Chemical and Biological Thermodynamics: Principles to Applications
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Lecture – 19
Chemical potential of Liquids, Raoult's Law, Henry's Law

In the previous lecture based on the pressure dependence of molar Gibbs function we have discussed chemical potential of gases. Now let us develop a relationship for chemical potential of liquids and hint in this discussion we will make use of the definition of chemical potential of a perfect gas.

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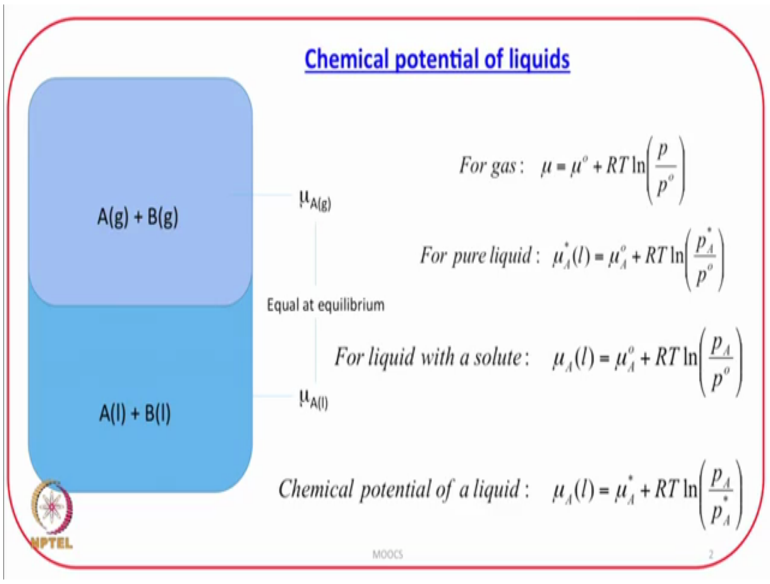

Chemical potential of liquids

For gas: $\mu = \mu^o + RT\ln\left(\frac{p}{p^o}\right)$

For pure liquid: $\mu_A^*(l) = \mu_A^o + RT\ln\left(\frac{p_A^*}{p^o}\right)$

For liquid with a solute: $\mu_A(l) = \mu_A^o + RT\ln\left(\frac{p_A}{p^o}\right)$

Chemical potential of a liquid: $\mu_A(l) = \mu_A^* + RT\ln\left(\frac{p_A}{p_A^*}\right)$

Let us consider in this figure the liquid forms of A and B in equilibrium with their vapors, whenever there is an equilibrium between the different phases of the same substance, remember the word equilibrium if there is an equilibrium then the chemical potential in each phase of that substance will be same and we will make use of that fact over here in this discussion let us take a look at the figure. If A liquid is in equilibrium with its vapor and an in an enclosed container then at equilibrium the chemical potential of A in the liquid form will be equal to chemical potential of A in the vapor form.

Let us now recall the definition of chemical potential of a perfect gas. This is the equation that we derived earlier for chemical potential of a perfect gas mu is equal to mu naught plus RT log P by P naught, where P is the pressure. Now since the different phases of the same substance for example, A in liquid form will have its chemical potential equal to that for A in the vapor form at equilibrium. So, I can replace this chemical potential for liquid form, although I am writing the expression for vapor or for a gas, but since the gas phase per a chemical potential will be equal to the chemical potential in the liquid phase it permits me to replace mu by mu A star l. Please try to understand the meaning of each term in this.

Let us assume that I have a pure liquid when you have a pure liquid just A and this liquid is in equilibrium with its vapors because of the vapor pressure of this, then at equilibrium the chemical potential in the liquid form and gas form will be same. So, therefore, I am writing this equation mu A star liquid this instead of mu I am writing for the liquid form and remaining thing I am writing mu star as same RT log P by P naught, where P A star it is the vapor pressure of pure liquid. Please note here when I am saying pure liquid I am using star, for purity I am using star. So, from the chemical potential for a gas I have written an expression for chemical potential for a liquid I have just what I have done is, I have just added a subscript A because I am writing it for A and I have added a star because in the beginning I am considering only pure liquid, I am not considering B I am only considering a in equilibrium with its vapor.

