Indian Institute of Technology Madras

NPTEL

National Programme on Technology Enhanced Learning

Chemical Engineering Thermodynamics

by

Prof. M.S. Ananth
Department of Chemical Engineering, IIT Madras

Lecture 15

Gaseous and Liquid Mixtures

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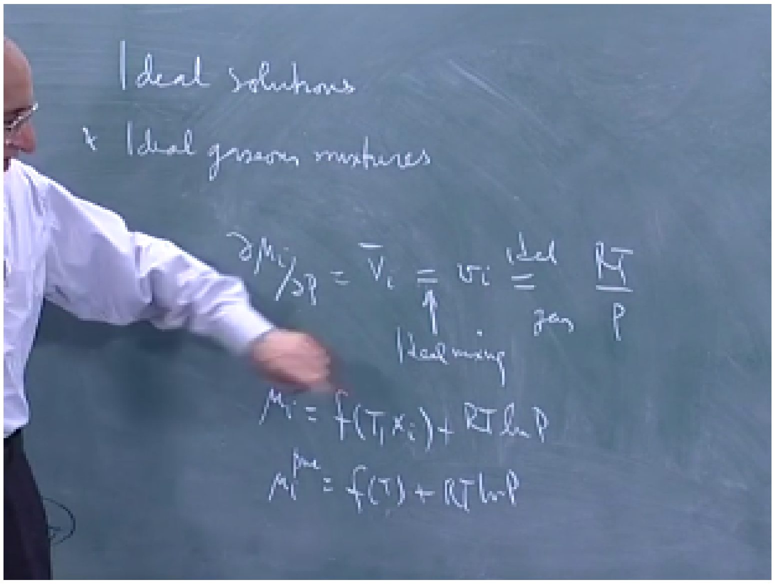

Okay we get started in order to discuss ideal solutions actually one topic I left out is equations of state discuss that couple of classes put on the line because we have gone on to liquid mixtures and also discuss ideal gageous mixtures and do equations of state later okay in the case of ideal gas gaseous mixtures is one redeeming features that helps you solve the Gibbs Duhem equation using experimental data.

The way this happen is you have ∂ μi/ ∂P = Vi bar is an exact expression in the case of ideal mixtures ideal gaseous mixtures first of all for ideal this is ideal mixing if the process of mixing is ideal there is no volume change on mixing because ideally molecules do not occupy volume so there is change in volume and ideally molecules do not interact with one other so there is enthalpy change.

So these are the 2 basic definitions of ideal mixing, if that is true this is then if it is an ideal gas that is with the pressure is sufficiently low Vi is simply RT/ P so you get μi = if you integrate this is done at constant pressure and composition and temperature in composition and temperature in composition so you will get some function of temperature and composition + RT/ lnP.

In particular you have μi pure is some function of temperature + RTlnP to find this function of composition you separate out Mi and RTlnP you have F(T) and Xi you know you have to solve the Gibbs Duhem equation now let us but down the I will come back to this in a minute.

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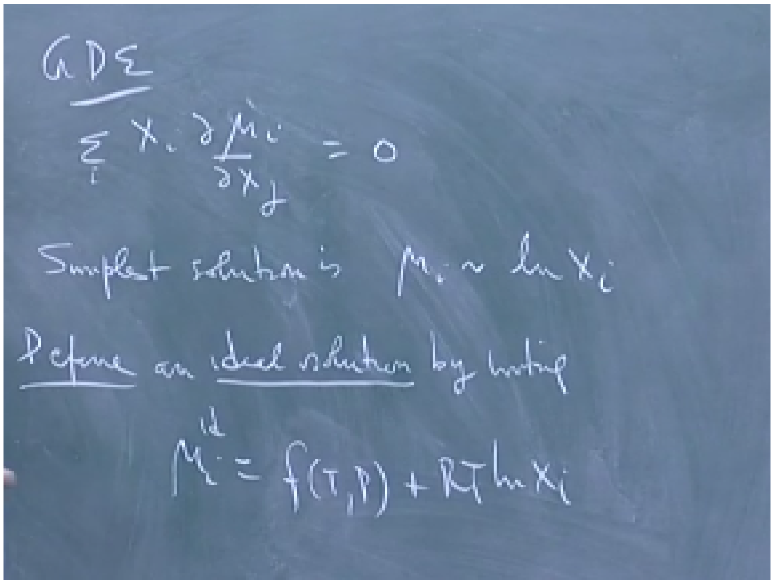

GDE

$$\sum_i X_i \frac{\partial \mu_i}{\partial X_j} = 0$$

Simplest solution is $\mu_i \sim \ln X_i$

Define an ideal solution by writing

$$\mu_i^{id} = f(T,P) + RT\ln X_i$$

But let me put down the Gibbs Duhem equation we have already seen this is simply Xi ∂ μi with respect to Xj I said the simplest solution is μi varying has log Xi right varying has because one left side is energy per the mole the right hand side is dimensionless so you have do some corrections, so I can defined this thing an ideal solution I will show you they I can also come from another root from the gaseous behavior and come to the same conclusion.

First of all define an ideal solution by writing μi ideal = μi if you okay I will just write or I will write this has function of T in fact tell me get this function of T, P this is the definition of solution now clearly as Xi goes to 1 f should go μi.

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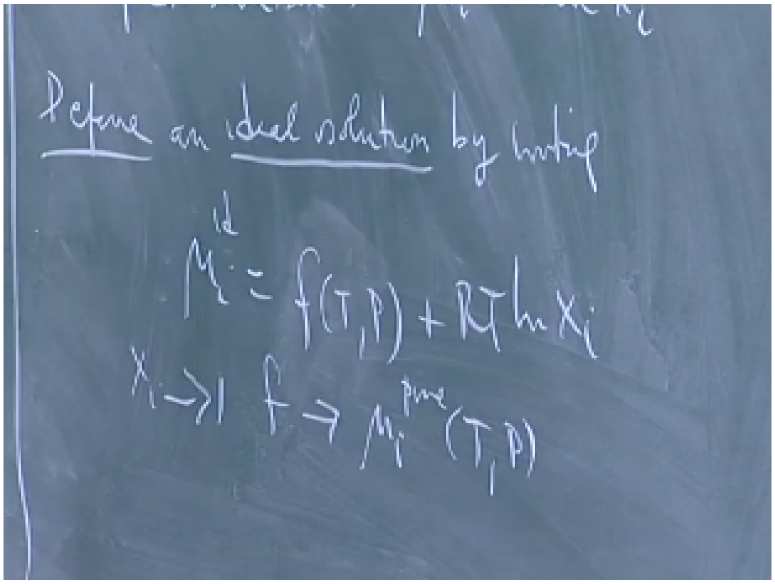

Define an ideal solution by writing

$$\mu_i^{id} = f(T,P) + RT \ln X_i$$

$$X_i \to 1 \quad f \to \mu_i^{pure}(T,P)$$

This ideal refers only to the mixture I mean only to this mixing process so in the limit has Xi goes to one you do not having mixing left hand side will become μi pure so f(T) as to be = μi pure wherever the value of the chemical potential at that temperature and pressure is.

