Indian Institute of Technology Madras

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National Programme on Technology Enhanced Learning

Chemical Engineering Thermodynamics

by

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

Lecture 21

Solvent-Solvent mixtures

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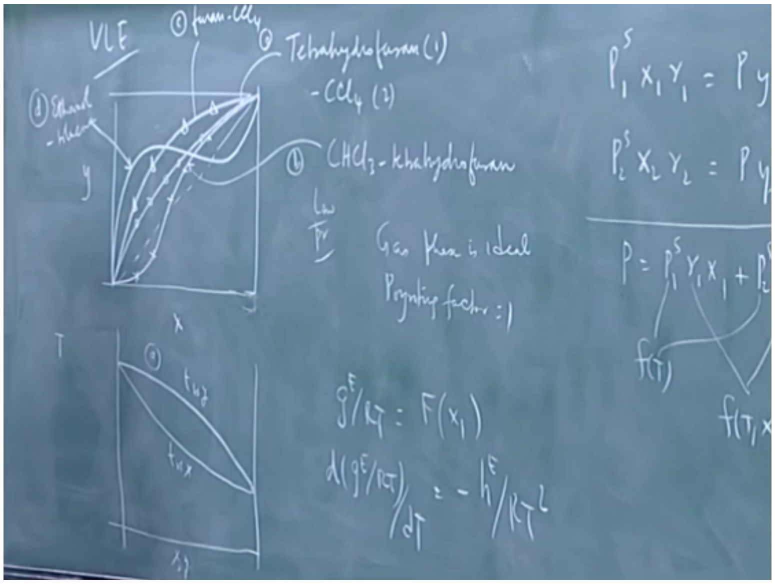

Just brought some data actual experimental data let us put on the curls in the names of the systems these are YX diagrams I want to discuss vapor liquid equilibrium really first one looking at qualitative curves the kinds of curves you get this, this is theatro hydro feuron CCL4 the second system behaves like this, this one is chloroform theatro hydro feuron sort of a convention that the more volatile component, component becomes component one know why he has this third one.

Because it does not illustrate anything different this is pure on carbon theatro chloride then is the last one it looks like this as ethanol toluene will mock them by you need to discuss only three this is one, this is the second one, the plane line can be the third one, and this can be another one these are examples of XY diagram in the corresponding txy diagram these are happen to be data at one atmosphere few T vs X, Y.

I told you X = 0 corresponds to pure less volatile component so it has a higher boiling point so normally the curves would look like this, this is T versus X this is T which is y this is for example for system 1 and call this A as he did and then B, C and D so this is system A for example.

Let us assume because this is at one atmosphere low pressure so gas phase is ideal and then you can assume that pointing correction is one so the phase equilibrium is simply governed by p1s x1 γ 1 = py 1 and p 2s γ1 X 1, X 2 γ2 =py 2 follows of course that the total pressure we are γ1, γ2 are known functions of composition these are functions of temperature.

So this is a function of temperature these two γ1, γ2 are functions of temperature and composition how many in curve fitting this is the equation you use in this case if P is one atmosphere you put it equal to one and find the parameters in this expression F T x1 has also has parameters in it for example if you have porters model this will simply be log γ1 will be ax 2 square that a is a parameter which is a function of both temperature and composition which is why actually from a theoretical point of view.

One prefers to do constant temperature data because prefers constant temperature data because this, this is a function of temperature alone automatically this becomes a function of temperature and X which is becomes then a function of composition law otherwise you have a temperature dependence as well actually the way you deal with the γ s through GX s /RT is equal to some known function x1 and the temperature dependence is handled by RT^2.

So if you know the values atone temperature you should be able to calculate other temperatures using this so you have an integral of this equation that will then lead to from experimental data on HX s HX s remember is actually ∂H of mixing because it is ∂H of mixing -∂H ideal ∂H ideal is 0 so from experimental data on hits excess you can get the temperature dependence of the parameters here.

