Course on Phase Equilibrium Thermodynamics
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Lecture 27
Fugacity(Contd.)

Well, I continue my class from the place where I had left my previous class just because this concept it is slightly difficult to understand, so I would like to revise from where I had left the last class. In the last class what did we do?

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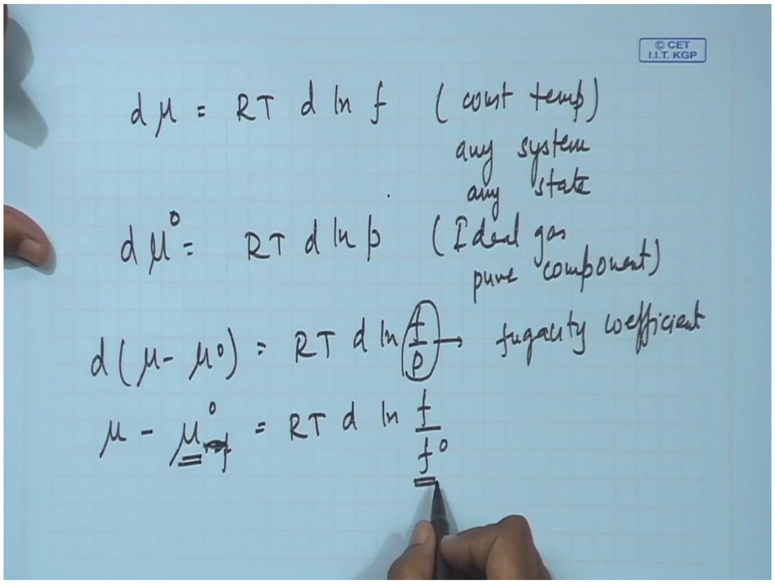

$d\mu = RT\, d \ln f$ (const temp) any system any state

$d\mu^0 = RT\, d \ln p$ (Ideal gas pure component)

$d(\mu - \mu^0) = RT\, d \ln \boxed{\frac{f}{p}} \rightarrow$ fugacity coefficient

$\mu - \underline{\mu^0} = RT\, d \ln \frac{f}{\underline{f^0}}$

I defined d mu as RT d ln f and this is constant temperature any substance, any system, any state and then I also defined d mu equals to RT d ln P ideal gas pure component and usually this is for an ideal gas. So therefore this and usually we find d of mu minus mu 0 this is equal to RT d ln f by P, right?

Now if we have to define and from there we found that this particular quantity is known as the fugacity coefficient. We also found out that if we have to move from one state to the other then in that case suppose I move from one particular state mu to some other reference state, so therefore in this particular situation or rather if I take the state as mu 0 itself this is also equal to f by f0 where I need to remember that the standards state of mu0 and the standard state of f0 they have to be the same but there is no other restriction on the selection of the standard states, we can select anything as the standard state as long as we can define mu0 and f0 at the same state.

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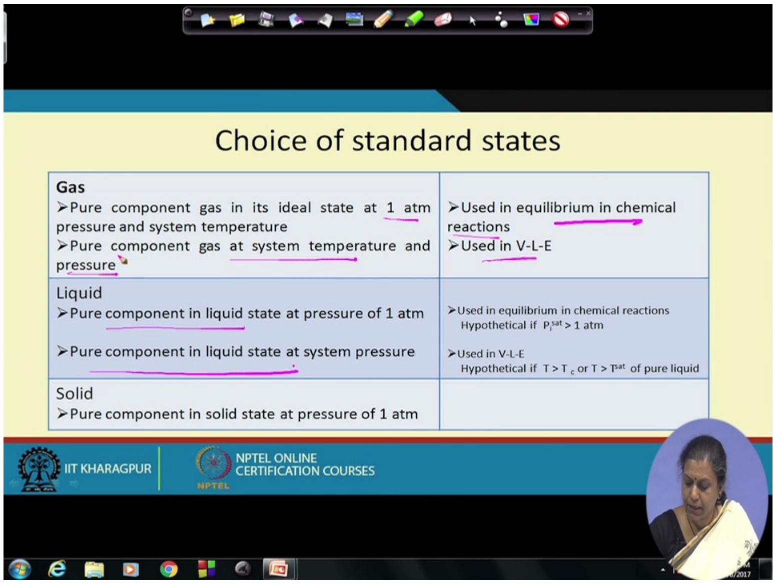

Choice of standard states

Gas ➢Pure component gas in its ideal state at 1 atm pressure and system temperature ➢Pure component gas at system temperature and pressure	➢Used in equilibrium in chemical reactions ➢Used in V-L-E
Liquid ➢Pure component in liquid state at pressure of 1 atm ➢Pure component in liquid state at system pressure	➢Used in equilibrium in chemical reactions Hypothetical if $P_i^{sat} > 1$ atm ➢Used in V-L-E Hypothetical if $T > T_c$ or $T > T^{sat}$ of pure liquid
Solid ➢Pure component in solid state at pressure of 1 atm	

I would also like to remind you that in fact we can also select any hypothetical state as a standard state as well and mostly we find that the different type of standard states that has been defined or there, which are mostly defined in literature are shown in this particular slide where we see that usually the standard states are selected for the different phases at say pure component gas in its ideal state at 1 atmospheric pressure everything has to be at the same system temperature or it or can also be pure component gas at the system pressure and the system temperature.

I just need to mention that the first standard state is usually used in chemical reactions while the second standard state we will be using very frequently in vapor liquid equilibrium because in this class we are going to deal mostly with vapor liquid equilibrium we are not going to deal chemical equilibrium same thing applies for a liquid as well it can either be a pure component in the liquid state at the pressure of 1 atmosphere or pure component in the liquid state at the system pressure.