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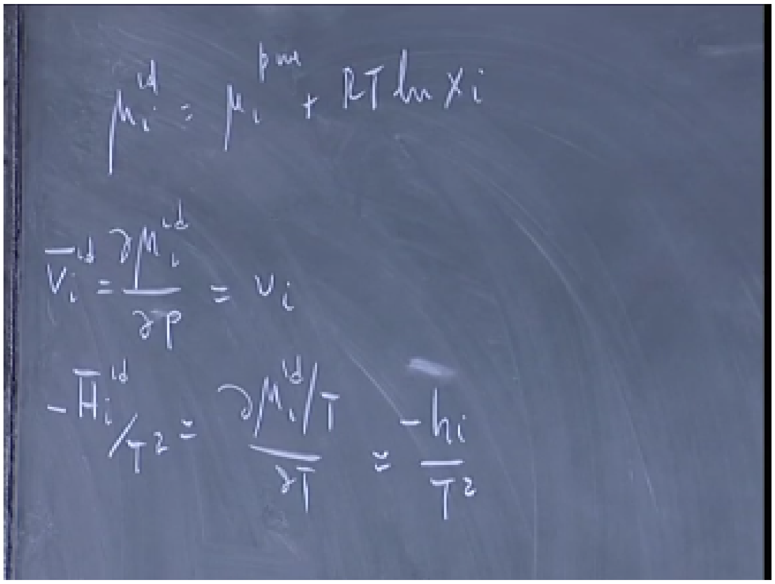

$$\mu_i^{id} = \mu_i^{pure} + RT \ln x_i$$

$$\bar{V}_i^{id} = \frac{\partial \mu_i^{id}}{\partial P} = v_i$$

$$-\bar{H}_i^{id}/T^2 = \frac{\partial \mu_i^{id}/T}{\partial T} = \frac{-h_i}{T^2}$$

So I have μi ideal this will give all the results that you need to define an ideal solution because μi ideal by P this side is simply Vi bar ideal on the right hand side I simply get Vi then Hi bar ideal by T^2 or – of this is ∂ μi ideal of T with respect to T this is regress thermodynamics but if I do the right side this comes from the right hand side on the right hand side.

If I divide by T and differentiate with respect to T ay constant pressure and composition is simply get ∂μi pure with respect to T μi pure by T with respect to T which is Hi sorry – hi/ T^2 so you get hi bar is equal to hi Vi bar = Vi which is a dentition of ideal mixing. Ideal mixing says mixing without change in volume and without change in energy enthalpy I can go further because of this if I have an ideal gas Then I μi – this + RTlnP.

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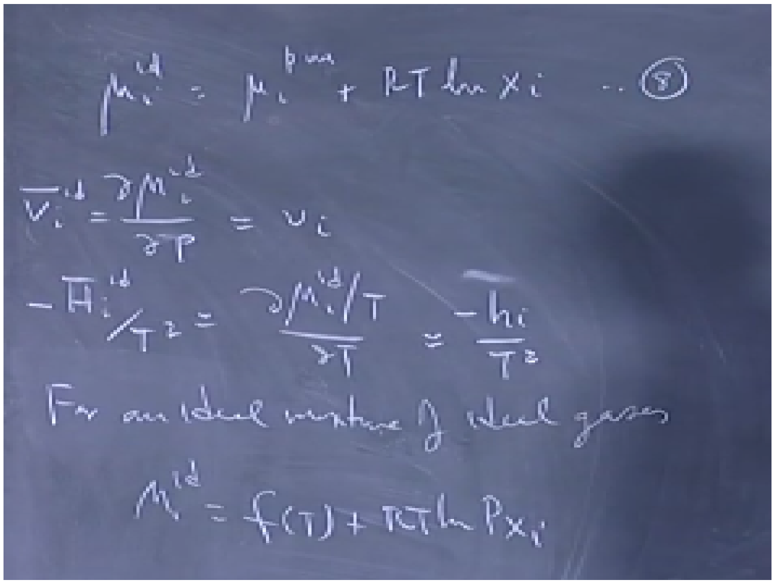

$$\mu_i^{id} = \mu_i^{pure} + RT\ln x_i \quad ..⑧$$

$$\overline{V}_i^{id} = \frac{\partial \mu_i^{id}}{\partial P} = v_i$$

$$-\overline{H}_i^{id}/T^2 = \frac{\partial \mu_i^{id}/T}{\partial T} = \frac{-h_i}{T^2}$$

For an ideal mixture of ideal gases

$$\mu^{id} = f(T) + RT\ln P x_i$$

I am sorry for a pure substance again this let me put this in here so if I have μi ideal for an ideal gas mixture for a mixture of ideal gases I have to write two lines there 2 words there for an ideal mixture of ideal gases the ideal mixing process in can be in the liquid phase can be in the gas phase but I am taking this special case of ideal mixture of ideal gases for μi pure for an ideal gas I got this result.

All of this is for this is for ideal gas right because I have substituted ideal gas here ideal mix of ideal gases so I get μi ideal = some function of T + RTlnP$_X$i you could have to give an interpretation for f(T) simply to say what it represents when Xi goes to 1 and P goes to 1 this term goes to 0 when Xi goes to 1 you get pure substance pure i so pure i at P = 1 is sufficiently low pressure we usually measure P in bars.

So if you use those units then when P is = 1 bar you get f(T) is simply μi the chemical potential of pure i at the temperature of the mixture at pressure = unit T.

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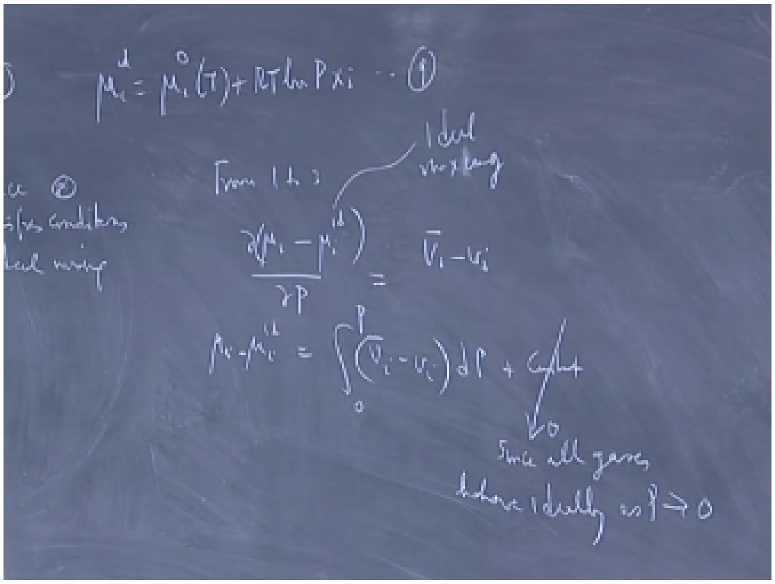

So we write this has μi = μi this is μi ideal μi0 (T) + RTlnPxi. Also from this equation I will be give these equations numbers this is 1 and Vi bar = Vi is for ideal mixing this is for ideal gas this is 3 so this is will be 4 this will be 5 this of course 1 number every day 6, 7 then 8, this simply proves that this is hence 8 satisfies conditions of ideal mixing are simply ∂V mix = 0 ∂h mix = 0 then finally this here 8 let us say this is 9 first of all from equations 1 to 3i have ∂ μi actual – μi ideal / ∂P this when I write ideal here it only means only ideal mixing from μi okay where I have detailed mixing of ideal gas from μi okay where I have detailed mixing of ideal gases I write it explicitly.

