Thermodynamics of Fluid Phase Equilibria
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Lecture - 39
Molecular Interactions in Dense Fluid Media

Welcome back. In this lecture, we are going to describe a molecular interaction in dense fluid media.

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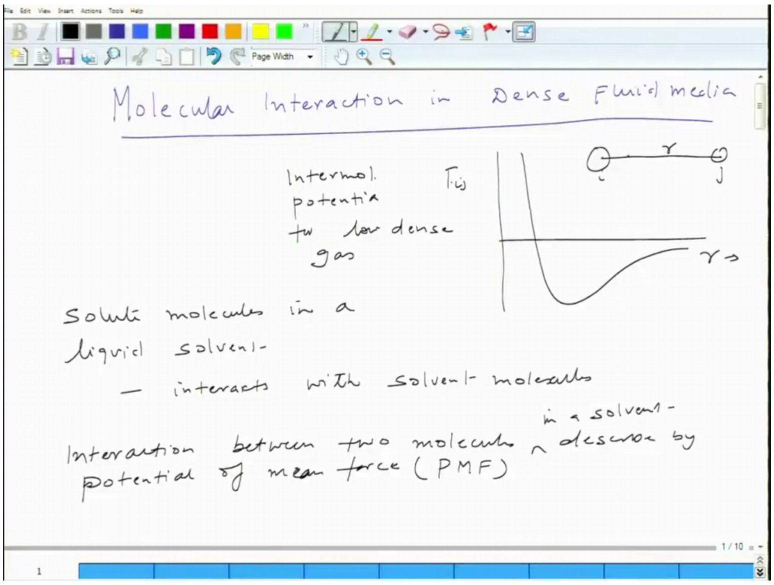

Molecular Interaction in Dense Fluid media

Intermol. potential for low dense gas

Solute molecules in a liquid solvent
— interacts with solvent molecules

Interaction between two molecules in a solvent - described by potential of mean force (PMF)

So, if you recall we looked into the different potential models in the last few lectures; however, they were kind of potential models in vacuum ok; that means, essentially when we consider two particles coming from very far only two particles; what would be the typical kind of potential energy.

So, we described using different kind of a potential models such as square wall then a zones models so the land exponential say (Refer Time: 00:55) and so forth, but in the solution when you bring two particles or tool that says solute closer to each other, it has to also experience if you know a solvent interaction in other word, it must repel the solvent molecules in order to come closer ok.

Thus the kind of effective interaction between the solid solute may not be the same as that seen in the case of a vacuum ok. So, let me just draw the typical interaction which we know when you; it is like a linear zones when you bring one particle i and particle j from very far from let us say distance r where r can vary from infinity to somewhere near the molecular size.

So, this is a typical interaction or intermolecular and potential for low dense gas. So, essentially for the low dense or gas system when you bring the two particles close enough they typically do not experience other molecules present in the system because they are extremely far because of extremely large volume ok. But in the case of a solid molecules; in a liquid solvent, it interacts with the solvent molecules.

So, molecules; so in this case how do you present the effective interaction between two solid molecules. So, we typically represent this kind of effective interaction between two solid molecules in a solvent medium by something we call it potential of mean force. So, the interaction between two molecules is described by two molecules in this you know solvent is described by potential of mean force; it is called sometimes PMF also.

So, remember like in the in vacuum our low dense gas medium the two particle interaction can be described by potential models such as linear zones which I have drawn here, but in case of a solvent molecules present in the system the two particle interaction could be represented by something called potential of mean force.

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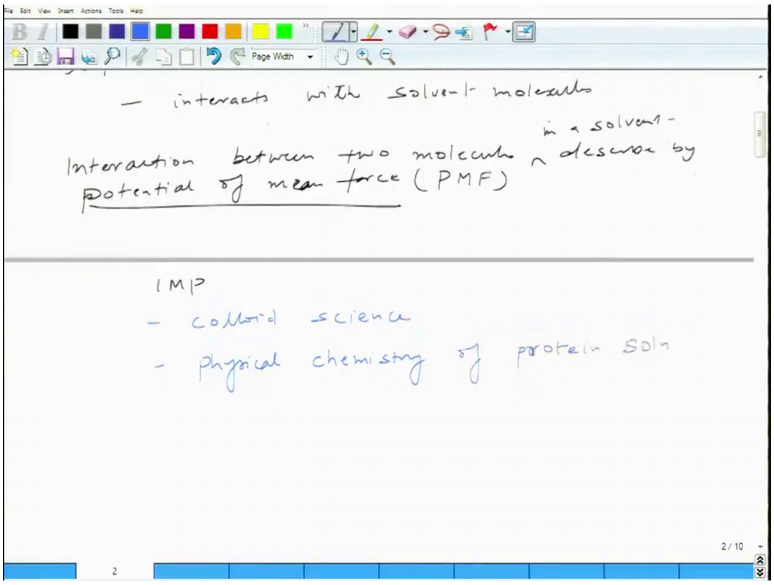

