Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
Department of Chemical Engineering
Indian Institute of Technology Kharagpur
Lecture 26
Concept of Fugacity

Hello everybody, so I would like to remind you that in the last class we had discussed the phase transitions of pure substances from one physical state to another. Now just one thing I would like to mention regarding that whatever transitions we have discussed in the last class all of these they are referred to as the first order transitions or the transitions of the first kind because in those particular transitions we found that the first derivative of thermodynamics potential, for instance in this case it is G.

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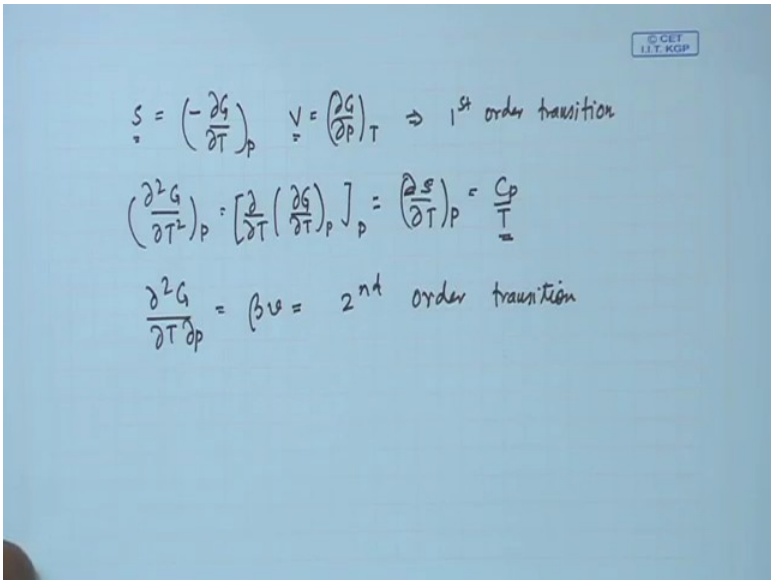

$$\underline{\underline{S}} = \left(-\frac{\partial G}{\partial T}\right)_P \quad \underline{\underline{V}} = \left(\frac{\partial G}{\partial P}\right)_T \Rightarrow 1^{st} \text{ order transition}$$

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = \left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial T}\right)_P\right]_P = \left(\frac{\partial S}{\partial T}\right)_P = \underline{\underline{\frac{C_P}{T}}}$$

$$\frac{\partial^2 G}{\partial T \partial P} = \beta v = 2^{nd} \text{ order transition}$$

The first derivative is s minus Del G Del T at constant P and the volume which is Del G Del P at constant T, so these 2 parameters they had undergone an abrupt discontinuity as a transition as a result these transitions they are known as the first order transitions or they are known as the transitions of the first kind.

Here I would just like to mention that in the second order transitions what happens is that, the first derivatives of the thermodynamic potentials namely in this case it is entropy and volume the first derivatives of the thermodynamic potential Gibbs free energy they remain constant while the second order the derivative it exhibits an abrupt discontinuity at the phase transition, for example what is the second-order rather second derivative.

It is suppose say Del 2 G Del T 2 at constant P, what is this? This is nothing but equal to Del Del T of Del G Del T everything at constant P. So therefore this is nothing but equal to minus yeah or in other words this is nothing but equals to Del S Del T at constant P which is nothing but equal to CP by T. So and in the same way we can also write Delta 2 G Del T Del P this is also this can also be found this is equal to beta v.

So therefore for the second-order transitions we find that these 2 parameters they would be undergoing an abrupt discontinuity while the first derivatives would remain constant and so therefore whatever transitions we had discussed in the last class all of these they refer to the first order transitions. Now along with that I would also like to remind you that in thermodynamics we have been dealing with equilibrium states. Now all these equilibrium states that we deal with all of these refer to stable equilibrium states.

We will be recalling from mechanics a very difficult diagram where this refers to the stable equilibrium, this refers to the unstable equilibrium; this refers to the metastable equilibrium states. Now for most of the cases we deal with stable equilibrium states while phase transitions they refer to metastable equilibrium states and some particular equilibrium states for example suppose water is existing below 0 degrees centigrade or in other words sub cooled water or maybe water existing above hundred degrees centigrade for example it is the super heated water or maybe steam existing below hundred degrees centigrade which is nothing but the sub cooled vapor. So these particular states which are extremely unstable, so these particular states they are known as the metastable states in classical thermodynamics.

We mostly deal with stable equilibrium states and during phase transitions we deal with metastable equilibrium states. I would also like to mention that just like in mechanics we have found out that the potential energy extremum in the state of equilibrium and that implies that when that extremum is maximum the state is unstable when the extremum is minimum then this equilibrium is a stable equilibrium.