But normally when I write μi ideal I only mean ideal mixing that is the gases need not be individually ideal but I am assuming the process of mixing is ideal this controller happen at very high pressures between say ethane, methane mixtures similar substance will mix without change in volume without change in so if I take this difference this is Vi bar first one if I take differentiae this I get Vi now μi – μi ideal therefore = I am ∫ from 0 to P of Vi bar – Vi dP + some constant.

Now I can determine the constant very simply in the case of gas phase because in the limit has P goes to 0 all gases behave ideally therefore this μi also becomes a mixing of ideal gases therefore I have μi – μ ideal is 0 at P = 0.So the constant is this is because this is 0 I will write here since all gases behave ideally as P goes to 0.

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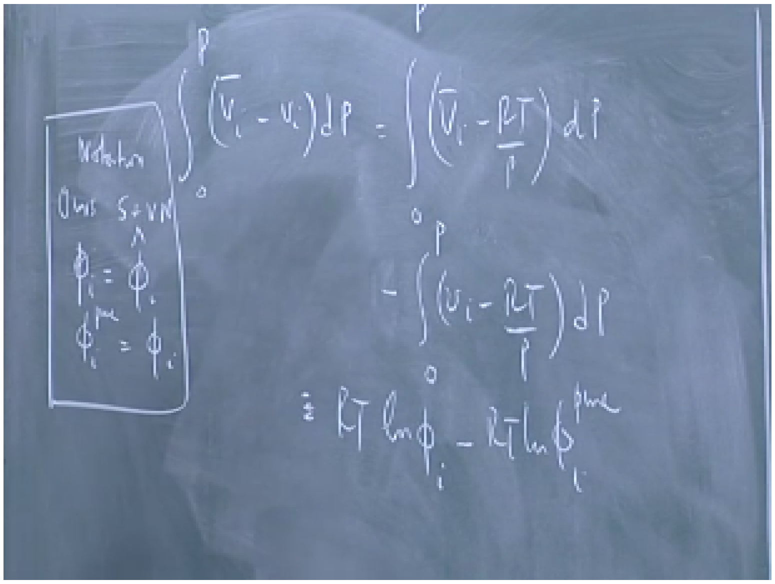

I have this ∫ 0 to P of Vi bar – Vi dP I write this as ∫0 to P or – I am adding and subtracting RT / P inside the ∫ and splitting the integral into two parts this is defined as this is 3 lines is just a definition write this as RTln (ϕi) – RTln(ϕi pure) when Vi bar is replaced by small vi this becomes the specific volume of the pure substance so I recognize this by writing ϕi pure indecently smith and van ness is a slightly different notion for ϕi here writes ϕi^ for this he writes ϕi so when he writes ϕi he is talking about pure fugacity.

The mixture value fugacity coefficients this is called fugacity coefficient I will come back to it in a minute ϕi is called ϕi^ is the value ion the mixture m2 used to this notion to change if I change ½ with ∂ will make a mistake again, I will stick to this notion, so ϕi for us is ϕi^ our notion smith and van ness our notion is ϕi pure and this is ϕi similar µi ^ in smith and van ness is chemical potential in the mixture and µi is the chemical potential of pure.

The reason we give these symbols is because you need default options in chemical engineering yiu can but ϕi = 1 as an approximation where as you would not know what the default option for chemical potential was, so we will not really done any significant at this stage we are not made progress in terms of defining the composition dependence is a chemical potential but we have expressed it in terms of quantity for example in a gas phase this is completely measurable Vi bar is measurable.

So if I know the composition dependence of the chemical potential if I know the composition dependence of this molar ∂ molar volume that is all I am saying so if I know 1 I can get the other I cannot make this connection in the liquid phase because liquids do not have a asymptotic

behavior either at a limit of temperature or a limit of pressure because all gases behave ideally at P = 0 this integration constant vanished for you we would not such a facility in the liquid phase.
S
On in the liquid phase you have stuck with solving this equation directly here if you experimental data on Vi bar you have a solution of the Gibbs Duhem equation because the Gibbs Duhem equation simply tells you then that μi – μi ideal is this and μi ideal is given by this so you got your whole this thing worked out so let me get back and write this equations.

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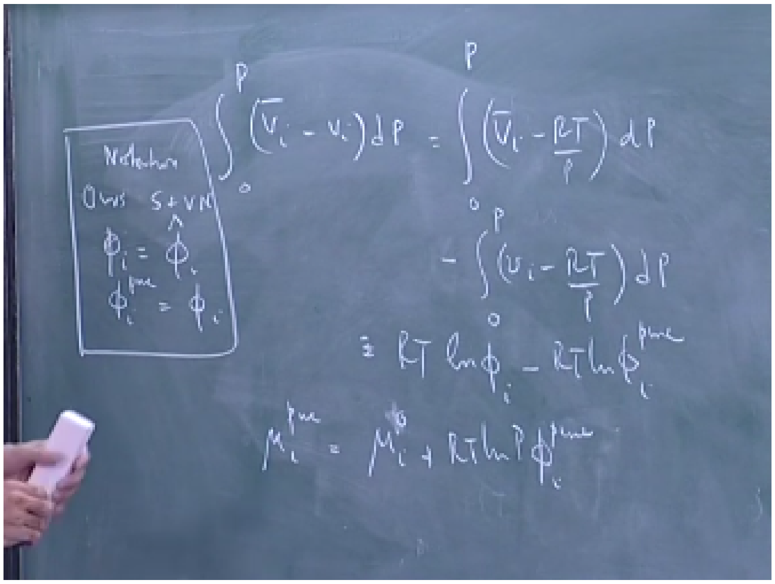

Notation
Ours S+VN
$\phi_i = \hat{\phi}_i$
$\phi_i^{pure} = \phi_i$

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

$$= RT\ln\phi_i - RT\ln\phi_i^{pure}$$

$$\mu_i^{pure} = \mu_i^0 + RT\ln P\phi_i^{pure}$$

μi pure in particular okay let me write this out μi pure is = μi 0 sorry this is μi 0 I can just simply write μi0 because μi0 that I have the notation I have used there is the chemical potential of pure i at the temperature in question and pressure = 1 + this would have been ideal case times Vi pure because if I did the same μi for the pure case μi pure -0.

