Thermodynamics And Kinetics Of Materials

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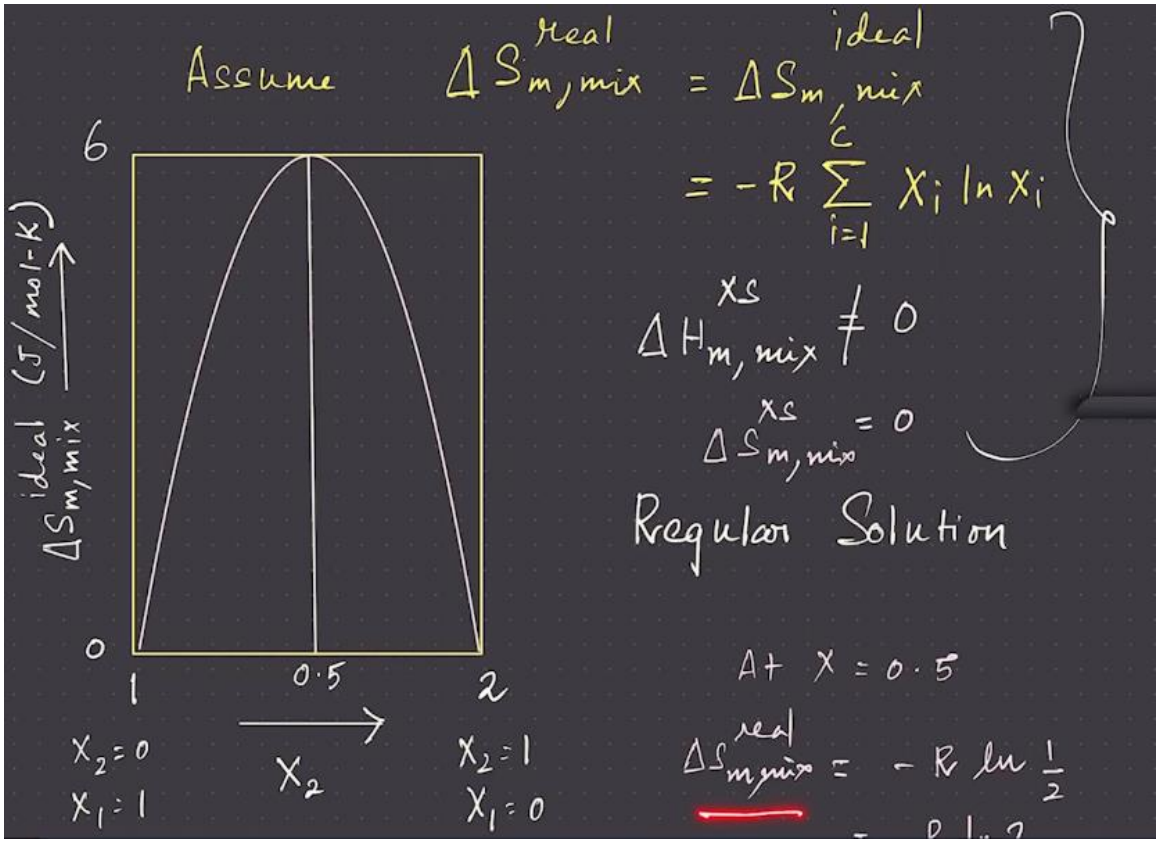
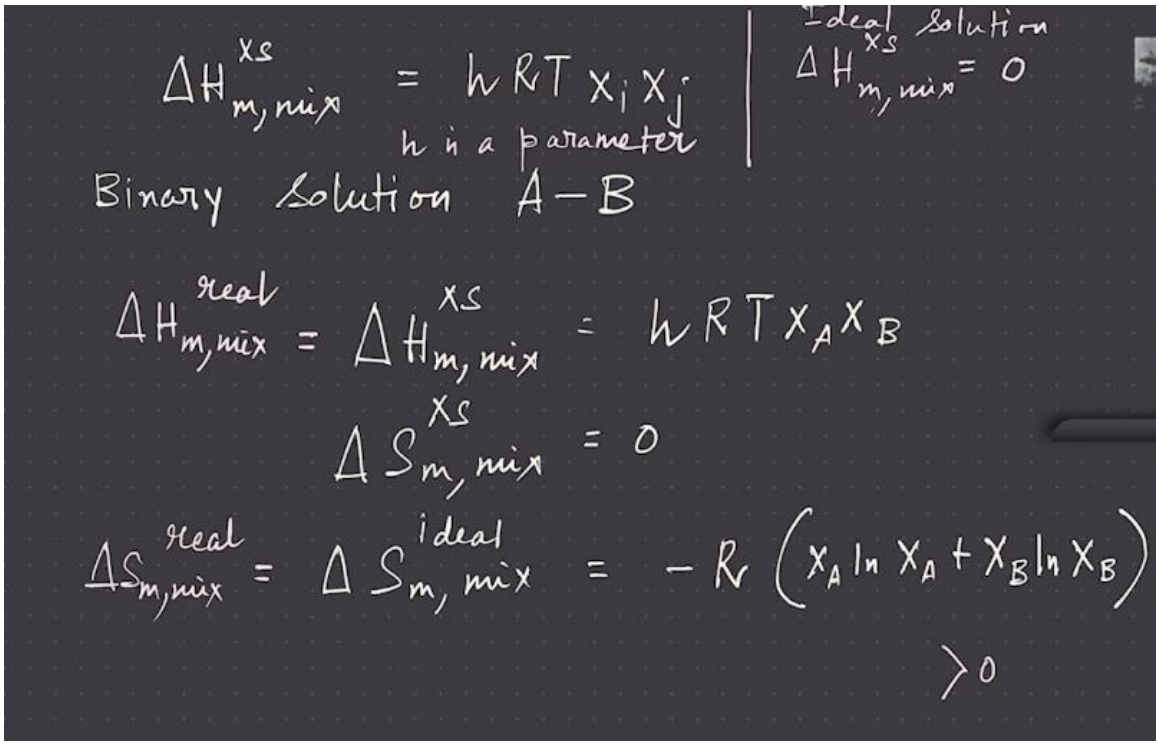
Lecture 27

Colligative Properties

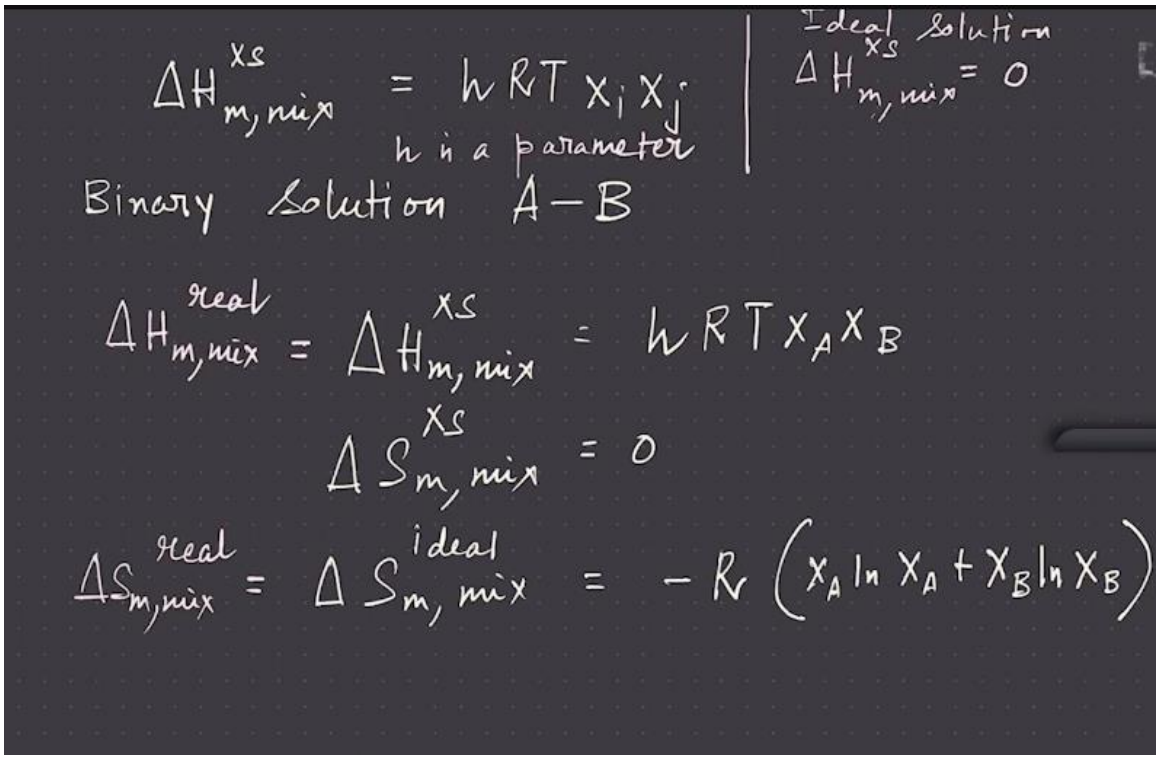
So, as I told the previous lecture, the molar entropy of mixing for real solutions have been taken with the same as that for ideal solutions. So, and the formula is given by minus r x i and x i. This is a formula that you can derive for multi component systems as we mean Boltzmann hypothesis s equals to k ln w, where w is the number of configurations that are a number of achievable micro steps for given for the most probable micro step. So, or basically the number of complete configurations or number of ways you can arrange a, b, c, b means as many components are there, atoms on the lattice side. Say for example, for a binding on the lattice sides, so totally available lattice sides are n and say out of which n a belong to a means n a atoms of a are there and n b atoms of b are there, then basically s equal to k ln w and w is nothing but n factorial by n a factorial n b factorial. This is something that we already know from there we used a Stirling approximation to get into this r minus r x i and x i or you can also get it through means assuming ideal solution.



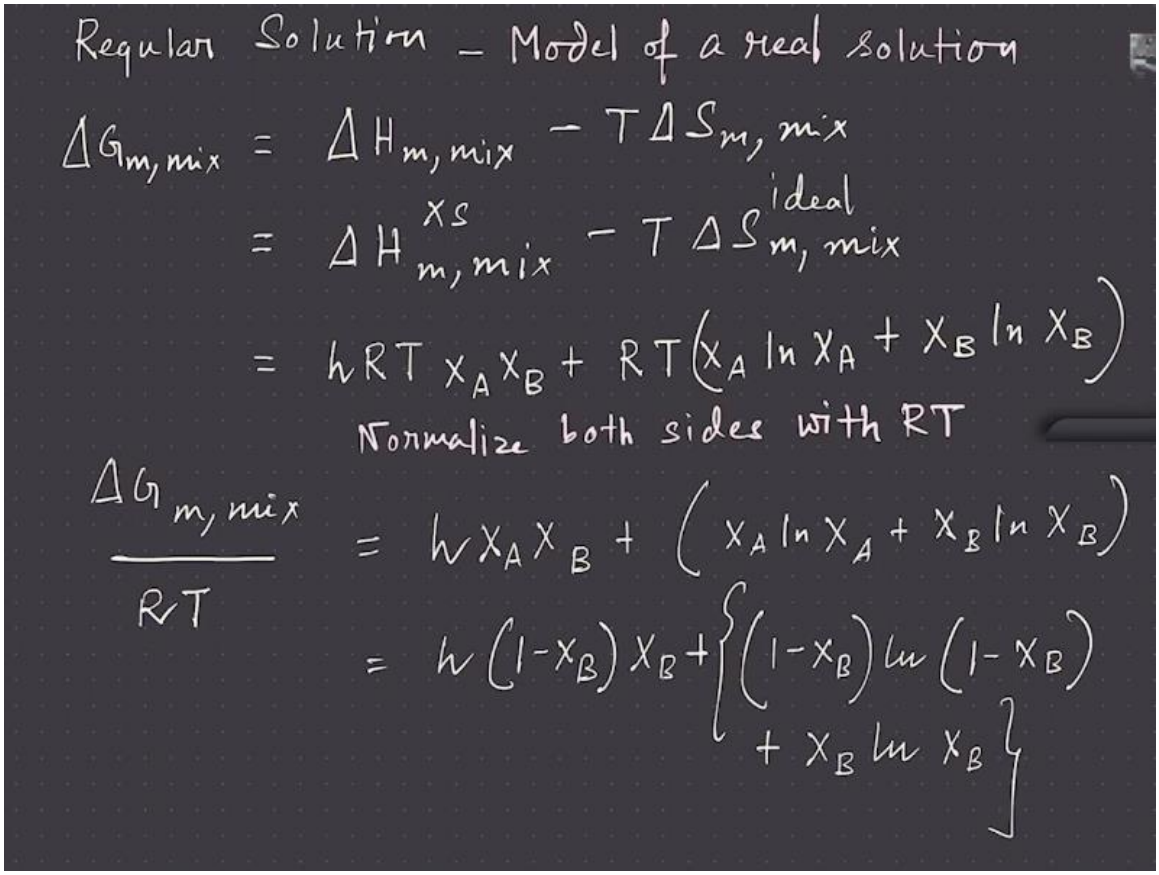
We also found flat from delta G that we arrive or delta G mix that we arrive for ideal solutions, we can derive the delta s mix and delta s mix for ideal solutions the same. So, basically for real solutions we have taken the delta s mix for ideal solutions and that is basically minus r x i and x i. So, please note that for regular solutions for regular solutions for the regular solution model that I will discuss there is no difference between delta s mix ideal and delta s mix ideal which is the and it will give you the same formula. Now, as you know the main difference in the real solution is that there are interactions, so delta s mix is not equal to 0.



We have already discussed that and remember again for real solutions the maximum delta s mix will be for r is equal to 2. However, the main difference comes in the delta G mix because delta H a mix excess is not equal to 0. Now, we are assuming a formula, so as if you follow the notes delta H a mix ideal is 0, delta H a mix excess is this H r t x i x j where H is the parameter. So, here H is a parameter and we are assuming say a binary solution a b. Also then this equation becomes delta H a mix excess actually you can write this as delta real equal to delta H a mix excess because delta H a mix ideal is 0.



This H r t x i x b where x a is the mole fraction of a and x b is the mole fraction of component p. Now, delta s m mix excess is 0 and delta s m mix real equal to delta s m mix ideal which is minus r x i l and x i sum over i. So, which is x l and x a plus x b and x b again you note that x a and x b are less than 1 and it lies between 0 and 1 and therefore minus sign makes sure that delta s mix is positive, delta s mix is positive greater than 0. So, the minus sign make sure that delta s mix is positive. So now, you have delta G a mix this is for a so this is the model for regular solution, regular solution is one model it is a model of a real solution, real solution differs from ideal in this that it has again I will tell differs from perfect in this that there are interactions.



See, there is a subtle difference between perfect solutions and ideal solutions I will come to that in ideal solutions there are no interactions this is not really means it is true that for ideal solutions we are telling that there is no interaction, but in general you can call them as perfect solution. So, there is a distinction here so I will come to that. In fact, these interactions that you can see for example, for example, you know a b binary solution what type of pair wise interactions are possible you can have a a interactions, you can have a b interactions and you can have b b interactions. Now, you can tell that there can be b a interactions, but they are equivalent because a b interaction or b a interaction does not really matter the order does not really matter. So, a b interactions or b a interactions and b b interactions.

So, these are the three major interactions that you can basically think. Now, in such a case you have come up with a model. So, you will just assume that the model is like HRT X X B. So, basically delta H m X is what HRT it is H times RT times X X B because we have assumed so, we have assumed so. We will show how a similar formula can be arrived for binary solutions.

So, you see that this part is equal to this and delta H m X has a minus R and there is a minus T here and there is a minus R there. So, because the definition has minus R. So, this becomes plus RT X Ln X A plus X B ln X B. Now, you normalize both sides by with RT.

