Introduction to Chemical Thermodynamics and Kinetics

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Lecture – 20
Mixtures – Part 2

In the last lecture, we discussed about mixing of two gases and we talked about how the free energy changes in the mixing process. And we showed that the associated free energy change in the mixing process is always negative, which means mixing will happen spontaneously. Now we will be discussing the mixing of two liquids, and we will be discussing a law which is now known as Raoult's law, this is after the French scientists Raoult who proposed how the free energy will change if we mix two liquids.

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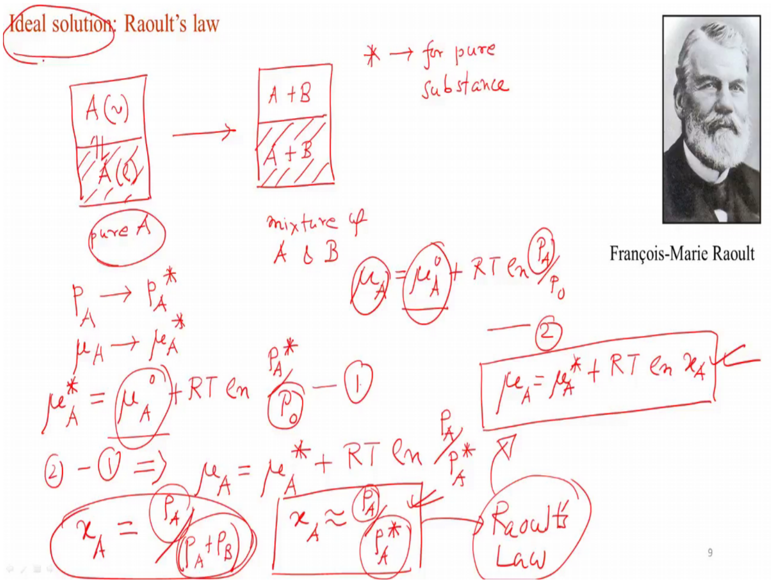

Ideal solution: Raoult's law

François-Marie Raoult

$* \to$ for pure substance

$P_A \to P_A^*$

$\mu_A \to \mu_A^*$

$\mu_A^* = \mu_A^0 + RT\ln \frac{P_A^*}{P_0}$ — ①

$\mu_A = \mu_A^0 + RT\ln \frac{P_A}{P_0}$ — ②

② − ① $\Rightarrow \mu_A = \mu_A^* + RT\ln \frac{P_A}{P_A^*}$

$x_A = \frac{P_A}{P_A+P_B}$

$x_A \approx \frac{P_A}{P_A^*}$

$\mu_A = \mu_A^* + RT\ln x_A$

Now, to begin with let us consider that we have a silt container and we have a liquid say liquid A, and this liquid which is liquid A. So, it is in equilibrium with its vapor.

So, this is when the liquid is in or the substance is in pure form, it is only one component system, now suppose we add a second component which we are denoting as B. So, right now in the liquid phase we have A plus B and in the vapor also, there is A plus B. So, this phase is liquid phase and this top portion is a vapor phase. So, this is mixture; this is mixture of A and B.

Now just to denote the pressure for at the vapor pressure for pure A, instead of writing it as P A will write it as P A star, but the star denotes for pure substance. So, initially the chemical potential was also we will write it in the similar notation instead of nu A we will write it as mu A star. So, before mixing what we had is mu A was equal to mu A 0 plus R T ln P A by P 0 now this P A is the initial pressure of the gas. So, if initial pressure means actually the partial pressure is nothing, but equal to the total pressure, P 0 as before is taken to be one bar.

Now since if the initially the liquid is in pure form we will use a star notation here, now see that mu is 0 star it is meaningless; because mu is 0 common corresponds to the chemical potential of the substance in one corresponding to one bar of the pressure. So, which is the standard state. So, we are not writing mu as 0 star. So, it is it; obviously, is equivalent to mu as 0. Now think about it, after we mix the solution or it is not a solution it is a pure liquid with another liquid B.

Now, it forms a solution or a mixture of two substances, then we are writing it as a mu A because it is not longer a pure substance and that mu A will be nothing, but mu A 0 plus R T ln P A by P 0 here I am writing P A not P A star and also mu A not mu A star, but note that the mu A 0 will be same, because it just corresponds to the standard state in either case. So, what Raouts law says is if we now compare that what is the mu A of the if we just take the difference between this equation.

So, let us call it as equation 2 and let us call it as equation 1 if we just take 2 minus 1 then we get mu A minus mu A star, and that mu A star I am just moving on the right hand side. So, it will be mu A is mu A star these terms cancel with each other and then we have R T lnp a by P 0 and here we have R T l n P A star by P 0.

So, we can take R T common and it will be just like ln x minus ln y is ln x by y, we can write this as R T ln P A by P A star now what is P A? P A is the partial pressure of component a in the mixture. Since it is partial pressure; obviously, it corresponds to a mixture and what is P A star P A star is the pressure of the same component or the vapor pressure of the same component when it is taken in the pure form. Now the mole fraction should be equal to P A by the total pressure which is nothing, but say P A plus P B. Now Raoult’s may then approximation he said that this mole fraction we can write as or we can approximate as the x A is nothing, but P A by P A star remember that this is not correct.

Because actually x A or the mole fraction should be equal to the partial pressure in mixture, divided by the total pressure, but Raoul approximated that the mole fraction is nothing, but the partial pressure divided by the pressure of the liquid or the vapor pressure of the liquid in its pure form.

So, this is known as Raoult's law, and using the Raoult's law if we just rewrite this equation, we will get mu is equal to mu A star plus R T ln P A by P A star will write it as x A. Now some textbook a write this as a Raoult's law, but it is not very correct because this is Raoult's law and this is Raoult's when applied to for ideal gases now the substances which follow this equation are the solutions, which follow this equation are called as ideal solution. Now let us try to understand why this approximation actually holds.

