Basic Thermodynamics
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Lecture - 32
Thermodynamics of Multi Component System – III

Good morning. I welcome you all to this session of thermodynamics. In the last class we just introduced the concept of fugacity so today we will discuss further on this property fugacity, if I continue the discussion in the last class as regarding introduction of fugacity.

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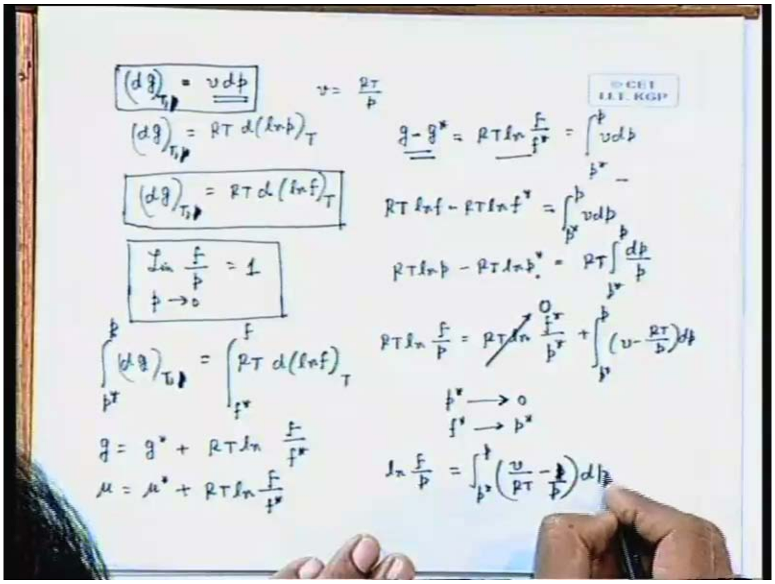

$$\boxed{(dg)_{T,p} = \underline{\underline{v\,dp}}} \qquad v = \frac{RT}{p}$$

$$(dg)_{T,p} = RT\,d(\ln p)_T$$

$$\boxed{(dg)_{T,p} = RT\,d(\ln f)_T}$$

$$\boxed{\lim_{p \to 0} \frac{f}{p} = 1}$$

$$\int_{p^*}^{p} (dg)_{T,p} = \int_{f^*}^{f} RT\,d(\ln f)_T$$

$$g = g^* + RT \ln \frac{f}{f^*}$$

$$\mu = \mu^* + RT \ln \frac{f}{f^*}$$

$$\underline{\underline{g - g^*}} = \underline{RT \ln \frac{f}{f^*}} = \int_{p^*}^{p} v\,dp$$

$$RT \ln f - RT \ln f^* = \int_{p^*}^{p} v\,dp$$

$$RT \ln p - RT \ln p^* = RT \int_{p^*}^{p} \frac{dp}{p}$$

$$RT \ln \frac{f}{p} = \overset{0}{\cancel{RT \ln \frac{f^*}{p^*}}} + \int_{p^*}^{p} \left(v - \frac{RT}{p}\right) dp$$

$$p^* \longrightarrow 0$$

$$f^* \longrightarrow p^*$$

$$\ln \frac{f}{p} = \int_{p^*}^{p} \left(\frac{v}{RT} - \frac{1}{p}\right) dp$$

Let us start a little repetition of the lass class that the molar Gibbs function dg at constant temperature and pressure can be written from the property relation $(dg)_T$ that means at constant temperature as vdp this was told in the class.

For an ideal gas we know v = RT / p. When ideal gas equation is used then we can write this as RT d of lnp at constant temperature. This is the relationship for an ideal gas at constant temperature $(dg)_T$.

For any other substance which is not an ideal gas, we can write the similar expression instead of pressure with f as the fugacity so this equation itself defines the fugacity. From this we know that any gas which is not an ideal gas at a very low pressure behaves as an ideal gas which means the limit of f/ p p tends to 0 =1 which means that when pressure tends to 0, the gas becomes very much radified then fugacity approaches to pressure.

Therefore in general we see that fugacity does the same role as done by the pressure in an ideal gas in defining the change of molar Gibbs function at constant temperature and pressure. This concept was given last class.

Now we proceed further, if we integrate this equation between two points, one is at a reference state p* to any other pressure p at a constant temperature then we get RT d(lnf) at constant temperature from f* to f, f* represent the fugacity at the reference state at T and p*.

Then we can write g is equal to g* plus RT ln f by f* this is one very important relationship. As we have seen earlier from the study of multi component system that the molar Gibbs function of any component is equal to its thermodynamic potential, as we define the thermodynamic potential m* plus RT ln f by f*, thermodynamic potential which came in relation to the multi component system but here we are using a single component system. From here we will derive one important equation g minus g* is RT ln f by f *.

Now, this g minus g* is the integration of dg at constant temperature from p* to p, which we can write as vdp because this relationship is valid for any gas which may not be ideal. Therefore we can also write equals to vdp from the reference state p* to p. If we do this integration, this vdp then what we do but we cannot do the integration until and unless we know v as a function of p.

Before that we write RT rather we write this lnf we equate this is equal to this. RT lnf minus RT lnf***** equals p* to p vdp. Now we can write another equation this RT lnp minus RT lnf* is nothing but RT integration of dp by p from this that means I just write an equation like that RT dp by p gives lnp from p* to p.

Therefore this is equal to this that means I use this equation this is an identity RT integral dp by p p* to p is RT lnp minus RT lnp star. If I subtract this one from this I get RT lnf by p is equal to RT ln f* by p* plus integral p* to p what will be there v minus RT by p dp.

If I consider p* very small that means the reference state is such that the p* that the pressure of the reference state approaches 0, what we know that f* approaches p*, which means f* by p* 1 so ln of this become 0. So we can write an equation that ln, now f by p RT we divide this side is equal to p* to p integration v by RT R is the universal gas constant v by RT minus 1 by p dp. This is a very important relationship regarding the important expression of fugacity in terms of pressure and volume.

For any real gas, if we can know the pressure and volume relationship from this equation of state we can find out the expression for the fugacity. This equation can also be written in another form.

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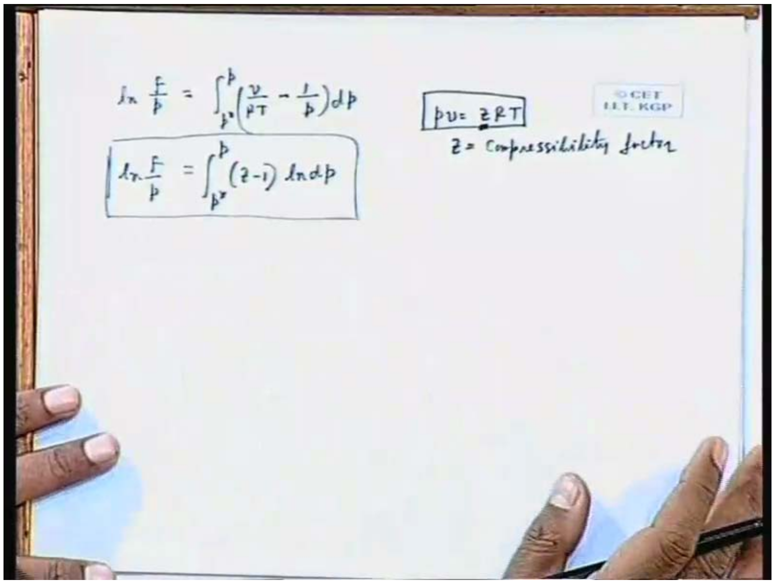

$$\ln \frac{f}{p} = \int_{p^*}^{p} \left(\frac{v}{RT} - \frac{1}{p} \right) dp$$

$$\boxed{\ln \frac{f}{p} = \int_{p^*}^{p} (Z-1) \ln dp}$$

$$\boxed{pv = ZRT}$$

Z = Compressibility factor

Let me tell you that this equation can also be written in another form of this equation ln little bit algebra is there in this part of this class that p* to p which we have done v by RT minus 1 by p dp. We know that for a real gas we can define the equation of state in terms of a compressibility function Z which takes care of the non ideality of the gasses that means for an ideal gas Z = 1.

If you define pv is equal to Z RT as the equation of state for any real gas then this can be written as you see v by RT is Z by p therefore we can write p* by p into Z minus 1 so dp by p can be written as ln dp because p v by RT is Z by p minus 1 by p so Z minus 1 dp by p has been written as, this is the same expression in another useful form.
Let us have some example before proceeding further. Let us find out the expression of fugacity

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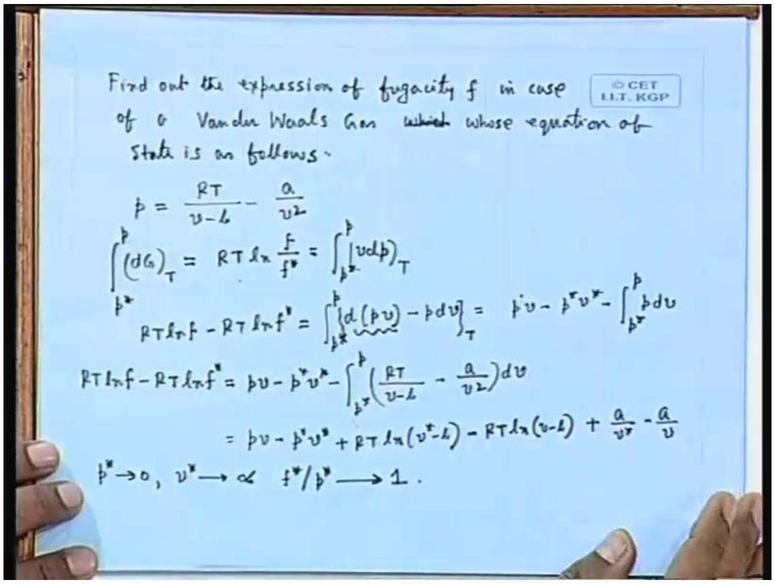

Find out the expression of fugacity f in case of a Vander Waals Gas ~~which~~ whose equation of state is as follows -

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$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$\int_{p^*}^{p} (dG)_T = RT \ln \frac{f}{f^*} = \int_{p^*}^{p} (vdp)_T$$

$$RT\ln f - RT\ln f^* = \int_{p^*}^{p} \{\underset{\sim\sim\sim}{d(pv)} - pdv\}_T = pv - p^*v^* - \int_{p^*}^{p} pdv$$

$$RT\ln f - RT\ln f^* = pv - p^*v^* - \int_{p^*}^{p} \left(\frac{RT}{v-b} - \frac{a}{v^2}\right) dv$$

$$= pv - p^*v^* + RT\ln(v^*-b) - RT\ln(v-b) + \frac{a}{v^*} - \frac{a}{v}$$

$$p^* \to 0, \quad v^* \longrightarrow \propto \quad f^*/p^* \longrightarrow 1.$$

Let us have some example before proceeding further. Let us find out the expression of fugacity with this example fugacity f in case of a Vander Waal Gas whose equation of state is as follows. Let us consider the equation of state of a Vander Waals Gas and we will find out the Vander Waals equation of state. This is given p is equal to RT you know the Vander Waals equation minus a by v square. Where a and b are the parametric constant in the Vander Waals equation of state.