And again this is the, this is of interest to us since we will be dealing with vapor liquid equilibrium, for solid it is pure component in the solid state at a pressure of 1 atmosphere. So we find that we can use different standard states, only thing which we need to remember in this particular case is that the standard state should be the same for chemical potential as well as for fugacity.

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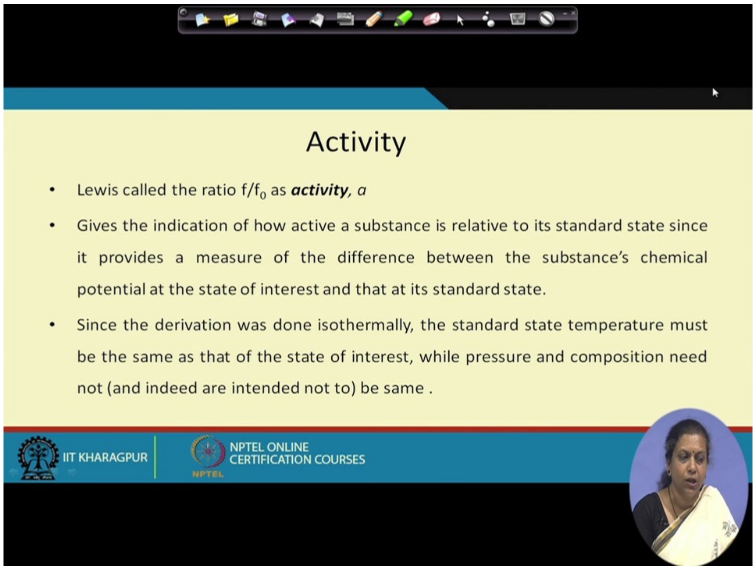

Activity

- Lewis called the ratio f/f_0 as ***activity***, *a*
- Gives the indication of how active a substance is relative to its standard state since it provides a measure of the difference between the substance's chemical potential at the state of interest and that at its standard state.
- Since the derivation was done isothermally, the standard state temperature must be the same as that of the state of interest, while pressure and composition need not (and indeed are intended not to) be same .

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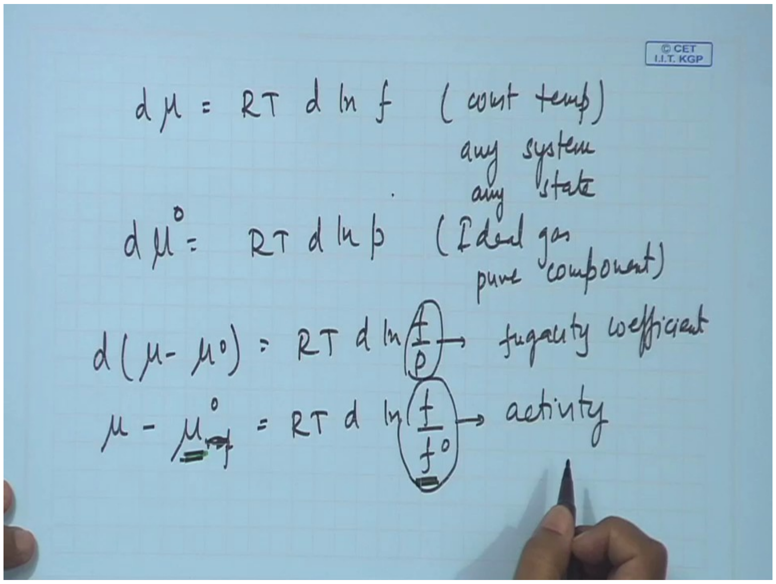


$d\mu = RT\, d \ln f$ (const temp)

any system

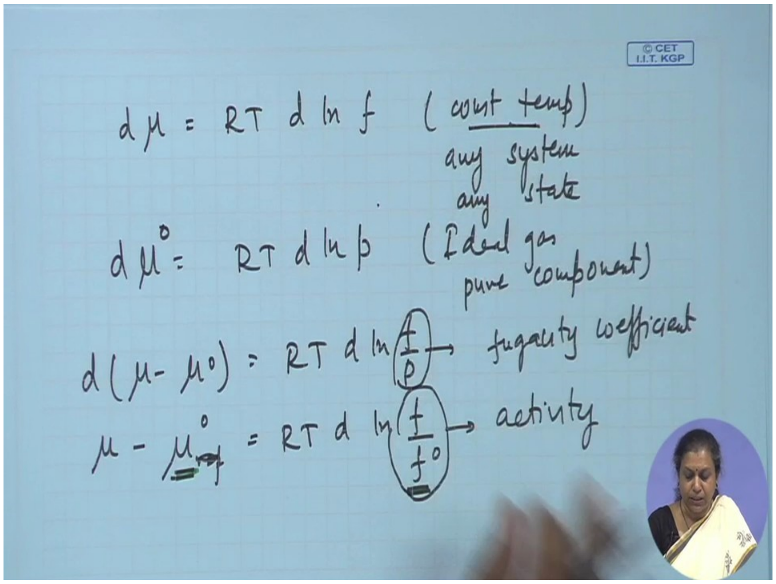
any state

$d\mu^{0} = RT\, d \ln p$ (Ideal gas pure component)

$d(\mu - \mu^{0}) = RT\, d \ln \boxed{\frac{f}{p}} \rightarrow$ fugacity coefficient

$\mu - \mu^{0}_{ref} = RT\, d \ln \boxed{\frac{f}{f^{0}}} \rightarrow$ activity

And the other thing which I would like to mention here is that there was another term which we had defined the term was defined as activity, why? Because again we find that this is another term which we come across this term was defined as activity as I had mentioned in the last class since it gives the indication of how active a substance is. It gives an indication of how active a substance is relative to its standard states and this one thing which we need to remember.



