Indian Institute of Technology Madras

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Chemical Engineering Thermodynamics

by

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Lecture 22

Liquid – liquid equilibria

It started I am going to discuss.

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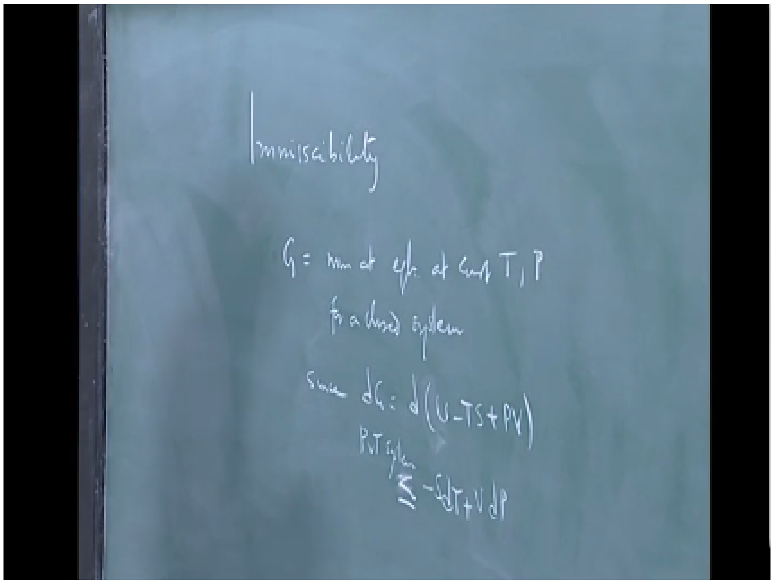

Immiscibility

G = min at eqb. at const T, P

for a closed system

Since $dG = d(U - TS + PV)$

PVT system

$\leq -SdT + VdP$

Invisibility basic idea is the following that the Gibbs frees energy = equilibrium criteria are minimum at equilibrium. This is a thermal thermo dynamic result because at constant T and P G should be a minimum for a close system, this is because d G d (U – TS + PV) = for PVT systems d (U – TS + PdV) therefore this is – SdT or there it should ≤. This is using the 2 laws where d U

= d Q – ΔW is Pdv – or + Pdv and the Q is ≤ TdS. Since so G can only decrease at constant T and P therefore G should be a minimum at equilibrium. G is a minimum at equilibrium.

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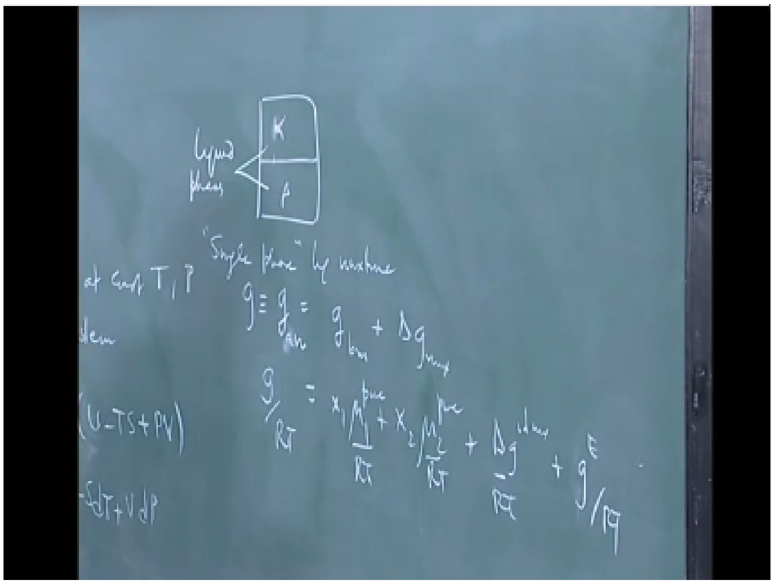

Let me write down G for a system of 2 phases, there is liquid phase α phase and a beta β phase, these are both liquid phases, the example we had and water in your talking was I directing the distributed between these two phases. So I have 2 liquid phases G if Interviewee: rite it per mole, this is g before mixing this is g for mixture as g before mixing, I am writing per mole of the total contents + Δg mixing. This is the same as g after mixing and looking for a single phase, liquid mixture.

You want to know if first of all let me write this out g before mixing is x1 μ1 pure + x2 μ2 pure, do everything at constant temperature I will divide by RT + Δg ideal mix + Δg non ideal mix or g excess sorry.

