Chemical Engineering Thermodynamics
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Lecture 33
Fugacity

Welcome back, in the past week we have gone through equational state and intermolecular interactions. Now, we are going to discuss a new topic, but before getting there, let me just try to explain the need for introductions of specific terms, this is something which mathematically or in general is driven by the experience which we have usually when we undertake problems and make use of the equations.

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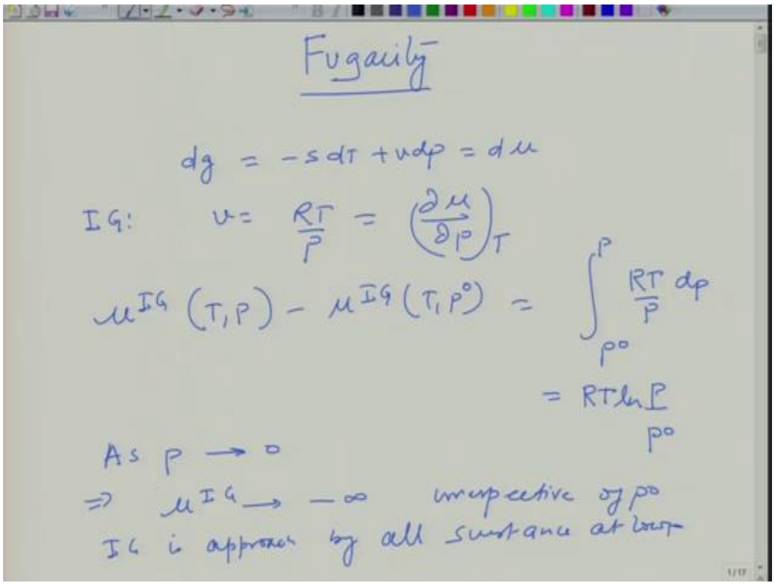

Fugacity

$$dg = -sdT + vdp = d\mu$$

$$IG: \quad v = \frac{RT}{P} = \left(\frac{\partial \mu}{\partial P}\right)_T$$

$$\mu^{IG}(T,P) - \mu^{IG}(T,P^0) = \int_{P^0}^{P} \frac{RT}{P}\,dp$$

$$= RT\ln\frac{P}{P^0}$$

As $P \rightarrow 0$

$\Rightarrow \mu^{IG} \rightarrow -\infty$ irrespective of P^0

IG is approach by all substance at low

So, one of such exercise is something called original fugacity. So, let us consider a case where we have a pure fluid and we write down the expression for differential form of Gibbs free energy in molar terms.

$$dg = -sdT + vdP = d\mu$$

$$IG{:}\, v = \frac{RT}{P} = \left(\frac{\partial \mu}{\partial P}\right)_T$$

$$\mu^{IG}(T,P) - \mu^{IG}(T,P^0) = \int_{P^0}^{P} \frac{RT}{P} dP = RT ln\frac{P}{P^0}$$

$$As, P \rightarrow 0;\;\; \mu^{IG} \rightarrow -\infty$$

Now considering this condition or this limiting condition this equation becomes a little difficult for us to use for different substances because ideal gas is approached by all substance had low pressure, okay. So, this is something which is highly undesirable, okay.

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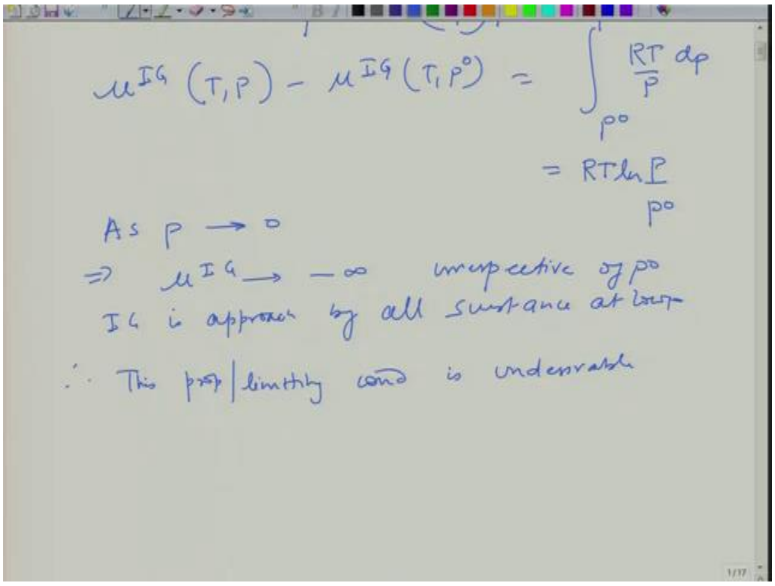

$$\mu^{IG}(T,P) - \mu^{IG}(T,P^{\circ}) = \int_{P^{\circ}} \frac{RT}{P}\,dp$$

$$= RT\ln\frac{P}{P^{\circ}}$$

As $P \rightarrow 0$

$\Rightarrow \mu^{IG} \rightarrow -\infty$ irrespective of P°

IG is approach by all sustance at low

$\therefore$ This prop | limiting cond is undesirable

Now, why this is undesirable? Therefore, this property or limiting condition is undesirable mathematically because we always consider a reference state as ideal gas for our calculation of thermodynamic property almost always this is the case and hence, the issue is that now this chemical potential tends towards minus infinity as the pressure is low, so we must come over some alternative solutions for that, okay.