– interacts with solvent molecules

Interaction between two molecules in a solvent described by
<u>potential of mean force</u> (PMF)

IMP
- colloid science
- physical chemistry of protein soln

Now, this is this plays a very important role. So, it is important this potential of mean force is important in colloidal science and physical chemistry of protein solution Now this potential of mean force incorporates the nature of the solvent what does it mean that if you change the solvent there and you keep the solute fixed the effective interaction between the solute will also change ok.

So; that means, the nature of the solvent will affect the potential amaze force or intermolecular interaction between the solute. Let us try to understand little more schematically this concept. So, let me just draw effect kind of a solvent molecules like a this sphere.

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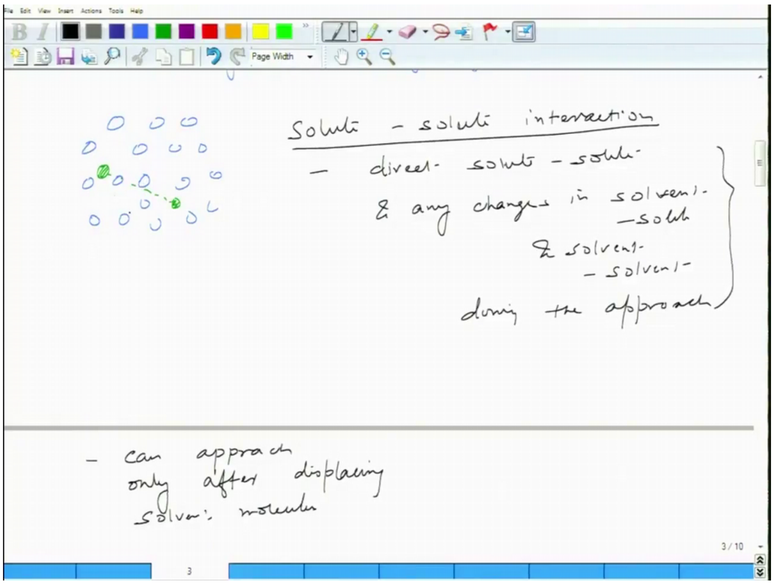

Solute - solute interaction

- direct solute - solute
  & any changes in solvent - solute
  & solvent - solvent
  during the approach

- can approach only after displacing solvent molecules

Now, let us say this is this is a one solute and this is another solute. Now in order to this solute come closer ok; when you are bringing this close enough it must repel this blue circles. Now effective solute-solute interaction now includes a direct solute-solute. So, this will be direct solute-solute interaction and as well as any changes in solvent and solute solvent and solute and solute solvent and solvent ok; during the approach. So, effective solute-solute interaction will have all this contribution. Now let us consider a case like you have a solute which typically is attractive to each other in vacuum. So, when you bring it closer, it can be represented by simple inner zones potential which has a minima essentially means that another solute will try to approach to the minimum value.

Now, consider the same solute in solvent, it can approach only after displacing solvent molecules ok; which is the case if you consider this; for example, you let us assume that you trying to keep this fixed and you bring it from here to here in order to this to come here you must displace this and this as well ok.

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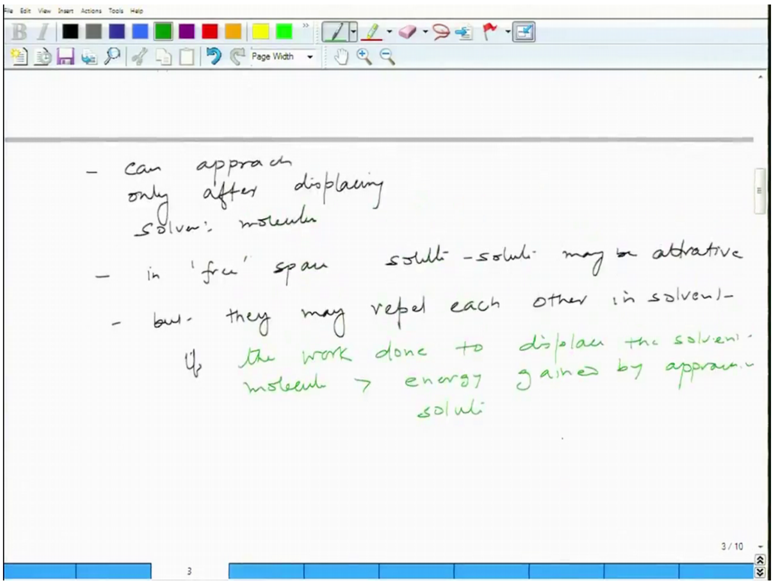

