Thermodynamics of Fluid Phase Equilibria
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Lecture – 19
Chemical Potential and Fugacity

Let us discuss Chemical Potential more in detail.

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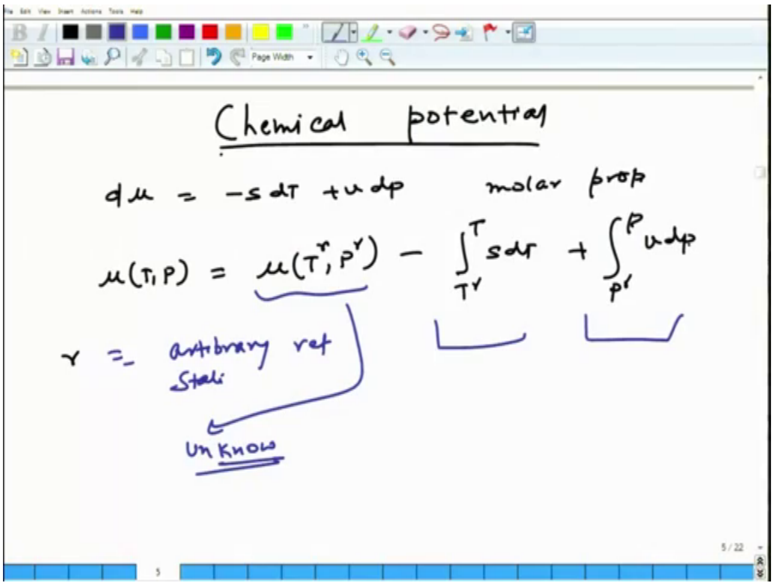

Chemical potential

$d\mu = -s\,dT + v\,dp$ molar prop

$$\mu(T,P) = \underbrace{\mu(T^r,P^r)}_{} - \underbrace{\int_{T^r}^{T} s\,dT}_{} + \underbrace{\int_{P^r}^{P} v\,dp}_{}$$

r = arbitrary ref State

Unknow

For a pure substance; one can write del mu as minus sdT plus udp. Now these are in molar properties; now the question is that how do you connect chemical potential to more physically measurable quantities right? And that is basically the challenge though Gibbs was the one who basically obtained thermodynamic solution to the phase equilibria by introducing chemical potential, but this is an abstract concept right.

So, what we are trying to do is to understand the issues with the chemical potential calculation. So, let us try to integrate this; if you integrate this ok; I can write mu as T P this would be equal to mu at some reference temperature and pressure because you have integrated minus Tr minus T; sdT plus Pr to Pv dp ok.

Now, r here is an arbitrary reference state. So, in principle you can calculate this using thermodynamic expressions and volumetric data. We have shown this that we should be able to calculate the changes in entropy, if you can convert make use of Maxwell relations and so, forth. So, in principle you should be able to calculate thermodynamic expressions and the volumetric data.

But there is a issue of reference temperatures or reference conditions. More importantly this we do not know this is unknown and thus due to the need of an arbitrary reference or standard state; the successful application of this expression depends on the judicial choice of the reference ok. And that makes it difficult for practical applications ok; it is not a problem if you want to find out changes in the chemical potential. Because this will cancel out ok, but for creating absolute; so, that is not feasible with this kind of expressions.

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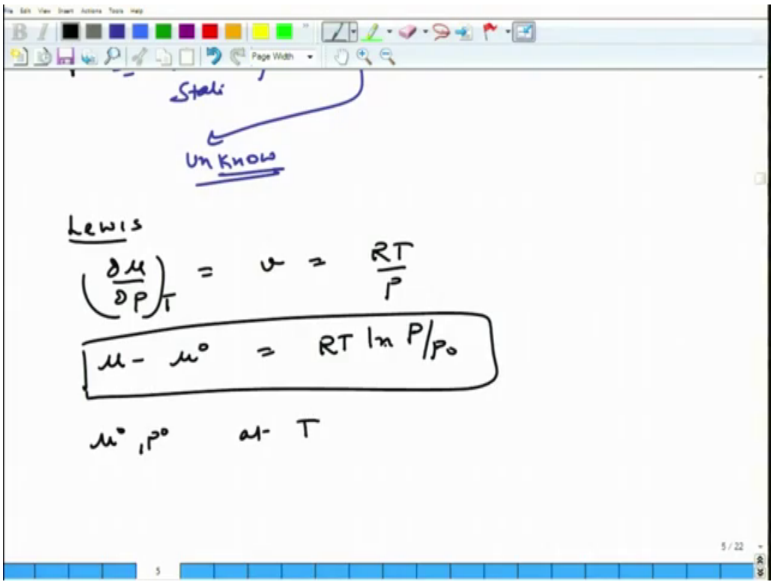

