Indian Institute of Technology Madras

NPTEL

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Chemical Engineering Thermodynamics

by

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Lecture 12

The Gibbs Duhem equation

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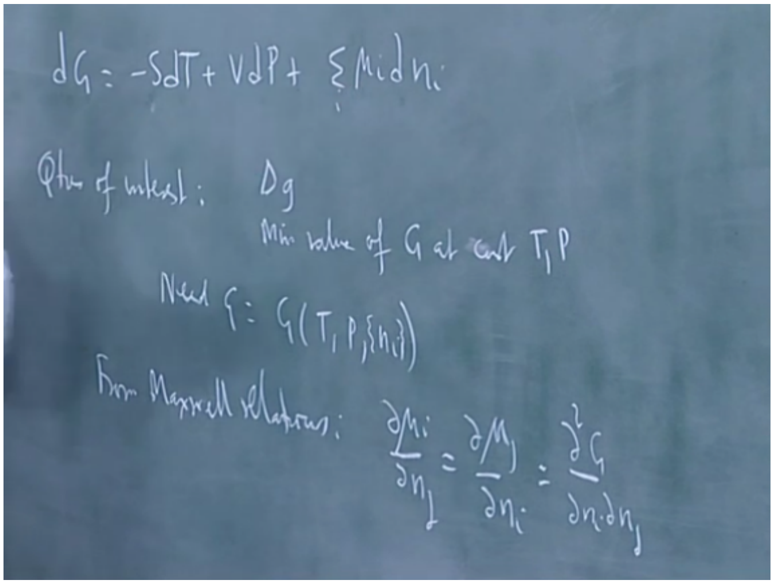

$dG = -SdT + VdP + \sum_i \mu_i dn_i$

Qtys of interest: Δg

Min value of G at cnst T, P

Need $G = G(T, P, \{n_i\})$

From Maxwell relations: $\frac{\partial \mu_i}{\partial n_j} = \frac{\partial \mu_j}{\partial n_i} = \frac{\partial^2 G}{\partial n_i \partial n_j}$

The fundamental equations of thermodynamics I just start with fG equation nod you can do similar treatment with other so we seen quantities of interest are essentially ΔG correspondingly ΔA, ΔU, ΔH and so on. And minimum value of say G at constant T and P so these are the two quantities even in the order to do this we need G this is your work calculation this is your equilibrium calculation you need G as a function of temperature pressure and composition.

This could be brackets indicate NI from I equals 1 to the number of components usually you get these relationships through Maxwell relations that is you find out how it depends on T how it depends on various quantities through the Maxwell relations so you have a $\partial G/\partial T$ is this is –s $\partial g/\partial P$ is V $\partial G/\partial I$ is μ_i but therefore what you need really these quantities you know for example S with if you want to know how S varies again you go back to Maxwell's relation.

You got S with respect to P and so on, so all that you can do the only thing you cannot get from here S from Maxwell relations if I keep all the variables constant except say N1 and N2 I get the equations like this or I and J $\partial\mu_i$ with respect to ∂nj both rae equal to of course $\partial^2G/\partial n_i\ \partial n_j$ normally if you want S with respect n_i for example what you do is to keep $S\partial t$ and μ_i n_i the n_i alone all the others you will keep constant.

Then your Maxwell relation will give you the second partial of G with respect to T and n_i is S with respect n_i that is equal to you will get the derivative of μ_i.

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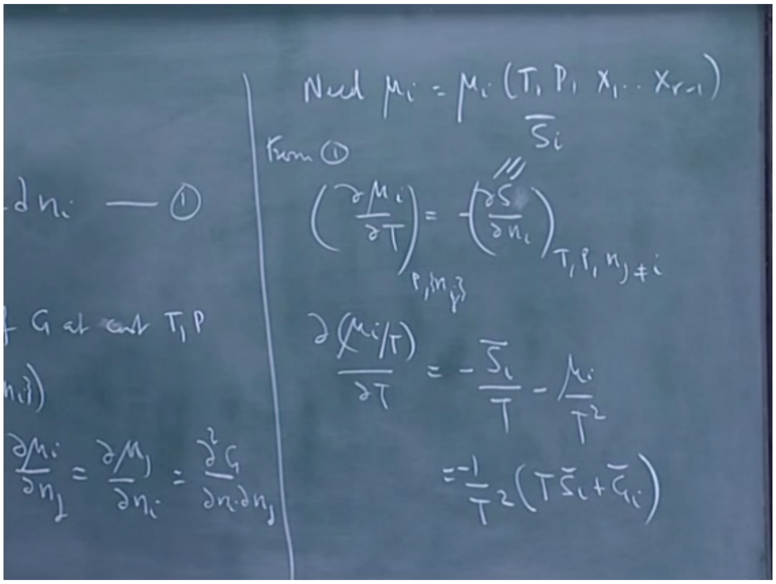

$d n_i$ — ①

G at cnst T, P

$n_i\})$

$$\frac{\partial\mu_i}{\partial n_j} = \frac{\partial\mu_j}{\partial n_i} = \frac{\partial^2 G}{\partial n_i \partial n_j}$$

Need $\mu_i = \mu_i(T, P, x_1 \ldots x_{r-1})$

$\bar{S}_i$

From ①

$$\left(\frac{\partial\mu_i}{\partial T}\right)_{P,\{n_j\}} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

$$\frac{\partial(\mu_i/T)}{\partial T} = -\frac{\bar{S}_i}{T} - \frac{\mu_i}{T^2}$$

$$= \frac{-1}{T^2}(T\bar{S}_i + \bar{G}_i)$$

Let me do this first of all let me say this is been reduce to and equation in the chemical potential so will say need μ_i as a function of T, P X $_{r-1}$ some from 1 I get partial of μ_i with respect to T is the same as partial of – of partial of S_i with respect to n_i S with respect to n_i this is μ_i with respect to T holding P and all n_j constant.

This is better way of getting this is not a measurable quantity I told you to stop whenever the right hand side is a measurable quantity so if you differentiate μ_i/T with respect to T you get this quantity this is the same as Si bar usual all partial quantities are claimed by differentiating and extensive variable with respect to n_i holding T and P constant that is important other mole numbers but T and P are important variables.

