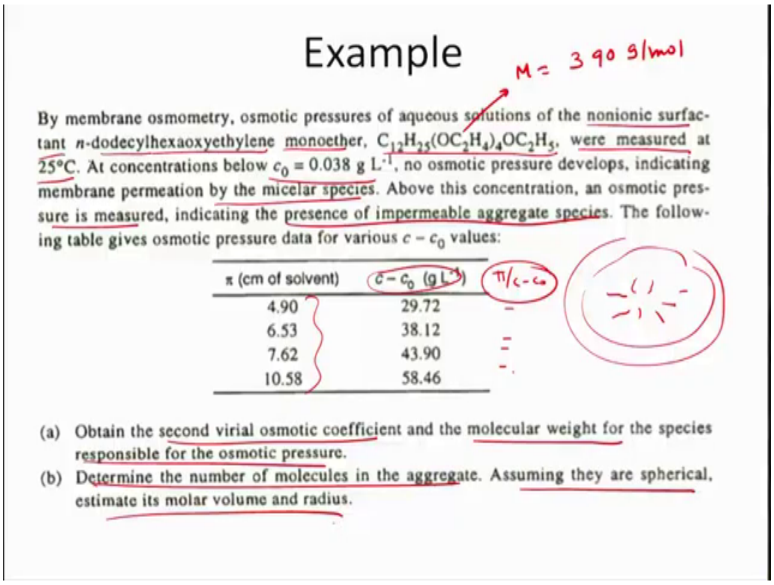
Thermodynamics of Fluid Phase Equilibria
Dr. Jayant K Singh
Department of Chemical Engineering
Indian Institute of Technology, Kanpur

Lecture - 41
Membrane Osmometry

Welcome back. So, in this short lecture I am going to take an example. So, this is an example on Membrane osmometry.

(Refer Slide Time: 00:23)



Example

$M = 390$ g/mol

By membrane osmometry, osmotic pressures of aqueous solutions of the nonionic surfactant *n*-dodecylhexaoxyethylene monoether, $C_{12}H_{25}(OC_2H_4)_4OC_2H_5$, were measured at 25°C. At concentrations below $c_0 = 0.038$ g L^{-1}, no osmotic pressure develops, indicating membrane permeation by the micelar species. Above this concentration, an osmotic pressure is measured, indicating the presence of impermeable aggregate species. The following table gives osmotic pressure data for various $c - c_0$ values:

π (cm of solvent)	$c - c_0$ (g L^{-1})	$\pi/c-c_0$
4.90	29.72	-
6.53	38.12	-
7.62	43.90	-
10.58	58.46	-

(a) Obtain the second virial osmotic coefficient and the molecular weight for the species responsible for the osmotic pressure.

(b) Determine the number of molecules in the aggregate. Assuming they are spherical, estimate its molar volume and radius.

Where osmotic pressures of aqueous solution of a nonionic surfactant n-dodecylhexaoxyethylene monoether which is the complex here, you can see the formula which was measured at 25 degree Celsius ok, at concentration below this 0.038 gram per liter there was no osmotic pressure developed, indicating that the membrane permission by the micelar species.

Say remember that osmotic pressure means that certain will develop only when you have some specific one of the ion, one of their compound moves for example, for the case as a solvent the solute, solute is also only diffusing then there will be a osmotic pressure developed here or vice versa.