So, what you get on the left hand side is delta G m X or this is the free energy of mixing of a real solution again or a regular solution let us call it delta G m X regular normalized by RT.

R is the gas constant RT equals to now if you look at the right hand side it is H X Ln H X X B plus X A ln X A plus X B ln X B. Now, we can assume let X equal to X B then X A equal to 1 minus X. Now, if I substitute that way, so this becomes H into 1 minus X into X and 1 minus X 1 minus X plus X 1 minus X. Now, if you have this function for different values of this parameter H you can plot it. For different values of this parameter H you can plot it.

```
In [1]:
1 import numpy as np
2 import matplotlib.pyplot as plt

In [2]:
1 x = np.linspace(0.0001,0.9999,100)

In [3]:
1 for i in np.arange(-4,6,2):
2     h = i
3     hm = h*x*(1-x)
4     plt.plot(x,hm,label=str(h))
5 plt.xlabel('x -->')
6 plt.ylabel('<-- Exo - Enthalpy of mixing - Endo -->')
7 plt.legend(bbox_to_anchor=(1.05, 1.0), loc='upper left')
8 plt.tight_layout()
9 plt.show()
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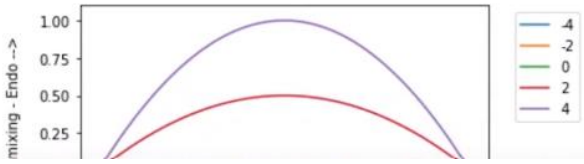
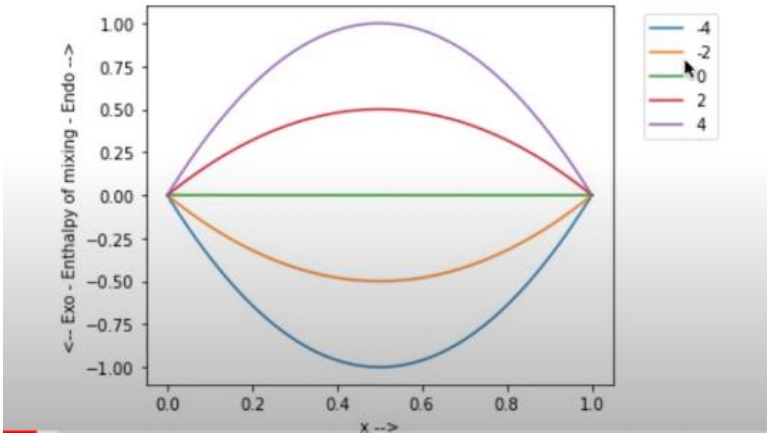
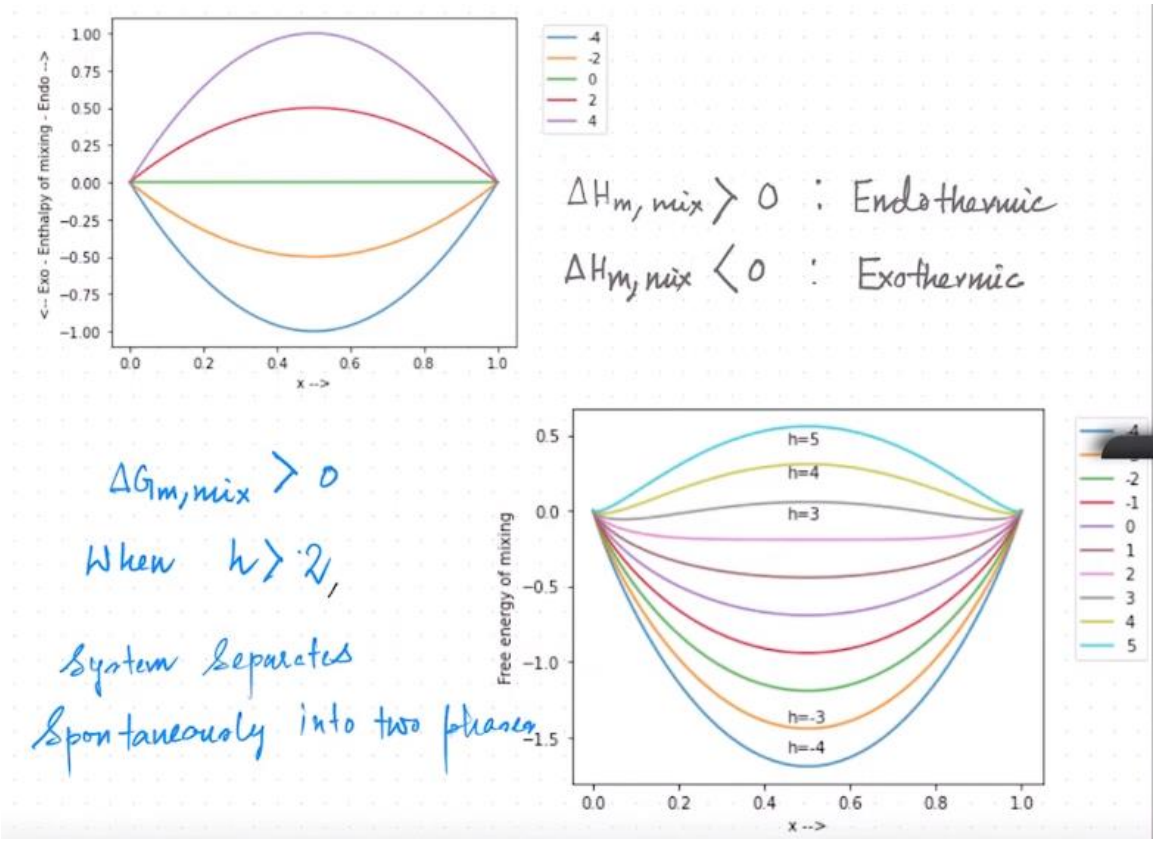


In fact, I will share with you small python code that I have written for this purpose for visualization of this function. So, as you can see here I am importing this library is called dump pi and matplotlib and I take an X between 0.0001 and 0.9 and 0.9 why not exactly 0 and 1 because log 0 is undefined right because 1 minus X when X equal to 1 1 minus X is 0 log 0 is undefined or it becomes minus infinity and again for 0 when I take X equal to 0 then there is again a log 0 which is undefined.

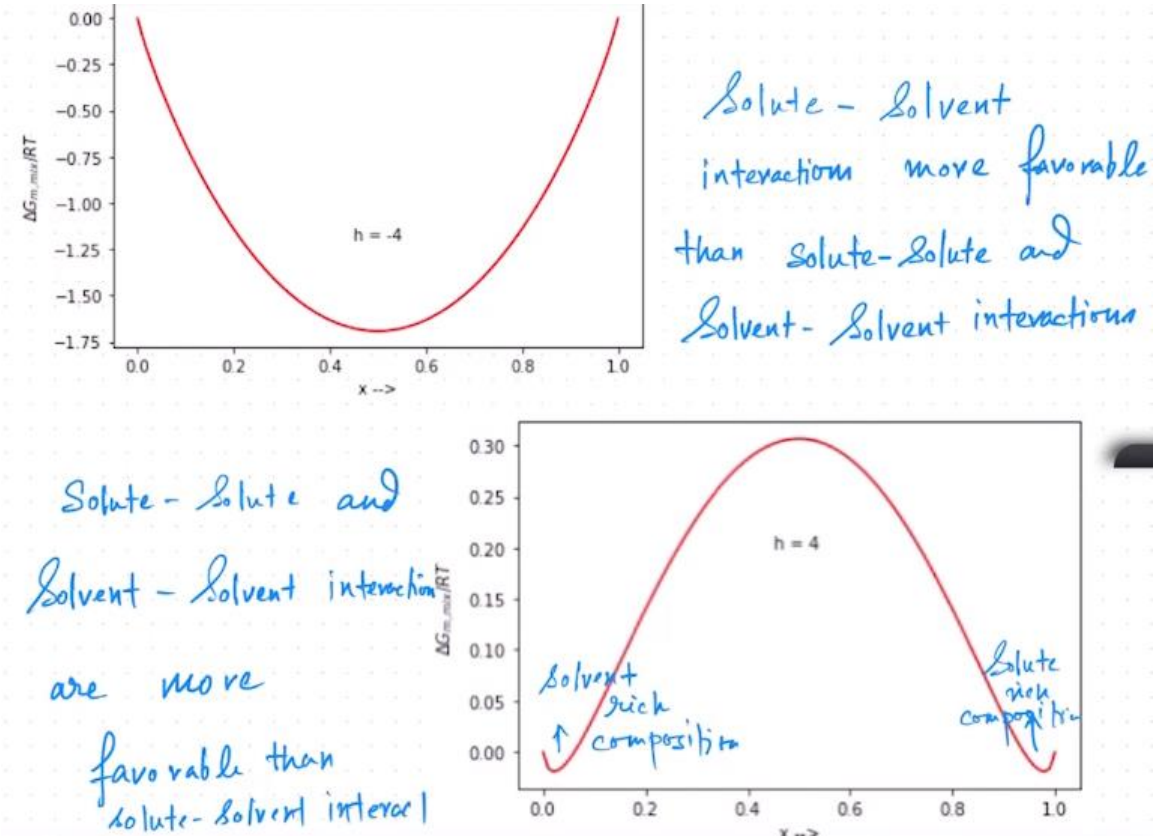


So, I take very small values 0.0001 and 0.99999 you can take even smaller values not a

problem and I use something called n p dot ln space to take this independent variable. So, this is the independent variable axis that I have set and then you can see I am varying H from minus 4 to 4 minus 4 to 4 in steps of 2 and this is the enthalpy of mixing and if you plot it you will see that if you plot it you will see that at 0 when H equal to 0 you have the ideal solution delta H m mix is 0 and then as you go to positive enthalpies of mixing which is basically endothermic process like positive enthalpy of mixing means you are basically absorbing basically absorbing heat for making the mixture of the solution for 2 for example, for 2 you have a positive enthalpy of mixing for 4 you have a positive enthalpy of mixing which indicates an endothermic process of mixing. For however, when H is negative like minus 2 or minus 4 you have a negative enthalpy of mixing that means that heat is evolved during the mixing process it is evolved during the mixing process.



Now, you know the H m mix and you can also now write the entire g m mix that is the solution the free energy of mixing the solution of the real solution or regular solution which is H x 1 minus x plus x times log x plus 1 minus x times log 1 minus x and you have again normalized with R T remember that then you can basically see again I go from minus 4 to 6, but in steps of 1 instead of in steps of 2 in fact here also I can make it steps of 1 then you will see more curves here. So, you will see more curves here. So, from minus 4 to till 5 you will see the curve and see blue the 5 1 has a very large enthalpy of mixing right the enthalpy of mixing is very large and it is really really big at x equal to 0.5 right at x equal to 0.5 you are seeing all the maxima and the minima right only for this purple line that you see that corresponds to H equal to 0 that corresponds to ideal mixing right.



So, ideal mixing is nothing, but a special case of this regular solution model right and now if you do this if you plot this guy here the g m which is H x 1 minus x plus x log x plus 1 minus x log x and you are plotting this you can see that you have a very interesting phenomenon you can see till the for negative for negative values of H you can like H equal to minus 4 H equal to minus 3 minus 2 minus 1 and 0 you basically have a the free energies which are negative all through. However, when you go to sufficiently large positive say H equal to 1 itself H equal to 1 itself you can still see that it is a H equal to 1 corresponds to this case the H equal to 1 or H equal to 2 because want to still the free energies being negative, but just go beyond that you start at H equal H equal to up to H equal to 2, but at H equal to 2 you can start seeing the change there is a change in the character of the free energy curve H equal to 3 you can definitely see there is a change in character you are actually seeing 2 minima and 1 maxima instead of 1 minimum when H was negative when H was negative you saw 1 minimum even H was slightly positive like up to 1 up to 1 or up to 2 I can tell up to 2 up to 2 you can still see that there is only 1 minimum in the gm curve right this free energy of mixing curve there is only 1 minimum. However, as soon as you go to H equal to 3 or H equal to 4 or H equal to 5 you can clearly see 1 maximum and 2 minima in fact to demonstrate that we have taken 2 special cases 1 say for example, if I take H equal to minus 4 if I take H equal to minus H equal to minus 4 and plot then basically I see 1 minimum right at x equal to 0.5 for the solution right this is delta gm mix by RT which has a minimum at x equal to 0.

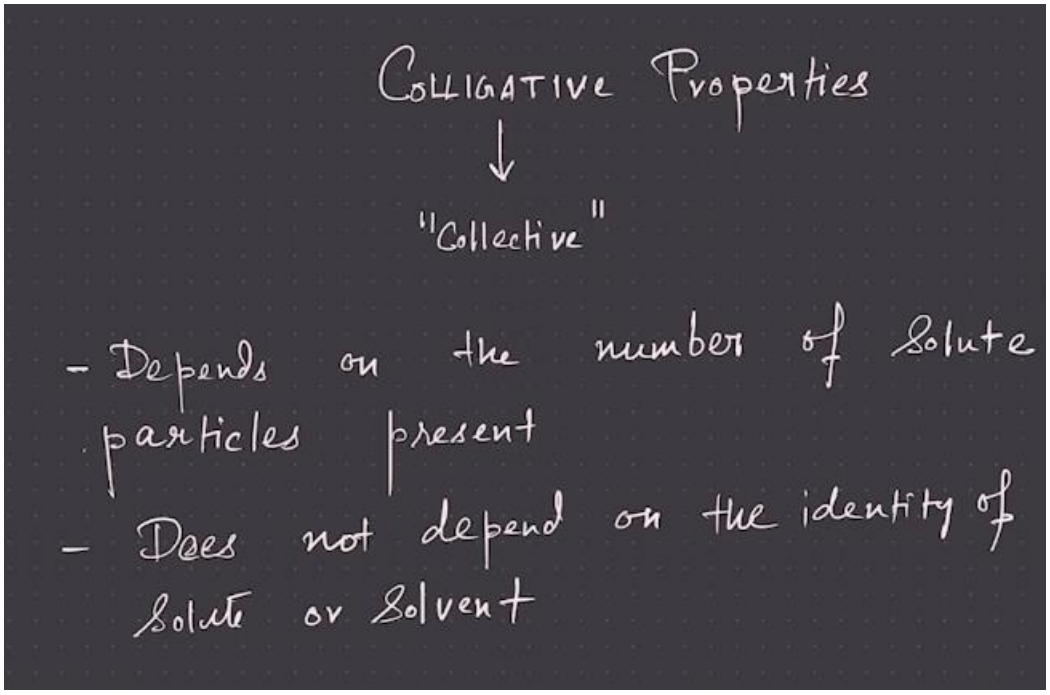
5. However, if I take now H equal to 4 case H equal to 4 case then basically as you can see there is 1 minimum here and 1 minimum here and there is 1 maximum here. So, basically you will see means in this solution there will be an unmixing that will happen and then an unmixing will produce 2 phase separated mixture phase separated mixture where you have 1 side corresponding to 1 minimum and the other sides composition the other phase of the. So, you have a phase separation and you have this last string and you have 2 minima you will have 2 compositions corresponding to this 2 minima. So, it that solution. So, basically you will see a A rich solution and a B rich solution if you think of a binary alloy there are binary solid solution or binary liquid solution or a binary gas mixture with H which is positive and H equal to 4 say then you will basically see that at the given temperature and pressure for which this guys are drawn you will see that you will see that there will be the solution will contain compositions of 2 minima 1 is a A rich side A rich composition another is a B rich composition.

