Indian Institute of Technology Madras

NPTEL

National Programme on Technology Enhanced Learning

Chemical Engineering Thermodynamics

by

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Lecture 17

Chemical potentials in gas and condensed phases

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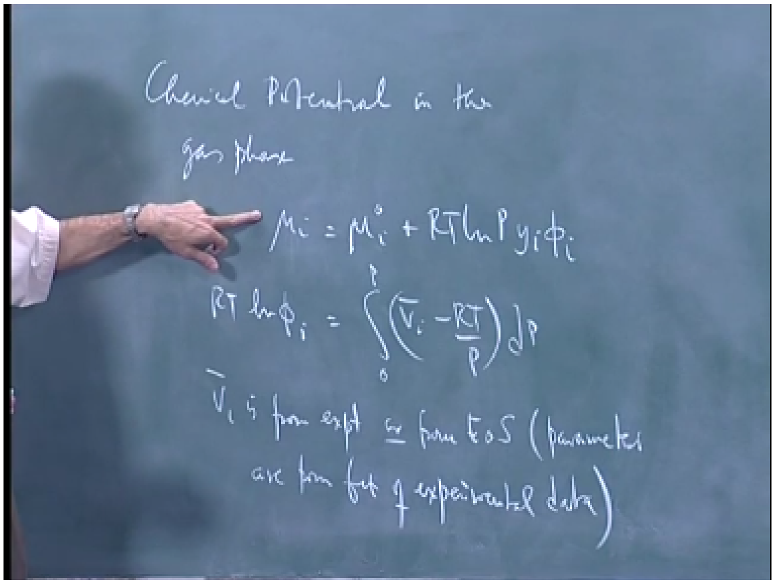

Chemical Potential in the gas phase

$$\mu_i = \mu_i^0 + RT \ln P y_i \phi_i$$

$$RT \ln \phi_i = \int_0^P \left(\bar{V}_i - \frac{RT}{P}\right) dP$$

$\bar{V}_i$ is from expt or from EoS (parameters are from fit of experimental data)

We are going to discuss in the gas phase I do, so you lnϕ suppose I have to write the chemical potential first, so the model for the chemical potential is somewhat unique if you have different kinds of models in the condensed phase but for the gas phase the model have almost always like this where P by convention is an atmospheres because μ_i^0 is the chemical potential at the temperature t and pressure equal to 1, 1 atmosphere because μ_i^0 represents one atmosphere this P also an atmospheres if actually P/1.

So you will get observed answers if you use millimeters in mercury for example, sometimes the data is given in that form then you will get 760 times the answers that you want. So we are doing this calculation $\bar{v}_i$ I told you about equation substrate so $\bar{v}_i$ is from experiment or again it is always from experiment or equation state from in which here again parameters are from experimental data from fit of experimental data.

In the chemical potentials have to satisfy the Gibbs duhem equation, but in this case the chemical potentials satisfy the Gibbs duhem equation if lnϕi satisfies the Gibbs duhem equation. Because μi0 is a constant RTlnP is a constant RTlnyi will satisfy the Gibbs duhem equation anyway right, they have shown that is the ideal mixture so the only other term left is RTlnϕi, if RTlnϕi satisfies the Gibbs duhem equation then you are through, RTlnϕi will satisfies the Gibbs duhem equation if v̄I satisfies the Gibbs duhem equation, the Gibbs duhem equation is basically a linear equation so I can go term by term and I can move through.

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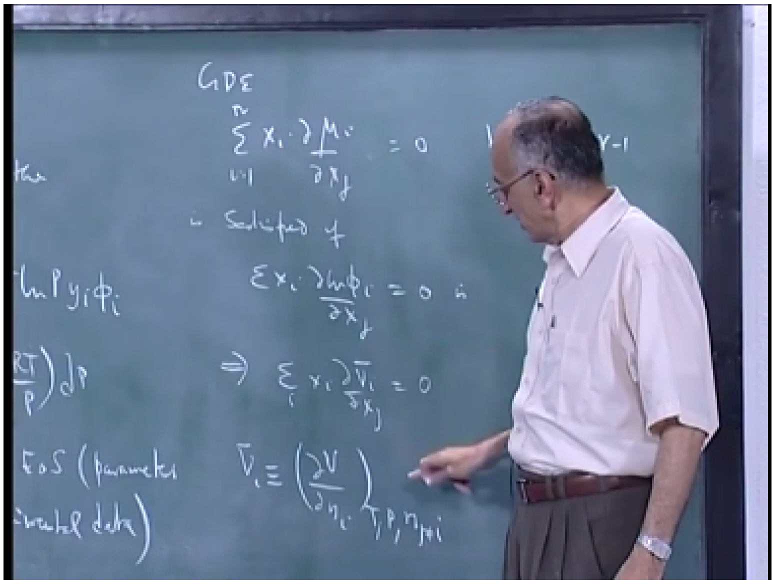

This is the equation is simply ∑xi partial of μi with respect to xj=0 ∑i=1 to r, this is for all j said that there are onlt r-1 independent mole fractions so this is satisfied see DGE is satisfied if ∑xi partial lnϕi is this implies xi partial of v̄i with respect to xj=0 so as far as the gas phase is concerned while the Gibbs dehum equation is central to the determination of composition dependence of the chemical potential we would not worry about it because we talk v̄i from experimental data or from equation substrate when you take it from equation state v̄i again is derived from the expression for v from it is definition, right.