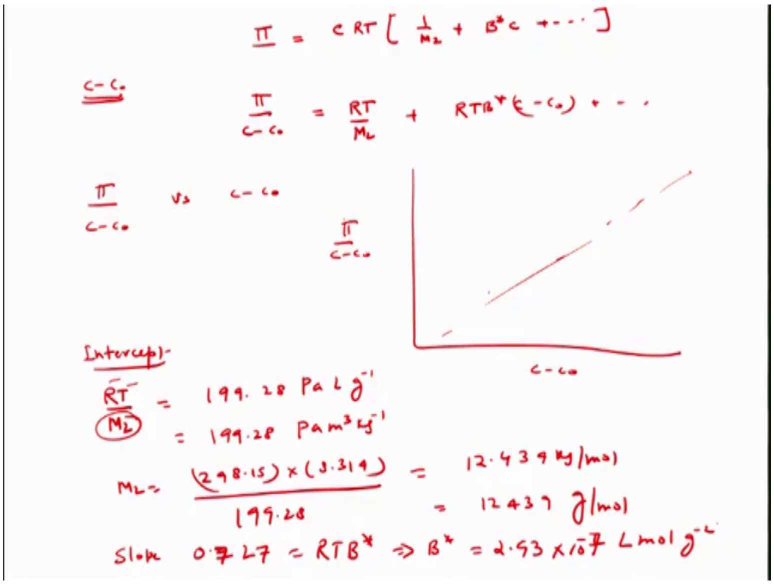
So, in this case a of this concentration that the concentration 0.038 and osmotic pressure is measured indicating the presence of impermeable aggregate species. So the reason why they are showing aggregate species? Because when you put any surfactant in a solution they tend to also aggregate, but that aggregation depends on the concentration. So, what is saying that f of this concentration and osmotic pressure is measured indicating the presence of impermeable aggregate species.

Whereas below this the membrane permeation by the molecular micelle a species ok, which essentially means it was trying to have some kind of micelles like this right and, it was kind of diffusing permeate, it was allowed to permeate and because the base was permeating then there was no specific protect pressure difference across it, but where after certain concentration; there is a aggregate this becomes bigger and because of that there was impermeable aggregate species.

So, only solvent was diffusing, but no species or aggregation aggregate species were diffusing. There could be monomers and dimers and so forth as possible, they may diffuse, but this aggregate was not refusing ok. So, what they measure this osmotic pressure for concentration greater than c 0 and it was tabulated in this way. So, the question is to find out the second virial osmotic coefficient and the molecular weight of the species responsible for the osmotic pressure.

There is a very many practical examples you can think of right and determine the number of molecules in the aggregate that is the second part. Assume they are spherical, estimated molar volume and radius ok. I will try to solve some part of it and leave others you know you to you to ponder on certain other part. Now what about the first part? First part is actually straightforward; if you look at the expression of the pie with respect to the concentration which we have written.

(Refer Slide Time: 03:44)



$$\pi = cRT\left[\frac{1}{M_2} + B^*c + \cdots\right]$$

$c - c_0$

$$\frac{\pi}{c-c_0} = \frac{RT}{M_2} + RTB^*(c-c_0) + \cdots$$

$\frac{\pi}{c-c_0}$ vs $c - c_0$

Intercept -

$$\frac{RT}{\boxed{M_2}} = 199.28\ \text{Pa L g}^{-1}$$
$$= 199.28\ \text{Pa m}^3\text{kg}^{-1}$$

$$M_2 = \frac{(298.15)\times(8.314)}{199.28} = 12.439\ \text{kg/mol}$$
$$= 12439\ \text{g/mol}$$

Slope $0.727 = RTB^* \Rightarrow B^* = 2.53\times10^{-7}\ \text{L mol g}^{-2}$

We considered not much dilute solution we wrote something like this, pi is equal to some concentration C R T 1 by M 2 plus B star C and so forth ok, this was what we written.

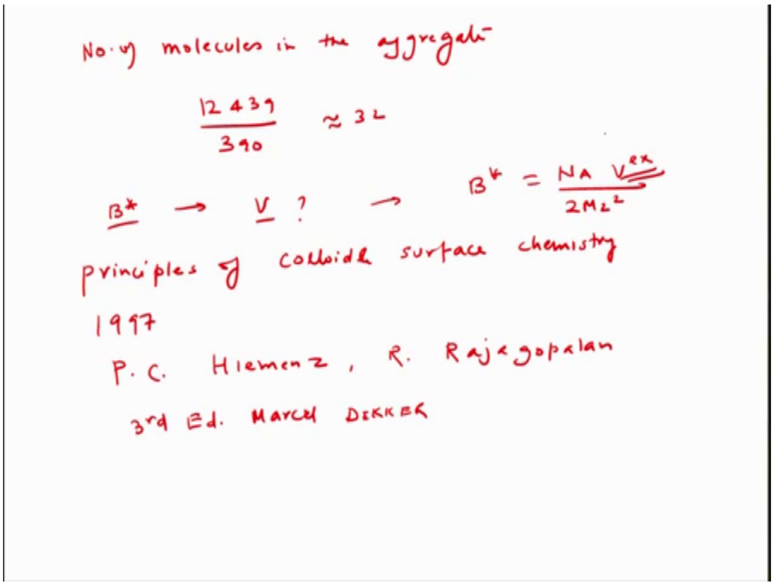
Now, what about the C here, C considering that this concentration is C minus C 0 because this is the amount, which you are talking about so, this we are going to write it like this C minus C 0 is equal to R T by M 0 M 2 plus R T B star C minus C 0 ok, I am not interested in the higher order terms. So, if you plot pi by C minus C 0 versus C minus 0, then I should be able to calculate.