Lewis

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

$$\boxed{\mu - \mu^0 = RT \ln P/P_0}$$

μ^0, P^0 at T

So, in order to express this chemical potential is more reasonable expressions first Lewis considered the case of ideal gas ok. For the ideal gas and if you consider the expression of del mu by del P for a pure system this is nothing, but molar volume that is what we have derived earlier and following idle gas this is RT by P ok.

So, if you integrate this what do you get mu minus mu 0 this is RT ln of P by P 0. So, you can relate chemical potential difference to the changes in the pressure in the logarithic value, but there is an issue ok. So, note here that what is mu 0? Mu 0 and P 0 are at this particular temperature [noise; so, all the substances you know approaches an ideal gas behavior at very low pressure or very high temperature.

So, if you consider a very low pressure then mu is the pressure is tending 0 what is the value of mu?

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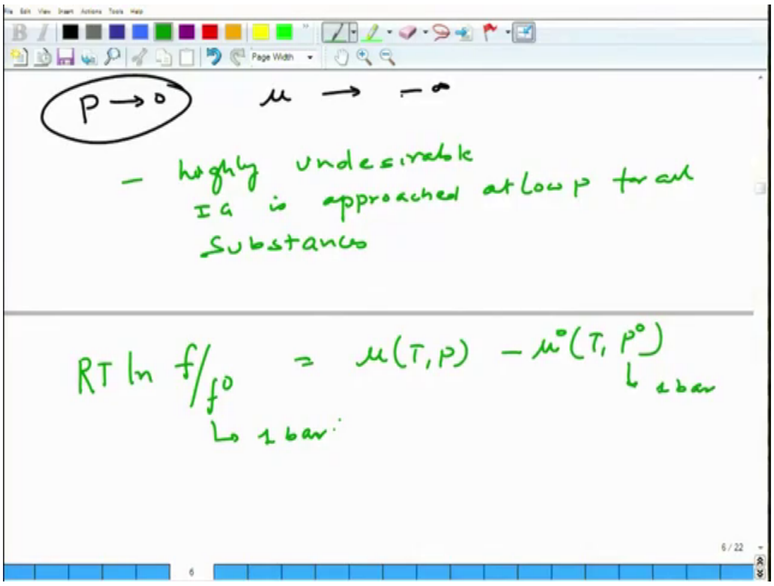

$P \to 0 \quad \mu \to -\infty$

- highly undesirable
IG is approached at low p for all substances

$$RT \ln f/f^0 = \mu(T,P) - \mu^0(T,P^0)$$

Mu is going to be minus infinity, but this is where all the substances approaches ideal gas. So, which essentially means we have an issue here; that this is a very unusual condition. So, this kind of situation is highly undesirable right; the reason is because ideal gas is approached at low pressure for all substances ok.

And this expression or the chemical potential is a key to the thermodynamic you know analysis ok. So, how do you avoid this like logarithmic divergence of chemical potential at low pressure? So, Lewis introduced fugacity in order to avoid such a situation. So, the definition of the fugacity is ln f by f 0 this is mu of T P minus the reference mu; T at the pressure P equal to 0 ok; this is the reference pressure, temperature is kept same.

Usually this is taken as 1 bar ok; note this is the ratio. So, this is this can be any arbitrary unit ok, but in practice people take this to be 1 bar ok, but fugacity is certainly not a pressure ok, it relates to the chemical potential. So, it is not a equivalent of pressure; the other thing which one should notice that since chemical potential is depends on two intensive variable T and P; the fugacity also depends on T and P ok.

