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

Lecture – 20
General Discussion on Fugacity

We are going to now discuss about fugacity and its particular role in phase equilibria.

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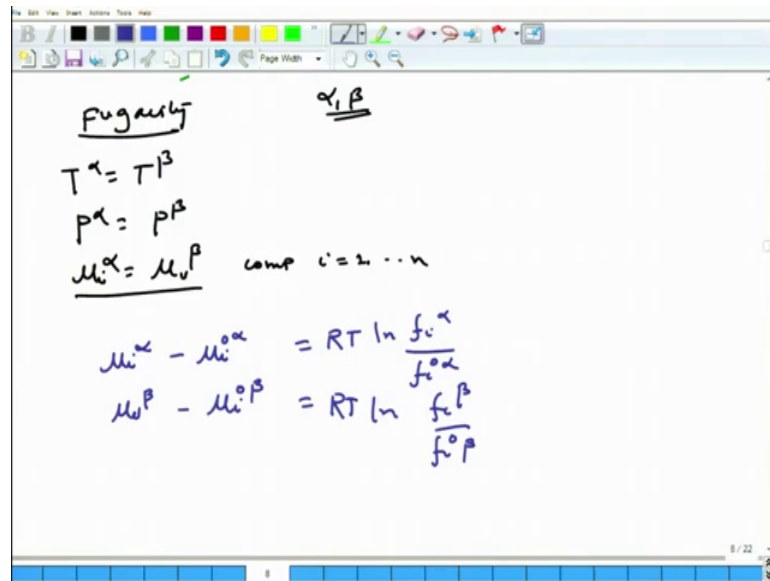
So, for the ideal gas we have already considered you know or discussed earlier that fugacity is nothing, but pressure for an ideal gas right. So, for the pure system; so, for component i in a mixture of ideal gas; f i will be P i where P i is a nothing, but partial pressure ok.

So, this is partial pressure P i is nothing, but partial pressure. Now as we know that for all the system whether it is pure or mixed, they approach to ideal gas at low pressure. So, in other word f i by y i P tends towards 1; by looking at this expression as P goes to 0; because at P goes to 0, the fluid starts behaving like ideal gas and thus this expression holds.

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Now, what we are interested is basically to make use of fugacity in our phase equilibrium ok. The question is can we replace chemical potential by fugacity by using transformation or some other criteria? So, fugacity it turns out is basically a convenient variable for fundamental equations of phase equilibria. So, we know the fundamental equations or the conditions for phase equilibria R right.

For two phases alpha and beta so, let us try to see try to make use of this equality of the chemical potential of component i ok. So, from mu i is equal to mu ib i can write it has by the definition of the fugacity this would be mu i alpha minus mu i 0 alpha this is RT ln fi alpha fi 0 right for a specific i similarly I can do the same exercise for mu i beta.

So, knowing this that this condition should hold; so, what we do is we write this expression ok. So, mu i; I put it here and move i beta i put it there.

I get the following expression. mu i 0; alpha plus RT ln fi alpha fi 0 alpha this should be mu i 0 beta plus RT ln fi beta fi 0 beta ok. So, I have this relation which connects the chemical potential in the reference state of alpha to beta and the fugacity ratios.

So, what we are going to consider is two cases consider two cases ok. So, let us assume that for both the phases the reference conditions are same ok. So, that is the reference potentials are same; so, we are going to consider case 1 where we consider that reference chemical potential of component i is same.

If you consider this since chemical potentials are related to fugacity which essentially means fi; fi 0 alpha should be same as a fi 0 beta and that case this implies that fi alpha should be same is fi beta ok. So, this is directly it implies taking this as assumption that this must be considered that you consider the reference chemical potential to be same ok.

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So, now what is the second condition; case second. So, suppose that standard states of alpha and beta. So, I am going to write this now; so, what is your case two? The case 2 is suppose that standard state for alpha and beta are at the same temperature, but not at the same pressure and composition which means basically you cannot just take it mu as 0 alpha is equal to mu i is 0 beta.

Why because it depends on T and pressure 0 is there the reference pressure is also considered. So, we have to now relate the chemical potential of reference state of alpha and beta ok. So, in that case there is a relation between the referenced chemical potential of alpha and beta; considering the difference we can straightaway make use of the definition of the chemical or the definition of the fugacity ok.

Now, this is the relation now you can plug this equation into the basic chemical potential equality and so, you can show that mu i 0 alpha which essentially means; so, plugging in mu i alpha is equal to mu i beta. This clearly shows because this is nothing, but same which means basically fi should be equal to fi beta.

So, what it tells you that the equality of the chemical potential can be replaced by the equality of fugacity of for a given component in two phase system.

Or in general you can now represent the convenient fundamental equation or phase equilibrium which is going to be T alpha is equal to T beta; P alpha go to P beta and fi alpha is equal to fi beta where i is equal to 1 to n ok.

Now, I am going to make use of this expression and for a simple application which is nothing, but Raoult's law. So, what we are interested is that for a arbitrary system vapor liquid at equilibrium, we are seeking a simple relation describing the distribution of the

component between the this phases alpha and beta ok; that means, we are interested in to connect mole fractions x in the liquid phase and y in the vapor phase ok.