So if you do this you get $-S_i$ bar of course by T differentiating μ_i I get $-S_i$ bar $-\mu_i/T^2$ this is the same as $1/T^2$, $-1/T^2 * T$ S_i bar+Gi bar μ_i is same as G_i bar because G we saw that last class G with respect to n_i holding T, P and other mole numbers constant is taken as J bar and this is $-H_i$ bar/T^2 so I have one equation that says μ_i/T.

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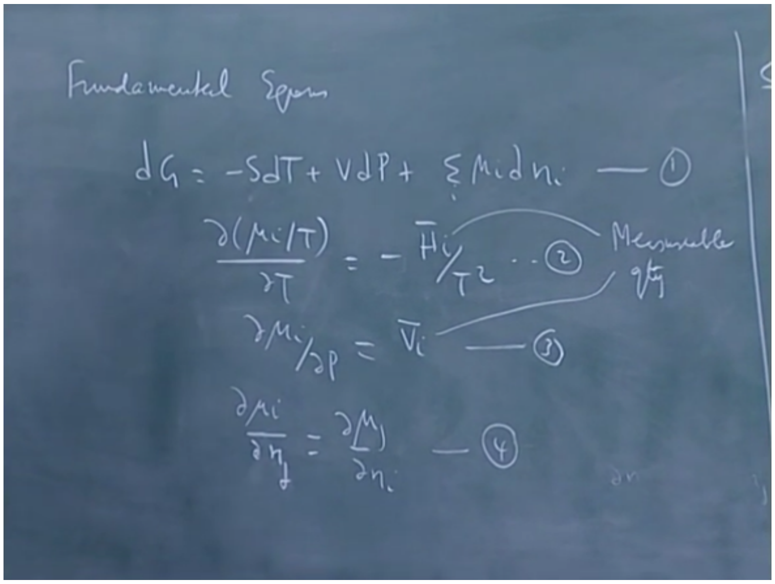

Fundamental Eqns

$$dG = -SdT + VdP + \sum_i \mu_i dn_i \quad — ①$$

$$\frac{\partial(\mu_i/T)}{\partial T} = -\bar{H}_i/T^2 \cdots ②$$

$$\partial\mu_i/\partial P = \bar{V}_i \quad — ③$$

$$\frac{\partial\mu_i}{\partial n_j} = \frac{\partial\mu_j}{\partial n_i} \quad — ④$$

Measurable qty

H_i bar is simply the partial molar property with respect to enthalpy changes in enthalpy are measurable so will show that this is a measurable quantity so this is the equation 2 I will show how it is exactly measured little later will simply note that this is our measurable quantity you can get a lot of data on H_i bar so since a I am interested in this equation here the chemical potential as a function of T, P, H.

Because my chemical equilibrium is governed in phase equilibrium by $\mu_i\alpha$ is going to be $\mu_i\beta$ if I have μ_i as a function of temperature pressure and composition I can solve the phase equilibrium problem and principle so I have got this I need to know μ_i as a function of P this is very straight forward here μ_i with respect to P will be the second partial of G with respect to n_i and then with respect to P.

That will give you the first partial of V with respect to n_i this is V_i bar this is equation 3 and this is also a measurable quantity volume changes, enthalpy changes are measurable and from these changes I can actually calculate Hi bar and Vi bar now when it comes to composition dependence if I take two of these the third equation is the hardest μ_i with respect to X_j or n_j sorry I should finally differentiate with respect to X_j but right now I will do it.

As it stands here I take μ_i ,n_i and μ_j and d_{nj} all others I hold constant I simply get μ_j with respect to n_i all it says this the chemical potential of the component I, it depends on the number of moles of j exactly like the chemical potential of j depends on number of moles of I but since I do not know either I am left in square 1 this is actually the basic problem of mixed thermodynamics or challenges essentially you do not know the chemical composition dependence if the chemical potential uniquely.

And there probably no unique solution because different mixtures behave differently the question is how do we describe this composition dependents in some meaningful form how do we modulate you have a of course be derived last class you know we integrated this in different obtained the Gibbs Duhem equation.

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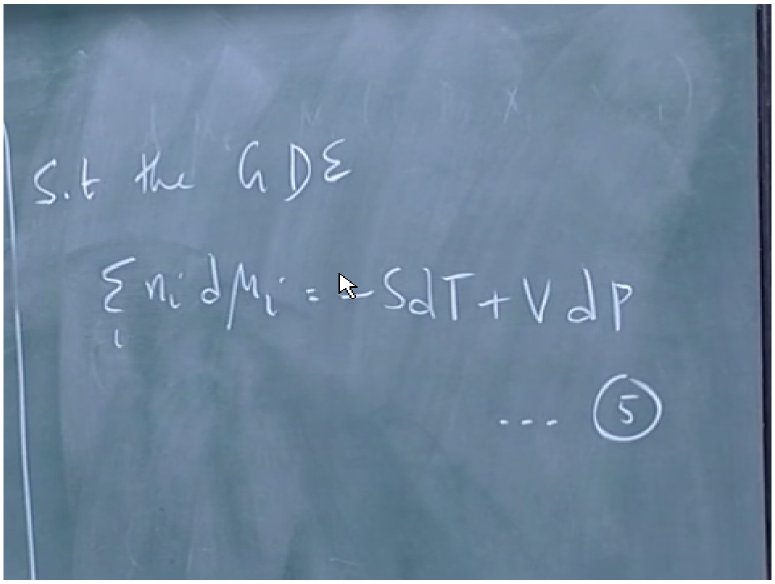

S.t the GDE

$$\sum_i n_i \, d\mu_i = -SdT + VdP \quad \ldots \text{⑤}$$

Subject to I will say 0=we got this ni some over i, ni d μ_i subject to Gibbs Duhem equation so these five equations are the fundamental bases of all mixture thermodynamics although you can play the same dm with A U or H you can play the equivalent game of all those equations this is simplest question explicitly here.

And for chemical engineers T and P are the most natural variables so what I have to do out of all this I should derive see first of all let me say this having by writing this equation down I am saying all the chemical potential together the changes in the chemical potential are constraint by one equation and then I have this equation if between my claim has between these equations I have a essentially one independent chemical potential which I cannot whose composition dependents I cannot described.