Now how to find out this?

We start from this dgt is vdpt therefore we can write dg at constant T is equal to RT ln this is integral if we make this integration from p* to p we get RT ln f by f* which equals to integration of p* p vdp which we already used earlier I just show you that this one. g minus g* RT lnf by f* this is nothing but dg at constant temperature from p* to p.

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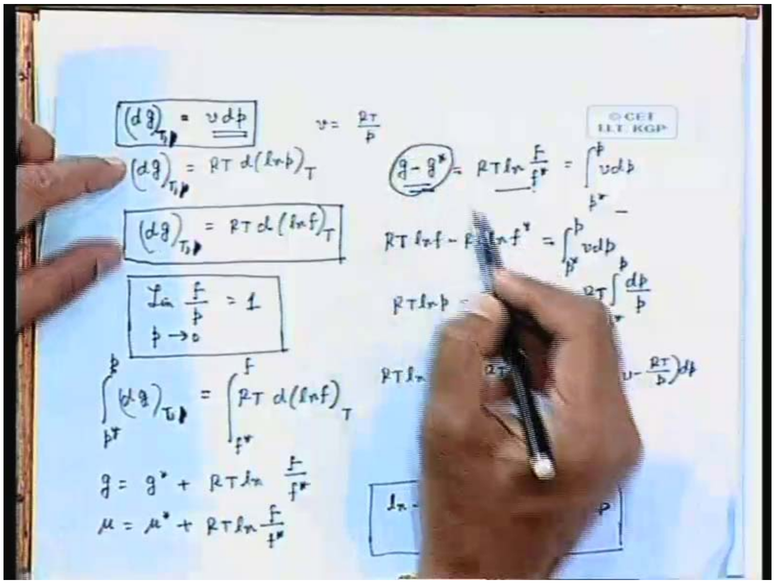

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$$(dg)_{T,p} = RT\,d(\ln p)_T$$

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$$\int_{p^*}^{p} (dg)_{T,p} = \int_{f^*}^{f} RT\,d(\ln f)_T$$

$$g = g^* + RT\ln\frac{f}{f^*}$$

$$\mu = \mu^* + RT\ln\frac{f}{f^*}$$

$$(g - g^*) = RT\ln\frac{f}{f^*} = \int_{p^*}^{p} vdp$$

$$RT\ln f - RT\ln f^* = \int_{p^*}^{p} vdp$$

If we equate this we get RT lnf minus RT lnf* here we have to make a tactful substitution or we have to arrange reorganize this thing in way that we can integrate it properly because v is explicitly in terms of p so that we can integrate it with the variable dp that means integration is made with respect to dp. So p is not explicitly given to p so that we can substitute and integrate.

What we do in state? we write this p* vdp we can write as td of pv minus pdv and this can be written as integral d of pv from p* to p that means we can write this as pv minus p* v*. If we integrate this part so v* is the corresponding volume at the reference state p* and v is the corresponding volume at this state p so pv minus p* v*. These are all done at constant temperature then minus p* to p pdv. Therefore we can write RT lnf minus RT lnf* equals to pv minus p* v*.

I just substitute p explicitly in terms of which is possible from this type of equation of state p* to p then what is this? T is RT v minus v minus a by v square dv. If we integrate it in the next step, if you write you see that RT v minus v is ln v minus and p to p* so the minus is there therefore we can first write RT ln v* minus b minus RT ln v minus b minus now this is minus minus plus a by v square this minus so plus a by v* minus a by v.

So a by v square integration is minus a by v, if you take the limit it will be like that where again I am telling v* is the volume when p is v* and v is the volume and p is p. If we use certain relationship like this as p* tends to 0 the reference state pressure is very low then v* tends to infinity and one thing is that f* by p* tends to 1 therefore, if you just write this from here you can see that….

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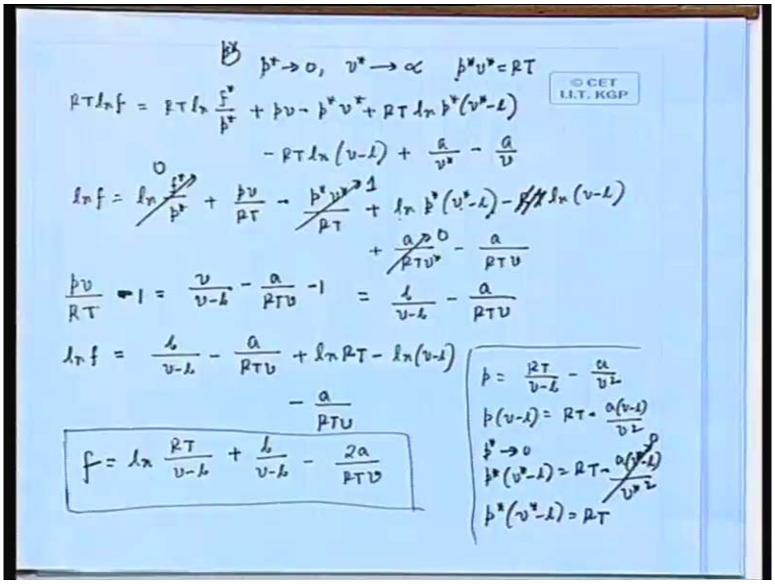

$$p^* \to 0, \quad v^* \to \propto \quad p^* v^* = RT$$

$$RT \ln f = RT \ln \frac{f^*}{p^*} + pv - p^* v^* + RT \ln p^*(v^*-b)$$

$$- RT \ln (v-b) + \frac{a}{v^*} - \frac{a}{v}$$

$$\ln f = \ln \cancelto{0}{\frac{f^*}{p^*}} + \frac{pv}{RT} - \cancelto{1}{\frac{p^* v^*}{RT}} + \ln p^*(v^*-b) - \cancel{RT} \ln (v-b)$$

$$+ \cancelto{0}{\frac{a}{RTv^*}} - \frac{a}{RTv}$$

$$\frac{pv}{RT} - 1 = \frac{v}{v-b} - \frac{a}{RTv} - 1 = \frac{b}{v-b} - \frac{a}{RTv}$$

$$\ln f = \frac{b}{v-b} - \frac{a}{RTv} + \ln RT - \ln (v-b)$$

$$- \frac{a}{RTv}$$

$$\boxed{f = \ln \frac{RT}{v-b} + \frac{b}{v-b} - \frac{2a}{RTv}}$$

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$p(v-b) = RT - \frac{a(v-b)}{v^2}$$

$$p^* \to 0$$

$$p^*(v^*-b) = RT - \cancelto{0}{\frac{a(v^*-b)}{v^{*2}}}$$

$$p^*(v^*-b) = RT$$

RT lnf is equal to RT ln minus RT ln p* plus RT ln p* so plus pv minus p* v* that means I keep this RT ln f* here I take this on the right hand side RT lnf* so 1 minus RT ln p* is there so plus RT ln p* into v* minus v then I write the rest part RT ln v minus b plus a by v* minus a by v.

Our next task will be like this, we will just divide from both the sides so we get ln f is ln f* by p* plus pv by RT minus p* v* by RT plus ln p* v* minus b minus RT ln v minus b plus a by RT v* minus a by RTv.

We will use this equation of state in this fashion that the equation of state can be written as pv by RT minus 1 is equal to v by v minus b minus a by RTv minus 1. How do I get it?

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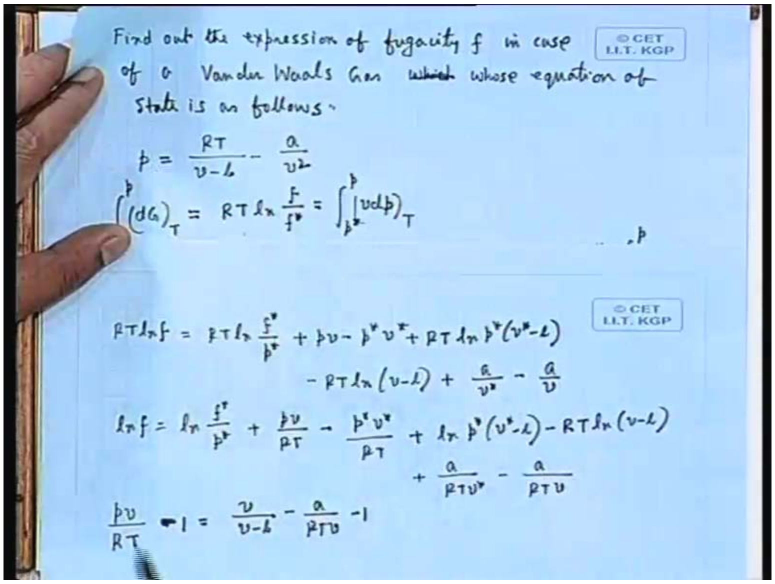

Find out the expression of fugacity f in case of a Vander Waals Gas ~~which~~ whose equation of State is as follows.