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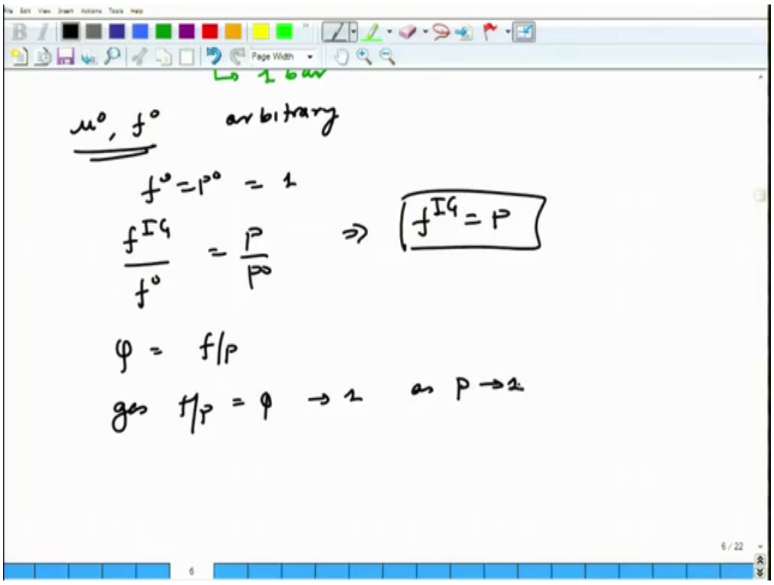

↳ 1 bar

μ^0, f^0 arbitrary

$f^0 = P^0 = 1$

$\frac{f^{IG}}{f^0} = \frac{P}{P^0} \Rightarrow \boxed{f^{IG} = P}$

$\varphi = f/P$

gas $f/P = \varphi \to 1$ as $P \to 1$

Now, this mu 0 and f 0 are arbitrary again ok, but are they independent and says no once you fix mu 0 the corresponding f 0 is fixed ok. The other thing is unlike the chemical potential f does not diverge; so, when you consider f 0 is equal to P 0 that says 1 ok. And if you compare this expression with the earlier expression mu 0, this expression when you consider f 0 is equal to P 0 is equal to 1 and you plug in here you can show that because that other expression is for ideal gas. So, this is for ideal gas right ok.

For an ideal gas f 0 is equal to P 0 is equal to 1; that is a difference would mean that f G f IG by ok. So, this you can derive because mu minus mu 0 is basically nothing, but RT ln P by P 0 ok. Find the ideal gas and since f 0 is equal to P is equal to 1; you should be able to find out you should be able to get this expression ok.

Now, the other thing is the sometimes we also defined terms like an auxiliary from quantity f by P and for gas f by P or phi tends to 1 as P tends to 1. So, when you choose of course, f 0; P 0 is equal to 1 ok. So, let me further continue with this fugacity expression let me go back to the definition of or the relation of the partial derivative of mu with respect to P which is related to v ok.

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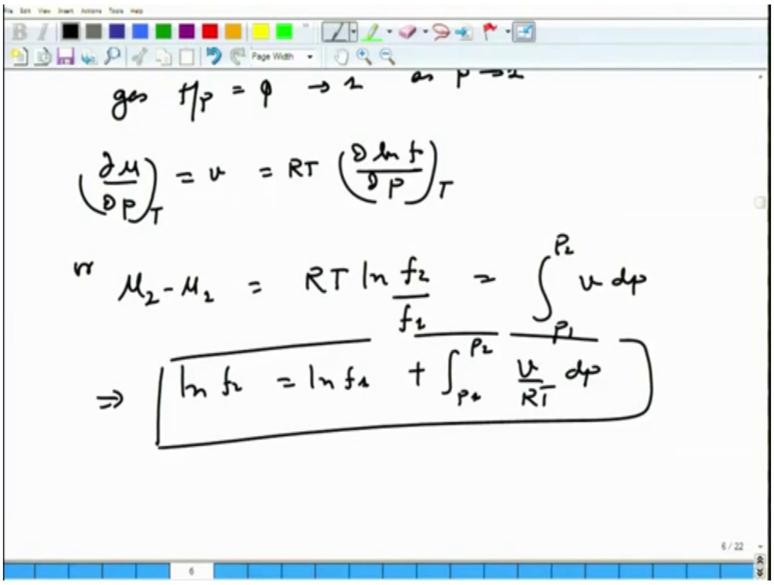

