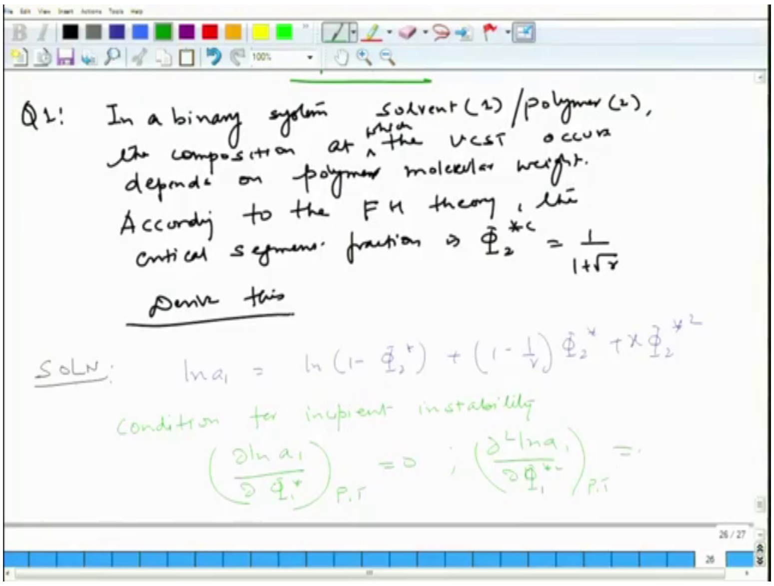
Thermodynamics of Fluid Phase Equilibria
Dr. Jayant K Singh
Department of Chemical Engineering
Indian Institute of Technology, Kanpur

Lecture – 51
Example Problems on Polymer Solutions

Welcome back. In this last lecture of the course I will be describing 3 problems.

(Refer Slide Time: 00:21)



Q1: In a binary system solvent (1) / polymer (2), the composition at which the UCST occurs depends on polymer molecular weight. According to the FH theory, the critical segment fraction is $\Phi_2^{*c} = \frac{1}{1+\sqrt{r}}$

Derive this

SOLN: $\ln a_1 = \ln(1-\Phi_2^*) + \left(1-\frac{1}{r}\right)\Phi_2^* + \chi\Phi_2^{*2}$

Condition for incipient instability

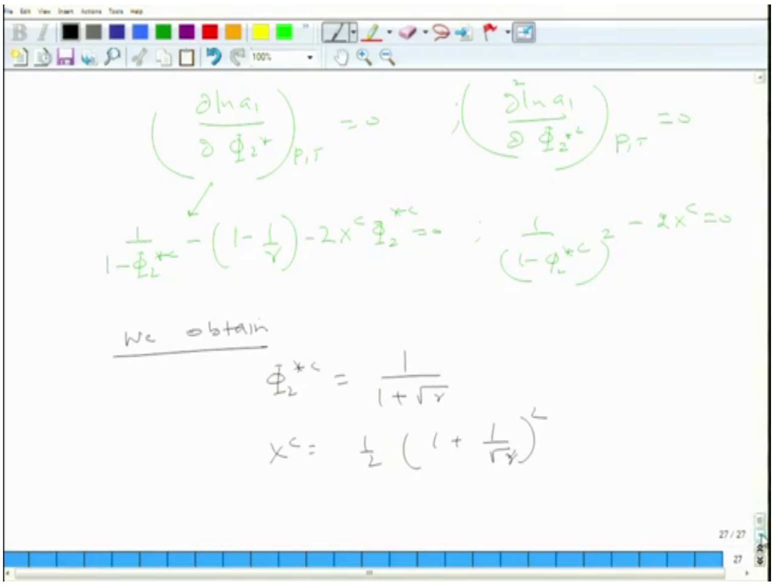
$$\left(\frac{\partial \ln a_1}{\partial \Phi_1^*}\right)_{P,T} = 0 \; ; \; \left(\frac{\partial^2 \ln a_1}{\partial \Phi_1^{*2}}\right)_{P,T} =$$

So, let us start with the first problem. The first problem states that in a binary solution system of solvent and polymer solvent is represented by 1 and polymer by 2, the composition at which the UCST occurs depends on the polymer molecular weight.