Now, suppose if I have something else in the solution. For example, now if I have a solute let us say I have B along with it then I will remove star because it is no more a pure liquid. So, when I remove star instead of mu A star l I will write mu A liquid, mu is not plus RT P A by P naught I am again removing star from here because the liquid is no more pure.

Now next step what I need is I need to eliminate mu A not from these two, these are two equations and once I eliminate mu A naught from these two equations the resulting equation is mu A for liquid is equal to mu A star plus RT log P A by P A star. Please note that this equation comes by substituting for mu A naught into this equation and then rearranging we get mu A liquid is equal to mu A star for that liquid plus RT log P A by P A star, where mu A star for that liquid is the chemical potential of the liquid A when it is in its pure form and mu A l is the chemical potential of A when it is in the presence of another solute.

So, what we have here is a term which is log P A by P A star it has an interesting meaning into it, P A is the vapor pressure of A in a mixture a mixture of A and B and P A star is the vapor pressure of A when A is pure liquid. It was experimentally observed by Raoult that when you plot P A that is the vapor pressure of A when it is in a solution it is a mixture against its mole fraction for closely related liquids, closely related means the liquids like benzene and toluene. So, for closely related liquids it was observed that when you plot P A that is the vapor pressure of A against mole fraction then the slope is a constant and it varies linearly.

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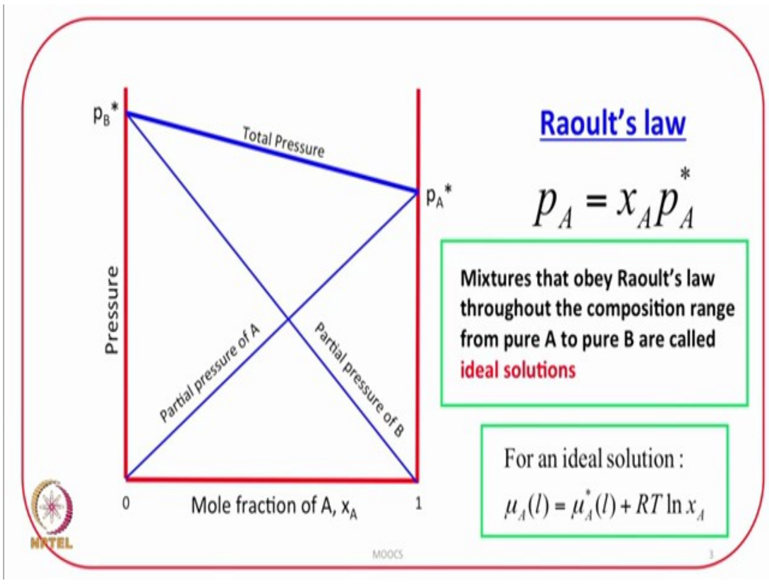

Raoult's law

$$p_A = x_A p_A^*$$

Mixtures that obey Raoult's law throughout the composition range from pure A to pure B are called ideal solutions

For an ideal solution :

$$\mu_A(l) = \mu_A^*(l) + RT \ln x_A$$

So, that was the basis of the Raoult's law this is what I was trying to explain that what he observed that for closely related liquids if you plot P A against x A the slope is equal to P A star, P A star is the vapor pressure of pure liquid A. And this is the variation for example, if you plot pressure against mole fraction for a 0 to 1, you see it leads to a straight line and the intercept when x A is equal to 1 or the slope of this float is P A star. For B the mole fraction here will be 0 for B and 1 here for B. So, again it will follow linearity and when x B is equal to 1 you see the vapor pressure is equal to vapor pressure of the pure liquid. Thus P A is equal to x A times P A star this is called Raoult's law.

Raoult's law has a greater meaning the mixtures that obey Raoult's law throughout the composition range from pure A to pure B are called ideal solutions. Earlier we have discussed about ideal gases we have discussed about the perfect gases. Now we have come to discussion on ideal solutions. In fact, this is one of the definitions which can be used for an ideal solution that in an ideal solution both the solute and solvent obey Raoult’s law that is what is commented over here. That mixture that obey Raoult’s law throughout the composition range from pure A to pure B are called ideal solutions.

