

**Indian Institute of Technology Madras**

**NPTEL**

**National Programme on Technology Enhanced Learning**

**Chemical Engineering Thermodynamics**

by

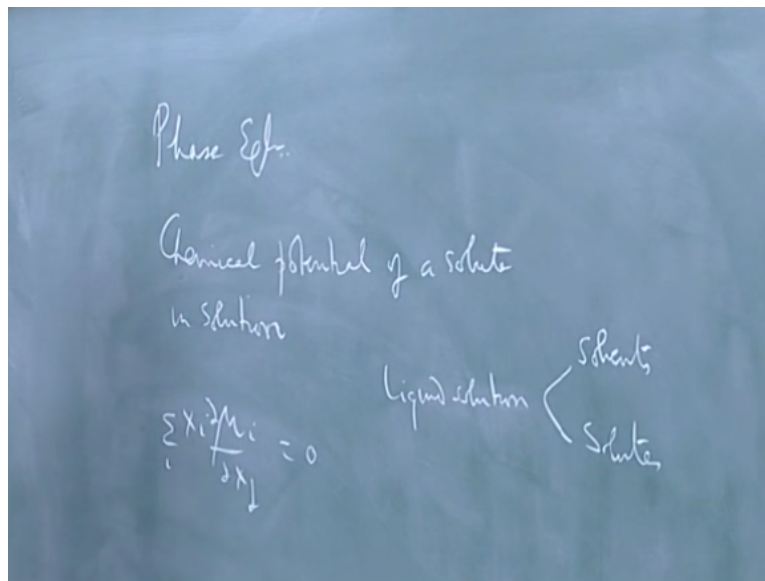
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**Lecture 21**

**Solvent-solute mixtures**

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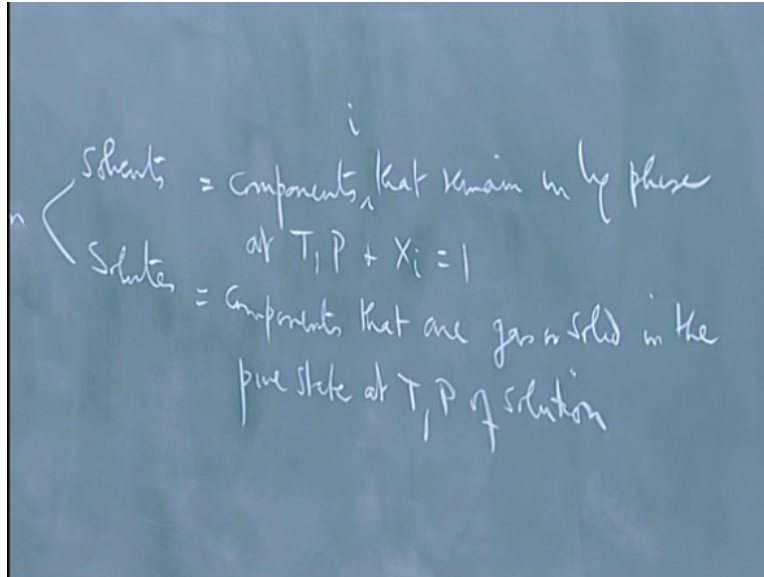


Mole discuss phase equilibrium again I am going to discuss the chemical potential of solute once I have a module for a chemical potential of the solute I can discussed topics like solubility of the solids in liquid solids in gases solubility of liquids and liquids and gases and liquids, these are the areas I have interest in direct interests.

Basically use the chemical potential you know it has to satisfy the Gibbs Duhem equation this is the chemical potential in any phase has to satisfy this equation so if you are talking of a liquid

solution, liquid solution consists of solvents and solutes it may not particular it may be all solvents in which case for the solvent case we have the nice model this is within quotes in our contexts the solvent is defines as a substances which does not change phase.