So, this is the B rich composition and this is the A rich composition because x increases this way x equal to x B right we have assumed x equal to x B. So, coming back coming back to the notes you see that the plot exactly I have shown here. So, delta as I told you that when delta H. So, when H is greater than 0 say for example, here H equal to 2 and here H equal to 4. So, in such cases what you will see is for H equal to 4 for example, you see this right.

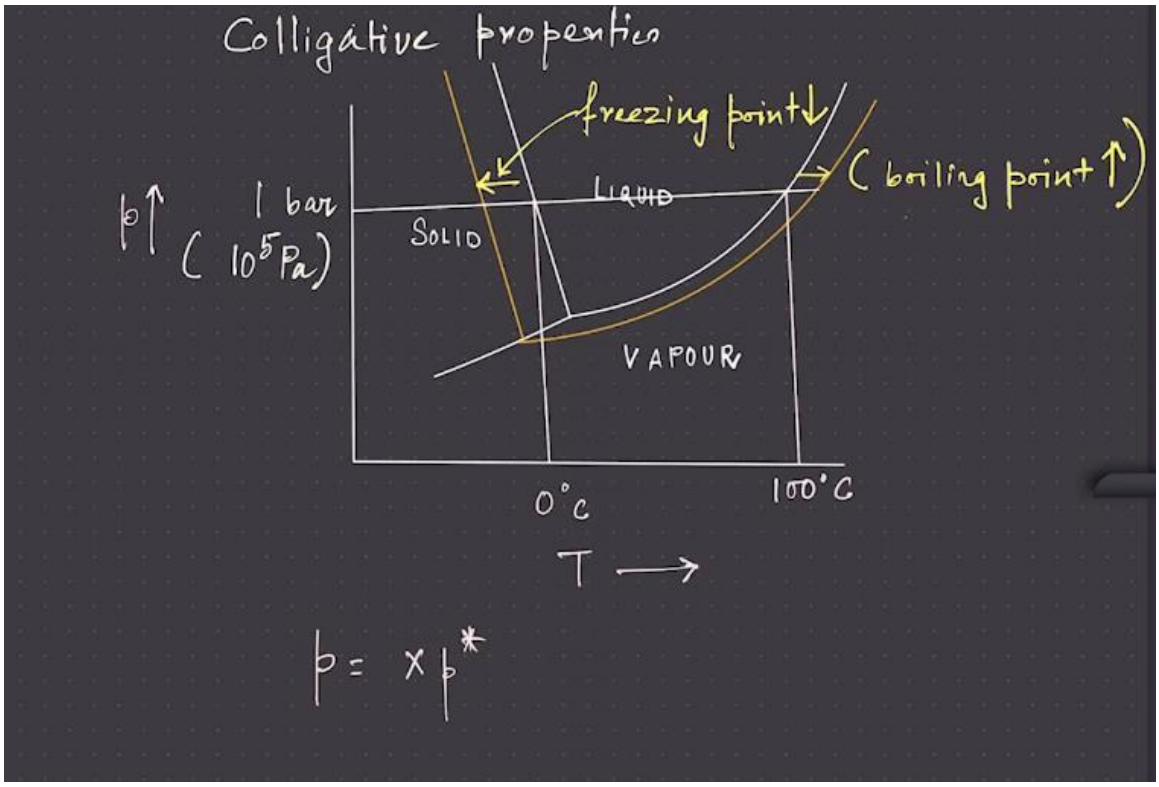
So, you basically see this and for H equal to 3 again you see a is very good to me again for or H equal to however for H equal to 2 for H equal to 2 which is basically this one you see that it is very nearly flat with us minimum here. So, basically you see beyond H equal to 2 at least for a model beyond H equal to 2 you start seeing system is separating spontaneously into 2 phases correspond and with the compositions corresponding to the 2 minimum. In fact, I have demonstrated here the same curve we have put. So, in this case what happens is solve in this case H equal to minus 4 is for a real solution remember solute solvent interactions are more favorable than solute solute and solvent solvent interactions. That means solute solvent interactions have less energy more favorable means less energy than solute solute solvent interactions put together.

So, if you take solute solute solvent solvent interactions put together the energy is more than the solute solvent interactions solute solvent interactions are favored and as a result you see this deep minimum deep minimum in the delta G m x by R T curve right. This is this indicates that their solute solvent interactions are more favorable right are more favorable. On the other hand it is solute solute and solvent solvent interactions are more favorable and since they are more favorable you see solute you will see here this minimum say for example this minimum corresponds to solvent rich right solvent rich composition and this is basically. So, x is the solute as room and this is solute rich composition. So,

solute is rich composition.



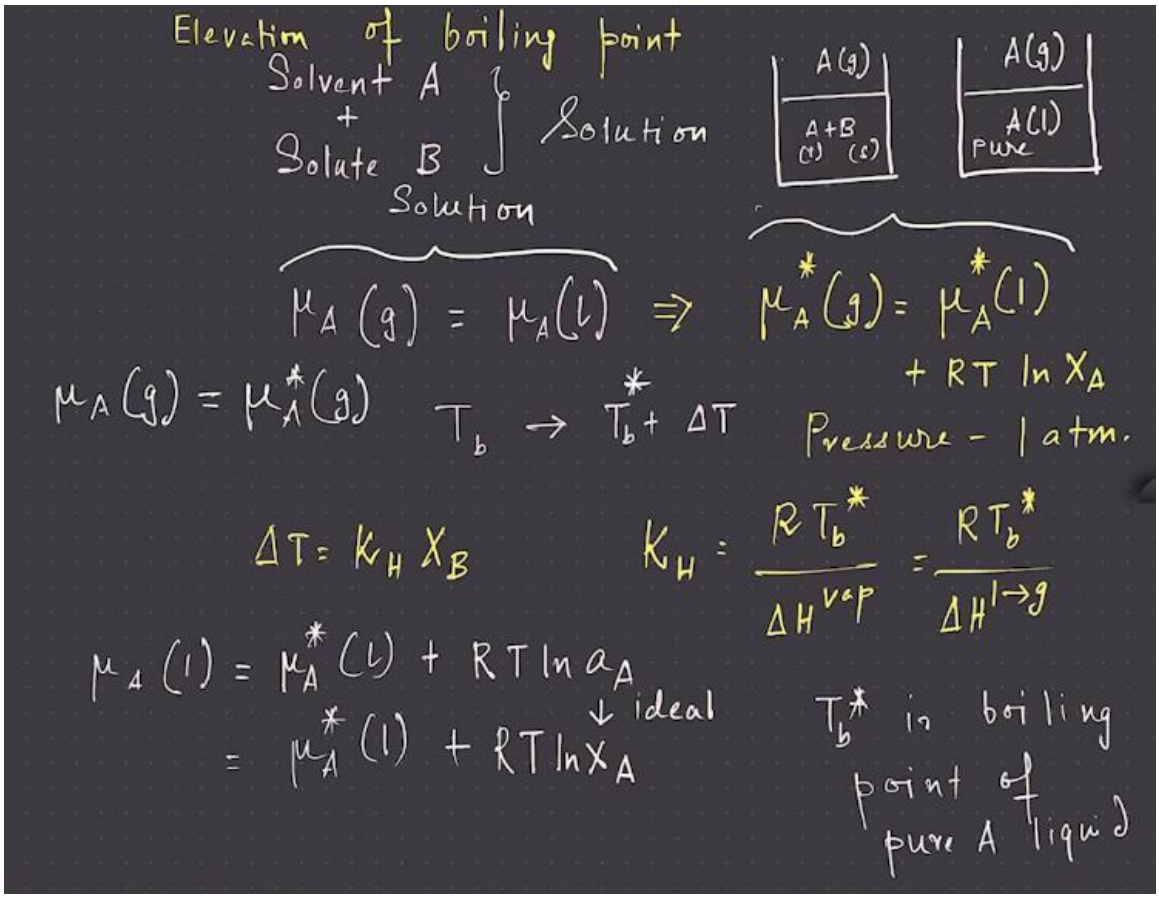
So, this is this can only happen this can only happen when solvent solvent interactions and solute solute interactions are more favorable than more favorable than what than solute solvent interactions. So, now understanding real solutions we come to colligative properties colligative means collective properties collective means it depends only on the number of solute particles present the solvent it does not depend on either the identity of the solute or that of the solvent it only depends on the number of solute particles present the solvent. So, once we understand colligative properties. So, we understood we already revised the distinction between ideal and real solutions. In fact, we constructed a real solution or a regular in the form of a regular solution where delta is a mix what the real solution was that was the same as that of the ideal solution.



However, delta HM mix was not 0 was not 0 and we took some function right how did this function come along and stuff we will discuss further when we discuss quasi chemical models, but right now let us discuss a very interesting idea called colligative property or collective property which basically the property that depends on the number of solid particles present, but not on their identity not on their character. So, it does not depend on the identity of solute or solvent, but the collection of particles of the number of solid particles that represent the solution right. So, what happens very interestingly if you see this is like pure water diagram. So, if you look at this pure water diagram which defines which shows distinct three distinct regions one is solid, one is liquid and one is vapor and if you look at this one bar pressure the systemic pressure you see for pure water these was your freezing point or this was your melting point this is 0 degree. So, one bar pressure and the temperature reading is 0 degree Celsius you have for water the melting point of the freezing point below the freezing point you have solid below the and above the freezing point you have liquid right.

Again if you go further up towards the right then you will see again another point on this one bar line and that line corresponds to liquid vapor equilibrium and that is at 100 degree Celsius this is called the boiling point or the or the vaporization point and this point basically below this point or condensation point and below this point liquid is below this point means to the left of it liquid is in liquid is the most stable phase and above this point vapor is the most stable phase. However, if you see so again how did this come along we will this colligative property come along you will see. So, if you now dissolve some

sodium fluoride in water right sodium chloride is your solute and you dissolve some sodium chloride in water you will see a very interesting thing you will see that your this curve basically shifts to the this guy shifts to the left right it shifts to the left. So, it is just this side that means your freezing point of this brine solution that is a solution of water and salt of basically the freezing point has reduced at one bar pressure at one bar pressure it freezes below 0 degree Celsius. Now, if you look at the other part that for the brine solution the same brine solution you see that the boiling point which was initially there the boiling point that was there has now shifted to the right and there is an increase in boiling point of the solution the solutions boiling point is here the solutions boiling point is now here instead of here.



So, not this point but this point so that boiling point has elevated right. Now, how do you understand that how do you understand that you can understand that by again looking at the equilibrium between liquid solid and liquid or liquid and vapor. For example, if we think of elevation of boiling point the first point that we talk about is this the elevation of boiling point that is the boiling point right at atmospheric pressure one bar pressure right it is more than 100 degree Celsius for a solution why is that so we will discuss that. So, what we want to discuss is so you take A to be the solvent and B to be the solute and the solvent plus solute makes a solution so that is a solution. Now, if you look at this when the when solvent and so when the vapor so basically if you have that you have say mixture

of solute A plus B and this is like a liquid and B is solute you can have like two liquids also B can be some other liquid which is in the or B can be some solid that is also possible which is dissolving in liquid.

But if you have this solution this A liquid is in equilibrium with its vapor right with its vapor. So, A liquid is in equilibrium with its vapor and as the vapor pressure goes towards atmospheric pressure as soon as the vapor pressure goes towards atmospheric pressure you will start seeing what you will start seeing what correct. So, now you consider this one where you have this type of configuration where you have this configuration compared to another one that we talk about is like you have A liquid that is pure liquid and then you have A vapor right in the liquid state. So, there is an equilibrium between them now one day when there is equilibrium between these two systems one is the gas one is the vapor phase of A and one is the liquid phase of A then obviously the chemical potentials have to be equal right mu A G for the for equilibrium between the vapor and the liquid there should be an equilibrium mu A in the vapor phase equal to mu A or chemical potential of A in the liquid phase. Now what does it mean is this so basically you can tell that A in the so when A is pure say for example this is the pure phase right this is the pure phase.

So, in that case mu A so gas for example even when there is a solute like sodium chloride the vapor phase still consists of water vapor right. So, it is like water vapor. So, A is in the solvent phase. So, A you can think of mu A star G is nothing but the chemical potential of A in the gaseous phase. So, basically chemical potential of the vapor of A right A vapor.

So, basically the vapor constant of A right A is the solvent. So, these are the solvent vapor. So, chemical potential of A in the vapor phase chemical potential of A in the liquid phase, but see that in the liquid phase when there is solvent when there is solute then basically it is not mu A L now becomes when there is solute mu A L is mu A star L which is like a pure solvent chemical potential plus RT ln AA. However, if we assume ideal solution we can write it as mu A star L let us assume that the solute the amount of solute that we put in it is still very dilute then we can write mu A star L plus RT ln right. Now, so this is basically assuming ideal solution means ideal nature of the liquid.

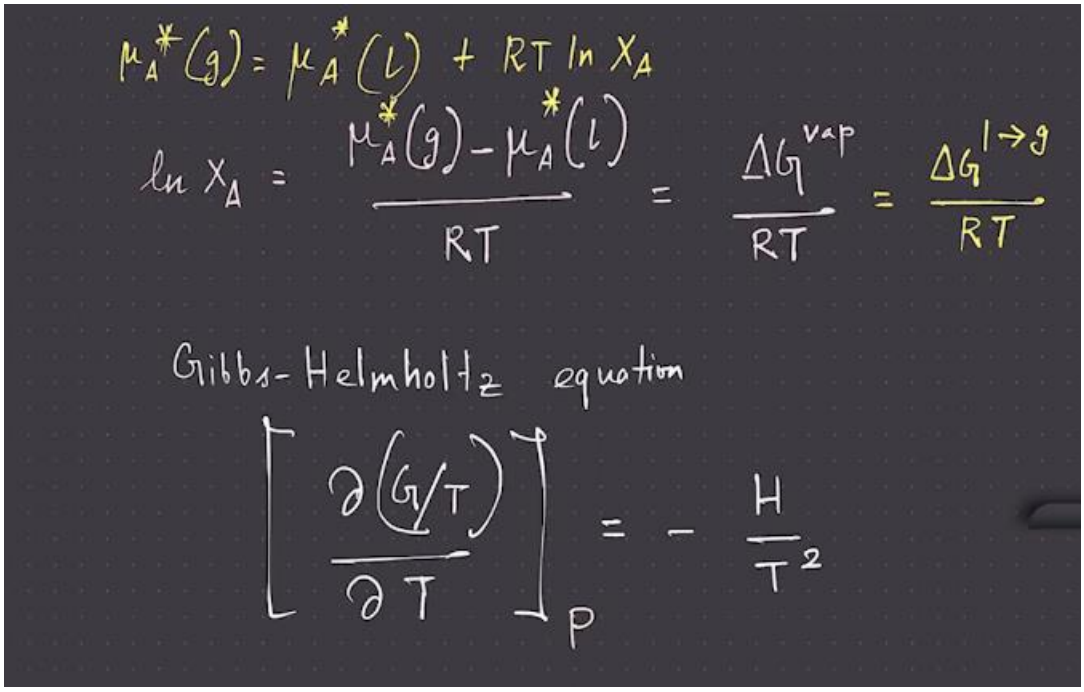
So, the means we are assuming ideality that means we are assuming Raoult's law and AA equal to XA and therefore, but remember this is the very important point here in the vapor phase A is pure in the liquid phase A is mixed with B right in the liquid phase A is mixed with B B has dissolved in A right. So, you have now mu A star L plus RT ln XA. Now, you can show that in such a case there is an elevation boiling point which is proportional to the fraction of solute and this KH you can prove that and that is what we were going to prove is RT B star, TB star corresponds to the boiling point of pure A TB star is boiling point of pure liquid boiling point of pure A liquid. Now, C which is equal to RT B star by

delta H L to gas.