So, if I use pi by C minus C 0 ok, then I should be able to get some data part this turns out to be linear ok. So, without scaling anything I do not want to draw a scale here, but the idea is you have to use this data; which is shown here and given to us. So, this data is available right. So, you right here pi by C minus C 0 and get the data so, you can plot this versus this ok and if you get that then you should be able to obtain the intercept ok. So, you use least square fitting in this such a case.

So, if you do that you get intercept which turns out to be 199.28 Pascal liter gram per gram, you have to convert into the units well because, this is an important part of calculation. Now I know R, I know T so I can get M 2; M 2 turns out to because this is the 25 degree Celsius experiment.

Now, I can comfortably write 199.28 because, everything in the SI unit and this is nothing, but 12.439 kg per mole ok, or you can write as gram per mole also which is going to be 12439 gram per mole. Now what about the slope; slope is 0.727 which is nothing, but R T B star. So, I have now B as 2.93 into 10 to the power minus 7 liter mole gram square per gram square B is a coefficient which provides you the idea about their interactions, whether the instructions are effectively attractive or repulsive.

(Refer Slide Time: 07:17)



No. of molecules in the aggregate

$\frac{12439}{390} \approx 32$

$\underline{B^*} \rightarrow \underline{V} \; ? \rightarrow B^* = \frac{N_A V^{ex}}{2M_2^2}$

principles of Colloid surface chemistry

1997

P. C. Hiemenz, R. Rajagopalan

3rd Ed. Marcel DEKKER

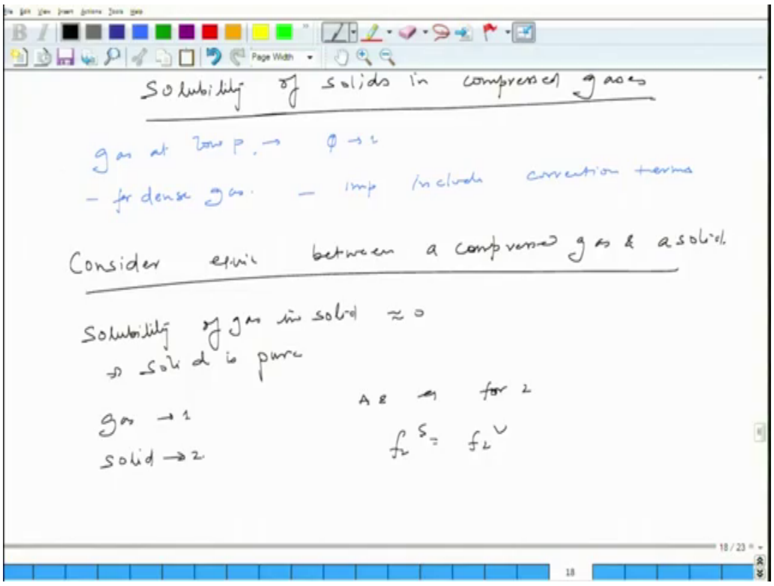
So, now you have datas you have calculated your molecular weight. Now the question is what is the number of molecules in the aggregate? That is a question. Now, let us look at this ok. So, this is the nonionic surfactant for a monomer the what is the molecular weight of this? This is this will turn out to be 390 gram per mole ok, 390 gram per mole and what is the value we got for M 2 12439.

So, certainly is a aggregate so we can simply divide it. So, 12439 divided by 390 is 32. So, this is the aggregate in the molecule, but what about the other part of the question which is; if you assume this aggregate to be spherical estimate is more of volume and radius. Now, this is a bit tricky because this is something which you need to connect B star to V.