So, we are going to consider a simple system simple system whose behavior can be approximated closest to ideal gas or ideal solution ideal behavior ok. So, let me just take component let us say 1 in the in this mixture. So, f 1 let us say in the vapor phase should be equal to f 1 in the liquid phase ok. Now this is what we know for as far as equality for a given temperature and pressure.

So, what we interested is basically connecting this and relating to the mole fractions and the other variables pressures. For example, so what is the assumption here? So, let me just take assumption number 1 ok. Assumption 1 is f 1 v at T P constant temperature pressure is proportional to the mole fraction of 1 ok; in other word we are saying f 1; v is y 1 1 vapor of pure ok.

So, this is what we are trying to say that this is proportional to y 1. Now this is the assumption 1; now we are going to take another assumption. So, this is assumption 2.

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Ok that f of l is proportional to x. So, this is basically saying that these are all ideal solutions where the fugacity is proportional to the mole fraction.

Now, remember this f 1 pure in the vapor; this is at the same temperature and pressure of the mixture same T P is same. So, in this case for the case of assumption 2; what we are

saying is that f 1 l is x 1 f l pure 1 pure alright. So, this is a again the liquid fugacity of the liquid component in the liquid phase temperature T P ok.

So, this assumption says that this is basically an ideal solution and is reasonable for conditions, where the components are of similar type ok. So, let us put it in there in the condition of the equality of the fugacity when you do that we get f V pure this is x 1 f l 1 pure alright.

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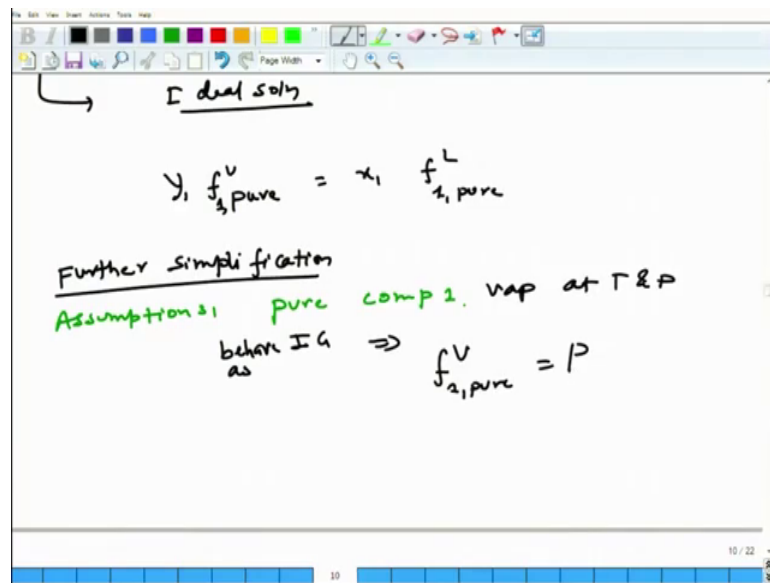
Now, we can make it further simplify this expression ok; so, let us say that is further simplify it. So, this is going to be assumption 3. So, we are saying that the gas the pure component at pure component 1 vapor at temperature and pressure behaves like an ideal gas. So, pure component vapor at T and P behaves like ideal gas which essentially means that f vapor 1 pure is nothing but pressure.

So, that is what the ideal gas we have shown that fugacity is same as pressure now. So, that we got rid of the fugacity and put it in the pressure, but what about the f L ok. So; that so, that would be assumption 4.

So, we are saying that the effect of the pressure on the fugacity of liquid which is in the condensed phase is negligible within the range; we are going to consider as far as the pressure is concerned.

So, the effect of the pressure is negligible for moderate range of the pressure now the second thing which we are considered that f remember that f 2 is equal to f 1 exponential integral of this which for the liquid phase we can write this as this right. So, we are going to ignore this and f 1 would be tons can be replaced by simply f 1 of liquid saturated liquid which we essentially means that if we assume this f 1 liquid; then we can consider that the since it is at equilibrium with his own vapor for the pure then this can be considered as a pressure or saturation pressure of it ok.

So, this can be replaced by the f 1 vapor in saturation and f 1 vapor of that can be considered as a vapor phase; that means, this can replace by simply P 1 sat. So, in summary what I am assuming is that we as we assume that the vapor in equilibrium with pure liquid one at T is ideal gas and we assume that this is nothing, but 1 ok.

Let it that is no effect of the pressure and then we assume this. So, this allows us to write f L pure 1 as simply P 1 sat ok. Now we have written these two expression, we plug in there what we got is a classic expression.

Y 1; P is equal to x 1; P 1 sat and this is nothing, but Raoult's law which holds within the assumption which we have made. So, which means basically tells you that you can actually make use of the fugacity relations and apply these assumptions and for a specific set of conditions.

So, with this I will stop and we will continue gas mixtures and in general mixtures properties in the next lecture.