So, therefore, going back to previous equation where we have discussed that mu I is equal to mu A star l plus RT log P A by P A star. So, in place of P A by P A star I am writing mole fraction. So, please note the comment over here for an ideal solution mu A that is chemical potential of a component in the liquid is equal to chemical potential of the same component in the pure form plus RT log x A, x A is the mole fraction of A. And if this law is obeyed by all the components of the solution then the resulting solution is ideal solution. In other words we can also use this as the definition of an ideal solution that is in an ideal solution this equation or alternatively Raoult’s law is obeyed by both solute and solvent.

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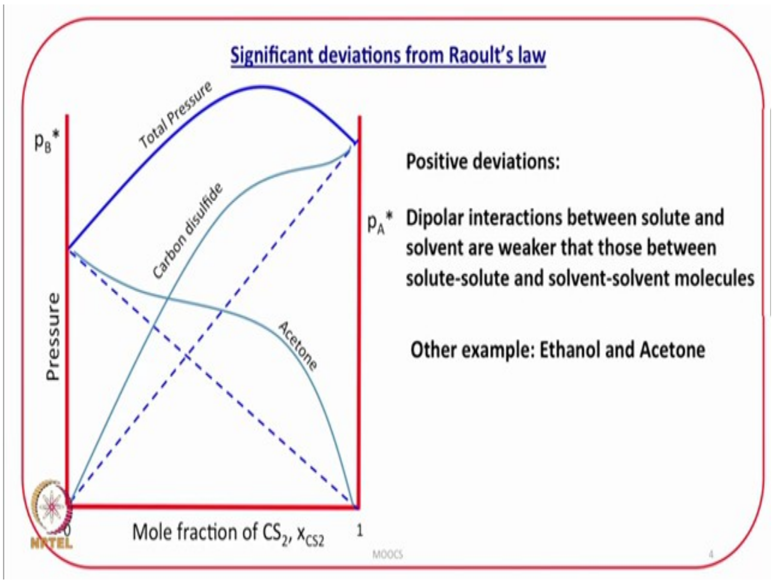

Significant deviations from Raoult’s law

Positive deviations:

Dipolar interactions between solute and solvent are weaker that those between solute-solute and solvent-solvent molecules

Other example: Ethanol and Acetone

Let us continue our discussion, do the deviations exist from Raoult’s law that definitely two types of deviations can occur from Raoult’s law - positive deviations and negative deviatio. When do the positive deviations is start? Let us first take a look at what do we understand by positive deviations. Look at the plot of pressure against mole fraction of carbon disulfide in a mixture of carbon disulfide and acetone. Here if we look at this plot this is pressure against mole fraction of carbon disulfide from 0 to 1, this dotted line is

Raoult’s law this is how the dependence would have been had the solution been ideal had there been no deviation. But you see there is a positive deviation the actual pressure vapor pressure varies like this.

When are the positive deviations possible? Before mixing you have one solvent and other component is a solute there are solute solute interactions there are solute solvent interactions. Now if the interactions which could be even dipolar in nature between solute and solvent are weaker than those between solute solute and solvent molecules; that means, now the components of the solution have more tendency to vaporize because them intermolecular interactions are weaker and if they have more tendency to escape; that means, their vapor pressure is more than what it would have been in ideal solution. And that is what is commented over here, the dipolar interactions between solute and solvent are weaker than those between solute solute and solvent solvent molecules in such a case we will get positive deviations and that is what happens in the case of carbon disulfide and acetone. And overall you see is also shows a positive deviation, if it were ideal it would have just shown a straight line over here, but we see positive deviations. If there are positive deviations from Raoult’s law then the negative deviations are also possible.

Let us take a look at a case of negative deviation, but before that another example which can show positive deviation is ethanol and acetone. And here you see ethanol molecules can form strong hydrogen bonding amongst themselves and when acetone is added to ethanol acetone can interfere in the intermolecular hydrogen bonding of ethanol and that is the reason that the mixture of ethanol and acetone shows positive deviations from Raoult’s law.