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$\int^{p}(dG)_T = RT\ln\frac{f}{f^*} = \int_{p^*}^{p}(v\,dp)_T$$

$$RT\ln f = RT\ln\frac{f^*}{p^*} + pv - p^*v^* + RT\ln p^*(v^*-b) - RT\ln(v-b) + \frac{a}{v^*} - \frac{a}{v}$$

$$\ln f = \ln\frac{f^*}{p^*} + \frac{pv}{RT} - \frac{p^*v^*}{RT} + \ln p^*(v^*-b) - RT\ln(v-b) + \frac{a}{RTv^*} - \frac{a}{RTv}$$

$$\frac{pv}{RT} - 1 = \frac{v}{v-b} - \frac{a}{RTv} - 1$$

If you see this slide, that p is equal to RT v minus p into v minus b that means pv by RT rather I just multiplied with v and RT so you multiply it v. If you see that pv by RT that means a by RTv v is multiplied minus 1so form this equation of state I can write this so that pv by RT minus 1 becomes equals to v by v minus b minus n, if I take this that means b by v minus b minus a by RTv.

Now, if I take p* tending to 0 and v* automatically tending to infinity so p* tending to 0 means this is ln 0. Now when p* tending to 0 and v* tending to 1 at this reference state the gas behaves like an ideal gas that means p* v* is RT that means p* v* by RT equals to 1. We can write lnf is equal pv by RT minus 1 so pv by RT minus 1 is again this one that is b by v minus b minus a by RTv.

Again, we see that RT ln v minus b. Now ln p* v* minus this so this also can be shown equal to…. If I write this ln p* v* minus b from the equation of state something here I do that equation of state if you remember p is equal to RT v minus b minus a by v square then p into v minus b, if I multiplied is equal to RT minus a into v minus b by v square.

When p tends to 0 that means if I just substitute p*, For example, that is p* tends to 0 then v* minus b is RT minus av* minus b divided by v* square so here you see the terms are getting 0 because denominator is v* it is 0 that means p* into v* minus b is RT that means this part I can write RT plus ln RT minus ln v minus b. There will be no RT because I have divided by RT so RT is not there.

Again v* tends to infinity v* means 0 so minus a by RTv so this remaining term. Ultimately we get ln, if these two things are taken together RT by v minus b then this term is b by v minus b and these two terms minus 2a RTv this is one of the very important expression. Finally fugacity f for Vander Waal gas equal to this one f is equal to ln RT v minus b this is the expression of fugacity for Vander Waals Gas.

Now, we will go for a multi component system. How to define fugacity for a multi component system?

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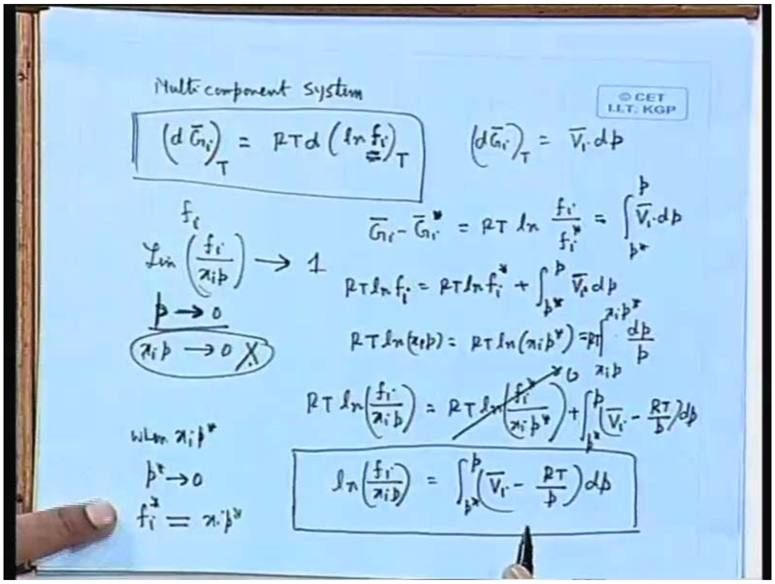

Multi component system

$$\boxed{(d\bar{G}_i)_T = RT\,d(\ln f_i)_T} \qquad (d\bar{G}_i)_T = \bar{V}_i\,dp$$

f_i

$$\bar{G}_i - \bar{G}_i^* = RT\ln\frac{f_i}{f_i^*} = \int_{p^*}^{p}\bar{V}_i\,dp$$

$$\lim\left(\frac{f_i}{x_i p}\right) \to 1$$

$p \to 0$

$x_i p \to 0$ X

$$RT\ln f_i = RT\ln f_i^* + \int_{p^*}^{p}\bar{V}_i\,dp$$

$$RT\ln(x_i p) = RT\ln(x_i p^*) = RT\int_{x_i p^*}^{x_i p}\frac{dp}{p}$$

$$RT\ln\left(\frac{f_i}{x_i p}\right) = \cancel{RT\ln\left(\frac{f_i^*}{x_i p^*}\right)} \to 0 + \int_{p^*}^{p}\left(\bar{V}_i - \frac{RT}{p}\right)dp$$

when $x_i p^*$

$p^* \to 0$

$f_i^* = x_i p^*$

$$\boxed{\ln\left(\frac{f_i}{x_i p}\right) = \int_{p^*}^{p}\left(\bar{V}_i - \frac{RT}{p}\right)dp}$$

For a multi component system, the fugacity is defined like this that for a multi component system if we define in terms of the partial molar Gibbs function at constant temperature is defined as RTd ln f_i. f_i is the fugacity of the ith component so this is the definition of the fugacity of an ith component in a mixture of multi component system, where G_i bar is the partial molar Gibbs function of the component and f_i is the fugacity of the ith component. This is the definition and here also the limit we can write f_i by the pressure of the component in the mixture that means its mole fraction times the total pressure, this tends to 1 when the total pressure tends to 0 do not make a mistake that x_ip or the partial pressure 0 this is wrong.

When the total pressure goes to 0 then this f_i behaves as the partial pressure that means x_ip of the component why? because it is very simple and you can understand that in a mixture of gas, if one component has a marginal amount that means a real gas whose amount is very marginal in a mixture or a very dilute mixture of a real gas in other gasses does not make the mixture as an ideal gas.

Until and unless the total pressure approach is 0 that means in a mixture of real gasses one real gas may have a very marginal quantity that means it is infinitely diluted with that particular real gas that means the partial pressure of that gas is approaching 0 but that does not mean mixture will behave as an ideal gas therefore very important thing is that p tends to 0 not x_ip tends to 0 this is wrong. This is the basic concept of the fugacity of an ith component in a multi component system.

We can find out the expression for fugacity in a multi component system in the similar way as we have done for the single component system. How we can do it? We can integrate this

equation and can write this way G_i bar minus G_i bar* where this is a reference state is RT if we integrate this ln fi fi* that is the reference state and that equates $v_i$dp that means the partial volume instead of the molar volume it is the partial molar volume which means that d G_i bar at constant T is nothing but v_i bar dp that is our relationship therefore if I integrate that I get this thing.
In the exactly similar way I can do f_i is equal to RT ln f_i* plus integration of p* p v_i dp bar that means the partial molar volume of the ith component in the mixture. In a similar way I can write RT ln instead of f_i I can write x_ip is equal to RT ln x_i p* is equal to just a mathematical identity. That means it will be dp by p from x_i p to x_i p* that means here connotations of thing that fi is the fugacity of the ith component at a state p then f_i* is the fugacity of the ith component at the reference state p and there it is integration of v_i bar where this is the partial molar volume of the ith component.

Here I am giving an identity where x_ip is the partial pressure of the component whose mole fraction is x_i and x_i p* is the partial pressure of the component i when the total pressure is at the reference state that means p* that means this is a mathematical identity. Similar way we did for the single component. We are going for the multi component system also then we just subtract and we get RT ln f_i by x_ip is equal to RT ln f_i* by x_ip* plus p* by p and your RT that means here has to be RT that means v_i bar minus RT by p dp.

When x_ip* is very small then what happens? When f_i* is p so f_i* is p_i when p* is going to 0 then what is the fugacity? Here p* going to 0 then fugacity is equal to the x_i p* that means this is one so this is the reference is at a very low pressure. Therefore we can write ln f_i by x_ip is equal to this is p* by p into v_i minus RT by p dp. Similar relationship I will show you just now we have developed for a component for a single component.

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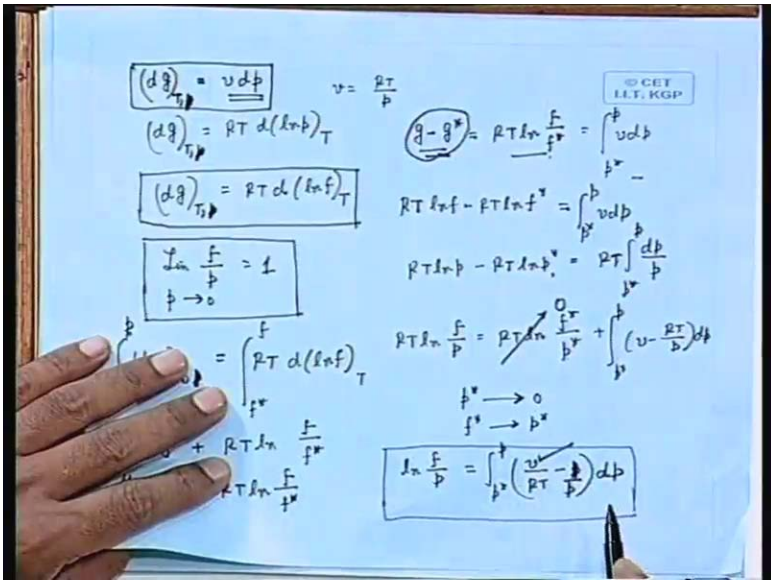

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$\boxed{(dg)_{T,p} = v\,dp}$ $\quad v = \frac{RT}{p}$

$(dg)_{T,p} = RT\,d(\ln p)_T$

$\boxed{(dg)_{T,p} = RT\,d(\ln f)_T}$

$\boxed{\lim_{p \to 0} \frac{f}{p} = 1}$

$\int^{p} \ldots = \int_{f^*}^{f} RT\,d(\ln f)_T$

$+ RT\ln\frac{f}{f^*}$

$RT\ln\frac{f}{f^*}$

$g - g^* = RT\ln\frac{f}{f^*} = \int_{p^*}^{p} v\,dp$

$RT\ln f - RT\ln f^* = \int_{p^*}^{p} v\,dp$

$RT\ln p - RT\ln p^* = RT\int_{p^*}^{p} \frac{dp}{p}$

$RT\ln\frac{f}{p} = \cancelto{0}{RT\ln\frac{f^*}{p^*}} + \int_{p^*}^{p}\left(v - \frac{RT}{p}\right)dp$

$p^* \longrightarrow 0$

$f^* \longrightarrow p^*$

$\boxed{\ln\frac{f}{p} = \int_{p^*}^{p}\left(\frac{v}{RT} - \frac{1}{p}\right)dp}$

There is a molar volume and difference, this is the component fugacity for the pure component, it is the fugacity of the ith component in a mixture. This is the partial molar volume of the mixture of the component i in that mixture so this is multi component this definition of fugacity in the multi component system. Now, we will derive the dependence of fugacity with pressure and temperature.