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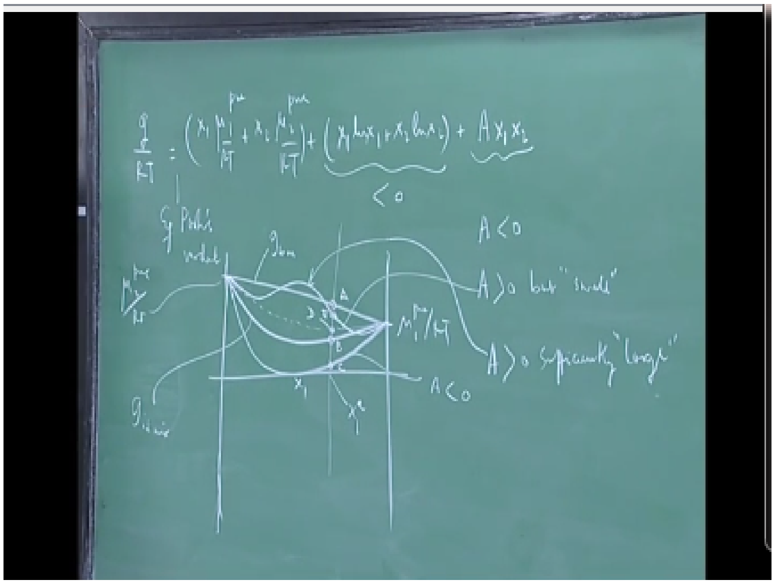

Now I have g/RT = ideal mixing is x1 log x1 + x2 log x2, + the excess free energy. I will take the example in this case, simplest model will be put as model, you have to write a model for a excess free energy for this system in this case it could be potters x1 x2. Say µ1 as some value this µ1 pure / RT, this is µ2 pure / RT, this is x1. So before mixing this value is the value before mixing it is simply a straight line.

Because a tongue of two pure components x1 µ1 pure / RT this is the discussion I have done some calculation in plotted numbers. If you look at the ideal case this one is always < 0, x1 x2 < 1 so log x1 log x2 are negative. So that number is < 0, so the free energy of a mixture at any point is lower than the free energy of this is g before mixing, this is g ideal mixture. Ideal mixture would have a g which will always be lower than the g before mixing.

So ideal mixing means all components are always visible in all proportions because at any given T and P if you fix the composition the free energy of the mixture is lower than that of the separate components. So if you keep them together and allow them to mix they will mix because this as the lower g than this and according to thermo dynamics this is some come to equilibrium at the lowest possible g.

So this will be if you take any line here you fix the composition this is the g before mixing this is g after mixing if the mixing was ideal, that means as far as ideal mixtures theory is right all components are visible in all proportions and the equilibrium status always that of a mixture. The idea in statistical thermo dynamics is and the system in this state still has the choice of being like this.

I mean I mix the components they do not have to mix they can stay apart but that is not the equilibrium state because that state as the higher fuel energy than this, but if you take real mixtures there is interaction between parameters this as to do only with entropic effectively. It can rearrange itself it has more configurations available than it had before. If you mix than you can have a component 1 and the middle 2 around it and so on, various configuration whereas here it was one and one only around it.

2 and 2 only around it and no interactions whereas that co9nfiguartion is still available to it, it has additional configuration in which it can re arrange any numbers of twos around 1. Therefore this is larger entropy and if there is no energy of interaction this always will be at equilibrium state. Equilibrium state is one in which there will be more and states available microscopic for the system then they were before mixing.

But if you add this energy contribution a x1, x2 for example if A is < 0 A x1, x2 is – and then again you will get miserable solution. If A < 0 you will get one more addition here could shift things, so this is A < 0. If A > 0 and sufficiently small you will get somewhere in between this is A > 0 but small I will define what is small in a minute. But A>0 and sufficiently large and what you could get initially of course it will be below the line this is the ideal mixing line.

So this case A > 0 you will still get to begin with it will go like this as suppose I have to draw this, you will get a curve like this because A x1, x2 is a maximum at x1 = x2 = ½, it can become positive or it can become positive at slightly there is the range over which the net result can be positive. So this will be the result when A > 0 and sufficiently large. So look at this mixture for example fix this x1 you put a certain amount of 1 and 2.

This is A is the point here A B, C this is D or I have chosen another point here let me redraw this curve to illustrate and then but it does not matter this can stay. So I have A, B, C, D, E of which B, C, D, E are < than the free energy of the separate components. So upto this point at this composition this is x1 let us call it at that composition they are still is miserable in al proportions. But if you go to this composition here for example draw a line here x_1B.