And that will have to go into this equation here for but if you take a look at this curve for example incidentally these are compounds that are actually we did some measurements on these compounds on that are of direct importance in the chemical industry and what you do in vapor liquid equilibrium I know systems basically the question in thermodynamics is how do you stop having to measure experimental data for all systems.

So you have to classify systems make a measurement for one and guess the parameters for the next system if you do that at least if you measure all the binaries can you tackle the ternary that is the question so if I have G Xs/ RT for all the three binaries in a ternary system suppose I have a ternary system consisting of theatro hydro feuron CCL4 and CCL3 if I know the GXs/RT for each of the binaries and I know the parameters can I predict GXs/RT for the ternary system.

This assumes that basically all interactions are pair wise and they are independent of the third body if this is true you can make a prediction and what you do is if you are doing experimental measurements primarily what you do is look at systems for which the ternary data is already available and two binary data are available then you measure the third binary data and test out a theory that says how to predict the ternary data and take that up very briefly because basically in an undergraduate course.

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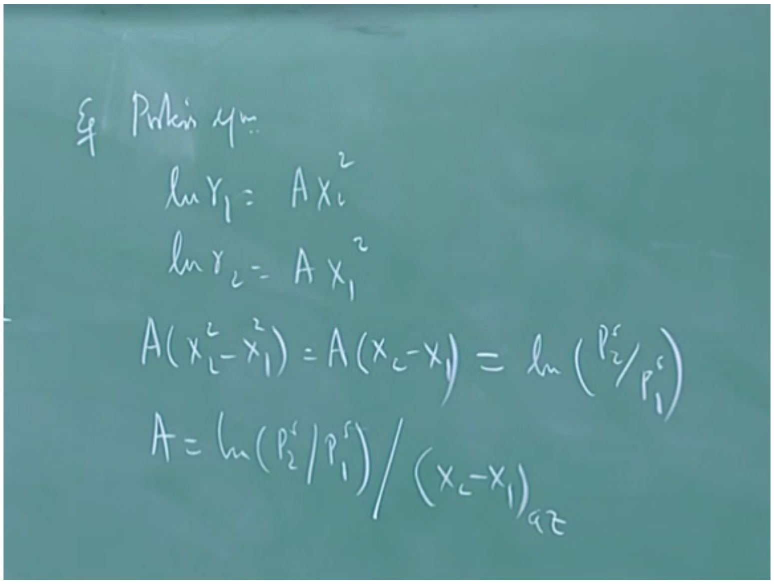

Eg Porter eqn:

$$\ln \gamma_1 = A x_2^2$$

$$\ln \gamma_2 = A x_1^2$$

$$A(x_2^2 - x_1^2) = A(x_2 - x_1) = \ln\left(P_2^s / P_1^s\right)$$

$$A = \ln\left(P_2^s / P_1^s\right) / (x_2 - x_1)_{az}$$

It is only more of the same we do not normally include ternary calculations but good for you to do one solute at least include that in the assignment but let us look at theazeotropic problem this is case B I have an isotropy as your trophy is simply defined as, as the phenomenon in which a mixture when distilled gives you vapor of the same composition that means you cannot use ordinary distillation to enrich the mixture if X 1=Y 1then P 1 s γ 1=Py1.

Sorry, P so you have γ 1/ γ 2 = P 2 s /P 1 s what you normally get from your models is log so log γ 1/ γ 2 is simply log of P 2 s / P 1s in the example Porter's equations you have log γ1 =ax $_2^2$ and log γ 2 is equal to ax$_1^2$ so you get a into X$_2^2$ - X$_1^2$ is the same as A* X$_2$ -X$_1$ this is log γ 1 -log γ2 which is the same as this, this is equal to log of 3 to s given as S, so if you measure the isotropic composition this is known you measure this.