It is v̄i is simply by definition partial with respect to ni of v at constant TP, so the v̄i bars will automatically satisfied to Gibbs dehum equation, you got when the Gibbs dehum equation was first introduced in the universities is it derived by Gibbs very casually this big monograph 1880’s or something took about 1920 before it came into the books 1910 or 1909. So then at that time the experiment researchers are not sure the Gibbs dehum equation satisfies.

So they do experiments extensively calculate this number, calculate the right hand side and see if it actually went to 0, so there are many papers in the early up to 30s or even 40’s that will say hence the Gibbs dehum equation is verified then they got by that time Gibbs said become a icon everybody understood that he was near as near God as you could get in, in thermodynamics as we understand it.

So they said here after the Gibbs dehum equation we assume to be correct and if you collect partial experimental data you can complete the data by using the Gibbs dehum equation which is what is done very often, so the Gibbs dehum equation is assumed to hold but here you could get mistakes with v̄i if your data is wrong, if the Gibbs dehum equation is not satisfied then it is the fault of the data is no longer the fault of Gibbs. The theory is assumed to be more correct than the experiments you do unless you are extraordinarily careful.

So as far as the gas phases concerned we do not use this equation at all, we simply go with v̄i data and calculate this, there are hundreds of ways of doing this calculation you can make life simpler by various means.

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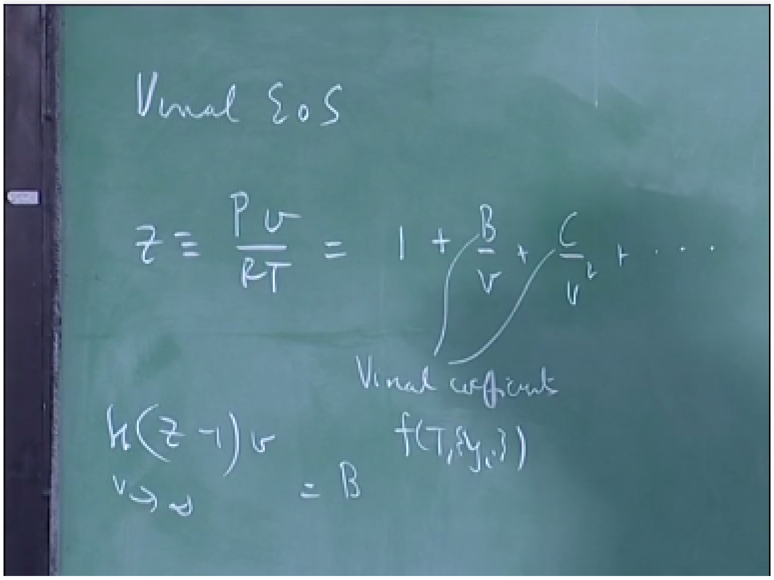

Virial EoS

$$z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \dots$$

Virial coefficient

$f(T, \{y_i\})$

$$\lim_{v \to \infty} (z-1)v = B$$

Let me take for example, first of all let me okay let me take the virial equation state it is just easy to use it most equations of state are not explicit in the volume, it is volume comes out as one of many roots and you have to choose the correct root and then you have to use the differentiation, so it is very difficult equation substrate only relate PvT after calculating v you have to do a differentiation you can do it numerically trivially but you do it in analytically is a better one new sense.

Since I am only looking at the concept it may just a virial equation of state is the following this is also very important Camberley Owner said this he said Pv/RT can be expanded in a density series he know it is 1 for a ideal gas $+B/v+C/v^2$+etc, he said he can write an expansion like this you can show in molecular theory that B corresponds to first of all the first term corresponds no interaction between molecules.

The second term corresponds to pair interactions between molecules two at a time and C corresponds to interactions of three molecules at a time without counting the pair interactions that is the total interactions will be.

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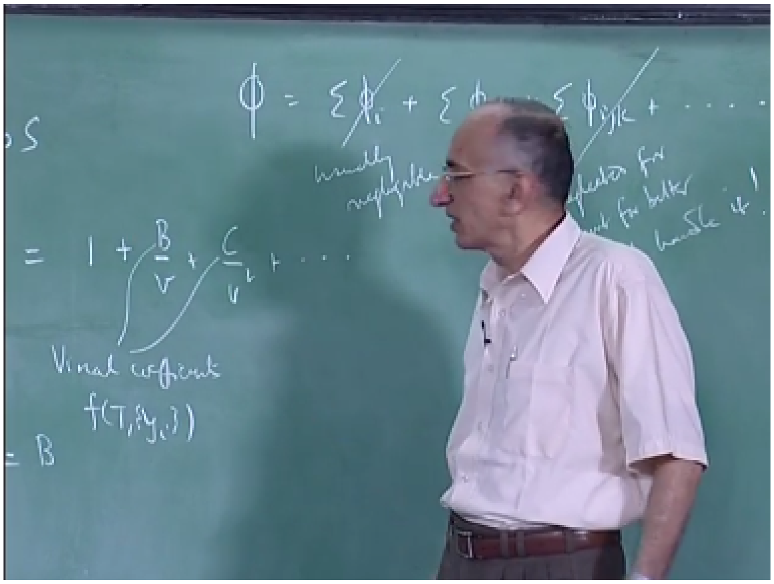