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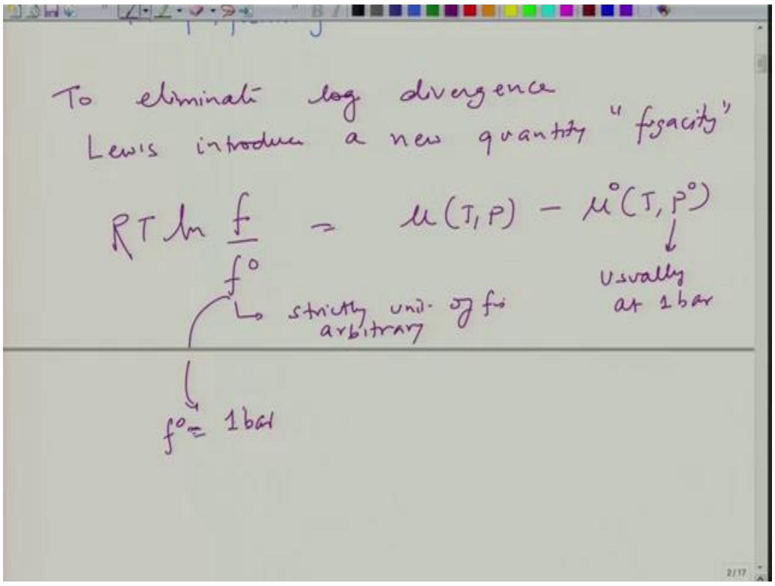

To eliminate log divergence

Lewis introduce a new quantity "fugacity"

$$RT\ln\frac{f}{f^{\circ}} = \mu(T,P) - \mu^{\circ}(T,P^{\circ})$$

f° → strictly uni. of fi arbitrary

P° ↓ Usually at 1 bar

$f^{\circ} = 1\text{bar}$

$$RT ln\frac{f}{f^0} = \mu(T,P) - \mu^0(T,P^0) \quad f^0 = 1bar$$

So this log divergence can be removed by considering a new property or by considering a new term, this is what Lewis state, so to eliminate log divergences, okay. What Lewis did, he introduced a new quantity which we called fugacity, okay. So, this is something which was introduced and thus something which we can write now based on, of course, due to Lewis is RT ln f by f0 can be written as mu of T and P minus mu0 which is at T , P0, okay.

So remember this mu0 reference is at P0, so P0 is some arbitrary pressure, usually we keep it at 1 bar, okay. Now this is a ratio, hence f has actually no, strictly has no units here which all could be any arbitrary units, so strictly unit of f is arbitrary, okay? But usually we refer, we provide of the u something like bar, but it is not a pressure, that is something which should be clear from this expression, it is not a pressure but for the sake of some reference value f here f0 is also considered to be 1 bar, okay?

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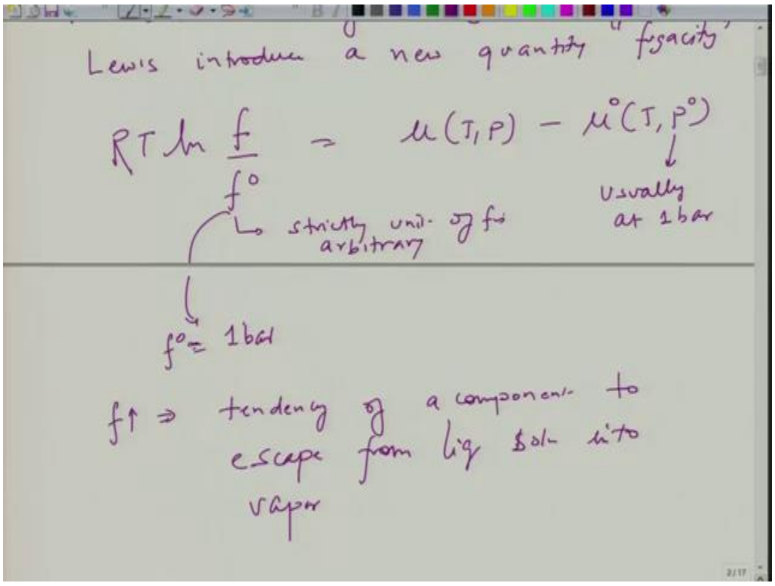

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usually at 1 bar

↳ strictly unit of f° arbitrary

$f^\circ = 1$ bar

$f\uparrow \Rightarrow$ tendency of a component to escape from liq soln into vapor

Now, if you look at it this expression, this will tell you that if f increases, your mu increases which is a tendency to escape, so f increase indicate tendency of a compound or component to escape from liquid solution into vapor, okay? So this is an indicative so as fugacity increases this is a indicative that it will go towards in the vapor phase.

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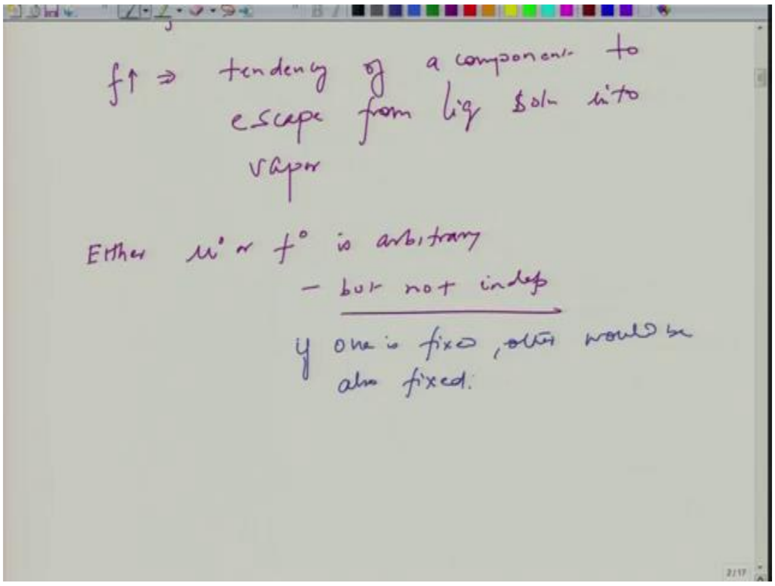

$f\uparrow \Rightarrow$ tendency of a component to escape from liq soln into vapor

Either μ° or f° is arbitrary

— but not indep

if one is fixed, other would be also fixed.

