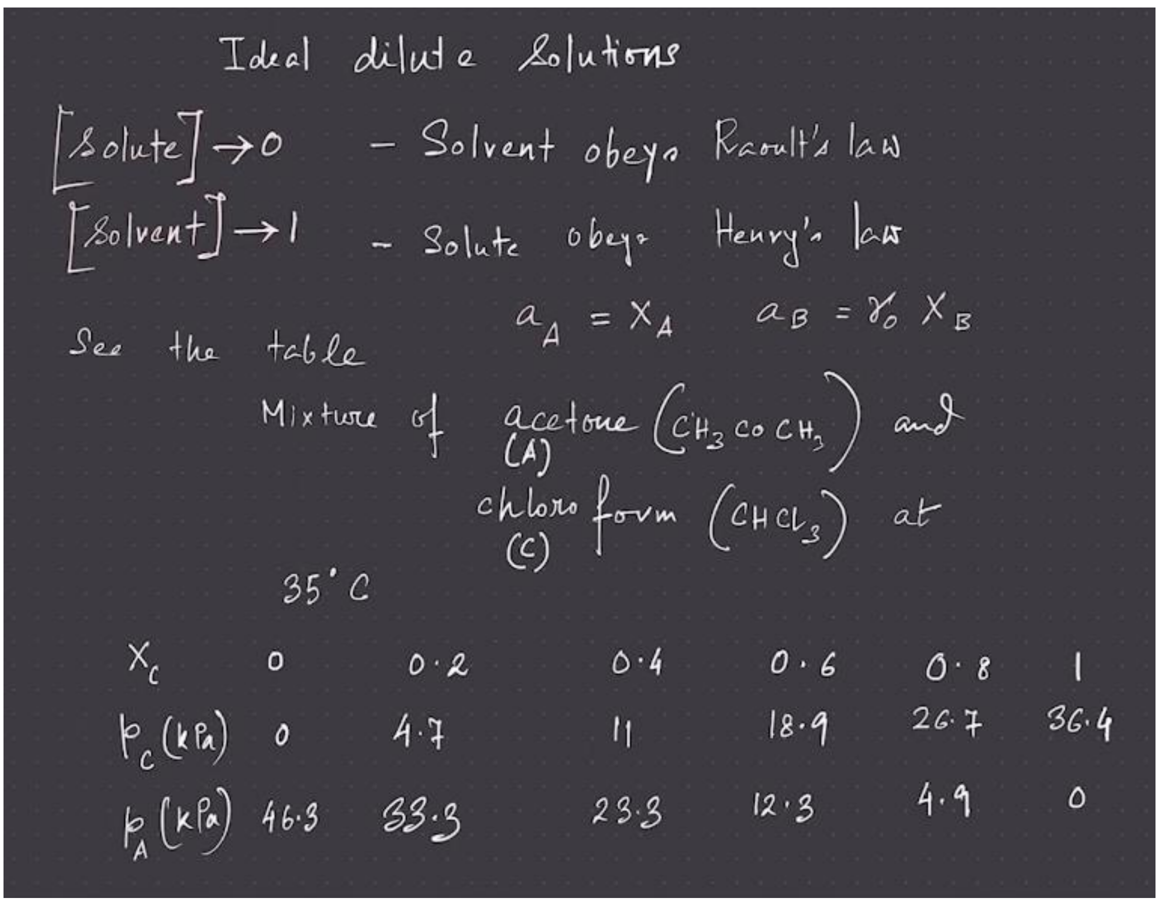
Thermodynamics And Kinetics Of Materials

Prof. Saswata Bhattacharya
Dept of Materials Science and Metallurgical Engineering,
IIT Hyderabad