$d\mu = RT\, d\ln f$ (const. temp)

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any state

$d\mu^0 = RT\, d\ln p$ (Ideal gas pure component)

$d(\mu - \mu^0) = RT\, d\ln \left(\frac{f}{p}\right) \rightarrow$ fugacity coefficient

$\mu - \mu^0_{\cancel{ref}} = RT\, d\ln \left(\frac{f}{f^0}\right) \rightarrow$ activity

The first thing is mu0 and f0 have to be at the same standard states the other thing we need to remember that the standard state is with reference to the pressure and composition it is not with reference to the temperature because we have been dealing with, the derivation was done under isothermal conditions for each and every case this particular thing this particular condition was maintained.

So therefore the standard states temperature must be the same as the temperature of the state of interest it is only the pressure and composition which can vary between the 2 states. So therefore to summarize the whole thing it's the thing which I would like to mention and this particular slide has been prepared primarily keeping in mind the confusion which students have when they are asked what is fugacity?

This is a problem which I have also faced several times whenever we try we ask the students what is fugacity? They try to say that it is a corrected pressure and then they are asked why I need to 2 to correct pressure and then the whole thing they just get confused. So therefore to make matters simpler I have just summarized the concept of fugacity and it is just like this which you need to remember for understanding chemical potential and fugacity it is that since it is difficult to wish, sorry.

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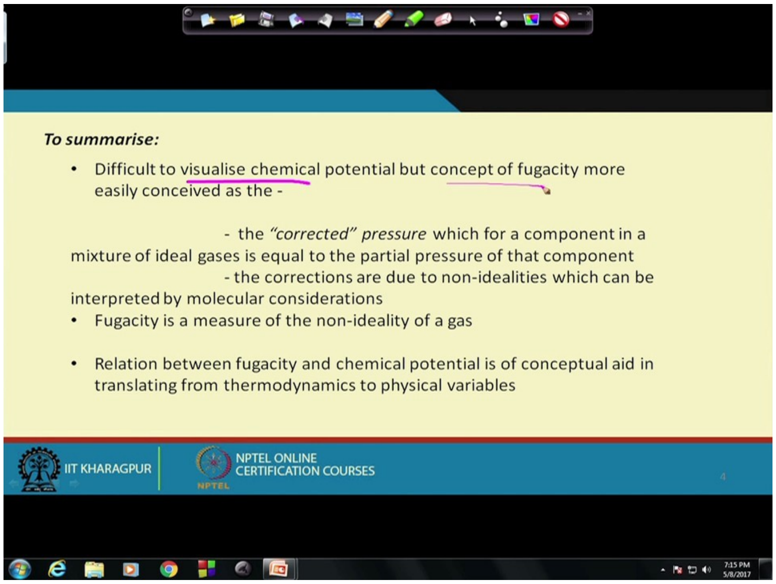

To summarise:

- Difficult to visualise chemical potential but concept of fugacity more easily conceived as the -

  - the *"corrected" pressure* which for a component in a mixture of ideal gases is equal to the partial pressure of that component

  - the corrections are due to non-idealities which can be interpreted by molecular considerations
- Fugacity is a measure of the non-ideality of a gas
- Relation between fugacity and chemical potential is of conceptual aid in translating from thermodynamics to physical variables

Since it is difficult to visualize chemical potential therefore the concept of fugacity it has been introduced it can be more easily conceived, what is it? It is a corrected pressure which for a component in a mixture of ideal gases is equal to the partial pressure of the component just as I had shown in the last class this tends to 1 for limit P tends to 0, right? And why do you need to correct pressure? It is we need to correct pressure just because they are typical non-idealities which can be interpreted by their molecular consideration.

So therefore if it is if you are concerned with gas, fugacity is nothing but a measure of the non-ideality of the gas. If it is for any other substance, it just notes the deviation of that substance from the ideal gas behavior and by defining fugacity what have we done? We have actually it is a conceptual aid by which we have translated thermodynamics to the physical variables.

We have actually related abstract concept of chemical potential to the concept of fugacity which can be understood or related to the physically realizable world the only condition which we need is to find out a straightforward way of defining fugacity but before that there are certain other things that we need to do. First thing is we need to remember that the whole concept of fugacity or chemical potential it came up just because we were trying to define chemical equilibrium.

We were trying to find under what conditions chemical equilibrium is achieved? What is the best composition that we can get? What is the best separation that we can get from our process? And all those things were dictated by chemical potential and accordingly what did we do in the last to last class?

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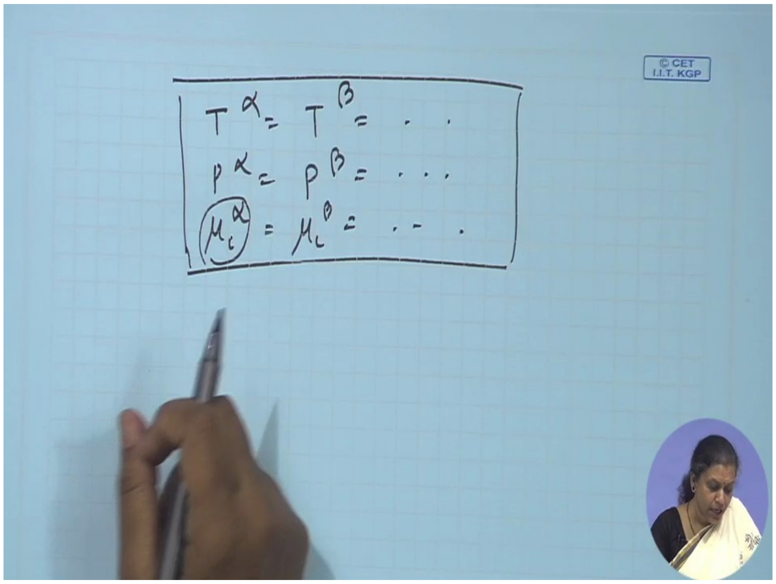