gas $f/P = \phi \rightarrow 1$ as $P \rightarrow 1$

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

or $$\mu_2 - \mu_1 = RT \ln \frac{f_2}{f_1} = \int_{P_1}^{P_2} v\, dp$$

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

Now, with this definition this definition is irrespective of whether the fluid is idle or not ok, but the relation of the chemical potential to pressure in this form depends on whether the fluid is ideal gas or in other word this holds for ideal gas. So, we again go back to this expression del mu by del P at constant v ok. And this mu we know now with respect to fugacity; so, we have this relation mu minus mu 0 is equal to RT ln f for a constant temperature ok.

This can be now written as RT del and f by del P at constant T or in other word mu 2 minus mu 1 is RT l n f 2 by f 1 this is nothing, but because you and you are integrating with respect to pressure. So, this is nothing, but d P; P 1 to P 2 ok.

So, now I can rewrite this expression I can also write it like ln f 2 is equal to ln f 1 plus P 1 P 2 v by RT dp right. Now this is a basically a generic expression and what we have done is we have not made any assumption. Here if you look at it very carefully, now for the case of a liquid and solid we can try to assume that it is incompressible; that means, molar volume is almost constant we can take it out.

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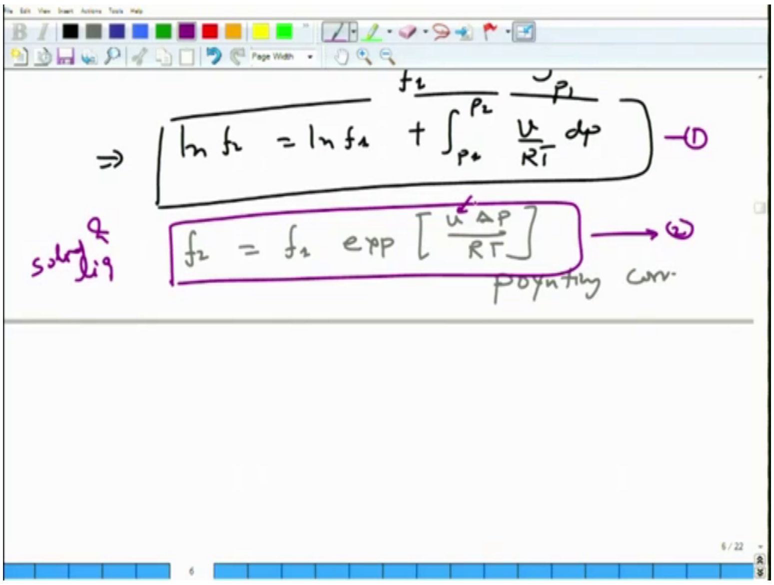

$$\Rightarrow \boxed{\ln f_2 = \ln f_1 + \int_{P_1}^{P_2} \frac{v}{RT}\, dP} \quad \text{—}①$$

solid & liq

$$\boxed{f_2 = f_1 \exp\left[\frac{v\,\Delta P}{RT}\right]} \longrightarrow ②$$

Poynting corr.

In that case I can write f 2 is equal to f 1 exponential and this is nothing, but pointing correction ok. So, in other word I should be able to calculate the fugacity at least the ratio of the fugacity from the known value of the molar property ok and the changes in the pressure for a given temperature for any system.

So, let me just do a simple example; why we can simply consider in this way and not necessarily integrate it. So, there are two equations right one is the case where we have this where it talks about just integration of v by RT dP and this is another one which approximate it, but this is first solid and liquid assuming this is more or less constant ok. So, this is a problem which we can look at this is an example.