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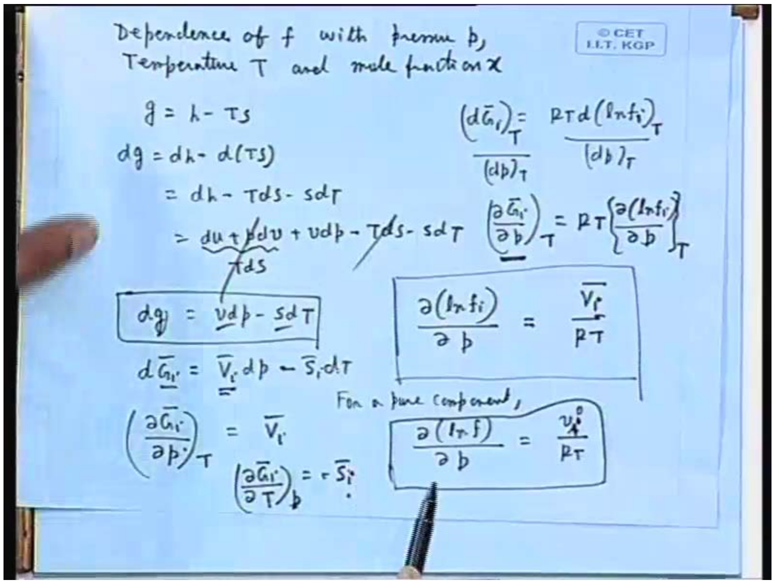

Dependence of f with pressure p,
Temperature T and mole fraction x

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$$g = h - Ts$$

$$dg = dh - d(Ts)$$

$$= dh - Tds - sdT$$

$$= \underbrace{du + pdv}_{Tds} + vdp - \cancel{Tds} - sdT$$

$$\boxed{dg = vdp - sdT}$$

$$d\bar{G}_i = \bar{V}_i dp - \bar{S}_i dT$$

$$\left(\frac{\partial \bar{G}_i}{\partial p}\right)_T = \bar{V}_i$$

$$\left(\frac{\partial \bar{G}_i}{\partial T}\right)_p = -\bar{S}_i$$

$$\frac{(d\bar{G}_i)_T}{(dp)_T} = \frac{RTd(\ln f_i)_T}{(dp)_T}$$

$$\left(\frac{\partial \bar{G}_i}{\partial p}\right)_T = RT\left\{\frac{\partial(\ln f_i)}{\partial p}\right\}_T$$

$$\boxed{\frac{\partial(\ln f_i)}{\partial p} = \frac{\bar{V}_i}{RT}}$$

For a pure component,

$$\boxed{\frac{\partial(\ln f)}{\partial p} = \frac{v_i^0}{RT}}$$

Dependence of fugacity f with pressure p temperature T and mole fraction x we will define in case of a multi component system and mole fraction s. We start from here from the very basic we know that the definition of g is h minus Ts for a single component system molar Gibbs function so dg is dh minus d of Ts which equals to dh minus Tds minus sdT. Again this has been done several times dh is du plus pdv plus vdp minus Tds minus sdT and you know du plus pdv is dts Tds, Tds so Tds cancels so vdp minus sdT this is our starting point definition.

Multi component system as we have already studied, we know that the same relationship holds good if we just substitute molar Gibbs by the partial molar properties that means in case partial molar Gibbs function partial molar property of the ith component. For a pure component this was molar Gibbs function, molar volume, molar entropy.Here partial molar Gibbs function of ith component, partial molar volume of ith component, partial molar entropy of ith component.

From here we see del G_i that means the partial molar volume bar by del p at constant temperature will be nothing but the v_i del G_i del p. We have already dealt with this expression, what is this? This is by definition RTd ln f_i this was the definition of the fugacity. These are all at constant temperature

If I divide it by dpt that means if divided by a change in pressure at constant temperature dp at T then we can write this thing change of pressure at constant temperature if I just divide that means in other way this integration of del G_i bar del p at constant T can be written as R del ln f_i del p and this is at constant T. If I equate this with this then we can get del ln f_i del p is equal to v_i bar by RT so this is the most important relation of f_i with pressure that means dependence of f with p is del ln fi del p is vi bar by RT.

For a pure component counterpart will be del lnf that means the fugacity of the component del p is simply v_i sometimes I write 0 on the subscript which means the for the ith component as a pure component. If we compare these two you should write this way where vi bar is the partial molar volume of the ith component at that mixture and v_i o is the partial molar volume rather partial molar volume or simply molar volume I will not tell partial molar volume of the component i as the pure component at that same pressure and temperature so del ln fb is v_i o by T this is for a pure component i, i itself when exists as a pure component this is for the pure component.

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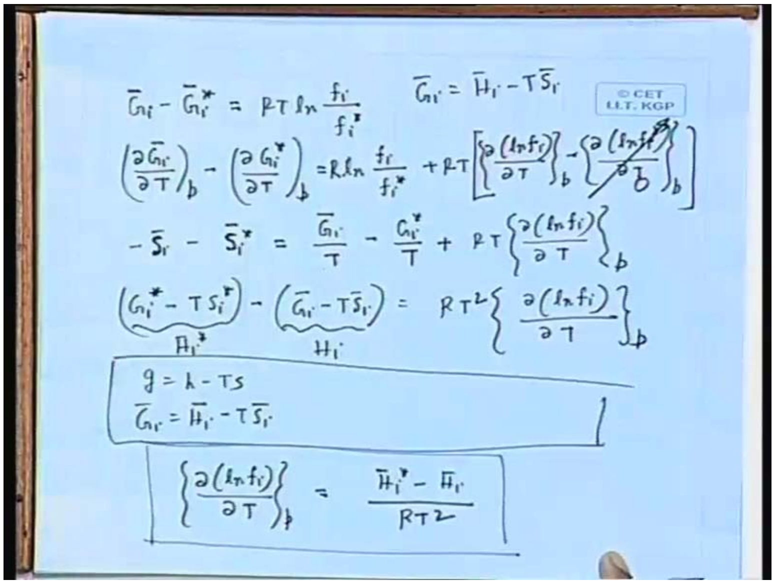

$$\bar{G}_i - \bar{G}_i^* = RT \ln \frac{f_i}{f_i^*} \qquad \bar{G}_i = \bar{H}_i - T\bar{S}_i$$

$$\left(\frac{\partial \bar{G}_i}{\partial T}\right)_p - \left(\frac{\partial G_i^*}{\partial T}\right)_p = R\ln\frac{f_i}{f_i^*} + RT\left[\left\{\frac{\partial(\ln f_i)}{\partial T}\right\}_p - \cancel{\left\{\frac{\partial(\ln f_i^*)}{\partial p}\right\}_p}\right]$$

$$-\bar{S}_i - \bar{S}_i^* = \frac{\bar{G}_i}{T} - \frac{G_i^*}{T} + RT\left\{\frac{\partial(\ln f_i)}{\partial T}\right\}_p$$

$$\underbrace{(G_i^* - TS_i^*)}_{H_i^*} - \underbrace{(\bar{G}_i - T\bar{S}_i)}_{H_i} = RT^2\left\{\frac{\partial(\ln f_i)}{\partial T}\right\}_p$$

$$\boxed{\begin{array}{l} g = h - Ts \\ \bar{G}_i = \bar{H}_i - T\bar{S}_i \end{array}}$$

$$\boxed{\left\{\frac{\partial(\ln f_i)}{\partial T}\right\}_p = \frac{\bar{H}_i^* - \bar{H}_i}{RT^2}}$$

We come to the dependence of temperature. For the dependence of temperature we start from here we have already seen that G_i bar minus G_i* that means the reference state the difference between this partial molar Gibbs function of the ith component this is equal to RT ln f_i by f_i *.

If I differentiate this with temperature at constant pressure then what I will get del G_i del T at constant pressure minus del G_i* del T at constant pressure is equal to…. if I differentiate this at constant pressure then what it will be at constant pressure the temperature? So, R ln f_i by f_i* plus RT then del ln f_i by del T at constant pressure minus del ln fi* by del T at constant pressure.

If we go back to this definition del G_i v_i dp minus sdt then what is del G_i del T? at constant pressure the partial differential with respective T at constant pressure is minus si bar so these are all known things we did earlier that this is the relationship property relationship therefore del G_i bar that mean del T that means the partial differential of partial molar Gibbs function of ith component with temperature at constant pressure is nothing but minus s_i bar, s_i bar is the partial molar entropy of the ith component.

Therefore minus s_i bar so this will be minus s_i bar minus si* bar that means the partial molar entropy at the reference state and this is equal to Rln f_i by f_i* so what is that value of fi by fi* Rln f_i f_i*? From this equation again I can write G_i bar by T minus Gi* by T Gi by T minus Gi* by T plus now fi* is a constant that is a fugacity at the reference state so we can neglect this. We can make this to 0 therefore we get plus RT del ln f_i del T at constant pressure.

If we just multiply T on this side what we get? We get, if you just multiply this side and this take this side G_i* multiplied T on both side G_i* minus T s_i* minus G_i just little algebraic manipulation minus T s_i bar is equal to RT square because we have multiplied T into del ln f_i by del T at constant pressure.