- can approach only after displacing solvent molecules
- in 'free' space solute-solute may be attractive
- but they may repel each other in solvent
  - if the work done to displace the solvent molecule > energy gained by approaching solute

So, you should get it should displace in order to come closer. Now, as I said that in free space the solute-solute may be attractive, but now it is possible that they can repel. So, while it is attractive in the free space, but when you consider the solvent and you try to bring it closer, it is quite, it is also possible that the solute will repel and the repulsion depends on two things ok, let me just write down that; that means, they can repel each other insolvent.

If the work done to displace the solvent molecule is less; is greater than the work done to displace the solute molecule is greater than the energy gained by approaching solute. So, what is this statement says that that if the final state where their solute-solute is close enough that energy is less than the work which requires to bring the solute together or closer in that case the solute will not prefer to be close and they will repel ok; for simple reason is that it will take more energy to bring in and the gain is much less.

And we know the system prefers to have a minimum energy and thus they would not like to come. So, a case where the solute-solute are attractive in the free space will become repulsive in solvent that is something which is a common case.

Now, in addition to that the solute can perturb the solvent molecules and then local ordering of this now due to that there is another contribution which is basically the solvation force which may arise ok.

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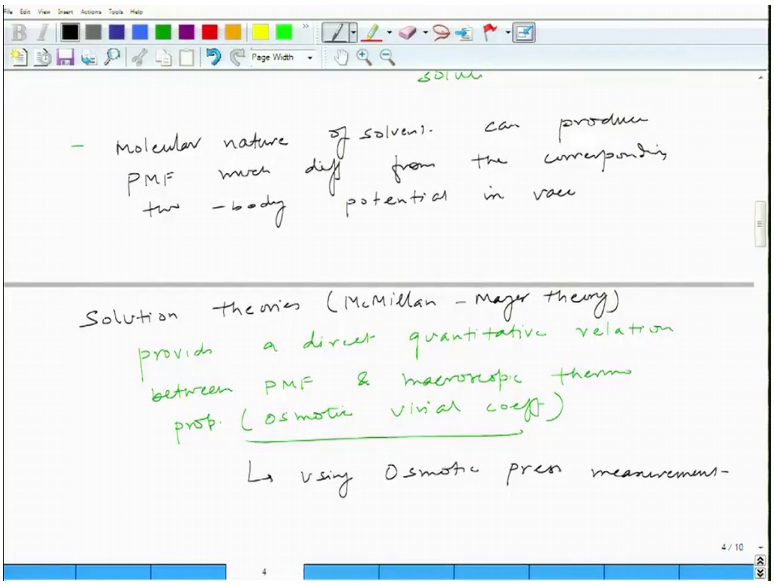

- Molecular nature of solvent can produce PMF much diff from the corresponding two-body potential in vac

Solution theories (McMillan - Mayer theory)
provides a direct quantitative relation between PMF & macroscopic thermo prop. (osmotic virial coeff)
↳ using Osmotic press measurement

Now, considering that the solvent can be of different type which essentially means that that molecular nature all solvent can have effective can affect the potential of mean force or effective interaction between the solute significantly.

So; that means, molecule nature of solvent can produce PMF much different from the corresponding two body potential in two body potential in vacuum ok. So, this is something which is already clear in this discussion here. So, what is a PMF; PMF is nothing but the measure of intermolecular forces between the solute molecule in solvent ok.

And this is something which is going to be different from the corresponding to the to the body potential in vacuum. Now this is why we are discussing this because we would like to provide a quantitative information of PMF and macroscopic thermodynamic property which apparently many solution thermo dynamics many many solution theories have looked into.

So, for example, solution theory such as Mc Millan Mayer theory, it provides a direct quantitative relation between PMF and macroscopic thermodynamic property. So, what is this property this property such as osmotic virial coefficient and this is something which we can obtain using osmotic pressure measurements, ok.

So, now what I am going to do is I am going to describe this osmotic pressure. So, let me describe this osmotic pressure and which is extremely useful for large molecules to evaluate their molecular weight and so forth. So, come to that very soon. So, what is this osmotic pressure? This before going into the details this is something which is often encountered in nature ok; especially in biological systems ok.

