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

Lecture - 26
Thermodynamics Properties from Volumetric Data – II

Welcome back. In the last lecture we derived the expression of fugacity as a function of molar volume, and this was a the derivation which connects to the integration of this term from 0 to P to the this fugacity coefficient ok.

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I can continue this exercise particularly we can look at for pure fluid when y i is equal to 1, V i bar is our volume in that case this expression is a fi by P for pure of is 0 to P V i minus RT by P dp ok.

I can also rewrite this expression by taking this RT in to the right hand side and this could be simply z i minus 1 divided by P dp where z i is nothing but compressibility factor, ok.

Now, consider one approximation. So, consider an approximation before I write that we should make a note that this expression which we have got for a component I in a mixture connecting to the fugacity to the molar volume for the mixture and for the pure these are exact expression there is no approximation involved in this expression. Now, we can make certain approximation to simplify and look at how from here we can come up with this Lewis fugacity rule which we have imposed earlier ok.

So, if I consider this approximation where I said that well, if the mixture follows Amagat's law which is nothing, but the additivity of the volume concept ok. This is i equal to m so; that means, you are simply adding up the volume this means that V i by is equal to V i for the mixtures or when somebody writes this actually means this also and which all will which essentially also means from here is mix this is equivalently also implies that this is equal to 0 or V access is also 0. So, this is the Amagat's law ok.

Now, if you have this information; that means, I can write the partial molar volume of component I as simply molar volume of component i and I can plug in here now, this right this if I using this kind of approximation then what we get RT ln fi yi P is equal to 0 to P V i. Instead of V i bar I am writing V i minus RT by P dp this expression looking at this ok. What is this? This is nothing, but RT ln f by P of pure i that is what by by definition, if you look at this is what the by definition right, this is the definition.

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So, you have this now, left hand side this and right hand side this. Now, if you can simplify what you get is the following expression f i T P composition is y i times f pure i add T P

This is nothing, but Lewis fugacity rule ok. So, note that this is at the fugacity of the pure component i add the temperature pressure of the mixtures ok. Now, I will try to describe this the validity of such a rule Lewis fugacity rule by taking an example from the literature.

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So, the one which we just derived was based on the additivity of the volume for all the components ok. So, that it is a very simple equation which inherently depends on the fact that the volume should be additive for the mixtures ok. So, it turns out that at high temperature they this is a good approximation because in liquid like densities fluid tend to mix with little or no change in volume ok. So, let us look at the example of nitrogen butane volumetric data at a specific temperature 171 degree Celsius ok.

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Compressibility factors for nitrogen/butane mixtures at 171°C
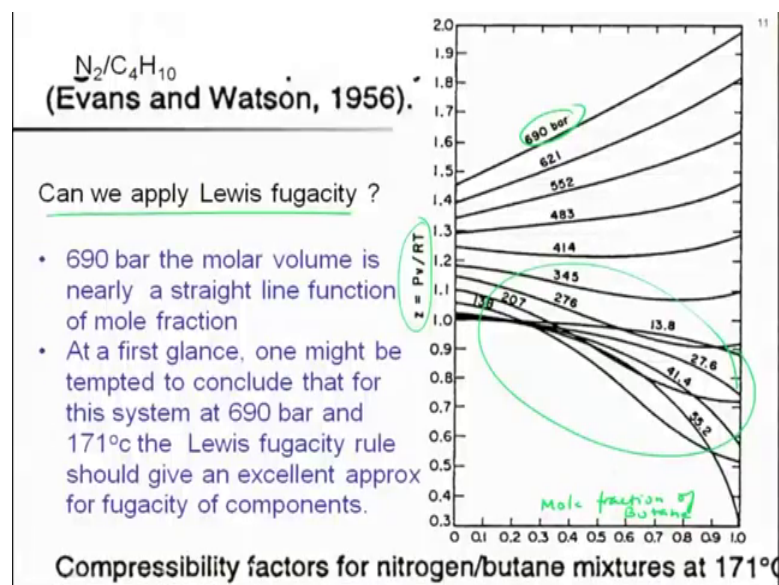
So, this is an example taken from the literature due to Evans and Watson and the data is 1956 data. So, what we have is the following that this is compressibility factor right as a function of the composition of nitrogen and beauty the nitrogen is close to 0.9. So, this is a basically the compressibility factor as a function of mole fraction of butane ok. So, this is the data directly from Evans and Watson work in 1956. So, the question is can we apply Lewis fugacity rule here.