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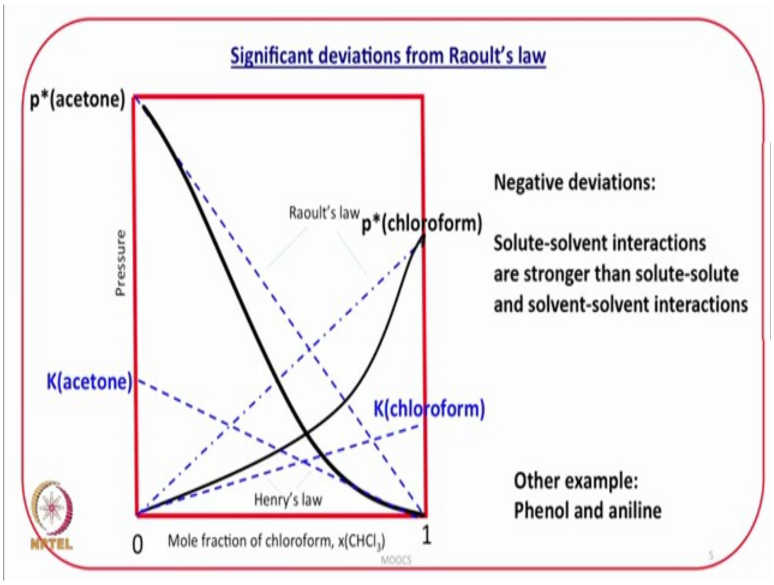

Significant deviations from Raoult's law

Negative deviations:

Solute-solvent interactions are stronger than solute-solute and solvent-solvent interactions

Other example:
Phenol and aniline

Now, let us take a look at the negative deviation now here the situation is reversed. Here if the solute solvent interactions are stronger than solute solute or salute solve or solvent solvent interactions, in that case there will be negative deviation.

Now, what I said is if the solute solute interactions are stronger, solvent solvent interactions are stronger than solute solvent that was the earlier case. Now when the solute solvent interactions are more; that means, the molecules would like to stick to each other we like to get bonded to each other, will not have easier tendency to escape and therefore, the vapor pressure will be low and that is what is commented over here. If the solute solvent interactions are stronger than solute solute and solvent solvent interactions then negative deviations are observed this should be radars solvent solvent interactions. And this is what is seen over here you see there are negative deviations in both - one example is acetone and chloroform and another example is phenol and aniline, because phenol and aniline will form a stronger bond than intermolecular interactions within phenol and within aniline molecule when these are in the pure forms.

One observation even if we let us take a look at the previous figure that this is this dotted blue line is Raoult's law and this Raoult's law is obeyed when the mole fraction of that component approaches one. You see here although there are positive deviations on the midway, but eventually when mole fraction is approaching a value of one it is obeying Raoult's law. Similarly when we see for acetone for acetone the mole fraction here is 0 and it is increasingly obeying, it is obeying Raoult's law when it is approaching purity. The same thing is seen in this figure, here you see when it is approaching purity it is almost matching this Raoult's law and the same thing is seen for acetone that Raoult's law is obeyed when it is obeying it is approaching purity. How do we explain this? The explanation is simple that is when the solvent is approaching purity means the concentration of solute is very less.

Therefore because there is a lot of solvent therefore, each solvent will experience almost a similar environment as if that solvent molecule were in a pure liquid. I repeat when the solvent is approaching purity or when in a solution the solvent is in large excess then each solvent volume molecule will view its surrounding as like in the presence of a pure solvent and therefore, it will act like an ideal system. Whereas, this is not the situation for solute, solute will see a different environment because solute is surrounded by solvent. So, it will depend upon the interactions of the solute and solvent that whether the solute will obey Raoult's law or not. Of course, if the nature of intermolecular interactions are similar then it will as I will discuss a little later.

