressure and allows any process because; it is a multi component system.

In a single component system, if the temperature, pressure and other properties are fixed; then the system is at a fixed state. Therefore, no process takes place. But, in the multi component system this may happen. As we have already recognized earlier in case of reactive system, that reaction can take place at constant temperature and pressure. Mass transfer process can take place at constant temperature or pressure. This can happen because of the flow of material in and out, that means there may be a change in the number of mole.

If a system changes its state, like a multi component system at constant temperature and pressure, then the change in the Gibbs function with respect to the change of the number of moles of a system, which can be caused by mass transfer, addition or removal of the materials or by chemical reaction, is the index of the chemical potential of that particular constituent or component. If the chemical potential is high, that means for a small change in the number of moles there is a large change in the Gibbs function, which is an index of the energy. At constant temperature and pressure the change in the Gibbs function gives a change in the energy quantity.

If you remember in case of availability, if there is a single component system interacts with the surroundings and the temperature and pressure remains constant with that of the surrounding. The change in Gibbs function gives the maximum useful work that we can get out of the system. This gives energy is a concept of work potential. Here you see these are the short term energy potential.

They are derived with respect to the number of moles, which means change with the change in the number of moles of a particular component with some constant in the process executed by the system is physically the concept of a chemical potential which can be defined in terms of internal energy, in terms of enthalpy that means, the change of internal energy with respect to change in the number of moles in terms of enthalpy change; in the enthalpy with the change in the number of moles in terms of Helmholtz energy and in terms of Gibbs energy as given by these equations which we have written.

Any of these equations can be the definitions of the chemical potential of the ith element. Usually this definition is used to symbolize or to express the chemical potential of an ith component. If I use the nomenclature; mu_i then I can replace all these by mu_i and can write,

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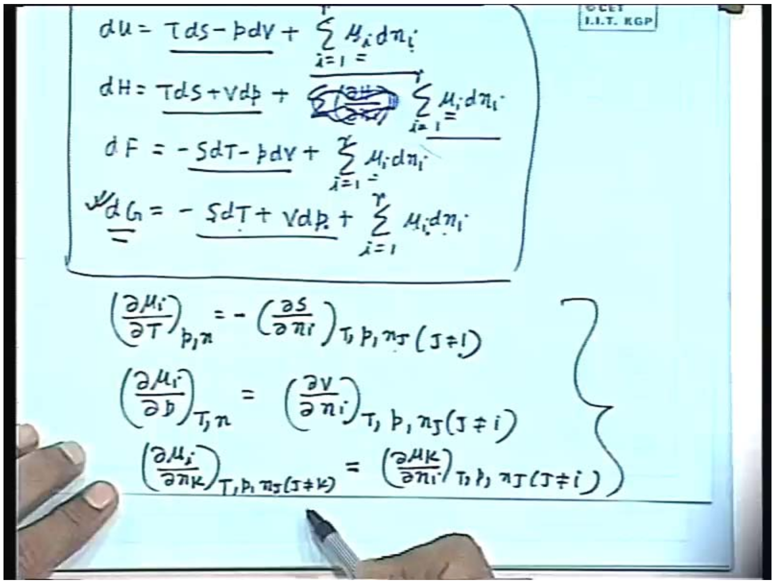

$$du = Tds - pdv + \sum_{i=1}^{r} \mu_i dn_i$$

$$dH = Tds + vdp + \sum_{i=1}^{r} \mu_i dn_i$$

$$dF = -SdT - pdv + \sum_{i=1}^{r} \mu_i dn_i$$

$$dG = -SdT + vdp + \sum_{i=1}^{r} \mu_i dn_i$$

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,n} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,p,n_J(J \neq I)}$$

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,n} = \left(\frac{\partial v}{\partial n_i}\right)_{T,p,n_J(J \neq i)}$$

$$\left(\frac{\partial \mu_i}{\partial n_K}\right)_{T,p,n_J(J \neq K)} = \left(\frac{\partial \mu_K}{\partial n_i}\right)_{T,p,n_J(J \neq i)}$$

du = Tds - pdv + sigma mu$_i$ dn$_i$; i = 1 to r. Similarly, I can write d$_H$ is Tds + vdp + sigma mu$_i$ dn$_i$. We can write in short, and we do not have to write all the differential terms; -sdT - pdv + mu$_i$ dn$_i$. But, in all equations the definitions of mu$_i$ are different; that they are expressed as different quantities. So, dG = - sdT + vdp, in terms of the chemical potential. I can write mu$_i$ dn$_i$ = 1 to r. Therefore, we see that in a multi component system the additional terms, apart from these two which we recognized earlier in a single component system, here is an additional third term.