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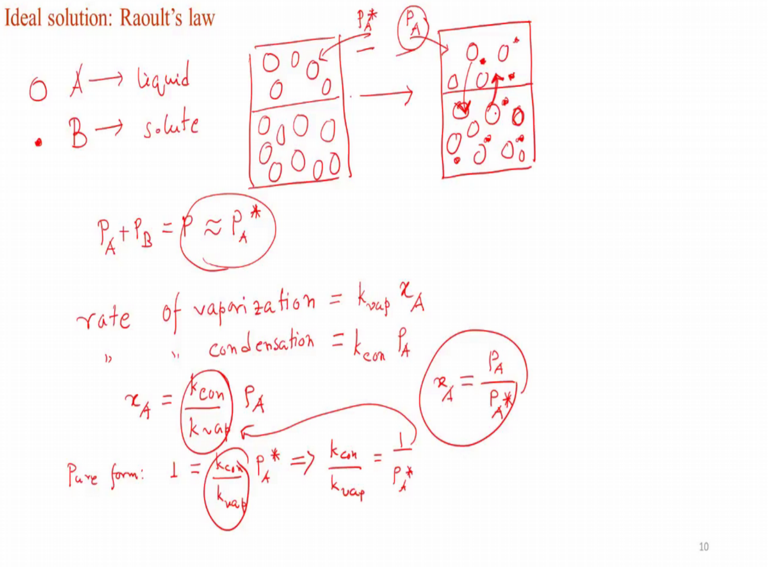

Ideal solution: Raoult's law

○ A → liquid

● B → solute

p_A^*

p_A

$$p_A + p_B = p \approx p_A^*$$

$$\text{rate of vaporization} = k_{vap}\, x_A$$

$$\text{" \quad " condensation} = k_{con}\, p_A$$

$$x_A = \frac{k_{con}}{k_{vap}}\, p_A$$

$$x_A = \frac{p_A}{p_A^*}$$

$$\text{Pure form: } 1 = \frac{k_{con}}{k_{vap}}\, p_A^* \Rightarrow \frac{k_{con}}{k_{vap}} = \frac{1}{p_A^*}$$

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Now think about situation suppose A is a liquid and suppose B is a solute, which is say for example, A is water and B is some salt, and then what will happen is that we are trying to give again a molecular level picture. So, in the liquid you have all these liquid molecules suppose or molecules of A. So, these are molecules of A and suppose I am writing the molecules of B like this, there are also few molecules of A in the vapor phase.

So, this was the initial condition and then from pure A we added salt, where the situation is like this. So, we have it is also some salt molecules here, but usually in the vapor phase we will still have only molecules of B molecules of A because usually the salt is nonvolatile. So, you can approximate this pressure which is basically the partial pressure of A here and which is basically a partial pressure this one has P A star, there will be of course, different I am coming to that.

But then you can approximate the total pressure in this case it will be equivalent to the liquids original pressure. Now why we are making that approximation? The reason being when the solute is present the evaporation of the solvent molecules into the vapor phase will be little bit suppressed.

So, definitely P A star and P A will be different; however, the total pressure expression which is which we took as instead of P A plus P B which is the P and that we approximated as P A star is not a very bad approximation, the reason being usually the P A star will correspond to a pressure which is largely which is purely contributed by a and similarly the total pressure here, when the suppose the solute also has few very few molecules is also largely contributed by A.

So, the total pressure can be approximated by P A star itself. So, this is the molecular origin for Raoul's law, now you can actually have a kinetic model to describe this entire process. Remember that at equilibrium every equilibrium is a dynamic equilibrium which means there will be some molecules of A going into the vapor phase, and some molecule of the B a going into the Conan's phase and the same thing is happening also for the molecules of B which is a solute, but which has very less number in the in the vapor phase. So, what will have is that P A plus P B we are approximating it to be P A star and then we can think that at any particular temperature the rate of vaporization.

That will be proportional to the mole fraction of A, because if you think that it has to be proportional to the mole fraction of it because it is proportional to the density of A in the mixture, but now instead of the pure density we have to calculate the mole fraction because now the solids are present and they will influence the evaporation of the or the vaporization of the liquid. So, it will be proportional to mole fraction of A which were the proportionality constant where is suppose writing as k vaporization.

Similarly there will be a rate of condensation meaning all these A molecules are also coming back and that rate will be proportional to now the partial pressure of A, because if the partial pressure is high. So, there will be higher tendency of the vapor to go back into the liquid. So, if that it is proportional to P A we can also consider some kind a rate constant which is in the condensation.

So, in equilibrium or at equilibrium we know that these two rates must be equal. So, we can write that x A is nothing, but k vaporization divided by k it will be the other way it will be k condensation divided by k vaporization times P A. Now if you take a pure form then for the pure form, we could write that x A is 1 and then k condensation by k vaporization is basically this pressure then is nothing, but P A star and then you can easily compare that this ratio of the constants, which is k con condensation by k vaporization is nothing, but 1 over P A star.

So, you can use it in this equation again and eliminate this arbitrary red constants and you can easily figure out that p x A will be nothing, but P A divided by P A star, and that is what was the essence of Raoult's law. So, Raoult's law is originating due to the fact that when I have solute solvent mixture then of course, some part of the solute may go into the vapor phase, but more than that the solute also suppresses the vaporization of the solvent.

So, the vapor pressure of the solvent must change which means P A must change from P A star, but when you take the total pressure the total pressure can be approximated as the vapor pressure of the pure solvent, the reason being usually in the mixture only a few amount or few tress amount of the solute goes into the vapor phase. So, it is largely contributed by the solvent molecules; so, we can have this situation.

However, there is a problem in if we want to have a solution of the have a change if we want to plot this how the vapor pressure or how the pressure is actually changing with respect to addition of the solute or the solvent, then we see a very very interesting situation. Now for if we there are two liquids sometimes we do not it is not a very ideal to call one substance as the solute, and the others all substances solvent. So, these are just two solvents.