If I fix that I can solve for all the others so I will show the explicitly what I wanted to do is that derives set of partial different equations for the chemical that will give you a method of solving for the chemical potential all chemical potential, all chemical potential except 1 and 1 will be completely arbitrary and then you actually call on some ideas in which you say you cannot model μ_1 why did you chose 1 why did you choose component 2 why did you choose component 3.

So this question will arise so we will find the common property which is the free energy change of mixing ∂G of mixing what we will do this take the pure components form the mixture and though experiment and ask what is the change in free energy and if I show the model that change I get all the chemical potential so that is what I am going to do in the next probably half an hour of it or 45 minutes.

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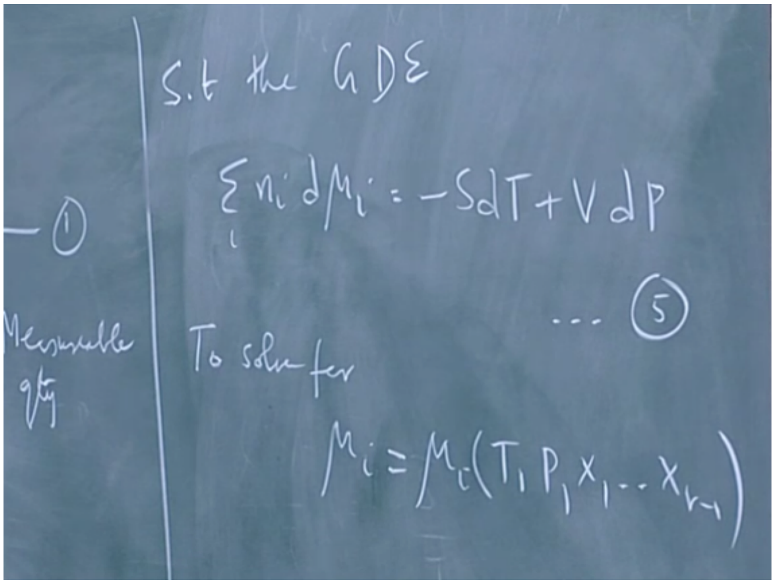

S.t the GDE

$$\sum_i n_i d\mu_i = -SdT + VdP \quad \ldots ⑤$$

To solve for

$$\mu_i = \mu_i(T, P, x_1 \ldots x_{r-1})$$

Let me start here all I wanted to do is I want to simplify this equation to simplify this equation the aim is to get I will say to solve for μi because it is intensive variable we can be only be function of T,P X_{12} X_{r-1} the only r-1 independent composition variables so I should be able to solve for the chemical function of these in fact if I give you that the rest of the thermodynamics is trivial.

This because you do not know this that you have to make so many extensive measurements in thermodynamics and go through complicated to predict phase equilibrium and reaction equilibrium so to do this what I do is to go back here and substitute for $d\mu_i$ if μ_i is this $d\mu_i$ is going to be partial of μ_i with respect to T dt+partial of μ_i with respect to P dp=some over ik μ_i with respect to X_k $d_{xk.}$

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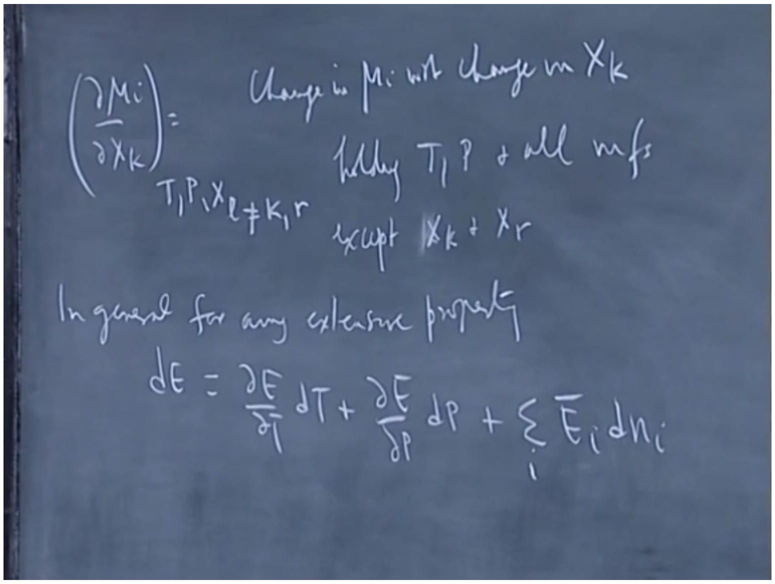

$$\left(\frac{\partial \mu_i}{\partial x_k}\right)_{T,P,x_{l\neq k,r}} =$$ Change in μ_i with change in X_k holding T, P & all mfs except X_k & X_r

In general for any extensive property

$$dE = \frac{\partial E}{\partial T} dT + \frac{\partial E}{\partial P} dP + \sum_i \bar{E}_i dn_i$$

Where I have written dμ_i with respect to Xk this is actually the partial in this equation its T, P held constant +XL any arbitrary composition which is not equal to say I am differentiating here μ_i with respect to Xk x1 through Xr-1 Xk cannot be held constant but since more fractions cannot independent I also have one more to vary which is Xr I have written as Xr-1 so here L should not be equal to k or r.

That is this change in μ_i with respect to change in Xk more reflection of K holding T,P and all mole fractions except XK and Xr, I will not write this explicitly it sort of understood in the context all the time come back again and again all just put this back in here remember that this is μ_i with respect to T at constant P and all the mole fractions that means it is same as what we got here or μ_i this can be written as right now I will not bothered whether it is Si bar or this is the original equation or this.

Again write it neither form this equation I will use μ_i with respect to T is holding all the mold numbers constants and P constant it is equivalent to that and the mixture except you are talking about one mole or the mixture so this term is the same as –Si it is still –Si bar dT+Vi bar Dp this is also0 the same+ this as it is and you have to recall I am write this in general in general this is what we showed in general for nay extensive property dE you can dE=partial of V respect to tdt+ partial of V with respect to P d+ some over Ei bar dni.

This going to be large amount manipulation but the final form of the equation is so nice it makes the whole process worth well this is really this is what philosophers called an anthropocentric point of view you stuck with the notions of equality even if not realized in real life you stuck with your ideal notion of the equality impartiality and so on.