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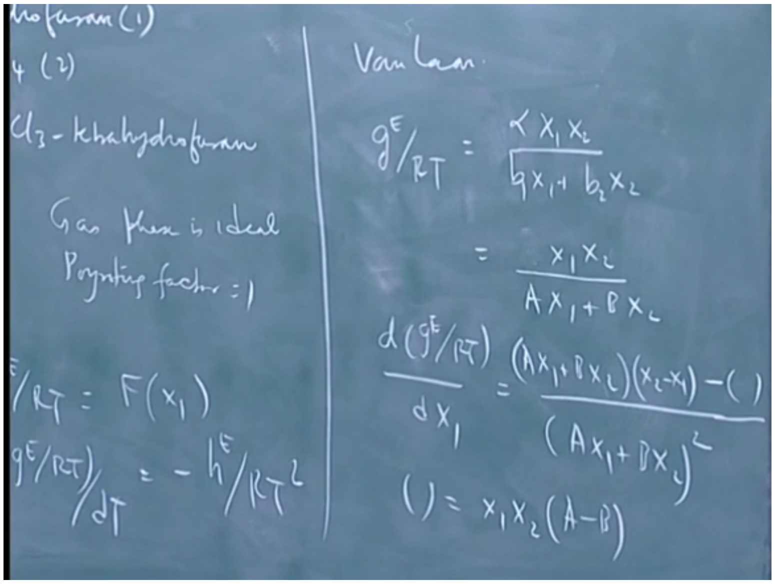

So A is simply equal to log of p 2s /p 1 s /X2 - X1 isotropy it is easy to measure the isotropic composition so you can get the parameter if actually in this in fitting data just take algebraic advantage of the form if I have for example one large situation another model is often used in a isotropy especially for in this case for ether methanol toluene alcohol water alcohol hydrocarbon systems the one layer equation works very well.

You had an expression GXs /RT equal to you just rewrite this is equal to A X1 X 2 we just divide by B 1 /α and so I will just write it as say X1 X 2/ AX 1 + BX 2 and B 1 B 2 are actually volumes liquid volumes it is, it is equal to the liquid volume so these should be known but the way the equation has been used this is the empirical form of this is this where you forget the fact that B 1 B 2 are actually volumes to the liquid and you treat capital A capital B as independent parameters.

If you do that let me derive the expressions for log γ and log γ2 all I have to do is to get D of gxs/RT /DX 1 you need the derivative then I have ax 1 +BX 2 the whole square numerator is ax 1 +BX 2 the differential of this is X 2 -X 1- X 1 X 2 this is in the numerator I have X 1 X 2 into the differential of this which is A- B.

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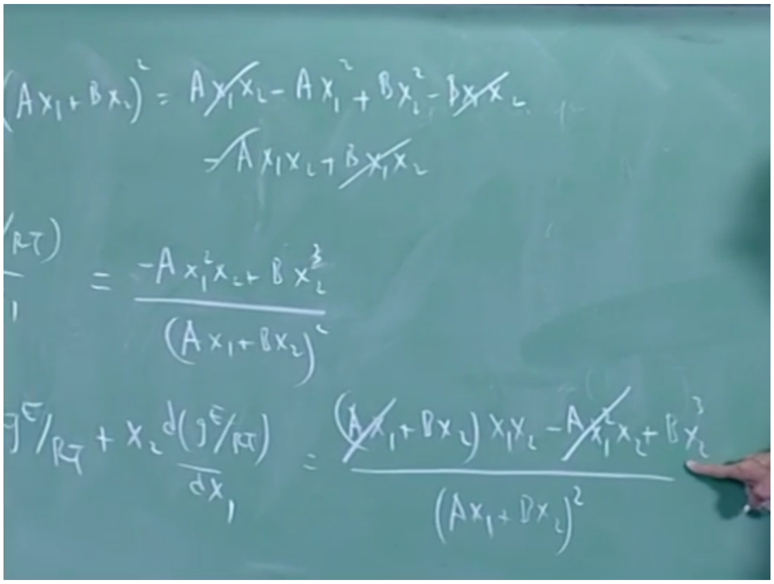

$$(Ax_1+Bx_2)^2 = A\cancel{x_1}x_2 - Ax_1^2 + Bx_2^2 - B\cancel{x_1}x_2$$

$$= \cancel{A}x_1x_2 + B\cancel{x_1}x_2$$

$$/RT)$$

$$= \frac{-Ax_1^2x_2+Bx_2^3}{(Ax_1+Bx_2)^2}$$

$$g^E/RT + x_2\frac{d(g^E/RT)}{dx_1} = \frac{(\cancel{A}x_1+Bx_2)x_1x_2 - \cancel{A}x_1^2x_2 + Bx_2^3}{(Ax_1+Bx_2)^2}$$