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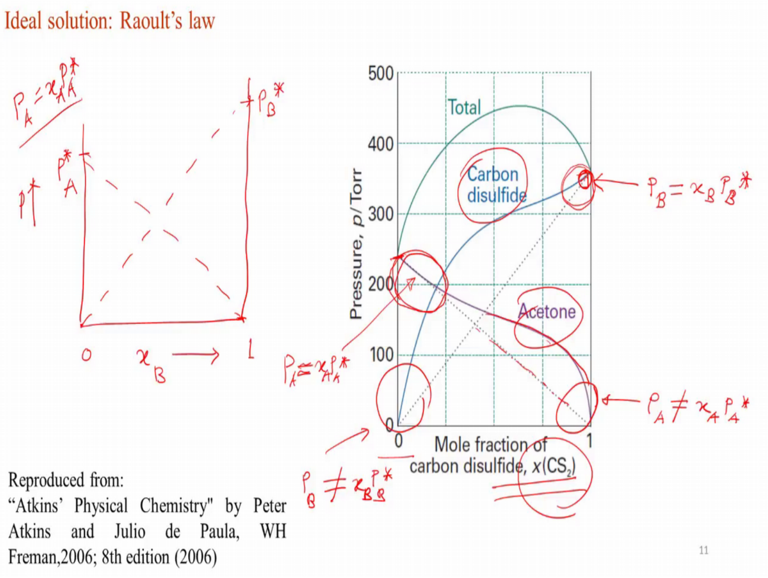

Ideal solution: Raoult's law

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Now, let us just try to have a look how it looks like in real life. So, if one plots the pressure versus the mole fraction of one component, in this case the plot is shown for acetone and carbon disulphide, and we are plotting the mole fraction of carbon disulphide.

Who had actually both are in liquid phase. So, it is not a solute solvent system, but it is a solution of two solvents. So, you can think that at a very zero concentration of carbon disulphide, when we have a pure acetone. So, we have some pressure which corresponds to P A star of acetone and then once it keep we keep on increasing the amount of solute in this case, if we think that it is a kind of solute at this carbon disulphide.

If we keep on increasing and if you watch the expression for Raoult's law, now how the expression for the Raoult's law should look like or remember the Raoult's law is a very smart simplification, it just says that P A will be nothing, but x A into P A star. So, suppose I am adding x B the second component, and it goes from 0 to 1.

So, when x B was 0 the plot for a if it is a pressure versus x B plot. So, that pressure should be equal to P A star because when x B is 0 x A is 1. So, a is in pure form. So, that pressure will be just P A star and when x B was one so; that means, actually it is pure form of x pure form of B. So, there is no a present.

So, then it should come here, it is basically 0 pressure. Now according to Raoult’s law this variation is just linear variation. So, it will just come like this and for similarly for the other component which is B if we ask this question how B varies or the pressure of B varies. So, for x B equal to 1 it will be the pure form of the B. So, it will have some pressures let us say the pressure is the P B star is somewhere here, and then the Raoult’s law says that it will again go from 0 to P B star.

So, this is a very ideal case, but what you see here when you vary the mole fraction of carbon disulphide and if you follow the acetone curve, remember that in that case acetone acts as a solvent at least in the is in the very dilute case we will come to that, and then you see that this actually matches with Raoult’s law very nicely, but sooner or later there is a huge deviation you can see this curve that the deviates a lot. And this is the ideal Raoult’s law curve and similarly if we think in terms of carbon disulphide you can see that these curve.

Actually starts from here and then there is a huge deviation. So, what is C from the Raoult’s law or the picture of the Raoult’s law is that this is very important. So, if you think in terms of the solute say carbon disulphide and initially when we are adding the carbon disulphide into acetone. So, initially when the mole fraction is very small. So, that solution, solution in the sense that it is a solution of carbon disulfide in acetone where acetone is the solvent that is a very dilute solution with respect to carbon disulfide and in the dilute solution, limit actually it works very nicely.

So, it is a kind of a proportional proportionality is maintained; however, the same opposite thing also happens. So, and you think about the other way meaning you are adding say acetone in carbon disulphide. So, acetone acts as a solute. So, then in this region one carbonyl sulfide is in excess. So, you see that this this actually I mean not soil matches with the curve, but it somehow I mean matches not so, badly also at a very very early stage.

So, the deviation is less there when the acetone is in prison. So, what it tells us is that when you think about a solute solvent mixture, and when the solute is present in very small amount or meaning that solution is very ideal solution, at that condition you see a nice matching for the solvent, but not for the solute.

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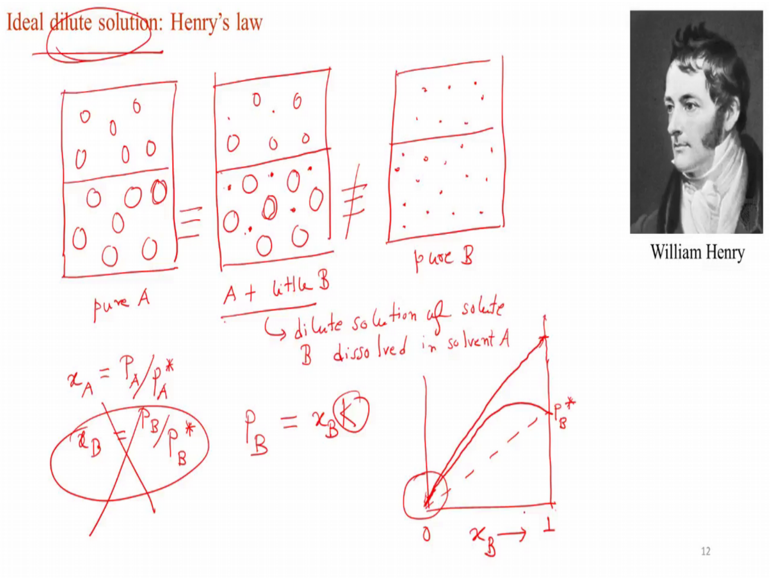

Ideal dilute solution: Henry's law

William Henry

Now, that was explained by another scientist William Henry, and he proposed an alternative law which is known as Henry's law, but Henry's law let us just try to conceptually a h analyze, what is Henry's law. Now Henry's law says that before we discuss about Henry's law. So, let us discuss about the solid solvent system as before we will just consider the A B situation.