According to the Flory Huggin's theory the critical segment fraction is known as 1 by 1 plus root r ok, where r is number of segments. Now, what is being asked is to derive this particular segment fraction ok. So, let us first write down the expression. So, we know that for critical or for incipient instability we need to find out the first and second derivative of log of activity or you can replace that also in terms of the activity coefficient or basically the activity it is basically originates from the conditions of the g E which we have looked at into earlier.

So, let me write the expression of activity based on the Flory Huggin's theory ok. So, this is something which you can write and this particular question is from the test book. So, you should let me try to, now use this expression and then what is the condition for the for incipient instability ok. This is going to be log or tau ln a 1 by tau phi 1 star P T is going to be 0 and the second derivative ok.

(Refer Slide Time: 02:40)



$$\left(\frac{\partial \ln a_1}{\partial \Phi_2^*}\right)_{P,T} = 0 \qquad ; \qquad \left(\frac{\partial^2 \ln a_1}{\partial \Phi_2^{*2}}\right)_{P,T} = 0$$

$$\frac{1}{1-\Phi_2^{*c}} - \left(1-\frac{1}{r}\right) - 2\chi^c \Phi_2^{*c} = 0 \qquad ; \qquad \frac{1}{(1-\Phi_2^{*c})^2} - 2\chi^c = 0$$

We obtain

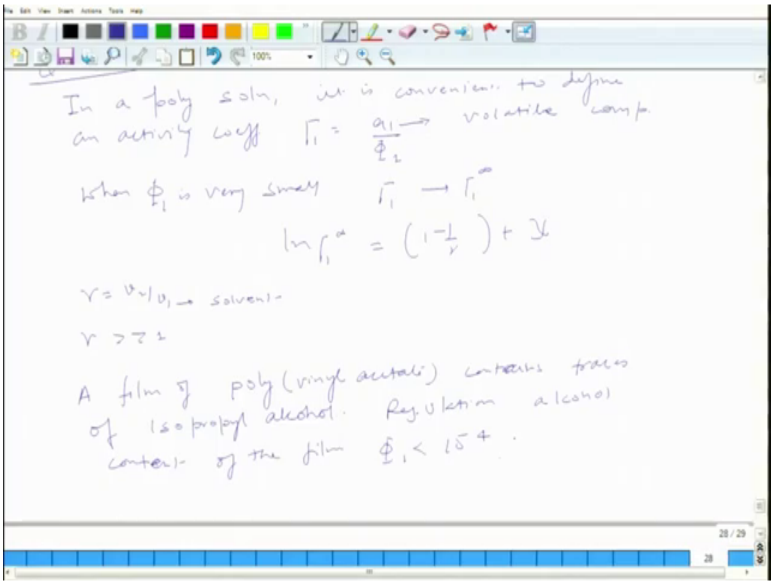
$$\Phi_2^{*c} = \frac{1}{1+\sqrt{r}}$$

$$\chi^c = \frac{1}{2}\left(1+\frac{1}{\sqrt{r}}\right)^2$$

So, this is equivalent to state that d ln a 1 d phi 2. So, the statement is equivalent these two statements are equivalent this ok. Now, if you plug in this expression here. So, you should be able to get from here 1 minus phi 2 c, minus 1 minus 1 by r minus 2 chi c phi 2 c equal to 0 and this one would be 1 pi phi 2 c 2 minus 2 chi c equal to 0.

So, using this two expression one should be able to find out what is phi 2 c phi 2 c n as well as chi c. So, if you solve this then we obtain phi 2 c as 1 by plus r and chi c is 1 by 2, 1 plus r to the power square ok. So, this is a very simple way of solving this problem where we have just made the use of the expression of the activity based on Flory Huggin’s theory and then we use the condition of incipient instability. So, let me now describe the second problem.

(Refer Slide Time: 04:33)



In a poly soln, it is convenient to define an activity coeff $\Gamma_1 = \frac{a_1}{\Phi_1}$ → volatile comp.