So I cannot model 1 chemical potential μ_1 so you will be try a model a common property of the mixture and then derive values for μ_1, μ_{12}, μ_3 etc. so it sort of stuck with that mole may be it is easier to model μ_1 and be done with it each mixture you can choose one component for which you can guess it is physical behavior and do it.

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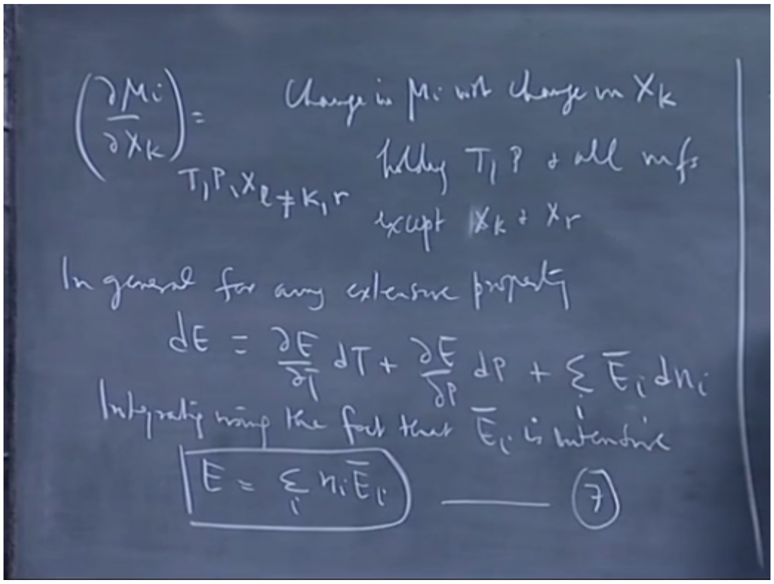

$\left(\frac{\partial \mu_i}{\partial x_k}\right)_{T,P,x_{l \neq k,r}} =$ Change in μ_i with change in x_k holding T, P & all mfs except x_k & x_r

In general for any extensive property

$$dE = \frac{\partial E}{\partial T} dT + \frac{\partial E}{\partial P} dP + \sum_i \bar{E}_i dn_i$$

Integrating using the fact that $\bar{E}_i$ is intensive

$$\boxed{E = \sum_i n_i \bar{E}_i} \quad \text{———} \quad ⑦$$

There will be general theory used this principles all the time so I have this equation you know by integrating what you will get integrating assume this is at constant T and P you will integrate exact we did it before E_i bar is an intensive variable so using the assumption or the hypothesis not actually using the fact that E_i bar is intensive I told you the big difference is between intensive and extensive properties.

If it is intensive property if I change only the mole numbers but keep the composition this same E_i bar will not change I will get E is equal to some over ni, E_i bar and then by differentiating this or this is the important one you get the Gibbs Duhem equation for every property E_i bar for differentiating this and comparing with this in particular the most useful Gibbs Duhem equation is this equation here.

The five as a particular case of that result and this is what we use repeatedly and therefore this is generally this is referred to as Gibbs Duhem equation but we have hold series and Gibbs Duhem equations but this result is important whenever I get n_i times V_i E_i bar I simply get E back so if you look at this result if I substitute this d μ_i here if I put Si bar here I get n_i, s_i bar some over n_i s_i bar as S.

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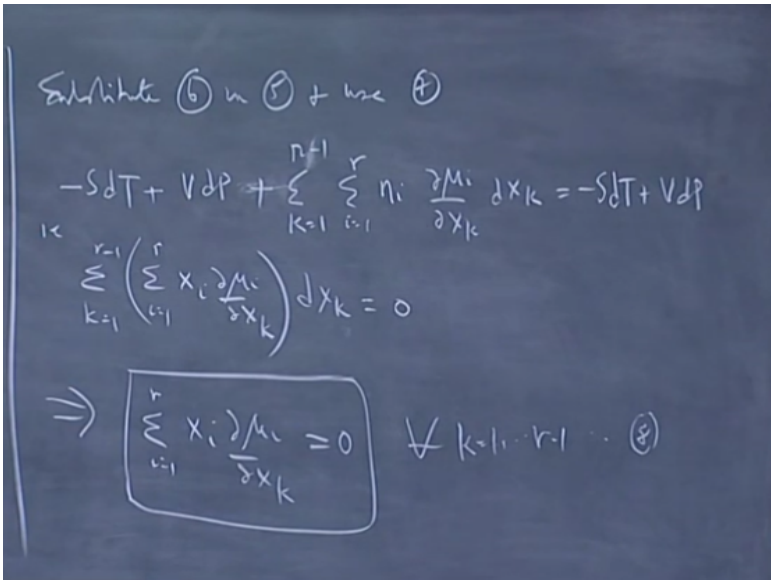

Substitute ⑥ in ⑤ + use ⑦

$$-SdT + VdP + \sum_{k=1}^{r-1}\sum_{i=1}^{r} n_i \frac{\partial \mu_i}{\partial x_k} dx_k = -SdT + VdP$$

$$\sum_{k=1}^{r-1}\left(\sum_{i=1}^{r} x_i \frac{\partial \mu_i}{\partial x_k}\right) dx_k = 0$$

$$\Rightarrow \boxed{\sum_{i=1}^{r} x_i \frac{\partial \mu_i}{\partial x_k} = 0} \quad \forall\, k=1, \dots r-1 \quad ⑧$$

The E_i bar if I put it here n_i e_i bar is V so I will get back sdt and vdb that cancels the right hand side so what I have left is this here so let me write it out so will substitute this is 6 this equation is 6 substitute 6 in 5 some over the left hand side becomes –sdt and use let us use this will call this 7 you get –sdt+vdb+ the last term there which is some over k or incidentally this some over k is not over all mole fraction r is not included.

Because the variables are X12 or Xr-1 so you must write here K normally this is denoted by prime on the ∑ that means one mole fraction does not come in ∑ usually the last mole fraction by convention so I will put some here prime or I will write explicitly K= 1 to r-1 and then I have this ∑ anyway ∑ over i=1 to r of ni times ∂μi/∂xk bxk this is equal to –sdt +vdb.

The right hand side I am copying as it is the left hand side if I substitute this I get –sdb if I substitute this and some I get -+vdb in the last term using the double ∑ so the results simply says some over k equals 1 to r-1 some over i=1 to r I will pull the total number of moles xi ei that is if I divide this by total number of moles I will get Xi.