How we are going to do that. So, apparently without going into details I would like you guys to check take a look at the book, which is principle of collides and surface chemistry. So, here in this book the B is well connected or is related to the excluded volume, through this relation ok. This is the excluded volume and from there we can obtain the using this a spherical nature of the aggregate to obtain the volume ok.

So, you need to know how to get use of this you know this excluded volume concept, but I would like you to look into this, if your interest is to obtain this all right. So, with this I can now move on to another topic which will be very short again. So, I will just talk about a solubility of solids and I want to talk about the liquids as well, but since we have not discussed much Henry's law. So, I will defer this expect once we cover the liquid mixtures part.

(Refer Slide Time: 10:15)



Solubility of solids in compressed gases

gas at low p. → $\phi \to 1$

– for dense gas. — imp include correction terms

Consider equi between a compressed gas & a solid.

Solubility of gas in solid ≈ 0

⇒ solid is pure

gas → 1

solid → 2

At eq for 2

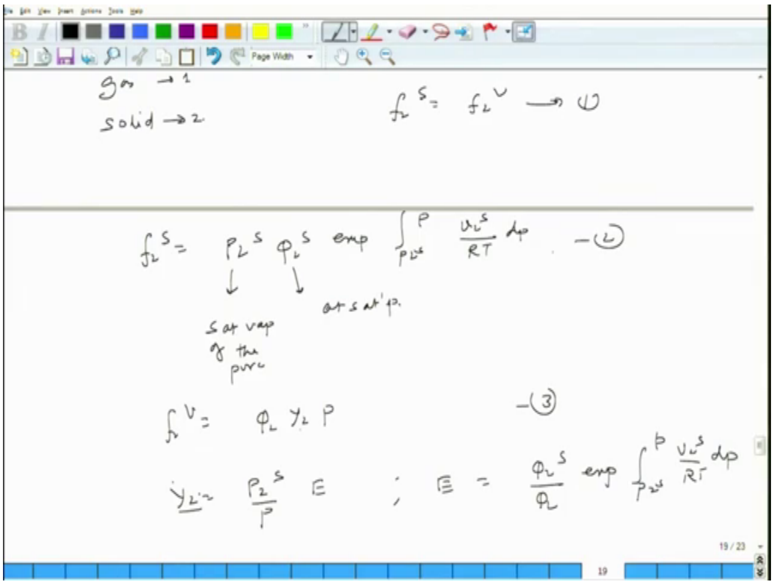
$f_2^S = f_2^V$

So, we will just talk about only the solids in compressed gases ok. For the case of the gas at low pressure, we can take the vapor pressure of vapor phase fugacity as simply one right, but this the vapor phase fugacity becomes an important parameter when you consider let us say solubility of a solid or high you know volume liquid; that means, they are very dense for particularly the densest dense gases.

So, if the gas is dense you have to understand how to get the fugacity coefficient of the gas phase. So that means, that for dense gas, it is important to include correction terms right; that means the fugacity coefficient; which will capture the non-ideality. So, let me describe the system to pressure this. Consider equilibrium between a compressed gas and solid ok.

Now so we are talking about a compressed gas and a solid and solid will not have any diffusion of the gas. So, we assume that basically the solubility of gas in solid is negligible 0 ok and thus which means basically solid is pure right. So, we consider a gas as 1 and solid as 2. So, at equilibrium let us say for 2 for solid f of 2 S is f of 2 V ok, which means basically the fugacity of a solid component in the solid phase should be same as a fugacity of the solid component in the vapor phase; that is what we are talking about ok.

(Refer Slide Time: 13:30)



gas → 1

solid → 2

$$f_2^S = f_2^V \rightarrow ①$$

$$f_2^S = \underset{\substack{\downarrow \\ \text{sat vap} \\ \text{of the} \\ \text{pure}}}{P_2^S} \; \underset{\substack{\downarrow \\ \text{at sat' p.}}}{\phi_2^S} \exp \int_{P_2^S}^{P} \frac{v_2^S}{RT} dp \quad -②$$