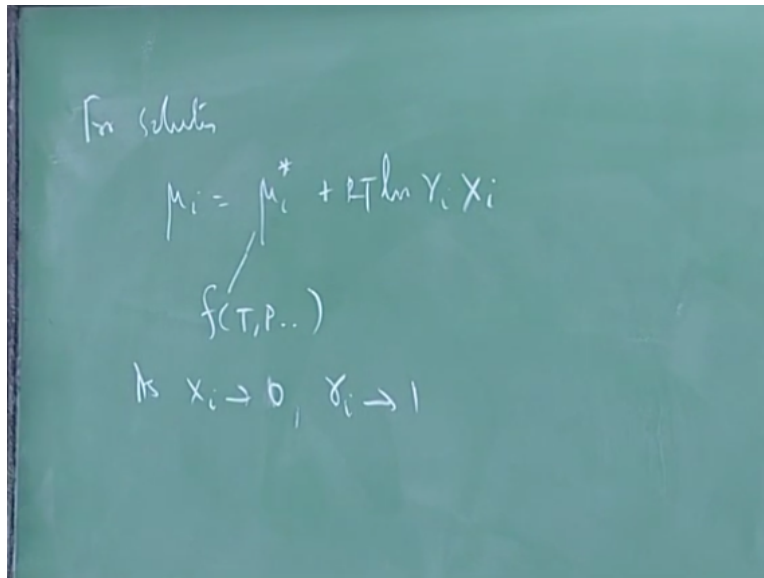
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If you change the mole fraction to unity without changing the temperature and the pressure this all solvents are essentially components that remain in liquid phase at  $T, P$  and  $X_i$  and say components I set as  $X_i=1$ , these are components to change phase that gather a gas or solid the pure state at  $T, P$  of solution.

So for solvents we have  $\mu_i = \mu_i^{\text{liquid pure at } T \text{ and } P \text{ of the solution}} + RT \ln \gamma_i X_i$ ,  $\gamma_i$  goes to 1 as  $X_i$  goes to 1 this is automatic because of the way you define this quantity the left hand side when  $X_i$  and  $\gamma_i$  this term is 0 so this as we equal to this which is the correct limit so if you have a solute you have a difficulty here.

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For solute we still write the same kind of model this is the function of T and P alone and T were double dot there I will explain what I mean it is not a function of composition but it actually has to do with the factor it depends on the environment I will explain that in a minute the physically realizable state without change of phase is not exact going to 1.

If I have for a example carbon dioxide dissolved in water at room temperature as I go to  $X_i$  it going 1 for carbon dioxide it become a gas so I can only realize a physical limit of  $X_i$  going to 0 so the reference point for me I have to therefore what I assume is that  $X_i$  as  $X_i$  goes to 1, 0  $\gamma_i$  goes to 1.

That is I have given myself an additional degree of freedom and defined a  $\mu_i^*$  and  $\gamma_i$  because I want  $\mu_i^*$  to be independent of composition that is why I am doing this formulation is useful then I need to fix  $\gamma_i$  as equal to unity at some point, this point can be either  $X_i$  going to 1 or  $X_i$  going to 0 I choose the limit as  $X_i$  goes to 0 then infinitely dilute solution of the solid in the solvent in that limit I choose  $\gamma_i = 1$  that defines  $\mu_i^*$  at this stage  $\mu_i^*$  is hypothetical it may not be an experimentally accessible quantity.

But I will show how I can get values for it or how I can get it affect from the equations so what I do is to make this limit but as  $X_i$  goes to 0 this logarithm it function will go to  $-\infty$  you have a problem of  $\log X_i$  going to  $-\infty$  I will circumvent that problem by the following method first of all, I look at let us look at individual cases.

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Gas solubility in liq of CO<sub>2</sub> in water

(1) (2)

$\mu_1^l = \mu_1^g = \mu_1^0 + RT \ln P y_1 \phi_1$  ✓

$\mu_2^l = \mu_2^v$

$\mu_1^* + RT \ln \gamma_1 x_1 = \mu_1^0 + RT \ln P y_1 \phi_1$

$\ln \frac{P y_1 \phi_1}{\gamma_1 x_1} = \frac{\mu_1^* - \mu_1^0}{RT}$

Let us look at gas liquid equilibrium or gas solubility liquids this is the correct of the phase let you get when you drink a coke when you drink a coke there is carbondipoxide dissolved in it your temperature you have to drink it cold the temperature goes up and the solubility decreases so the gas comes out you get a phase you know that is the only reason you are able to get that phase.