$$T^{\alpha} = T^{\beta} = \ldots$$

$$P^{\alpha} = P^{\beta} = \ldots$$

$$\boxed{\mu_i^{\alpha}} = \mu_i^{\beta} = \ldots$$

We had defined the conditions of thermodynamic equilibrium if you remember the conditions it was T alpha equals to T beta equals to so on, it was P alpha equals to P beta equals to so on and it was for each and every component it was mu i alpha equals to mu i beta equals to so on. So now since we want to replace mu with fugacity we should be in a position to reframe the conditions of thermodynamic equilibrium in terms of fugacity particularly we need to reframe the chemical potential condition in terms of fugacity.

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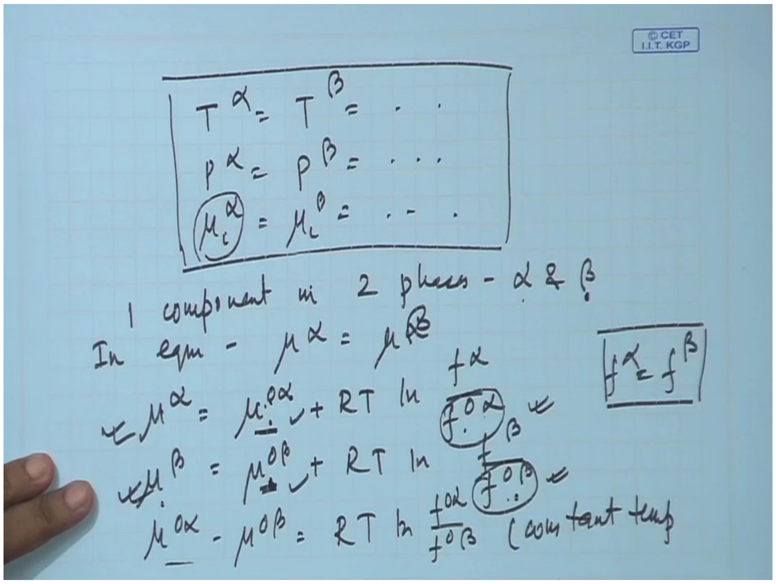

$$\boxed{\begin{aligned} T^{\alpha} &= T^{\beta} = \dots \\ p^{\alpha} &= p^{\beta} = \dots \\ \mu_i^{\alpha} &= \mu_i^{\beta} = \dots \end{aligned}}$$

1 component in 2 phases - α & β

In eqm - $\mu^{\alpha} = \mu^{\beta}$

$$\mu^{\alpha} = \mu^{0\alpha} + RT \ln \frac{f^{\alpha}}{f^{0\alpha}}$$

$$\mu^{\beta} = \mu^{0\beta} + RT \ln \frac{f^{\beta}}{f^{0\beta}}$$

$$\boxed{f^{\alpha} = f^{\beta}}$$

$$\mu^{0\alpha} - \mu^{0\beta} = RT \ln \frac{f^{0\alpha}}{f^{0\beta}}$$ (constant temp

Let us see how we can we can do, we can come about do doing this? Let us start from the beginning, simplest case we have say one component in 2 phases, the 2 phases are say alpha phase and the beta phase. Now in equilibrium, what do we know? We know mu alpha must be equal to mu beta, what is, how is mu alpha related to fugacity?

It should be equal to some standard state mu alpha plus RT ln f alpha by f0 alpha. Similarly what is mu beta? It is nothing but equals to mu 0 beta plus RT ln f beta by f0 beta. Now we are stuck up here, why? Because we cannot proceed further unless we have some idea regarding the standard states in the 2 phase’s alpha and beta, what are the standard states? They may be same they may not be same.

Suppose for the time being we assume that they are the same. If they are the same then what do we have? We have this equal to this under equilibrium this equals to this and if these 2 are equal automatically these 2 are equal because as I have said we cannot very these and these separately. So when these 2 are in under the same standard states these 2 are also under the same standard states.

So with these 2 equal, this and this equal and these 2 equal, what does it imply? It implies automatically that f alpha equals to f beta but this was under the condition where we assumed equal standard state same standard states for both. Suppose we assume that the standard states are not the same in what can they vary? They cannot vary in temperature remember because everything we have done, we have done under isothermal conditions.

So they can just vary in terms of pressure or in terms of composition if that is so they do not vary in terms of temperature then we can also have a equation relating the chemical potentials of the 2 standards states with the standard fugacity's of the 2 standard states, isn't it? We find that these 2 standard states are not the same the temperature has to be same. So either the pressures are different or the compositions are different, the same thing should be applicable to both of them.

So therefore we are simply relating the change in chemical potential to the change of fugacity under constant temperature conditions. So therefore the same equations which we had used should hold for this condition as well.