In thermodynamics also as I’ve already mentioned in one of my previous classes stability of a thermodynamic system in terms of the extremum of some thermodynamic property it can be either maximization of entropy or minimization of energy. Well, so with this I come to the topic which we are going to discuss today. We are going to discuss little more about the phase transitions or rather phase equilibrium thermodynamics and here I would like to mention that the task of phase equilibrium thermodynamics is to describe quantitatively the distribution at equilibrium of every component among all phases which are present.

For example suppose we are performing distillation of a mixture of alcohol and water and we would like to know that under a certain temperature and pressure conditions, how much amount of alcohol or water would be distributed between the liquid phase and the vapor phase. Again suppose we would like to extract acetic acid from a solution of toluene, acetic acid in toluene using water as the solvent.

We would like to know how much amount of acetic acid would be distributing itself between the 2 liquid phases or in other words what is the maximum amount of acetic acid that can be extracted from toluene using water under the same conditions of temperature and pressure. Now the thermodynamic solution to such phase equilibrium problems was obtained several years ago by a person Gibbs who we will be referring very frequently during the course of this phase equilibrium thermodynamics.

He gave a solution to this problem by introducing the abstract concept of chemical potential which we have defined and we have discussed some aspects of it in the last 2 classes. Now we just know that all the chemical potential it has got a profound influence on phase equilibrium thermodynamics it is basically an abstract concept. It does not have an imagent equivalent in the physical world and therefore it is desirable to express chemical potential in terms of some auxiliary function which might be more easily identified with physical reality.

In this class we would attempt to relate the abstract concept of chemical potential of a substance through a physically measurable quantities like temperature, pressure, composition etc. Now I am attempting to simplify the abstract equation or rather the abstract concept of chemical equilibrium, GN Lewis he first considered the chemical potential of a pure ideal gas and this I guess I had already derived in one of the previous classes.

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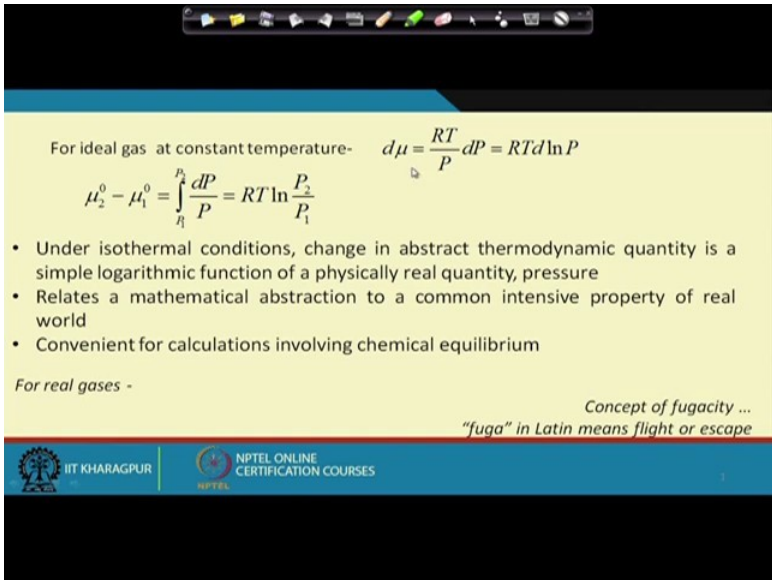

For ideal gas at constant temperature- $d\mu = \frac{RT}{P}dP = RTd\ln P$

$$\mu_2^0 - \mu_1^0 = \int_{P_1}^{P_2} \frac{dP}{P} = RT\ln\frac{P_2}{P_1}$$

- Under isothermal conditions, change in abstract thermodynamic quantity is a simple logarithmic function of a physically real quantity, pressure
- Relates a mathematical abstraction to a common intensive property of real world
- Convenient for calculations involving chemical equilibrium

For real gases -

Concept of fugacity ...

"fuga" in Latin means flight or escape

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We found out that chemical potential for ideal gas at constant temperature can be obtained from this particular equation. He observed that under isothermal conditions the change in the abstract thermodynamics quantity that is chemical potential is a simple logarithmic function of a physically real quantity that is pressure and so in this particular way he could relate a mathematical abstraction to a common intensive property of the real world but we need to remember that this was applicable just for an ideal gas.

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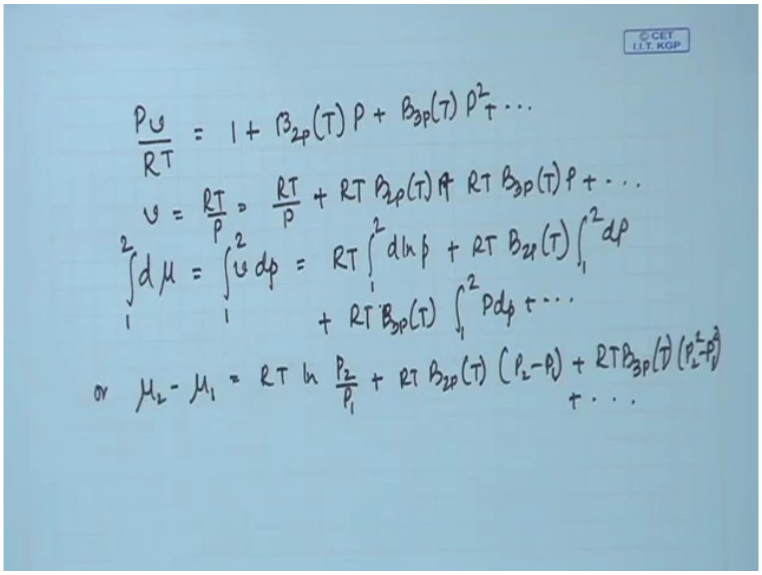