So let us say for example this would be for system D alcohol hydrocarbon mixtures so you have D of G X s /RT okay have I will multiply this by X 1 +BX 2 the whole square this gives me a X1 X 2- A X 1^2+BX_2^2- BX1 X 2 then there is a -A into A - B - AX 1 X 2+ B X 1 X 2 so these cancel so I simply get B of G Xs/ RT by DX1. I am going to multiply this by X to get γ1 finally it is simply a X $_1{}^2$ -AX_1^2 X $_2$ +B X_2 X $_2{}^3$ /AX1 + B X2 the whole square so log γ 1 as you know is simply G X s /RT + X 2* D of GX s .

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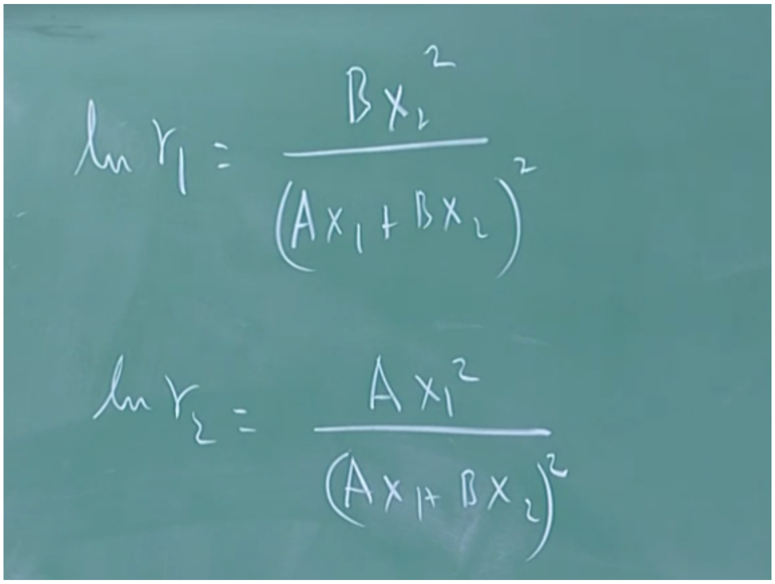

$$\ln \gamma_1 = \frac{B x_2^2}{(A x_1 + B x_2)^2}$$

$$\ln \gamma_2 = \frac{A x_1^2}{(A x_1 + B x_2)^2}$$

So I have to add this X 1 X 2 so the numerator of this would be a X 1 + BX2*X 1 X 2 -A X 1^2 X2+BX $_2^3$so this is a X $_1^2$ X $_2$ will get cancelled out so I get B X_2^2 *X 1 + X 2 so it is just be X_2^2 so finally log γ1 = BX_2^2 /AX 1 + BX2 the whole square this that looks right it is the final expression for log γ1 and log what you normally do is okay we will leave it as it is log γ2is I just have to replace exchange 1 & 2remember when you do replace 1 & 2.