So, suppose this is the pure form of A and then this is the mixture, where we just added little bit amount of B. So, with respect to B so, this is pure A and this is A plus little amount of B by little amount. So, which means actually it is a dilute solution of B, which is dissolved or let us write it as a dilute solution of solute B dissolved in solvent A.

Now, what Raoult's says is for any component, you can write x a is nothing, but the partial pressure of A into the or we can write it in this way P A by P A star. Similarly for x B Raoult's law also says that the vapor pressure if we follow the same equation it will be P A by P B star, but Henry's law by argument Hentry said that this is very unlikely because when at the limit of very dilute condition dilute with respect to always remember one component which is the B component and B is very less in amount it is very highly unlikely to consider the vapor pressure or the vapor pressure of B in this mixture, to be equal to the vapor pressure of the pure B.

Because remember that pure B will be something like this. So, this is pure B and where there are also it is in equilibrium with this vapor here, also we have equilibrium with its vapor and here we have both, but of course, the amount of B will be less. Now what Henry's law says is that when you are making an approximation with respect to the solvent for a dilute solution.

So, then the solvent which are basically the A in this case, which we denoted as this large circle they are present in large excess and they somehow resemble this thing. Because if you can see that there are still there are a large number of solvent molecules here and here actually it is just the pure solvent molecule. So, in presence of a trace amount of solute it does not matter; however, from the solid per perspective.

If you are thinking that the, this condition is same as the pure solid that will be erroneous very much erroneous; because in the pure B form it is in much excess whereas, in for the dilute solution it is in much much less. So, Henry said that for solute you cannot use this approximation, and then he just said that for solute it will be something like we cannot since you cannot approximate it the ideal case as the P B star.

So, the pressure he said instead of writing it as like this, let us write it in this way that he said that P B will not be x B into P B star, but it will be x B times some constant and this constant was an empirical constant which henry tries to try to measure from experimental quantities and what he showed is that for many solutes he showed that whether whereas, Raoult's law actually tells you that if I change the amount of x B or the mole fraction of xp.

Then this will be the ideal situation where the final pressure will be nothing, but the pressure of vapor pressure of B in its pure form and the initial pressure will be 0 and then the ideal behavior is something like the real behavior is something like this, and what Henry's law says is that the initial part if we draw it more carefully.

So, suppose it will be something like this at what henry said is we can approximate it the initial part to be equal to a constant, but of course, at a very very high concentration of the solute, Henry's law will also fill, but Henry's law matches more in a better way than Raoult's law for many solids. Because it just talks about only that part where the solute was in where basically the solvent was in large excess or the solid was increase among, which means with respect to B or respect to one particular component it was a dilute solution.

Now, this A and B notations are just purely arbitrary, when you keep on increasing the solute concentration at a very high solute concentration in this case, if these two miscible solvents then in that solution the second or the earlier solvent which is basically A from its perspective it is a dilute solution.

So, let us keep that in mind these are all arbitrary because it is depending on the mole fraction, and when the mole fraction of one component is less which means the other component is in large excess, then it is a very dilute solution with respect to that particular component, but the situation will be just reversed when you keep on increasing the concentration of that particular component and reach to a situation, where it is almost equal to one.

So, then the original component the original solvent has now become solid. So, this is just arbitrary notation. So, usually by convention we always say that the B component is the solute and the A is a large excess to begin with, and which will off course be reversed eventually and in the dilute limit when B is in much less compared to A, you will see linearity behavior.

But this linearity will not be proportional basically to the P V star, and the physical reason is something like that. So, when this is a very dilute solution with respect to B then you see a very large departure from your Henry's from your original Raoult's law. Now if you can see it here also now like for example, when we have this acetone water mixture, when we had carbon disulfide adding in a very little amount.

So, with respect to carbon dioxide carbon disulfide, when it was a very tress amount, then the ideal solution will be this part and you see that in that part actually deviates very largely. So, the approximation that P A; P B is proportional to P B star is wrong; however, P A is proportional to P A star is still correct because of this picture that we can still approximate that in the solution the vapor pressure of A will be proportional or the mole fraction will be proportional to the vapor pressure in the pure liquid form.

So, for acetone it matches very correctly. So, this is all with respect to only Raoult's law is plotted. So, where P A is we can write it as x A into P A star that is more or less valid, but with respect to B it is very wrong to write as x B into P B star. Similarly the exactly the opposite situation happens. So, when you have it here that when you write it in terms of P A more A is the solute as x A into P A star. It is just very wrong because it has a huge a departure; however, with respect to A not A it will be B with respect to B, when the B is in large excess you can actually write x B into P B star.

So, Henry's law very cleverly poses this entire situation of defining the solute and the solvent in a very different way, and he says that we have to consider only for the dilute solution a dilute means one component is much less and when one component is much less then Raoult's law fells for that component for the other component of course, it will be very good agreement because it acts as a solvent, and the solvent is in large excess which is equivalent to saying that it is equivalent it has these properties will be equivalent to the properties of the pure solvent itself.

So, Henry's law is just trying to understand or reformulate Raoult's law in a newer way in in some sense.