Because gas solubility decreases temperature as temperature increases okay let me get, let me equate chemical potential of the solubility let me take example Co2 in water will call CO2 as component 1, water is component 2 so you have  $\mu_1$  liquid phase is equal to  $\mu_1$  vapor phase or gas phase. Similarly I have  $\mu_2$  liquid phase is equal to  $\mu_2$  vapor phase.

I write g and v to distinguish the factor that 1 as blow the critical temperature if there both is critical temperature okay this you know how to do because this vapor phase is simply the vapor liquid equilibriums problem this is  $\mu_2$  liquid  $\mu_2^0 + RT \ln Y_1 P_1$ ,  $P Y_2$  if it is, this is simply you are pointing correction and  $\mu_2^0 + RT \ln$  of the saturation pressure if the gas is equal at coefficient at saturation pointing correction  $\gamma_2 X_2$ .

So this you have done already so this is the equation I have to worry about it even this is not this is simply  $\mu_1^0 + RT \ln P y_1$  times  $\phi_1$ , in  $\phi_1$  of course satisfies the Gibbs Duhem equation  $\log \phi_1$  satisfies the Gibbs Duhem equation but you get it from  $V_1$  bar which satisfies the Gibbs Duhem equation anyway which is experimentally measure so this part is well known. Now this part you

have this equation here let me write this out and I will write  $\mu_1^* + RT \ln \gamma_1 X_1$  I am looking at  $\ln \frac{P_1 \phi_1}{\gamma_1 X_1}$  okay this is equal to  $\mu_1^* - \mu_{10}/RT$ .

Usual trick and thermodynamics if you do not know the quantity try and produce the same quantity on both sides of the equation this is what we did so far in vapor liquid equilibria we cancel  $\mu_1$ , both sides you had words for it but you did not know the number so you produce  $\mu_{10}$  here for  $\mu_2$  for example you produce  $\mu_2$  both sides cancelled it so we did not have to talk about it.

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The image shows a chalkboard with the following handwritten equations and notes:

$$\frac{P_1 \phi_1}{X_1} = \frac{P_1 \phi_1}{\gamma_1 X_1} = k_{H,12} \equiv \text{Henry's law constant}$$

As  $X_1 \rightarrow 0$ , the expression is labeled as "infinite dilution".

$$\frac{\partial \ln k_{H,12}}{\partial T} = - \frac{\bar{H}_1^* - h_1^0}{RT^2} = - \frac{(\bar{H}_1^* - h_1^0)}{RT^2}$$

$$\ln k_{H,12} = - \int \frac{(\bar{H}_1^* - h_1^0)}{RT^2} dT + C$$

$$\frac{\partial \ln k_{H,12}}{\partial P} = \frac{\bar{V}_1^* - v_1^0}{RT}$$

Now you have to get it as  $\mu_1^*$  the other thumb rule in thermodynamics whenever you do not know free energy divide it by T and differentiate with respect to T okay let me do that so you have and also this number will this quantity will keep appearing all the time  $T \gamma_1 \phi_1 / \gamma_1 X_1$  let us

give it the name  $H_1$  we want to write  $H_{12}$  because it turns out as far as this is concerned I am going to the limit as  $X_1$  goes to 0.

When  $X_1$  goes to 0 this can only represent a quantity that is a characteristic of the solvent of the medium in which 1 is dissolved in this case I have a binary of 1 and 2 and they should depend on the nature of 2 not on composition but on nature of 2 this quantity is called Henry's law constant normally this  $\Phi$  and  $\gamma$  are omitted because you look at dilute solutions in the limit as  $X_1$  goes to 0.