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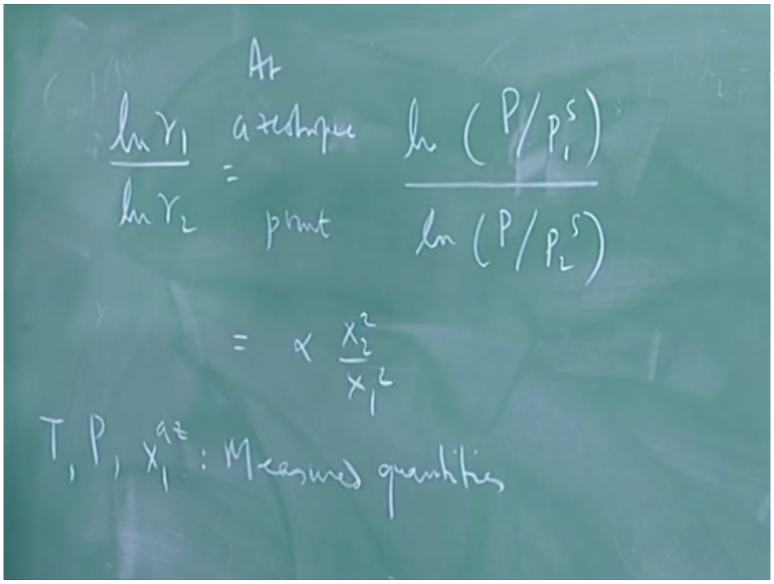

You also have to replace A and B when you do the interchanging they go together so you will get a X_1^2/Ax1+BX_2^2 you get log γ1/ log γ to remember γ1 is the same as in the case of isotropy you get log or@ isotropic point, point log log γ 1 is py 1/ P 1 s divided by log of P by P 2 s because P 1 s γ1 is equal to P and P 2 s γ2 is equal to P again if you take the ratio of these two and you put B by A equal to α you simply the denominator disappears.

So you get α into X_2^2 / X_1^2 so P is known what is measured is P temperature is known P is known X1 isotropy is known so if you have an isotropic point and you can measure these quantities and have got this left hand side log P / P1 s and log P /P 2 s therefore I can get α once I get α again the calculation of the other quantity.

A say for example that is you can rewrite this as if I divide numerator and denominator I will rewrite log γ 1 if I did divide numerator and denominator by B^2 whatever I said I have set B by a is α okay then I will divide this by A^2 and get B/A^2 maybe is α/a sorry and this log coming is log of P.

So what you do is use this equation 1 calculate α then use equation 2 to calculate A therefore B, so you use to this is measured again to calculate and be is simply α time say so the zoetrope point becomes a very useful point all you need to is make one measurement and then you can predict the whole curve, if I make one measurement namely if I make the measurements of TP and x1 so the zero tropic composition of the zero tropic mixture then I can calculate in two parameter equations.

I can get both quantities you may have to do some curve fitting if it is a different algebraic expression but basically you can get both parameters you get two parameters then you have the entire curve predicted because your equation simply is Py1 is P 1has γ on x1 you know γ 1, so from1 as your Tropic point measurement you can get the entire really. Now the interest here is if you want to purify a mixture like this suppose you want to get pure ethanol out of it this is the one that we are working with this is the isotropic point question is can you shift the co tropic point this way or this way.

In a curve like this is at constant pressure, so you can change the pressure or you can do have a similar diagram at constant temperatures can I shift the zero drop by changing the temperature and you can obviously because your isotropic point as you have seen here the calculation of the isotropic point depends upon the parameters n, B which are functions of temperature. So the relative volatility the volatility one component versus the other will change with temperature.

If one of them changes faster with temperature then you should be able to shift this is your table this way that way, so one way of shifting does your drop is simply changing the temperature of operation or changing the total pressure the pressure has a smaller effect than temperature. So you normally change the temperature and try to shift a zero and again it depends on this the temperature dependence of the parameters depends on the enthalpy of solution mixing.

Let me look at this clear as far as vapor liquid equilibrium is concerned the main problem is that once you get to this point you cannot purify the substance any more at this point it is the intersection with the 45^{0} line at this point sorry this is the isotropic point question is can you shift it this way all the time, so you can do so by changing T or P. Another method of doing this is to add a third component if you for instance if I add salt to this mixture the salt addition of any substance will see that also.

When you do solid liquid equilibrium addition of any substance the solvent is a solute solvent will lower its vapor pressure in general if the lower the vapor pressure is lowered more for toluene than for a than then this will also shift thee as your top, so one way of braking as your drops is by adding a third component but you have to pay a penalty after you break the third component you will get a make sure the salt end which you can have to separate again.