But first argument here as bxk are independent thermodynamics demands that this should be 0 the left hand side should be 0 the left hand side should be 0 under all conditions since dxk are arbitrary I can change these mole fractions because this goes only r-1 this one I can change nay of the mole fractions exactly as I substitute still be 0.

Therefore this implies that some over i=1 to r of Xi partial of μi with respect to Xk=0 and you pulling out the k so for all k, for all k=1 to r-1 you know derive the theory it has to be proof against all power so on if you give me any I will choose the mixture where I change the moles fraction of only one component and then if you told me this was not 0 for that component.

Then you will get the contradiction here essentially you will get the contradiction of two laws because you can traced back all the way and go back to laws from mixture derived this so this is the Gibbs Duhem equation now it looks so little nicer it looks as a fall became potential circuit equally but even this is not good enough notice that Gibbs Duhem equation now explicitly appear as r-1 equations.

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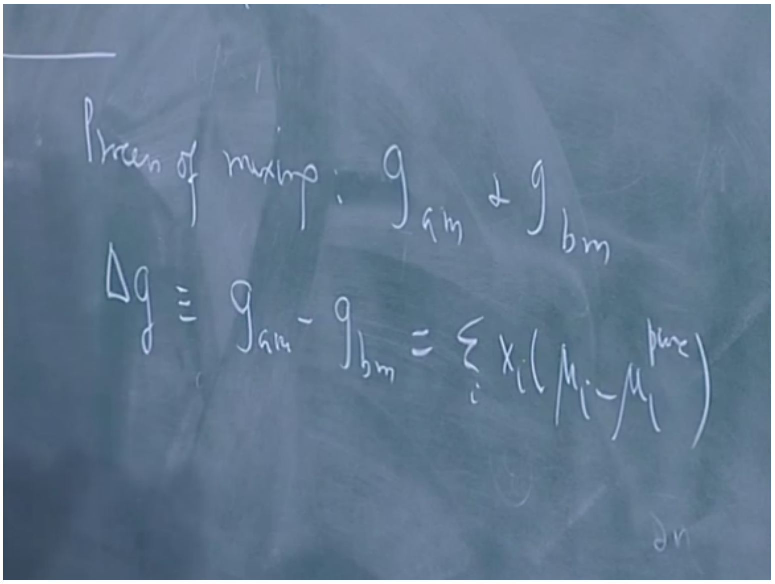

For every k you can write that equation so it is set of r-1 equations it is not obvious from the original Gibbs Duhem equation right this is actually a set of r-1 equations for r unknown μ_1,μ_2,μ_r for r unknowns namely μ_1, μ_2 etc μ_r and r-1 equations, you have equation 8 for k=1 to r-1 it has be a valid for every k so you have one degree of freedom is no way you can uniquely solve that set of equations.

If you assume one of the chemical potentials then you have -1 equation for r-1 and again I am assuming given as set of equations you have solutions to it but having said this I want to set this as straightly different quantity let me go back and look at the process have mixing all this thermal because of the process mixing so if I examine that this process I can show you that this one way of getting of the thing.

From a combination of the chemicals potentials that does not specify anyone chemical potential uniquely if I look t the processes of mixing I look at G after mixing and G before mixing like ad and bc after mixing and before mixing so G I m looking at ∂G for this processes ∂G is actually g after mixing and this is the definition g before mixing I cannot measure ∂g but I can measure ∂H of mixing ∂v of mixing.

The change in enthalpy change in volume those are measurable quantities but let me derived this here in expression for this, this difference is simply some over i xi μi-μi if you look at G before mixing all the components are pure components I take X1 moles are X2 moles etc. so I have Xi, μi pure I submit up I get the free energy before mixing but because μi is a partial property after mixing it is simply Xi μi.

You can write this for any extensive property you will have to write Ei bar and small ei similarly this is Gi bar- μi nut Gi bar bas a normal curvature but now we call it as μi symbol okay so let me write dg again now let me will do this sorry let me write d of ∂Δg partial of ∂Δg with respect to say X1 let me do this for a binary and then we will do this for more complicated it is very straight forward but if I do it for binary it will be easier.

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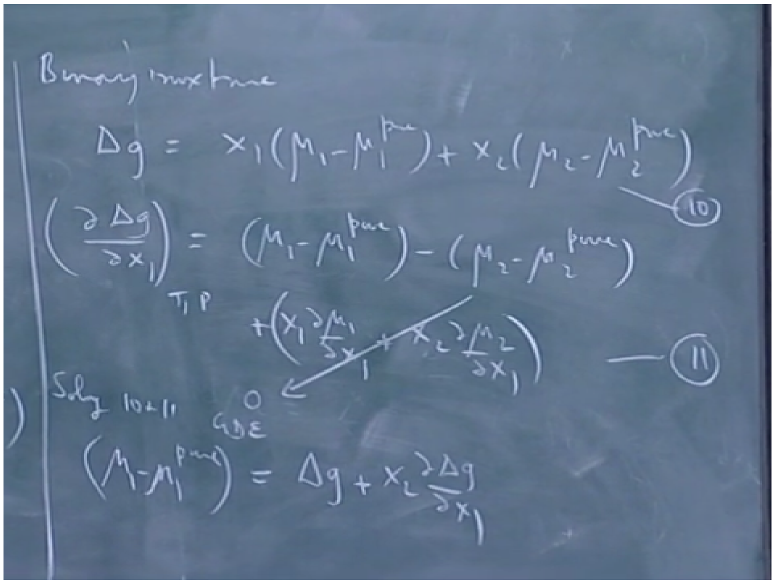

Binary mixture

$$\Delta g = x_1(\mu_1-\mu_1^{pure}) + x_2(\mu_2-\mu_2^{pure}) \quad (10)$$

$$\left(\frac{\partial \Delta g}{\partial x_1}\right)_{T,P} = (\mu_1-\mu_1^{pure}) - (\mu_2-\mu_2^{pure}) + \underbrace{\cancel{\left(x_1\frac{\partial \mu_1}{\partial x_1} + x_2\frac{\partial \mu_2}{\partial x_1}\right)}}_{0 \ \text{GDE}} \quad (11)$$

Solg 10 & 11

$$(\mu_1-\mu_1^{pure}) = \Delta g + x_2\frac{\partial \Delta g}{\partial x_1}$$

Let me first do this for a binary I will show you the results and then will go on to the mixtures let us take the binary mixture so Δg is simply X1 µ1-µ1 pure+x2*µ2-µ2 pure and I want to ask what is partial of Δg with respect to X1this is done at constant T and P in case of binary mixture I can hold only T and P constant as allow X1 to vary so I cannot hold X2 constant for differentiate this if I differentiate this I get µ1-µ1 pure so I get – sign.

