Thermodynamics of Fluid Phase Equilibria
Dr. Jayant K Singh
Department of Chemical Engineering
Indian Institute of Technology, Kanpur

Lecture - 27
Fugacity of Pure Liquids and Solids

Welcome back. In the last few lectures we were discussing about Thermodynamic Properties from Volumetric Data. We will continue this discussion and in particular this lecture we will look at the fugacity of pure liquids and solids ok.

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Now, often many times we would like to calculate the fugacity of liquid, particularly fugacity of pure liquid at temperature T P. So, since it is let us say liquid is i in this case. Now, if you would like to evaluate this we can make use of the earlier expression which we have evaluated for the pure liquid system that is ln fi by P pure this is equal to 0 to P compressibility factor minus 1 by P dp.

But in this case what we are going to do is we are going to break this integral from 0 to P to 2 parts this is mainly because what we are interested is basically the compressed liquid state or the point.
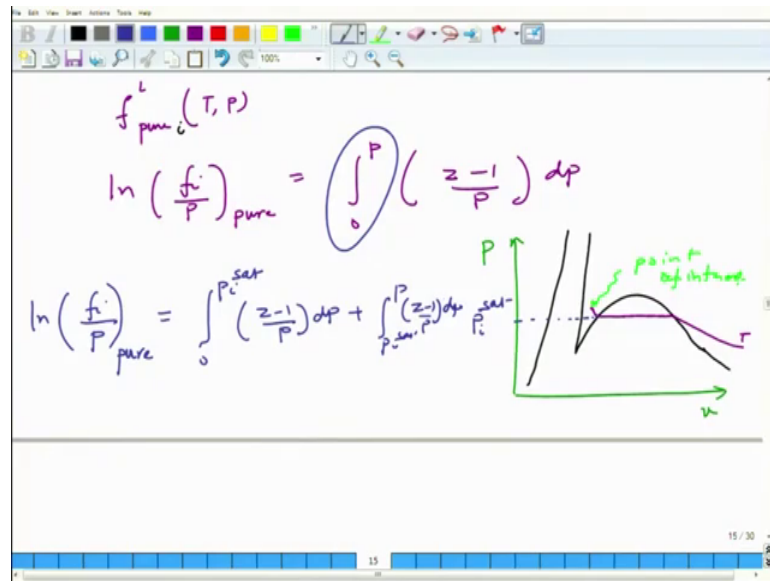
So, let me first draw a generic phase diagram here. So, this is a pressure P against molar volume this is typical two phase region and this is basically kind of low liquid vapour region ok. Now, since our interest is somewhere here this would be our point of its interest and the corresponding line I can use solid line here and so this is basically isotope. So, our point of interest is this point of which basically we are trying to calculate the fugacity ok.

Now, this is at P and T ok, this is the corresponding P is here, but this point corresponds to P i for the pure system i sat ok. So, we can break this expression because this expression in two parts. So, the left hand side still remains the same ok, but now, I will break it into P i set from 0 pressure which is somewhere way down way down here it will be 0 pressure from here till the point we reach P saturation. I can actually write this also as plus P i sat P z minus 1 P by T P i can simplify this expression also in terms of the molar volume directly then in that case.

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The equation will be RT fi L, let us say T P that is going to be 0 to P i sat and here now we have V i. So, this is basically rearranging this because z nothing but P V by RT. So, this second term is P i set P V i minus RT by P dp ok. Now, this part we can relate to the fugacity at saturation condition. Since RT f I, f pure i sat T but now, corresponding to P sat; that means, this point cause went to this point would be P sat this is going to be simply 0 to P i sat I will put P i here V i minus RT by P dp. So, this term is in fact, but definition from here we can directly get putting P as P is sat indicate this fi is basically corresponding to saturation condition, ok.

Now, we plug this expression back here because this for generic T P this part is nothing, but RT f pure set. So, let me write down here RT from here RT fi L T P by P this is nothing, but RT this term is going to be RT f pure i sat T P i sat plus this integral P i sat to P and this expression get here ok. So, I can now, rearrange this expression. So, if I rearrange this expression the following I should get ok.