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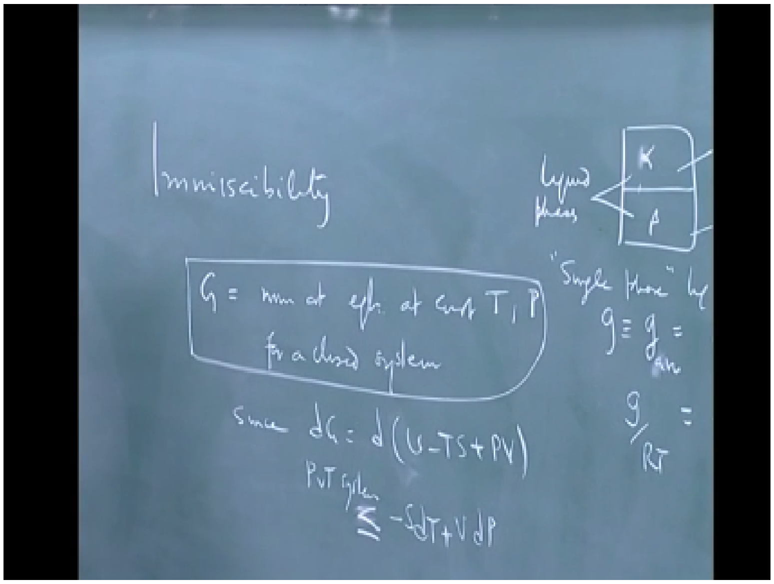

So we will say first x1 = x_1A mixture always as a lower free energy than the individual components before mixture, this is the individual components before mixture the separate there free energy was at A it reduce to B because of the ideal mixing, it reduce to C in case of mixture where A < 0, it reduce to a point D where A > 0 but small, it still reduce to the point E when A was large, was sufficiently large to cause.

D stabilization but not enough at this composition but if move to composition like x_1B we will draw the same point A, B, C, D, E. A is here, B is still here below C is still here and then D is here but E is above, in this case if x1 = x_1B point E as a g greater than g before mixing. Thermodynamics tells you that cannot be the equilibrium situation. At the same time if you look at this curve I can draw a tangent here, there are 2 minima in this curve and then maxima.

If you look at these two minima these two constitutes solutions of this composition x1 low and x1 high, we just call it has x1 low and x1 high. This is the mixture of composition homogeneous mixture of composition x1 low, homogeneous mixture of composition x1 high and if you kept these two as pure components and mix them that is suppose, you always had the solution of mixture x1 composition x1 and solution of mixtures of composition x1 high.

And they formed a physical joint entity rather than a single solution then the free energy would lie on this line right the free energy would be number of moles of this times the free energy here + the number of moles of 2 phase because the total moles is 1 and it always as the fraction, so along this line the free energy is lower than here. So this point here F as x1 = x_1B a heterogeneous mixture of two phases of composition, x1 low and x1 high as a g < g at F.

You can take the case of g before mixing which would be this point A g after the real mixing because of the value of A the energy would have been at E had it continued remain as a homogeneous phase. This is higher than the separate components so it will stay at A but there is another state where the free energy is even lower, that is the point F here which corresponds to mixture of 2 phases x1 low and x1 high.

Therefore thermodynamics tells you that let us settle for that, you will two phases, this one will have x1 low and x1 high, I am talking about only two components here suppose I had ethyl and water I was not talking about as a directant for example water rich layer, where say 1 as ethyl and 2 is water. When I discuss the problem as a directant I was talking about a liquid mix, 2 liquid, liquid phases + a solute distributor between them our interest was our directant.

I realized that I have not discussed invisibility itself basically what we find is sometimes a system split into two parts and this will explain why a system should separate into two phases.