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$$\frac{Pv}{RT} = 1 + B_{2p}(T)P + B_{3p}(T)P^2 + \cdots$$

$$v = \frac{RT}{P} = \frac{RT}{P} + RT\,B_{2p}(T) + RT\,B_{3p}(T)P + \cdots$$

$$\int_1^2 d\mu = \int_1^2 v\,dp = RT\int_1^2 d\ln p + RT\,B_{2p}(T)\int_1^2 dP + RT\,B_{3p}(T)\int_1^2 P\,dp + \cdots$$

$$\text{or}\quad \mu_2 - \mu_1 = RT\ln\frac{P_2}{P_1} + RT\,B_{2p}(T)(P_2 - P_1) + RT\,B_{3p}(T)(P_2^2 - P_1^2) + \cdots$$

Let us see what happens when we are dealing with a real gas situation. Say for example a real gas which is obeying the virial equation of state, what is the virial equation of state? We have already discussed in, while we were discussing the PVT Behavior of the gases. This we write it down in the pressure explicit form where the constants or functions of temperature only. So this can be written in this particular form.

From here we can very well-define V as RT by P which is nothing but equal to dividing throughout by RTP RTP by P, sorry multiplying throughout we get the equation in this particular form plus RT B3P as a function of (T) P plus so on and so forth. Now suppose we we try to compute dmu for this particular condition. We know that for constant temperature this is equals to vdp, so therefore if we compute this from say state one to state 2, we try to compute this from state one to state 2, what do we get?

The expression is something like 1 to 2 d ln p plus RT B2p (T) integral 1 to 2 dP plus RT B3p as a function of (T) 1 to 2 Pdp plus so on and so forth. On integration we can write it down as mu2 minus mu1 equals to RT ln say P2 by P1 plus RT B2p as a function of (T) into P2 minus P1 plus RT B3p (T) P 2 square minus P1 square plus so on and so forth. Now this is applicable for any other equation of state as well.

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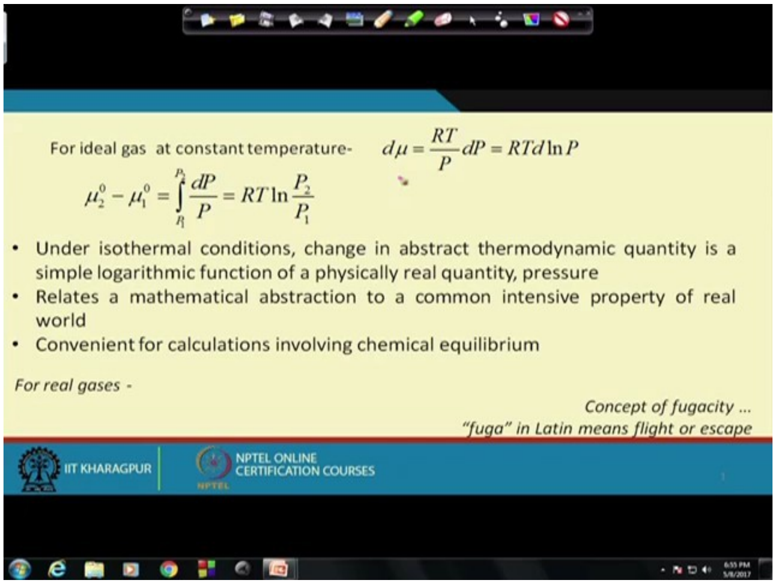

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Now we find that this equation is exact but this will be different for each and every gas and it turns out to be more convenient particularly for calculations involved in chemical equilibrium to maintain the form of equation which is shown in to the form of the equation which is represented here. So what Lewis he attempted, he wanted to maintain this form of an equation by defining a property or an auxiliary function which is fugacity where fuga In Latin means flight or escape.