When Φ_1 is very small $\Gamma_1 \rightarrow \Gamma_1^{\infty}$

$$\ln \Gamma_1^{\infty} = \left(1 - \frac{1}{r}\right) + \chi$$

$r = v_2/v_1 \rightarrow$ solvent

$r >> 1$

A film of poly (vinyl acetate) contains traces of isopropyl alcohol. Regulation alcohol content of the film $\Phi_1 < 10^{-4}$.

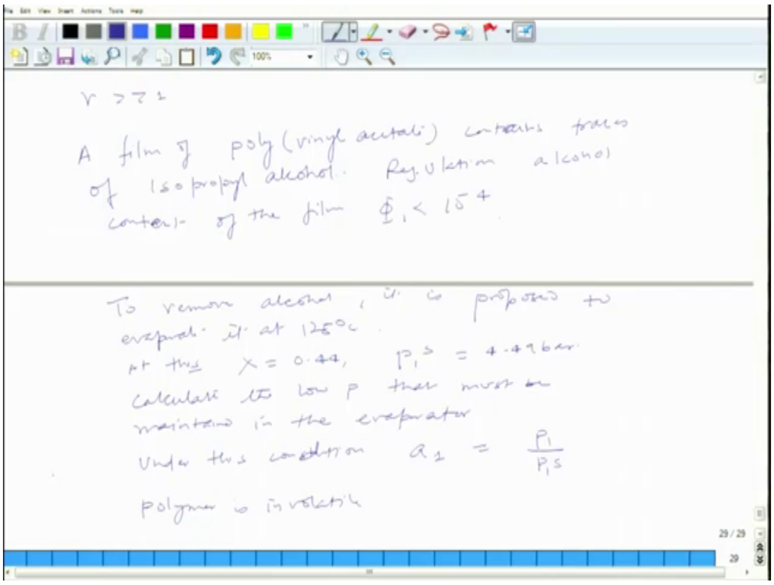
So, this is question 2, a problem 2. So, let us say in a polymeric solution it is sometimes convenient to define an activity coefficient as a 1 by phi 1 ok, where a is of course, the activity and phi is the volume fraction one represent the volatile component ok.

So, when phi 1 is small gamma 1 is written as gamma infinity and that case the Flory Huggin's theory or equation gives us the following expression ok, where chi is Flory interaction parameter and r is v 2 by v 1 where v is basically molar volume of the polymer v 2 and v 1 is for the solvent. And what we are considering is basically r is much much greater than 1 ok. So, this is the statement of the problem.

Now, let us consider specific case. So, let us assume a film of poly vinyl acetate which contains a trace contains traces of isopropyl alcohol, ok. Now, for the health reason the alcohol content of the film must be reduced to a very low value and the government regulation says that, so the regulation requires that alcohol contained of the film should be less than 10 to minus 4 ok.

So, in order to remove the alcohol it is proposed that to evaporate it at 125 degree Celsius, so to remove alcohol it is proposed to evaporate it at 25 degree Celsius 125 degrees Celsius, at this temperature the chromatography experiments gives chi as 0.44 and vapour pressure of the isopropyl alcohol is 4.49 bar ok.

(Refer Slide Time: 07:30)



$\gamma >> 1$

A film of poly (vinyl acetate) contains traces of isopropyl alcohol. Regulation alcohol content of the film $\phi_1 < 10^{-4}$

To remove alcohol, it is proposed to evaporate it at 125°C.

At this $\chi = 0.44$, $P_1^s = 4.49$ bar.