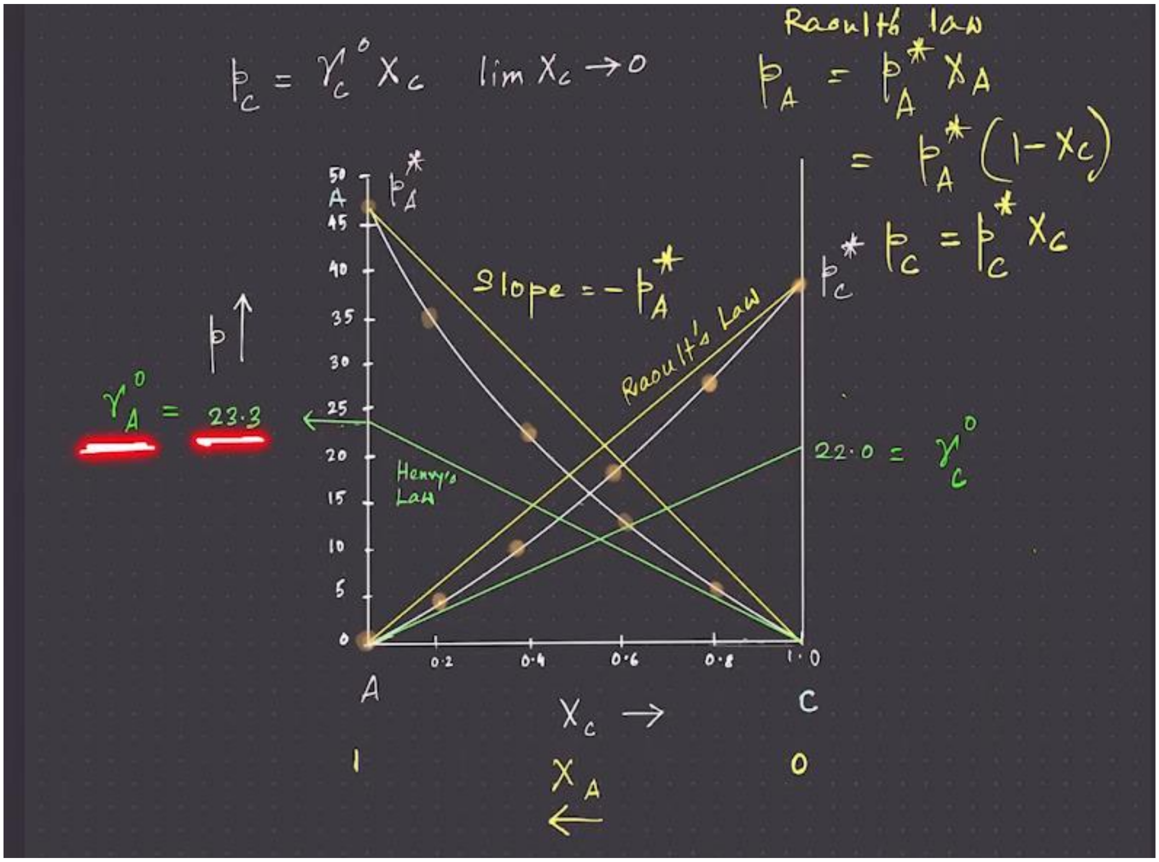
Lecture 26

Regular solutions and thermodynamic properties of mixing

We start with the revision of solutions, then I will discuss something called colligative properties or collective properties because of solute in solvent. And we will also discuss one very important type of model to describe some solutions or liquid solutions or different types of solutions. It can be gas mixture also and these are called quasi-chemical models. So we will go into that and we will also discuss colligative properties. So initially in fact I will start with real solutions again so I will emphasize. So before I go to quasi-chemical models or colligative properties, we will briefly recollect real means ideal versus real solutions.



So as we know in ideal dilute solutions for example, we know that there is this solvent which so dilute solution means that the sol the concentration of solute say V is the solute then it is V tends to 0 and XA that is the solvent tends to and we also have seen. So basically the amount of solute tends to so amount of solute we can write this way solute concentration tends to 0 and solvent tends to a pure solute. So in these case solvent to base routes now but the solute so solvent to base routes now and solute to base in base line. So this is some although it is an ideal dilute solution and we are talking about Raoult's law so Raoult's law is something that is obtained by the components in an ideal solution.