So, liquid to gas. So, delta H liquid to gas means what we are basically telling liquid goes to gas that is delta H evaporation. So, this is our vaporization. So, we can write delta H vaporization process right liquid goes to gas or boiling process. Boiling means when the vapor pressure of A becomes equal to the atmospheric pressure means that the ambient pressure then basically the liquid starts boiling right that is the idea. Now, as you can see as you have seen you start with this equation mu A star G equals to mu A star L plus RT ln XA then ln XA is nothing but mu A star G minus mu A star L by RT right.

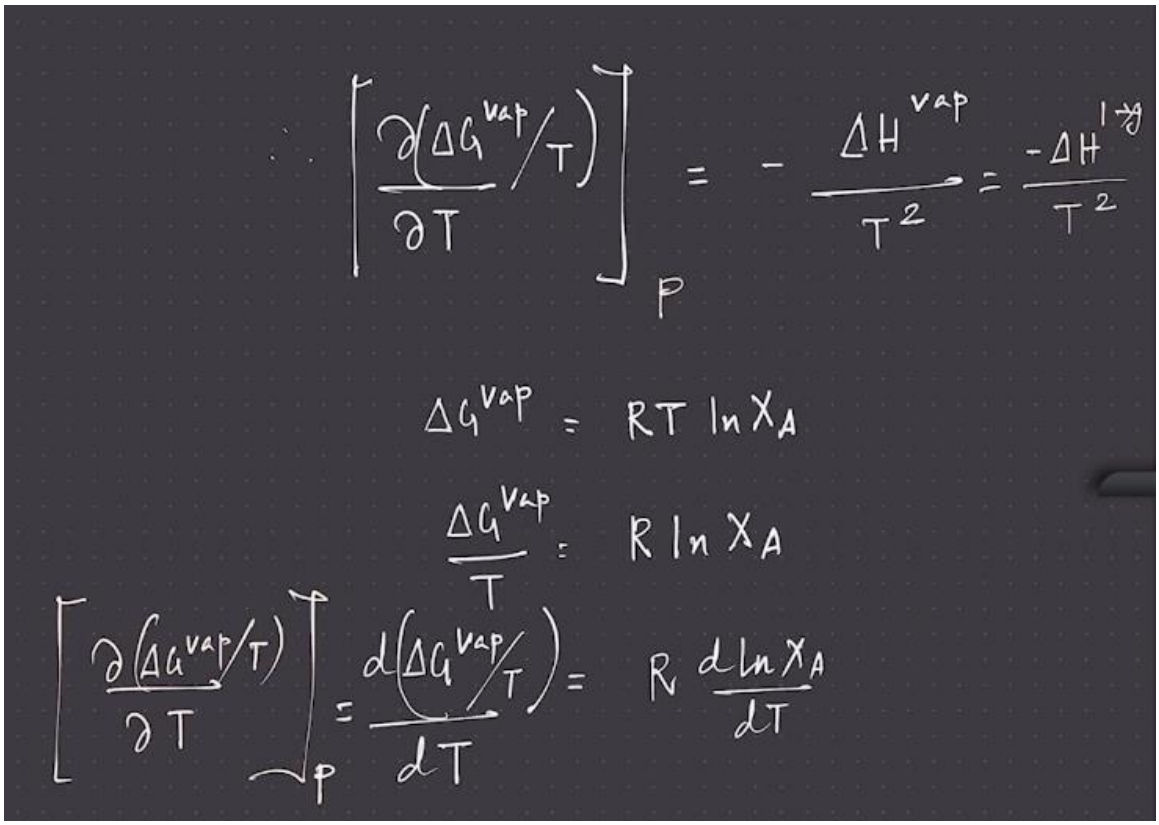
You can call it RT B or RT but that is like that transition temperature. Now, if you see ln XA is mu A star G minus mu A star L by RT right this by RT this is the RT. So, you have now what is mu A star G minus mu A star L that is the delta G vaporization for the pure A liquid right that is the delta G vaporization for pure A liquid right. So, because it is so liquid is here. So, from so liquid is the initial state gas is the final state.

So, that is what you please note the convention. So, it is G minus L G minus L means this is liquid to gas this is liquid to gas transformation is what we are talking about or liquid to vapor transformation. So, delta G vaporization by RT where delta R delta G l2 G by RT. Now, you know give Selmon's equation I do not want to prove it you please again check the proof I have done it in the previous week or maybe week 7. So, you please look up Keef Selmon's equation it is del G by T del T is minus 8 by T square by the way if you take on. So, del G by T del T if you see the partial pressure the so this the derivative of G by T derivative of G by T with respect to temperature with pressure fixed with pressure fixed remember pressure is fixed here pressure is fixed del G by T del T is minus of H by T square.



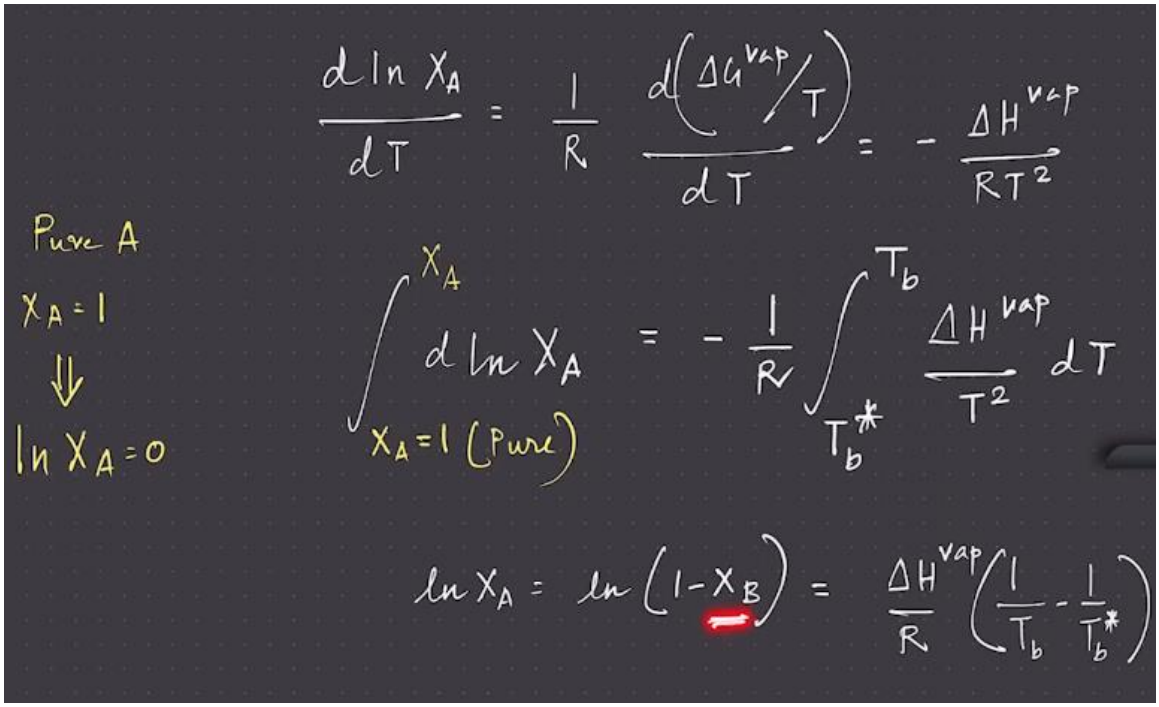
This is easy to prove you can prove it by yourself if you are not sure you refer to the lectures a few weeks back and you will see that I have derived that use of the Selmon's equation. So, I will use this identity I will use this identity because you see it gives you a very useful relation particularly this identity was very useful when we discussed Clausius-Lepidin equation. So, you go to those lectures and you please find out the derivation of use of the Helmholtz equation. Now, once you have this Helmholtz equation you can now put it like this. So, you have delta G by T so you are telling del delta G by T and this delta G is nothing but so instead of G you are substituting by delta G vaporization.

So, delta G vaporization by T so partial derivative of delta G vaporization by T with respect to temperature. So, basically delta G vaporization by temperature is so the derivative of delta G by delta G vaporization by temperature with respect to temperature at fixed pressure pressure is 1 bar. Remember the pressure we are considering as 1 bar at fixed pressure is minus delta H vaporization which is minus delta H liquid to gas by T. Now, remember when it is delta H liquid to gas so liquid to gas means you are absorbing heat the liquid has to absorb heat to convert to gas or they both this. So, this is basically an endothermic process so that means delta H is positive.

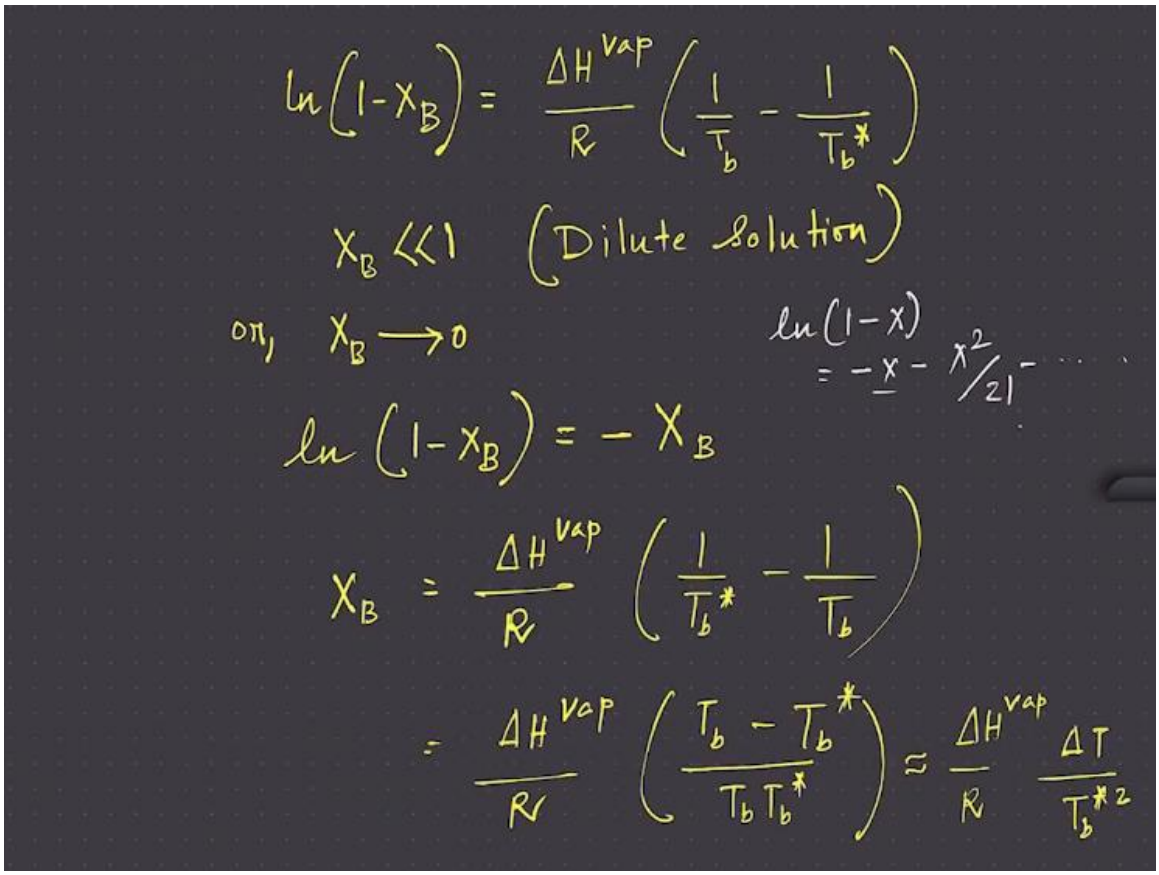


So, minus of delta H means negative because delta H itself is positive for a liquid to vapor transmission. Now, that is something that you please take a note of the delta H liquid to gas is liquid to vapor transmission is an endothermic transformation because the system the liquid has to absorb it that it has to absorb it to transfer to vapor. So, delta H is positive and minus delta H therefore is negative by T square T square again is positive. So, minus delta H by T square in this case has to be negative because of this minus. Now, delta G vaporization is nothing but as you know from where do you know from here you know delta G vaporization is nothing but RT ln XA if you take RT from here to here then delta G vaporization is RT ln XA or delta G vaporization by temperature is basically RL n XA delta G vaporization by temperature see this is what is the argument here in the Grisselmoles equation.

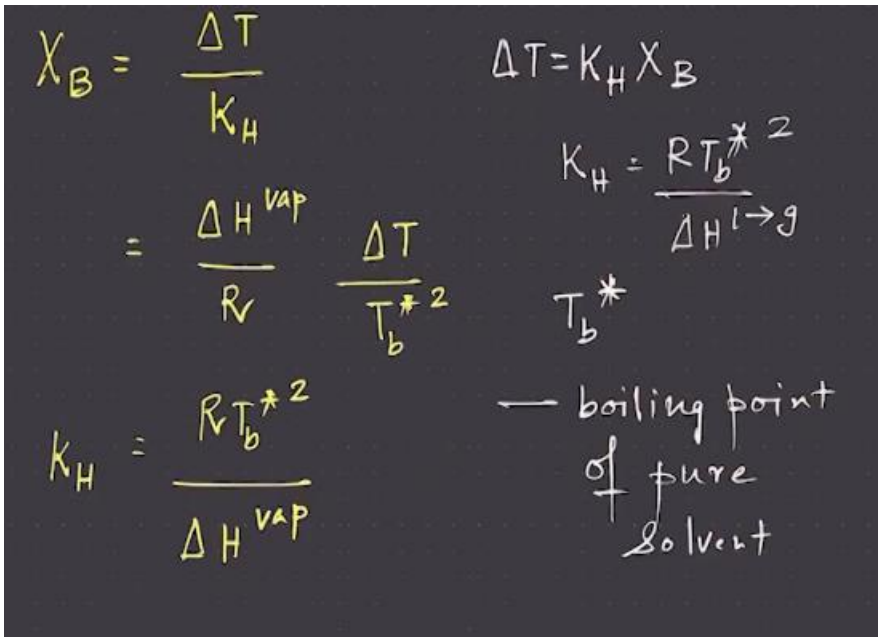
This is the numerator delta G vaporization by temperature. So, delta G vaporization by temperature comes out to be RL n XA in our model. So, now if you now look at this again remember I am writing d by dt this is basically why can I write this because I know that pressure is fixed so I have fixed the pressure. So, basically this is nothing but at constant pressure equals to this equals to RT d ln XA dt. Now d ln XA dt is nothing but now if you see that means d ln XA dt is 1 by bar d delta G vaporization by t by dt which is minus delta G vaporization by RT square.