Calculate the low P that must be maintained in the evaporator

Under this condition $a_1 = \frac{P_1}{P_1^s}$

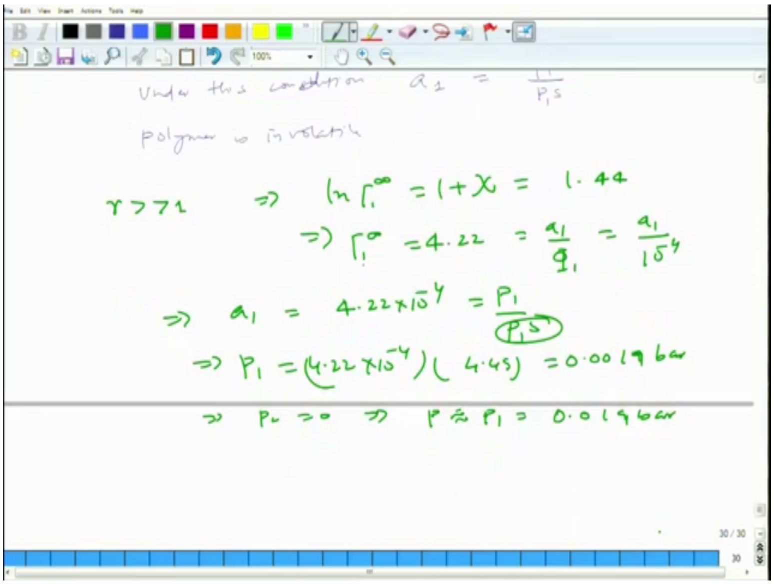
polymer is involatile

So, what we need to find out is calculate the low pressure that must be maintained in the evaporator to achieve this kind of purity of the film.

Now, under this condition what is be given is condition, so we given that activity is given as a ratio of the partial pressure by the vapour pressure and the polymer basically is in volatile ok. So, this is a very long description of the problem ok, it is very straightforward. So, what we need to find out is basically the content of the alcohol should be less than 10 to minus 4 and chi value is given the saturation pressure is given and activity is given in this ratio and polymer is basically in volatile.

So, how are you going to solve that? The very against theory is already staged that from here ln gamma 1 infinity I actually considering that the gamma is the greater than 1 this can be written as simply 1 plus chi ok. So, let me just try to solve here.

(Refer Slide Time: 09:47)



Under this condition $a_1 = \frac{}{P_{1S}}$

polymer is involatile

$\gamma >> 1 \Rightarrow \ln \Gamma_1^\infty = 1 + \chi = 1.44$

$\Rightarrow \Gamma_1^\infty = 4.22 = \frac{a_1}{\phi_1} = \frac{a_1}{10^{-4}}$

$\Rightarrow a_1 = 4.22 \times 10^{-4} = \frac{P_1}{\boxed{P_{1S}}}$

$\Rightarrow P_1 = (4.22 \times 10^{-4})(4.45) = 0.0019$ bar

$\Rightarrow P_2 = 0 \Rightarrow P \approx P_1 = 0.019$ bar

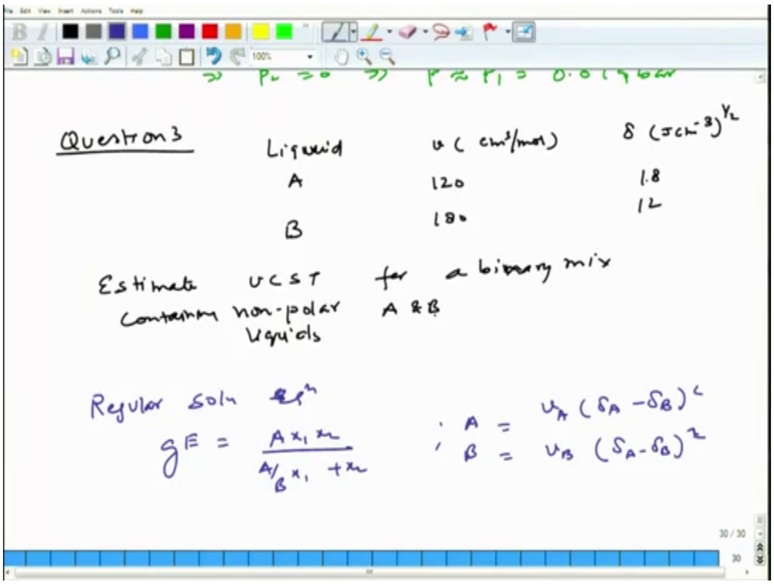
So, gamma is greater than 1 indicate ln, so that is 1 plus chi and a chi is known this is 1.44 this is, that means, this is 1.44 which essentially means gamma infinity is 4.22 ok. So, as defined what is gamma infinity? Gamma infinity definition wise is this ok. So, gamma 1 infinity I can write now, here at these conditions a 1 by phi 1 and phi 1 4 our condition need to be less than or should be less than minus 4.