Now G_i - Ts what is that? By definition G is equal to Hi you know the definition and G = H - Ts and this hold goods we know now here we do that we know the definition of G is molar Gibbs function for a pure component s therefore for a multi component system s these molar properties will be replaced by the partial molar properties so this becomes H_i bar* and this becomes H_i. Therefore we can write del ln f_i del T at constant pressure is equal to H_i* - H_i all with bar H_i bar* minus H_i bar divided by RT square.This is the required expression for this is the dependence of fugacity with temperature. What will happen for a pure component? We will repeat for a pure component,

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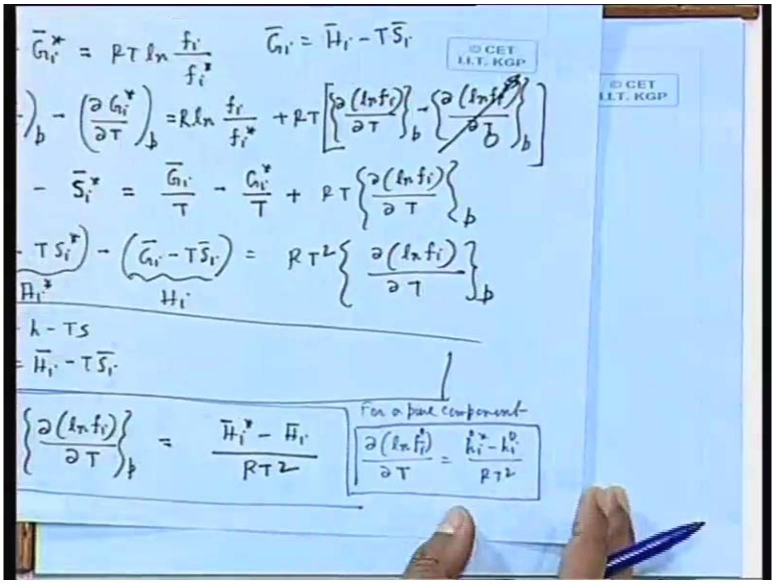

$$\bar{G}_i^* = RT\ln\frac{f_i}{f_i^*} \qquad \bar{G}_i = \bar{H}_i - T\bar{S}_i$$

$$)_p - \left(\frac{\partial G_i^*}{\partial T}\right)_p = R\ln\frac{f_i}{f_i^*} + RT\left[\left\{\frac{\partial(\ln f_i)}{\partial T}\right\}_p - \cancelto{0}{\left\{\frac{\partial(\ln f_i^*)}{\partial T}\right\}_p}\right]$$

$$- \bar{S}_i^* = \frac{\bar{G}_i}{T} - \frac{G_i^*}{T} + RT\left\{\frac{\partial(\ln f_i)}{\partial T}\right\}_p$$

$$\underbrace{- TS_i^*)}_{\bar{H}_i^*} - (\underbrace{\bar{G}_i - T\bar{S}_i}_{H_i}) = RT^2\left\{\frac{\partial(\ln f_i)}{\partial T}\right\}_p$$

$$h - Ts$$

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

$$\boxed{\left\{\frac{\partial(\ln f_i)}{\partial T}\right\}_p = \frac{\bar{H}_i^* - \bar{H}_i}{RT^2}}$$

For a pure component

$$\boxed{\frac{\partial(\ln f_i^0)}{\partial T} = \frac{h_i^{0*} - h_i^0}{RT^2}}$$

this will be del lnf divided by del T that means for a pure component where I will denote f_i o that means the ith component when it exists as a pure component then what will be H_i* minus H_i divided by RT square these are the molar enthalpy of the pure component so this I give as the 0, it means that when ith component exists as a pure component at the same state of the mixture so del del T ln f_i into 0 is h_i 0* minus hi 0 by RT^2 so this is valid for the pure component.
Now I will come to the mole fraction so dependence with mole fraction

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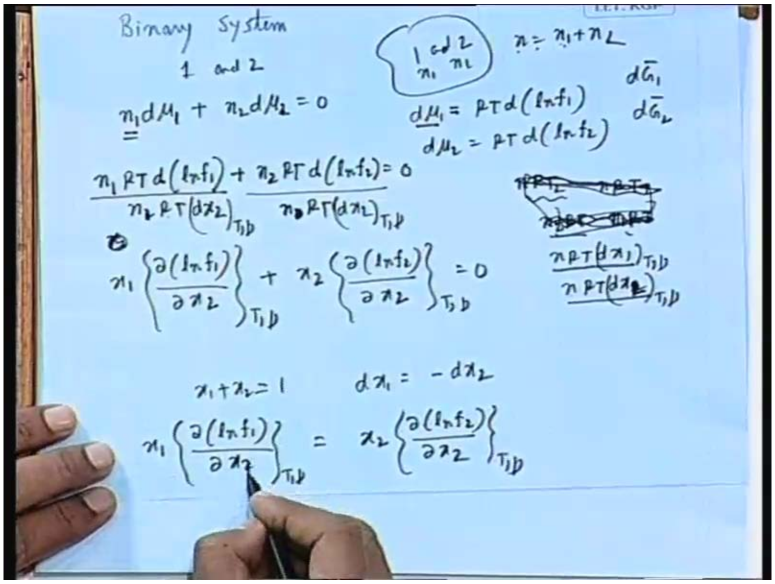

Binary System

1 and 2

$n_1 d\mu_1 + n_2 d\mu_2 = 0$

1 and 2, n_1 n_2 $\quad n = n_1 + n_2$

$d\mu_1 = RT\,d(\ln f_1) \qquad d\bar{G}_1$

$d\mu_2 = RT\,d(\ln f_2) \qquad d\bar{G}_2$

$$\frac{n_1 RT\,d(\ln f_1)}{n_2 RT(dx_2)_{T,p}} + \frac{n_2 RT\,d(\ln f_2)}{n RT(dx_2)_{T,p}} = 0$$

$$\frac{nRT(dx_1)_{T,p}}{nRT(dx_2)_{T,p}}$$

$$x_1\left\{\frac{\partial(\ln f_1)}{\partial x_2}\right\}_{T,p} + x_2\left\{\frac{\partial(\ln f_2)}{\partial x_2}\right\}_{T,p} = 0$$

$x_1 + x_2 = 1 \qquad dx_1 = -dx_2$

$$x_1\left\{\frac{\partial(\ln f_1)}{\partial x_1}\right\}_{T,p} = x_2\left\{\frac{\partial(\ln f_2)}{\partial x_2}\right\}_{T,p}$$

I will start with a binary system 1 and 2. We know for a binary system we have already deduced this equation n_1 d mu_1 plus n_2 d mu_2 is 0 where n_1 is the number of moles considered in mixture of 1 and 2 with n_1 and n_2 so n is the total number of moles n_1 plus n_2 and mu_1 mu_2 are the chemical potentials of component 1 and 2 so this equation we know and we also know, just now we have learnt that d mu1is equal to RTd ln f_1 in terms of the fugacity.

d mu_2 is RTd ln f_2 ,d mu_1 is nothing but dG_1 bar and d mu_2 is nothing but dG_2 bar so this we know so RTd ln f_2. If you now substitute this then we get n_1 RTd ln f_1 plus n_2 RTd ln f_1 is equal to 0. We can divide both the sides by either nRT_2 or nRT_1 results will be same you can do it. Let me do it by dividing nRT_2 so n_1 by n will be x_1 mole fraction and it will be either n_2 RT or n_1 RT result will be same.

Let me divided it nRT dx 2, n2 RT you can divide by n_1 RT also the result will be same. Now we divide by nRT dx_2. n either nRT dx_1 or by nRT dx_2 not n_2 RT not n so either nRT dx_1 or nRT dx_2 so I divide by nRT dx_2 so it is x_1 now dx_2. This is defined at constant temperature and pressure only this mole fraction is changing so that RT is cancelled out so n_1 by nx.

You can write this lnf_1 by del x_2 at constant temperature and pressure that means mathematically this is at constant temperature and pressure. Either you multiply with this or you multiplying with dx_2 at constant temperature. I am multiplying with nRT dx_2 then what will be that? X_2 and del ln f_2 del x_2 at constant temperature and pressure is 0.

You know that x_1 plus x_2 is 1 why? n is equal to n_1 plus n_2 divided by n_1 is x_1 plus x_2 therefore dx_1 is minus dx_2, if I take this minus of this side then I can write x_1 del lnf1 by del x_2 is equal to is a very important relation x_2 del lnf_2 del x_2 all are at constant temperature and pressure and we can take this x_1 inside, now it will be del x_1 by x_1 and del x_2 because del x_2 is minus del x_1 so that it has gone that side so this equal to this.

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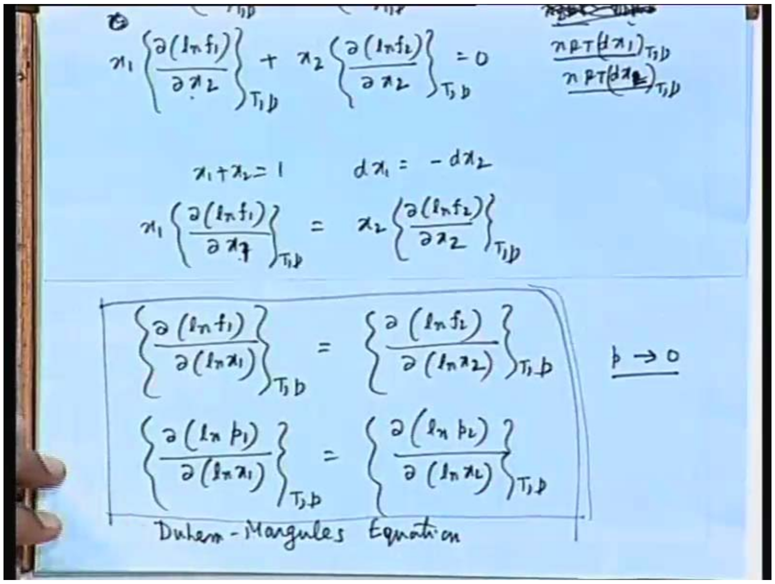

$$x_1\left\{\frac{\partial(\ln f_1)}{\partial x_2}\right\}_{T,p} + x_2\left\{\frac{\partial(\ln f_2)}{\partial x_2}\right\}_{T,p} = 0$$

$$\underline{nRT(dx_1)_{T,p}}$$

$$\underline{nRT(dx_2)_{T,p}}$$

$$x_1 + x_2 = 1 \qquad dx_1 = -dx_2$$

$$x_1\left\{\frac{\partial(\ln f_1)}{\partial x_1}\right\}_{T,p} = x_2\left\{\frac{\partial(\ln f_2)}{\partial x_2}\right\}_{T,p}$$

$$\boxed{\begin{gathered}\left\{\frac{\partial(\ln f_1)}{\partial(\ln x_1)}\right\}_{T,p} = \left\{\frac{\partial(\ln f_2)}{\partial(\ln x_2)}\right\}_{T,p} \\ \left\{\frac{\partial(\ln p_1)}{\partial(\ln x_1)}\right\}_{T,p} = \left\{\frac{\partial(\ln p_2)}{\partial(\ln x_2)}\right\}_{T,p}\end{gathered}}$$

$$\underline{p \to 0}$$

Duhem - Margules Equation

If I take del x_1 by x_1, this can be written as del ln f_1 by del ln x_1 at constant temperature and pressure is equal to del of ln f_2 divided by del of ln x_2 at constant temperature and pressure and it can be written when the pressure tends to 0 very low pressure this fugacity is can be expressed as partial pressures of the component.

del lnp del ln x_1 this is another form at very low pressure. This dependence of the partial pressures with the mole fractions del ln x_2 at constant temperature and pressure and this equation is very important equation and known as Duhem Margules equation. This equation is an important equation.