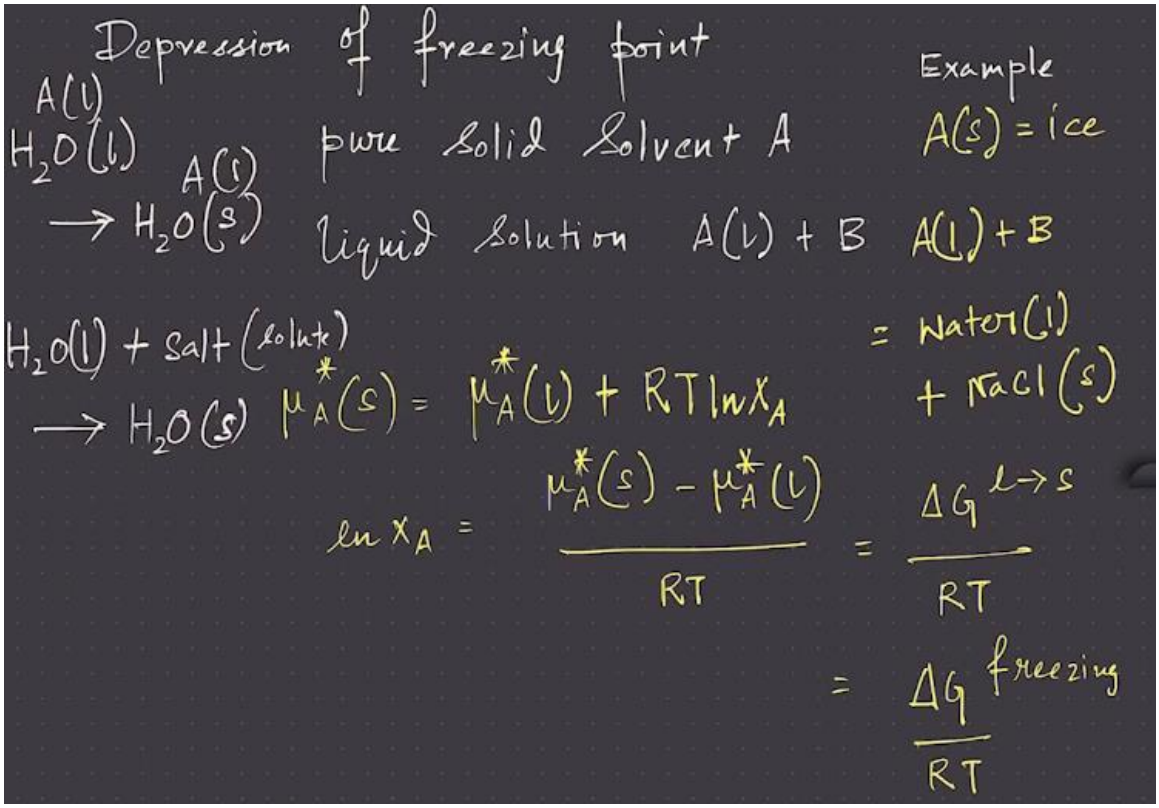
So, basically now if you look at that you can take this guy here so there is a dt here and this is here d ln XA here. Now when XA equal to 1 means XB equal to 0 that means pure solvent and your initial state is pure solvent state and the final state is a solution with XA mole fraction of the solvent and XB mole fraction of solute. So, this is the final state. So, the final state is the new boiling point the new the change in boiling point that the new boiling point this is the boiling point of the solution Tb is the boiling point of the solution and Tb star is the boiling point pure A. Now if you do that then you see remember XA equal to 1 means ln XA or ln 1 is 0.



So, basically now you have only ln XA which is nothing but ln 1 minus XB because XA is 1 minus XB XA plus XB equal to 1 equals to if you now see if you want to absorb the minus sign you have now T square but by T square. So, it is minus 2 to the power minus 2 plus 1 by minus 2 plus 1 there is a minus sign outside minus and minus becomes plus. So, you basically get 1 by Tb minus 1 by Tb star you can check this integration you have done this in even when you beat the clauses integration of classes that we have done in this equation we got into this equation. So, delta H for the evaporation condensation systems or very considered evaporation condensation type phase transition we came up with a very similar derivation. Now if you look at that then this is but only thing you do not have an XB there.



Now XB is the mole fraction of solute. Now if you look at that if solute is very very small so that is XB is less than 1 that is valued solution then ln 1 minus XB is nothing but so you can take so if XB is very very small so if you know ln 1 minus X equal to minus X minus X square by 2 factorial minus dot dot dot. But if you can see here that X is very very small so X square will be small even smaller so you can neglect all of these terms all of these terms and you can only take the linear term and that is what I have taken. So, ln 1 minus XB has become minus XB writing that so minus XB equals to minus XB equals to if you remember minus XB equals to delta evaporation by R 1 by TB minus 1 by TB star. So, now if I take XB so then it becomes 1 by TB star minus 1 by TB so from this equation itself you can see that this is what comes in because ln 1 minus XB is minus XB in the dilute solution limit. Now, you get XB equals to delta evaporation by R TB minus TB star by TB into TB star.

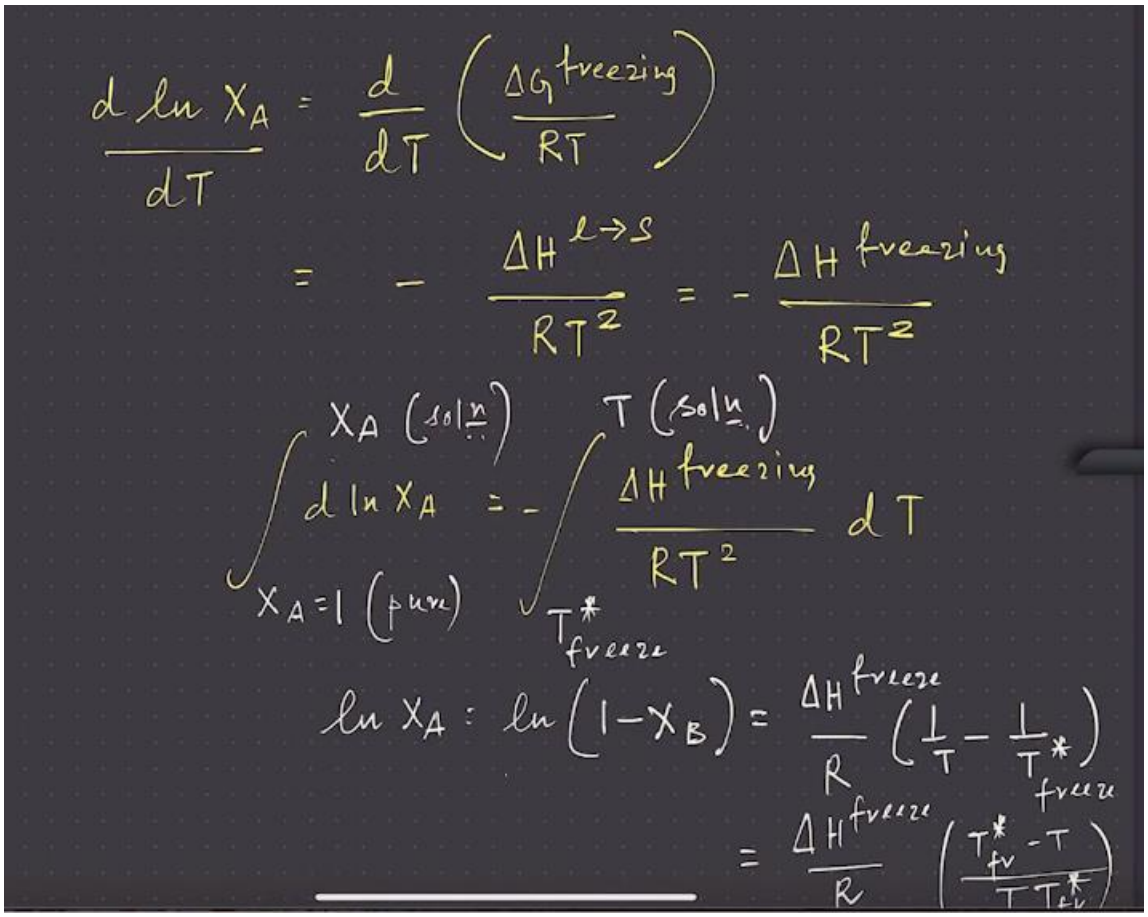


Now, if you see that TB star and TB are very close if you think of that then TB TB star can be written as TB square TB star square and delta T is the change in volume point which is TB minus TB star and as you can see here delta T by so you can write this as delta T by KH equals to XB and that means so what does that mean? This is delta H evaporation by R into TB star square and TB star is the volume point of the pure solvent then basically KH that is this constant that we wrote right in the initials initially so the constant. So, basically what you are getting is nothing but delta T equals to KH times KH times XB right the amount of solvent KH as you can see is R TB square R TB star square R TB star KH is R TB star square remember that and TB star square by R TB star square by delta H liquid to that star vaporization right. So, delta H evaporation is positive and this is R TB star square is also positive remember that TB star is the boiling point of your solvent. So, we can explain dilution of boiling point now think of depression of freezing point think of like a solid now you can you are thinking like pure solid solvent you are thinking of pure solid solvent and there is a liquid solution of A liquid plus B and so the solvent is like ice right it is so ice and you have also A liquid plus B mixture. So, basically the major component is the solvent component and we are taking that component in two forms.

So, basically you are thinking of water H2O so you are thinking of an example is H2O liquid to H2O solid. So, basically this is like A liquid to A solid transformation. Now, instead of this is called freezing right A liquid to A solid. So, it is called freezing and this

is basically again now see interestingly when we talk about the boiling point and we were talking about liquid to vapor transformation we were talking about an endothermic process. But now think of liquid to solid transformation which is an exothermic process right it is an exothermic process.

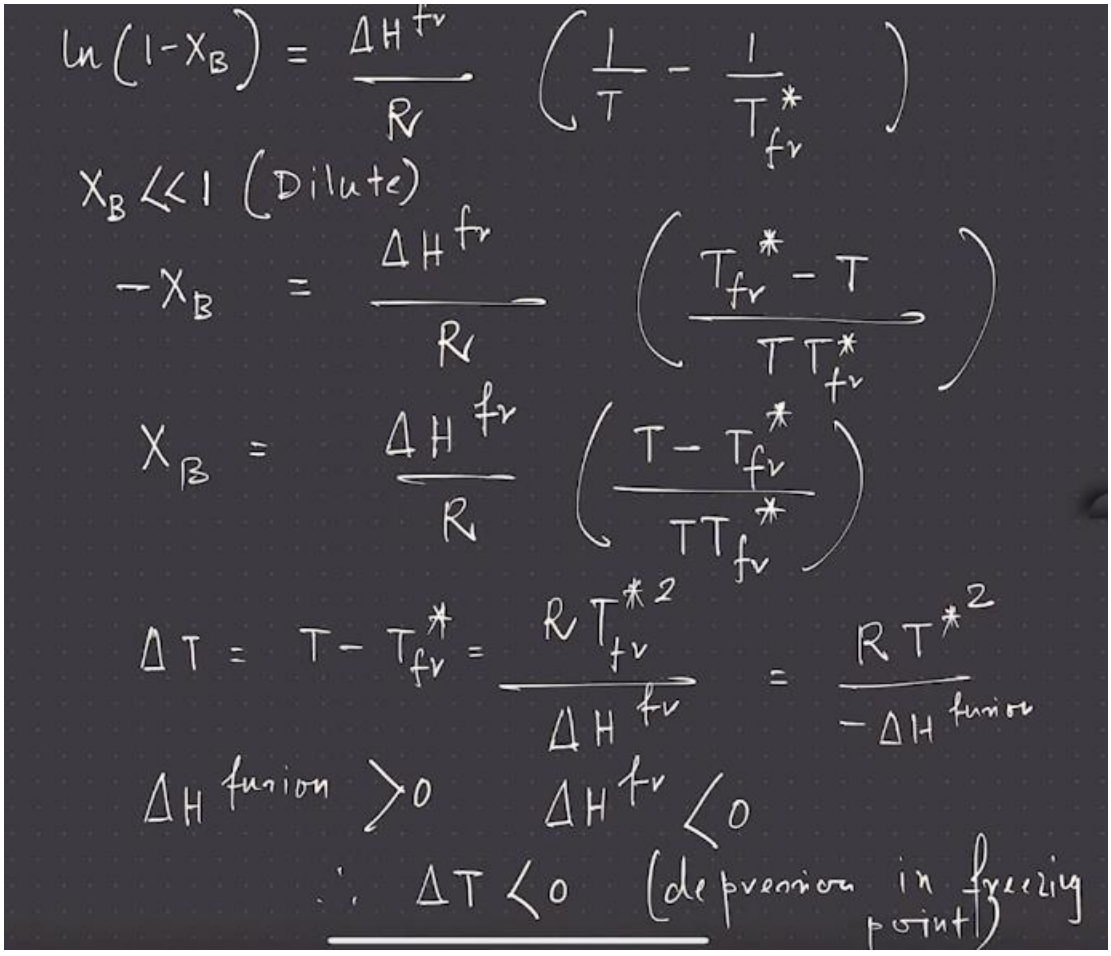
Now, this instead of this I am telling now you have H2O liquid plus some salt which is basically the solute that is like solute and then you are trying to transform this to H2O solid. Now, this is not really H2O this is basically the solution. So, basically you want to transform it to solid right. So, water so you have some amount of very little amount of sodium chloride that you have added to water and you are trying to in the liquid state and you have dissolved it and you now want to freeze this solution and you are seeing the freezing point whether it will be depressed or whether it will be elevated. Immediately you can see in a very common intuitive way that delta H vaporization is an endothermic process on the other hand freezing is an exothermic process.



So, you know that if boiling point is elevated with the same idea with a very similar idea the freezing point should be depressed right, but we will prove that right we will prove that why is it so. So, as you know again we are looking at solid we are assuming solid to the pure one and liquid is a solution right liquid is a solution and that is what is going to be frozen. So, basically now if you think of that we can write this way mu s star s is mu s

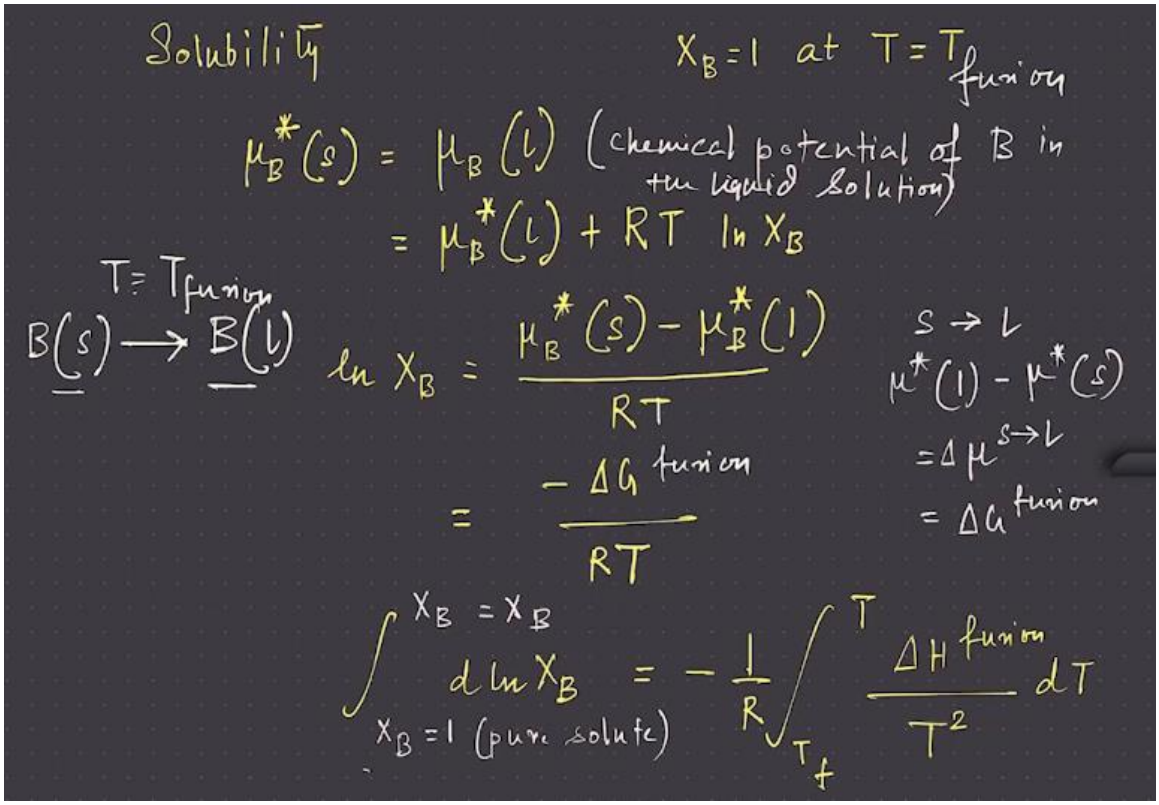
star l plus RT ln xa where ln xa is mu s star s minus mu s star l by RT which is delta G liquid to solid remember delta G liquid to solid right. This is like delta G freezing by RT right delta G freezing, freezing is opposite to fusion or melting right freezing is opposite to melting. So, again we can proceed the same way you get d ln xa dt which is d dt of delta G freezing by RT which is minus delta H right again we are using the Gibbs-Helmholtz equation or Gibbs-Helmholtz identity we can write d dt of delta G by RT is nothing but minus delta H by RT square.