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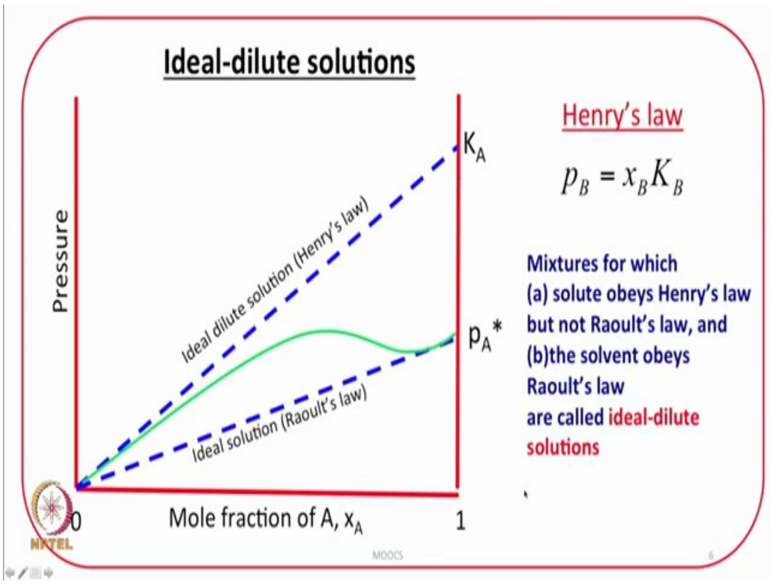

Ideal-dilute solutions

Henry's law

$p_B = x_B K_B$

Mixtures for which
(a) solute obeys Henry's law but not Raoult's law, and
(b)the solvent obeys Raoult's law
are called ideal-dilute solutions

Now, let us see what is ideal dilute solution. We have discussed what is an ideal solution, we have discuss the definition of ideal solution a solution in which both the solute and solvent obey Raoult's law is an ideal solution. In terms of intermolecular interactions I will discuss further. There was another observation by Henry that in a dilute solution if you plot the vapor pressure of component B or let us say if I treat B as a solute against its mole fraction still you see linearity, but the constant of proportionality is not the vapor pressure of pure component rather it is another constant and this K is called Henry’s law constant. So, this law P B is equal to x B into K B is called Henry’s law. Let me explain this Henry’s law or Raoult’s law how it is obeyed by considering one component system.

Raoult, actually treat that there is only one component in a solution because the solution is always made when there are more than one components, but let me explain on the basis of this plot of pressure against mole fraction of A. See when the mole fraction of A is very low in a mixture it will act like a solute and when the mole fraction of A is very high in the mixture it will act like a solvent. So, when it is acting like a solvent you see although there is a deviation positive deviations indicated by the green line, but when x A is approaching one it is increasingly obeying the Raoult’s law it is obeying the Raoult’s law.

And when its concentration is very low, very low that is what I was saying the vapor pressure is still proportional to mole fraction, but the proportionality constant is something else, you see here the proportionality constant is K, K is Henry’s law constant. So, in a given solution, in a given dilute solution I will say the solvent will obey Raoult’s law and the solute will obey Henry’s law. So, this diagram is for a dilute solution very dilute solution in which the solvent obeys Raoult’s law and the solute obeys Henry’s law. Henry’s law is the upper dotted curve, the Raoult’s law is the upper dotted line and the Raoult’s law is the lower dotted line. So, such solutions are called ideal dilute solution.

Therefore mixtures for which solute obeys Henry’s law, but not Raoult’s law and the solvent obeys Raoult’s law are called ideal dilute solutions. So, we should be able to clearly distinguish between in an ideal solution and an ideal dilute solution. In an ideal solution both the solute and solvent will obey Raoult’s law, in ideal dilute solution solute obeys Henry’s law, but not Raoult’s law and the solvent obeys Raoult’s law.