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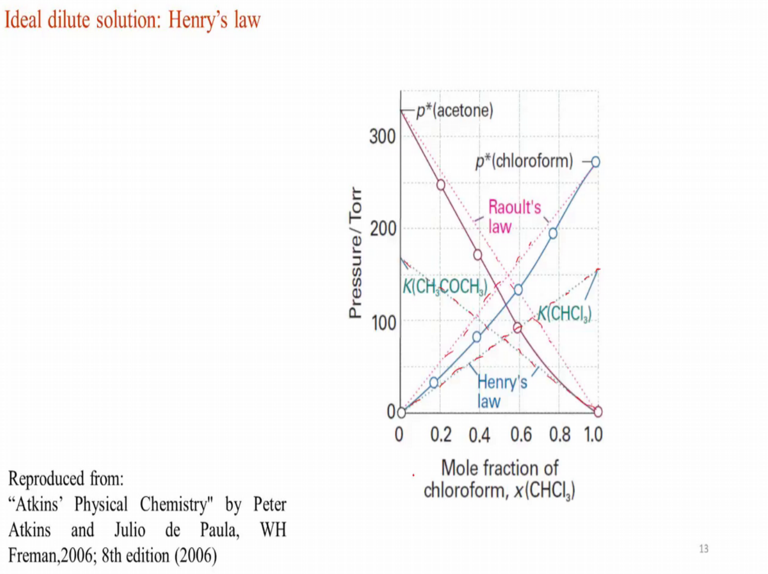

Ideal dilute solution: Henry's law

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And then if this is a real curve experimental data for two solvents acetone and chloroform, and also you can see there are other solvents also is here like acetic acid and chloroform, now you can see that these dotted lines are the Henry's law these dotted lines and you can see that, this is basically Raoult's law. So, both actually are linear variation and Henry's law were formulated only for dilute solution.

So, just to summarize for Raoult's law it whatever we got is a this relationship that the mole fraction will be equal to the partial pressure divided by the total pressure instead of the total pressure we are writing it as equivalent to the pressure of the component when the component is in pure form, that will hold only for some solvents of course, our reality is very different and those solvents of those systems we call as ideal systems or the solution we call as ideal solution.

Now, within the ideal solution Henry's law says that you form solute perspective solid means the component which is very less, the Raoult's law fails because of the situation that the solute is in very less amount and then you see a large departure. Now here are some experimental data again. Now coming back to the last part of this section on mixtures so we have so, far discussed about the thermodynamics of mixture, and then we discussed about how Gibbs free energy changes with respect to addition of one particular component, keeping pressure temperature and all other components constant or unchanged.

And then we discussed how basically the pressure of a particular component in a two component system changes by addition of one particular component, and we discussed the Raoul's law and Henry's law. Henry's law actually talks about limiting case of Raoul's law how to modify it, with respect to the solute which is present in trace amount or in less quantity compared to the other component. And now the last thing which we are going to discuss is some phenomena or some collection of phenomena which are known as colligative properties.

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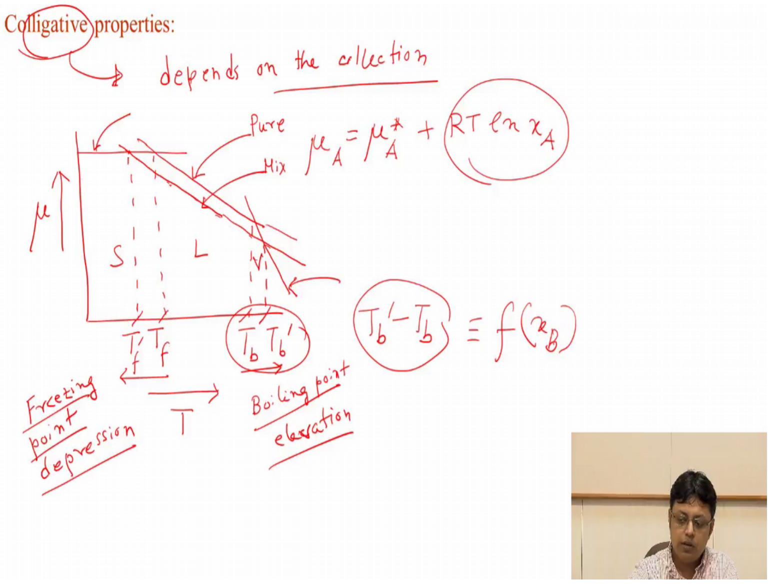

Colligative properties:

depends on the collection

$\mu_A = \mu_A^* + RT \ln x_A$

$T_b' - T_b \equiv f(x_B)$

Now, this name a colligative means actually its depends on the collection meaning it is a collection of phenomena we are about to discuss. Now suppose it is when we start to begin with suppose you have a pure liquid say pure water and you add some salt. Now the question we are asking we know that pure water under one atmosphere freezes at a 0 degrees centigrade or to 73 kelvin, now the question is whether if we when we add little bit salt to it how the freezing point changes.

And we know that of course, freezing point changes because salt water phase is such a much lower temperature than the freezing point of water which is 0 degree centigrade. Another question is how does it happen? Now you can easily think about it in terms of say the chemical potential or the equation for the chemical potential.

So, one way to quickly understand is that suppose when we talked about it, that mu versus T curve. If you remember we discussed it when we are discussing the phase transition, and this was the first thing we discussed that how the Gibbs free energy varies with temperature and we said that for solids it if the variation is much less, and then for liquids there will be some variation and for gas there will be a much more variation.

So, here where we have a phase transition from solid to liquid, this is a solid region this is liquid region. So, that we called as the melting point or the freezing point equivalently and similarly this is nothing, but the boiling point. So, this region is the vapor region. Now suppose we are adding some solute in that liquid.

So, what will happen is that now the chemical potential initially the chemical potential of the liquid was basically pure liquid it will be nothing, but equal to the I a mu A start, because the equation is mu A is equal to nu a star plus R T ln x A, if it is a in pure form then x A is equal to one which means mu A is equal to mu A star with addition of pinch of salt or so, now, the x A will change it will drop from one, which means this quantity it will be negative which means actually mu A will be less than mu A star. So, if this curve for the liquid is in liquid for a liquid which is in pure form, the in the mixture will have a new curve for the liquid which will lie below to this curve because it is now less.