I will come to that  $X_1$  goes to 0,  $\gamma_1$  will go to 1 and normally the pressure you are talking about is low enough for ideal behavior so this ratio is called Henry's law constant so it just given a name because Henry is suggested a some point that  $Y_1$  is proportion to  $X_1$   $Y_1 = H_{21} X_1$  or  $P_{y1}$  the partial pressure is  $H_{12} * X_1$  this one Henry's Law constant.

So Henry's Law constant will if I have experimental data for it then I have got a correlation between vapor phase composition and the liquid phase composition I have  $\partial \ln a_1 / \partial T$  as I told you if I differentiate with respect to  $T$   $\mu_1 / T$  will give you a  $H_1 / T^2$   $\mu_{10}$  is pure so you will get  $-H_1 / RT^2$  actually this is pure substance it as an ideal gas so this is simply  $H_1$ ,  $H_1$  if you like in the vapors phase or the gas phase  $\mu_{10}$  is a chemical potential of pure 1 at temperature  $T$  and pressure equal to 1 atmosphere.

So  $\mu_1 / T$  for the pure substance will give me  $H_1 / T^2$  it is  $H_1$  for the ideal gas for component 1 as an ideal gas at temperature  $T$  and pressure equal to 1 because enthalpy is independent of pressure I do not have to write that 0 there for ideal gas it is simply  $H_1$  it simply the enthalpy of pure 1 this is symbolic when you differentiate  $\mu_1$  you will get  $H_1 / RT^2$  it indicates the same state as the  $\mu_1$  that I have there.

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Gas solubility in liq. Eq. CO<sub>2</sub> in water  
 (1) (2)

$$\mu_1^l = \mu_1^g = \mu_1^o + RT \ln P y_1 \phi_1 \quad \checkmark$$

$$\mu_2^l = \mu_2^v$$

$$\mu_1^* + RT \ln \gamma_1 x_1 = \mu_1^o + RT \ln P y_1 \phi_1$$

$$\ln \frac{P y_1 \phi_1}{\gamma_1 x_1} = \frac{\mu_1^* - \mu_1^o}{RT} = \lim_{x_1 \rightarrow 0} \ln \frac{P y_1 \phi_1}{\gamma_1 x_1}$$

Now look at this quantity the whole idea of writing an equation like this is I have all the composition dependents on left hand side the right hand side is independent of the composition therefore the left hand side remains same if I go to limit as X1 goes to 0 right so this is equal to the left hand side in the limit as X1 goes to 0.

A  $\gamma_1$  X1 goes to Y1 or also goes to 0 I do not have to worry  $\gamma_1$  is 1 this is equal to this because the way I have separated I have written them for the model chemical potential is to dump all the composition dependents in  $\gamma$  here and  $\Phi$  here other than this X1 and Y1 the rest of the composition dependents is dump in  $\gamma_1$  and  $\Phi_1$  these are the reference quantities the only thing I know about dump this I know only thing I know about this animal is independent of the composition.

Because it is independent of the composition if I rearrange the equation this quantity becomes independent of composition therefore it is the same this ratio remains a same in the limit as X1 goes to 0, in the limit as X1 goes to 0  $\gamma_1$  is 1 that I have a liberty to do because that is defined as  $\mu_1^*$  then Y1 will also go to 0 you do not have to worry about X1 going to 0 because Y1 /X1 will remain finite.

Then you have pressure and you have  $\Phi_1$  so H12 is actually Henry's law constant is usually defined in books as  $P y_1 / X_1$  it is a correctly  $P y_1 \Phi_1 / X_1$ ,  $\Phi_1$  is normally small X close to 1 so I have this in the limit is X1 goes to 0 this is written as  $H_1 \bar{\infty} -h_1 \text{ gas} / RT^2$  this  $H_1 \bar{\infty}$  is partial mole all enthalpy of component 1 in a solution in a given solvent I think infinite dilution.

So the  $\infty$  indicates infinite dilution it is actually a measurable quantity I will show you it is measurable in a minute actually what you do is measure enthalpy of solution this is actually been experimentally measured by long ago Henry's law constant have been reported for long time because you do not actually measure it infinite dilution you measure it in low dilution in the next half let to 0.