For example, if you have an AB binary solution then AA that is activity of A or apparent concentration of A equals to XA and even for the other component we can write AB equal to XB but here for solute it is not Raoult's law but Henry's law. So we will see what does this mean so what does this mean AA equals to XA and AB equal to gamma 0 XB where gamma 0 or k h is the Henry's law coefficient right. So and this is drawn basically as XB tends to 0 right as XB tends to 0. So if you look at the plot that gamma 0 is obtained or the slope is obtained by drawing a tangent to this curve or to this at where XB tends to 0. So if I look at a real solution for example of mixture of acetone and chloroform which we have discussed the earlier class you see this is the concentration of chloroform and as a function of concentration the partial pressure of chloroform given the partial vapour pressure of chloroform is given by 0, 4.

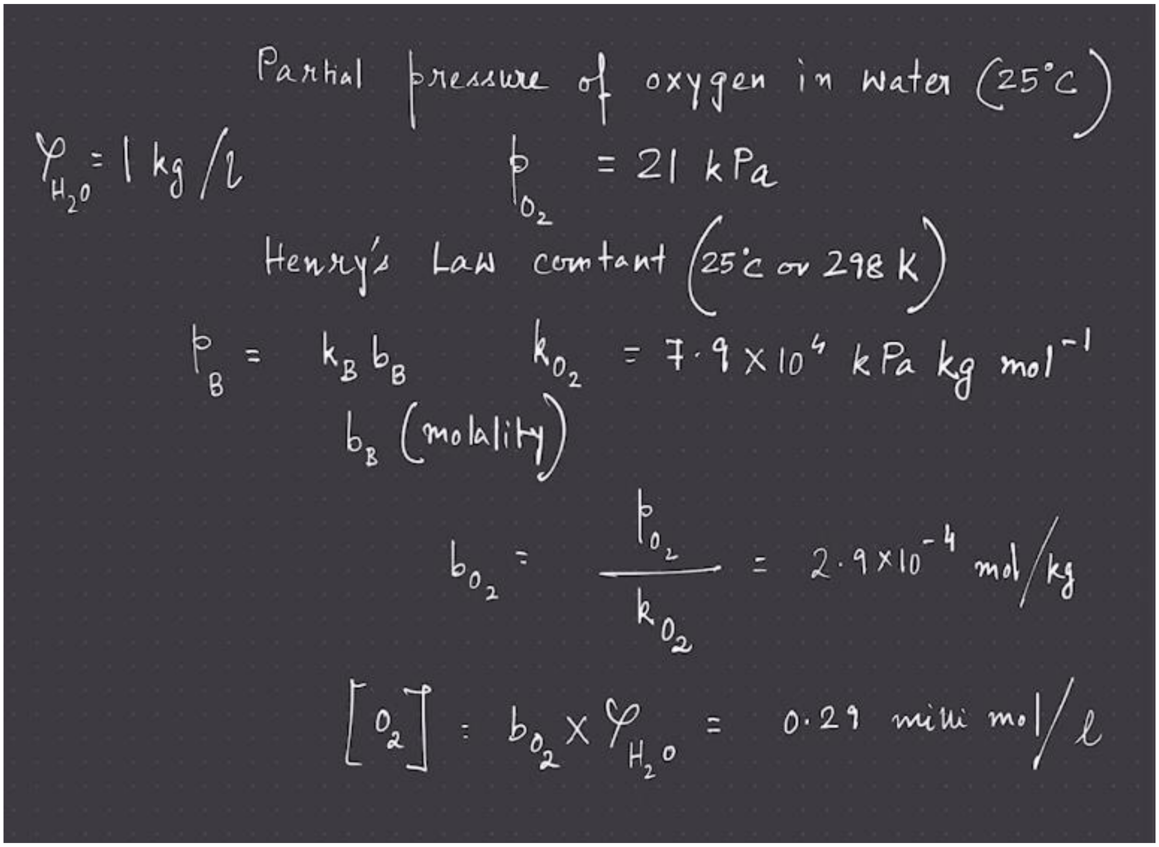
7, 11, 18.9, 26.7 and 36.4 it is increasing. So as you increase chloroform the vapour pressure due to chloroform is increasing from 0 to 36.