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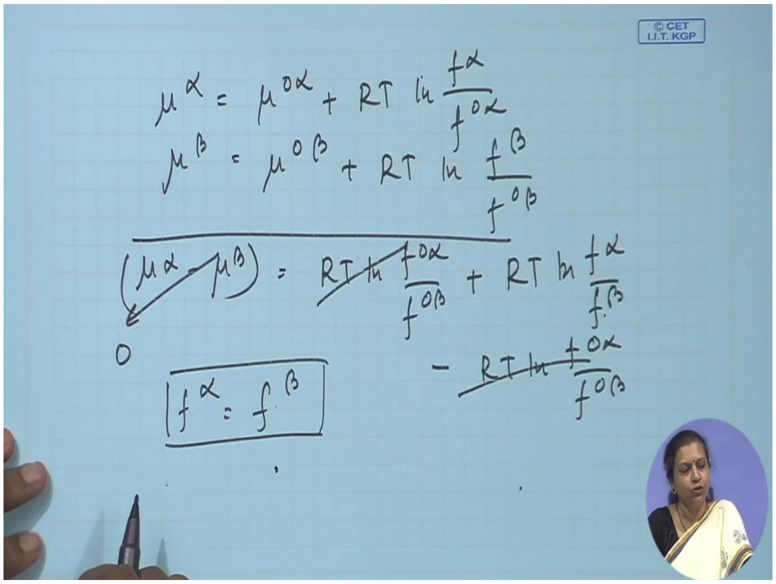

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$$\mu^{\alpha} = \mu^{0\alpha} + RT \ln \frac{f^{\alpha}}{f^{0\alpha}}$$

$$\mu^{\beta} = \mu^{0\beta} + RT \ln \frac{f^{\beta}}{f^{0\beta}}$$

$$\underbrace{(\mu^{\alpha} - \mu^{\beta})}_{0} = \cancel{RT \ln \frac{f^{0\alpha}}{f^{0\beta}}} + RT \ln \frac{f^{\alpha}}{f^{\beta}} - \cancel{RT \ln \frac{f^{0\alpha}}{f^{0\beta}}}$$

$$\boxed{f^{\alpha} = f^{\beta}}$$

So now we can replace this particular condition in these 2 equations if we replace what do we get let us see? The first condition was mu Alpha equals to mu0 alpha plus RT ln f alpha by f0 alpha. Second thing was mu beta was equal to mu0 beta plus RT ln f beta by f0 beta, if we subtract one from the other what do we get? Which is equal to 0 and this minus this, this is nothing but RT ln f0 alpha by f0 beta.

Now if you subtract from this what do we get? Can we write it down as f alpha by f beta minus RT ln f0 alpha by f0 beta just rearranging this part? So therefore in this particular condition also what do we get? We find that RT ln f alpha by f beta equals to, so therefore from this condition also we find that since this part is equal to 0 this should be equal to this and we get this condition.

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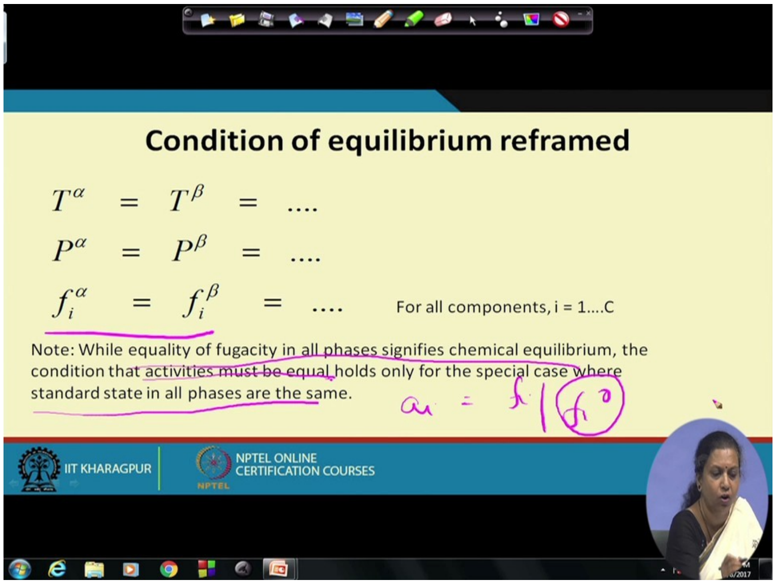

Condition of equilibrium reframed

$$T^{\alpha} = T^{\beta} = \ldots.$$

$$P^{\alpha} = P^{\beta} = \ldots.$$

$$f_i^{\alpha} = f_i^{\beta} = \ldots.$$ For all components, i = 1....C

Note: While equality of fugacity in all phases signifies chemical equilibrium, the condition that activities must be equal holds only for the special case where standard state in all phases are the same.

$a_i = f_i / f_i^0$

So therefore what do we deduce from here? We find that whatever be the standard sate, we find that irrespective of the standard states the condition of equilibrium reframed is this, for all components i equals to 1 to C whatever components we have there is just one note of caution which I would like to mention here that while equality of fugacity signifies chemical equilibrium the condition that activities must, this equality of fugacity does not imply that activities in all the phases should be equal.

The activities will be equal only for the special case where the standard state in all the phases are the same because what is activity again if I recollect ai equals to fi by fi0. So even if fi is same for all the states if fi zeros are different for all the states the ai is different.