By looking at the data you may be tempted that well since Lewis fugacity rule stays that the fugacity of a component i in a mixture is nothing, but the mole fraction multiplied by the fugacity of the pure component at the same temperature and pressure. So, it is like a linear relation. So, looking at here if you looking at the high at this pressure at here it is a linear region as a function of the mole fraction. So, you may be tempted well is a straight line function as a mole fraction at first glance you might be tempted to conclude that this

system at here and 171 degree this Lewis fugacity rule should give an excellent approximation for fugacity of component.

So, it looks very obvious that you know well this should be fine you know I can simply apply it because if I am interested in the pressure let us say 69 bar I should be able to apply. It looks from the derivation that well this is not from the derivation from the final expression, but this is simply f is equal to f y i multiply f of pure. But then if you carefully look at it the pressure has a significant effect on this z as a function of mole fraction it is not linear and this is the region which clearly tells you at low pressure it is certainly does not behave similarly as in the case of higher pressure higher pressure you can see the linearity, but low pressure it is not ok.

Now, does it affect this data or it does not affect? I mean can I actually apply this relation at 69 bar this Lewis fugacity rule. I cannot because at low pressure it behaves completely different. In other word in a linear case you can add the volume, but when it is non-linear can we simply add the volume in the way which we expect in the assumption for the Lewis fugacity rule.

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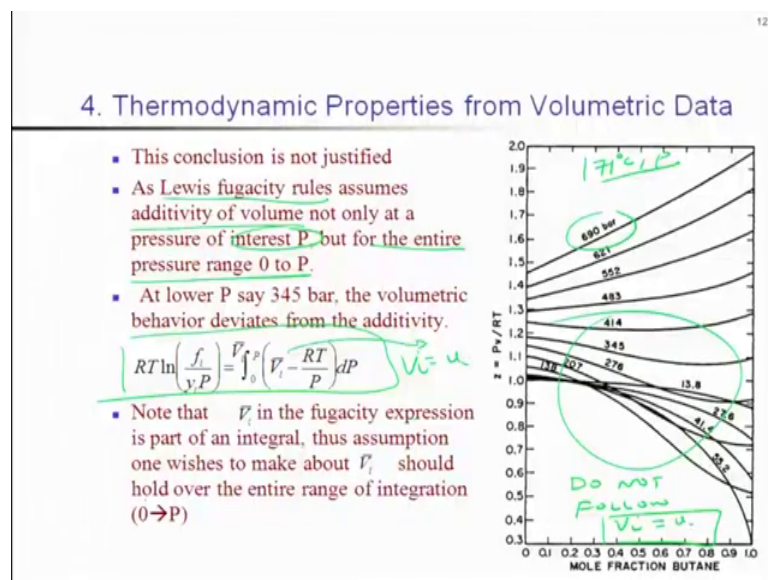
So, the answer is actually the conclusion which we wanted to apply is not justifiable ok. And the reason is that when we made use of the Lewis fugacity relation or rather when we derive their Lewis fugacity relation the assumption valid the assumption was that this additivity will valid from pressure 0 to the pressure P its from 0 to P, that integration is

from 0 to P. So, it assumes the additivity of volume the Lewis fugacity rule assumes the additivity of volume not only at the pressure of interest which we thought here, but also for the entire range from 0 to P.

Look at this derivation we made use of this right we due to the additivity we replaced V i is equal to vi, but this assumption is not at P it is for the whole range. So, if you are blindly applying this fugacity at 690 bar ignoring the fact that it behaves differently then naturally the results are going to be incorrect, ok.