Let me correct this is going to be P ok. So, before I rearrange this expression this right hand side can also be written as f sat pure i T ok. And why is that? Here this P is not the same as P here because its 0 to P sat. So, if I look at it this should have been actually P i sat corresponding to this basically T here the corresponding to temperature T here ok. So, this should be P i sat ok, T.

So now, we are saying that this itself is going to be only T because once you say basically e saturation it indicates that this corresponds to a specific temperature that temperature. So, this is only dependent on just one variable T due to the fact that this is a pure system. So, right here P i sat again T here plus term ok.

So, let me further simplify this. So, this is going to be T fl pure i T P divided by P can now be broken into two parts, one due to the contribution from 0 to P sat, where by P i sat T plus the other contribution which is from P i sat P V i L dp this is the first part of this minus, minus of P i P can take minus outside the integral make it here this is going to be RT by P dp which is nothing, but RT ln P by P sat ,ok. So, I can write this as simply this is nothing, but RT ln P by P sat ok.

Now, I can further simplify this expression and rearrange this expression to make it a much more simpler looking expression rearranged we obtain the following expression, f of L pure i at temperature T P this will be equal to this is equal to f of saturation saturated a figure f of f of liquid at saturation which will be only dependent on this T once you fix the T the corresponding saturation pressure is fixed at that point the fugacity is also fixed. And the other term is basically the correction due to the change in the pressure from P i sat to P V i L by RT dp ok. So, this is the term we got. This is a multiple of two terms due to the saturation fugacity this plus the correction term ok.

I can also make use of fugacity coefficient to express this term.

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So, I can write this as f of L pure i T P this is nothing, but this is nothing, but P i sat at T and phi i sat T. Note that the definition of fugacity coefficient is nothing, but phi i T P is nothing, but f of pure T P divided by P. So, basically the fugacity coefficient is nothing, but f by P ok. So, now, I can replace this expression in terms of the fugacity coefficient I can write this expression as P i sat multiplied by phi i sat these are both dependent on temperature ok; then this term exponential P P i sat V i L by RT dp ok. Now, note that f i f i sat note that phi sat is a function of T n P i sat since the constraint due to the condition of the saturation this can be written as simply phi i sat T ok. So, it is independent of or it is dependent on only one variable ok.

So, if you look at carefully this expression here basically tells you that fugacity of the pure liquid i is equal to the saturated vapour pressure. So, if you look at very carefully this equation tells you that fugacity of a pure liquid i is equal to the saturation pressure P i sat corresponding to T multiplied by 2 corrections. The first correction this is fugacity coefficient ok.

So, this is basically fugacity coefficient of the saturated vapour and what its account for its account for non ideality of the saturated vapour. So, that is a fugacity coefficient. So, its accounts for of saturated vapour and then you have this another term ok.

Now, this is as I said already this is nothing, but we call it often as pointing correction ok. And what it accounts for? So, it accounts for compression of the liquid from P i sat to P ok. So, this is exponential ok. So, it accounts for ok. So, it will call for compression from P i sat to P compression of this of the liquid from P i sat to P. Often we try to

approximate this term pointing correction, so this approximation typically we give we make is V i L P minus P i sat divided by RT ok.

Now, what is the reason for such an approximation because we have taken this molar volume outside which means we have assumed that the liquid is incompressible. Now, in addition to that where the other approximation which are which we can make use of it depends on the condition.