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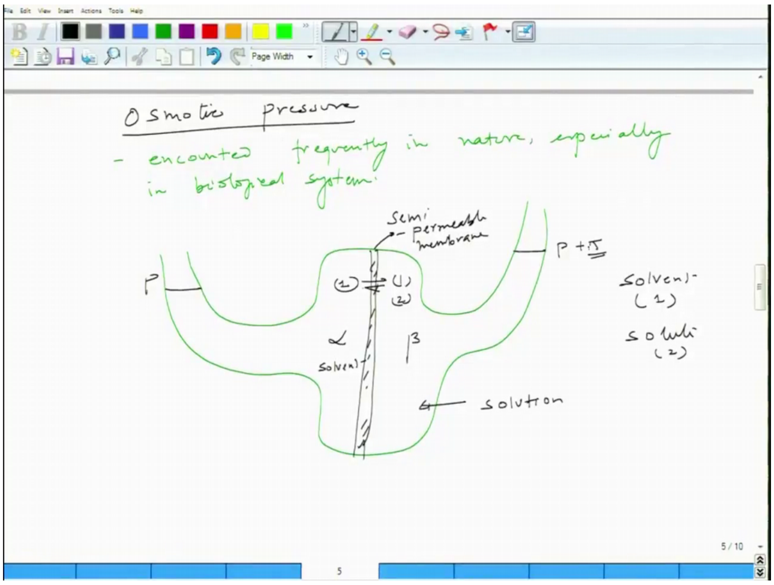

Osmotic pressure

- encountered frequently in nature, especially in biological system.

So, let me first draw a schematic representation where this osmotic pressure comes into consideration. So, let us consider a system; something like this where you have this at pressure P, this is at pressure P plus pi and this vessel this could be a biological system this is separated by a semi-permeable membrane which allows only solvent to pass through, but does not allow the solute ok.

So, let us consider the solvent here is one and. So, this is a solute plus solvent. So, this is a solution where you have 1 and 2s solute is 2 and it allows only one to pass so; that means, here you have 1. So, there are two phases here. So, this is phase alpha and this is phase beta ok; and this is only solvent here. So, in such a case the left hand side is at pressure P and the right hand side at pressure P plus additional term called pi which is basically nothing but the osmotic pressure.

Now, I would like to come up with a relation of this pi with thermodynamic quantities such as temperature pressure and concentration. So, that is the objectivity of this exercise here ok. Now initially they may not be at equilibrium, but after certain time it reaches an equilibrium and then we can we can consider that at chemical at equilibrium you have a chemical equilibrium condition which you can evoke.

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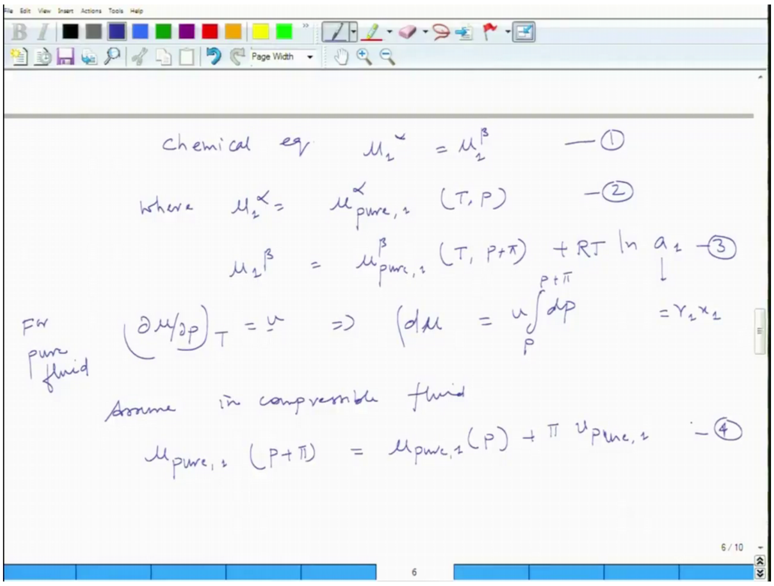

Chemical eq $\mu_1^\alpha = \mu_1^\beta$ — ①

where $\mu_1^\alpha = \mu_{pure,1}^\alpha (T, P)$ — ②

$\mu_1^\beta = \mu_{pure,1}^\beta (T, P+\pi) + RT \ln a_1$ — ③

$\downarrow$

$= \gamma_1 x_1$

For pure fluid $\left(\partial \mu / \partial p\right)_T = \underline{v} \Rightarrow \int d\mu = v \int_P^{P+\pi} dp$

Assume incompressible fluid

$\mu_{pure,1} (P+\pi) = \mu_{pure,1} (P) + \pi \, v_{pure,1}$ — ④

So, mu 1 again we are looking at solvent is 1, solute is 2, alpha is phase should be same as mu 1 beta ok. So, this tells you that the chemical potential of solvent in phase alpha should be same as chemical potential of solvent in phase beta. Now the next thing which we need to do is to connect this chemical potential to other properties or thermodynamic variables which we can evaluate.