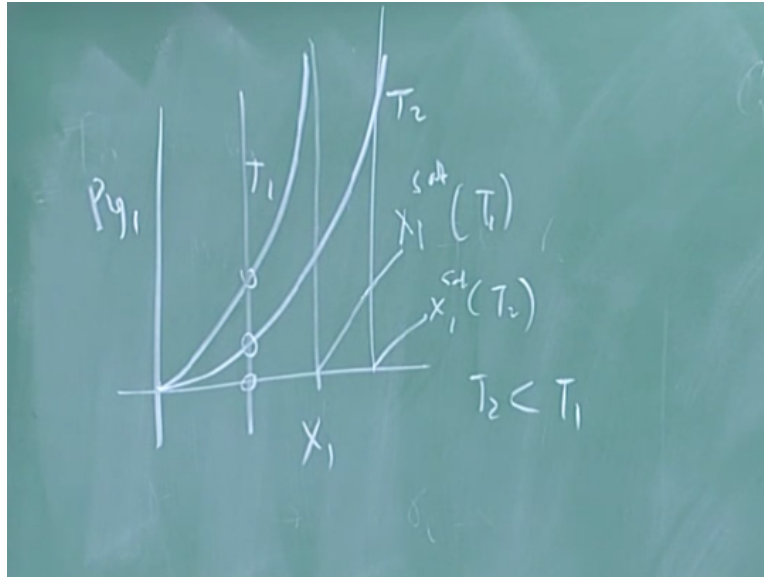
Having done this, this is only subject in which you can do this now integrate this and you get a slightly difference here if you integrate this you get  $\log H_{12}$  is equal to integral of I think laws of constant because now you have an interpretation you had no one star by  $t$  which you did not know but when you differentiate you got  $H_1/T^2$  which you know so you can integrate this the only difference is that this integral you can do this integration actually from experimental data on  $H_1$  bar.

Let me also write down that other expression that is differentiation with respect to pressure since this quantity can only dependent on temperature and pressure I have to worry only about temperature and pressure dependents and of course it dependents on nature of the solvent that vary from solvent to solvent this is by you will get  $V_1$  bar  $\infty - V_1/RT$  differentiation of  $\mu$  with respect to  $P$  will give me  $V$  or  $V_1$  bar.

This again is measurable and what is more if I integrate this over  $P$  I can go to 0 pressure will discuss the constants later on that means I need to access if experimentally the Henry's law constant at some sufficiently low pressure if I do it at low pressure then  $\Phi$  is 1.

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So what I do is measure  $P_{y1}$  for carbon dioxide and plot it against  $X_1$  typically the curve will go like this it will start at 0,0 course and it will go off vertically because as you increase the pressure at a given temperatures you reach the saturation limit this is the  $X_1$  saturation or solubility at temperature  $T$  this is typically the experimentally observed curve as you increase the pressure the solubility will increase and then it will stop at certain value.

So I said I can this is the given temperature at in other temperature may be slightly different this is at  $T_1$  this is a  $T_2$  so this will be a  $T_1$  and this will be  $X_1$  saturation at  $T_2$ , and  $T_2$  is less than  $T_1$  this is an experimental observation in case of gas it also follows from here if you look at this Henry's law constant here this is enthalpy in the solution this is enthalpy in the vapor phase so this enthalpy is always greater than this, this number is with the order of latent heat.

This is not exactly this actually normally little less than a latent heat but it is positive number so  $D/dt$  is negative so the Henry's law constant will decrease as temperature increases this  $H_{12}$  will decrease as the increases if  $H_{12}$  decreases  $P_{y1}$  decreases with the same quantity so what you do is actually you operate at some temperature is lower you will actually be I am sorry at some you not working at saturation you work at some temperature like this at some composition liquid composition like this and the solubility you will find the vapor pressure here of carbon dioxide above the solution at temperature  $T_2$  is this at  $T_1$  is this.