4 kilopascal. On the other hand that for acetone goes from 46.3 when there is 0 chloroform that is pure acetone the vapour pressure reduces to 0 when acetone becomes very very small. If you plot that you see neither it is not following any law neither Raoult's law or this law basically as you can see if you look at it is a function of C. So this is XC there is a mole fraction or atomic fraction of chloroform.

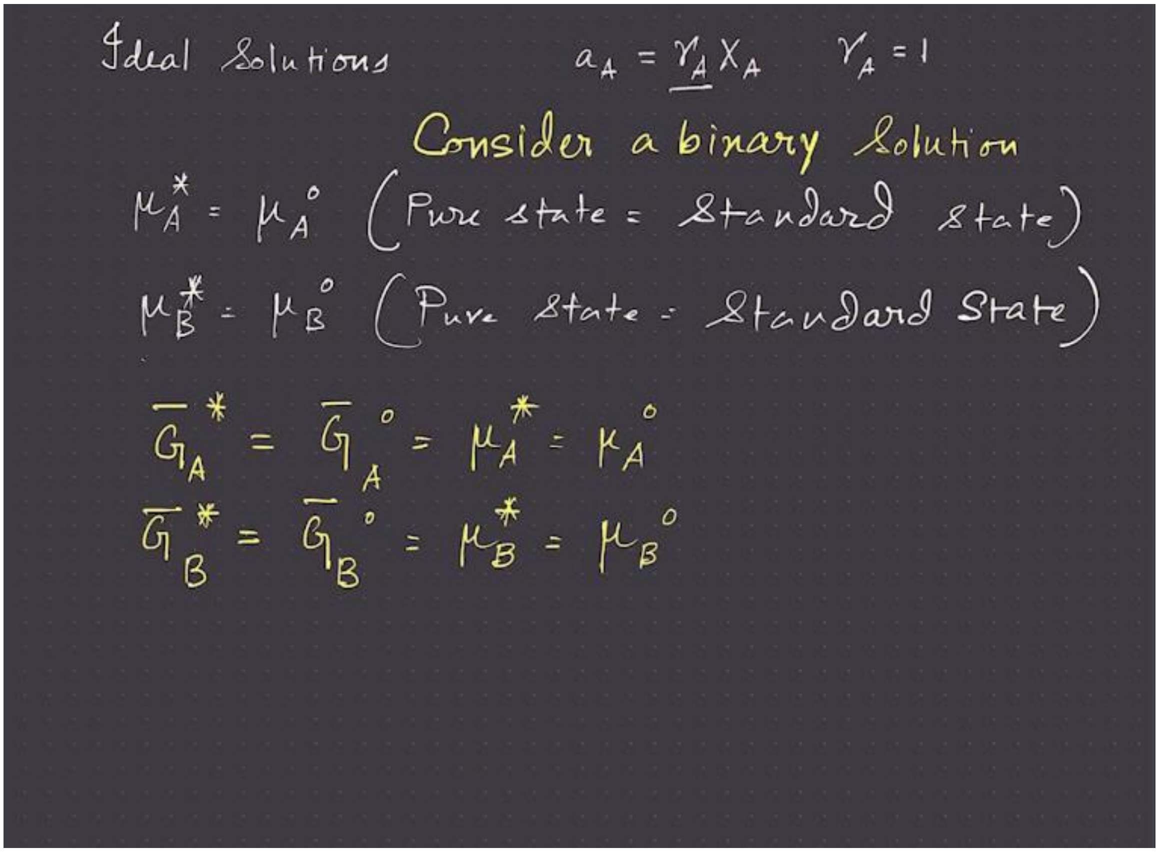
So chloroform is 1.0 here and this is specifically acetone this is basically acetone and XA goes the other way right to left. So XA increases from right to left while XC increases from left to right and you can see the point if you follow my line then you can see that there is deviation from identity right there is deviation from identity here as well as from in here. So this is basically for this is from A to C as you can see A to C there is an increase in vapour pressure. So A to C as you go to pure C there is an increase.