So, let us consider a phase alpha; now phase alpha contains pure solvent. So, what I can write here mu 1 alpha is mu alpha pure one at temperature T P whereas, mu 1 beta is mu beta pure one at T P plus pi, but considering that; now this is a solution you are going to write RT ln a 1; a is the activity which is given as gamma 1 activity coefficient multiplied by composition ok.

This is something which we have briefly we touched upon but we are going to look into this activity more in detail in very soon as few lectures from now ok. So, now, this is the important part, let me just write down this is equation 1 2 and 3 ok.

Now considering the alpha phase is pure in general what we can do is in general if you are looking at pure fluids we can write down this expression del mu by del p at constant temperature is equal to molar volume this is for pure weight ok.

Now, assume in incompressible fluid. Then I can write down this I can expand this considering u is going to constant then I can write mu pure 1 at if you integrate this as this would be on P plus pi is equal to mu pure one P and this delta p is nothing but pi u pure 1. So, this is now expression.

Now, I can plug the same in equation 3; therefore, three can be written as minus l n a 1. So, if I plug in here ok; then I get this expression pi V pure 1 divided by RT ok. So, this is the expression; now I can make use of this expression to simplify. So, for by considering dilute solution where, basically, the concentration of the solvent is almost close to 1 and the concentration or the mole fraction is almost close to 1 and that for the solute is close to 0.

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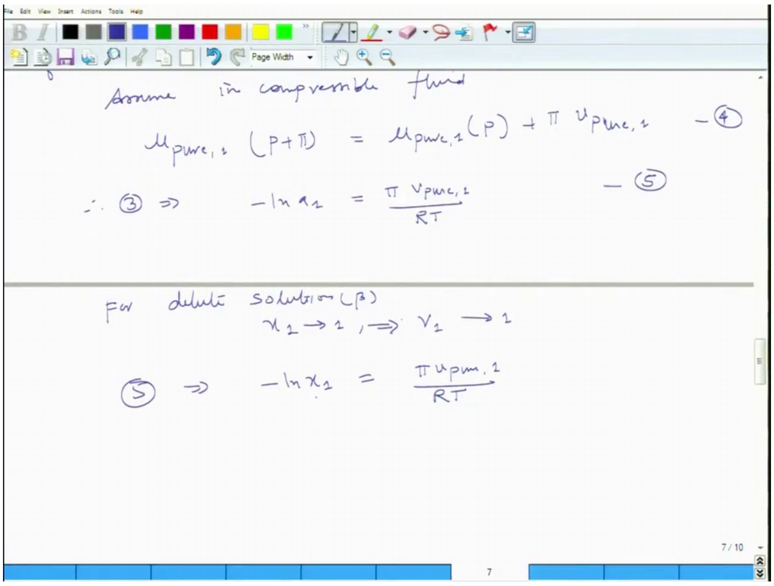

Assume in compressible fluid

$$\mu_{pure,1}(P+\Pi) = \mu_{pure,1}(P) + \Pi\, v_{pure,1} \quad - ④$$

$$\therefore ③ \Rightarrow \quad -\ln a_1 = \frac{\Pi\, v_{pure,1}}{RT} \quad - ⑤$$

For dilute solution (β)

$$x_1 \rightarrow 1, \Rightarrow \gamma_1 \rightarrow 1$$

$$⑤ \Rightarrow \quad -\ln x_1 = \frac{\Pi\, v_{pure,1}}{RT}$$

So, in other word; for dilute solution that is beta phase or dilute solution; a x 1 is 1 when x 1 is 1. So, this is beta phase right and then basically we are saying this implies that gamma 1 is 1 ok. In other word I can write 5; equation 5 will become minus l n and x 1 is equal to pi v pure 1 by R T ok.