So, naturally the fugacity of vapor would be much more higher than that of the liquid, right? So that is something which one can prove also that at higher pressure you should have higher fugacity. Okay, for the pure fluid. Now, the other thing which you can also look at it this f0 and mu0 are they independent? So based on this constraint either mu0 or f0 is arbitrary, okay, but they are not independent, that means once you fix mu0 the corresponding f0 is also fixed because that depends on the conditions which you are imposing, which is at TNP0.

All right, so this is a statement which we must remember, this essentially means that once if one is fixed other would be also fixed, okay? So, now the reason we introduced this is, of course, to eliminate the log divergences so unlike mu is diverges as pressure goes to 0, f does not, okay. That is something which should be clear here, okay, because it is not the relation which we are using here in this case which is this, okay?

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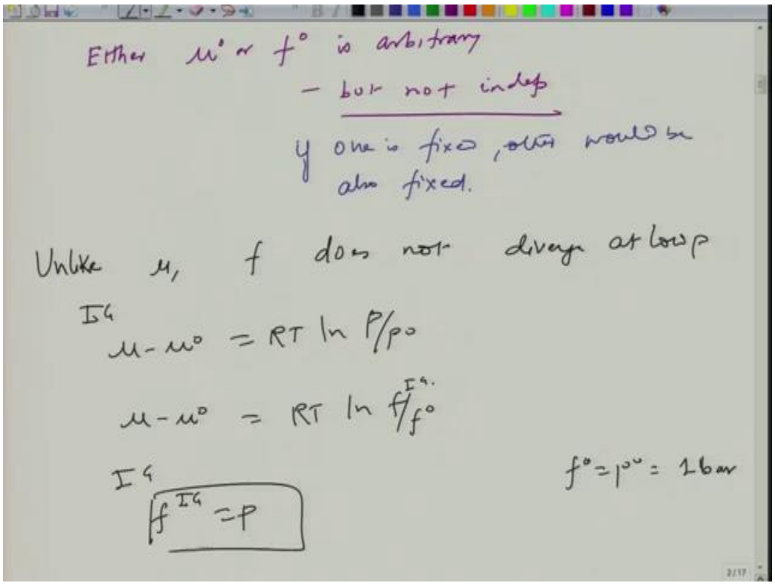

Either μ^0 or f^0 is arbitrary

— but not indep

If one is fixed, other would be also fixed.

Unlike μ, f does not diverge at low p

IG

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

$\mu - \mu^0 = RT \ln f^{IG}/f^0$

IG

$\boxed{f^{IG} = P}$

$f^0 = P^0 = 1$ bar

So, that is important to note that unlike mu f does not diverge at low p, okay. Now, let us look at again comparison between ideal gas and for this particular relation, we know from other relation, which we have used earlier that mu minus mu0 for ideal gas is nothing but RT ln P by P0. So, for a case of our definition of fugacity we can write it there. Now, these two terms, of course, get cancelled so considering these that Pf0 is nothing but P0, so if we consider f0 is equal to P0 is equal to 1 bar. So, this indicates that for ideal gas, f of ideal gas is nothing but pressure, okay?

$$IG\colon\ \mu - \mu^0 = RTln\frac{P}{P^0}$$

$$\mu - \mu^0 = RTln\frac{f^{IG}}{f^0}$$

$$for\ ideal\ gas\colon\ \ f^{IG} = P \qquad f^0 = P^0 = 1\ bar$$

$$\phi = fugacity\ coefficicent = \frac{f}{P} \quad ; \quad \phi^{IG} \to 1$$

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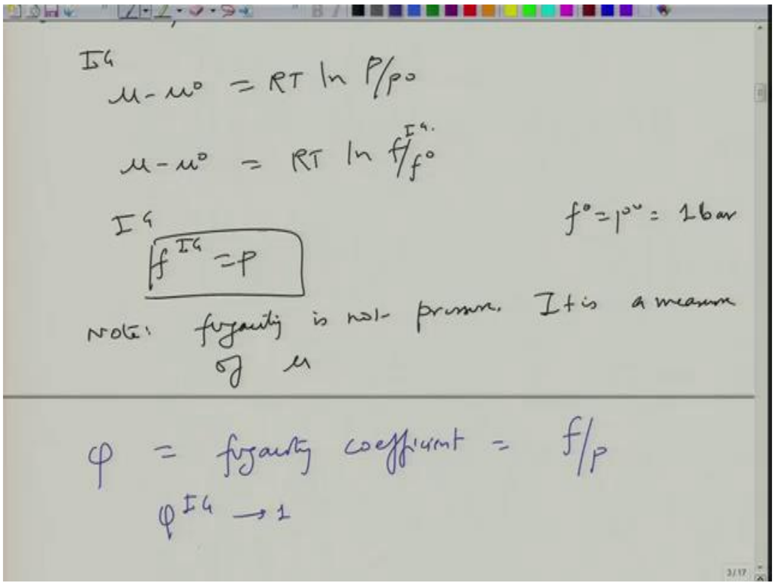

IG

$\mu - \mu^0 = RT \ln P/p_0$

$\mu - \mu^0 = RT \ln \overset{IG}{f}/f^0$

IG

$\boxed{f^{IG} = P}$

$f^0 = p^0 = 1\,bar$

Note: fugacity is not pressure. It is a measure of μ

φ = fugacity coefficient = f/p

$\varphi^{IG} \to 1$

But remember this is numerically it is a pressure because fugacity is again not a pressure, okay; it is a measure of a mu, okay. Note that fugacity is not pressure, it is a measure of chemical potential or basically it tells you, what is the behavior of the fluid to escape from the liquid phase. Now, in order to define deviation from ideal gas we can come up with another auxiliary parameter, which we call it fugacity coefficient, which is nothing but the ratio of f by p, okay.