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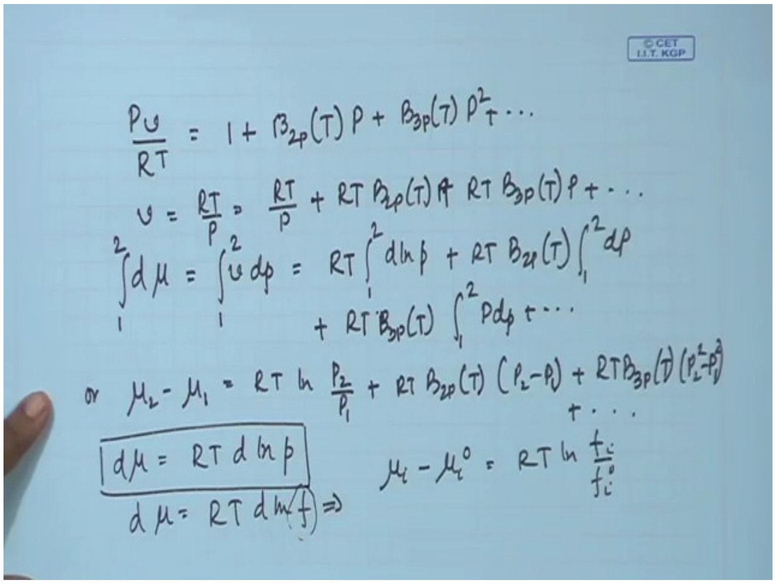

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or $$\mu_2 - \mu_1 = RT\ln\frac{P_2}{P_1} + RT\,B_{2p}(T)(P_2 - P_1) + RT\,B_{3p}(T)(P_2^2 - P_1^2) + \cdots$$

$$\boxed{d\mu = RT\,d\ln p}$$

$$d\mu = RT\,d\ln(f) \Rightarrow \mu_i - \mu_i^0 = RT\ln\frac{f_i}{f_i^0}$$

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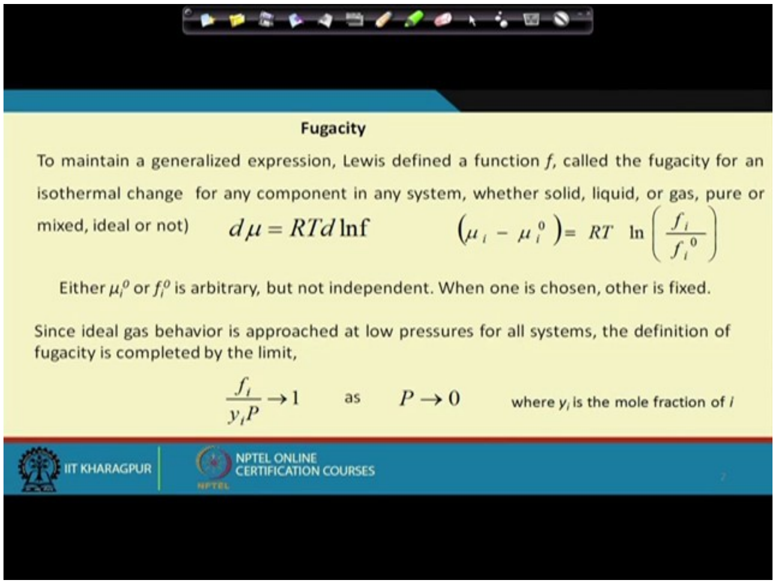

Fugacity

To maintain a generalized expression, Lewis defined a function f, called the fugacity for an isothermal change for any component in any system, whether solid, liquid, or gas, pure or mixed, ideal or not) $d\mu = RTd\ln f$ $\quad (\mu_i - \mu_i^0) = RT \ln\left(\frac{f_i}{f_i^0}\right)$

Either μ_i^0 or f_i^0 is arbitrary, but not independent. When one is chosen, other is fixed.

Since ideal gas behavior is approached at low pressures for all systems, the definition of fugacity is completed by the limit,

$$\frac{f_i}{y_i P} \to 1 \quad \text{as} \quad P \to 0$$ where y_i is the mole fraction of i

So therefore what he did? The equation which was developed for or rather which was obtained for ideal gas he tried to maintain this particular form of the equation for all substances whether it is substance or a component in a mixture for all substances he tried to retain this particular expression simply by replacing P with F the fugacity of the mixture, from where we can get just like we had got for the case of an ideal gas we can get, on integration of this equation we can get this as RT ln f by f0, right? It’s better we write fi referring to a component i.

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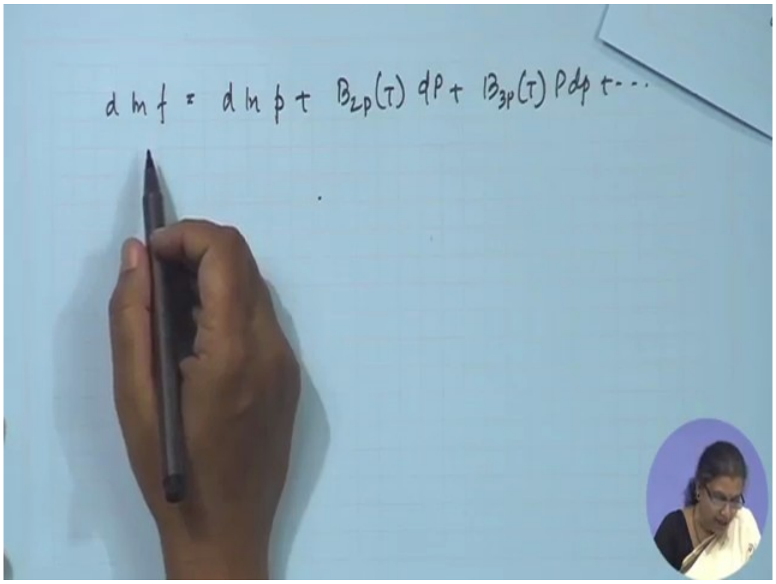