Now, I am interested it basically in the mole fraction or the x of 2. So, in such case; when x 1 is 1 or in the word, when x 2 is much less than 1; then l n x 1 is equal to l n 1 minus x 2 and since x 2 is very small, I can write this as x 2. So, 6 now can be written as pi v pure 1 is equal to x 2 RT ok. Now I can place this x in terms of the moles also. So, because x 2 is much less than one it this implies that n 2 is much less than n 1 and we can write x 2 as approximate as n 2 by n 1 because n 2 is very small. So, n 1 plus n 2 here in the denominator can be simply written as n.

So, therefore, pi v pure one is nothing but n 2 by n 1 RT or pi v is equal to n 2 by RT; where v is basically nothing but n 1 v pure 1 this is a total volume available to n 2 moles ok. And this expression is very famous expression pi v is equal to n 2 by RT is called Vant Hoff equation where it connects the osmotic pressure pi to the volume and to the other thermionic variables ok.

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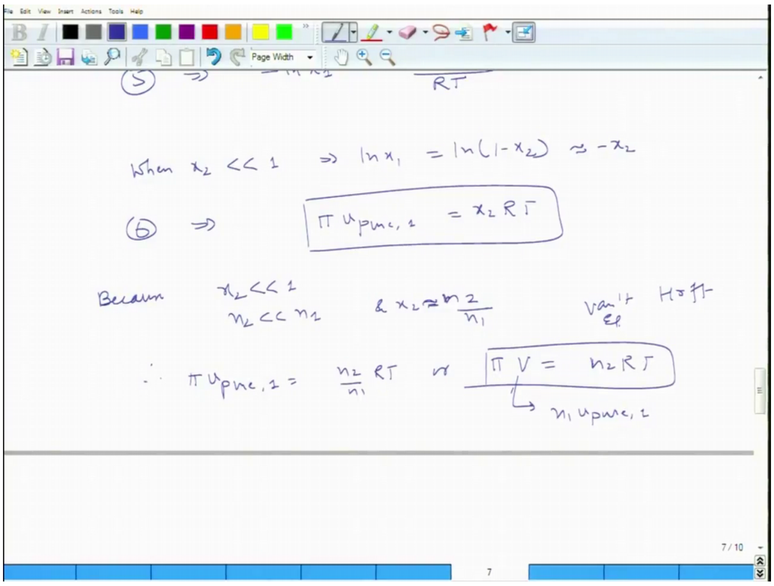

⑤ ⇒ RT

When $x_2 << 1 \Rightarrow \ln x_1 = \ln(1-x_2) \approx -x_2$

⑥ ⇒ $\boxed{\pi v_{pure,1} = x_2 RT}$

Because $x_2 << 1$

$n_2 << n_1$ & $x_2 \approx \frac{n_2}{n_1}$

Van't Hoff Eq.

$\therefore \pi v_{pure,1} = \frac{n_2}{n_1} RT$ or $\boxed{\pi V = n_2 RT}$

$\hookrightarrow n_1 v_{pure,1}$

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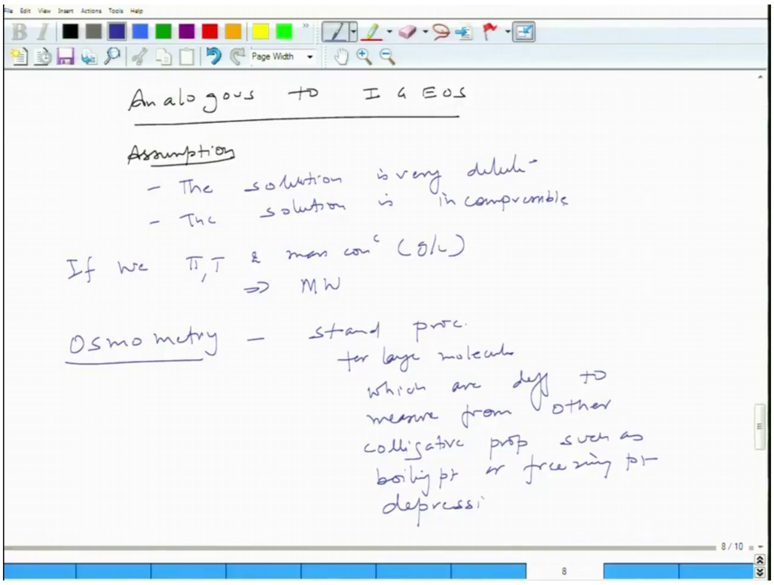

Analogous to I G EOS

Assumption

- The solution is very dilute
- The solution is incompressible

If we π, T & mass conc (g/L)

$\Rightarrow$ MW

Osmometry – stand proc. for large molecule which are diff to measure from other colligative prop such as boiling pt or freezing pt depressi

Now, if you look at this expression very carefully. Then this is analogous to ideal gas equation of state it and but the most important thing is that it all is based on certain assumptions. So, what are the assumption here; that the solution is very dilute and the solution is incompressible

So, if you look at very carefully this equation if we can measure if we measure pi; that means, the pressure. So, you can measure the pressure in the left hand side of the membrane and you can measure the pressure on the right hand side of the membrane; you can take the difference and you get pi. So, if you can measure pi if you can measure temperature and as well as the mass concentration of solute then we should be able to find out the molecular weight of the solute and this is something which is the very common way to obtain molecular weight of a large molecules.