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So, 0 to P the assumption of the volumetric should be.

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No, this is not a linear (Refer Time: 10:58), this is the data which we got it from the literature. So, you have done an experiment and you calculate the compressibility and you plotted against the mole fraction that is what. So, it shows that when you have linear z is a function of linear which essentially means since here in this line, if you look at in this line that the temperature and the pressure is fixed because temperature is 171 the temperature and pressure is fixed.

So, in this along this line what is happening is z is increasing as a function of mole fraction; that means, the volume is basically changing linearly as a function of mole fraction and thus it is linear; that means, it is additive whereas, in the other case is not, and this is the reason that in here just looking at this higher pressure. So, you cannot do that you cannot make use of this approximation, but at lower regime you can what I wanted to say was at higher you may look like at this regime it works fine, but the lowest ones they do not follow you know the Maggot's law follow this relation. So, that means, this relation do not hold ok.

So, this is what I was mentioning here that V i bar in the fugacity expression is a part of an integral this assumption one wishes to make about V i should whatever assumption if not just assumption of Maggot's law. But whatever is assumption you are going to make it for V i bar should hold over the entire range of integration ok. So, this is an important part.
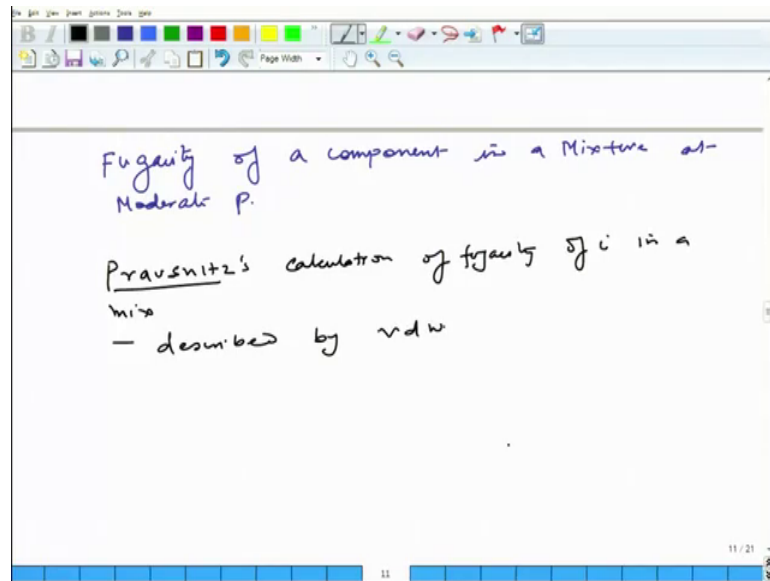
So, now, think on through the bit of example. What we can now, do is talk about fugacity of a component in a mixture add moderate pressure what the idea behind this one is basically that P is not equal to 0 or not even close to 0 we are considering pressure which is reasonably moderate. So, the best way to explain is to make use of some equation of straight.

So, what we are going to do is we are going to make use of what Pravsnitz's came up with to explain this. So, here we are going to make use of Pravsnitz's calculation of fugacity of component i in the mixture described by modified Vanderwall equation. So, Vanderwall equation ok, valid which is valid up to moderate pressure. Now, because Vanderwall equation has some limitation, so you is not like valid for all conditions.

So, what does Vanderwall equation talks about? So, I will write in a way which is simpler to understand.

So, if you look at V. So, here P V P multiplied by molar volume for a pure state let us say is equal to RT then it is a ideal gas correct it adds up the term b minus a by RT by P ok. So, if you rearrange you get a wonderful equation. So, what I am going to do is I am going to you know you can expand this a bit and then this will become like modified Vanderwall equation and this would be the higher in term you know this would be higher terms in P square and P 3 ok.

So, so what project this was the he made use of Vanderwall equation he wrote in this form and now, the question is given this relation of the pressure volume as we said the volumetric data is are given in terms of equation of state how do you calculate now the fugacity; so fugacity how do you calculate, right. So, we know that for calculation of fugacity we need to find out partial molar volume.