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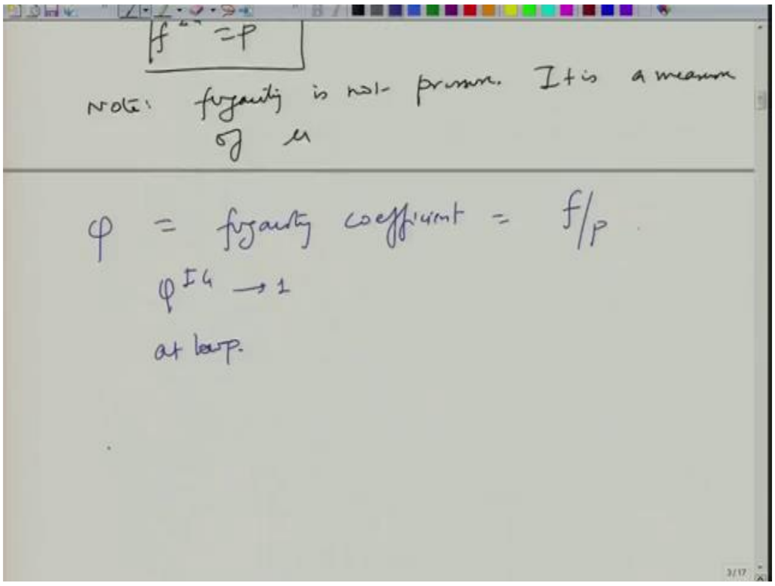

$f^{IG} = P$

Note: fugacity is not pressure. It is a measure of μ

φ = fugacity coefficient = f/p

$\varphi^{IG} \to 1$

at low p.

Hence, for ideal gas this will be 1, right? And in other words we can say that fugacity, the coefficient, fugacity coefficient will approach towards 1 at low pressure, okay; with, of course, the convenient reference is this f0 p0 is equal to 1 bar.

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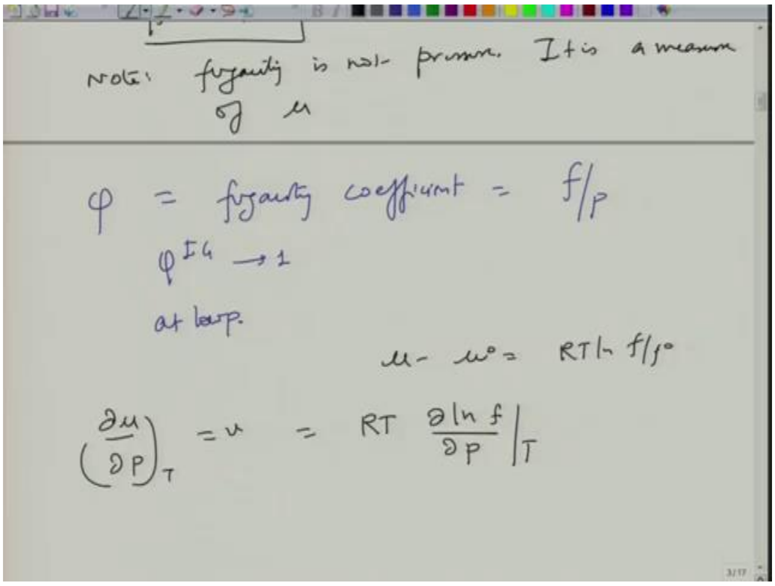
Note: fugacity is not pressure. It is a measure of μ

φ = fugacity coefficient = f/P

$\varphi^{IG} \to 1$

at low p.

$\mu - \mu^{\circ} = RT \ln f/f^{\circ}$

$\left(\frac{\partial \mu}{\partial P}\right)_T = v = RT \frac{\partial \ln f}{\partial P}\Big|_T$

Okay, so using this expression, now I can little bit expand a bit of this fugacity understanding, okay.

$$\left(\frac{\partial\mu}{\partial P}\right)_T = v = \frac{RT\partial lnf}{\partial P}|_T$$

$$or, \qquad \mu_2 - \mu_1 = RT\ln\frac{f_2}{f_1} = \int vdP$$

$$\ln f_2 = \ln f_1 + \int_{P_1}^{P_2}\frac{v}{RT}dP$$

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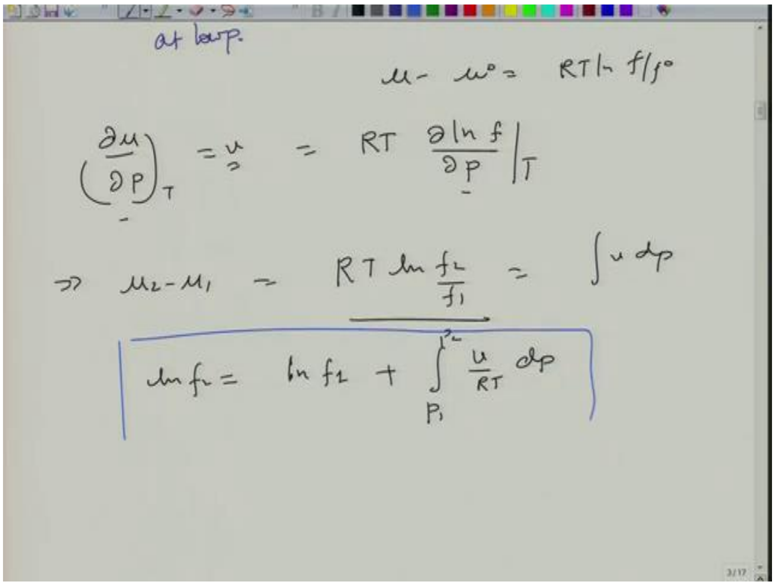
at low p.