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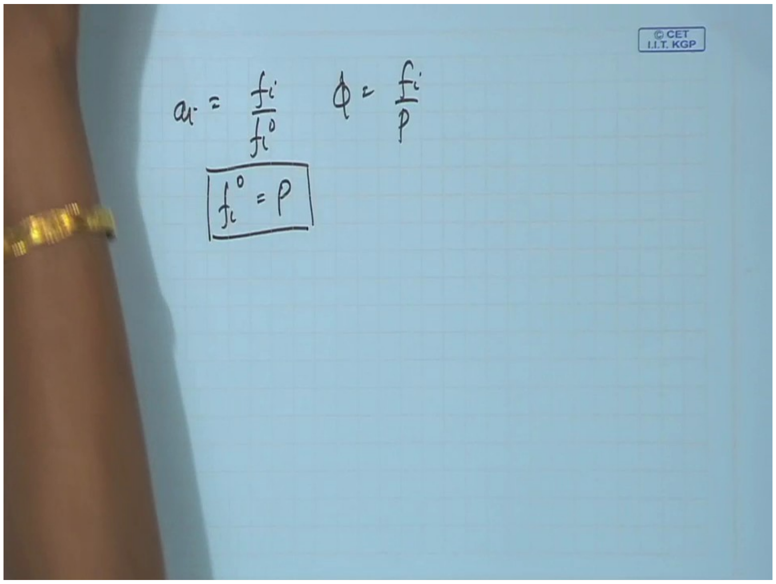

$$a_i = \frac{f_i}{f_i^0} \qquad \phi = \frac{f_i}{P}$$

$$\boxed{f_i^0 = P}$$

In fact here I would like to pose a question for you, what is the difference between fugacity coefficient and activity? Or rather under what conditions will activity and fugacity coefficient be equal activities fi by fi 0 phi equals to fi by P, so it is very evident when fi0 equals to dv when we define the standard state such that the standard state is the total pressure of the system under that condition fugacity and activity are the same.

Well, so once having defined the or rather reframed the condition of equilibrium the next thing which I would like to do before I go into the estimation of fugacities for solid, liquid, gases etc. since whenever we define any new quantity we would like to find out the effect of temperature and pressure on it.

So I would like to find effect of temperature and pressure on fugacity. Let us define it and we are going to, our starting point will be the variation of chemical potential with temperature and pressure we know that, why? Because in a in one of the classes I had spend 1 whole class rather discussing the affect of temperature and pressure on molar Gibbs free energy. The reason for doing that was that molar Gibbs free energy is equal to the chemical potential for a pure component.

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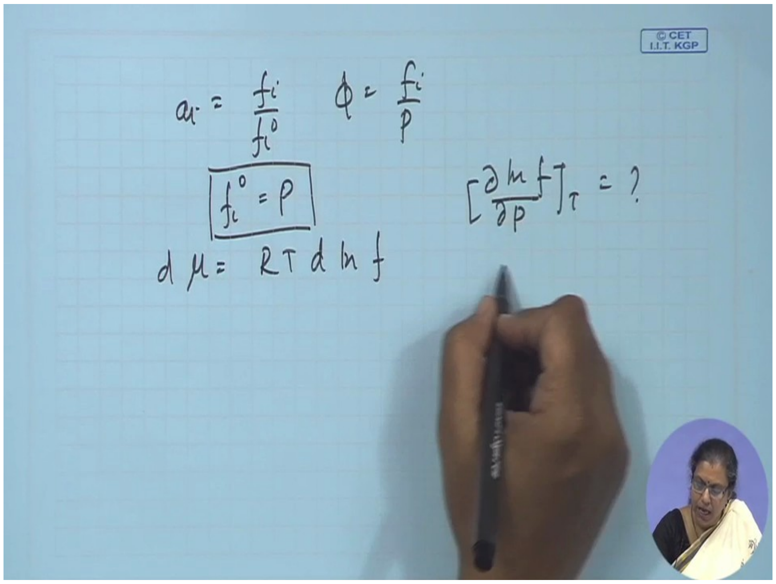

$a_i = \frac{f_i}{f_i^0}$ $\phi = \frac{f_i}{P}$

$\boxed{f_i^0 = P}$

$d\mu = RT\, d\ln f$

$\left[\frac{\partial \ln f}{\partial P}\right]_T = ?$

So therefore whatever equations we have derived for the molar Gibbs free energy is applicable for the chemical potential and using the relationship between chemical potential and fugacity we should be in a position to find out, how fugacity it varies with pressure under constant temperature conditions? And how fugacity varies with temperature under constant pressure conditions?

Let us start doing the equations, we know this equation and what is this equals to? Minus sdT plus vdp we already know that, so therefore what is del ln f del P at constant T and the total number of moles? This is nothing but equal to del mu del p at constant T and total mole and we know what is this? This is equals to v. So therefore what is, just a minute there has to be an RT here sorry, so therefore we deduce that del ln f del P at constant T, n is nothing but equals to v by RT or in other words ln f by f0 equals to again if f0 is defined at P equals to 0 v by RT dp.

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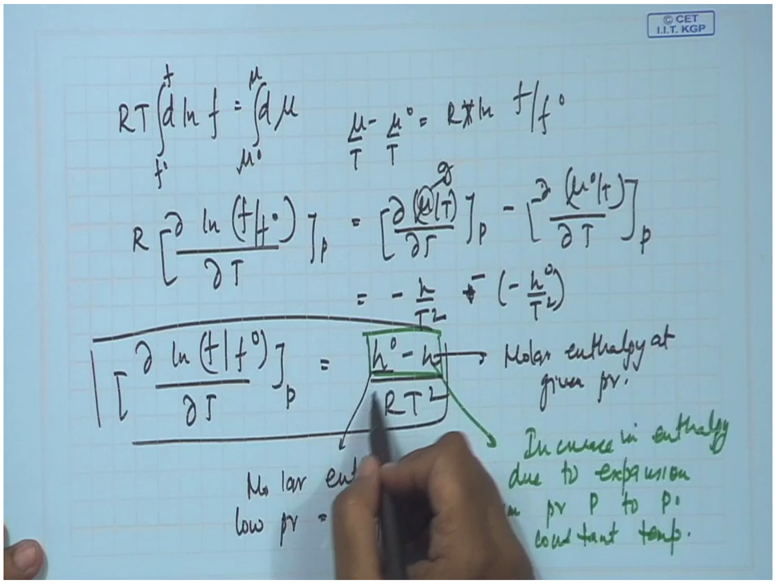