$$d \ln f = d \ln p + B_{2p}(T)\, dP + B_{3p}(T)\, P dp + \dots$$

So therefore if we do this then in the process, what have we done? We have varied the entire non-ideality of the gas in the expression for f. In this particular case what is the expression of f, if we assume the gas to obey the virial equation of state? This will be equal to, then d ln p plus say B2p (T) dP plus say B3p (T) Pdp plus so on and so forth. So therefore what do we find? What have we done in this particular case?

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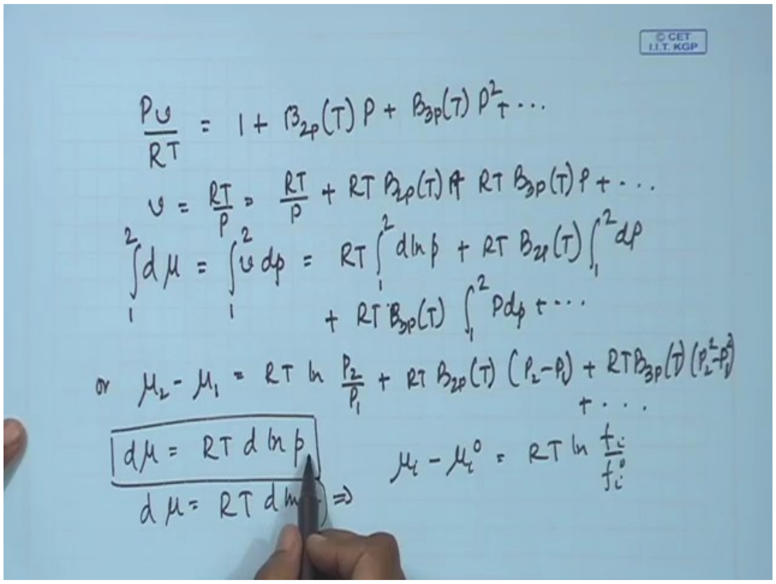

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$$d\mu = RT\,d\ln f \Rightarrow \quad \mu_i - \mu_i^0 = RT\ln\frac{f_i}{f_i^0}$$

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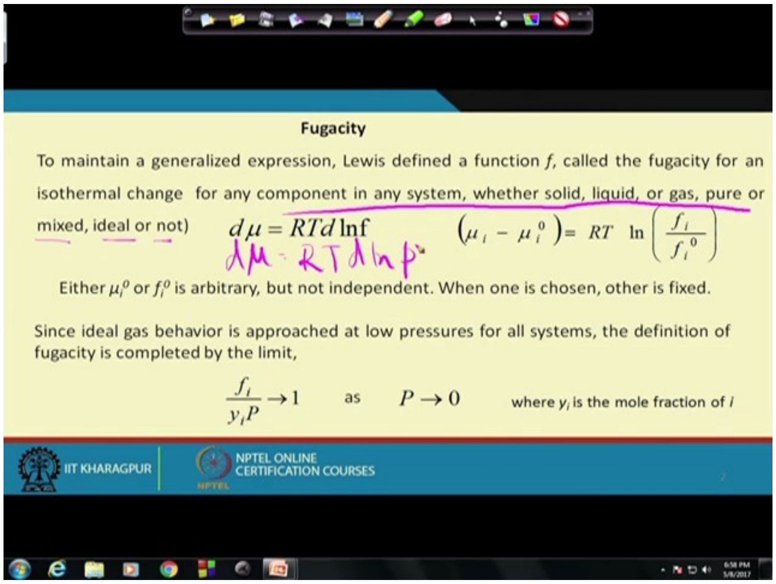

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Since ideal gas behavior is approached at low pressures for all systems, the definition of fugacity is completed by the limit,

$$\frac{f_i}{y_i P} \rightarrow 1 \quad \text{as} \quad P \rightarrow 0 \qquad \text{where } y_i \text{ is the mole fraction of } i$$

We have just retained the type of the expression which we have obtained for an ideal gas and in and this particular equation this is varied for any component in any system whether it is a solid, a liquid, a gas whether it is a pure whether it is mixed whether it is ideal whether it is non ideal and everywhere we can we can use this particular function or this functional form of fugacity and we would like to remember that this particular equation will reduce to the equation RT d ln P when we would be dealing with ideal gases.