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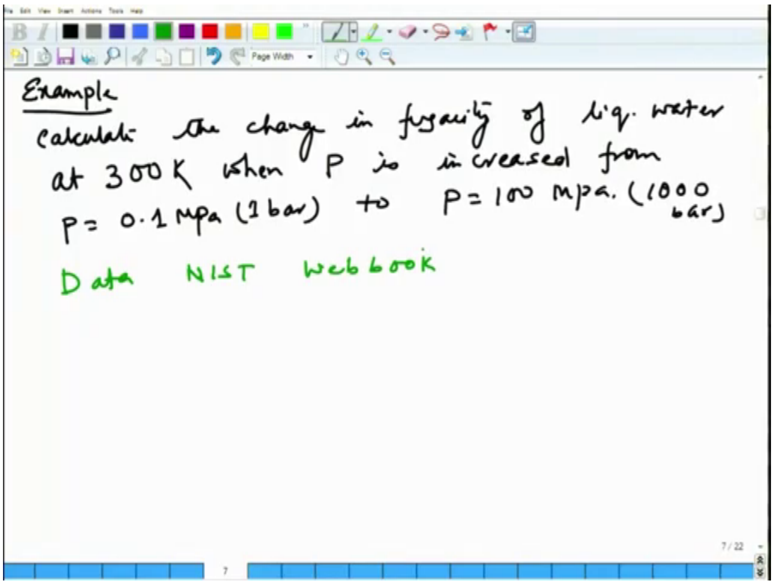

Example

Calculate the change in fugacity of liq. water at 300 K when P is increased from $P = 0.1$ MPa (1 bar) to $P = 100$ MPa. (1000 bar)

Data NIST web book

So, the question is we have to calculate the change in fugacity of liquid water at 300 Kelvin when pressure is increased from point 1 mega Pascal to 100 mega Pascal ok. So, basically thousand times increasing the pressure and the data for this can be obtained from NIST web of science or a NIST web book which is available without any special privileges, you can just type it and you can get this information.

What are the information you need? Temperature is already given; what you need is basically nothing, but molar volume of the water liquid; water as a function of pressure because we are going to make use of the expression.

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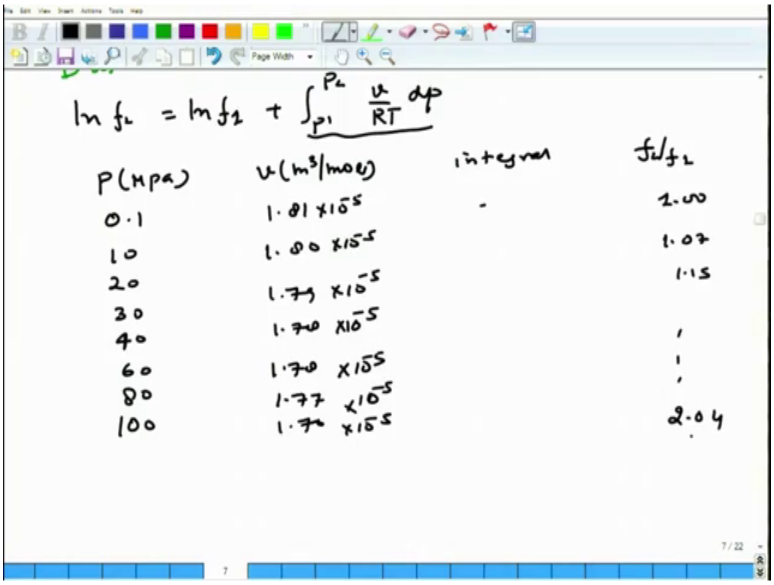

$$\ln f_2 = \ln f_1 + \underbrace{\int_{p_1}^{p_2} \frac{v}{RT} dp}$$

P (MPa)	v (m³/mol)	integral	f_2/f_1
0.1	1.81×10^{-5}	-	1.00
10	1.80×10^{-5}		1.07
20	1.79×10^{-5}		1.15
30	1.78×10^{-5}		
40			,
60	1.78×10^{-5}		'
80	1.77×10^{-5}		,
100	1.76×10^{-5}		2.04

So as I said there are two expressions which we have considered, this is the one without any approximation right. So, we can use (Refer Time: 12:32) rules for numerical integration.