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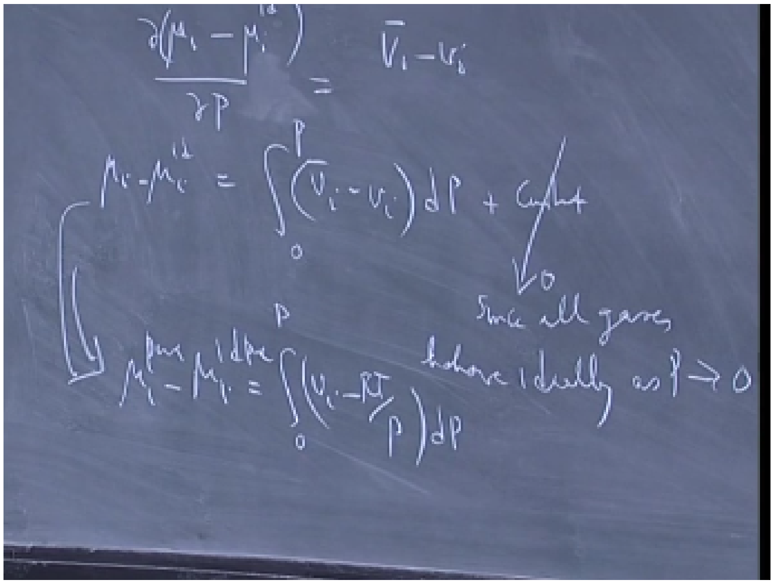

$$\frac{\partial(\mu_i - \mu_i^{id})}{\partial P} = \bar{V}_i - v_i$$

$$\mu_i - \mu_i^{id} = \int_0^P (\bar{V}_i - v_i)\, dP + \text{const} \to 0$$

Since all gases behave ideally as P → 0

$$\mu_i^{pure} - \mu_i^{ideal} = \int_0^P \left(v_i - \frac{RT}{P}\right) dP$$

μi ideal pure would have been simply Vi – RT/ P may be is should write it here same follow us that μi pure – μi ideal simply = 0 to P because it is pure Vi bar becomes simply Vi the second case because it is ideal it becomes way – RT dP this is μi ideal pure in μi ideal pure we had already that is μi 0 you would have μi ideal pure would have been μi 0 + RTlnpXi or RTln if I multiply by oh there is no xA P ϕ pure μi 0 + RTlnP would be the value for μi pure ideal add on a correction for non ideality which is ϕi pure.

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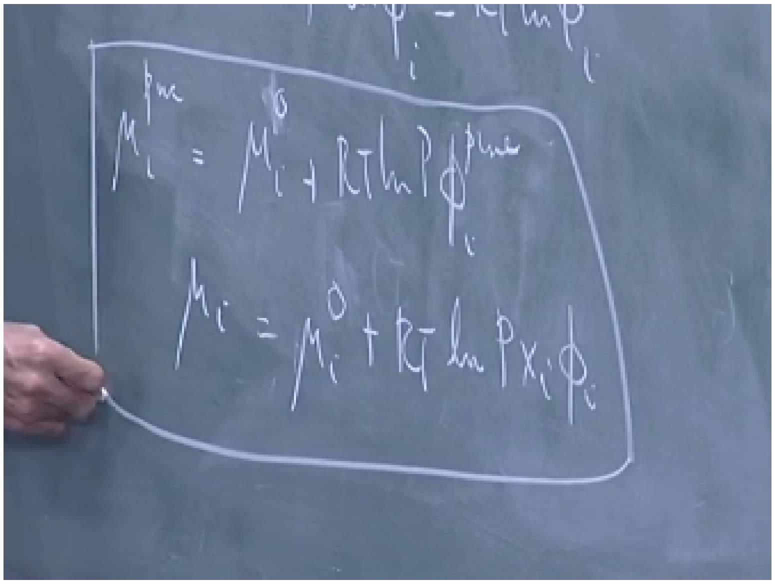

Then I have µi in the actual mixture = µi ideal mixture ideal mixture + RTln Pxi into ϕi I have actually µi = µi 0 µi ideal mixture is already there Pxi is there so this is µi0 sorry I have to come back. These are the unique models for gas phase ϕi is given in terms of Vi bar- RT/ PdP ϕi pure is simply Vi RT/P for gases this completes a description remember that the Gibbs Duhem equation is different return for a homogeneous phase.

When you write Dg = - STT+ VdP now writing for a homogeneous phase so you have to solve this since luckily we have only 3 phases of aggregation you have to solve it for the solid state the gaseous state and the liquid state separately so I have done the gas phase now we will do the liquid phase.

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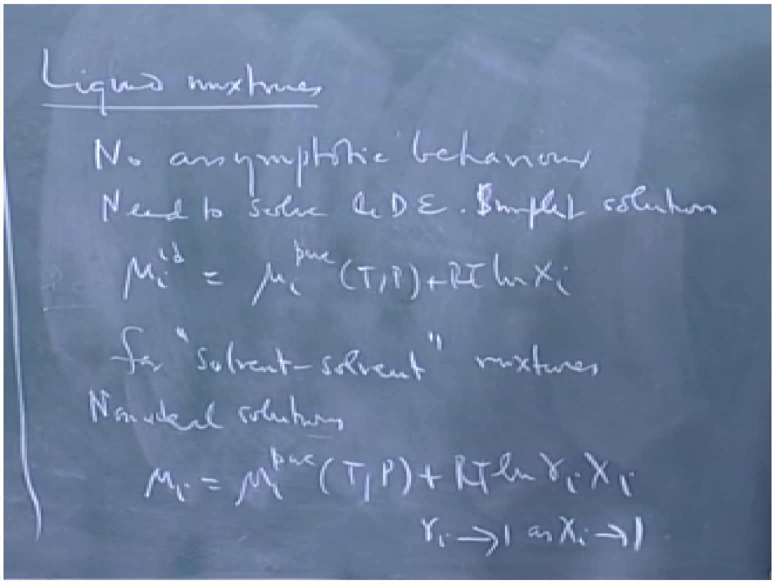

Liquid mixtures

No asymptotic behaviour

Need to solve G.D.E. Simplest solution

$$\mu_i^{id} = \mu_i^{pure}(T,P) + RT\ln x_i$$

for "solvent-solvent" mixtures

Nonideal solutions

$$\mu_i = \mu^{pure}(T,P) + RT\ln \gamma_i x_i$$

$$\gamma_i \to 1 \text{ as } x_i \to 1$$

Liquid mixtures for liquid mixtures first know asymptotic behavior if your able to find an asymptotic behavior you are in for a noble price here but some of these things are not worth searching when the liquid range has been covered people have looked everywhere so you have to solve need to solve Gibbs Duhem equation what we do is to simplest solution is μi ideal again I still have okay possible simplest solution is however you must notice that in liquids you have all kinds of mixtures I can have gas dissolved in liquid.