$\mu - \mu^{\circ} = RT \ln f/f^{\circ}$

$\left(\frac{\partial \mu}{\partial P}\right)_T = v = RT \frac{\partial \ln f}{\partial P}\Big|_T$

$\Rightarrow \mu_2 - \mu_1 = \underline{RT \ln \frac{f_2}{f_1}} = \int v\, dp$

$\boxed{\ln f_2 = \ln f_1 + \int_{P_1}^{P_2} \frac{v}{RT}\, dp}$

So, this is the expression we get here, now this is a very important relation again here we have not made any assumption so this is the exact expression we get here. Now, this is a very important relation again here we have not made any assumptions so this is the exact expression.

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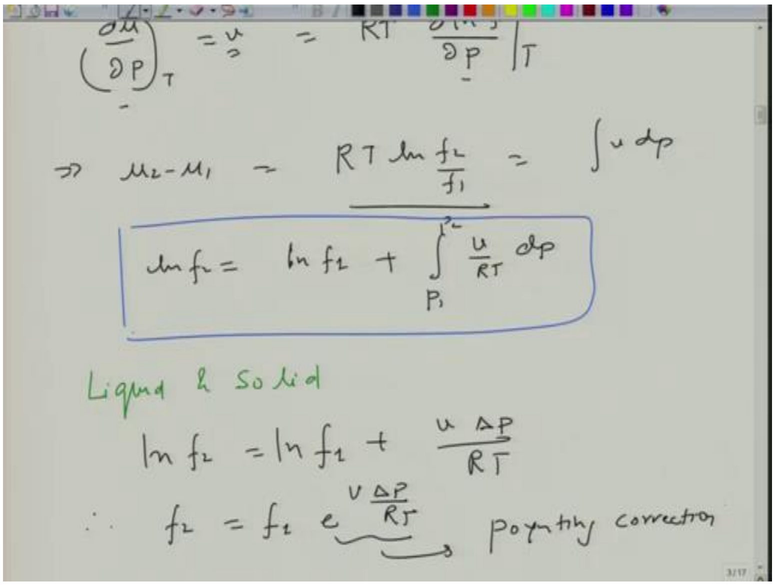

$$\left(\frac{\partial \mu}{\partial P}\right)_T = v = RT \left.\frac{\partial \ln f}{\partial P}\right|_T$$

$$\Rightarrow \mu_2 - \mu_1 = RT \ln \frac{f_2}{f_1} = \int v \, dp$$

$$\boxed{\ln f_2 = \ln f_1 + \int_{P_1}^{P_2} \frac{v}{RT} \, dp}$$

Liquid & Solid

$$\ln f_2 = \ln f_1 + \frac{v \Delta P}{RT}$$

$$\therefore f_2 = f_1 \underbrace{e^{\frac{v \Delta P}{RT}}}_{} \rightarrow \text{Poynting correction}$$

$$Liquid\ and\ solid: \quad \ln f_2 = \ln f_1 + \frac{v\Delta P}{RT}$$

$$Therefore, \quad f_2 = f_1 e^{\frac{v\Delta P}{RT}} \quad Poynting\ correction$$

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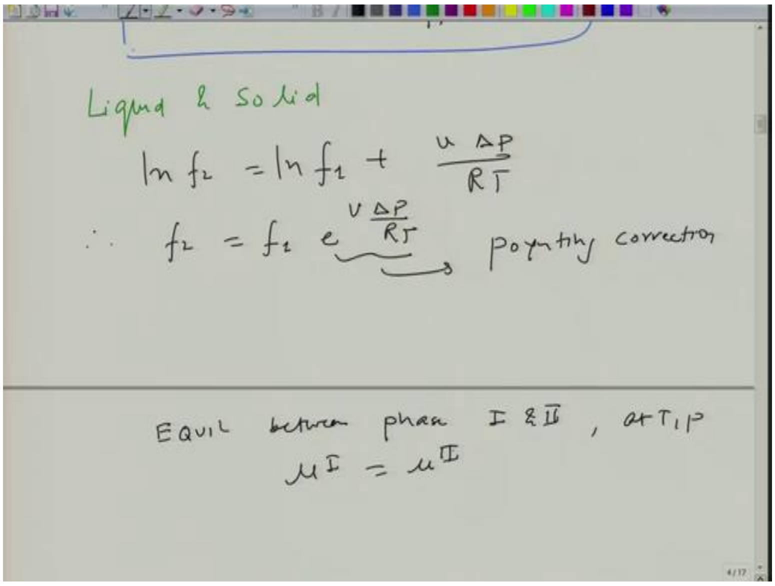

Liquid & Solid

$$\ln f_2 = \ln f_1 + \frac{v \Delta P}{RT}$$

$$\therefore f_2 = f_1 \underbrace{e^{\frac{v \Delta P}{RT}}}_{} \rightarrow \text{Poynting correction}$$

EQUIL between phase I & II, at T, P

$$\mu^{I} = \mu^{II}$$

Now, this becomes a valuable tool for us particularly to connect, particularly for the case of equilibrium conditions. So, for example, if you are interested in a equilibrium let us say two phases, between phase 1 and 2, then you know that one of the condition at a given at temperature and pressure the condition is mu 1 or mu of a specific component in phase 1 should be same as in phase 2, right? For the pure substance.