$$RT\int_{f^0}^{f} d\ln f = \int_{\mu^0}^{\mu} d\mu$$

$$\frac{\mu}{T} - \frac{\mu^0}{T} = R\cancel{T}\ln f/f^0$$

$$R\left[\frac{\partial \ln(f/f^0)}{\partial T}\right]_p = \left[\frac{\partial(\overset{g}{\mu}/T)}{\partial T}\right]_p - \left[\frac{\partial(\mu^0/T)}{\partial T}\right]_p$$

$$= -\frac{h}{T^2} \cancel{+} - \left(-\frac{h^0}{T^2}\right)$$

$$\boxed{\left[\frac{\partial \ln(f/f^0)}{\partial T}\right]_p = \frac{h^0 - h}{RT^2}}$$

→ Molar enthalpy at given pr.

Increase in enthalpy due to expansion ... pr P to P0 constant temp.

Molar ent... low pr =

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And what is the variation of fugacity with temperature? Again we start from the same thing we know that RT, for everything we are going to start with the same thing, we integrate this equation, again this is from mu 0 to mu, this is from f0 to f from where we get mu minus mu0 equals to RT ln f by f0, we can divide this by T, we can divide this by T. Now we know what, now suppose we want to find out R del ln f by f0 as a function of T for constant pressure, what is it? Del mu by T del T at constant pressure minus del mu 0 by T del T at constant pressure, you must recall that this is nothing but equal to G.

So we had already defined it or rather derive the Gibbs Helmholtz equation. We can straightaway substitute it here and therefore this is equals to minus h by T square plus of minus or rather minus of minus h0 by T square. So therefore we can very well write it down as del ln f0 by del t at constant P this is nothing but equal to h0 minus h by RT square.

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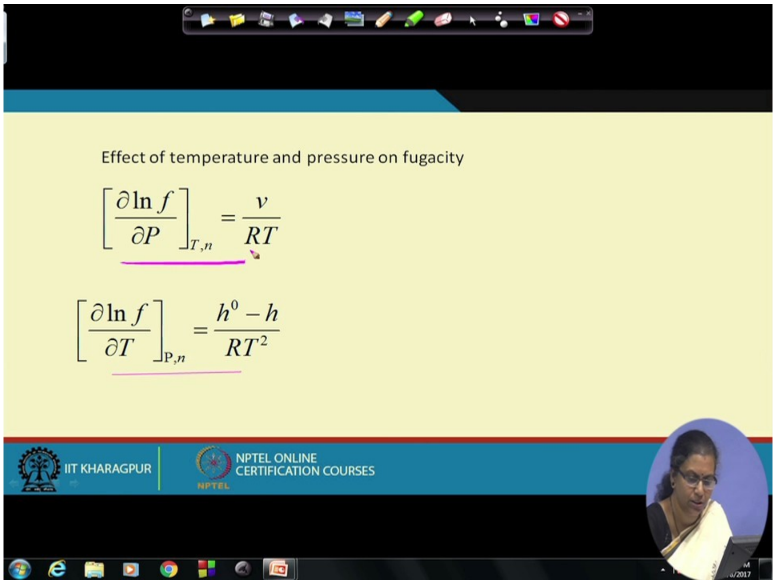

Effect of temperature and pressure on fugacity

$$\left[\frac{\partial \ln f}{\partial P}\right]_{T,n} = \frac{v}{RT}$$

$$\left[\frac{\partial \ln f}{\partial T}\right]_{P,n} = \frac{h^0 - h}{RT^2}$$

The same equation which I have just jotted down and the derivations are here, where what is h0 equals to? This is the molar enthalpy at low pressure which is nothing but equal to Cp0 dT, what is h equals to? It is the molar enthalpy at the pressure of interest at given pressure and therefore what is this term? Term h0 everything is right. What is this term h0 minus h? This term is nothing but the increase in enthalpy due to expansion from pressure P to P0 at constant temperature.

So well, once we have understood this one more interesting thing since we know that all these are properties of the system, so therefore we can arrive at the same particular expression by using an alternative route.

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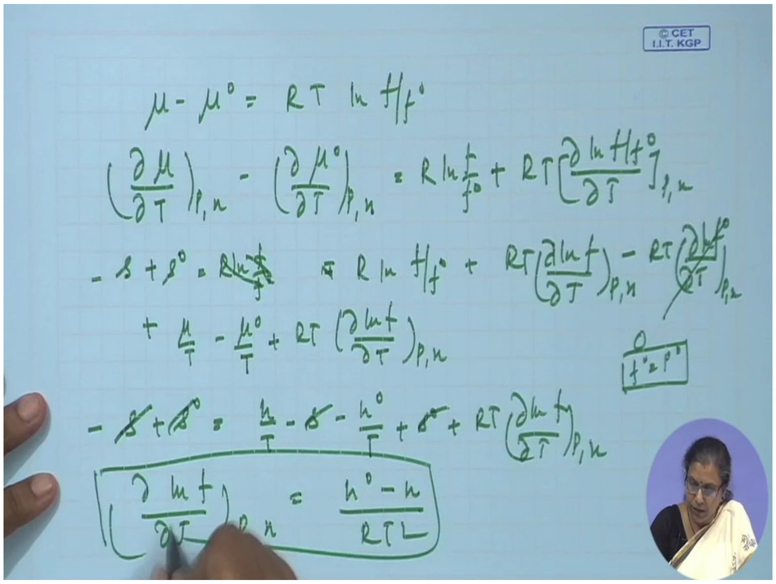