So, the since the chemical potential is less, you will have a curve like this. So, what do you see here is that now this curve actually crosses the solid curve which means the freezing point now is here after addition of the salt. So, we see here that we have a freezing point depression. Depression means actually it is lowering down it has been lowered down.

So, this phenomena is called as freezing point depression, similarly if you follow this to curve now this is for the mixture, remember this is for the pure form and this is for the mixture and now the cross here the with the vapor out. So, the boiling point unlike the freezing point is actually enhanced or increases; so our it is elevated.

So, we call it as boiling point elevation. So, it is just like opposite to depression in the freezing point. Now you might ask a question that well what about the solid curve because we are only considering the change in the chemical potential of the liquid, we do not consider the solid how it behaves from the pure or in the mixture.

Now, here the assumption is that when the liquid forms the solid, the solute separates out suppose when you act some salt to the water. Then the assumption here is that when solid ice is forming it is a pure solid ice or when water is vaporizing to a water vapor it is a pure water vapor. So, those two curves for solid and the vapor curve those are not the chemical potential for those two curves are not changed; only it is shown in the solution form which is in the liquid form. So, only in the liquid state the solution exist and the chemical potential of the solute sorry chemical potential of the solvent in this case.

So, which is the pure which was pure liquid and when we added the solute it becomes a solvent and then that solvent is actually suppressed in presence of a solute. But the solid and the vapor their chemical potential remains unchanged, which means the solute is a nonvolatile solute which also does not freezes along with the liquid.

Because the solid suppose the solute freezing temperature is it basically separates out, and that is the assumption here, but in may encounter some instances where the solute actually freezes along with the solvent, and then this approximation or the way you have drawn the curves will not be correct because then the solid also will go a little bit down because the chemical potential should change because x A is fraction.

So, should be the ln x should be negative, but we are not considering this thing here. Now think about it, just like we discussed about how the freezing point is changing of the boiling point is elevated, we can actually discuss the thermodynamics of this processes in much more detail.

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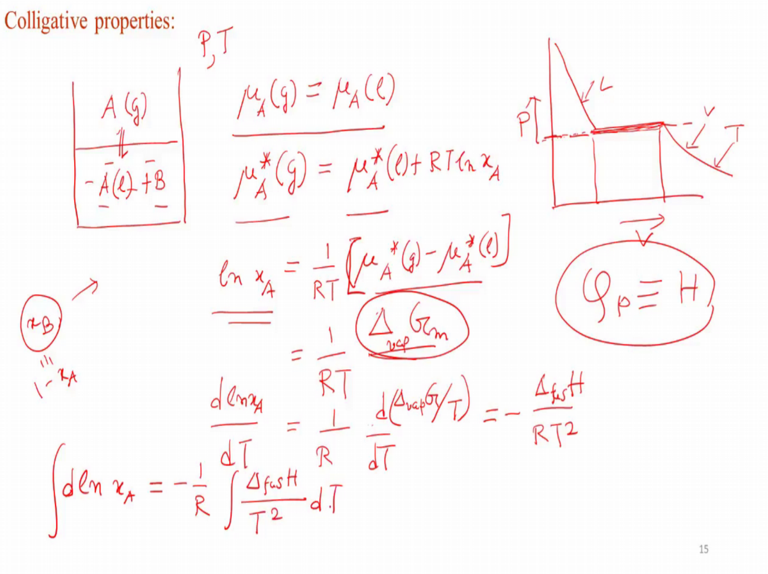

Colligative properties:

P, T

$\mu_A(g) = \mu_A(l)$

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

$\ln x_A = \frac{1}{RT}\left[\mu_A^*(g) - \mu_A^*(l)\right]$

$= \frac{1}{RT} \Delta_{vap} G_m$

$\frac{d \ln x_A}{dT} = \frac{1}{R} \frac{d(\Delta_{vap}G/T)}{dT} = -\frac{\Delta_{fus}H}{RT^2}$

$\int d \ln x_A = -\frac{1}{R} \int \frac{\Delta_{fus}H}{T^2} dT$

$q_p \equiv H$

Now, let us start with the elevation of the boiling point. Now what is boiling? Now if you ask this question think of it like we have a solvent here, and then it is always in equilibrium with its vapor. So, suppose I write it as a liquid A gas and when boiling happens, what it means is that the chemical potential of A in the gas phase must be equal to the chemical potential of the liquid itself.

Because at that temperature which is known as the boiling temperature, and also at that particular pressure. Now if the chemical potentials are equal then it is basically the conditioner for boiling. So, the liquid is in equilibrium with the vapor and it starts falling and we discussed it in various context actually, if you remember that to when you discussed the (Refer Time: 43:57) curve or the Andrew's curve not the (Refer Time: 44:02) curve.

So, you showed that this nice pressure volume curve, when I discuss that over a large range of volume because the volume should change pressure is kept constant you see here that the pressure is gets constant and this is also an isotherm, which means temperature is also constant and at that at a particular temperature, if you just keep on increasing the pressure you will you can actually boiling also or a for a fixed by pressure you can think of for a particular temperature, will have boiling temperature.

So, for water it is say one atmospheric pressure it corresponds to the 100 degree centigrade. Now when volume happens the volume of course, changes, but the thing is that that liquid is now in equilibrium with the vapors. So, this is the liquid and this is the vapor we already discussed it. So, if we start from that and suppose we have a second component now, which is B here which is a solute say some salt we add it into water, and then what will happen that when the boiling we are considering it is the boiling of water not boiling of the salt it is the boiling of the water only.

So, this condition still holds; however, the mu of the liquid will not be the mu of the pure liquid, because now the mu A has to be replaced for the liquid state by the partial quantities, but for the gas we can still say or the vapor phase, it is basically the mu s star or the pure form, because in the gas phase there is no B because we just added a salt which does not come into the gas phase, but for the liquid phase instead of mu A we can we should write mu s the liquid plus R T ln.