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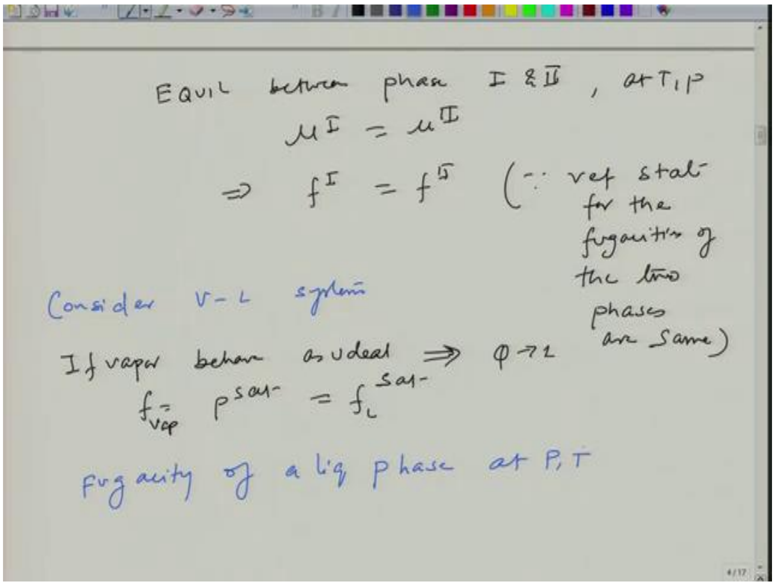

EQUIL between phase I & II , at T, P

$\mu^{I} = \mu^{II}$

$\Rightarrow f^{I} = f^{II}$ (∵ ref state for the fugacities of the two phases are same)

Consider V-L system

If vapor behave as ideal $\Rightarrow \phi \rightarrow 1$

$f_{vap} = P^{sat} = f_L^{sat}$

Fugacity of a liq phase at P, T

$$Equilibrium\ between\ phase\ I\ and\ II, at\ constant\ T\ and\ P,\quad \mu^{I} = \mu^{II}$$

$$or,\ \ f^{I} = f^{II}$$

$$Considering\ V - L\ systems:\ \ ideal\ vapour:\ \ \phi \rightarrow 1$$

$$f_{vap} = P^{sat} = f_L^{sat}$$

Now based on our analysis of the chemical potential relation with the fugacity you can show that this is nothing but also that fugacity should be same, okay, given that the reference state for the fugacity that is f0 of the two phases are same, okay? So, this is something which you can show. Now consider case particular for vapor, liquid systems.

Vapor liquid system, okay. Often for the case of vapor for common fluids, we consider them the vapor phase to behave in ideal like gas, so if we consider vapor behave as idle then you are talking about or you are implying that fugacity coefficient is 1, in that case f is equal to vapor is nothing but p of sat, right? Because the pressure of the vapor in the vapor liquid equilibria would be that of the pressure of saturation at the particular temperature. So, the fugacity of the vapor will be nothing but the pressure of the saturated vapor which will be p sat.

Now, p sat has to be same as liquid fugacity and that too at saturation, okay? So this is something which we come now. If you are interested to find out let us say fugacity of liquid at temperature P and T, then essentially I can make use of this expression here, so for example this could be the fugacity at T and P and is essentially could be a fugacity at the saturation condition and the v would be the saturation or the molar volume at the saturation and Delta p would be the pressure difference from the saturation to the pressure p which we are interested in, all right?

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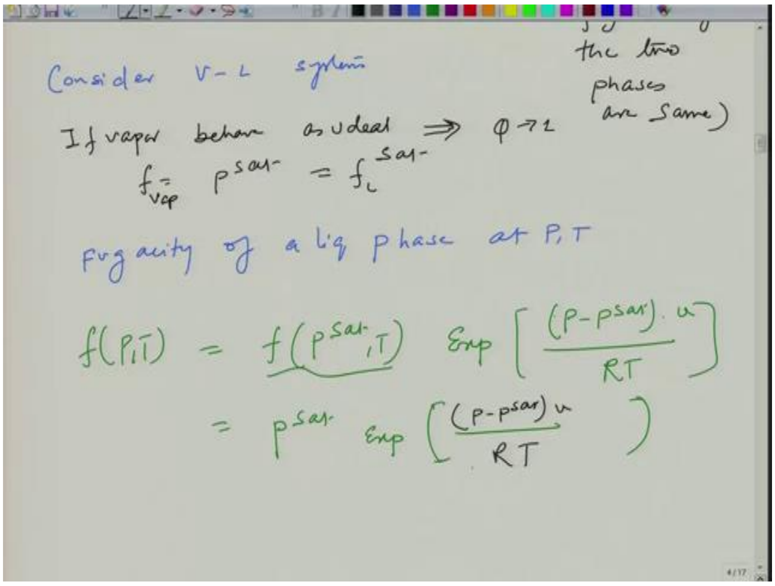

the two phases are same)

Consider V-L system

If vapor behave as ideal $\Rightarrow \phi \to 1$

$f_{vap} = P^{sat} = f_L^{sat}$

Fugacity of a liq phase at P, T

$$f(P,T) = \underline{f(P^{sat},T)}\ Exp\left[\frac{(P-P^{sat})\cdot v}{RT}\right]$$

$$= P^{sat}\ Exp\left(\frac{(P-P^{sat})v}{RT}\right)$$

$Fugacity\ of\ a\ liq\ phase\ at\ P,T$:

$$f(P,T) = f(P^{sat},T)\exp\left[\frac{(P-P^{sat})v}{RT}\right] = P^{sat}\exp\left[\frac{(P-P^{sat})v}{RT}\right]$$