Then I have to differentiate what is inside X1 this is a function of composition this is not so I will get Δµ1/Δx1+x2 Δµ2/Δx1now notice that this term this identically 0 according to Gibbs Duhem equation, like Gibbs Duhem equation there tells you for binary in case of binary k can be only one so you get X1 partial of µ1 with respect to X1+µ2 with respect to X1 the denominator variables is the same.

In the Gibbs Duhem equation so you will get X1, Xk the same as denominator numerator will run through all the indices because this is 0 I can now look at these two and solve for one of these for exampleµ1-µ1 pure if I want to solve from µ1-µ 1 pure al I do is multiply this equation by X2 and add give these numbers again we call this 9 this is 10 and this is 11 so µ1-µ 1 pure I will simply say solving 10 and 11 this is simply equal to Δg+x2*Δ partial of Δg with respect to X1.

If I switch this indices 1 and 2, I will get the equation for 2 so what this tells you is that I can get the chemical potentials 1 and 2 from ΔG itself we can do this in a mixture the multi component mixture clearly because you will get those r-1 equations and this one you simply solve for this differences µ1-µ2 and so on.

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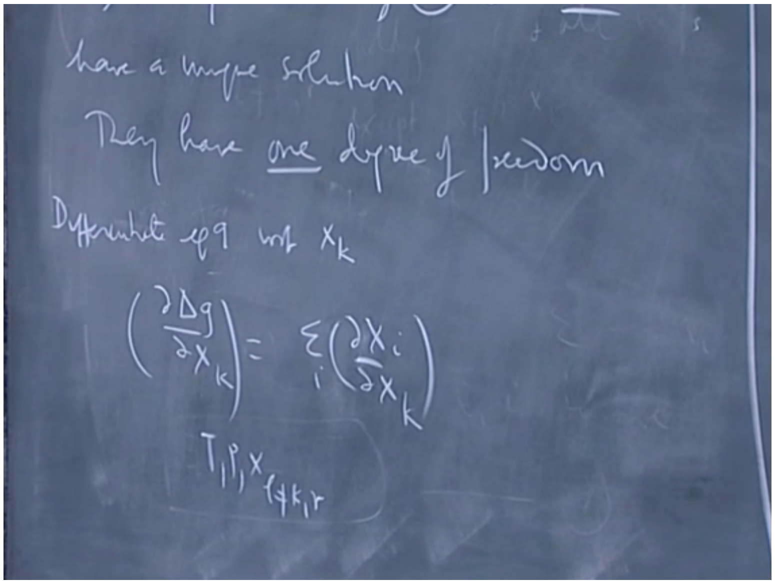

have a unique solution

They have one degree of freedom

Differentiate eq 9 wrt X_k

$$\left(\frac{\partial \Delta g}{\partial X_k}\right)_{T,P,X_{l\neq k,r}} = \sum_i \left(\frac{\partial X_i}{\partial X_k}\right)$$

But essentially now solving the Gibbs Duhem equations you cannot solve manipulate the we simply say the Gibbs Duhem equations represented by 8th do not have a unique solution they have one degree of freedom regardless the number of components if I do this in the general case let me just write this down now I take equation 9, differentiate the equation 9 with respect to whenever you make these differentiations you choose index other than domain x here.

So with respect to Xk then you will get partial of Δg with respect to Xk is equal to some over I xi know Δxi with respect to Δxk the hold doing this holding T,P Xr is not a variable in the problem the differentiating with respect Xk so we have to allow Xk to change so Xk Xr are not hold constant all others are held constantly.

You doing this differentiation here Xi with respect to Xk, holding again Xl not equal to k and R times μi-μi pure+ some over Xi partial of μi with respect to Xk because μi pure is not a function of composition at differentiate this term first and then I differentiate this term I will differentiate that term I get luckily the exact thing that I have in the left hand side of the Gibbs Duhem equation so this term is 0.

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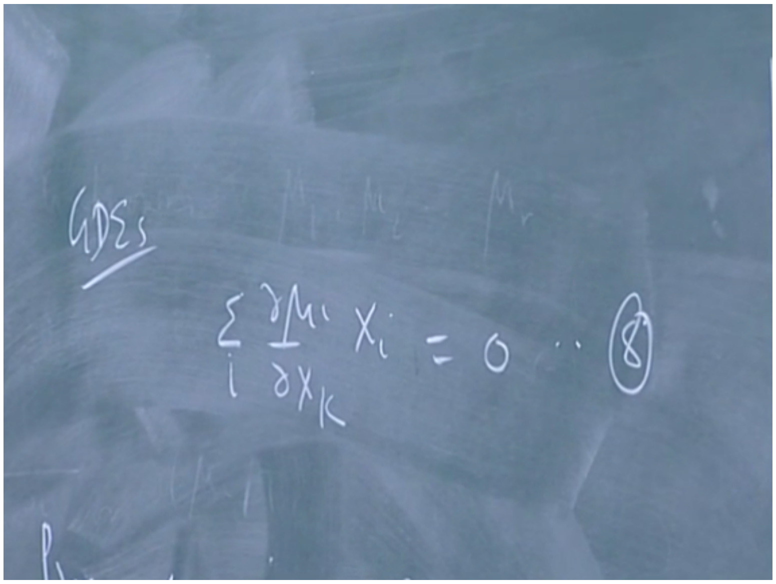

$$\sum_i \frac{\partial \mu_i}{\partial x_k} x_i = 0 \quad ⑧$$

So I will copy this here and I can erase that also okay now xi with respect to xk because all others are held constant when Xi is equal to I is equal to k you get 1 when I is equal to r this ∑ is over all components and I is equal to r you will get R Xr is 1-x1, x2, xk etc. so you will get -1 that is only difference so partial of Δg with respect to Xk as only two terms one is μi-μi pure sorry μk-μk pure.