So suppose i refers to carbon dioxide in water and I referred to carbon dioxide then has if you go to the temperature of the solution if you go to the temperature in pressure of the solution go to the pure state the pure state is a gaseous state it is not realizable in practice that is I cannot take a mixture of composition Xi where Xi represents the composition of carbon dioxide mole fraction of carbon dioxide in a mixture and take their mole fraction continuously to one without change of phase and Gibbs Duhem equation is written for a single phase.

So I have to solve within that phase so what we do is write this has simplest solution for give name for mixtures in we classify mixtures into solvents, solvent mixtures and solvent solute mixtures, so this is valid only for solvent – solvent mixtures in solvent – solvent mixtures you can take the mole fraction of all the components individually to unity without change of phase that is the definition of a solvent – solvent mixture.

For every component I can go to mole fraction unity and still get preserve liquid state so this is a simplest solution this is A solution so what you do in practice is write for non ideal solutions or real solutions as here you have μi – μi pure at TP again for solvent – solvent mixtures only will treat the other case separately.

I write μi = that where I have to tell you what γi is in this case when Xi goes to one left hand side becomes equal to this so γi is 1 in the pure state so I you write a along with this you notice that γi goes to one as Xi goes to 1.

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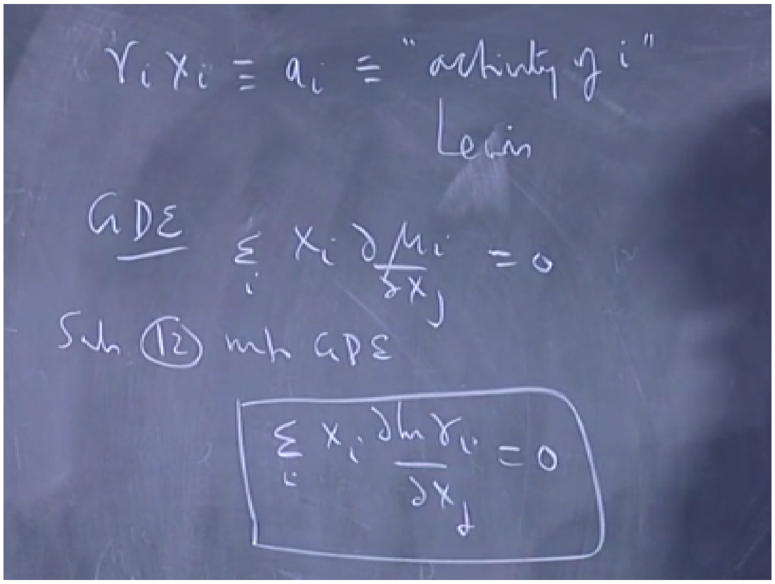

$\gamma_i x_i \equiv a_i \equiv$ "activity of i"

Lewis

GDE $\sum_i x_i \frac{\partial \mu_i}{\partial x_j} = 0$

Sub ⑫ into GDE

$$\boxed{\sum_i x_i \frac{\partial \ln \gamma_i}{\partial x_j} = 0}$$

This quantity γi x Xi is called ai is been called activity and to the term coined by Louis long ago incidentally Louis is credited with being the first expositor of classical thermodynamics because Gibbs need an interpreter what Gibbs said was absolutely right but very tedious Gibbs would say in the foot note obviously and he will say in the foot note if necessary this can be derived and so on then Louis will do the derivation.

So Louis is book at all the just like he took notice from the master and filled them up so in ideal solutions the role of non ideal solutions the role of mole fraction is played by ai the activity and the activity default option and all chemical engineering design programs as I said γa = 1 but yiu can go terribly wrong, there are mixtures in which γi can be 1500 which means Xi being the being a representative of μi is meaningless log Xi does nor any longer represent.

But those are exceptions but typical γ values of 2, 1.5 2, 3 etc very common many mixtures so we will do lots of examples in which these and that will make a lot of differences I told you finally you are going to use ΔG is the work done ΔG is Xi μi – Xi μi for the of μi pure so that is the change when you do mixing or unmixing you take air separated into oxygen and nitrogen you can calculate how much work is done in the process.

I will do that calculation when you do difference essentially this RTln γ log γ aXi represents the work in bring you show that it is equal to the work in bring 1 mole of a i into a mixture of j so if you have a binary system and since the work depends on log of Xi if it is log γaXi and γi turns out to be 2 you will make a mistake of Rtln2 it can be large differences that is all so this is your activity coefficient.

Now you have not really done anything only change words because if substitute this into the Gibbs Duhem equation now let me go to the Gibbs Duhem equation it will play it you solve it in some way or other now substitute this quantity give these finished 9 I think last we will call this 10 this can be 11, 12 so substitute 12 into the Gibbs Duhem equation do this by inspection μi pure non function of Xj at all so if it will cancel RTlnXi satisfies the Gibbs Duhem equation.

So when I do sum over i of Xi ∂ of log Xi with respect to Xj you know we get 0 right for come ij i=j you will get 1 for the last component r you will get – 1 so you will get 0 so only thing that remains is log I and RT is constant so this will give you sum over i ∂ of log γi with respect to Xj = 0, to solve this you go back to the other formalism remember we wanted to look at ∂ G you model ∂ G and you get all your equations for μi instead of μ I now you will get log γi so the equation.

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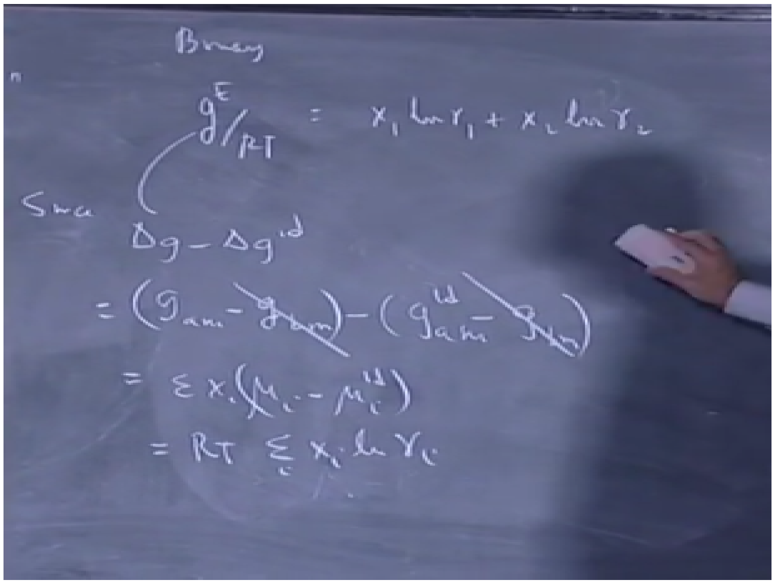

Binary

$$g^E/RT = x_1 \ln\gamma_1 + x_2 \ln\gamma_2$$

Since

$$\Delta g - \Delta g^{id}$$

$$= (g_{am} - \cancel{g_{pure}}) - (g^{id}_{am} - \cancel{g_{pure}})$$

$$= \Sigma x_i(\mu_i - \mu_i^{id})$$

$$= RT \sum_i x_i \ln\gamma_i$$

So the equations are very simple you get g excess by RT I will write this for a binary X1 now log γ1 + X2 lg γ2 reason is g excess is Δg - Δ g ideal Δ g is g after mixing – g before mixing – g after mixing ideal – g before mixing g excess / definitions Δ g - Δ g ideal so this g after mixing – g after mixing ideal g after mixing is sum over Xi μi these 2 will cancel before mixing these 2 will cancel I am looking at the ideal mixing process now.