The only thing which we, there is 2 things which we need to remember in this particular respect. First thing is we need to remember and in fact I had mentioned this earlier regarding other properties as well here also we need to remember that the defining equation of dmu be it for a real gas or for an ideal gas we find that we cannot compute the absolute value of mu because the defining equation of mu is in terms of a differential equation which on integration gives a difference quantity.

So therefore the important part here to remember is that we can define the entire equation but the standard state that we select that is arbitrary. We can select anything as the standard state but we need to remember that the standards states have to be same for both mu i0 and fi0. If suppose for mu i0 I select the lower limit of integration to be at P equals to 1 bar then fi0 also has to be computed at 1 bar, this is the first thing which we need to remember the entire thing arises because the equations which we are dealing with in phase equilibrium thermodynamics most of these are differential equations or the difference equations.

In fact let me remind you that phase equilibrium thermodynamics becomes much more complex not due to the concepts of the equations but more due to the need or the importance of the reference states which are known as the standard states. The other thing which I need to mention is that if I have defined the quantity fugacity then it is very important and I would like to find out this particular quantity fugacity at any particular conditions of temperature and pressure and that has to be provided I perform this integration with respect to some particular condition where I know the value of fugacity, is it clear to you?

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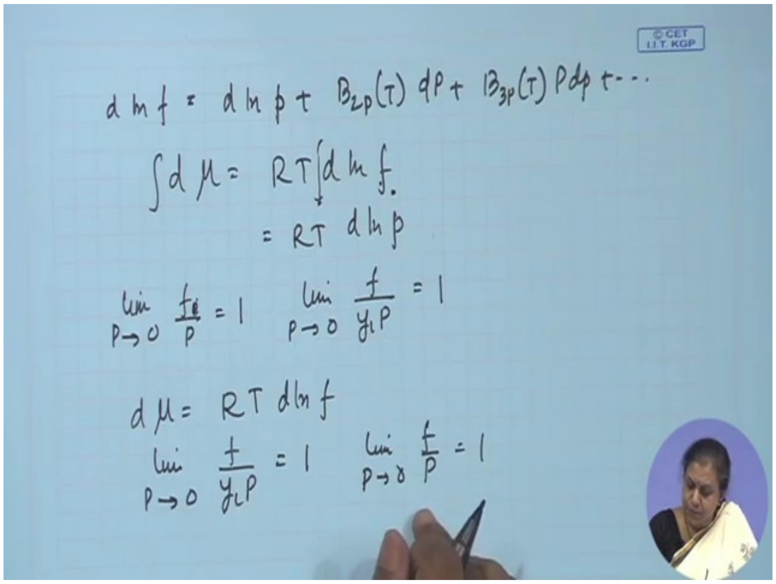

$$d \ln f = d \ln p + B_{2p}(T)\, dP + B_{3p}(T)\, P\, dp + \cdots$$

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

$$= RT\, d \ln p$$

$$\lim_{P \to 0} \frac{f_i}{P} = 1 \qquad \lim_{P \to 0} \frac{f}{y_i P} = 1$$

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

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What I mean to say is that if I want to calculate or rather if I want to find out the utility of this particular equation then I need to integrate this particular equation and if I am integrating this particular equation it has to start from some particular reference condition where the value of fugacity is known. Now where do I know the value of fugacity? I know the value of fugacity at very low pressure under which condition all substances can be assumed to be in the gaseous state and the gas at such low pressure behaves as an ideal gas because I know when the gas behaves like an ideal gas then under that condition the equation is d ln p.

So therefore the point is that this particular definition it is not complete unless I specify the lower limit or I specify the limiting condition of fugacity and this particular limiting condition is suggested in this particle form, when we are dealing with a pure gas or single component gas then the condition is limit P tends to 0 f by P equals to 1 and suppose I'm dealing with a mixture of gases which behave ideally at low pressure then under that condition it becomes limit P tends to 0 f by the partial pressure of the gas at 0 at the very lower pressures.

So therefore it's very important for us to remember that once we have defined fugacity it is important to remember that in order to define fugacity we need to equations, the first equation as I have already mentioned it is d mu equals to RT d ln f and along with that we need to mention the a subsidiary equation which states this where for pure gas yi becomes equals to 1 and condition becomes limit P tends to 0 f by P equals to 1, unless this is specified the definition remains incomplete because just a differential equation without an idea of the value at any of the end points of the integration is definitely meaningless.

Now here I would like to mention that it might appear to you that we are just going around and around in circles, what are we doing? First we defined chemical potential; it was an abstract quantity, we did not know what to do with it? Or rather we wanted to find out a straightforward way of defining it. You wanted to keep matter simple, so therefore we define fugacity this is another unknown quantity adding to our problems.