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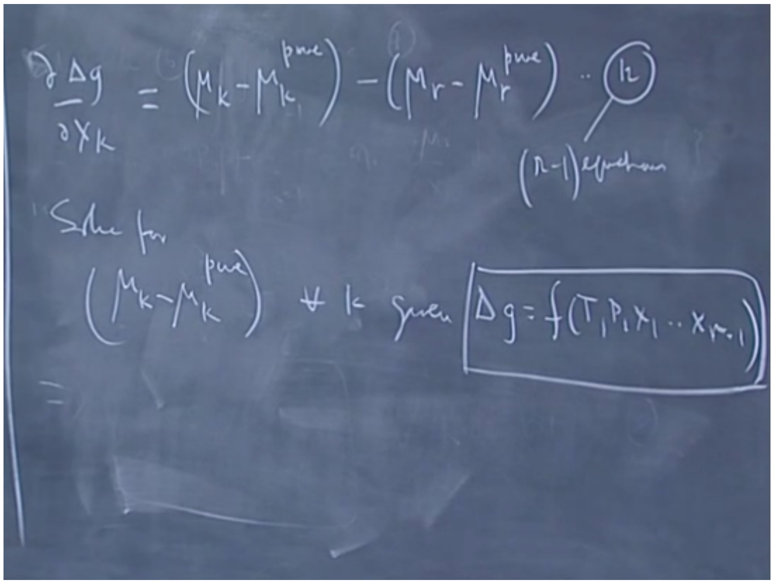

$$\frac{\partial \Delta g}{\partial x_k} = (\mu_k - \mu_k^{pure}) - (\mu_r - \mu_r^{pure}) \quad \cdots ⑫$$

$(r-1)$ equations

Solve for

$$(\mu_k - \mu_k^{pure}) \ \forall k \text{ given } \boxed{\Delta g = f(T, P, x_1 \cdots x_{r-1})}$$

When i=k you will get a contribution and then when i=r you get a – contribution μr-μr pure is called the equation 12 so if you look at equation 9 and equation 12 this is actually a set of equations this is r-1 equations because you have to write one set equations for each value of k other than r so k=1k equal to r-1 so you have r-1 equations and I have one additional equations that I have introduced here.

So I have r equations for r unknowns so you can solve for say μk-μk pure I simply say μk for μk I simply say μk for k given Δg as a function of T P X1 through Xr-1 I have to give you this function if I tell you what Δg is as a function of the composition if I give this as function of composition then by solving these equations simultaneously I can get everyone of the chemical potentials.

What do I want to mix tells you is that this not unique so when you say modeling and thermodynamics it invariably boils down to guessing a function F and you can guess any function f you can produce your own functions everyone have you can model thermodynamics except the use a model and less the result you derived from the model agree with the experimental data.

For a large class systems now point having a model for each individual systems that means you are only measuring data are to describing it but if you have the many classes of systems that you can describe that one function I can have model for Δg which describes all ideal mixtures that all colonel polar and non polar mixtures and so on.

So if you can find the models for a class of system then you have essentially the thermo dynamics is to guess a Δg, the Δg should have some boundary conditions you cannot get a Δg function that is non-zero when you have only pure substances that is when I do not have a mixing processes it should go to 0.

So when all the moles fractions goes to 0 except 1 which is 1 then Δg should be 0 so the some boundary conditions you have to for example for a binary mixture you right Δg as X1 X2 times of function arbitrary function like function cannot be infinite it has to be a bounded function that is all if you write X1and X2 infinite automatically when X1 goes to 1 or X2 goes to 1 that goes to 0 you are safe.

So they use some games and then you can say you can use theorem and say what I can whatever it is I can approximated by polynomial so I will rewrite the polynomial so I will write the polynomial and you can write the whole series of models like that because that is called the whole models the polynomial expansion so you can get this several initially people derived models of different ways.

The most interesting model though was the very first on which is quite exciting so given is derived by 1 hour, it is one of the most beautiful papers in mixture thermodynamics after that people discovered that you could write arbitrary functions from real analysis they say after all what can this function be polynomial and so on.

So the difference forms of this and what I will do is go through I start with 1 that incidentally there are two this whole all these theories the thing that I would derived and the Δg expression at which you get all physical theory of solutions this come under theories of liquid mixtures because they assume you know the components in any given mixture in 1890’s there was another guy called Doss laic.

In this guy said actually you guy are all mistaken first of all I will show you the concept of theorem of ideal mixture you can show what is the simplest solution to Gibbs Duhem equation and that is called the ideal mixture he said all mixtures of ideal you behave non and you observed non ideal behavior because you are fool and you are looking at wrong components actually in mixture of 1 and 2 the real substances say A and B the real substances may be A 22 B1 or it may be and A 12 B is 13 you do not know there may be associated that way.

And if you look that the right components all mixtures are idea and if it is look at this mixture of A 22 B and A 12 B 13, it is ideal mixture but if it look at the mixture the A and B as some foolish this is from Doss laic but let me first look at I think this is the simplest thing that I should start with ideal solutions.

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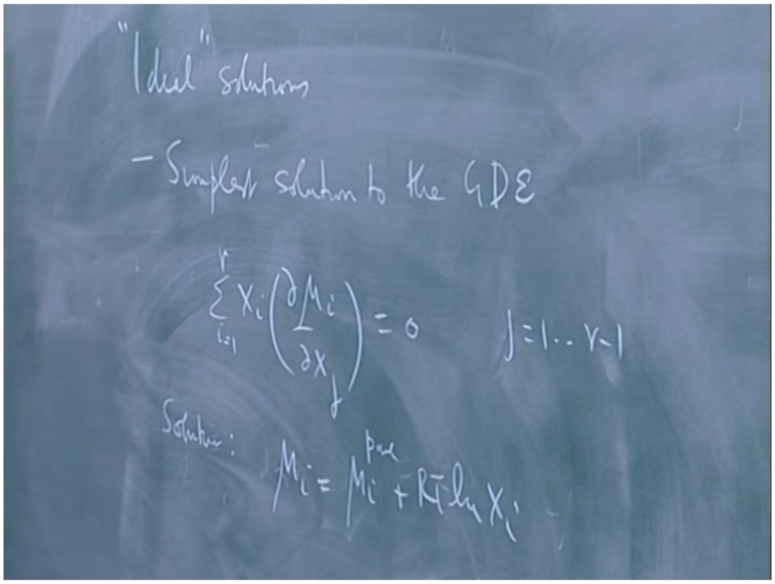