Xiμi – μi ideal so μi ideal is μi pure + RTlnXi μi non ideal is μi pure + RTln γaXi so the only difference is log γi so this is = RT Σ SO g excess for binary this in particular will give you x1 log γ1 + x2 log γ2 okay suppose I should say here since this is okay so then do the same thing that I did before.

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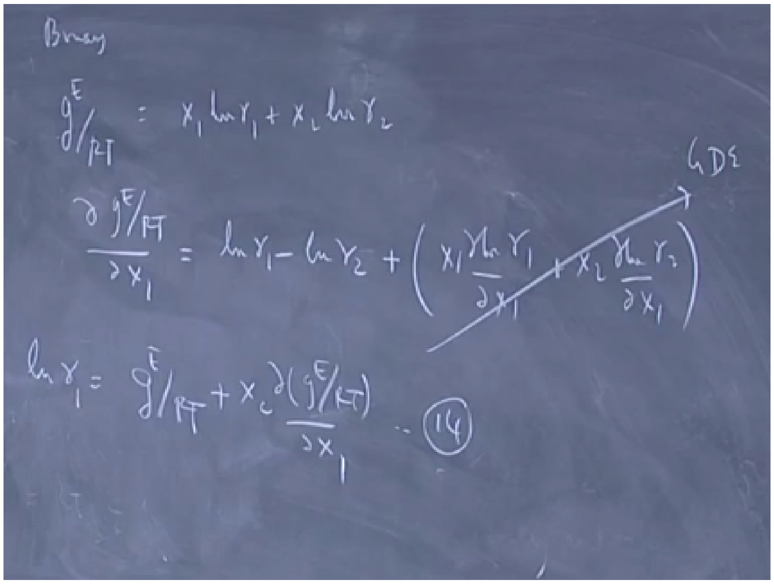

Binary

$$g^E/RT = x_1 \ln\gamma_1 + x_2 \ln\gamma_2$$

$$\frac{\partial g^E/RT}{\partial x_1} = \ln\gamma_1 - \ln\gamma_2 + \cancel{\left(x_1 \frac{\partial \ln\gamma_1}{\partial x_1} + x_2 \frac{\partial \ln\gamma_2}{\partial x_1} \right)} \rightarrow \text{GDE}$$

$$\ln\gamma_1 = g^E/RT + x_2 \frac{\partial (g^E/RT)}{\partial x_1} \quad .. ⑭$$

Differentiate this ∂ of ∂g excess by RT/ ∂X1 is log γ 1 – log γ 2 + and this term is 0 because is the Gibbs Duhem equation I just to solve these two equations algebraically equation 12 this is 13 this 14 and if you recall and we did one last equation we really got an expression for g excess not for ∂g the models for solid mixtures are identical we do not often use them in chemical engineering.

We use them in metrological engineering because basically between solids and liquids is not really much difference they both represent the condense phase molecules reasonably closely packed in the density of the solid is not very different from that of the liquid we have very well defined crystal structure in solids in a amphora solids you do not have a crystal structure but you have a well defined reasonably well defined structure in the case of the liquids you have a little more entropy.

So the model for solids mixtures are similar but we do not use them often in chemical engineering to it main solid mixture problems are in metrological thermodynamics so primarily we will deal with liquid mixtures we will of course deal with gaseous mixtures but most of the time your gaseous mixtures will behave themselves when you will have to calculate frigorific coefficient but you will know the equation of state and you can calculate it that way.

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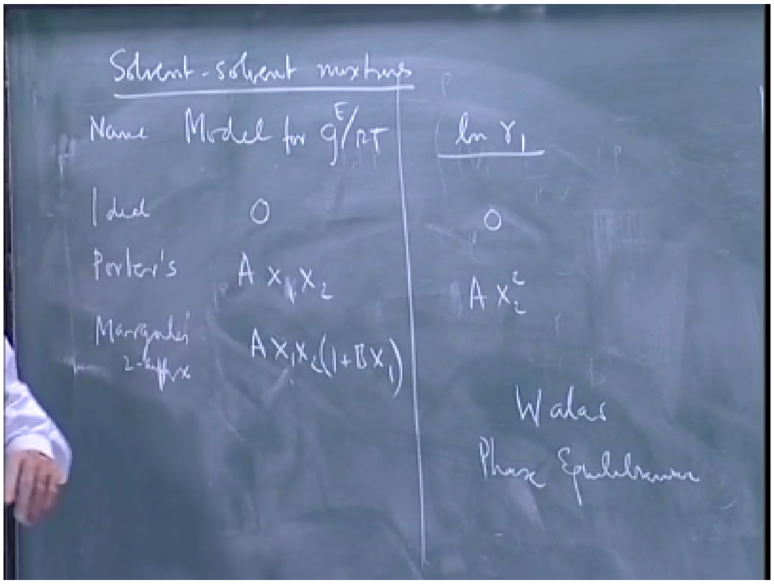

Solvent-solvent mixtures

Name	Model for g^E/RT	$\ln \gamma_1$
Ideal	0	0
Porter's	$A x_1 x_2$	$A x_2^2$
Margules 2-suffix	$A x_1 x_2 (1+B x_1)$	

Walas
Phase Equilibrium

For this you will have to go through for liquid mixtures I will write the model for g excess in the corresponding log γ1 you can get this from tables this is you will have to write this separately for 2 classes of mixtures and deal with solvents solute mixtures later for solvent solute mixtures the model for the solvent will rennin the same but for the solute I will have to write it differently gx as can be 0 is a ideal solution γ1 = 1or I will just write γ its is okay log γ or not gx is can be A x_1

x_2 gx/R_T this is called the misses ideal given name for the model this is called porters equations and if you do that solution that I have given in 14 you take this expression differentiate it and so on.