These are the two forms for the dependence of fugacity with the mole fractions. fugacity is a partial pressure when the pressure tends to 0 this equals to the partial pressure for a component in a multi component system.

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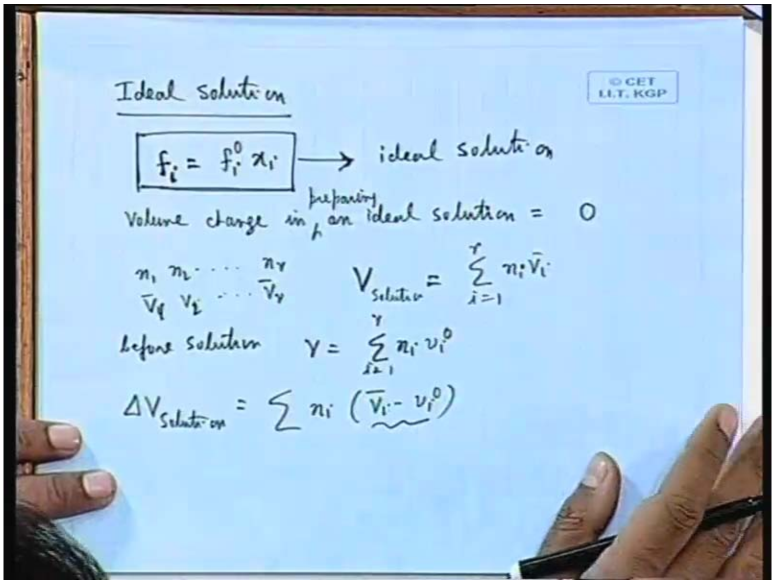

Ideal solution

$\boxed{f_i = f_i^0 x_i} \longrightarrow$ ideal solution

Volume change in preparing an ideal solution = 0

$n_1\ n_2 \cdots n_r$ $\qquad V_{\text{Solution}} = \sum_{i=1}^{r} n_i \bar{V}_i$

$\bar{V}_1\ V_2 \cdots \bar{V}_r$

before solution $\quad V = \sum_{i=1}^{r} n_i v_i^0$

$\Delta V_{\text{Solution}} = \sum n_i \left(\underset{\sim}{\bar{V}_i - v_i^0}\right)$

We will go to another section that is an ideal solution. What is an ideal? After discussing all these things, we will come to ideal solution, what is an ideal solution? How do you define an ideal solution? First of all what is solution?

Mixtures of many components are known as solution that may be in solid state, that may be in liquid state, that may be in gas state that means a mixture of real gas is a solution, a mixture of many liquids we can tell at solution even the mixture of many solids, we can tell at mixture solution so solutions is a mixture of many components and a solution is told as an ideal solution when this expression is valid.

This is the expression which defines an ideal solution means the fugacity of any component in that solution equals to the fugacity of that component as a pure component at the same state of the solution multiplied by the mole fraction.

f_i is f_i 0 x_i that means in an ideal solution the fugacity of any component equals to the fugacity of that component as a pure component at the same temperature and pressure and the aggregation of the solution that means the same state of the solution times the mole fractions so this simple relationship hold goods for ideal solution or other way we can tell that for each and every component in a solution this equation is valid. This solution is an ideal solution.

With this hypothesis of an ideal solution, we have certain corollaries of ideal solution that is the volume change in an ideal solution in an ideal solution or in preparing an ideal solution is equal to 0.

How do I prove it? Let us consider an ideal solution is made up of n_1 n_2 like that r number of components and each has a partial molar volume in the solution that means mixture as v_1 v_2.... vr. Therefore, their total volume of the solution $V_{solution}$ is equal to the sigma of n_i v_i i goes to v_i bar 1 to r. You know that thing we have already discussed that the extensive property of a solution is equal to sum of the product of the number of moles times the partial molar property of that property which we are finding. For example, volume, so sum of the products of this n_i v_i. Before solution total volume v is equal to sigma of n_i into v_i 0 i=1 to r. Therefore change delta v change in the volume to make the solution is sigma n_i into v_i minus v_i 0. How to prove this is 0? Very simple, we have already derived these two properties. Just now we have derived thing.

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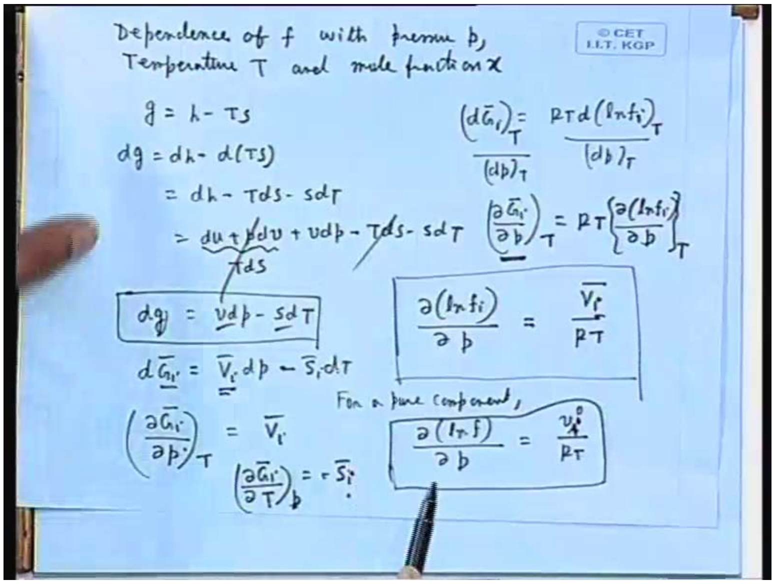

Dependence of f with pressure p,
Temperature T and mole fraction x

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$$g = h - Ts$$

$$dg = dh - d(Ts)$$

$$= dh - Tds - sdT$$

$$= \underbrace{du + pdv}_{Tds} + vdp - \cancel{Tds} - sdT$$

$$\boxed{dg = vdp - sdT}$$

$$d\bar{G}_i = \bar{V}_i dp - \bar{S}_i dT$$

$$\left(\frac{\partial \bar{G}_i}{\partial p}\right)_T = \bar{V}_i$$

$$\left(\frac{\partial \bar{G}_i}{\partial T}\right)_p = -\bar{S}_i$$

$$\frac{(d\bar{G}_i)_T}{(dp)_T} = \frac{RT\,d(\ln f_i)_T}{(dp)_T}$$

$$\left(\frac{\partial \bar{G}_i}{\partial p}\right)_T = RT\left\{\frac{\partial(\ln f_i)}{\partial p}\right\}_T$$

$$\boxed{\frac{\partial(\ln f_i)}{\partial p} = \frac{\bar{V}_i}{RT}}$$

For a pure component,

$$\boxed{\frac{\partial(\ln f)}{\partial p} = \frac{v_i^0}{RT}}$$

We have derived that del ln f_i del p is this and del n f_i 0 that means for a pure component v_i 0 t, if I write it it will be like this, let me write it.

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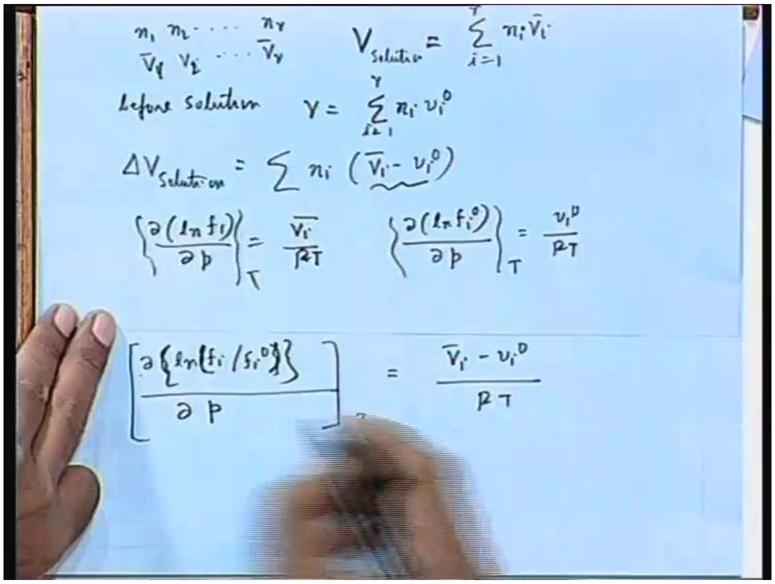

$n_1, n_2 \cdots n_r$

$\bar{V}_1\ \bar{V}_2 \cdots \bar{V}_r$

$$V_{\text{Solution}} = \sum_{i=1}^{r} n_i \bar{V}_i$$

before solution $V = \sum_{i=1}^{r} n_i v_i^0$

$$\Delta V_{\text{Solution}} = \sum n_i \left(\underbrace{\bar{V}_i - v_i^0}\right)$$

$$\left\{\frac{\partial(\ln f_i)}{\partial p}\right\}_T = \frac{\bar{V}_i}{RT} \qquad \left\{\frac{\partial(\ln f_i^0)}{\partial p}\right\}_T = \frac{v_i^0}{RT}$$

$$\left[\frac{\partial\{\ln(f_i/f_i^0)\}}{\partial p}\right]_T = \frac{\bar{V}_i - v_i^0}{RT}$$

del ln f_i del p is v_i bar by RT, just now I have done it and for a pure component del ln f_i 0 that means when the component i is as the state pure component at the same state of the mixture is equal to v_i 0 by RT this is at same temperature always when I differentiate with pressure here is the same temperature.