The total potential energy will be ∑ϕi this is the external potential suppose you had gravity and it counted then you have to take that mg, xh into account. So if you had a box of molecules one molecule is at a higher level than the other so will be small differences in potential unit. But this is generally negligible unless you have a system with magnetic materials inside and you apply 500 test law magnetic force, magnetic field from outside then you can have them dancing then you better take this into account, then the molecule on top will have a different to it in properties from the molecule at the bottom.

Next is ϕij pair interaction sum over all pairs ∑ϕijk+etc this ∑ijk the potential includes up to here all the pair interactions then there is a correction due to triple at interactions the effect of the third molecule on the pair interaction, if I 1,2,3, and these are important if you have an electro static forces it stops here which is why electronics and electrical engineering is so easy, it is true that they tassel you with all kinds of effects but they understand that theory very well because electrostatics stops here.

All electrical charge interactions do not have a triple act interaction the third charge does not influence the first two charges except in that there are three now that is if you have 1,2,3 your ϕ12+ϕ23+ϕ31 you have to take all three into account but it stops here. In most of chemical engineering and in chemistry we are make this assumption and you can stop here this is generally negligible so from here on you say neglected for want for better tools to handle it, a slight difference here.

This is negligible at low densities but at higher densities it is not clear that it is negligible and it can make a 10% difference in properties and so on you can go on. Let me come back here that was shown later the Camberley Owner is actually anticipated this result, but he mainly pointed out that each of these terms this these are called virial coefficients and he said these are all only functions of temperature. Well I should say F(T) and composition in a mixture they are not function of pressure or density if you make f(T) I scrubby bracket simply means to set of mole fractions y1, y2 etc.

The argument for that if you take a pure substances for example, if you take the limit as v goes to ∞this simply goes to 1, then you take v into this is z compressibility factor take (z-1) multiply by v and take the limit as v goes to ∞, this will give you B right, I take (z-1)v the rest of them as if at least a v in the denominator so it will all go to 0 so this in the limit as v goes to ∞ since all properties in a pure substances are functions are only two variables we are talking one mole of the substance it can only be a function of T.

You start with everything as a function of T and v and because you are taking the limit as v goes to ∞ the property is defined and the limit as v goes to ∞, because that how it is determined. What you do is plot z-1, z-1 verses 1/v verses density and take the limit as density goes to 0, then you will get B. similarly you can do the same thing next step what you do is take z-1 –B/vxv^2 and take the limit as v goes to ∞ you show that C is a function only a T, so the argument the first simplification here is you have a series of coefficient so functions only have temperature.

Here functions of composition the function of composition again goes back to the same principle, it is thermodynamics will not give you the composition depends you have to guess the composition depends.

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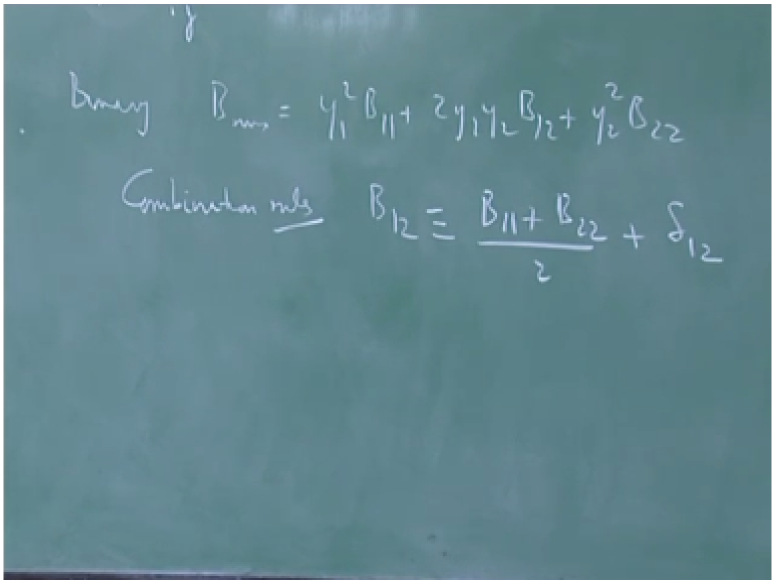

Binary $B_{mix} = y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22}$

Combination rules $B_{12} = \frac{B_{11} + B_{22}}{2} + \delta_{12}$

In this particular case Bmix is exactly this, sum over i and j because you do not want to count it twice you have to write i<j no not i<j sorry, I think this is bad here this is just ∑i and ∑j because this is goes this is the random mixture result but it is exact in the case of the virial equation this can you can only show the exactness in molecular theory simply tells you if you had a random mixture then the probability of finding i molecule if yi the probability of finding at j molecule is yj, the ptobability of finding an ij pair is yi yj.