It is basically the way we are writing it is we can write it as x A. Now because P A by P A star are we approximated P A by P 0 we approximated as a x A. Now what we are seeing what you just saw here is that we can take the difference which is basically the if we write these in terms of ln x A, we will get it will be 1 over R T into mu A star of the gas minus mu A star f of the liquid.

Now, this is basically the difference in the chemical potential, in the vapor phase minus the gas phase which means it is the associated free energy change per mole because it is mu. So, we can write it as the associated delta G per mole, and this is a vaporization process. So, this is delta vaporization of G and this quantity we want to estimate. Now remember that instead of writing how the ln x is changing, we could also I mean we are trying to figure out a relationship between how much xp we can add so, that we see a change in the boiling point something like the curve we wrote.

So, here we want to get an expression for this quantity as a function of the solute added, which is the x B here. So, x B you can easily write as one minus x A at any point. So, this x A we just have to replace by x 1 A, x B you have to replace by one minus x A or the other way x A can be replaced as one minus x B, but the question is how will you get the delta t equation now if you remember that we use the Gibbs Duhem equation, where we talked about the variation of delta g with respect to temperature and that was connected to the enthalpy. And since this boiling is happening at constant pressure and also the temperature is also constant from this curve we can easily see that from Andrews curve.

So, we can actually write instead of the delta G a irrelevant quantity will be how much heat is supplied, and heat transfer that constant pressure is nothing, but enthalpy and then you can always argue that I can use the Gibbs Duhem equation to get this. So, Gibbs Duhem equation is nothing, but the derivative of delta G with respect to temperature at constant pressure.

So, on left hand side I have to take d ln x a d T, I am not writing the del notation because the term pressure is always constant it is already there. So, that will be one over R T and then we have you can write it as d d T sorry this is capital T of delta G, this is a delta of vaporization of G divided by T. So, this T actually got inside. So, that is nothing, but del h by R T square with a negative sign. So, it will be one over a t square and the numerator is nothing, but the associated change in enthalpy of fusion. Now we can integrate this equation and see how it appears.

So, you can easily see that if we integrate it. So, we take the temperature on the other side. So, we will get ln d ln x A integrated will be equal to minus 1 over R integral of delta fusion h divided by t square d T. Now when we easily integrate it, I will just use this space and the integration or the integrand will be if we take the lower limit of the integration to be 0 or when we have l n x A is to be 0. So, then we are saying that ln x A to be 0 means think about it that x A must be equal to 1 which is the liquid in the pure form.

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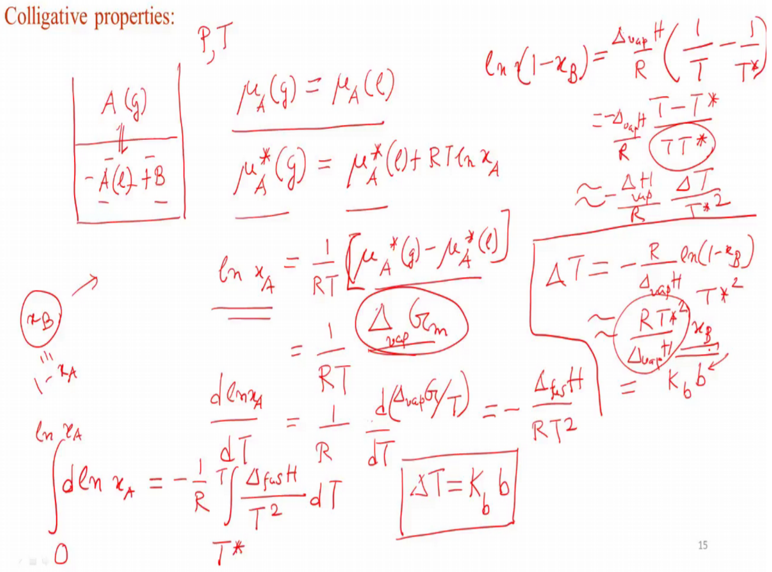

Colligative properties:

$$\mu_A(g) = \mu_A(l)$$

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

$$\ln x_A = \frac{1}{RT}\left[\mu_A^*(g) - \mu_A^*(l)\right] = \frac{1}{RT}\Delta_{vap} G_m$$

$$\frac{d \ln x_A}{dT} = \frac{1}{R}\frac{d(\Delta_{vap}G/T)}{dT} = -\frac{\Delta_{fus}H}{RT^2}$$

$$\int_0^{\ln x_A} d\ln x_A = -\frac{1}{R}\int_{T^*}^{T}\frac{\Delta_{fus}H}{T^2}\,dT$$

$$\ln(1-x_B) = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right) = -\frac{\Delta_{vap}H}{R}\frac{T-T^*}{TT^*} \approx -\frac{\Delta_{vap}H}{R}\frac{\Delta T}{T^{*2}}$$

$$\Delta T = -\frac{R}{\Delta_{vap}H}\ln(1-x_B)\,T^{*2} \approx \frac{RT^{*2}}{\Delta_{vap}H}x_B = K_b b$$

$$\boxed{\Delta T = K_b b}$$

So, then the t is nothing, but the T star or the boiling the pure liquids boiling point and the upper limit let us call it as T and let us call it as ln x A. So, we have ln x A which we can write as ln 1 minus x B and the right hand side will become minus 1 over R. So, the integration of 1 over T square is minus 1 over T. So, that minus gets cancelled with this minus and if we just calculate the limits, it will be 1 over T minus 1 over T star.

So, what we will get is delta H vaporization by R and del be are delta H vaporization by R and then we can write it as a T minus T star divided by T into T star with a negative sign, and that we can further approximate as this T into T star we can approximate as T star squared. So, we can write it as delta vaporization divided by R into delta T which is the elevation in the boiling point, divided by T star squared. This is just an approximation. So, what we just saw is that. So, there will be a negative sign here somewhere it is 1 over T minus 1 over T star.