So, we can contain that this is the minimum which we have to get the volume fraction. So, from here we should be able to find out a 1 is equal to 4.22 into 10 to the minus 4 which is nothing, but p 1 by p 1 stat p 1 stat we know ok, p 1 sat is given as 4.49 bar which essentially means p 1 is 4.49 this turns out to be 0.0019 bar ok.

Now, considering that the was all polymer is non volatile which essentially means p 2 partial pressure of this polymer can be considered to be 0 therefore, p is just the pressure of the evaporator can be considered as simply p 1 which is 00.19 bar ok. So, this is how we solve a very simple problem. Our description was much much lengthier, but the problem statement in general the problem was very straight forward ok.

So, now, I am going to describe the third problem which would be the last problem of the this lecture.

(Refer Slide Time: 11:55)



$\Rightarrow P_2 \to 0 \Rightarrow P \approx P_1 = 0.0196$ bar

Question 3

Liquid	v (cm^3/mol)	δ $(\text{J cm}^{-3})^{1/2}$
A	120	1.8
B	180	12

Estimate UCST for a binary mix containing non-polar liquids A & B

Regular soln eq^n

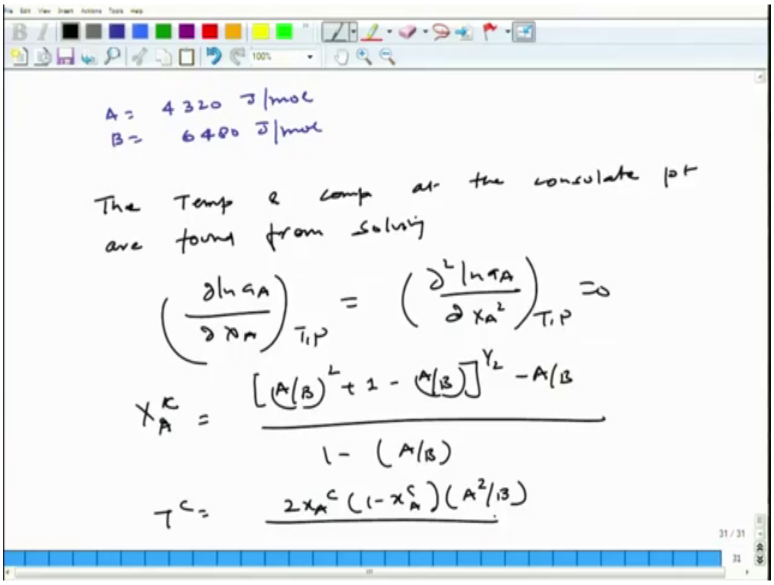
$$g^E = \frac{A x_1 x_2}{\frac{A}{B} x_1 + x_2} \quad ; A = v_A (\delta_A - \delta_B)^2 \quad ; B = v_B (\delta_A - \delta_B)^2$$

So, this is question 3. So, you have two liquids given they could let us say A and B and this is the molar volume given in centimetre cube per mole ok, this is 120, this is 180, and this is solid solubility parameters given in J joules per centimetre cube half this is 18 and 12 ok.

Now, what we need to find out is estimate upper critical solution temperature for a binary mixture containing non polar A and B ok, non polar liquid ok, all right. So, this is the problem statement and the considering is a non polar liquid solution what we can take is we can make use of regular solution theory and if you use a regular solution equation then we can we can write g E as A x 1 x 2, A by B x 1 plus x 2, where A and B are related as if you make use of Scatchard-Hildebrand expressions this would be v A delta A minus delta B square this will be v B delta A minus delta B square.

Now, this is g E from here we can of course, get the other expressions, but let us first find out what is A and Bb because we have the information of v's and delta ok.