So this basically corresponds to PC right. So PC 0 to 1 there is a monotonic increase in the pressure but if you see the increase in the pressure you look at the increase in the pressure the vapour pressure you see that it is not following a straight line because this is P and this is XC if Raoult's law would have been followed then P A should have been P A star X A and P A star is nothing but the slope or PC goes to PC star XC so that PC star is nothing but the slope and you see it is a straight line but it is definitely not if you join this points if you join this points it is definitely not a straight line so it is deviating or there is a departure from Raoult's law but if you want to use Raoult's law then you can basically for either A or C you can start from here and you can draw this yellow line here so this is for C so this is for C which is PC goes to PC star XC and what you basically get is nothing but the slope is basically here PC star so for this yellow line for PC 0 line you see the slope is PC star okay while for this yellow line for the other line that is for acetone you see there is a decreasing trend right there is a decrease in pressure from acetone it is going to 0 for it was pure chloroform basically the slope is minus P A star now how do you basically tell so if you look at P A it goes to P A star X A so the slope is basically minus P A star if you look at this line so the slope is negative right it's minus P A star so if you can see it is plotted against X C so P A star minus into X A is nothing but P A star into 1 minus X C so basically P A star so minus P A star X C as you can see and then there is also an intercept so minus P A star X C and the intercept is basically P A star so this is basically P A star this point is basically P A star P A star is the vapor pressure of the pure solvent so this is P A star and this is nothing but P C star right and the slope is minus P A star for acetone because for acid the way we have plotted X C increases from left to right X C increases from left to right and therefore for acetone the vapor pressure continuously decreases from pure acetone to pure chloroform right now if you look at Henry's law what we are doing Henry's law is basically giving you so for any component is basically P C goes to gamma C 0 X C then limit X C tends to 0 right X C tends to 0 so if you look at for chloroform you will basically draw a tangent to this white curve that you have interpolated the interpolated curve through the data point so you have these data points if you look at this data points you have this data point this is the point this and this and this guy and this guy now if you look at this is a curve is a curve right this is a this is basically as you can see here this is a this white line is a curve for this curve in the limit X C tends to 0 is here right at the origin here so because here A equal to 1 that means acetone is 1 therefore chloroform is 0 so at this point if you now draw tangent to the curve at X C equal to 0 you are drawing a tangent to the curve now that tangent line gives you the value of gamma C 0 which comes out to be 22.0 kPa so gamma C 0 is 22.0 kilo Pascal for chloroform similarly for acetone we will go to the chloroform end where acetone is 0 and we will draw this curve again draw this green line is tangent at this point at the limiting point of X A tends to 0 and where it meets the y-axis and that that value is like 23.3 kPa and for acetone that means the Henry's law of propagation is 23.