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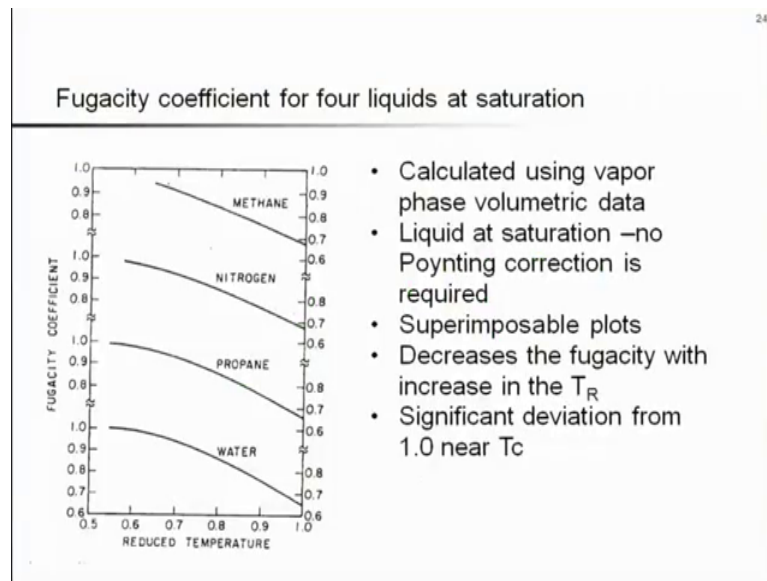
So, for example, approximation at low pressure we can make use of i sat is equal to 1 approximately at low pressure since with behaves like ideal system. So, we can as well as the pointing correction factor is also close to 1 ok.

So, let us try to understand this how does this approximation looks like for different systems ok. So, in order to understand this pointing correction or in general the fugacity we will take an example ok.
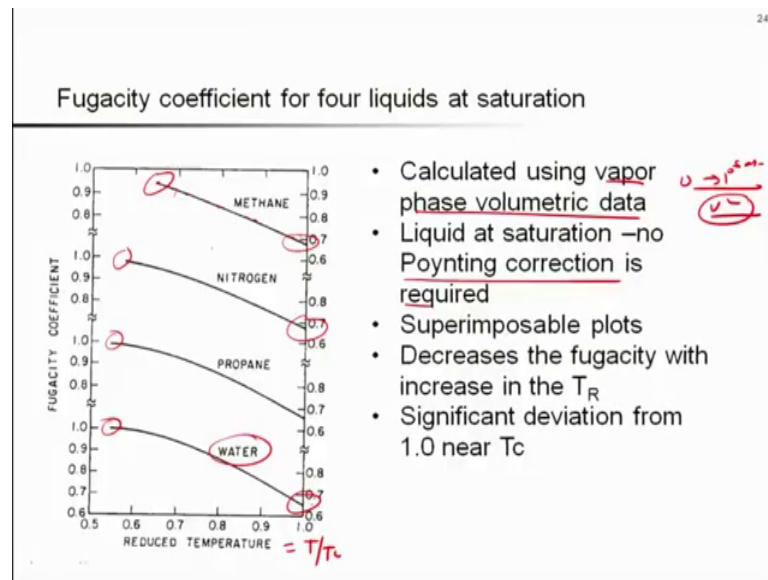
So, let us discuss the fugacity coefficient behaviour for liquids at saturation condition by considering 4 molecules. So, this is an example we have taken methane nitrogen propane water and in order to plot this on the same scale we have made sure that we have to taking that reduce the temperature. So, this is reduced. So, this temperature is nothing, but T by T C ok.

So, in order for you to understand this let us let me just provide more details. So, this particular point corresponds to a state condition where the liquid is a liquid or vapours are saturated at a specific reduced temperature. So, once you fix this temperature the corresponding it tells you that this is this it has a certain pressure which of course, I am not plotting here, but this all this point are at saturation.

And of course, with this is the temperature is different the corresponding saturation pressure will be also different. But since it is the saturation we do not require pointing correction first of all. The second is that we have made use of the expression which we have derived earlier and the vapour phase volumetric data from 0 to P sat has been used and V L the 0 to P sat volumetric data has been used ok.

Now, if you look at this fugacity coefficient it is something which is very clear that this are very much alike; that means, there are more or less super imposable plots the important thing is basically the fugacity decreases with increasing in the reduced temperature; that means, when the temperature is change is increasing and is

approaching towards this critical point the fugacity coefficient drops or decreases dramatically ok.

But at lower T C is very close to 1 which is very visible particularly water it around is close to 1. So, that means, the approach towards ideality is visible at lower values of T R otherwise if you look at it at very close to T C there is a significant deviation from the non ideality ok, from 1 to 0.7 ok, that is a significant division.