So, let us assume that you have pressure given in mega Pascal like 0.1, 10, 20, 30 and the molar volume is given as 1.81 into 10 to power minus 5; 1.80 into 10 to the power minus 5; 1.79 ok. So, these are all the values directly from the NIST web book ok.

Now, ah; so, what is the value of this integral ok? So, we can consider since it is being asked the change in fugacity not the value of the fugacity. So, we can consider this as a reference 0.1 ok. So, if we consider this as a reference; then we should be able to find out the fugacity ratio at 10 mega Pascal with reference to the fugacity at 0.1 mega Pascal. So, this is the values of the integral and this would be your f by ot f 2 by f 1 ok.

So, if you just; this is if you were just considering this there of course, this is going to be 1 this is going to be 1.07, 1.15 and so, forth up to 2.04. So, this is the value 2.04 which comes at 100 mega Pascal ok; so, in other word getting from 0.1 to 100 mega Pascal; the ratio of change and the fugacity is 2.04 ok.

Now, if you use the second expression which is a pointing expression ok; what how you going to do that? You can consider the molar volume at 0.1 mega Pascal to be constant.

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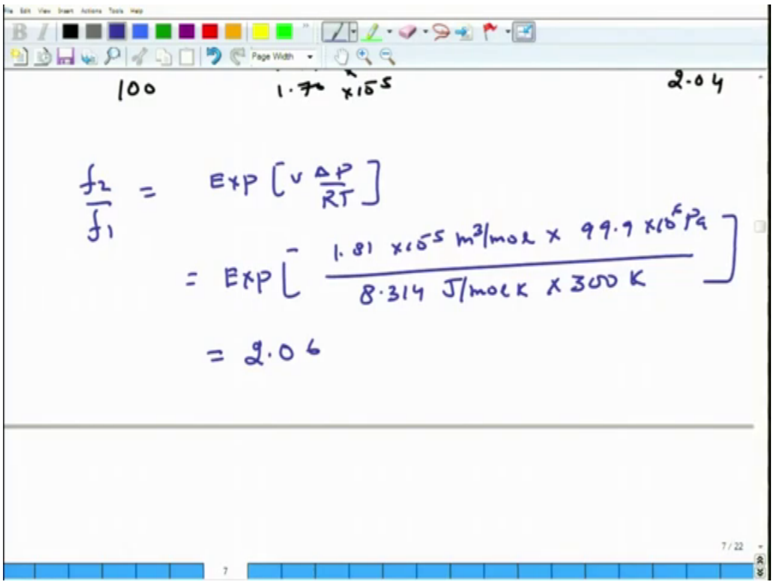

100 $\quad 1.7 \times 10^{-5} \quad$ 2.04

$$\frac{f_2}{f_1} = \mathrm{Exp}\left[v\frac{\Delta P}{RT}\right]$$

$$= \mathrm{Exp}\left[\frac{1.81\times10^{-5}\ m^3/mol \times 99.9\times10^{6}\ Pa}{8.314\ J/mol\,K \times 300\ K}\right]$$

$$= 2.06$$

So, f 2 by f 1 is exponential v delta P by RT right. So, this is exponential what is v? v is whatever we have considered here this is the molar volume at 0.1 mega Pascal.

So, this is 1.81 into 10 to the power minus 5 meter cube per mole multiplied by the change in the pressure which is 100 minus 0.1 mega Pascal; which is 99.9 into 10 to power 6 Pascal divided by gas constant which is 8.314 joules per mole Kelvin multiplied by the temperature; the temperature was a 300 Kelvin ok.

So, we just put 300 here now this turns out to be 2.06 ok. So, on one hand you have done away regress (Refer Time: 16:05) based calculations which you can of course, do using excel without writing codes; also the value turns out to be 2.04. And on the other hand, if you use simply the point in expression the value turns out to be almost close enough ok. And the reason why it is negligible because water in this condition turns out to be incompressible ok.

So, I will stop here and now in the next lecture I am going to continue the general discussion on the fugacity as the relation to the phase equilibria.