So it is simply a matter of economics how you work out this thing normally this score is called salt effects in vapor liquid equilibrium it is quite an important topic by itself, depending on the kind of substance. You are producing what happens is now in the pharmaceutical industry some of these substances have medicinal value and there is a market value automatically for such compounds then some of these methods that were considered an economical earlier have become very economical.

It is worth adding a third component to the whole thing too is in separating it out, so what I will do is give you an assignment with vapor liquid equilibrium examples you give you anisotropic system and I also cover all the models that you have to know.

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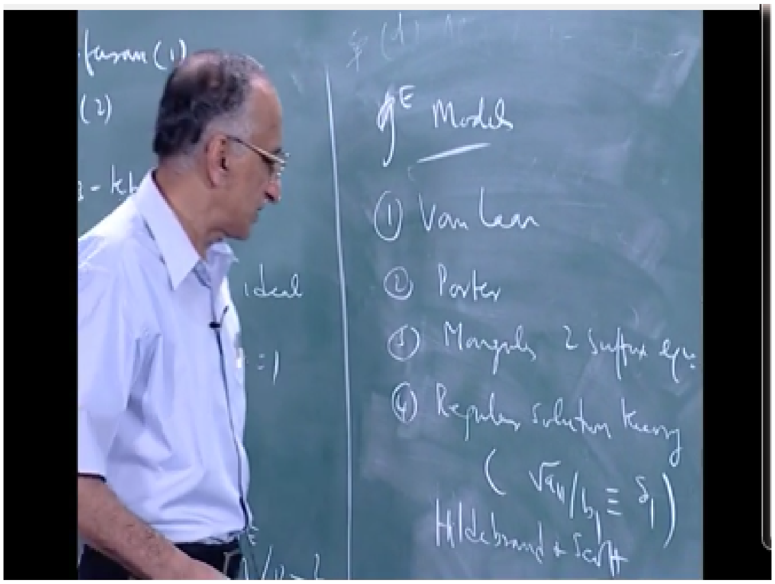

The models that I expect you to know are these the g^E models don't know if I listed them already of course the for historical reasons and also for the fact that it is very good for alcohol containing mixtures, in general alcohol water and alcohol hydrocarbon mixtures you have to know the simple exporters equations third you have to know the modules to suffix equation 2 parameter equation.

It is rental van Laar model also what you do is write a and B as A 1 2 and A 2 1, so if you switch 1 & 2 the parameters get automatically switched. 4 you need some of the rest of the equations are from molecular theory there is a regular solution theory actually in this what you do is √ of a 1 1 by B 1 that you got in one large theory if you set it = what is called solubility factors derives independently but if you call that a parameter Δ that is characteristic of substance 1 this is called solubility parameter.

You get essentially the regular solution theory, the regular solution theory was divided derived by Hildebrand and Scot I think I told you about Hildebrand he was at Berkeley and he passed away as a chemist, he is the one who was a mountaineer till 40 and then took the thermodynamics and then anyway and Scot derived it separately is.

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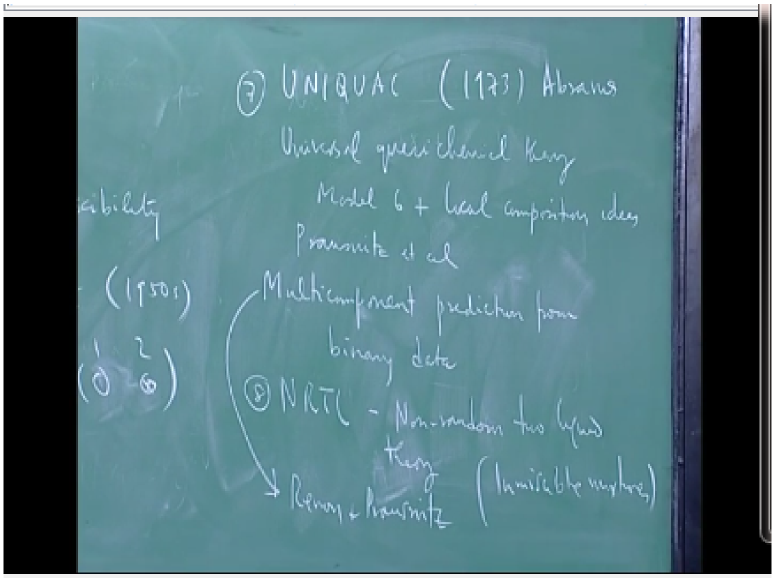

ibility

(1950s)