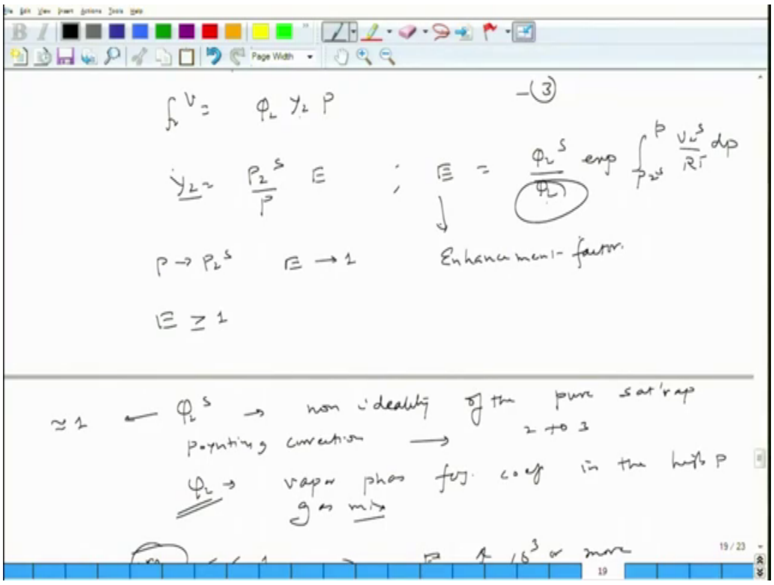
$$f_2^V = \phi_2 y_2 P \quad -③$$

$$\underline{y_2} = \frac{P_2^S}{P} E \quad ; \quad E = \frac{\phi_2^S}{\phi_2} \exp \int_{P_2^S}^{P} \frac{v_2^S}{RT} dp$$

Now, since f 2 S is a pure we can straight away connect this f 2 S as P 2 S, phi 2 S, exponential P 2 S, P v 2 S by R T dp right, this we can write and this is nothing but the saturation vapor of the pure solid right. Because we are talking about solid and this is at saturation pressure right ok and for the vapor phase we can simply write the standard expression that f 2 V is phi 2 y 2 P; I have this relation and I can I can make use of this.

So, this is 1, this is 2 and 3 using 2 and 3 plugging in to 1, I can write as y 2 here as P 2 S by P and some factor E ok, where E contains everything E contains phi 2 S by phi 2 exponential P 2 S P V 2 S by R T ok. So, this is what which is so y 2 is nothing, but the solubility of the solid phase in the vapor right; that is a composition or mole fraction ok.

(Refer Slide Time: 15:11)



$$f^V = \phi_2 y_2 P \qquad -③$$

$$y_2 = \frac{P_2^S}{P} E \quad ; \quad E = \frac{\phi_2^S}{\boxed{\phi_2}} \exp \int_{P_2^S}^{P} \frac{V_2^S}{RT} dp$$

$E \downarrow$ Enhancement factor

$P \to P_2^S \quad E \to 1$

$E \geq 1$

$\simeq 1 \leftarrow \phi_2^S \to$ non ideality of the pure sat vap

Poynting correction $\longrightarrow$ 2 to 3

$\phi_2 \to$ vapor phase fug. coef in the high P gas mix

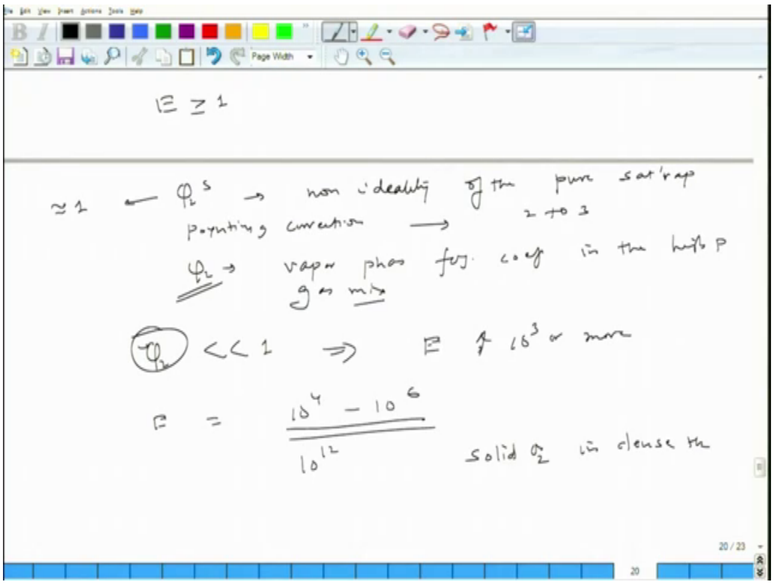
$E \uparrow 10^3$ or more

So, now we can just talk about what is E; E is nothing, but the enhancement factor so, when E is 1 when P approaches to P P 2 S and, when P approaches to P 2 S basically E approaches to this. So, E is greater than or equal to 1 in fact, many times for many cases this E is much larger than 1.