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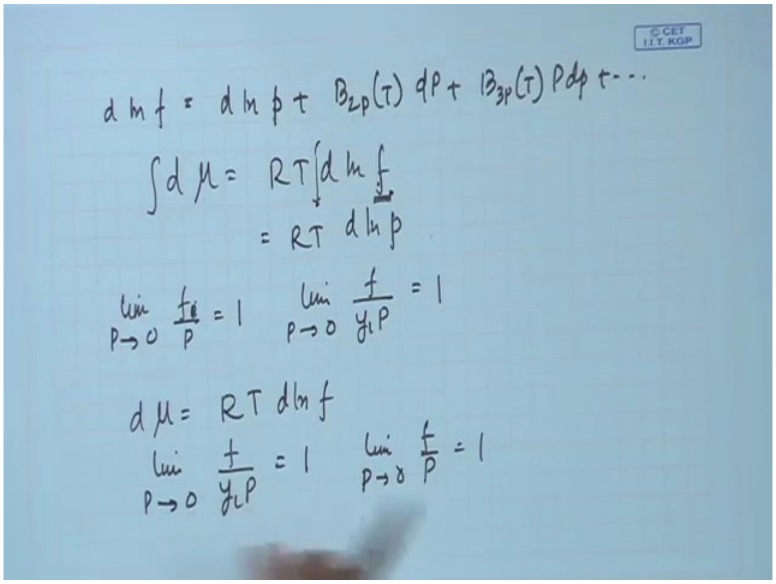

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So therefore immediately it appears that we are we are just going on in circles and we are not doing exactly we are not achieving anything useful we are not going in a straight road, road towards understanding more of phase equilibrium thermodynamics but the reality is, in defining fugacity, what we have actually done? We are now in a position to use all thermodynamic functions which have been defined for ideal gases just by replacing pressure with fugacity.

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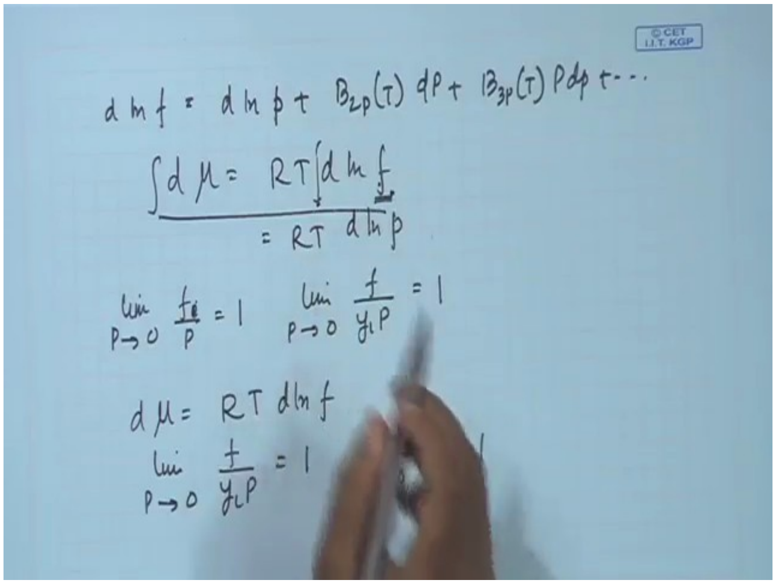

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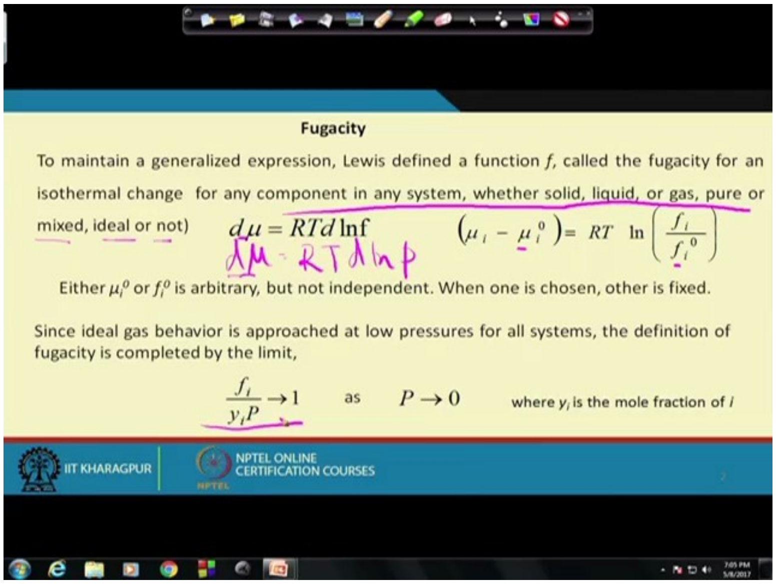

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$$\frac{f_i}{y_i P} \to 1 \quad \text{as} \quad P \to 0 \qquad \text{where } y_i \text{ is the mole fraction of } i$$

So the only thing that we need now at this moment is to find out or rather to devise a straightforward way to define fugacity and the other important part is, it’s very important to remember that is particular equation this is applicable, as I’ve already mentioned this is applicable for solids, liquids, gas, the gas is pure, mixture everything it is applicable.