So for example in a binary you will get, where B11 B22 are pure results from pure substances and 12 is a hypothetical interaction hypothetical's again virial coefficient that arises in a system which has only one two interaction in it you cannot realize it by experiment because when you have one two interactions you will have 11 and 22 with them. Then you have these are the mixing rules this is mixing rule, you have mixing rules these are exact rules you have combinate or rules or combination rules.

Combination rules you will have to tell you what B12 is like, now this could be for hard sphere this is an exact result. But actually the way these values are derived is through another route through what is called corresponding states, so I will come back when I discuss corresponding states I will show you how to do this. In practice what you do is say B12 is equal to this +δ12 this is just a definition and δ12 can be obtained from experimental data by fitting the results. You sort of expect that the 12 interaction will be intermediate between 11 and 22 and then since we are not very imaginative characters we either use arithmetic mean or geometric mean.

For temperatures if you want a Tc you use that geometric mean and for all volumetric properties B is a volumetric property if you use the arithmetic mean there are justifications for it you can show an asymptotic conditions that these rules are exact. But they are not generally true so let me write that out here so you have for a virial equation you have.

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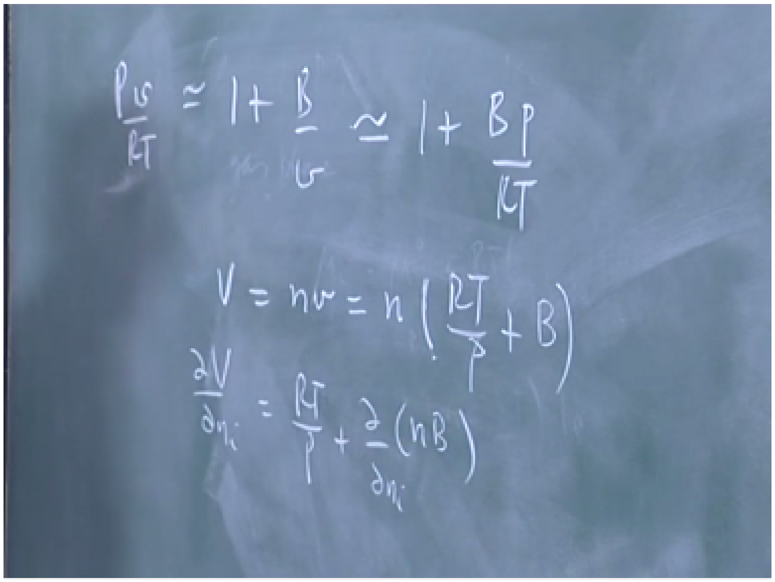

$$\frac{Pv}{RT} \simeq 1 + \frac{B}{v} \simeq 1 + \frac{BP}{RT}$$

$$V = nv = n\left(\frac{RT}{P} + B\right)$$

$$\frac{\partial V}{\partial n_i} = \frac{RT}{P} + \frac{\partial}{\partial n_i}(nB)$$

z=+B/v I thought Pv so let me use this equation and I am going to approximate this even further by 1/B P/RT instead of v I am going to write RT/P this is not a theoretically based equation this is the original virial equation this equation is sometime described as a pressure virial equation, pressure explicit virial equation of state. But I will use that simply because it is right now it simplifies my life in algebra.

So if I now calculate v from here this nv, n is the number of moles n(RT/P+B) so I want δv/δni so if I differentiate this n here this nRT/P I will simply get RT/P+B and then I have to differentiate in what is inside plus or I will write it like as it is, RT/P+ partial with respect to ni okay nB. So nB= because of this rule here we call this equation 1 so like 2.

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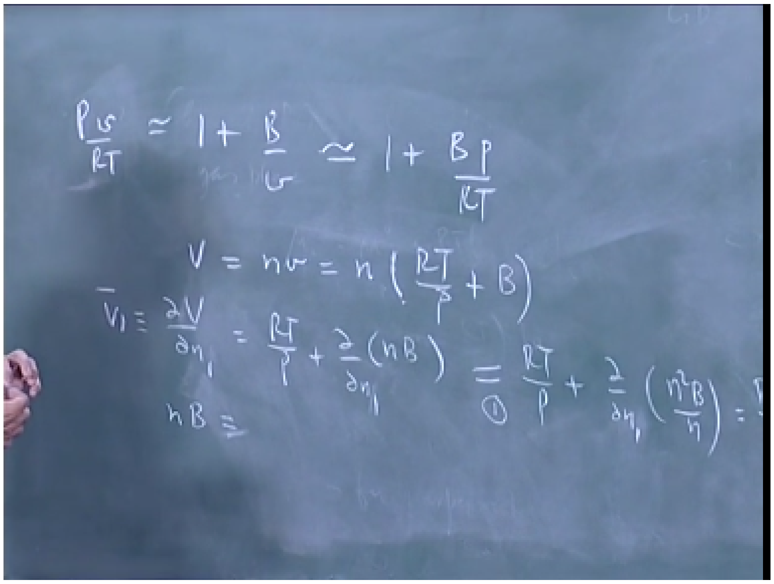