If I subtract this from this then what we get? We get del ln f_i by f_i 0 divided by del p at constant temperature is equal to then you just v_i bar minus v_i 0 by RT. You see f_i by f_i 0 is x_i which is constant at constant composition therefore this is constant so this is 0 therefore del v solution is 0.

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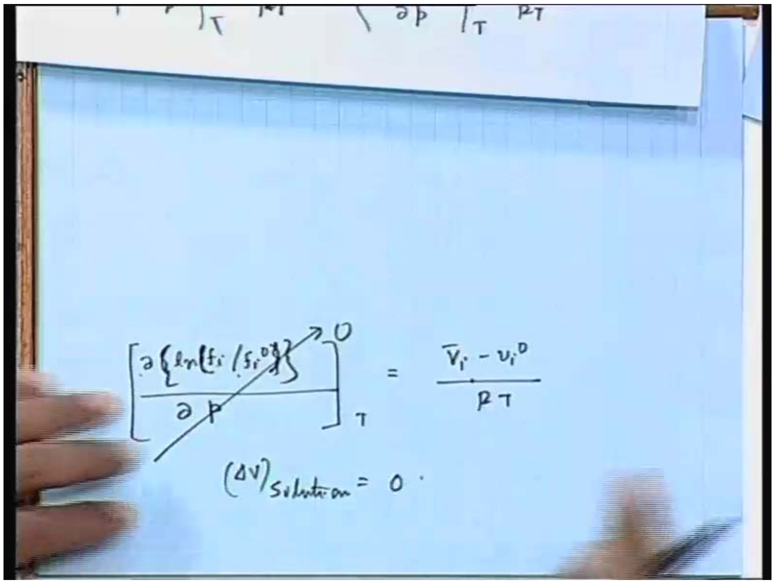

$$\left[\frac{\partial\{\ln(f_i/f_i^0)\}}{\partial p}\right]_T \xrightarrow{} 0 = \frac{\bar{V}_i - v_i^0}{RT}$$

$$(\Delta V)_{Solution} = 0$$

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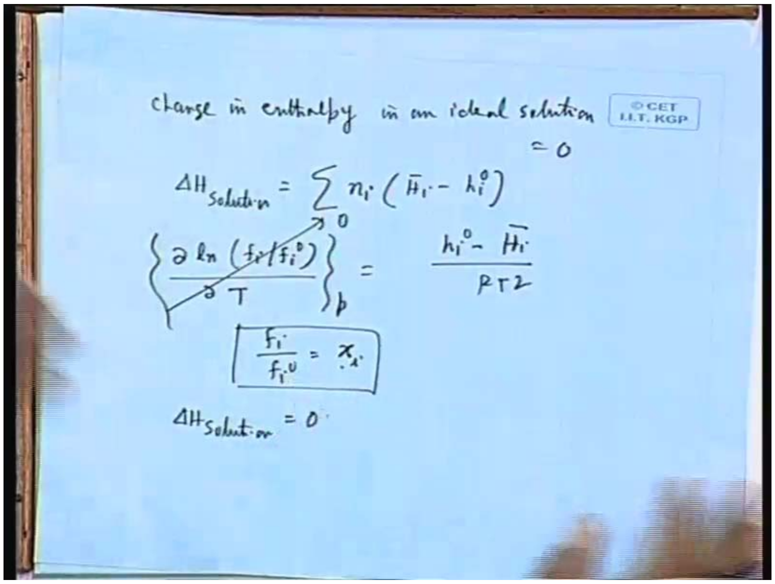

change in enthalpy in an ideal solution $= 0$

$$\Delta H_{Solution} = \sum n_i (\bar{H}_i - h_i^0)$$

$$\left\{\frac{\partial \ln(f_i/f_i^0)}{\partial T}\right\}_p \xrightarrow{} 0 = \frac{h_i^0 - \bar{H}_i}{RT^2}$$

$$\boxed{\frac{f_i}{f_i^0} = x_i}$$

$$\Delta H_{Solution} = 0$$

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In the similar way we can tell that the change in enthalpy in an ideal solution is 0. In the similar way we can tell that delta H in an ideal solution is sigma n_i into H_i bar minus h_i 0. Obviously n_i H_i bar is the total enthalpy of the mixture n_i h_i o is the total enthalpy of all the pure components so enthalpy change of solution and also we can write out in the similar fashion, if we see this expression earlier that these two del ln f_i del T at constant pressure is for a multi component system ith component present in a multi component system and at its pure state which we have defined earlier.

We can write you also see and do it at your home everything line by line I will not do in the class so del T this is at constant pressure it becomes is equal to RT square. In the similar way we did for the volume change. Again this is 0 because fi by f_i 0 by the definition of the ideal solution is x_i so therefore it is constant for constant composition therefore this is 0 and delta H solution is also 0. Change in the enthalpy of the solution is also 0.

After this we will come to dilute solutions. So far we have told about the ideal solutions. What are ideal solutions in practice? You must know that the mixture of real gases at low pressures is an ideal solution which means the mixtures of ideal gases are ideal solutions. Again the mixture of non electrolyte liquid solutions at high dilutions behaves as an ideal solution. What is non electrolyte solution?. A non electrolyte solution means a solution of non electrolyte liquid solutions where all the components exists as uncharged species rather charged ions and this non electrolyte solutions at high dilution What is meant by high dilution? That means with respect to a component it is diluted that means one component is in a very meager amount so that is known as a high dilute solution so it behaves as an ideal solution. These are the examples of ideal solution.

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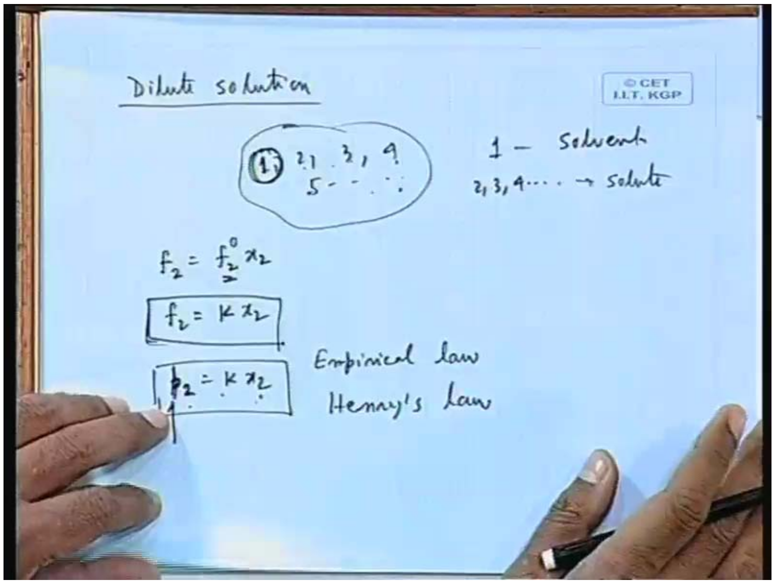

Dilute solution

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① 2, 3, 4
5 . . . .

1 – Solvent
2, 3, 4 . . . . → Solute

$f_2 = f_2^0 x_2$

$\boxed{f_2 = K x_2}$

$\boxed{p_2 = K x_2}$

Empirical law
Henry's law

Continuation of dilute solution what is a dilute solution?. Dilute solution means if there is a mixture of many components in a solution 1, 2, 3, 4, 5…. like that number of solution and if one of the component say for example one predominates by its amount and other components are very meager in its amount then this what is known as a dilute solution. This solution behaves an ideal solution with respect the solutes that means I can write for any of these 2, 3, 4 f_2 is f_2 0 x_2 and f2 expressed as a constant because this is constant this is the fugacity of the pure component of any of these 2, 3, 4 at the same state of the mixture x_2. So this is the definition or this is the law where this valid for all these components which are meager amount.

In a dilute solution where one component dominates, this is known as solvent and the components which are exist by meager amount are known as solutes so for any solute this is the equation because they behave as an ideal equation. In fact this was stated in terms of the partial pressure, this is an empirical law and it was found by Henry and known as Henry's law.

Henry's law states that in terms of the partial pressure or partial vapour pressure in a liquid solution of a component which is a solute in a dilute solution is proportional to its mole fraction with this we can prove the similar thing for this solvent. How we can prove?