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$$\mu_1^l = \mu_1^* + RT \ln \gamma_1 X_1$$

$$P y_1 \phi_1 = H_{12} \gamma_1 X_1 \quad \text{--- Solute}$$

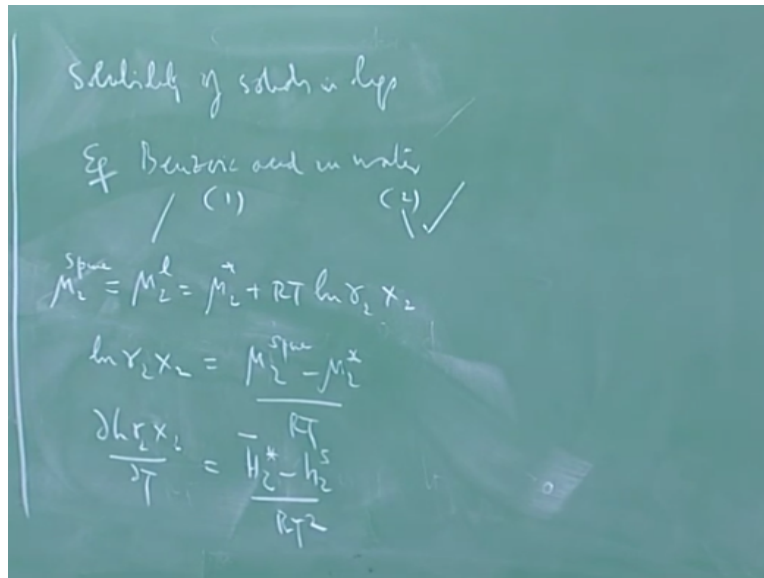
$$P y_2 \phi_2 = P_2^{\text{sat}} \phi_2^{\text{sat}} (P y_2) \gamma_2 X_2 \quad \text{--- Solvent}$$

So you will get a difference in the carbon dioxide in the vapor phase that is what you get this phase in this solution so having said this let me now write out what the chemical potential is therefore  $\mu_1 = \mu_1^{\text{liquid}} = \mu_1^* + RT \ln \gamma_1 X_1$  or I write  $P y_1 \phi_1$  these two are equivalent  $\gamma_1 X_1$  it is necessary for you to measure the Henry's law constant, Henry's law constant for gases and liquid for example usually very large so at very high partial pressures you get very low solubility.

Typical solubility carbon dioxide in water is to -3 solubility from most of the gases is very low in terms of mole fraction now let us look at so this is how look at so this is how what you do is then as for as solid vapor liquid equilibria or concerned involved in solvents and solutes for solutes will get an equation like this for solvent component this is for solute like components and this is solvents.

Even you can have any number of components you can just rewrite this equations we get the H<sub>12</sub> if you have many, many solvents that 2 will actually represent the solvent in environment it may be a mixture of solvents so you have to get Henry's law constant in that particular so vent or mixture of solvents so I can change this 1 to I and 2 to j I representing all solutes j representing all solvents in which case you will write this as H<sub>is</sub> s indicating the solvent in which solvent mixture and mix the solute.

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The Henry's law constant is measured for the solute okay this is one part of it the other thing is solubility of solids in liquids okay this is exactly the same way so I have now, now again solvent like substances in solute like substances now let us take the example Benzoic acid in water is a classical system in which many, many measurements have been done very convenient to measure Benzoic acid does not ionize so ideally like NaCl.

If you have highly ionizing solutes the treatment is slightly different it is not different at this stage but it is different because what counts in solution is the number of molecules present and if it ionizes or the ions present sodium and chlorine for example will be treated as two different ions is the sometimes call colligative properties the properties that depend on the number of species in solution the number of actual identities whereas benzoic acid will be just benzoic acid it does not ionize so you can be treated as one solute in water if you had NaCl it will be like three components system.