Now, of course, here if you have the equational state available for the specific fluid, then you can plug-in here v in terms of v by RT can be written in terms of z here or you know something which we can elaborate more.

$$EOS: f = f(Z)$$

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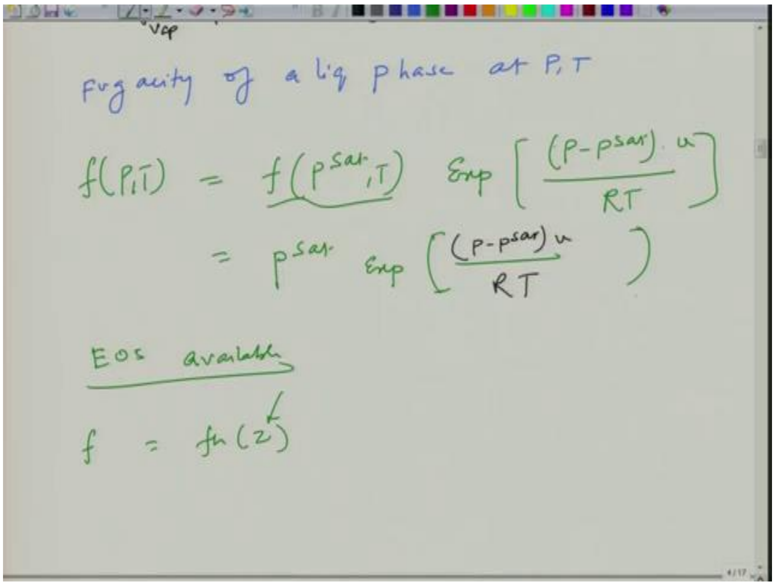

Fugacity of a liq phase at P, T

$$f(P,T) = \underbrace{f(P^{sat},T)} \; Exp\left[\frac{(P-P^{sat})\, v}{RT}\right]$$

$$= P^{sat} \; Exp\left(\frac{(P-P^{sat})\, v}{RT}\right)$$

EOS available

$$f = fn(z)$$

So, this can be further elaborated if equational states are available, okay. Then I can write this function, this f as a function of some function of z, okay, that could be the compressibility factors and other terms, for example, simple equational state could give you literally complicated expression of f, but that something which we can take care later I will not describe to start with now, okay, something I will explain it in a later part of the course.

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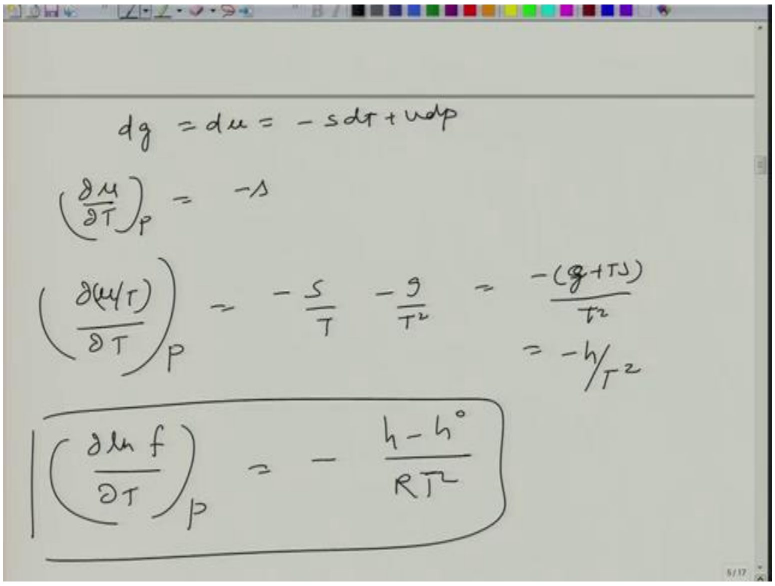

$$dg = d\mu = -sdT + vdP$$

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -s$$

$$\left(\frac{\partial\left(\frac{\mu}{T}\right)}{\partial T}\right)_P = -\frac{s}{T} - \frac{g}{T^2} = -\frac{g + TS}{T^2} = -\frac{h}{T^2}$$

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

So, let me just tell little bit more add to this understanding here and particularly in the fugacity, how the fugacity change can be related to other thermodynamic property. Let us go back to the equation first, the thermodynamic equations which they wrote in the early part of this lecture, okay, so this is the one and then essentially if you look at it the del mu by del T by constant pressure is nothing but entropy, right?

Okay and now here I can do a bit of exercise here to obtain the relation Del mu by T, okay, by Del T at constant pressure this can be further written as minus S by T minus g by T square, that I can show that this is g plus TS by T square which is nothing but minus h by T square, okay?

All right, so this is something which you can prove it and essentially the way to prove is by considering nothing but that mu in this case is g so essentially if you differentiate this you will get a term here, minus mu by T square which is nothing but minus g by T square, okay? So this is for the pure substance and hence here you can write it, so if you differentiate this the first will come this one and with the T in the denominator and a second term will be minus mu by T square which is nothing but g by g square.

So, this is something which we can prove now. Now, this is a one term, okay? Now make use of the expression of the, definition of the fugacity, and if you can take the definition of the fugacity which we have mu minus mu0 is equal to RT ln f0 and here you can prove that that this is d… This can be written as d ln f by dT at constant pressure nothing but minus h minus h0 by RT square, okay.

So this is something which tells you that the change in the enthalpy, Delta h by measuring the Delta h, okay, as a function of temperature you can find out the fugacity, okay. So essentially or in other words change in the fugacity as a function of temperature can be measured by finding out the change in enthalpy. So that is something which one can show that, okay.