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Now, let me also further point out a bit of a this pointing correction. Now, it is usually very small this is a pointing correction usually very small at low pressure, but it could be very large at high pressure to appreciate this point let us consider molar volume of an incompressible fluid which is at you know 100 centimetre cube per mole at 300 Kelvin ok. So, we are looking at only this term where we have put the molar volume at 100 centimetre cube per mole and the pressure this delta P V varied.

So, if you consider delta P or the pressure in the axis of saturation pressure, 1 the pointing correction is only this which is a close to 1, But if you consider ten it increases, but it is not to that extent is negligible, but one more 1 increase in another by 1 order increases this quantic correction significantly, and further increase my another order the pointing correction is like dramatically much higher ok.

So, thus it is it can be very large at high pressure this is something which we must understand ok.

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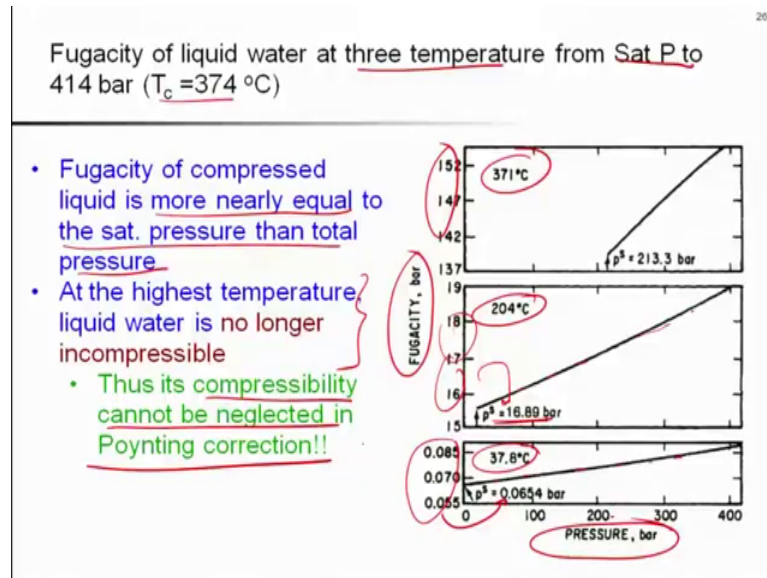
So, let me also try to give an example of particular molecule. So, let us consider liquid water and here what we are going to consider is basically 3 temperatures which can show the breadth of the temperature from low temperature to temperature closer to a critical point. And let us see what you what kind of behaviour for fugacity we have for water. Now, T C is basically of for liquid water for water itself is 374 degree Celsius and what we are wearing is the 3 temperature from saturation pressure to 414 bar.

So, let us look at this here this is the very high temperature, intimidate temperature and low temperature ok. So, we have fugacity here as a function of the pressure of the system ok. So, this point corresponds to the pressure or this point corresponds to the state of this liquid vapour of saturation at this particular temperature ok. So, at this temperature the P sat is to 13.3 bar ok, at this temperature the P sat is 16.89 bar, at this temperature the P sat is close to 0.654 bar and what we are doing is basically at keeping the temperature fixed and changing the pressure.

Now, what you can notice that here in this case these are all compressed liquid data's ok, from here to here these are all compressed liquid data's right. So, at lower temperature the fugacity of the compressed liquid is almost or nearly equal to the pressure total saturation pressure the restate this. So, this is a fugacity here. So, the fugacity of the

compressed liquid is more nearly equal to the saturation pressure than the total pressure. We can see this statement very clearly. So, for example, this is the fugacity this is more nearly to this saturation pressure than the pressures here ok.

So, for example, here also we can look at it. So, these are the fugacity of the compressed liquid at very high pressure, but this is very close to the saturation pressure. And the other important thing is that at high temperature liquid water is no longer compressible which is evident from these values the fugacity because it deviates significantly from here which indicates that that very high temperature the compressibility cannot be neglected in quantum corrections ok. So, this is a very practical example considering the real systems in order to understand the effect of the pressure or at different temperatures.

So, we will stop here and we will continue our exercise of understanding these thermodynamic property from volumetric data in the next lecture.