$$\mu - \mu^0 = RT \ln f/f^0$$

$$\left(\frac{\partial \mu}{\partial T}\right)_{P,n} - \left(\frac{\partial \mu^0}{\partial T}\right)_{P,n} = R \ln \frac{f}{f^0} + RT\left[\frac{\partial \ln f/f^0}{\partial T}\right]_{P,n}$$

$$-s + s^0 = \cancel{R \ln f/f} = R \ln f/f^0 + RT\left(\frac{\partial \ln f}{\partial T}\right)_{P,n} - RT\cancel{\left(\frac{\partial \ln f^0}{\partial T}\right)_{P,n}}$$

$$0 \quad \boxed{f^0 = P^0}$$

$$+ \frac{\mu}{T} - \frac{\mu^0}{T} + RT\left(\frac{\partial \ln f}{\partial T}\right)_{P,n}$$

$$-\cancel{s} + \cancel{s^0} = \frac{h}{T} - \cancel{s} - \frac{h^0}{T} + \cancel{s^0} + RT\left(\frac{\partial \ln f}{\partial T}\right)_{P,n}$$

$$\boxed{\left(\frac{\partial \ln f}{\partial T}\right)_{P,n} = \frac{h^0 - h}{RT^2}}$$

I very frequently do this particular exercise just to show you that since we are dealing with properties we can start and derive by any particular route, if you have done it correctly we will be arriving at the same results. For example this equation we can also start in a different form starting from the same equation, we are interested to find how this quantity varies with temperature? We can just write it down in this particular form, right? This is equals to R ln f by f0 plus RT del ln f by f0 del T at constant P and n, we can do it this is equal to R ln f by f0 plus RT del ln f del T at constant P, n minus RT del ln f0 del T at constant P, n, fine.

Now we know that this term it has to be equal to 0 because f0 is equal to P0 and that is definitely a constant quantity. So therefore what is this term then in that particular case? We can write this term as minus s, this term is plus s0 this is equal to R ln f by f0 plus mu by T minus mu0 by T and so therefore we can write down sorry this term was wrong, we can just write it down as this plus RT del ln f del T at constant P, n. So therefore from there what do we get?

It is nothing but minus s plus s0 equals to, this mu by T is nothing but g by t it can be written down as hT minus s minus h0 by T plus h0 plus RT del ln f del T at constant P, n. It is slightly more involved thing but from here we find del ln f del T at constant P, n all these terms they cancel out and we get this is nothing but equal to h0 minus h by RT square.

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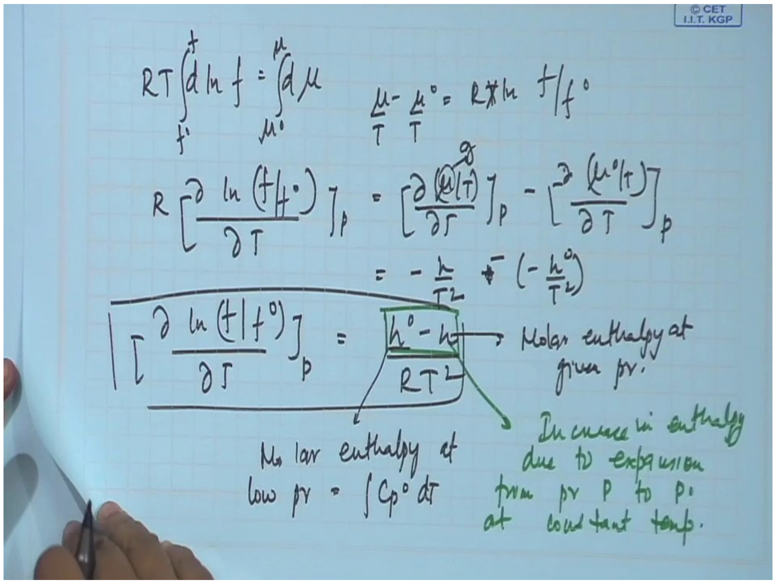

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$$RT\int_{f^0}^{f} d\ln f = \int_{\mu^0}^{\mu} d\mu$$

$$\frac{\mu}{T} - \frac{\mu^0}{T} = R\cancel{T}\ln f/f^0$$

$$R\left[\frac{\partial \ln(f/f^0)}{\partial T}\right]_P = \left[\frac{\partial(\overset{g}{\mu}/T)}{\partial T}\right]_P - \left[\frac{\partial(\mu^0/T)}{\partial T}\right]_P$$

$$= -\frac{h}{T^2} \cancel{+} - \left(-\frac{h^0}{T^2}\right)$$

$$\boxed{\left[\frac{\partial \ln(f/f^0)}{\partial T}\right]_P = \frac{\boxed{h^0 - h}}{RT^2}}$$

Molar enthalpy at given pr.

Molar enthalpy at low pr = $\int C_p^0\, dT$

Increase in enthalpy due to expansion from pr P to P0 at constant temp.

The same expression that I had obtained in this particular case as well, so therefore it hardly matters which route you use what type of approach you do, since if your approach your concepts are correct then by whatever way you do, you should be in a position to come to the correct answer.

Well, after this the next thing which I would like to do is to estimate rather to devise or rather to discuss different ways by which fugacity of a pure idea of a pure gas of a pure liquid can be found out once we have understood that then we go for mixtures and there we try to find out how the fugacity of component in the mixture can be estimated?