So, what are the components of E if you look at E contains pointing factor phi 2 S, phi 2; 3 parameter right. So, which one is the most important parameter what is the phi 2 S represent? Non ideality of the pure saturated vapor and pointing correction of course, we all know that pressure effect what is phi 2? This is the vapor phase fugacity coefficient in the high pressure gas mixture right.

Because it is dense the pressure will be very high, it is not a low pressure system at all. And this is the one which plays a bigger role, the pointing correction will continue to some number like 2 and 3 to E; phi 2 is typically small so, phi 2 will be close to 1 ok, but phi 2 S will be close to 1, but what about phi 2? Phi 2 will be much much less than 1, which essentially means because phi 2 is here right that E will increase ok, sometimes to 10 to the power 3 or more so, pointing fraction will give you 2 to 2 to 3 numbers like times and because of this phi 2 it is important that we calculate it very well.

(Refer Slide Time: 17:21)



$E \geq 1$

$\simeq 1 \leftarrow \varphi_2^s \rightarrow$ non ideality of the pure sat'vap

2 to 3

Poynting correction $\rightarrow$

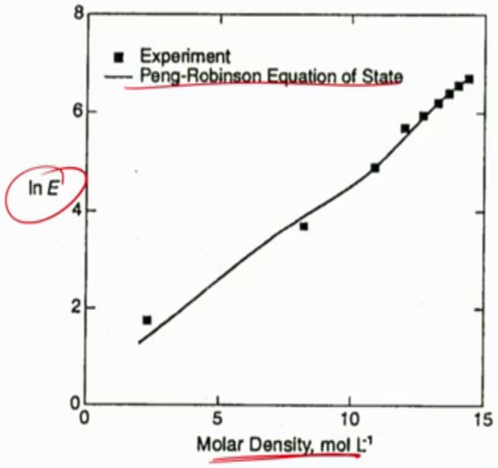
$\varphi_2 \rightarrow$ vapor phase fug. coef in the high P gas mix

$\varphi_2 << 1 \Rightarrow E \uparrow 10^3$ or more

$E = \frac{10^4 - 10^6}{10^{12}}$ solid O_2 in dense H_2

So, E will tend it to be typically in the range of 10 to power 4 to 10 the power 6 which are common, but you can also have 10 to the power 12 that large number and this is the case for example, in the case of solid oxygen in dense hydrogen ok, very specific case, but this is a common molecular system. So, E is a enhancement factor which plays an extremely important role in the solubility of solids and gases ok.

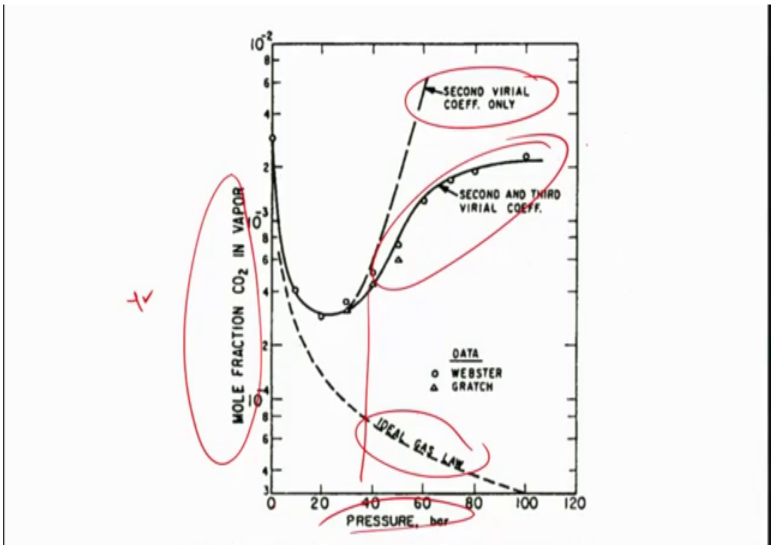
(Refer Slide Time: 18:00)



Enhancement factors for solid CCl_4 in supercritical CF_4 at 249 K.