$$\frac{Pv}{RT} \simeq 1 + \frac{B}{v} \simeq 1 + \frac{Bp}{RT}$$

$$V = nv = n\left(\frac{RT}{p} + B\right)$$

$$\bar{v}_1 \equiv \frac{\partial V}{\partial n_1} = \frac{RT}{p} + \frac{\partial}{\partial n_1}(nB) \overset{①}{=} \frac{RT}{p} + \frac{\partial}{\partial n_1}\left(\frac{n^2B}{n}\right) =$$

$$nB \equiv$$

This is you see using equation 1, this is going to be RT/P+ partial with respect to ni I will write this as $n^2B/$, n^2 if I take n^2 inside I will get $(n1^2B11+2n1n2B12)$ this is if I am doing if you do not mind I will change this to 1 I am going to calculate specifically $\bar{v}_1$ instead of i this will be 1.so I get $\bar{v}_1$.

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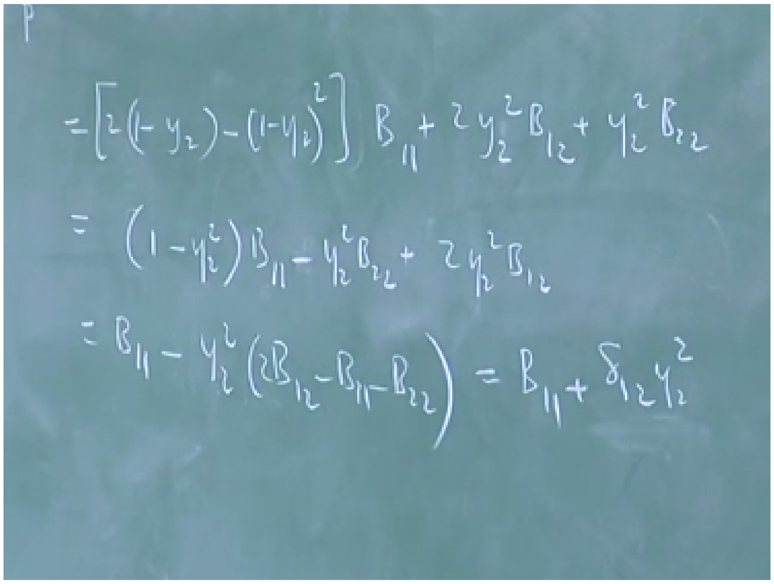

P

$$= \left[2(1-y_2)-(1-y_2)^2\right] B_{11} + 2y_2^2 B_{12} + y_2^2 B_{22}$$

$$= (1-y_2^2) B_{11} - y_2^2 B_{22} + 2y_2^2 B_{12}$$

$$= B_{11} - y_2^2 \left(2B_{12}-B_{11}-B_{22}\right) = B_{11} + \delta_{12} y_2^2$$

What I am interested in this $\bar{v}$1-RT/P I have to differentiate this so if I keep the 1/n and then differentiate this I will get 2n1B11 because there is an n there it is 2y1B11 then next one I keep n2 constant remember, so I will get again 2n1B12 so +B12 then the n2^2 does not contribute then I have to differentiate the n I will get essentially -1/n^2 if I get –n/1^2 I get back Bmix or –Bmix. I will write over Bmix because I am may as well cancel some terms with this Bmix is y1^2 B11+2y1y2B12+y2^{2}B2.

Okay, they should want to simply this a bit what I will do is so I have I will correct terms together 2y1-y1^2 this is 2y1- this is (1-y2)^2 no I think I should I rewrite everything in terms of y2, [2(1-y2) – (1-y2)^2]B11 then I have 2y1B12 – 2y1B12xy2 so it is 2y1^2 -2y1^2+2y1^{2}B12+y2^2 B22 I am going to substitute for this and we write it 2 x what cancels from here 1 will cancel no, okay 2 – 1 is one and I have a 2 y2 here and 2y2 here -2 y2 and +2y2 that will cancel then – y22 this is not 2 2-1 1 – y2 is all you will get B11 +y22 b22 + I will rewrite this keep this as it is in to 2y12 x or y12 x this is b11 + b22 + 2 δ 12 using equation 2.

Δ 12 is b12 – b11 + b22 / 2 when you do not have data you just put δ 1 2 = 0, you always have to develop this engineering practice you have to have a default option you have to have a quantity for which under ignorance under pressure you can either neglect or put equal to one. First I was kept this as y1 itself now let me rewrite this I get b11 I tell you what I am really looking at if this was a pure substance this would have been v1 v1 – rt / p would have been exactly b11 so I am separate out b11 I must separate out the pure and then look at what happens when there is, then I have b11 y12 – y22 this is y1 – y2 x y1 + y2 so y1 – y2 alone I have give on like it anyway I am keep it inside which I say.

Say that again here from here I am differentiating this 2n1 then 2n2 so I made a mistake yeah thanks, so this should be 2y1 b11 + 2y2 b12 right okay and does make a different finally you have to got stuck anyway so thanks for, so 2 x 1- y2 so this is -2 y2 no, what I have write here is correct 1 – y2 2 this is alright 2y2 x 1- y1 this should have been 2y2 right I will keep it as it is right now okay I am simplifying this necessarily.