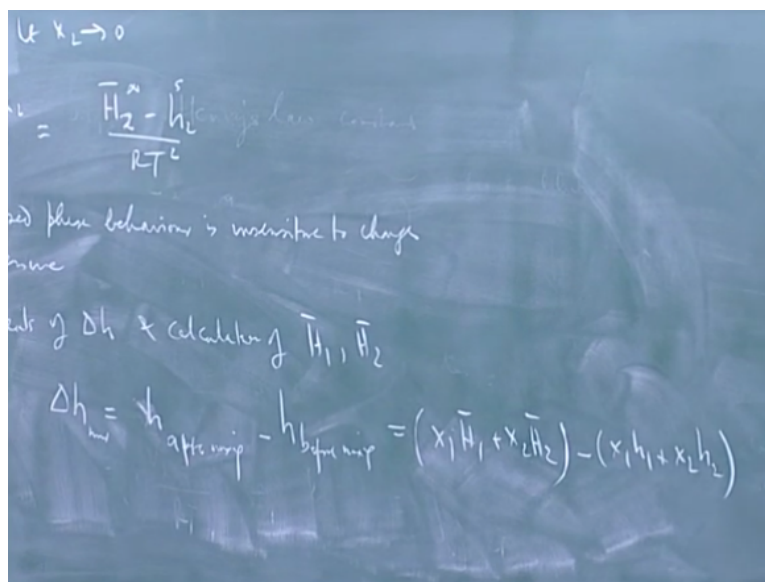
If it is Na<sup>+</sup>Cl<sup>-</sup> and water but let me come back to this let us say Benzoic acid is 1 and water is 2 for water it is the same equation so we know how to treat this, this is just a solvent here you are going to get  $\mu_2 = \mu_2^* + RT \ln \gamma_2 X_2$  this should be equal to under phase equilibrium conditions we are looking at solubility of solids you are looking at  $\mu_2$  solute pure at phase equilibrium demands certain both phases the chemical potential should be the same.

The solid phase in this case is pure solid this is  $\mu_2^{\text{solid pure}}$  should be equal to  $\mu_2^{\text{liquid}}$  which is equal to this now you do the same thing you ask simply what is  $\gamma_2 X_2$  which is  $\mu_2^{\text{solid pure}}$  –

$\mu_2^*/RT^2/RT$  if you differentiate this will give you  $H_2$  solids this will become  $H_2^*$  now reverse with to in order to take care of the sign.

I did not reverse that here only because the quantity  $H_1 \text{ bar } \infty$  I mean or  $H_1 \text{ gas } -h_1 \text{ bar } \infty$  is the positive untidy here this quantity is positive this is like a liquid enthalpy this is a solid enthalpy this is  $h_2$  solid so it is like the radiant heat of melting the order of magnitude of latent heat of melting.

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So let me reiterate this  $\partial \log \gamma_2$  by  $\partial T$  is equal to  $h_2 \text{ bar } \infty$  I am going to go to limit this side is independent of composition so this side both sides should remain independent when  $X_2$  goes to 0 so take limit as  $X_2$  goes to 0 to  $\text{bar } \infty - h_2 \text{ solid } /RT^2$  this is actually your  $\partial H$  of solution I will come back to that I am going to discuss heats of mixing heats of solution and so on in their measurement.

Then you can integrate this and get information you do not do differentiation with respect to  $P$  when it comes to the condensed phase because pressure the condensed phase behavior is insensitive to the changes in pressure is insensitive so essentially you lose a degree of freedom when you are dealing with the condensed phase pressure is not a significant variable for the engineer unless you use millions of points pressure unless you are talking of enormous changes in pressure.

We do not deal with normal such changes in pressure normally so in practice you will find effectively one degree of freedom is lost that pressure effectively should be counted out as a variable that it does not control anything in the condensed phase so as far as the condenser is concerned this is the equation you will use you will have to make these measurements and then do the integration but let me get back and show you measurement system.

So we have seen that these measurements are important measurements of  $\partial H$  and calculation of  $h_1$  bar and  $h_2$  bar  $\partial H$  of mixing maybe solution or in all cases it is simply  $h$  after mixing -  $H$  before mixing this is this is after mixing for mixing is  $H_1 + X_2 h_2$  small  $h_1$  is of course by our notation the enthalpy of the pure substance in the specific enthalpy of this incidentally I forgot to mention this if you look at sufficiently dilute solutions  $\gamma_2$  is one because  $X_2$  goes to zero  $\gamma_2$  is 1 so in dilute solutions.