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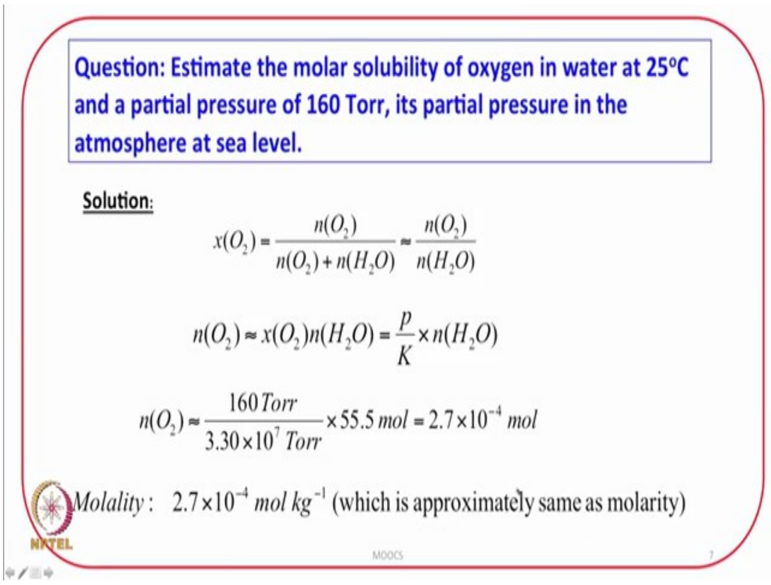

Question: Estimate the molar solubility of oxygen in water at 25°C and a partial pressure of 160 Torr, its partial pressure in the atmosphere at sea level.

Solution:

$$x(O_2) = \frac{n(O_2)}{n(O_2)+n(H_2O)} \approx \frac{n(O_2)}{n(H_2O)}$$

$$n(O_2) \approx x(O_2)n(H_2O) = \frac{p}{K}\times n(H_2O)$$

$$n(O_2) \approx \frac{160\,Torr}{3.30\times10^{7}\,Torr}\times 55.5\,mol = 2.7\times10^{-4}\,mol$$

$Molality:$ $2.7\times10^{-4}\,mol\,kg^{-1}$ (which is approximately same as molarity)

Now, let us discuss an application of what we have covered now. Estimate the molar solubility of oxygen in water at 25 degree Celsius and a partial pressure of 160 torr, its partial pressure in the atmosphere at sea level how do we approach this question. The molar solubility of oxygen is in water is to be determined and we know that the concentration is very low of oxygen in water and therefore, we can conveniently use Henry’s law.

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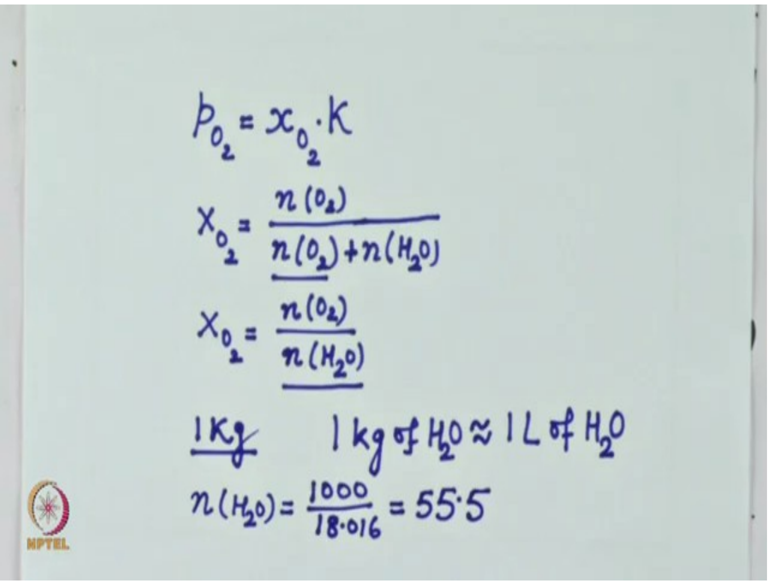