There are a number of terms because; the additional term is the sum of mu$_i$ dn$_i$. Chemical potential of the element multiplied with the change in the number of moles of that component. These are the extra terms added, and this is the concept of chemical potential. Now, I will write other relations; this is the routine and from these expressions if we can have several other thermodynamic property relations. For example, if we consider this one first; this is exact differential equation so we can use this to develop certain other relationship. If we use this, then we can write del mu$_i$ del T at constant p and n = - del s. Thus, we can generate a number of such nj j $\neq$ i.

For chemical thermodynamic relation; del mu$_i$ del T at p and n constant. del mu i del T will be equal to del s that means, del s del n$_i$ at constant Tnp and other range. This is the property of the exact differential. If, dG is the exact differential, differentiate these with respect to another variable, which will be equal to the differential of these with respect to these variables that we have already recognized earlier and derived other property relation.

Similarly we can write del mu$_i$ del p that means I differentiate this with respect to del mu$_i$ del p and constant T and n. It will be equal to del v del n$_i$, which will be equal to T and del v del ni T and p; except nit hat means nj j ≠ i. We can get this type of relationship from exact differentials for each of these, even their number of terms. I can write del mu$_k$ del mu$_i$. For example, i and k are the two general components.

Differentiation of the chemical potential of the ith component, with respect to the number of moles of the kth component at all these T p and nj j not equal to k equals to del mu$_k$ del ni T p and nj j not equal to i. These are the relationships which are being found thermodynamic relation; by exploiting the properties of the exact differentials of G. G is the exact differential, that means the coefficients of the differential quantity, dT dpd coefficient. They are being cross differentiated partially and can be equated like this.

We can write equations from similar property relations. We can derive from this equation dH and du. I just write the relationship which we can derive from this equation. If you differentiate mu$_i$ with respect to T, at constant v and n, it will be equal to the differential of s with respect to n$_i$ at constant T V and other. We can write the relationship as;

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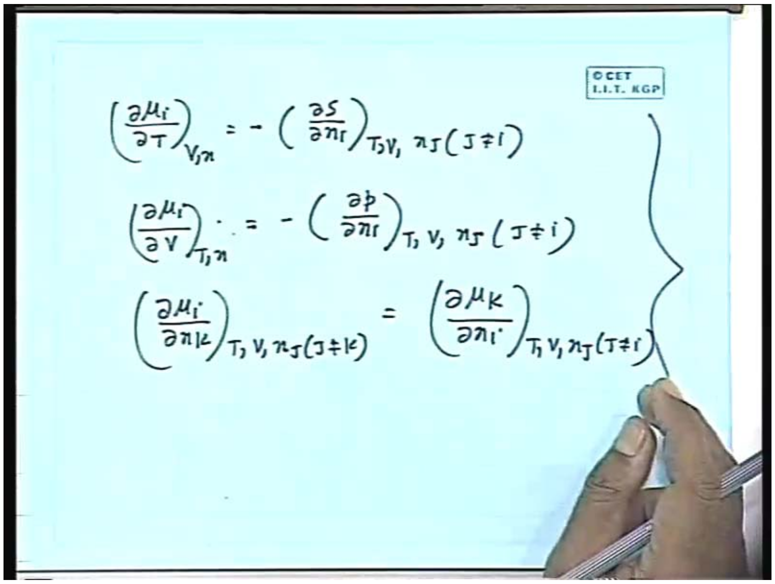