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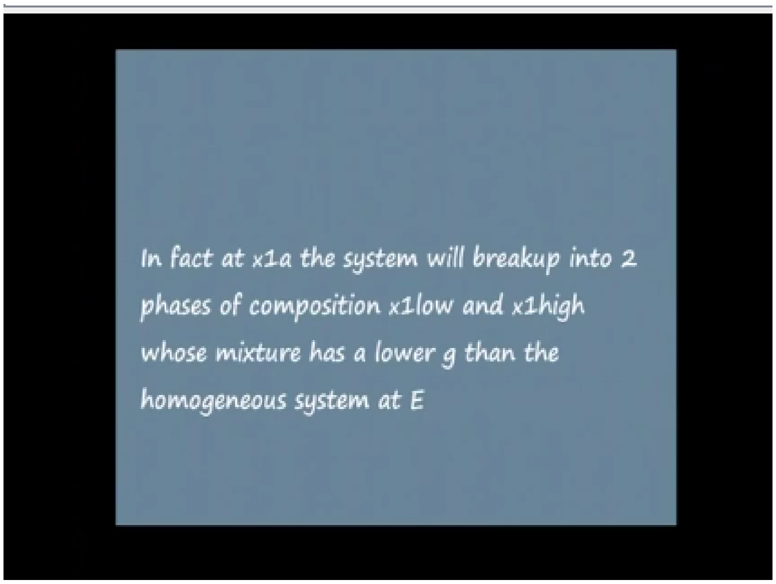

In fact at x1a the system will breakup into 2 phases of composition x1low and x1high whose mixture has a lower g than the homogeneous system at E

What I am giving you there is an example this A x1, x2, is simply to do the algebra, let me examine the algebra system a little more look at if you want to know whether there is minimum and maximum all that you are going to do differentiation.

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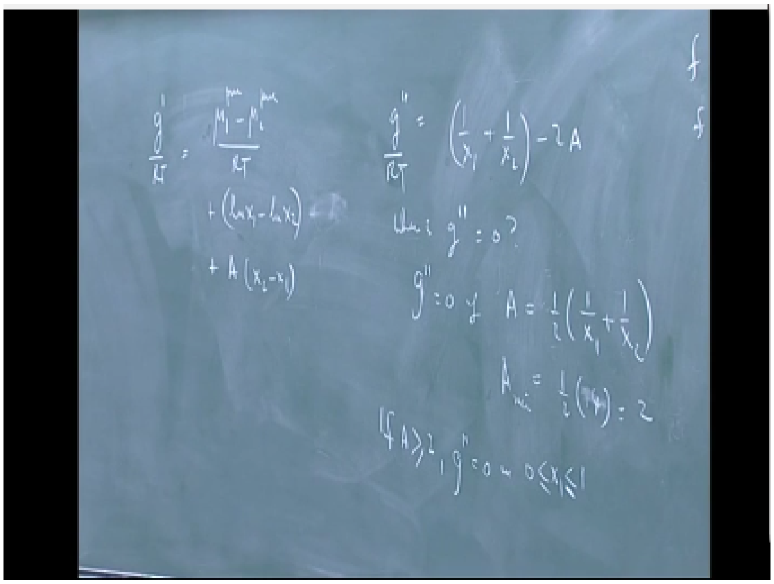

$$\frac{g'}{RT} = \frac{\mu_1^{pure} - \mu_2^{pure}}{RT} + (\ln x_1 - \ln x_2) + A(x_2 - x_1)$$

$$\frac{g''}{RT} = \left(\frac{1}{x_1} + \frac{1}{x_2}\right) - 2A$$

When is $g'' = 0$?

$g'' = 0$ if $A = \frac{1}{2}\left(\frac{1}{x_1} + \frac{1}{x_2}\right)$

$A_{min} = \frac{1}{2}(2+2) = 2$

If $A > 2$, $g'' = 0$ in $0 \le x_1 \le 1$

g` /RT at constant temperature if I take the derivative of that with respect to x1 I get μ1 pure – μ2 pure/ RT that is the 1st term the next term will give me x1 if I differentiate log x1 I get 1/x1,s o I get 1 then I get x2 if I differentiate log x2 I get 1/x2 x -1, so that is the -1 that will get cancel, so I have to only do log x1 – log x2 and the last one will give let me write below this A x x2 – x1. If you look at g ` `/ RT this term if I differentiate this further with respect x1 this will vanish.

This will give 1/x1 + 1/x2 this will give me A x2 will give me -1 this will give – 1 so – 2A, so if you look at this case that we are looking at. If I am looking at A sufficiently large I get a curve like this I get 1 minimum, 1 maximum and another minimum. So mathematically I should pick up 3 points here, g ` = 0 at 3 points. But if g ` vanishes here this slope keeps on decreasing then the slope increases and it decreases and so on.