"Ideal" solutions

- Simplest solution to the GDE

$$\sum_{i=1}^{r} x_i \left(\frac{\partial \mu_i}{\partial x_j}\right) = 0 \qquad j = 1 .. r-1$$

Solution: $\mu_i = \mu_i^{pure} + RT \ln x_i$

The word ideal is used in this context as the simplest solution to Gibbs Duhem equation this is done by inspection I have this Gibbs Duhem equation this is some over 1 to r j is 1 to r-1 this is Gibbs Duhem equation simplest solution I will write down the solution I will assume that μi dependents only on the composition you can treated it has pure gas or you can go back and apply everything to ideal gas mixture and derived those results.

But as far as I am concern the Gibbs Duhem equation always have one degree of freedom and I can make a guess this just to treat this as intelligent guess and ten we look at thermodynamics consequences I will show you that this corresponds in fact to an exact notion of an ideal mixture the ideal mixture is one and which it consists of molecules that do not have interactions between them.

So there should be no energy change when you mix inside and I will show you that this result agrees with that and I will also derive the result for the mixing which will be the same as what you get I will show you and we will come back here just substitute this as here if you substitute this as here and you going to differentiate with this respect J holding all moles numbers all mole fractions constant except J and K right J and R.

Because this one the differentiations is J=1 to r-1 we substituting this as here you get Xi log Xi with respect to Xj the only two variables that can change are i=j and i=r so you essentially get and substitute this here into what was the equation this equation is 8 substitute it as 8 Xj partial of log Xj with respect to Xj+Xr partial of log Xr with respect to Xj.

On the left hand side all others are held constant this equal to this is 1/Xj and which is 1/Xr*-1 because Xr is 1-x1-x2 etc of Xj if 1-1is identically 0 al I am saying is I have got it here that satisfies that equation you can actually guess this solutions to this equations by Hooker I do not care how you get the solution as long as you have a solution it is valid thermodynamic model for as valid thermodynamics model for chemical potentials.

From this you then derive the results in phase equilibrium you derive the results the reaction equilibrium and if does not agree with any experiment model the test of model is simply agreement of experiment finally otherwise it is as an thermodynamics concerned supremely in different anything that satisfies this set of equations is a valid model.

And in fact you may be able find for every model you write you may be in powers enough to write all kinds of complicated models involving in terms of fucntions but you will find one system that satisfies that one we can always find this system but that is not meaning but what you have to do eventually is to give some physical meaning to the model your parameters in a model you have to related to something.

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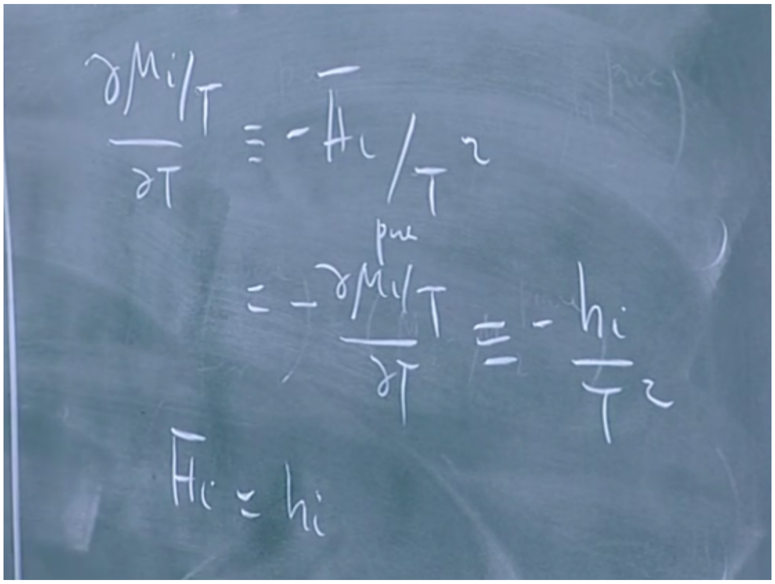

So this equation this is called the idea mixture let me show you the consequences of this µi/t with respect to T let me show you the consequences of this may have µi/t with respect to T is equal to H_i bar/t^2 this is thermo dynamics take this model if we differentiate µi/t I mean if you differentiate first divide by t and then differentiate you get µi/t on this side it is µi/t right.

From the model if I gets µi pure/t and then if I next term is 0 because if I divide by t and ten differentiate r log Xi with respect to T is 0 because I am differentiating with respect to T holding T and all mole fraction constant but this is again from the thermodynamics this is thermodynamics here H_i/T^2 small Hi is specific enthalpy of pure i, so it says Hi bar is equal to hi that means there is no enthalpy change for each equations it means Δh=0 because Δh mixing is H after mixing –H before mixing H after mixing is Xi Hi bar some and before mixing it Hi Xi times small hi this you know is the ideal behavior.

This is what you understand ideal behavior no interaction energies if there were interaction energies or equal interaction energies between all repairs right this out between all pairs of molecules this happens for example homologous series you mix methane and lithene really no inter molecules force difference between a molecules of lithene the molecule of methane.

So such mixtures often have ΔH=0 no energy changes occurring so the word ideal therefore ideologically it is acceptable it describes exactly what do you think of in a mixture of substances that had no inter molecules forces stop that for few seconds what I do is I continue next class sand complete ideal mixture then what I do is to introduce instead of chemical potential you write $\mu i=\mu i$ pure $+Rtl$ and γXi and activity coefficient.

The reason we engineers need an activity because it has a default option will always be system about which is ignorant so in your computer program you must be able to say if I tell you nothing $\gamma a=1$ where as for chemical potentials I did not have default option but here in the you have to say at the worst case I can guess $\gamma a=1$ or if you do an interactive calculation you will start with $\gamma a=1$ so in that sense it is better to use a variable that occurs that tells you the departure from the ideality than use a variable that is known.

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