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{V,n} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,V,n_j(j\neq i)}$$

$$\left(\frac{\partial \mu_i}{\partial V}\right)_{T,n} = -\left(\frac{\partial p}{\partial n_i}\right)_{T,V,n_j(j\neq i)}$$

$$\left(\frac{\partial \mu_i}{\partial n_k}\right)_{T,V,n_j(j\neq k)} = \left(\frac{\partial \mu_k}{\partial n_i}\right)_{T,V,n_j(j\neq i)}$$

del μ_i del T, V and n is - del s del ni T V and nj j not equal to i. Similarly, μ_i del v at constant T and n is equal to - del p del ni at T V nj j not equal to amongst all the moles. Then del μ_i del nk T V nj j not equal to k is equal to del mu k del n_i and T V will remain same and here nj j not equal to i. Like this we can derive three sets of relationship from these two equations also.

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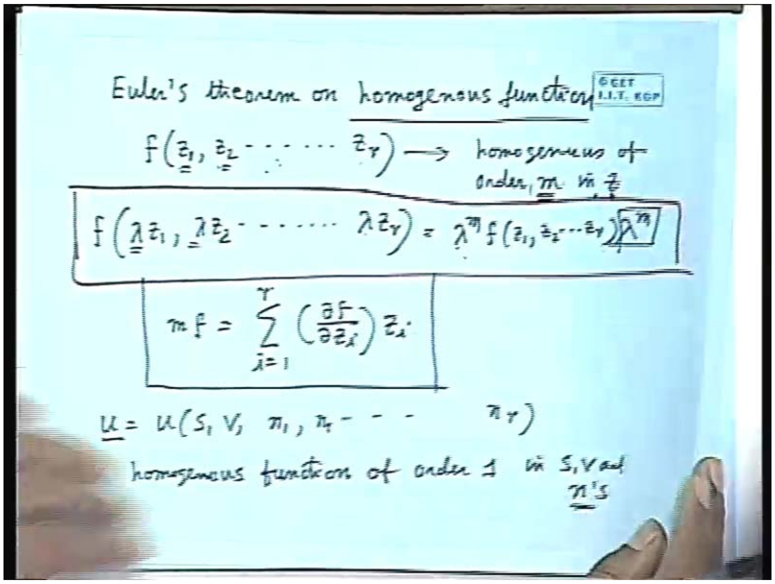

Euler's theorem on homogenous functions

$f(z_1, z_2 \cdots z_r) \longrightarrow$ homogeneous of order m in z

$$\boxed{f(\lambda z_1, \lambda z_2 \cdots \lambda z_r) = \lambda^m f(z_1, z_2 \cdots z_r) \boxed{\lambda^m}}$$

$$\boxed{m f = \sum_{i=1}^{r} \left(\frac{\partial f}{\partial z_i}\right) z_i}$$

$U = U(S, V, n_1, n_2 \cdots n_r)$

homogenous function of order 1 in S, V and n's

Now I will come to another thermodynamically important relation for multi component system, for which I would like to state a theorem known as Euler’s theorem on homogeneous function. There are various Euler’s theorems. This is a particular mathematical theorem on homogeneous function. If F is a function of number of independent variables, let Z_1 to Z_r are independent variables. They are the independent variables of a function of Z_1, Z_2…… Z_r. If this function is homogeneous of order m in Z, then these equations are the functions.

Let us first see, what is meant by homogenous or what are m and Z, by recapitulating basic mathematics. In all the Z variables, Z_1, Z_2 are multiplied by a multiplier then the function will be multiplied by m index of the multiplier. If it is homogeneous of order 1, then the function is multiplied by a constant multiplier. For example, if it is homogeneous in m, then for F, I make a constant multiplier lambda Z_2, which means in the function all the variables are multiplied by the lambda. This function will be equal to lambda to the power m, which will be common so that it can be again expressed as the same function Z_1 Z_2….. Z_i.

The function F is homogeneous in it. This is recapitulation of the basic mathematics, a function of multiple variables. If a homogeneous or all the independent variables are multiplied by some constant lambda, then the function becomes lambda to the power m. This is the definition of the homogeneity. If it is homogeneous of order 1, that means lambda into this.