So, the question turns out that how do we calculate partial molar volume. So, we write down this expression. So, this is a generic expression does not talk about anything about I did mention that written for pure system, but in this case it could be for mixtures also ok. So, if it is for mixtures you have to multiply V by N T that is it.

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So, we will rearrange ignore the higher terms and again we talking about V as a function of T P and now, I will write it here V as N T RT by plus N T b minus N T a by RT ok. So, you have this expression right.

Now, though of course, you know how to calculate the partial molar property we if we talk about only let us say a binary mixture then V one bar is del V by del N 1 T P N 2 and this will be RT by P plus del N type V by del N 1 minus 1 by RT del N T by del N 1 ok. The reason I did not just directly went and assumed b to be constant because b is a coefficient of the mixtures equation of state which depends on the composition of it ok, it depends on the interaction parameter of it ok. So, what is in general, what is a and b here in Vanderwall equation. So, b represents the size and a represent the there are attractive forces the interaction between the particles.

Now, what would be the a and b for mixture? And it depends on composition right. So, what would be the mixing rule? You must specify mixing role ok.

So, we will directly use what originally Vanderwall proposed which was a is equal to y 1 square a 1 plus 2 y 1 y 2, a 1 a 2 plus y 2 square a 2 and b was simply the weighted average of those individual sizes for this is for binary mixture ok. Now, I can actually make use of this expression and calculate N T a because the N T a here and N T, N T b is here N T a is here. So, I can write N T a as N 1 square a 1 plus 2 N 1 N 2 plus N 2 square a divided by N T and N T b is N 1 b 1 plus N 2 b 2.

Now, you can take the partial derivative because you have this the information of this term. So, when you take the partial derivatives V one is equal to del V by del N 1 T P N 2 this is nothing, but RT by P RT by P and then you take the derivative with respect to N 1, N 1 N T b is here. So, that is going to be only be 1, right. So, second term is nothing, but b 1 and the b 1 and then you have N T also which is which is of course, that is fine then you have minus RT and then you have this term which you have to worry about.

o, you have minus RT I am going to write down the expression how we got whatever the expression we got plus even a two and within here we have minus n T square a ok. So, this is ok. So, this is part of this numerator minus N T square a ok.

Now, you have this expression you can now, plug in this expression in the right hand side of the expression cross point to the fugacity, remember that ok. So, when you plug in this equation what you got you have phi 1 which is f 1 by y 1 P this is fugacity coefficient for component 1 this is nothing but exponential b 1 minus a 1 by RT P by RT that is one part because you have this part ok, this is one part ok. So, if you plug in here you got what RT by P which got cancelled right and then you can rearrange this expression. So, if you so, but this is V 1 minus RT by P. So, if you take it this here you got actually b 1 minus 1 by RT ok. So, and this is actually not the case.

So, you got a simplified expression here this is another term will come up here exponential multiplied by a 1 minus a 2 square y 2 square P RT square ok. So, this is the term which you are going get ok, this becomes simplified. Now, this two terms if you look at very carefully, so this phi which is your fugacity coefficient contains two terms based on Vanderwall equation of state. The second term these dependent on a 2 ok, but the first term is independent of a 2 ok.

So, if I consider y 2 goes to 0 which essentially means pure 1 then f 1 pure 1 is going to be simply P multiplied by exponential b 1 minus a 1 by RT multiplied by P by RT right that is what is saying right ok. So, which essentially tells you that this term or if you take this term is nothing, but your f pure 1 divided by P this is what he is saying. So, what you have this expression finally, f 1 by y 1 P f pure 1 by P and the second term right. So, you have f 1 as y 1 f pure 1 and then you have this exponential term ok. So, this is the point. Now, if you look at this expression and remember this is nothing, but the fugacity rules is talked about this is the additional correction. This is nothing, but correction to Lewis fugacity rule.

So, this expression you take a note. And then I will just take in one example this as I said here this is only when you have the condition where you are saying that this correction is added when you have situations which are that y 2 is not equal to not equal to 0 right and a 1 is not equal to a 2.