So, you please look at the proof here so you please validate this so you get delta H liquid to solid by RT square which is minus delta H freezing right liquid to solid is nothing but freezing process by RT square. So, this is called freezing conformation basically. Now, again we go to this integration again x equal to 1 is the pure case right x equal to 1 basically the solid is pure A then it is basically so now and you have xa is your final this is your final state which is like the solution. So, this is basically solution and again you have T star, T star is the pure the freezing point of the pure solid pure A freezing point of pure A, T star freezing point of pure A right. So, remember and T is the freezing point of the solution right T is the freezing point of the solution.



So, you basically now if you continue this if you continue this equation if you continue

again you can write ln xa equals to ln 1 minus xb which is delta H freeze by R 1 by T minus 1 by T star which is delta H freeze by R T star freezing like T star freeze minus T by T T star. So, basically very analog plus T you can write so you get xb is less less than 1 right this is a dilute solution. So, this is again minus xb and you have delta H freezing by R and this is T star F R minus T which is the new freezing point right this is the T is the new freezing point of the solution this is the freezing point of pure A this is freezing point of solution of A and B and you have T T star and again xb is dilute solution with limit. So, T T star can be written as T star square write T star square and you have this R. So, basically delta T again you can write as R T freezing square by delta H freezing.



However, as you know delta H fusion is greater than 0 but delta H freezing is less than 0 it is an exothermic process. Therefore, the delta T is basically because R is positive T star square is positive and but delta H freezing is negative right delta H fusion is positive but delta H freezing is so fusion or melting process is basically when the solid absorbs heat to melt right and freezing process is where a liquid is transformed to solid by giving out its latent heat or heat of transformation and therefore delta H freezing is basically you can write this as minus of delta H fusion. Now delta H fusion is positive right. So, you have this as less than 0. So, delta T is negative that means delta T is negative means there is a depression freezing point that we already intuitively understood because delta H vaporization was positive that time there was an elevation of boiling point now delta H freezing is negative as a result there is a depression the freezing point.

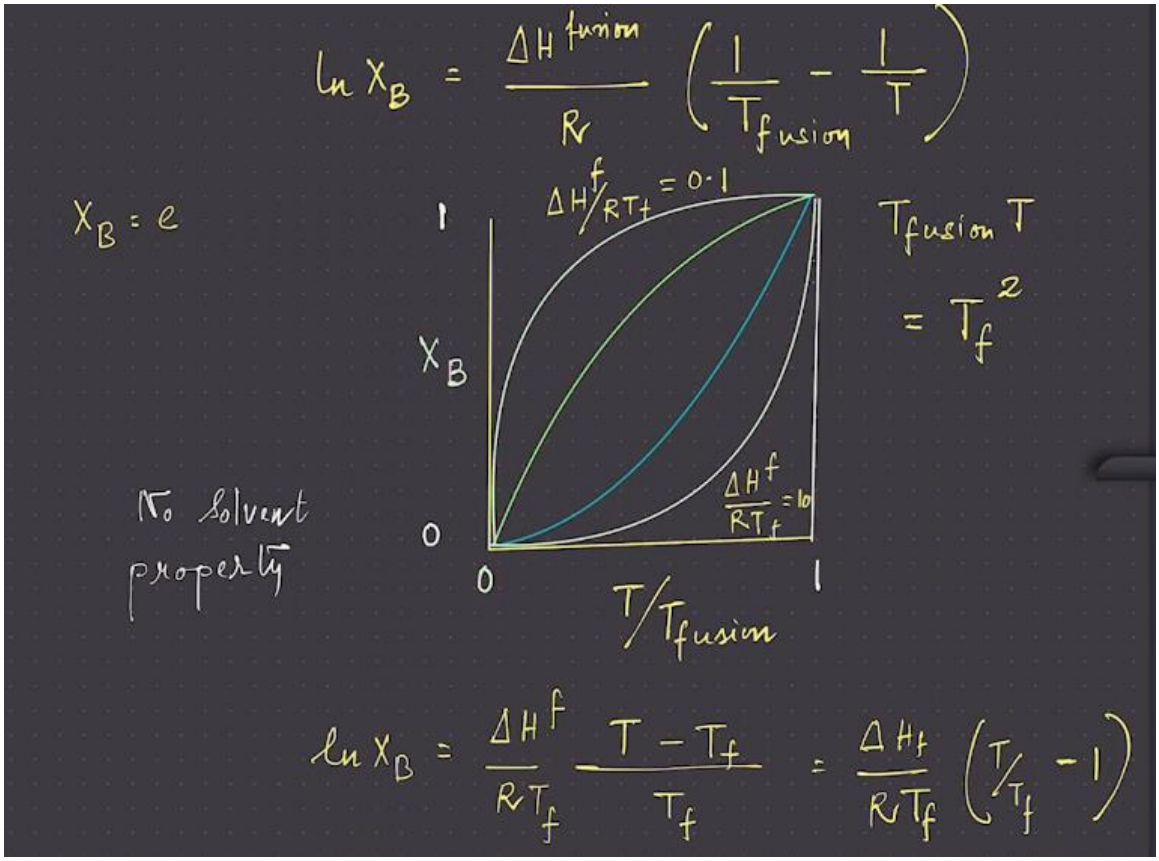
Now there is also another thing although it is not exactly colligative property you cannot

exactly call it a colligative property because you are now looking at the solubility of solute in the solvent right. So, basically if you think of that if you now you are looking at solute as the pure phase right in the solubility case. So, basically you are telling that mu B liquid is nothing but so mu B liquid is the B that the chemical potential of B in the liquid solution. So, mu B liquid is chemical potential of B in the liquid solution right. So, now you have that so now mu B star solid is basically the chemical potential of B in the solid state and in the pure state.

So, in the solid state in the pure state right B that is why you are writing mu B star right you are basically thinking of when you are thinking of solubility you are thinking of B which is the solid state is transformed to B in the liquid state right this is dissolving right this is transformed to the liquid state right at t equal to some diffusion for B right. So, basically mu B star liquid plus RT ln x B you can think of that now right in mu B liquid is nothing but mu B star liquid that mu B star liquid is the in pure liquid B what is the chemical potential of B right mu B star liquid is that plus RT ln x B is there because the RT ln x B and that x B again is the mole fraction of B in the solution right. So, ln x B is mu B star S minus mu B star L by RT which is basically so it is like solid to liquid transmission. So, but you are looking at solid minus liquid surface liquid to solid liquid to solid transmission.

So, solid to liquid transmission is what we are looking at. So, mu L minus mu S is what we are looking at right. So, we solve it to liquid transmission. So, S to L if I am thinking of then we should have taken mu star L minus mu star S is basically equals to mu or delta mu this is from solid to liquid right. But or that is like the delta mu fusion or delta G fusion right delta G fusion. So, this is nothing but see ours is the way we have written it the way we find it is mu B star S minus mu B star L.

So, basically it is like liquid to solid transmission. So, it is opposite to delta G fusion. So, there is a negative sign. So, as you can see here, there is a negative sign here, there is delta G fusion and there is RT again in the same integration. So, again you see d ln x B and again you can look at the integration limit this way that x B equals to x B and now there is an interesting point.



So, here x B equal to 0 or x B equal to 1. So, let us look at x B equal to 1. Now, if you do that, then basically what you basically get because x B equal to 1 is like pure, pure the x B equal to 1 basically means pure solid. And here it is x B equal to x B. Now, you do this integration limit again T f is that of pure B, T f is the fusion temperature of pure B or and you have like 1 minus 1 by R T f to T delta H fusion by T square. Now, again you have ln x B equals delta H fusion by R 1 by T fusion minus 1 by T or T fusion is a melting point of or T fusion is a melting point of B.

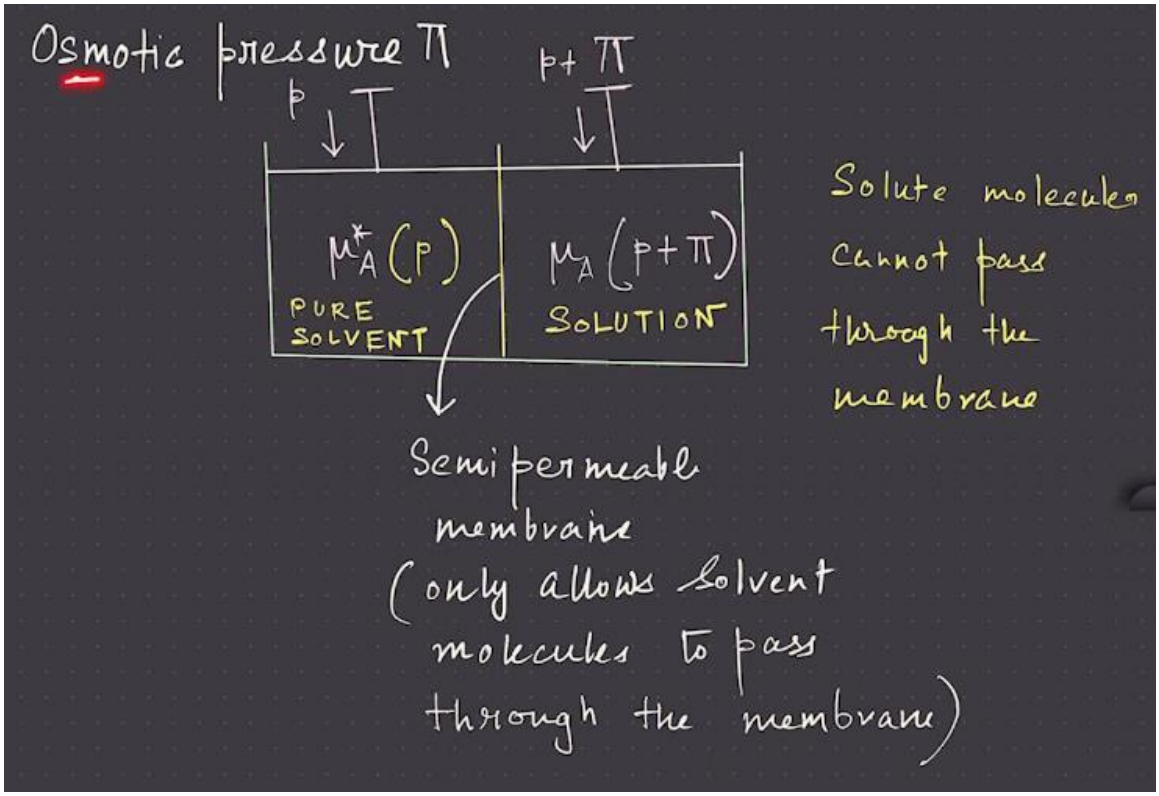
So, basically if you have that, you can plot x B. So, please understand this that you have delta H fusion is positive and then R which is positive and then there is 1 by T fusion minus 1 by T and T fusion T can be written as T fusion square. So, T fusion square or you can basically write this. So, basically if you look at this, what the plots you will see that I have plotted delta H f by R T f. So, basically delta H by R is there and then there is this and you get 1 by, so T fusion minus T. And again if you think of this, this is basically delta H f by R T f T minus T f by T f or delta H f by R T f T by T f minus 1.

So, then x B is there. So, x B is exponential of this entire term, x B is exponential of this entire term. Now, I am plotting x B as a function of T by T fusion. So, I basically get for different values.

So, delta H f by R T f for example, is 0.1 in this curve for this curve. For this curve, it is like slightly higher than 0.1 and here it is like 10. So, here the value is like 10.

This is 10, so it is I do not know how to write this here. So, it is equal to 10. And this is 0.1. So, as you can see how the solubility of x B varies between, varies as a function of T by T f, T by T f is plotted here. So, basically as you can see here that dissolution or the solubility, if you think of this as a colubatic property, there is no solvent property associated with it. There is absolutely no solvent property does not influence somehow it is solvent property at least in this approach does not influence the solubility of B in it.

It does not. So, in this the colligative treatment, you see that it really depends on the delta H fusion of pure B, the delta H fusion of pure B solute transforming from the solid state to the liquid state, from the solid state to the liquid state. And there is this R T f, where T f is the pure, the T f is nothing but T f. Remember, T fusion I am calling T fusion as in short form as T f. So, basically if you see T f is the melting point of B, of pure B solute.



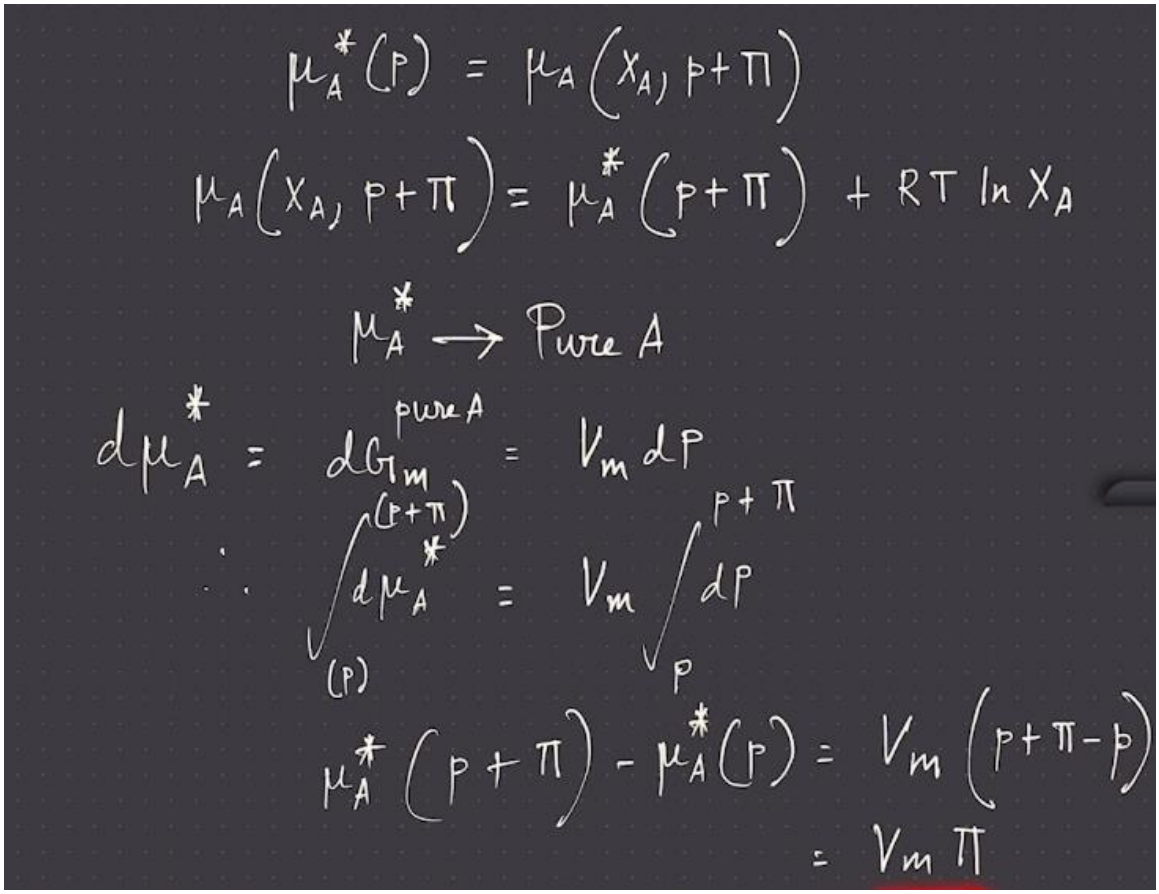
And T is the melting point in the solution. And if you look at that, if you look at that delta H f is again the transmission or the fusion transmission of solute from the solid phase to the liquid phase. And therefore, as you can see in this entire expression, in this entire expression that you have here, there is no solvent property that is included when we are expressing solubility. Again, there is another very important process called osmosis. So, osmosis is like preferentially, so you use something called a semi-permeable membrane, you use it in biology a lot. You use a semi-permeable membrane, which basically allows

only solvent molecules to permeate, only solvent molecules can grow, only solvent molecules can transfer.