$\begin{pmatrix} \overset{1}{0} & \overset{2}{\infty} \end{pmatrix}$

⑦ UNIQUAC (1973) Abrams

Universal quasi chemical theory

Model 6 + local composition idea

Prausnitz et al

Multicomponent prediction from binary data

⑧ NRTL - Non-random two liquid theory

→ Renon + Prausnitz (Immiscible mixtures)

Then you need to know Wilson is model, Wilson is model is the first local composition model at a molecular level he said that locally the composition could be different from the global composition you could have a 50/50 mixture of 1 & 2 but locally around every one you may have a point 7.5 mole fraction of 2 and around every molecule of 2 you may have 0.75 mole fraction of 1.

Since the immediate environment determines the work required to bring a molecule from infinity to here which is how these models have formulated, there is a difference in the difference in the local composition makes a difference in the excess free energy calculation but this is basically a molecular model and following this you have this is this is molecular theory. And so is this regular solution all these put a star here all these come under molecular theory.

Under classical models exactly like the instead of the local composition model you can have Guggenheims quasi chemical theory, what Guggenheim said was very simply this quasi chemical theory is a classical theory but it again depends on semi molecular arguments. What he said suggested was that if you have 1,1 pair in a pure substance and then you add a 2 2 you add 1 to 2 you have a 1, 1 pair in the first container you have a 2, 2 pair in the second container when you fix finished mixing them you get 2 12 pairs.

Let me mark 2 as something different if you imagined that everyone one pair and the two pairs were replaced by one two pairs in the mixture, then you would write a reaction equilibrium constant K as the 1 2 √ / 1, 1 x 2, 2 the concentration of 1 2 / the concentration of 1, 1 the number of 1 one person to number of two ways. If you treat this K as a constant then you can calculate the number of pairs and therefore calculate finally arrive at an expression for again you have to use molecular theory I am not going to derive that here but you will essentially get an expression for excess free energy.

I will do that a little later after I have and show you how you can start from molecular theory and do it do this but you essentially get what is called the quasi chemical theory because it assumes that this K is a constant exactly like your treatment of reaction equilibrium, this is not a reaction that actually occurs but you pretend that the reaction occurs and you get an expression. So this quasi chemical Theory has then been generalized to universal quasi chemical theory.

The universal quasi chemical theory is a universal of this is Guggenheim 6 model 6 plus local composition concept, this is due to projects and coworkers basically these this is good for alcohol good for alcohol containing mixtures these are for in some sense simple mixtures more or less hydrocarbons that are similar, if you have mixtures of hydrocarbons that are similar then the single parameter this is sometimes referred to as the marbles one parameter equation this is marbles because all these come from holes expansion.

The polynomial expansion for excess free energy the regular solution theory is like the van Lan theory it is also good for mixtures it also has other predictions for every useful as I told you one of the predictions, that came from one last theory and from regular solution theory is that substances that have the same critical pressure will mix ideally. So the critical pressure differences are a measure of the non-ideal T of mixing this is part of the irregular solution one.

Wilson is model I must tell you in addition to all these being used in vapor liquid equilibrium can also predict immiscibility I will do that in a minute because all I have to do is thermodynamics tells me that the Δ g of mixing should be a minimum g should be a minimum at equilibrium if I have constant temperature and pressure g should be a minimum. So the question is g a minimum for the two substances that remain unmixed or for them in the mixed state.