So this is okay this all I need b11 – thanks for baling me out in to b11 must be a –sin somewhere I am missing a – sin this b22 is a – sin here is ay this is minus of that so here I get – y2 2 x 2b12 – b11 – b22 so essentially this is equal to b11 you know b11 + b22 – 2 b1 2 is δ 12 so this is + δ 12 x y22 that is all. That is really what I was looking at.

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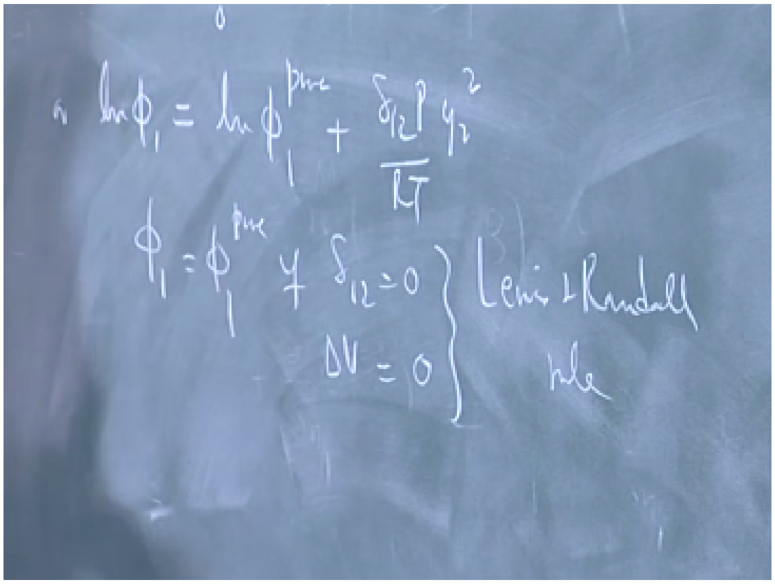

So look at log φ 1, is integral rt log φ 1 is v1 bar – rt / pdp from 0 to p this b11 etc all of them are functions temperature alone, so I can integrate directly with respect to pressure B11 P + δ 12 x y22 I am sorry δ y22 x P this is exactly log φ 1 pure + δ 12 p x y22 or log φ 1, so notice that φ 1 is a same as φ 1 pure if δ 12 = 0 or affectively if δ v = 0 if the volume change on mixing a 0 then v1 bar is a same as small v1 v2 bar same as small v2, this is call the Lesion and Randall rule.

Part of education is learning Jorgen we are suppose to know what is the Lesion Randall rule, lesion Randall rule it simply means that volume change on mixing a 0,which means instead of φ if you want to calculate φ 1 in the mixture you need to know only φ pure, pure component data reeducate the calculation. If you simply given the virial equation and note data on b12 again you do the same option anyway.

So as for as chemical potential of μ 1 it is concern a μ 1 0 this is gas phase + rtln py1 x φ 1 this is a few one this is alright okay, where log φ is simply given this what we do is defining a new quantity because you do not have to carry this μ 1 0 all the time this is a definition f1 is call the fugacity, which is actually why φ 1 was originally introduce thus the fugacity coefficient. Fugacity is corrected pressure in some sense and if you use a same μ 1 0 as a base in the liquid phase then instead of equating chemical potentials you can equate fugacity and fugacity is come out directly in terms of partial pressures and a correction which is calculate which can be calculated from exponential data.

And for which you now had default options we are do not know anything you put replace fugacity by partial pressures.

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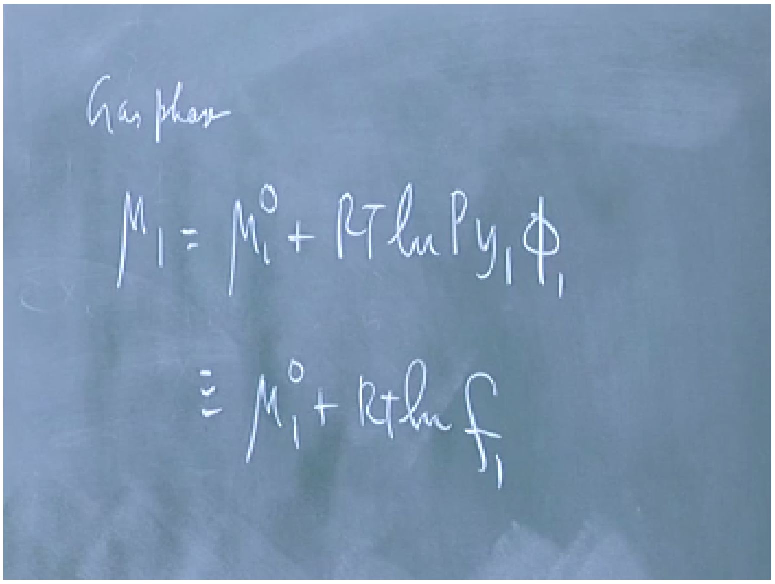

Gas phase

$$\mu_1 = \mu_1^0 + RT \ln P y_1 \phi_1$$

$$\equiv \mu_1^0 + Rt \ln f_1$$

So let me now do the liquid side then we can do vapor liquid equilibrium because all you have to do is calculate the fugacity of a component of a liquid mixture refer to the same μ 1 0 so I am going to look at liquid phase.