So, if you measure pi T and mass concentration gram by l you can find out molecular weight ok. So, this technique to obtain molecular weight for large molecules is called Osmometry; this is a standard procedure ok; for large molecules. So, for those particular large molecules such as protein polymers and usually for other colligative properties to evaluate the molecular weight such as a boiling point and freezing point let us say depression if those are difficult and this is an approach to obtain the molecular weight ok.

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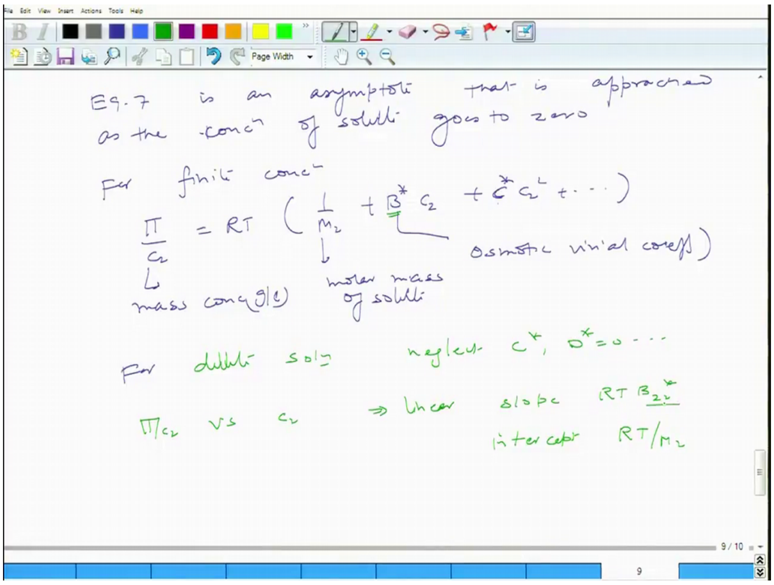

Eq. 7 is an asymptote that is approached as the conc^n of solute goes to zero

For finite conc^n

$$\frac{\Pi}{c_2} = RT\left(\frac{1}{M_2} + \underbrace{B^* c_2}_{\text{osmotic virial coeff}} + C^* c_2^2 + \cdots\right)$$

$\frac{\Pi}{c_2}$ → mass conc (g/L)

$\frac{1}{M_2}$ → molar mass of solute

For dilute sol^n neglect $C^*, D^* = 0 \ldots$

Π/c_2 vs c_2 ⇒ linear slope $RT B_{22}^*$

intercept RT/M_2

Now there are few points which we must make the one of the important thing is that if you look at this Vant Hoff equation and this is the limiting case it works only for the dilute conditions what about if the solution is not dilute then you have to come up with the some other terms which are missing in this equation.

So, equation 7 which we wrote here is basically is an asymptote that is approached as the concentration of solute goes to zero. So, so for the case of finite concentration what we can do is we can try to write down instead of saying x 2 we can simply say pi by C 2 is equal to RT 1 by M 2 plus B star C 2 plus C star C 2 square C here is a small C this is a capital C ok.

Where c is the small c's are the mass concentration in gram per liter M is molar mass of solute and B's and C stars are nothing but osmotic real coefficient ok. So, now, we have to come up with a kind of virial equation in state for osmotic pressure that is what this equation looks like it. Now you can recover Vant Hoff equation by putting B star and C star is equal to 0.

So, for the case of a dilute solution we can neglect C star and higher order. So, for dilute solution if we neglect C star D star and so forth and if you plot pi by C 2 versus C 2 then this; so, this part will be your intersection and this slope this will give you a slope; that means, we can come up with a linear equation having a slope RTB let us 2 2 star.

Because you are looking at only the B; that means, solution b star and then intercept this RT by M 2 ok. Now this B 2 star star basically is extremely useful interpreter you know useful information, because it gives you the interaction between the particles in solution and that is why this is valuable information which you can extract from the experimental data and you can understand how the solute molecules interact.