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So, if a 1 is equal to a 2 which essentially means similar component and if I 2 equal to 0; means basically nothing, but pure 1. So, you have a condition where you have to include a term like that and this is the reason that Lewis fugacity rule may not work in many cases. So, typically Lewis fugacity figures rule for a component i is often poor or is a bad approximation when why of that component is much less than 1 ok. Lewis fugacity rule usually good when y i is close to unity.

So, for example, if y 1 is close to 1 then of course, means that y 2 is close to 0 in that case this particular expression will hold. So, this is what is talking about y 1 is much less than 1 then considering f 1 is y 1 f pure is a bad approximation ok. When y 1 is much less than 1 then Lewis fugacity rule would be a bad approximation that is what is talking about you can say that because when y 1 is much less than 1, it means y 2 is going to be not 0 significantly more than 0 and as this collection has to be included.
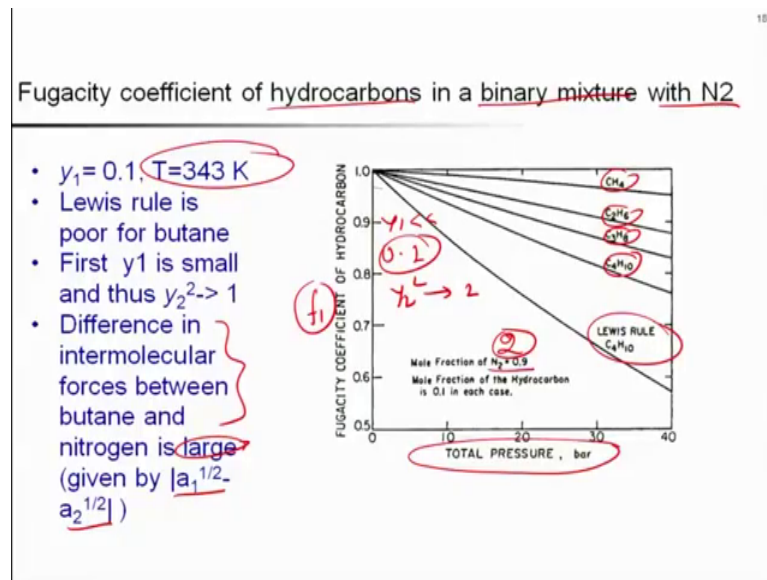
So, let us take an example here this is an example of fugacity coefficient of hydrocarbons in a binary mixture with N 2 nitrogen ok. So, what we have is fugacity coefficient of hydrocarbon as a function of total pressure for different hydrocarbons ok. So, here nitrogen is y is 2 and hydrocarbon is 1, ok. So, for each of this we have considered a mole fraction of 0.1 for hydrocarbon and then the temperature is fixed ok. So, this is a fugacity of y 1 of fugacity of component 1 sorry ok, f 1 here. So, this is nothing, but f 1 ok. Now, in this case y 1 is much less than 1, right, is not it 0.1, it is not 1, its very lower than 1.

But you look at this is the actual fugacity coefficient as a function of total pressure, but this is the one which is from the Lewis rule and thus it is very clear that in this condition since y 1 is much less than 0.1 and y 2 square is closer to 1 because y 2 square is part of this one, y 2 is closer to 1 ok. And thus this is this rule cannot be applied and this deviates from the actual value.

But there is another important thing is that in addition to the composition the sizes of this system hydrocarbon and nitrogen is quite different and the intermolecular forces also different. So, difference in the intermolecular forces between butane and nitrogen is large given that this; that means, this value is going to be nonzero ok; that means, this in addition to this term this is also playing a role in this case because these are dissimilar molecules and thus it deviates from this ok.

So, these are the considerations which you have to apply before making use of these a kind of expression because the expression such as Lewis fugacity rule based on assumptions ok. So, one need to take a judicious consideration of such a expression for any for any applications ok. So, this was the kind of example which we wanted to cover as far as this lecture is concerned.

We will end here. We will see you next time.