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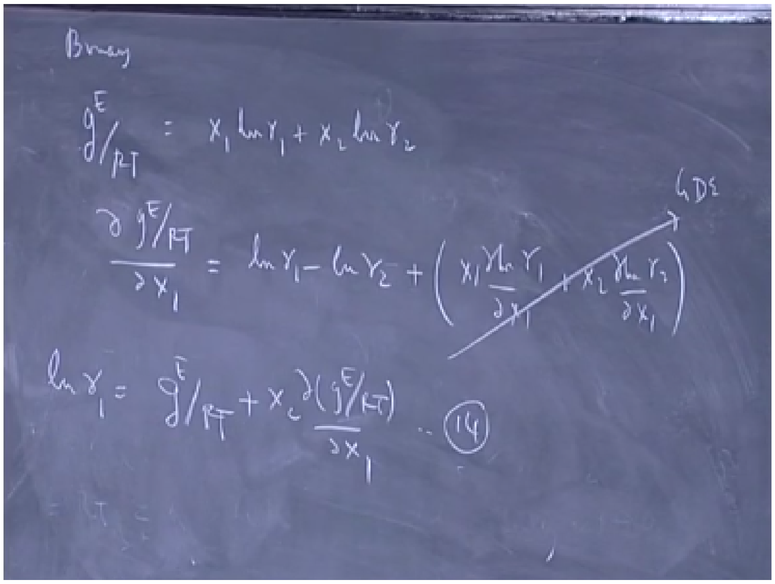

Binary

$$\frac{g^E}{RT} = x_1 \ln\gamma_1 + x_2 \ln\gamma_2$$

$$\frac{\partial\, g^E/RT}{\partial x_1} = \ln\gamma_1 - \ln\gamma_2 + \cancelto{\text{GDE}}{\left(x_1 \frac{\partial \ln\gamma_1}{\partial x_1} + x_2 \frac{\partial \ln\gamma_2}{\partial x_1}\right)}$$

$$\ln\gamma_1 = \frac{g^E}{RT} + x_2 \frac{\partial (g^E/RT)}{\partial x_1} \quad .. ⑭$$

With Aax22 for log γ1 to like for log γ1 here you get 0 γ1 is 1 log γ1 is equal, so you can built models of this kind get Ax1 x2 into 1 + Bx1 you can write higher polynomial models this is Margulies it is called two suffix mod.

As I told you, you can write this is A11 and this is B12 so it is called two suffix I think he even writes is AA12 and A2 1 or something does not matter two parameters existing and you have to solve that I do not remember the solution but you can solve those equations simultaneously and get the values what I will do is put a table of this instantly this is very nice personally do not like the book points but it is well written and it is written by an industrial practice so it is written typically with the law out of redundancy.

It is got everything worked for an open book examination it is ideal classify and tell you the model you do not have to start solving those equations and the examiner make mistakes and solving simultaneous equations because I will never find out where you know your thermo you will make a silly mistake there so the best thing is for you to keep these things wall as a table I will and put that table on the web itself, he has this model and he has the solution for log $\gamma 1$ log $\gamma 2$ is got it for ternary mixtures.

For any number of multi component mixtures in case you do not know how to simplify the multi component mixture equation for a binary he will separately give you a binary table, so he is got all that it is called I think phase equilibrium thing just got a phase equilibrium I do not remember exactly, but wall is a practicing engineer for 15 20 years okay so I just said once you have models with the chemical potential the various models in and your also have to go through the model for venlor.

Which is in expression for R_T / gx is only thing you have to be careful about is at gz is has to go 0 in the limits otherwise you can propose your own model.

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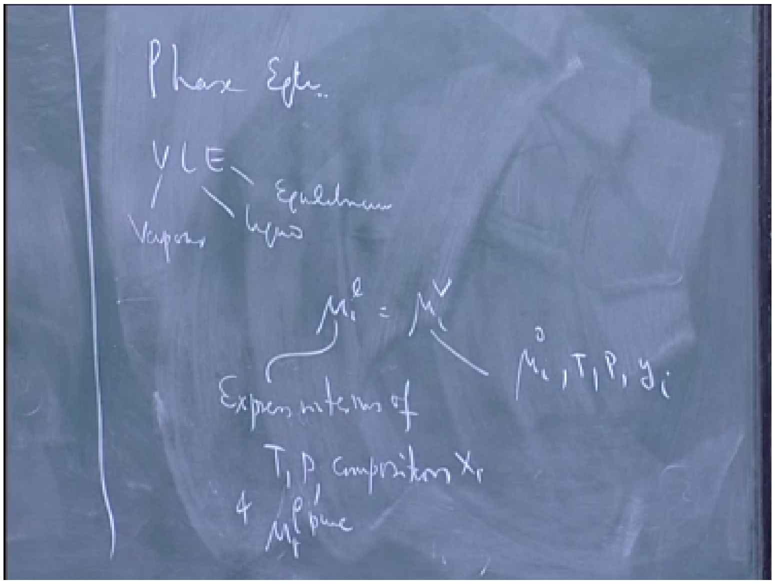

But if you have a phase equilibrium if you have vapor liquid equilibrium and you will get μ_i liquid = μ_i vapor this is we have already shown now the whole purpose of all this exercise was expressed μ_i liquid in terms of measurable quantities and we will shown that everything has measurable except the composition dependents the chemical potential, so this alone you have to do modeling so with the model you get it in terms of composition we get so what you do is when you solve this phase.

Equilibrium problem for μi liquid I have to go through a little more so here you express in terms of T,P and composition and you will get 1 term here that represents and μ_i liquid pure, beaks your model is μi = μi pure + R_T ln and γA x_i in your rated for the liquid phase this is μ_i liquid pure this will come out similarly in terms of μ this will come out in terms of μi is 0 always we will come out in terms of T,P what will do hereafter for composition and the gas phase will use y for liquid phase we use x it seems to be a convention.

Composition xi so the only thing that is that is still gives you a little difficulty is this μi 0 that appears in the gas phase equations in the μ_i liquid pure that appears in the liquid phase equations, so you have to related μ_i liquid to μ_i vapor and I will do that then I will go back and do in solids in solids solvent mixtures if you go back to your pure component phase diagram P was a H.

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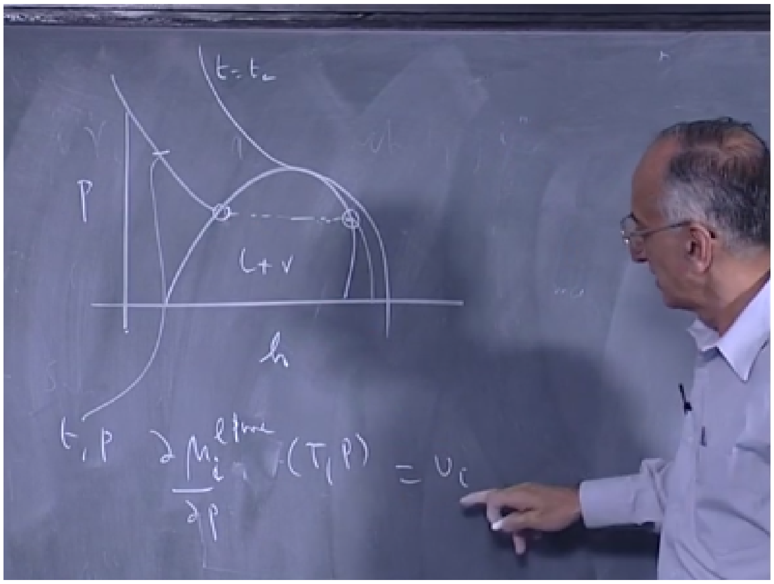

This t = tc and you have liquid + vapor diagram here so if you talking of liquid pure you are talking of substance below the critical point it has to be that is the ways of critical point right, so the way you connect the two which to recognize that at this point the chemical potential of the liquid is same as the liquid in chemical potential the vapor, so if I want to cancel this μi0 I have to express to μ_i liquid in terms of μ_i gas if I do that the μ_i gas will have the μi0 in it which will cancel on both sides.