So I want to know if there is inflection point I will ask when g ` ` = 0, this will happen if A = ½ 1/x2 + 1/ x2 but A is not composition dependents this will happen if the maximum value on the right hand side you can verify the maximum values occurs at x1 = ½ because if you take 1/x1 + 1/x2 then f ` is $– 1 /x1^2 + 1/ x2^2$ this is = 0 if x1 = x2. Since it is = ½, so at x1 = x2 = ½ this is A minimum I will say actually this is minimum because when x1 = 0, it will obviously go to ∞. So what you are discovering is at a maximum if you are discovering a minimum here, for this function, so the minimum value of A is ½ x 1 x 4 in another words as long as A > 2 that if A > 2, g ` ` = 0 in the range for x1 = 0 to 1 g `` will 0 at least 1 point at A = 2 it will 0 at exactly x1 = x2 = 1/2. That means the energy of the interaction is such that this constant A > 2 in this model you will predict In feasibility.

Again for immeasible mixtures for example the portals models may not describe the system at all very well if you have try out different models in order to see which one is satisfied because there is no unique model, but there is some interesting features as mathematical model set you have one of the interesting models is the Wilson model which describes alcohol water hydro carbon systems extremely well.

Now I can show the Wilson model cannot predict in feasibility that there is no value of the constants in the Wilson model that will give you miscibility that there is no value of the constants in the Wilson model that will give immiscibility. So you can look at a model and ask if it is applicable and if it is not applicable then you do not, if you have it since model you hit it on head on any number of times during the computer.

You will never get parameter values that will predict immiscibility, so if the mixture is actually immiscible then you can eliminate some models as being in practical. For example the most successful model for immiscible mixtures not involving electrolyte is the NRT model, I will take the Wilson and the NRT models, I am sure Wilson does not predict immiscibility. The procedure is the same all you do take write down the expression for g which will involve this term always involve this term always.

This will change this is g excess / RT this is model dependent term, so you will always get this straight line you will always get the ideal curve this depending on the values of the parameters in the value of gx / R T as a function of composition you will get different curves, if the free energy net free energy always lies below the ideal mixing line or below the before mixing line you will have complete solubility.

Anytime it crosses the line of g before mixing you will have a miscibility, so we will take a look at g excess models and take two examples one Wilson because one of the first models that was proposed and was very successful for many mixture when people discovered that it does not predict immiscibility at all, it has this logarithmic form and just write them down.

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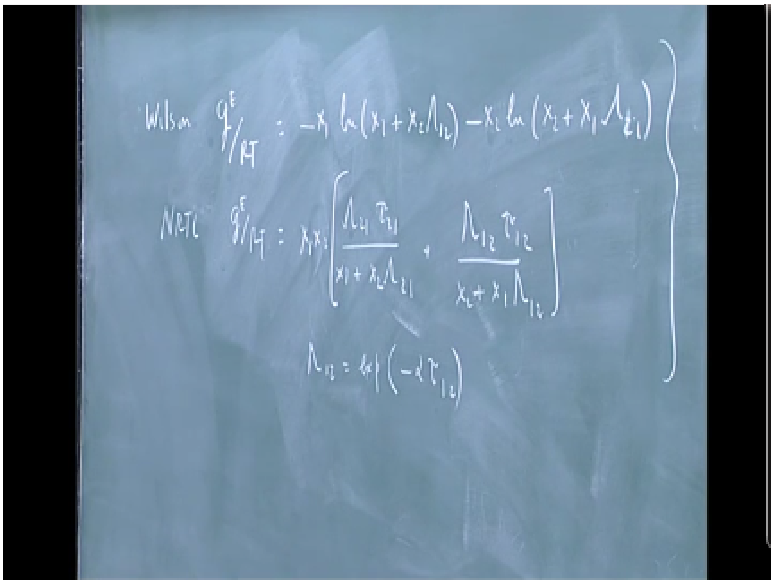

Wilson $$g^E/RT = -x_1 \ln(x_1 + x_2\Lambda_{12}) - x_2 \ln(x_2 + x_1\Lambda_{21})$$

NRTL $$g^E/RT = x_1x_2\left[\frac{\Lambda_{21}\tau_{21}}{x_1 + x_2\Lambda_{21}} + \frac{\Lambda_{12}\tau_{12}}{x_2 + x_1\Lambda_{12}}\right]$$

$$\Lambda_{12} = \exp(-\alpha\tau_{12})$$

G ^{E} model this is / RT incidentally his notation for capital G and my notation small g are the same right small g is a specific property for him capital G itself is a specific property, he uses n times that value for me number of moles. This is Wilson and then an RT- so it is got another two I must take it so x1 x2 into when to 1 2 is a constant at constant temperature this is constant all these parameters are constant and constant temperature.