So you have to look at g as a function of composition and ask if there is a minimum at some point if there is if the curve actually produces a situation where the two separate substances have a lower free energy than he mixture they will remain a separate substance. So I will show you that so Wilson is model is used where Wilson is model you can show cannot predict the only limitation of since product is it cannot predict immiscibility. You can show this theoretically the quasi chemical theory is gently used in all these cases and the universal quasi chemical theory is one of the most successful theories.

It has actually a fundamental flaw but it is so successful that the flaw is overlooked I will point out the mistake in it the mistake in it is actually that the quasi chemical the universal quasi chemical theory is much more successful than the quasi chemical theory, so people thought it was a great this thing this came in nineteen this came in nineteen fifties and this was1973 they called Abrams is a graduate student with browse Nets in Berkeley turned out that.

What they made a mistake in this theory that the number of pairs you know the Guggenheim worked with number of pairs, probes Nets worked with from molecular theory with the local composition concept he had a very nice way of deriving it, so you need one does not have to take away credit from cross nets but in the process of deriving it turned out that the theory had one defect that the number of one two pairs counted was not the same as the number of to one pairs.

ISn Guggenheim series the one two pairs in the to one phase number of one two pairs was contrast the same as number of two and pairs it was obvious in the way the theory was derived in this case it was not, so there was a mistake and because of that mistake it had one parameter in a binary more than Guggenheim's theory and that parameters correlated data so well that even now unique work has accepted as it is with the flaw in pair counting.

So this model you should know simplifies because the industry uses it very widely and it has a very natural generalization to multi-component systems, if you know binary calculations you can do ternary calculation. So for multi-component systems and say multi-component prediction from binary data, so this is its main part then you have to know one more this is it is called NR TL very pompous names this is non-random to liquid theory so NRTL.

This is again due to it is due to a guy called Rennin this is Abrams impersonates, the Hildebrand squad theory is sometimes referred to as the two liquid theory, you can derive this on the basis of I can show you how it is done later but this God is theory was called also to liquid theory. So non-random to liquid theory was a generalization of this does not assume random mixing and this is extremely good for immiscibility immiscible mixtures. This theory is even worse than unique whack because unique whack had a mistaken pair counting.

And not TL has a very fundamental flaw in its derivation which is now well known in fact if I derived it in class which I will try and do later after you finish the classical part I will reserve a few lectures for the molecular theory, I have to actually ask you to close your eyes and change internal g to free energy in order to derive that result. It is now well known that the test that defect but again it is one of those cases where the experimental correlation of liquid-liquid equilibrium data that is if you have two liquid phases.

And you correlate the equilibrium it is one of the most successful theories in correlating the data so there must be some compensation of errors that makes it, so good so as far as engineers are concerned this theory will continue to be used for quite a long time but this question is why does it work so well is there a good derivation of it that will show, that the assumption that it makes is actually valid as of now there is no justification for it.

So you should be aware of it and you should I mean although you use it as a tool you must know that there is no fundamental basis for it you can treat it all you can treat all of them as empirical models because them what a classical thermodynamics does not give you an expression for the composite independence. So any model you write for the composition independence that goes to zero for the pure substance is a valid model.

So as far as classical thermodynamics is concerned that the derivation is a flaw makes no difference there is finally an expression an algebraic expression that correlates data extremely well that is all that is important but if you are looking at it from a theoretical point of view it is very unsatisfactory. So the situation in molecular thermodynamics is very unsatisfactory as far as classic alter mina this course is concerned I only give you the final expressions in the final expressions.

In these theories are at the moment the best ways of correlating data, so this is an RTL again this is the same thing applies to a TL as well you can do multi-component prediction from binary data. So you have to know these are the models that you have to know I do most think you need anything else.

So you will need to know a total of eight models my suggestion is that actually Wallace has a summary of these, so you should have the expressions for gx s and for log γ so you start deriving it like I did now you just take a long time the whole idea of an open book example is that you can use, so you must get a little familiar with these.

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Kannan Krishnamurthy

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Post Production team
Subhash
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Karthikeyan
Ram Kumar
Ram Ganesh
Sathiaraj

Producers
K R. Ravindranath
Kannan Krishnamurty

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