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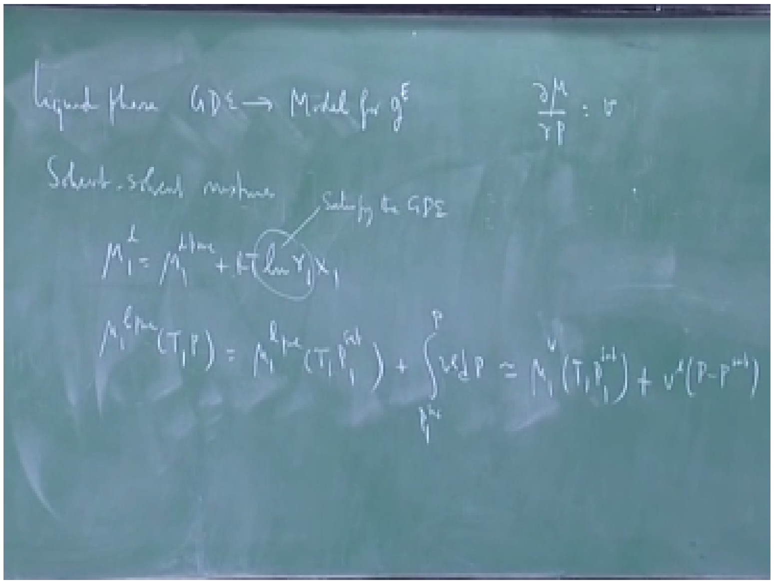

Liquid phase GDE → Model for g^E

$\frac{\partial \mu}{\partial P} : v$

Solvent-solvent mixture

Satisfy the GDE

$$\mu_1^L = \mu_1^{L\,pure} + kT \ln \gamma_1 x_1$$

$$\mu_1^{L\,pure}(T,P) = \mu_1^{L\,pure}(T,P_1^{sat}) + \int_{P^{sat}}^{P} v^L dP \simeq \mu_1^V(T,P_1^{sat}) + v^L(P-P^{sat})$$

The liquid phase you do not have any asymptotic behavior you cannot go to v1 bar v2 bar and calculate the chemical potentials so you have to use the GD equation, and you know it is all the GD equation you have to go to your model, model for GX and the way to modulate in some sense in asymmetric form is using the GX models which we have discuss in class,. So whenever I give you a liquid mixture I will have to tell what the model for the GX automatically.

I am going to look at first liquid solvent- solvent mixture so far these cases you remember when we went to the I draw this afterwards our model is simply μ 1 liquid is = μ 1 liquid pure + rtln γ 1 x1 where log γ 1 satisfies the GD equation that is GX is satisfies to GD or μ 1 satisfy to GD equation μ1 μ2 etc. similarly log γ 1 satisfies to gives you because this is pure rtl and x1 satisfies the GD equation so it is satisfy the but it is satisfying GD equation now simply means assuming a model for GX that goes to 0 at the right limits any model will do.

But what will agree with the experiment will depend open how good your physical intuitions I mean to said that I now write μ 1 liquid pure this is t np you are looking at temperature and pressure the solution this is equal to μ 1 liquid pure t you have to go to as point which you understand the saturation point + you know partial of μ with respect to p is small v this is the regress thermodynamics.

So plus integral vdp from p1 saturation reason you go to p saturation as because at such saturation pressure the liquid is equilibrium with the vapor so I can now go from here again simply replace l / v and if I know go to v then I can go back to this model I have this model for the vapor pressure vapor phase.

And if I go to that model I come back with the same μ 1 0 which I can then cancel,. Incidentally this is v liquid this whole thing is in the liquid region this is approximately constant so wrote this as approximately μ 1liquid now instead liquid I will write it as vapor pure actually I do not have to write pure because if I write t and p saturation it as to be pure as long as I write this saturation pressure here plus v liquid in to p – p saturation.

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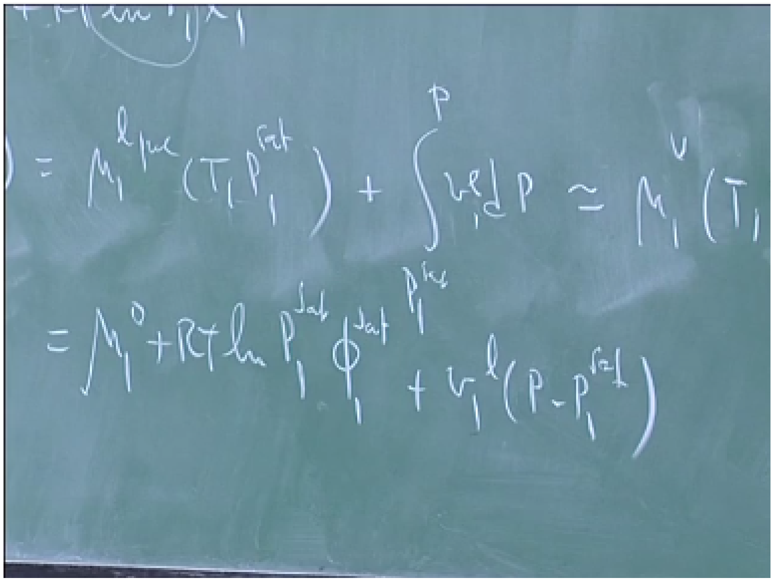