The solute molecules that say for example, B, B solute, B cannot cancel. So, only thing that happens is like you have a solution of A and B and you have pure solvent and you have the semi-permeable membrane, which only allows all molecules to pass through the membrane. So, basically you can adjust the dilution by transferring solvent molecules to the particles. So, basically solute molecules cannot pass, solute molecules cannot pass through the membrane. If you look at Atkins, you will see that this is very much useful in determining, this is in determining the molecular mass or molar mass of macromolecules or polymers.

It is also very important in biology and in biochemistry. So, basically there is a lot of application there. So, I will quickly briefly tell you. So, here we are talking about some pressure called osmotic pressure. When only, when there is a semi-permeable membrane between the pure solvent and solution and only solvent molecules are allowed to pass through.

So, as you can see here, you have two chambers, there is a semi-permeable membrane here. So, you have a semi-permeable membrane here and there are two chambers. Chamber 1 has pure solvent, chamber 2 has solution and there is this pressure. It is like you can see the piston here and there is this piston here. And so you can see pure solvent has a pressure of P while the solution has a pressure of P plus pi and this pi is basically called osmotic pressure. So, if you look at that again mu A star, again star denotes pure, star denotes pure that is what we use as a convention in the previous lectures also.



So, mu A star and P equals to mu A XA P plus pi. Mu A is a function of, function of solvent concentration or solute concentration and the pressure that you have is additionally there is a pi equation which is called the osmotic equation. We do not know what pi is and we will try to find out. So, if you want to find that out, you can write now this guy is XA P plus pi is mu A XA P plus pi is mu A star P plus pi. So, P plus pi for the pure solvent plus RTL and XA, now mu A star is basically corresponding to pure A.

So, d mu A star is d g m pure A because it is pure A. So, which is nothing but d g is basically v d p at a constant temperature, v d p minus s d t if d t is, if t is constant d t is equal to 0. So, we can write as d m d p where d m is the molar volume, molar volume of the solvent and molar volume of the solvent of A, molar volume of A. Now, if you see, if you integrate d mu A star, you have two pressures, one is mu A star d mu A star where mu A star changes from P pressure P. So, what is the change in the chemical potential of pure A when the pressure changes from P to P plus pi is what is this integral with them. So, this integral basically tells you how mu A star will change when the pressure changes from P to P plus pi, P to P plus pi, how mu A star will change.

So, mu A star P plus pi minus mu A star P equals to this is C, we are taking x A equal to 1 here, we have expanded it. So, mu A x A P plus pi we have written as mu A star P plus

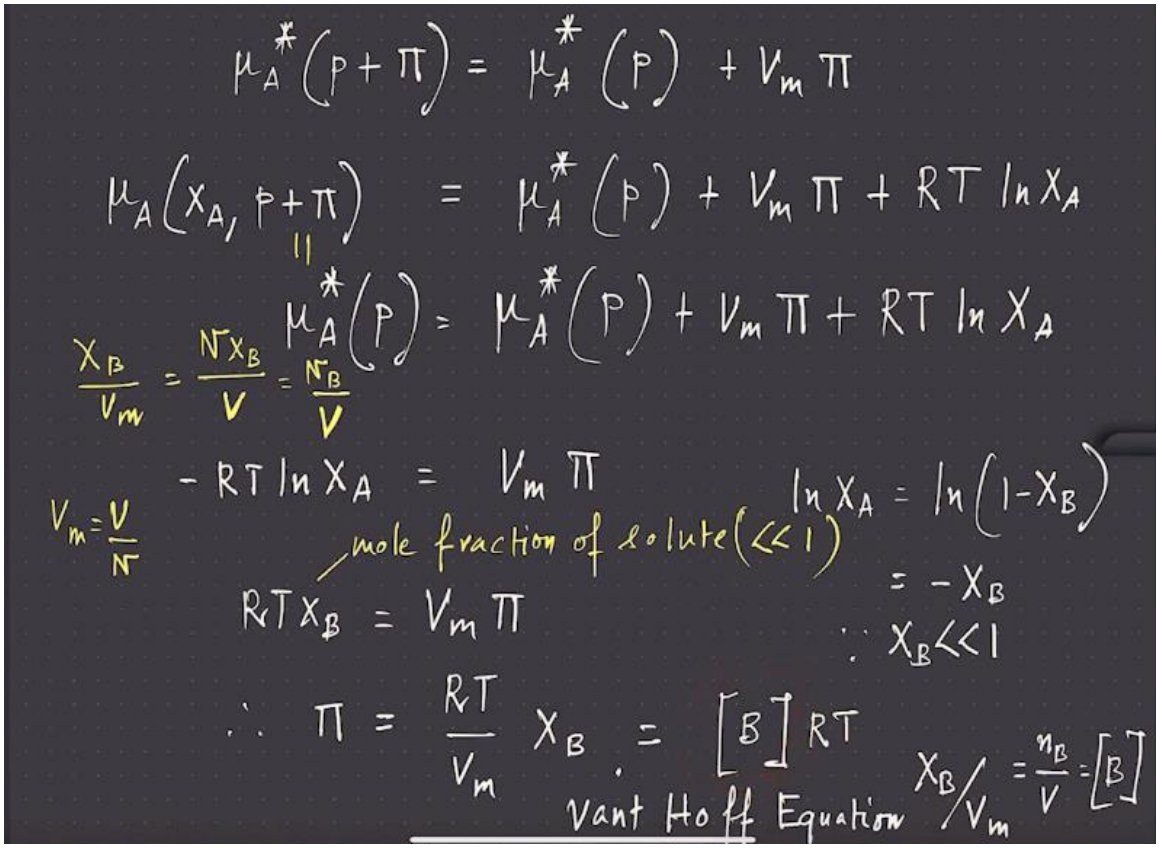
pi plus RTLn x A. So, we have separated this out, mu A star P plus pi plus RTLn x A. So, you now have mu A star P plus pi minus mu A star P is v m P plus pi minus P. So, as you can see the change in chemical potential of pure solvent when the pressure changes from P plus pi to P or P to P plus pi is nothing but is proportional to this increment in pressure or this osmotic pressure of v m, which is basically v m times pi.

Now, as you can see mu A star P plus pi is nothing but mu A star P plus v m pi, that is what we have written here, mu A star pi this one equal to this and so this one if I take this way, then what I get is this. Now, if you look at that mu A x A P plus pi is mu A star P, now mu A star P plus v m pi, v m pi plus RTLn x A. Now, as you can see here, we have made a very succinct approximation that we are telling the molar volume does not change even when it is a solution. So, molar volume remains unchanged, molar volume of A remains unchanged even when A is in solution.

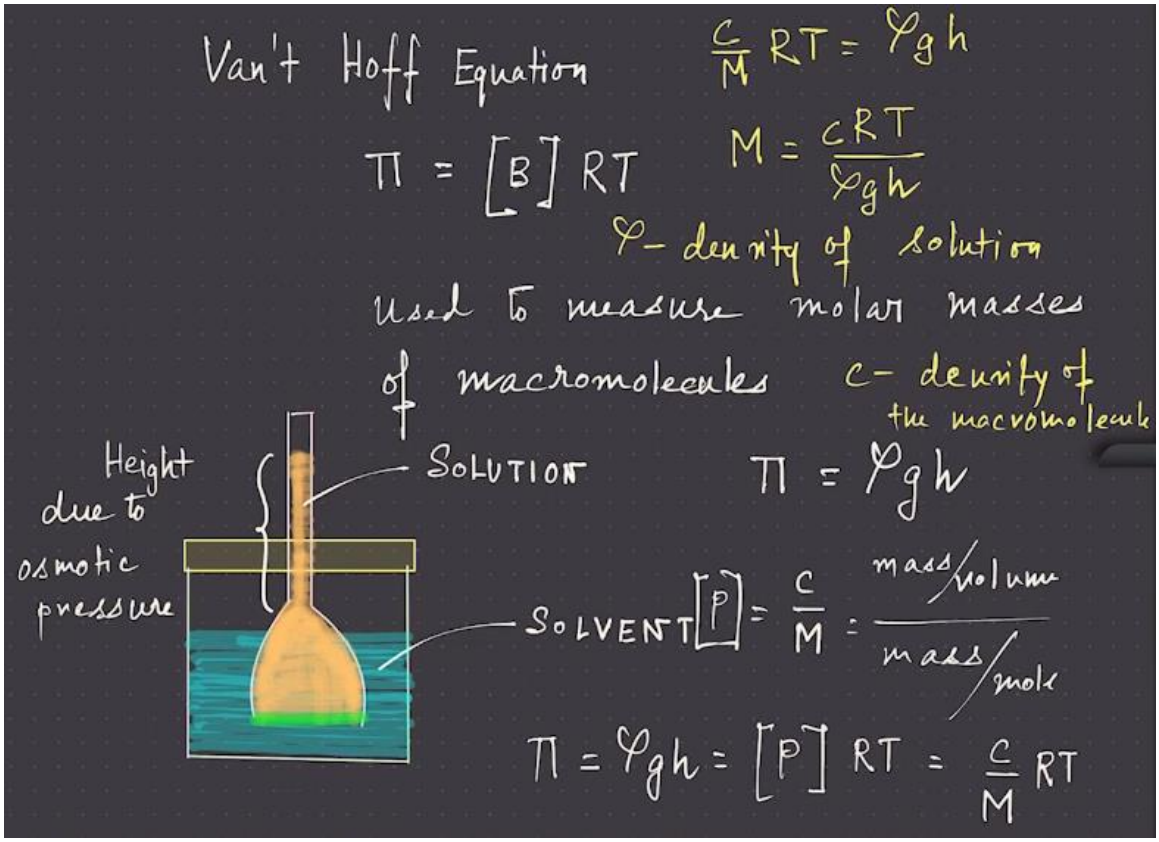
So, there is no change in molar volume and if you consider that you get mu A star P plus v m pi plus RTLn x A. Now, as you can see mu A x A P plus pi is now this equal to this pi because this is something we have already written, we have written because these are in equilibrium. This is there is a semi-permeable membrane and this and this, so the pure solvent and solution are in equilibrium and separated by a semi-permeable membrane. So, mu A star P equals to mu A x A P plus pi. So, mu A x A P plus pi equal to mu A star P, that was our initial condension.

So, this is equal to mu A star P and mu A star P here also there is a mu A star P plus v m pi plus this. So, basically you can basically now cancel this term. So, this entire term is equal to 0 and if this is 0 then v m pi is minus RTLn x A and Ln x A is with nothing but Ln 1 and x B and again for a dilute solution limit Ln 1 minus x B as we have shown is minus x B negative of x B because since x B is less than 1. So, basically you can write now RT x B again x B is the mole fraction of solid which is very, very in this equation it is less than 1, is less than 1 equal to v m pi. So, pi basically RT by v m, v m is a molar volume of the solvent times x B. So, if you see RT by v m times x B, now x B by v m is nothing but x B by v m, x B is mole fraction, v m is molar volume that is volume per mole.

So, if you think of this, if you, so x B by v m is nothing but, so if you have say for example, so it is volume per mole. So, basically if you think of this, this is nothing but total v and you have n moles. So, then n times x B by v because v m is v by n, v m equal to v by n, v by v. So, volume by mole number, the total number of moles, so n times x B is nothing but n B.



So, this is nothing but number of moles of B divided by the total volume, total volume. So, basically this is nothing but the concentration of B in moles per volume. This is the concentration of the solute in moles per volume by concentration of the solute. This indicates, this is nothing but concentration of solute in moles per volume and you have RT. So, basically what you get is the osmotic pressure equals to, is proportional to the concentration of solute in moles per volume and this is called Van't Hoff equation.



So, basically pi equals to P R T is called a Van't Hoff equation. Now, if you, as I told you, it is used to measure molar mass of macromolecules that result in the solvent. So, you can see how it is done. So, you have the semi permeable membrane here and then this is a solution of macromolecule with the solvent and this is a pure solvent and you have immerse this funnel and basically as you immerse this funnel, there is a osmotic pressure that develops here. There is an osmotic pressure and that osmotic pressure is equal to the height, basically the pressure due to this height.

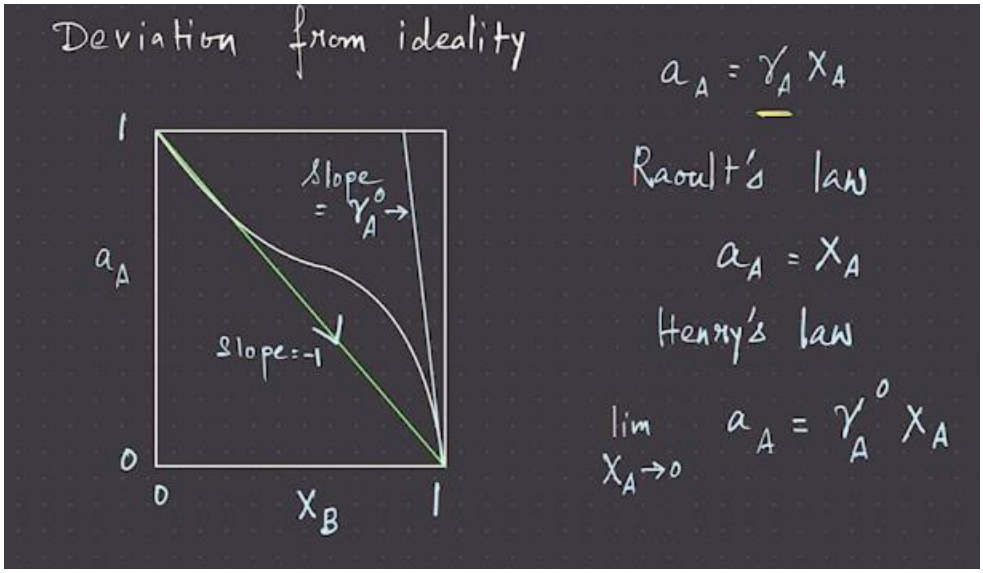
So, basically pi is equal to be the height that up to which the solution rises due to the osmotic pressure. So, basically you are dissolving the solution inside the solvent and there is this semi permeable membrane, a pressure develops and as a result, the solution will rise to some height and this height difference, the height difference that you have from this surface to here. So, this height to which that is risen is like rho gh because this is the height to which the solution is risen and rho is basically the density, rho is density, g is acceleration due to gravity and height is the height due to osmotic pressure. Due to osmotic pressure, the height to which the solution has risen, the solution column rises and solvent is nothing but and this pure solvent and p, so let us call this p, the within square box p, let it denote the concentration of polymeric moles per volume.