So, let us consider some example which has been done by a few researchers or workers. So, here what I am going to draw is 3 different bio-molecules as a function of protein concentration. So, what I am going to draw is. So, this is pi by C 2 as we said in the units of Pascal liter per gram as a function of protein concentration gram per liter.

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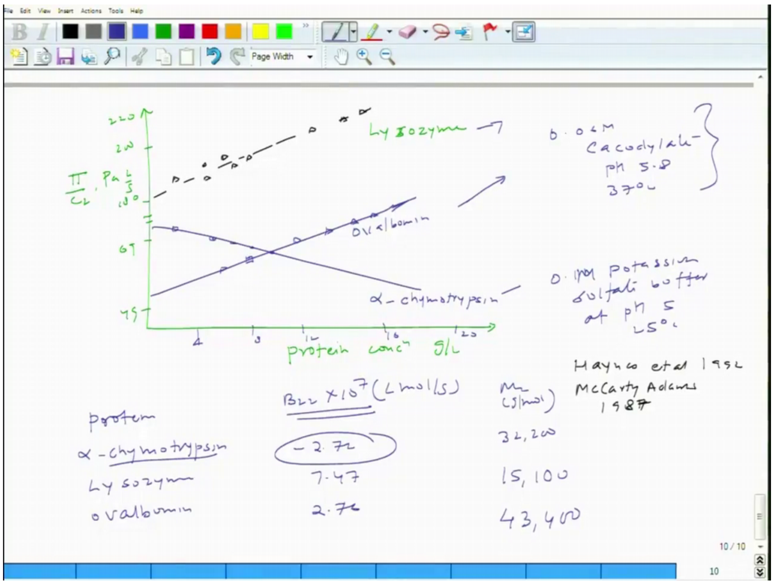

protein	$B_{22} \times 10^7$ (L mol/g)	M_w (g/mol)
α - chymotrypsin	-2.72	32,200
Lysozyme	7.47	15,100
ovalbumin	2.72	43,400

So, basically that is what we said pi by C 2 versus C 2. So, C 2 is basically the protein concentration; that means, solute here right. And what we are drawing is basically the case um. So, I am not going to draw exactly as in the paper of a Hayns et al in 1992 or McCarty Adams in 1987 ok. So, I am going to just draw to provide you the basic idea here.

So, the datas are something like this. So, this is the case for; Lysozyme; then and this is around 180 200 220; and this is around 69 49; and this will be the case for and this would be the case for this is your alpha Chymotrypsin and this is your Ovalbumin ok. And this is around 4, 8, 12, 16, 20 again these are experimental data this symbols are experimental data and lines they fit to the experimental data. So, what you can see is given this experimental data and you plotted it this value because you know the C 2 and you know the pi. So, you can plot this expression that is what we have done or by done by these people.

So, they plotted this Lysosome in different solution. So, Lysosome was in Lysosome and and over the mean was in 0.06 M Cacodylate and we are talking about ph 5.8 37 degree Celsius for the case of Chymotrypsin it is at 0.1 M potassium sulfate buffer at ph 5 25 degree Celsius ok.

Now, using this data; so this is a very dilute solution, but using this data you can obtain the slope and the intersection ok. So, if you obtain the slope you can get B 2 2 and from intercept you can get your molecular weight and that is what it has been done. So, this is the protein. So, let us say protein alpha Chymotrypsin, Lysozyme and Ovalbumin. So, the B 2 is calculated into 10 to the power 7 liter mole per gram.

And molecular weight is calculated which is something like 32, 200 in gram per mole what is more important is the value of this B 2 2 ok. So, Chymotrypsin turns out to be minus 2.72 Lysozyme is 7.47, 2.76.

So, what you can clearly see is that the slope is different in the case of Lysosome all domain in this solution as opposed to some it was seen in this potassium sulfate buffer and having a negative real coefficient indicates that it is effectively interact attractive to each other in the solution. Whereas, the other one Lysosome in Ovalbumin; they are not which is opposite to what you see in the Chymotrypsin.

Now, using this analysis, you could get certain the idea of the solutes behavioral solution and as well as molecular weight and as this kind of exercise is quite a valuable in solution thermodynamics or in general the experiments to evaluate the understanding of the behavior solute. So, that was my intent for today’s lecture and I hope that you got an idea a bit on the using basic concept of thermodynamics to evaluate understanding of the behavior of solute in solutions.

We will take up another topic and subsequently we will do some examples to appreciate this kind of concepts. So, that will be the end of today’s lecture, we will see you in the next lecture.