$$p_{O_2} = x_{O_2}\cdot K$$

$$X_{O_2} = \frac{n(O_2)}{n(O_2)+n(H_2O)}$$

$$X_{O_2} = \frac{n(O_2)}{n(H_2O)}$$

1 Kg   1 kg of H_2O ≈ 1 L of H_2O

$$n(H_2O) = \frac{1000}{18.016} = 55.5$$

According to Henry’s law the vapor pressure or partial pressure of oxygen will be equal to the mole fraction of oxygen into Henry’s law constant, therefore, how do we calculate this mole fraction of oxygen this will be number of moles of oxygen divided by number of moles of oxygen plus number of moles of water. And since water is in access I can ignore this because this is in excess. So, mole fraction of oxygen will be equal to number of moles of oxygen divided by number of moles of water. I can easily calculate number of moles of water provided I consider either o1ne kilogram or 1 liter. See K g of water is approximately one liter of water because the density is approximately 1. So, therefore, number of moles of water, number of moles of water will be equal to; if I consider 1 kg that is 1000 gram by 18.016 this is about 55.5 these many number of moles are there. With this information I can solve the question. The mole fraction of oxygen will be approximately number of moles of oxygen divided by number of moles of water and if I consider 1 kg we just discussed that I can use the 55.5 for this.

Now I am using Henry’s law as I just discussed that Henry’s law will be the partial pressure or vapor pressure of oxygen is equal to mole fraction of oxygen into K.

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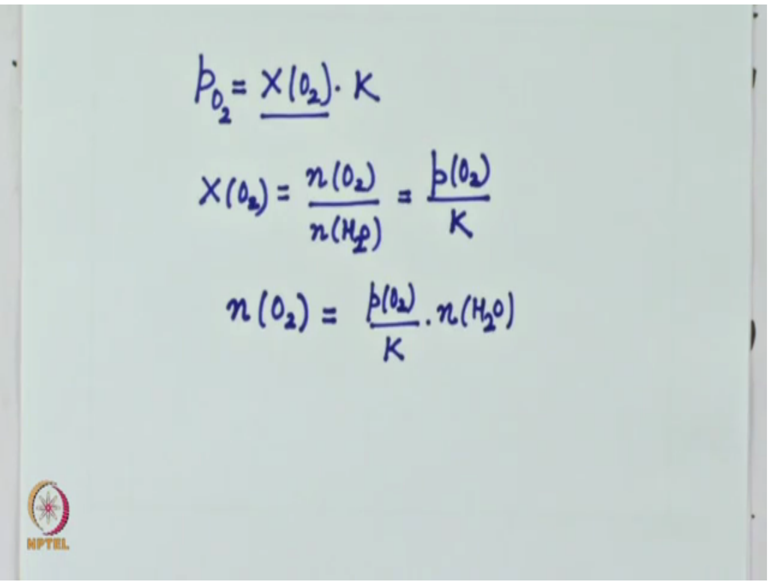

$$p_{O_2} = \underline{X(O_2)} \cdot K$$

$$X(O_2) = \frac{n(O_2)}{n(H_2O)} = \frac{p(O_2)}{K}$$

$$n(O_2) = \frac{p(O_2)}{K} \cdot n(H_2O)$$

And mole fraction of oxygen we have just discussed this is the number of moles of oxygen divided by number of moles of water, we have just discussed how it is approximately this; this is equal to P of oxygen divided by K. Therefore, number of moles of oxygen will be equal to P of oxygen by K into number of moles of water.

Now, let us go back to the slide and this is the expression that we just discussed substitute the numbers P is given 160 torr, its partial pressure is 160 torr and Henry's law constant that value will be supplied this is 3.3 into 10 raised to the power 7 torr. And number of moles of water in 1 kg is 55.5 - the answer is 2.7 into 10 raised to power minus 4 mole. And since we this is the number of moles of oxygen in 1 kilogram of water this is directly equal to molality because molality is defined as number of moles of solute in 1 kg of solvent therefore this is directly the molality and since for water the density is nearly 1, therefore molality is nearly same as molarity and that is what is commented over here which is approximately same as molarity.

So, in this lecture we discussed the chemical potential of a liquid and then we further extended the equations that we derived for chemical potential of a liquid to discuss Raoult's law and discuss Henry's law Raoult's law and Henry's law allowed us to describe the solutions into different categories one is an ideal solution and the other is an ideal dilute solution. We will discuss further on these concepts in the next lecture.

Thank you very much.