So, there will be a negative sign here. So, what we just discussed is that we have gave a formalism to understand the elevation of boiling point, similarly you can use the same formalism to understand the depression of freezing point. When you discuss the freezing point depression instead of the delta H fush and delta H of vaporization, we write it as delta H of fusion, but the maths is the exactly the same. Now alternatively sometimes you write it as instead of this delta expression for delta T is sometimes written as the expression what we got is R by delta vaporization H into l n 1 minus x B and times we have T star squared, and sometimes it is basically it is proportional to as we can see it is proportional to x B and then you can just manipulate all these terms.

So, ln 1 minus x B we can approximate to be minus x B and then you can further write it as R divided by delta vaporization H, we can write as T star squared into x B. So, this is some constant into x B, and you can further approximate that x B is proportional to the molality of B and then you can get it some other constant which is basically this constant multiplied by some other constant which is the proportionality constant between mole fraction and the molality.

And then you can write it in terms of the molality and you can in a shorthand notation, you can actually write it as k b into b, where b is the molality of x B molality of component capital B and case of it is B is nothing, but the sometimes it is called as the boiling point elevation constant and similarly for freezing point if we write it as case of it is f into b. So, you can connect it to molarity.

So, that delta T ultimately can be written as a constant which is the basically rearrangement of all the constants times the molality. So, this equation shows how one can connect the amount of B at the mole fraction of B which is x B or equivalently the molality of the B to the depression of freezing point or the elevation of the boiling point. We derived it for the elevision of the boiling point, but the similar mathematics also holds for the depression of the freezing point.

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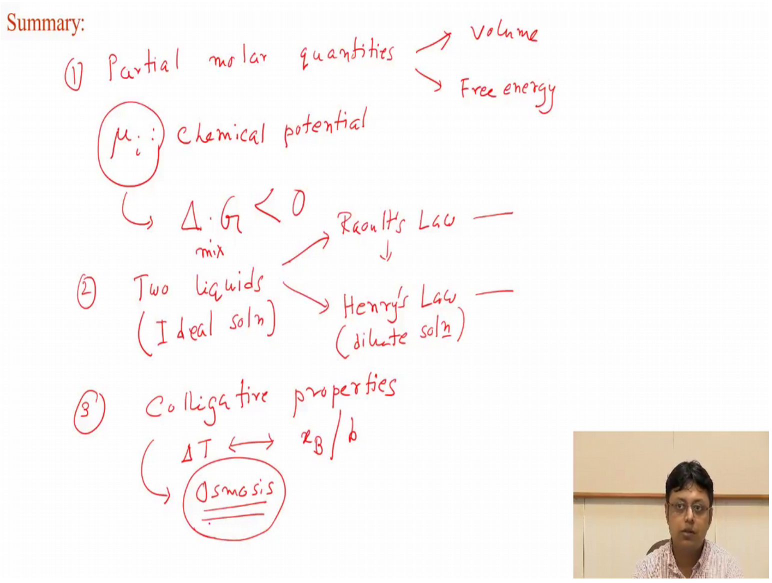

Summary:

① Partial molar quantities → volume, → Free energy

μ_i : Chemical potential

$\hookrightarrow \Delta_{mix} G < 0$

② Two liquids (Ideal soln) → Raoult's Law —

↓

→ Henry's Law — (dilute soln)

③ Colligative properties

$\Delta T \longleftrightarrow x_B / b$

$\hookrightarrow$ Osmosis

So, let me now summarize what we discussed in this lecture. So, we started with the partial molar volume and we talked about how we can use this partial molar quantities, one we discussed about the partial molar volume and then we switch to the partial molar free energy. And then we discussed that this free energy change which is basically the chemical potential is a very general concept, and it is not that you have to always use our all is express it in terms of Gibbs free energy you could also express it in many other things like the internal energy enthalpy and so on.

So, mu i is a very general thing and then we derived expression for mu i, first we talked about the gaseous mixtures if we have two gases and you are mixing it, and then we calculated the delta G of the process the process is mixing and we found it is negative. So, they mix two gases actually mix spontaneously, and then we talked about what will be the similar quantities for two liquids and in this case we showed that we have a general formalism which is the Raoult's law.

And then only for the and this these solutions which we have Raoult's law or Henry's law are called as a ideal solutions and for this ideal solution Raoult's law does not apply for the dilute condition dilute with respect to a particular component, and that component does not obey Raoult's law and for that there is Henry's law which is for the dilute gas.

So, it is for ideal dilute solution. And then we discussed the molecular origin for Raoult's law and Henry's law why it is valid in one limit and where the other one is valid in the other limit we talked about the solid solvent interactions, and then we talked about in the last part very briefly what is known as colligative properties.

So, then we talked about if we add pinch of salt in water why the freezing point is depressed or the boiling point is elevated, when we found the relationship between this depression or enhancement in the boiling point or freezing point or vice versa, it is depression of freezing point and elevation of all and connecting to the amount of the solute added to it the mole fraction of the solute added or equivalently the molality of the solute which is added to it.

And we could also discuss few other things like under colligative properties like one of the interesting thing is, how osmosis happens because if you remember that osmosis of a solution, where we have a semi permeable membrane and only the solute solvent is transparent to permeable to it, then we have a interesting phenomena which is osmosis, which we could also explain in terms of the diffusion of the solvent. Now we will have a problem set and we are we asked you to derive the thermodynamics or try to learn the thermodynamics of osmosis, through this through the concept which we just developed.

So, in the next lecture will be discussing about chemical equilibrium. So, we will talk about chemical reactions and what are the conditions for equilibrium, and how one can actually enhance the amount of one particular substance or say the product at equilibrium by just playing some tricks, but we would not be discussing any rate of the process, how the equilibrium how quickly the equilibrium is achieved at this point, and in the following lecture will be discussing about electrochemistry or the equilibrium electrochemistry what happens what are the thermodynamics of electrochemical cells.

Thank you.