(Refer Slide Time: 14:19)



A = 4320 J/mol

B = 6480 J/mol

The Temp & comp at the consulate pt are found from solving

$$\left(\frac{\partial \ln a_A}{\partial x_A}\right)_{T,P} = \left(\frac{\partial^2 \ln a_A}{\partial x_A^2}\right)_{T,P} = 0$$

$$x_A^c = \frac{\left[(A/B)^2 + 1 - (A/B)\right]^{1/2} - A/B}{1 - (A/B)}$$

$$T^c = \frac{2x_A^c(1-x_A^c)(A^2/B)}{\quad}$$

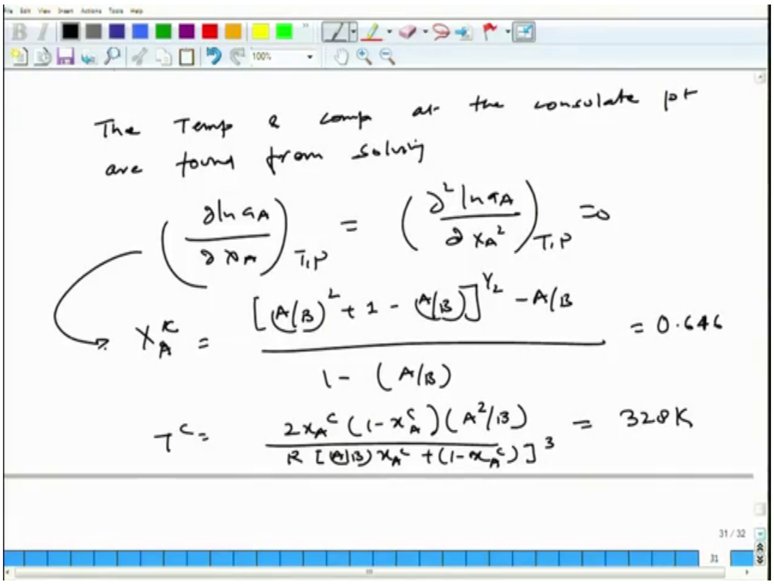
So, what would be A? If I plug in the expression from the table it turns out to be 4320 Joules per mole and for the case of B it turns out to be 6480 Joules per mole ok. Now, we need to find an upper critical solution temperature and for that you we need to find out the conditions the temperature and the composition at the consulate point.

So, again, so the temperature and composition at the consulate point that is the basically the upper critical solution temperature can be found by solving these conditions of incipient inequality or in this case we will consider the equality from solving d ln A by del x A, T P this is equal to 0 and similarly the second derivative is also equal to 0 ok.

So, now, so you can get this A’s because from here you can get the log of gamma and, so once you use that log on gamma and from there you can get this activity. So, basically you can obtain this log of A. So, this is something which we have done for regular solution theory straightforward.

So, I should be able to find, so I am going to directly write the expressions which you should be able to evaluate there is something which you can do at home. So, this is the expression which comes here 1 minus A by B, 1 by 2 A by B 1 minus A by B and T C is 2 x A C 1 minus x C A, A stand for considered point of critical composition, so divided by R A by B ok.

(Refer Slide Time: 16:59)



The Temp & comp at the consulate pt are found from solving

$$\left(\frac{\partial \ln a_A}{\partial x_A}\right)_{T,P} = \left(\frac{\partial^2 \ln a_A}{\partial x_A^2}\right)_{T,P} = 0$$

$$x_A^c = \frac{\left[(A/B)^2 + 1 - (A/B)\right]^{1/2} - A/B}{1 - (A/B)} = 0.646$$

$$T^c = \frac{2x_A^c(1-x_A^c)(A^2/B)}{R\left[(A/B)x_A^c + (1-x_A^c)\right]^3} = 328K$$

So, now, using the values of A and B you can find of x A C which turns out to be 0.646 and then if you plug in that value in this expression of T you get your critical temperature of the upper critical solution temperature is 328 Kelvin. So, this something which you can check upon doing this derivation from here to from here, till here something which you can do. So, this would be the end of the problem solving session, and the idea was to illustrate what kind of problem you can solve using this solution theories and in general the approach.

I hope that you get an expo you know you got some kind of understanding of the problem of this particular course particularly the solution theories and later part of the course ok. So, I will stop here and I hope you have wonderful learning in this course and you can always write to me over emails, on forum.

If you have some problems something which you interest you and if this was not covered is just because you know there are so many things to cover as far as the solution theories are concerned, and with this limited time we could only cover a limited scope and you probably have got an idea and you can take it from here by looking at the text book which we are looking as a reference text.

So, with that good luck wish you all the best for the exam and perhaps see you in the next time.