So in that case the power of the definition of fugacity arises from the fact that we are in a position to define fugacity for any particular component, for any particular system, for whatever we define the limiting condition that I have proposed here for the limiting condition that is written down here, it holds well and by defining this particular the quantity we are in a position to use whatever thermodynamic functions we have developed a device for ideal gas.

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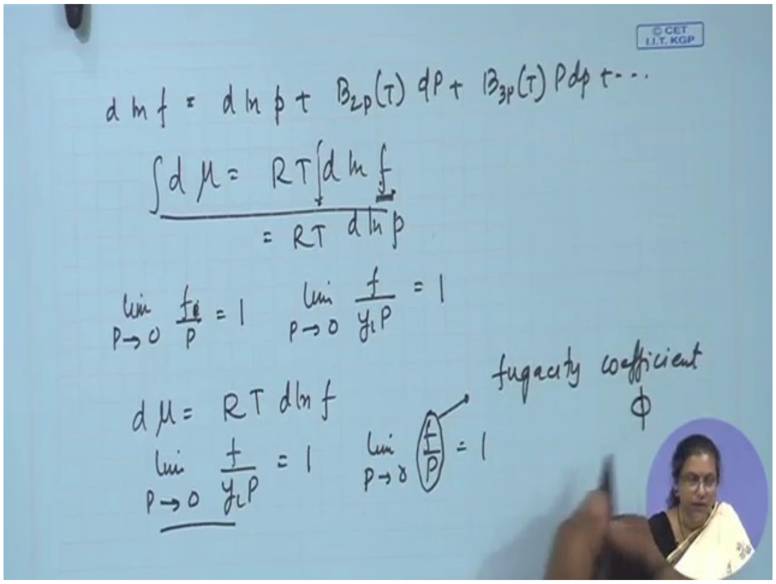

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fugacity coefficient

ϕ

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

$$\lim_{P \to 0} \frac{f}{y_i P} = 1 \qquad \lim_{P \to 0} \left(\frac{f}{P}\right) = 1$$

So therefore there are 2 other things which I would like to clarify before winding up this particular lecture. The first thing which I would like to mention is that very frequently we would be coming across a term like f by P this term we across very frequently. In fact we get this term more frequently than f because for most of the cases we would like to define fugacity with respect to pressure at the low-pressure.

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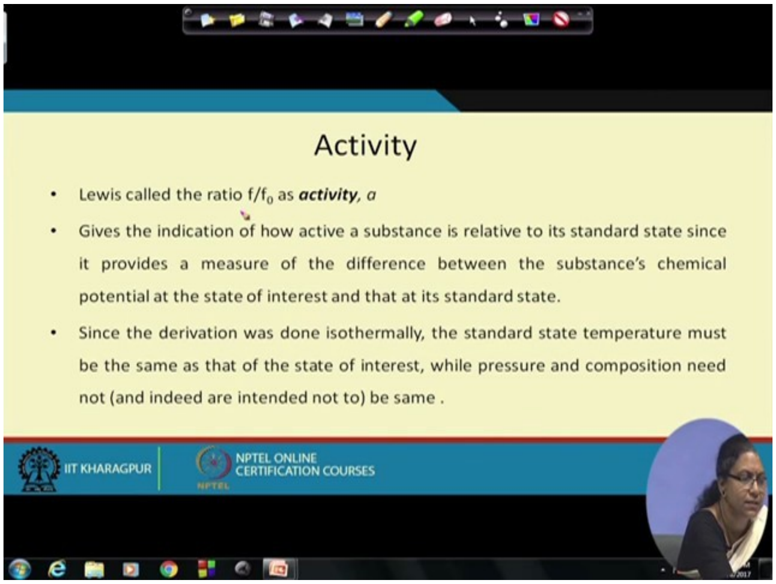

Activity

- 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 .

So this particular term is usually defined as a fugacity coefficient phi. The other thing which is very important is this particular term f by f0. We find what does this term signify you tell me this term signifies the activity or this term signifies how active the substance is in the state of interest compared to its standard state. So therefore this particular term f by f0 this is also defined as activity.

It gives an indication of how active a substance is relative to its standard state because we would like to remember that f by f0 or in other words ln f by f0 or RT lb f by f0 it gives the difference between the chemical potential of the substance at the state of interest and the standard state and we would also like to remember another very important fact that this particular derivation was done isothermally and therefore it is important to remember that when we are dealing with these equations the standard state temperature must be the same as the temperature of the state of interest while the pressure and composition need not and indeed they are intended not to be the same. We continue with the discussions regarding fugacity, fugacity coefficient activity in the next class as well.