He uses capital G here it is part of the trick in the derivation I will explain to you what happens but I have used λ that is all this is a molecular parameter which is of this form which so this is also another constant but because of the α, here this is different from the other one. So effectively this is a two parameter equation 212, 221 α is in third parameter. So α 2 1 2 and 1 there are three parameters in this equation there are two parameters in this.

One interest is that if you go to the limit as x1 goes to 0 for both of these he will write the limit as x1 goes to 0 as x1 goes to 0 this term will go to 0 this term this will go to 1 so you get gxs by RT is = x2 will go to 1 x1 goes to 0 so you will get log 1 you are getting the limit, I am sorry I should look it I do not want to look at this yet look at, γ I will come back to sorry I wanted to discuss the limiting activity coefficients γ 1 and γ 2.

I will do that later because I have to again copy the expression for γ and γ 2 but let us just get back to what we are discussing now, this is the gxs/ RT model so all I need is g ` and g ` ` I will do that and essentially show you that with gxs ` ` here I will never get g after mixing less than g before mixing I mean greater than g before mixing. Therefore this Wilson always predicts complete solubility.

So we will take Wilson is something you have remembered essentially you have to examine if the model is good enough for the situation if you know that there is a range of immiscibility and there is no point using Wilson is equations for such systems.

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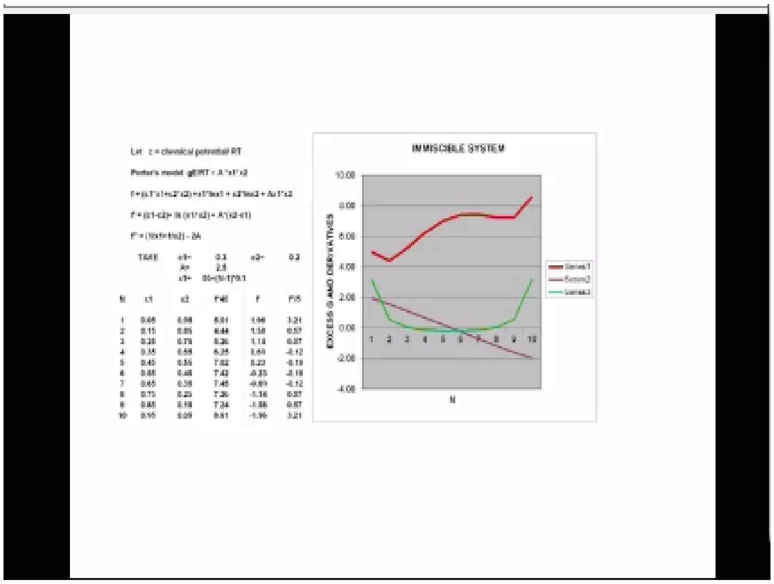

On this diagram that I have given there and actually this was for I forget which system I think it is isopropyl alcohol benzene or something, there is a miscibility data available and this is simply a calculation it was actually four porters model + one of the quiz paper some time ago. The curve is peculiar because that is the way Excel plots the curve that is all it is actually a smooth curve you can see the three that straight line is x1 µ 1 + 2µ 2 / RT µ 1 / RT taken as 0.3 µ 2 / RT as point two.

But those constant values make no difference the calculation because by the time you do g ` ` those constants will be µ1 do not appear, so g ` ` depends only on the ideal mixing which will give you 1 by x 1 + 1/x2 and then you have g excess model. So if you look at G double you would look at the equation for G which is the wonderful top essentially the excess free energy and its derivatives those are what are plotted there.

G ` ` is plotted on top this N a mistake I said that is actually x1 that is the way I calculated x1 was 0.o5 plus n - 1 x 0.1 I just give it steps ,you should have removed in the plot at x1 x2 etcetera but this is illustrative all you need to do is the same calculation for different values of the parameters in this case I have taken a is = 2.5 if I had taken less than 2 you would nost have got a miscibility because the energy is insufficient to compensate for the entropic change that occurs when you mix this if the 1/2 interactions are lower all interactions molecular interactions, interaction energies are negative.

That is the way they are all formulated so if the 1:1 interaction in the 2 interaction are larger than the 1/2interaction negative terms then you will they would prefer to stay in their neighborhoods rather than in the one to much, so that is when you have this problem this a is actually dependent on 1 2 1 1 and 2 2 it's actually the difference between effectively the difference between 1 to 2 times 1 2 & 11 & 2 2, actually will derive a small theory called the Flory Huggins theory which that term will be very important you.

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