If this quantity is reasonably independent of temperature I will say two things first  $\gamma_2$  goes to 1 secondly  $h_2$  bar  $\infty - h_2$  is approximately constant or approximately independent of temperature so I can rewrite I can integrate this equation and write  $\log x_2$  is equal to minus by acting plus the constant which means if you plot the solubility of 2 in 1 against  $1/T$  you should get a straight line.

But anyway this is a very well-known result  $\log X_2$  against  $1/T$  and many physical chemists have actually calculated  $h_2$  bar  $\infty - H_2^s$  from this so data on  $h_2$  bar  $\infty$  are reported from such calculations so you need to know the solubility at room temperature and then you need to know  $H_2$  bar  $\infty - h_2$  is usually known so from that you can calculate solubility at any other temperature.

This is another extreme case of this if the solution remained ideal if solution is ideal if the mixing process is ideal then  $H_2$  bar  $\infty$  is the enthalpy of two when dissolved in one that is in the liquid state if you go to the limit as  $X_2$  goes to 1 and treat this as still being in the liquid phase it is a pathetically now because you are talking about Benzoic acid in water suppose benzoic acid had remained a pure liquid at that temperature then  $H_2$  bar  $\infty$  would be actually  $h_2$  liquid which means the right-hand side is actually the latent heat of melting of component 2.

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$$\ln x_2^{id} = -\frac{L_2^m}{RT} + \text{const}$$

$$T = T_{m2}, x_2 = 1$$

$$\ln x_2^{id} = \frac{L_2^m}{R} \left( \frac{1}{T_{m2}} - \frac{1}{T} \right)$$

That means  $\log X$  to ideal the ideal denotes ideal solution is  $-L_2$  of melting/  $RT$  + a constant this was by integrating with respect to temperature I know one condition that is a temperature equal to  $t$  melting of two of component 2,  $X_2$  has to be equal to 1 so I can write  $\log x_2$  ideal for ideal solubility is equal to  $L_2$  melting by  $R \cdot 1 / T_m - 1 / T$  the most significant aspect of this result is that the ideal solubility of a solute to in any solvent is independent of the solvent.

And when you must have the same solubility in all solvents this has been observed for example for naphthalene in a series of hydro carbons you take propane butane etc, etc. you take a solution start with butane you have to start with even higher molecular weight so that is in the liquid state or go to sufficiently low temperature you take a whole series of hydrocarbon series the homologous series and look at the solubility of say something like naphthalene.

In that if you take the mole fraction solubility its independent of the this has been observed it is true for many systems and what actually what Hildebrand and Scott do say that  $X$  to actual is simply what you do is  $x_2$  ideal is actually  $\gamma_2 X_2$  is actual  $x_2$  ideal /  $\gamma_2$  so you can have a theory for GXS the excess free energy calculate  $\gamma$  from that and calculate  $X_2$  ideal divided by  $\Delta_2$  in fact the whole book on by Hildebrand and Scott on solubility of non electrolytes has a large volume of data that shows you that you can do this calculation very well.

You calculate the ideal solubility using this formula that is fixed for a solute so you can take a solute and tell me at any temperature what the solubility is then you calculate  $\gamma_2$  for that

substance from excess free energy information you divide  $X_2$  ideal by  $\gamma_2$  you did the actual sorry it becomes independent of composition therefore the right hand side has to be independent of composition therefore I can go to the limit of  $X_2$  going to 0.

Then I know this animal  $h_2 \bar{\infty}$  as the partial molar enthalpy at infinite dilution what I will do is to show you that I can actually measure these quantities by measuring heats of mixing I will discuss different units for measurement of for writing the models for chemical procedures we lose the polymer units for example and we will also talk about polymer solutions separately in polymer solutions when you say dilute solutions you mean parts per million you do not mean mole fractions 4.21 anything with it those are the only two cases I have discussed the rest of it is just applications so I will stop there.

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