Now, if a function is homogeneous, like all the Z’s, then Euler’s theorem is like this, m into F is sigma del F del Z_i into Z_i i 1 to r. This is the Euler’s theorem. It is needed to define or to derive very important thermodynamic relations.

In the beginning, we told, U as a function of S V and n_1, n_2….. n_r; and we have seen finally that U is a homogenous function of order 1 in S V and n. In this differential equation, U is a homogeneous function of orders 1 in a SV and all n’s.

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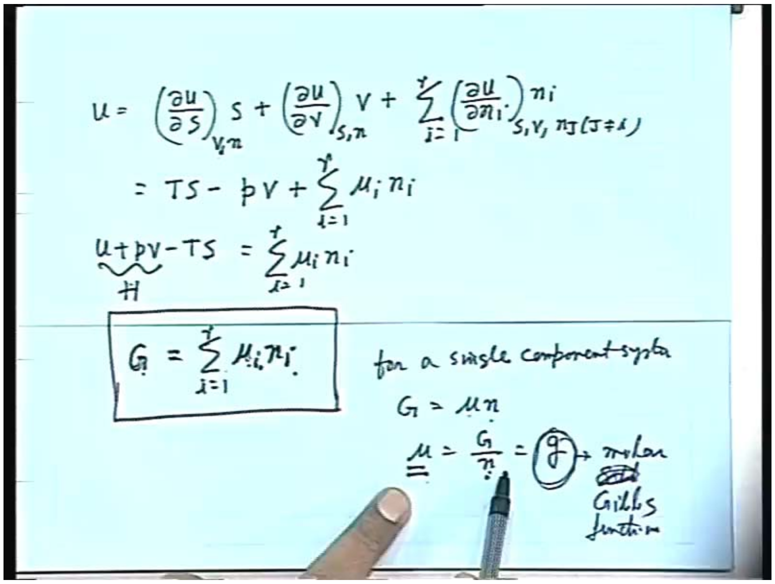

$$U = \left(\frac{\partial U}{\partial S}\right)_{V,n} S + \left(\frac{\partial U}{\partial V}\right)_{S,n} V + \sum_{i=1}^{r} \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j (j \neq i)} n_i$$

$$= TS - pV + \sum_{i=1}^{r} \mu_i n_i$$

$$\underbrace{U + pV}_{H} - TS = \sum_{i=1}^{r} \mu_i n_i$$

$$\boxed{G = \sum_{i=1}^{r} \mu_i n_i}$$

for a single component system

$$G = \mu n$$

$$\mu = \frac{G}{n} = g \rightarrow \text{molar Gibbs function}$$

If I exploit this thing, the information with the use for Euler's theorem, we can write, U is equal to del U del S into S del U del S, V and n will be constant S plus del U del V. del U del V at S and n V plus sigma of del U del ni times, S V and nj j not equal to i, i = 1 to r. As per Euler's theorem, U is equal to this. m is 1 in this case. By definition sigma of mu$_i$ n$_i$ i is equal to 1 to r. If I take this in the left hand side, it becomes U + pv - TS = sigma of mu$_i$ n$_i$ i = 1to r.

These things can be written as, U + pV is H and H - TS is G. Therefore we can write G = sigma mu$_i$ into n$_i$. It is a very useful relationship, i = 1 to r mu$_i$ n$_i$. From this relationship, we get a very important thing; for a multi component system, in Gibbs function for example; is the sum of the chemical potential times the number of moles, which means it is the molar weighted sum of the chemical potential.

For a single component system, G becomes equal to mu into n because there is no n$_i$ for 1 to r. Therefore, mu is equal to G by n which is small g. For a single component system the molar property for unit mole, is the mass that is the index of mass. The amount of the system mole is the amount of the system. Therefore, it is G by n, which is the molar Gibbs function.

For a single component system, thermodynamic potential becomes equal to molar Gibbs function. It will be clearer when discuss the partial molar property. Today, I will end at; G is sigma mu$_i$ n. For a single component system, we get mu$_i$ into n. In a multi component system, the Gibbs function is the sum of the product of chemical potential and the number of moles. For a single component system, the thermodynamic potential is the molarity function.

Thank you.