So, let me show you that how do we actually make use of equation of state by few examples. So this is the E in a logarithmic scale and for the case of a solid CC l 4 in supercritical CF 4 at this temperature and as you increase the molar density. Now, I make it more denser pressure is more the enhancement factor increases ok. This is the logarithmic scale and you can clearly see that this equation of state was well captured; you know could capture the behavior very well and is in line with the experiments ok.

(Refer Slide Time: 18:36)



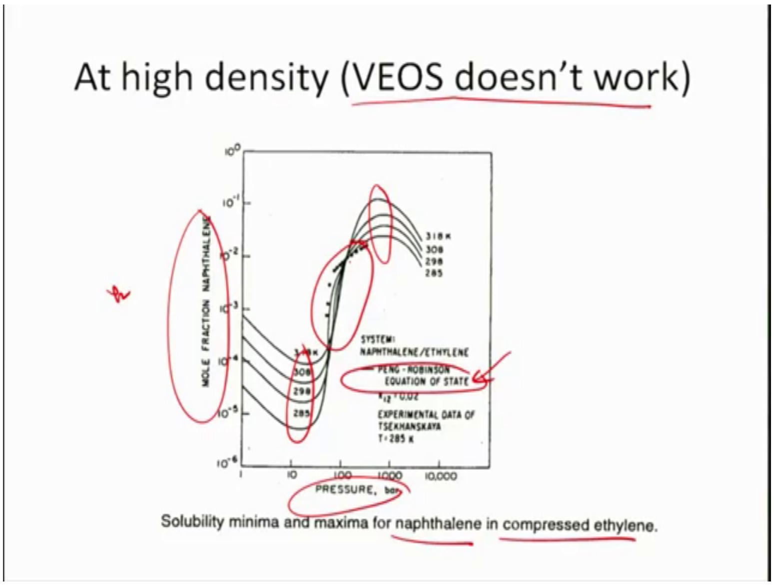
Solubility of solid carbon dioxide in air at 143 K.

Now, here this is the solubility of solid C a C o 2 in air at 143 Kelvin, this is a mole fraction of C o 2 the solubility that is what you talk of y 2 as a function of pressure and this is the symbols are the experimental data, if you would may, if you had used only the ideal gas it could capture only very little amount very low pressure. If you use only the second virial coefficient that. If you using the equation of state with the only second virial coefficient, then it can capture again up till certain pressure which is up till 40 bar.

So, if but for higher pressure you need to also add the third coefficient in order to get the right equation of state. So, virial coefficient has its own issues ok, if you want a correct equation of state you know, they are the equation of state, but such as Peng Robinson these are the equations well you know developed, but virial coefficient there is a possibility if you increase the density of this you may also need another term the fourth virial coefficient also.

But apparently for this for this condition third way the coefficient works very well for this region where, if you had used only the second little coefficient it fails to capture the high pressure you know domain ok. In addition you can also see a very unusual cases such as the maximum and, you know low minimum in the solubilities.

(Refer Slide Time: 20:00)



At high density (VEOS doesn’t work)

Solubility minima and maxima for naphthalene in compressed ethylene.

So, this is the case of naphthalene in compressed ethylene ok, at different temperature and this is a mole fraction again y 2 is vapor phase pressure and the virial equation on state in this case does not work; if you had to use this it will fail. So, the datas again here you can see this is this is here the datas are limited, but if you had used Peng Robinson equation of state then it captures this as well as shows that there is a maximum and there is a minimum solubility which depends on the pressure.

So, having also fitted this you can also predict this kind of thing using basically the equation of state which is this one. So, remember that this we do not have the data exponent so this is like a obtaining this information right from the equation of state where, this captures the intermediate pressure range all right. So, I hope that it gives you an idea of how this has played an important role in thermodynamics molecular thermodynamics in particular.

And in the next lecture we will start fugacity of liquid mixtures. So, hopefully you get to learn little more about liquid phase and as well as the utility of activity coefficients and we also talked about the Henry’s law. So, I will see you in the next lecture.