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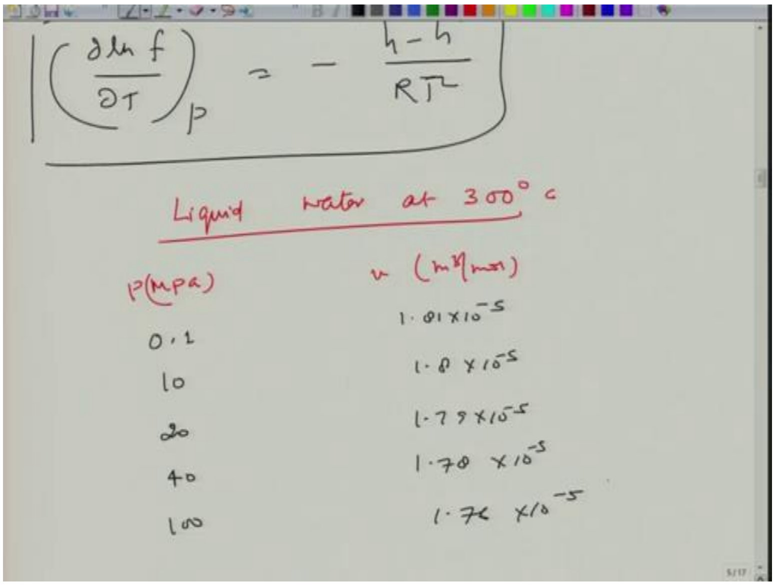

$$\left(\frac{\partial \ln f}{\partial T}\right)_p = -\frac{h-h}{RT^2}$$

Liquid water at 300° c

P(MPa)	v (m³/mol)
0.1	1.01×10^{-5}
10	1.8×10^{-5}
20	1.79×10^{-5}
40	1.78×10^{-5}
100	1.76×10^{-5}

Now, let me do a little, one exercise before we close this session. This is an example of liquid water at 300 degree C, okay? So what we have is the pressure in mega pascal and volume is meter cube by mol. And what we have is this information, that 0.15 mega Paschal the molar volume is this 10 is 1.8 into 10 to the power minus 5, 20 is 1.79 into 10 to the power minus 5, 40 is 1.78 into 10 to the power minus 5 and then 100 is 1.76 into 10 to the power minus 5 meter cube per mol.

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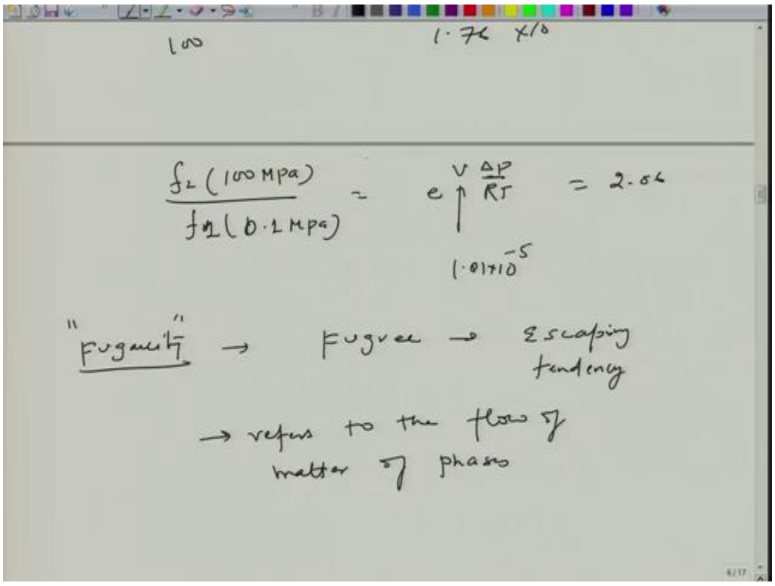

100 1.76×10

$$\frac{f_L(100\text{ MPa})}{f_L(0.1\text{ MPa})} = e^{v\frac{\Delta P}{RT}} = 2.06$$

1.01×10^{-5}

"Fugacity" → Fugere → Escaping tendency

→ refers to the flow of matter of phases

So, what we want to find out, what is the fugacity of this, Fugacity at hundred mega Paschal with respect to that at 0.1 mega Paschal. Okay, so we are interested in here this ratio. Now based on our expression which we have written earlier, the fugacity ratio is nothing but the poynting correction, right? So, if you look at it here I can simply write e to the power v Delta p by RT and here we can consider that the volume is more or less fix, so I can just take the volume at 1.81 which is at 0.1 mega Pascal and delta p is, of course, 100 minus 0.1, so if you plug in this, okay if you plug-in this values you are going to get 2.06 as a value.

$$\frac{f_2(100\ MPa)}{f_1(0.1\ MPa)} = e^{\frac{v\Delta P}{RT}} = 2.06$$

So, essentially it tells you the fugacity at higher pressure is much much higher, that means it has a higher tendency to escape to the vapor phase, okay. So that is something which you can evaluate from this exercise. So fugacity also sometimes, fugacity, the original fugacity of the particular the word comes from the word Fugree which actually means escaping tendency, okay? And this is something which you can clearly see from this example, that had a fugacity at this pressure indicates at this pressure is more; it has much more capacity to escape, okay.

And this fugacity provides you a kind of an idea or it refers to something to the flow of matter, right, of phases, right? So it gives you an idea about that and similar that is why it is not a pressure, at the end fugacity is not a pressure, it is a similar in nature of the chemical potential which is clear from our definition as well, because chemical potential also is the driving force for the mass exchange or mass flow and similarly fugacity also gives you a idea of the flow of the matter, okay. So, with that I will stop here and I will start a new topic, particularly I will start the property of the mixtures in the next lecture, okay, so I receive in the next lecture.