So having introduced a μi0 which is a hypothetical quantity which is the chemical potential of pure I at the temperature and pressure equal to 1 I do not care what it is it will cancel on both sides, so I will simply write the equations down and cancel so to do this all I do is to take at any temperature Tn let sy TP I write μ_i liquid pure this is what I want I know from thermo dynamics that this is equal to Vi so I integrate this between this point where I can make the connection with the gas along that temperature this is the saturation pressure.

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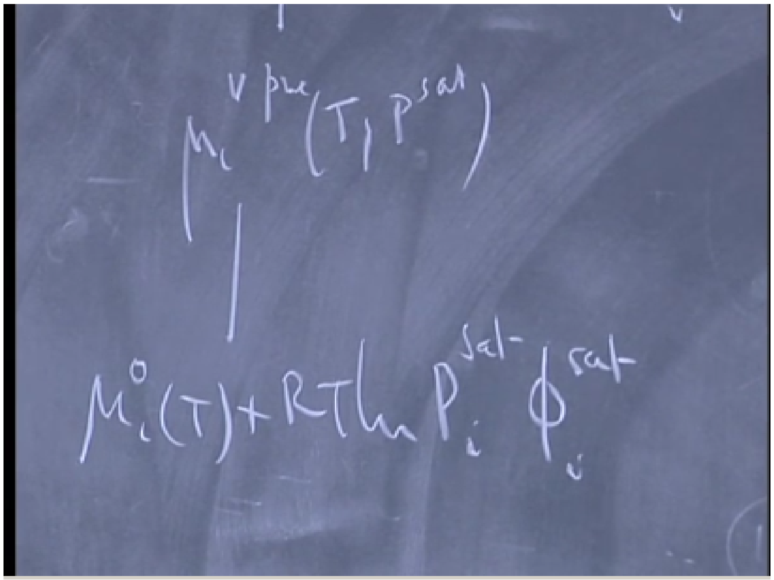

$$\mu_i^{v\,pure}(T, P^{sat})$$

$$\mu_i^0(T) + RT\ln P_i^{sat}\phi_i^{sat}$$

So integrate this I get μi liquid pure TP – μi liquid pure at T and P saturation = ∫ Vi liquid dT from P saturation to P but this is the same as μi vapor pure and TP saturation because the pure substance in the pure substance at this saturation pressure and temperature the vapor and liquid are at equilibrium, because this is given in term this is simply μi 0 of T + RT ln Ai saturation Vi saturation this is referring back to the way I treated this once I have got μi 0 on both sides of the equation.

I can cancel it of I do not have to worry what it is I do not even care if it goes to – it is the identical quantity on both sides, so to complete the picture let me go ahead and do solvents solute mixtures.

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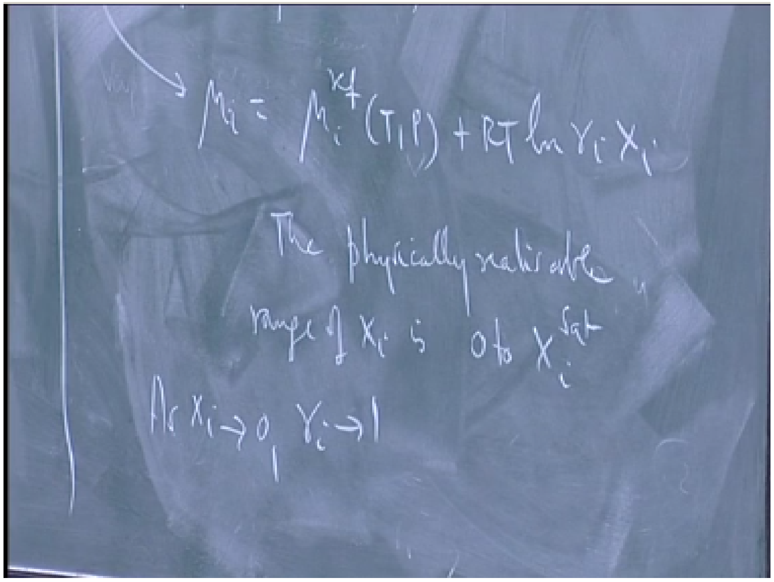

$\mu_i = \mu_i^{ref}(T,P) + RT \ln \gamma_i x_i$

The physically realisable range of x_i is 0 to x_i^{sat}

As $x_i \to 0$, $\gamma_i \to 1$

For the solvent the model is the same μ_i is μ_i pure liquid T,P this is the complete specification because γi will go to 1 as xi goes to for solute mixtures I still have log xi s an ideal solution and simply writ μi reference but for the solute the physical state that I can realize is between xi = 0 and xi = saturation value if it is carbon dioxide dissolved in water the saturation value at room temperature and normal pressure would be something like 10^{-2} mole fraction whatever the value so xi can varying.

Xi is physically realizable or it physically realizable range of x_i S0 to S_i saturation whatever the solubility limit is now there are two constants here one is this μ_i reference in this γ_i it is a function of composition add only one unknown to began with, so I must be able to specify one number uniquely so I will have to choose an xi reference at which I choose γ_i to be 1 in this case of pure substances I would go all the way to mole fraction 1 I could use the pure substances is a reference.

So here I will simply say since xi is going to 0 is a realizable we said γi = 1 you will have this conceptual difficulty that as γi goes to 1xi goes to 0 you get log of 0 so you get $-\infty$ there but we would not worry about it what I am going to do in thermodynamics we also cheat you on this actually it is very valid it is not just we think what you do is get an animal that diverges but the same animal on both sides of equation then you can cancel it, so that is one way of doing it the other things in simply ways.

Although this quantity this is an expression has a function of xi so I can divide this T and differentiate with respect xi differentiate with respect to T or P if I differentiate if I divide by T and differentiate with respect to T_i will get a quantity here which represents – enthalpy of I bar partial more or enthalpy by T^2 on this side I will get some reference enthalpy this term will vanish because I am differentiating with respect to temperature, so if I do that in the if I it will vanish in the limit as xi goes to 0.

So I got very dilute solutions so what I will do is although I do not know this animal I know it is derivative with respect to T or it is derivative with respect to T and I will show you in treating phase equilibrium I do not need to know μi reference I only need to know it is derivatives.

This lecture Series Edited by
Kannan Krishnamurthy

Online Recording&
Post Production team
Subash
Soju Francis
Selvam
Pradeepa
Robert
Karthikeyan
Ram Kumar
Ram Ganesh
Sathiraj

Producers
K R Ravindranath
Kannan Krishnamurthy

Recorded at NPTEL Video Studios
IIT Madras