So, concentration of polymeric moles per volume. So, C is the number of moles and M is the mass per moles. So, basically, so if you see, this is basically moles per volume is

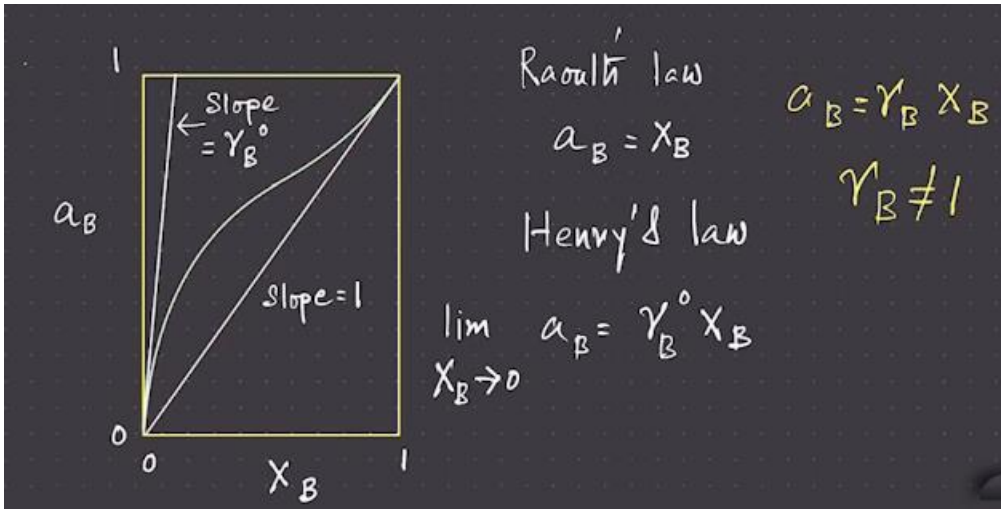
nothing but mass by volume, C is basically mass by volume and this is like, and this is mass by mole. So, basically this is going to be mass and mass cancels, it is moles per volume. So, you can write it as C by M and we know pi equals to rho gh, which is equals to, pi is nothing but concentration of p times RT, which is nothing but C by M RT. Now, if I know C, if I know RT, if I know pi, because I know rho gh, so I know rho gh, I know C, I know RT, so therefore I can get the M for that.

So, that is the molar mass. So, I can get the molar mass of the macromolecule for this equation, because C by M, so what we are writing is C by M RT equals to rho gh, I can measure everything, I can measure H, I know G, I know rho, that is the density. So, M equals to C RT by rho gh, M equals to C RT by rho gh, where C is basically mass per volume, C is basically the mass of the solute per unit volume, mass of the solute per unit volume and rho is the density of the solution, rho is the density of the solution. And C is basically density of the macromolecule. C is basically defined as mass by volume, so C is basically the amount of, the amount of macromolecule, the mass of macromolecule that is put into the volume in the solution. So, basically it is like a density, so you can call it like C is basically the amount of polymer, so mass of polymer by the volume of the solution.

So, basically C cannot be defined as density of the polymer, but it is basically mass of the polymer by the volume of the solution that you have taken. So, as you can see this is called osmometry, where Van't Hoff equation can be used and you can get the molar mass of macromolecules, this is something that you can do. Now, we will come to this again, once again we will quickly discuss and this part which is called this, we will discuss now this approach to create models, we have created actually two models, one model was this ideal solution model, ideal solution model means or you can call it a perfect solution model where there is no interaction between the atoms. So, now if you look at the deviation from identity that is basically expressed through the non-unity gamma. So, basically this gamma A basically corresponds to, so in Rouse's law A equals to XA and Henry's law as you know, but this gamma is the activity coefficient.



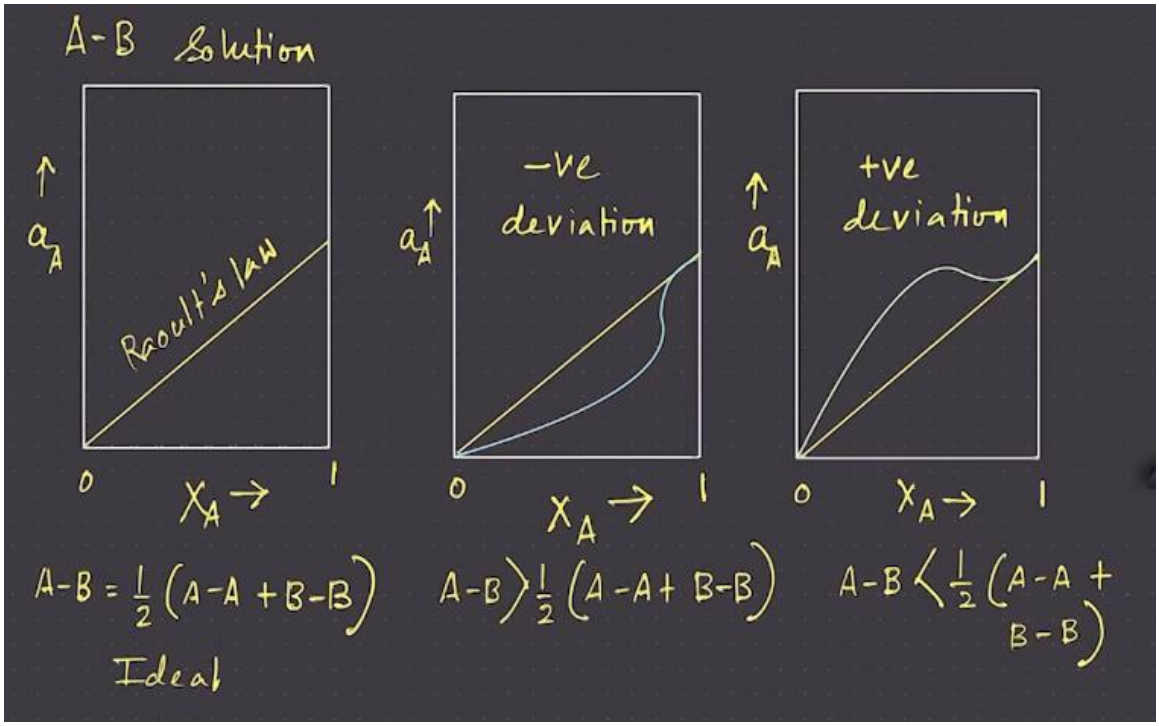
So, basically A is activity, gamma A is activity coefficient which is different, if it is different from 1 then you have deviation from identity or departure from identity. So, again for solve, you can do it for the solvent, you can also do it for the solute, you can also express it for the solute. So, AB goes to XB, but again you can write AB equal to gamma B XB and if gamma B is not equal to 1 then what you get is a deviation or departure. Now, departure can be positive or negative depending on the interactions that happen and that is what we will try to understand. So, let us think of a binary AB solution, so what are the interactions possible as I told, the interactions possible are AB, AA and BB.



Now, see if AB interactions exactly, remember there is a half here because there is double counting, see there are AA, 2 A's and 2 B's, here there is 1 A and 1 B. So, if you want to balance this then basically you have to create because there are 2 A's here and 2 B's here, so there is some sort, there is a double counting here, so you have to use half here. So, half of AA plus BB interactions equals to AB interactions, this basically gives you nothing but Raoult's law or ideal case. So, as you see there is this, that is why Atkins uses this distinction between perfect and ideal, ideal is where the interactions cancel out or

interactions are exactly cancel out or interactions exactly balance that means the AB interactions exactly balance the AA interactions and BB interactions and that is called ideal. But in perfect there is no interaction at all AA, BB, AB all are 0, basically there is no interaction between A and B in case of perfect solutions, but in case of ideal solutions there is interaction but the AB interactions are completely balanced by the AA interactions and BB interactions, in such case what we call is ideal.

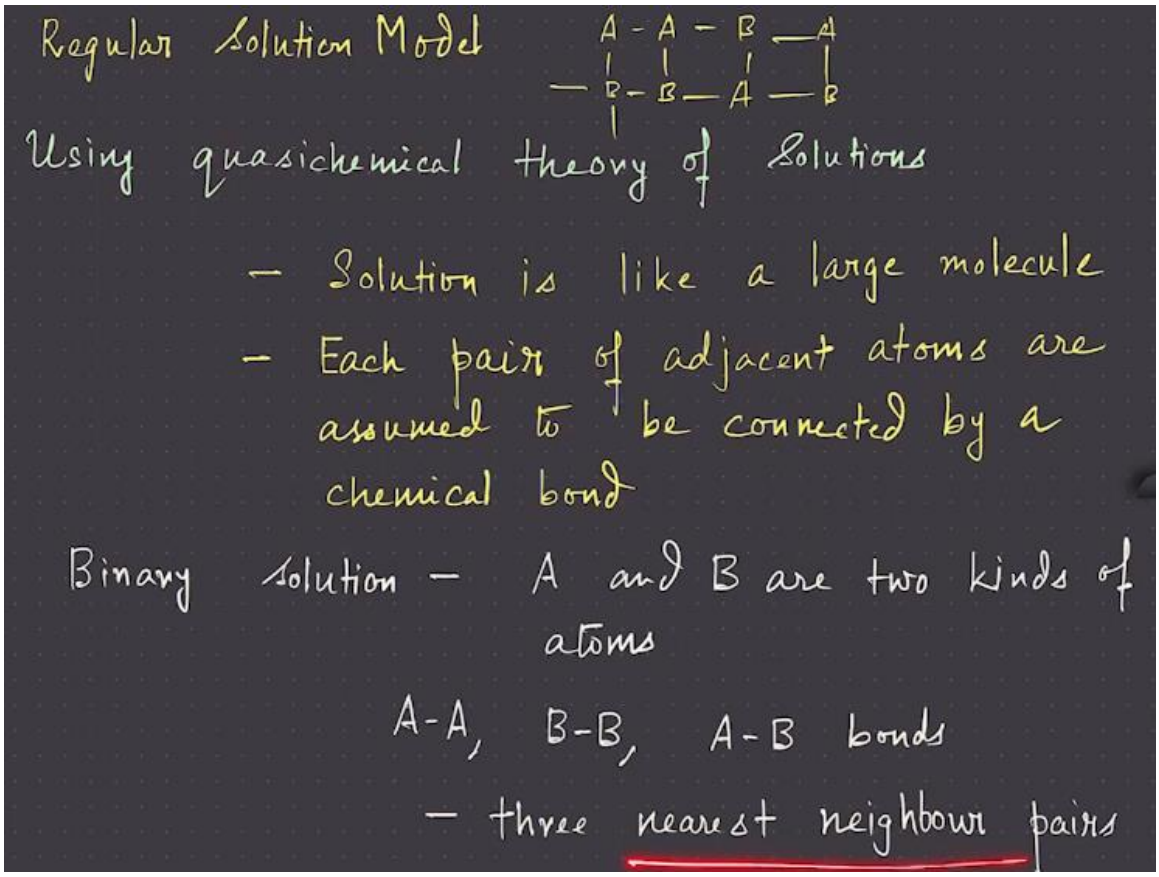
So, this is a very important point here because in ideal solution there are indeed interactions but the interactions are exactly balancing, the AB interaction energy is equals to the 2 half of AA interaction energy plus BB interaction energy. Again as you can see AA counted twice, BB counted twice therefore there should be a half and so as you can see this ideal means where there is exact balance between the different interactions, exact balance between the different interactions that the net interaction goes to 0, right the net interaction goes to 0. So, basically if you think of these interactions as EAB and this is EAA and this is EBV these are the interaction energies then you can see EAB minus of half of EAA minus of half of EBV will exactly go to 0 and that gives you the ideal solution that gives you the realization of ideality, that gives you the realization of ideality and you basically get nothing but Raoult's law. As you can see this is completely linear AA equal to XA, AA equal to XA and that is called Raoult's law. However, if AB is greater that the interaction of AB is greater than AA and BB then basically you start seeing something called a negative deviation, we will tell why.



So, you see if AB is greater that means you have more AA and BB, you will have more AA and BB that are preferred because AB is more that the interaction energy between A

and B is more than that of AA and BB, AA and BB interactions are more favorable. So, in such case you get negative deviation from Raoult's law, negative deviation from Raoult's law. On the other hand when AB is less than AA plus BB interactions the AABB interactions, AB is less then you get positive deviation from Raoult's law. Now I will tell why we will try to explain this by deriving a regular solution model from atomistic perspective where we look at this AA interactions, BB interactions and AB interactions. So, how will you do? So, you will use in regular solution model what is called, so there are various models that quasi-chemical models that you can construct.

So, we will consider one type of regular solution model for disorder, for a disordered solution of between two liquids or between two solids. We will primarily focus on the condensed phases right now, we will come to know phi very soon. So, basically you will use quasi-chemical theory of solutions. What is the quasi-chemical theory solution? So, we will tell solution is a large molecule, large molecules means a molecule which has a collection of atoms, A atoms, B atoms and we are talking about initially we will start with the binary solution, but you will see that regular solution model can extend to ternary, quaternary and so on.



So, it is a multi-component regular solution model, you can go to generalize it to multi-component, there is no problem at all. But remember, so in quasi-chemical theory, the approximation that we use is that the solution is like a large molecule and the molecule consists of atoms that are arranged in a lattice or atoms that are arranged in space and these atoms are like and where each in this large molecule, each pair of adjacent atoms are assumed to be connected back into bond, each pair of adjacent atoms are connected by a chemical bond. So, basically you have like A, A, B, B, this is completely random let us say A and so you have all these interactions that are possible B, A. So, this entire thing, so this weak structure on this lattice say for example, you go on between B here, A here, you can just do it in random way and you basically have this large molecules consists of different types of bonds like A, A bond, B, B bonds, A, B bonds also. So, only there are 3 types of bonds possible, there are 3 nearest neighbor pairs that are possible. In a binary solution, there are only 3 nearest neighbor pairs that are possible, there are only 3 nearest neighbor pairs possible when you have a binary solution.

So, A and B are 2 kinds of atoms, A, A, B, B and A, B bonds are only possible, there are only 3 nearest neighbor pairs that are possible. Now, we are also assuming volume of pure A and pure B are assumed to be because the volumes of pure A, then basically volume per atom of A or B are assumed to be equal. So, V M the molar volume of A and molar volume B are assumed to be equal, we are not assuming any difference between the molar bonds. So, and also when A and B mix together, then the volumes of A and B will not change during mixing, that is another really important thing that we have to consider. And also inter atomic distance and bond energy does not depend on composition. So, in the next lecture, we will continue this and we will stop here and in the next lecture, we will continue this and we will finish the description of regular solution model for a disordered solution.

And also later I will show in case of ordered structures or ordered lattices, how do you modify the regular solution model. And finally, we will show what gives negative division and what gives positive division from Raoult's law or from this ideal solution assumption. From this ideal solution assumption, what basically what the important thing that I want to say here is that what are means how does this differ, this is something that we will deal with in the next lecture. So, basically how what type of interactions or what interaction balance why does EAB greater than half of EAA plus EBB gives you a negative departure from Raoult's law or why does EAB less than EAA plus EBB half of again half comes because of this double counting of A and B bonds. So, basically if you look at that, we want to see how this negative or positive divisions from Raoult's law identity comes and but we have defined what is the identity and we are going to derive the regular solution model assuming these interactions. Again, these interactions are assumed to be pairwise, they are assumed to be nearest pairwise interactions and as you can see, we have this quasi-chemical theory that we have taken into account, but the solution is like a big molecule.

This big molecule contains a large number of AABB and AB bonds in a binary system. Again, in a ternary system, it can be AB, BC, AC as well as AA, BB and CC. So, if you have A, BC, 3 components in a ternary solution. So, you can basically as you can see, you can extend it from binary to ternary to partnary and so on. So, we will again discuss this further in the next lecture. Thank you.