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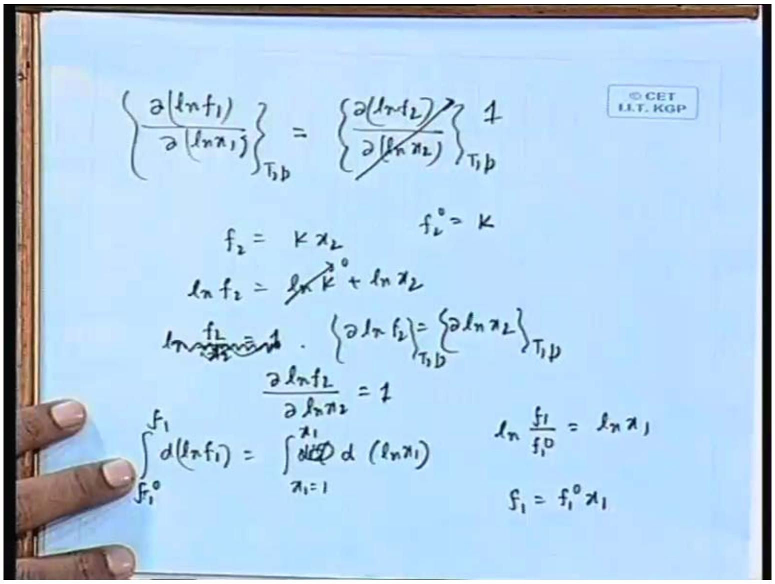

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$$\left\{\frac{\partial(\ln f_1)}{\partial(\ln x_1)}\right\}_{T,p} = \left\{\cancelto{1}{\frac{\partial(\ln f_2)}{\partial(\ln x_2)}}\right\}_{T,p}$$

$$f_2^0 = K$$

$$f_2 = K x_2$$

$$\ln f_2 = \cancelto{0}{\ln K} + \ln x_2$$

[illegible] . $\left\{\partial \ln f_2\right\}_{T,p} = \left\{\partial \ln x_2\right\}_{T,p}$

$$\frac{\partial \ln f_2}{\partial \ln x_2} = 1$$

$$\int_{f_1^0}^{f_1} d(\ln f_1) = \int_{x_1=1}^{x_1} d(\ln x_1)$$

$$\ln \frac{f_1}{f_1^0} = \ln x_1$$

$$f_1 = f_1^0 x_1$$

If you remember just now we have derived del ln f_1 by del ln x_1 so that we have just derived at constant temperature and pressure is equal to del ln f_2 divided by del ln x_2. If you remember just now we have derived this expression that this one. x1 this thing.

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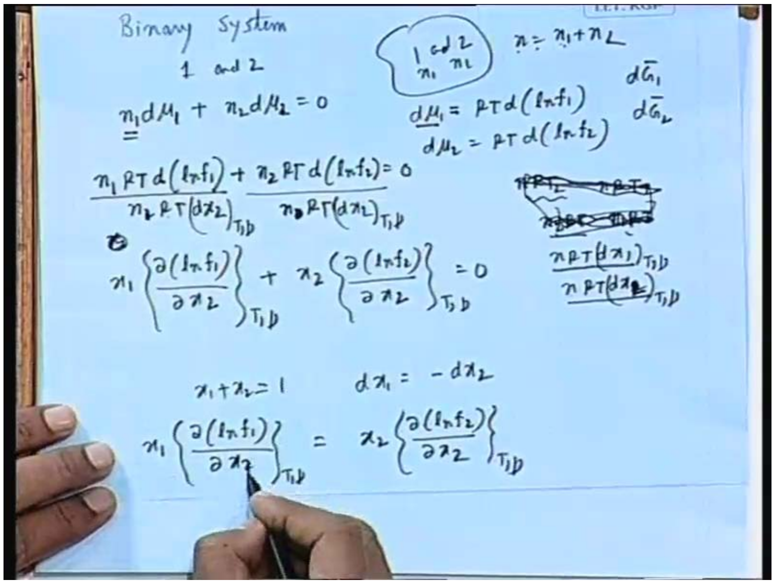

Binary system

1 and 2

1 and 2 n_1 n_2 $n = n_1 + n_2$

$d\bar{G}_1$

$d\bar{G}_2$

$n_1 d\mu_1 + n_2 d\mu_2 = 0$

$d\mu_1 = RT\, d(\ln f_1)$

$d\mu_2 = RT\, d(\ln f_2)$

$$\frac{n_1 RT\, d(\ln f_1)}{n RT (dx_2)_{T,p}} + \frac{n_2 RT\, d(\ln f_2)}{n RT (dx_2)_{T,p}} = 0$$

$$\frac{nRT(dx_1)_{T,p}}{nRT(dx_2)_{T,p}}$$

$$x_1 \left\{\frac{\partial(\ln f_1)}{\partial x_2}\right\}_{T,p} + x_2 \left\{\frac{\partial(\ln f_2)}{\partial x_2}\right\}_{T,p} = 0$$

$x_1 + x_2 = 1$ $dx_1 = -dx_2$

$$x_1 \left\{\frac{\partial(\ln f_1)}{\partial x_1}\right\}_{T,p} = x_2 \left\{\frac{\partial(\ln f_2)}{\partial x_2}\right\}_{T,p}$$

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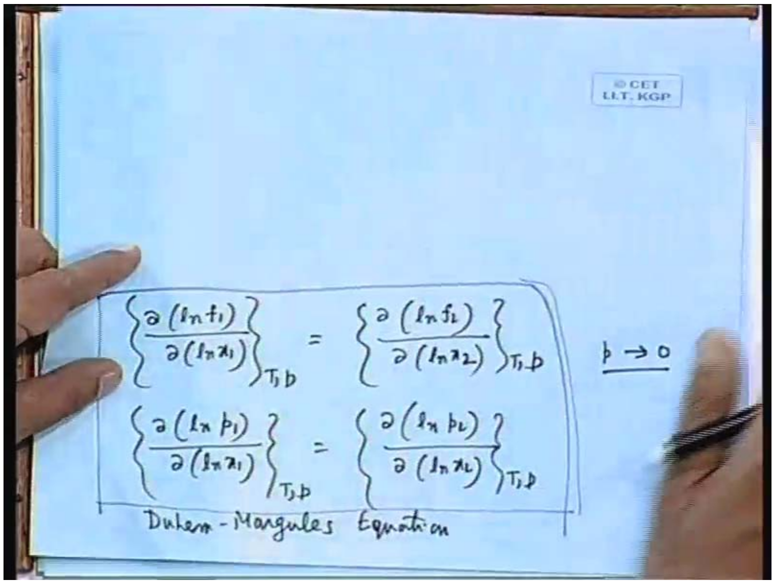

$$\left\{\frac{\partial(\ln f_1)}{\partial(\ln x_1)}\right\}_{T,p} = \left\{\frac{\partial(\ln f_2)}{\partial(\ln x_2)}\right\}_{T,p}$$

$p \to 0$

$$\left\{\frac{\partial(\ln p_1)}{\partial(\ln x_1)}\right\}_{T,p} = \left\{\frac{\partial(\ln p_2)}{\partial(\ln x_2)}\right\}_{T,p}$$

Duhem-Margules Equation

After that we have derived del ln f_1 x_1 del ln f_2 x_2. Then what we can write? that ln f_2 so f_2 is kx_2 so del ln f_2 is ln k plus ln x_2 so k is constant 0, this k is f_2 0 for the solute. Already we know behaving as an ideal that is the Henry's law therefore ln f_2 by x_2 is 1 therefore what we get? f_2 is ln f_2 so del ln f_2 by del ln fx_1 ln f_2 by ln x_2 is 1 so rather we can write this way ln f_2 is ln or we can write del ln f_2 this will be better del lnx_2 so del ln f_2 by del ln x_2 is 1.

If we write this is at constant T p. If we write this as 1so del ln f_1 del n x_1 that means we can write integration of d ln f is equal to integration of d ln d ln x_1 that means this is equal to 1so del ln f_1 I integrate this from what from x_1 is 1 to x_1 and x_1 1 means f_1 0 to f_1 pure state to f_1.

Which tells that ln f_1 by f_1 0 is ln x_1 which means f_1 is f_1 0 into x1 therefore for the solvent also sorry we have the same type of equation which is valid for the solute and if this solution is a liquid solution which are in equilibrium with its vapour.

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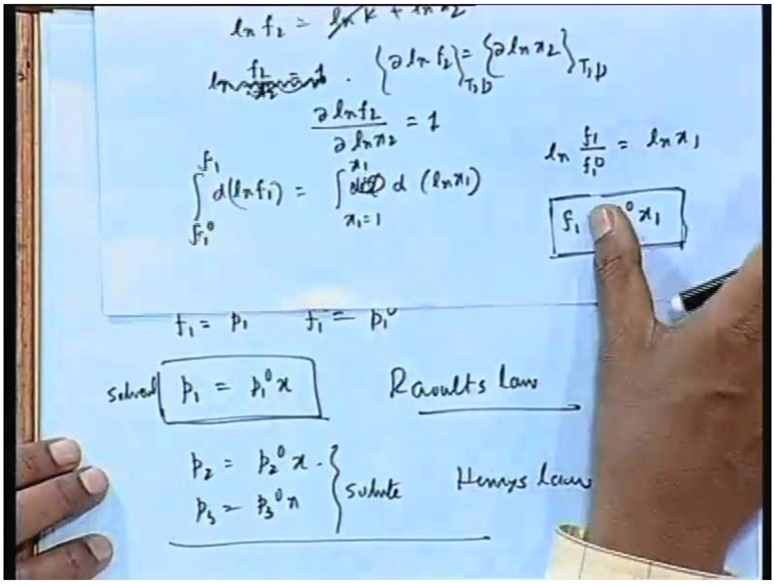

$\ln f_2 = \cancel{\ln} K + \ln x_2$

$\ln \frac{f_2}{\cancel{\quad}} \cdot \left\{\partial \ln f_2\right\}_{T,p} = \left\{\partial \ln x_2\right\}_{T,p}$

$$\frac{\partial \ln f_2}{\partial \ln x_2} = 1$$

$$\int_{f_1^0}^{f_1} d(\ln f_1) = \int_{x_1=1}^{x_1} d(\ln x_1)$$

$$\ln \frac{f_1}{f_1^0} = \ln x_1$$

f_1 [illegible] $^0 x_1$

$f_1 = p_1 \qquad f_1^0 = p_1^0$

Solvent $\boxed{p_1 = p_1^0 x}$ Raoults law

$p_2 = p_2^0 x$ } solute Henrys law

$p_3 = p_3^0 x$

Then f_1 can be written as the corresponding partial pressure and f_1 0 is p_1 0 so we can write p_1 is p_1 0 x and this is known as Raoult's law. If we compare the Raoult's law and the Henry's law then we see that whether when Henry's law is valid for a solute, the Raoult's law is valid for a solvent so this is Raoult law for solvent and p_2 is p_2 0 into x, p_3 is p_3 0 into x this is for solvent and this is for solute and this is the Henry's law .

When Henry's law is valid for the solute the similar law is valid for the solvent and is known as Raoult's law. These two laws are very important in dealing with the solutions or mixture of components but dilute solutions mind it and this is valid for dilute solutions, where Henry's law is obeyed by the solutes whose amount is very less and Raoult's law is the law obeyed by the solvent but the law is same that the fugacity of any component equals to the fugacity of the pure component times its mole fraction.