Okay so now I can write μ liquid this quantity I can write in terms of the vapor phase model so I write this as μ 1 0 + rt l and p1 saturation I am not assuming ideal behavior so I have to get for the pure substance will be μ 1 = μ 1 0 + rtln pc1 pure right y1 is one when you get pc1 pure I write ps p1 saturation because that is the pressure it which evaluating it φ1 is φ 1 saturation plus of course this term this is v1 liquid x p – p1 saturation. As soon as you get a μ 10 you can define a rest as μ 1 + rtln f1 this is f1 liquid this is f1 vapor, because you have started with μ 1 liquid = μ1 vapor.

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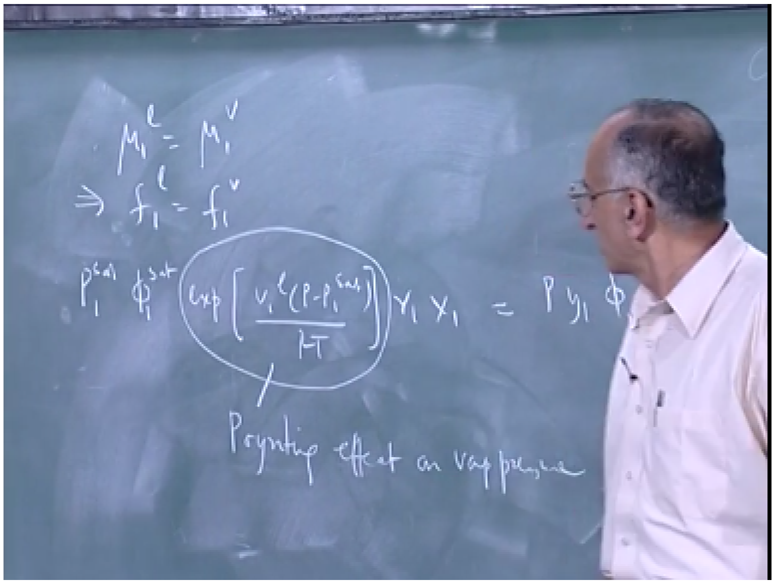

This is a same as f 1 liquid = f1 vapor remember looking at the systematic constant t and p, so μ 1 0 is the function only ft so if this is equal to that μ 1 0 will cancel because the same μ 1 0 the rtln f 1 temperature is the same so ln f1 is the same as same in both phases you have required. So we can now rewrite what exactly f1 liquid is, f1 liquid / this comparison here is p1 φ 1 this side is p1 saturation φ 1 saturation and then there is to if forgot a γ 1 x1 somewhere, this is only this part sorry so μ 1 liquid is equal to all this plus I must write log γ 1 x1 I forgot that or this is μ1 liquid pure so I have to add a log γ 1 x1, it is clear?

I wanted μ 1 liquid μ1 liquid is μ liquid pure plus this μ 1liquid pure is this, so if you like f1 liquid pure is f1 liquid is f1 liquid pure times γ 1 x1, so I have f1 vapor is py1 times p1 and f1q liquid is f1 liquid pure times γ 1 x1 this is valid only for this all event, so all went component only I solvent component I mean that component whose mole fraction can go to unity without change a phase at the same pnp.

So this is your this is equal to py1 times φ 1 put half the time you will use only this equation for vapor liquid equilibrium this is known for a pure substance this is non ideality correction of the pure substance this is effectively an increase in the saturation pressure when the total pressure is greater than this saturation pressure when there are two components the pressure above the liquid at equilibrium need not is not equal to a saturation pressure but it is different from the saturation pressure it is equal to this difference multiplied by v1 liquid / rt will give you the increase in effective increase.

In saturation pressure it was first pointed out to by a guy not punning for punning sake who was called pointing, so it is call pointing effect, it is call the pointing except you had a y pointing effect on vapor pressure he said most people measure vapor pressures at room temperature measuring the boiling point they are actually measuring it at atmosphere a pressure not a saturation pressure because the easiest measurement is at atmosphere equation just boil the liquid deep at our thermometer measure the temperature.

But the pressure is one that is the normal boiling point what you get is actually an increase in the saturation pressure if the e is a second component present for example if water had something dissolved in it, then the actual saturation pressure that you measure would be this saturation pressure times an increase because of what is call the pointing effect.

So you have a pointing effect and then you have a ideal liquid mixture and then a correction for non ideality, on the right hand side you have partial pressure correction for non ideality that is all, so I will stop there that is the basic equation when you just have to hit that equation to depth with of the course there is a so many systems, so many kinds of behavior, so many models for γ one, and so many ways of calculating φ 1.

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