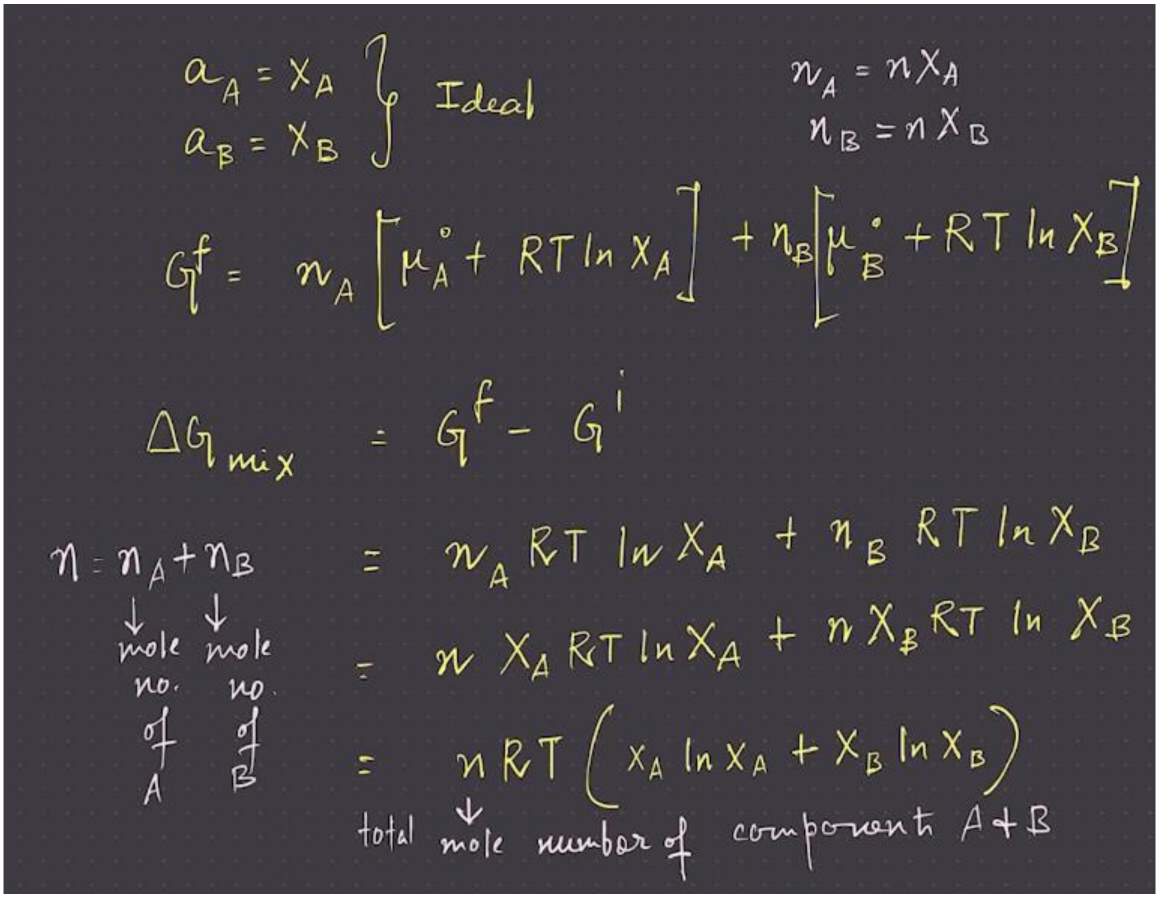
3 correct and as you know the partial pressures are basically measured in this way that you have pO2 is 21 so this is basically partial pressure of oxygen dissolved in water at 23.3 Celsius you have pO2 is 21 kilo Pascal and if I give you Henry's law constant 30 basically kilo Pascal kg per mole okay this is kilo Pascal kg per mole then basically you can also use basically what I am trying to see here this example tells you that you can express Henry's law in terms of molality that is molality means amount of solute per 1000 grams or per kg of the salt so PB goes to KB BV so BB is basically nothing but molality and if you know BO2 that is the molality of oxygen you basically can find out if you know KO2 which is the it is basically 7.9 10 power 4 kilo Pascal kg per mole so BO2 comes out to be 2.9 into 10 power 4 moles per kg that means the very small amount of moles per kg right per kg of the solvent right or per kg of this sometimes you can call it per kg of the solution but I think if strictly speaking the molality is per kg of the solvent so basically now so if you look at that if I know BO2 then O2 the concentration per unit volume of O2 right so that the in moles per unit volume the concentration is BO2 that is molality times rho water right so as you can see this kg is per solvent so basically BO2 times rho water will gives you 0.29 millimoles per liter of water solvent right 0.



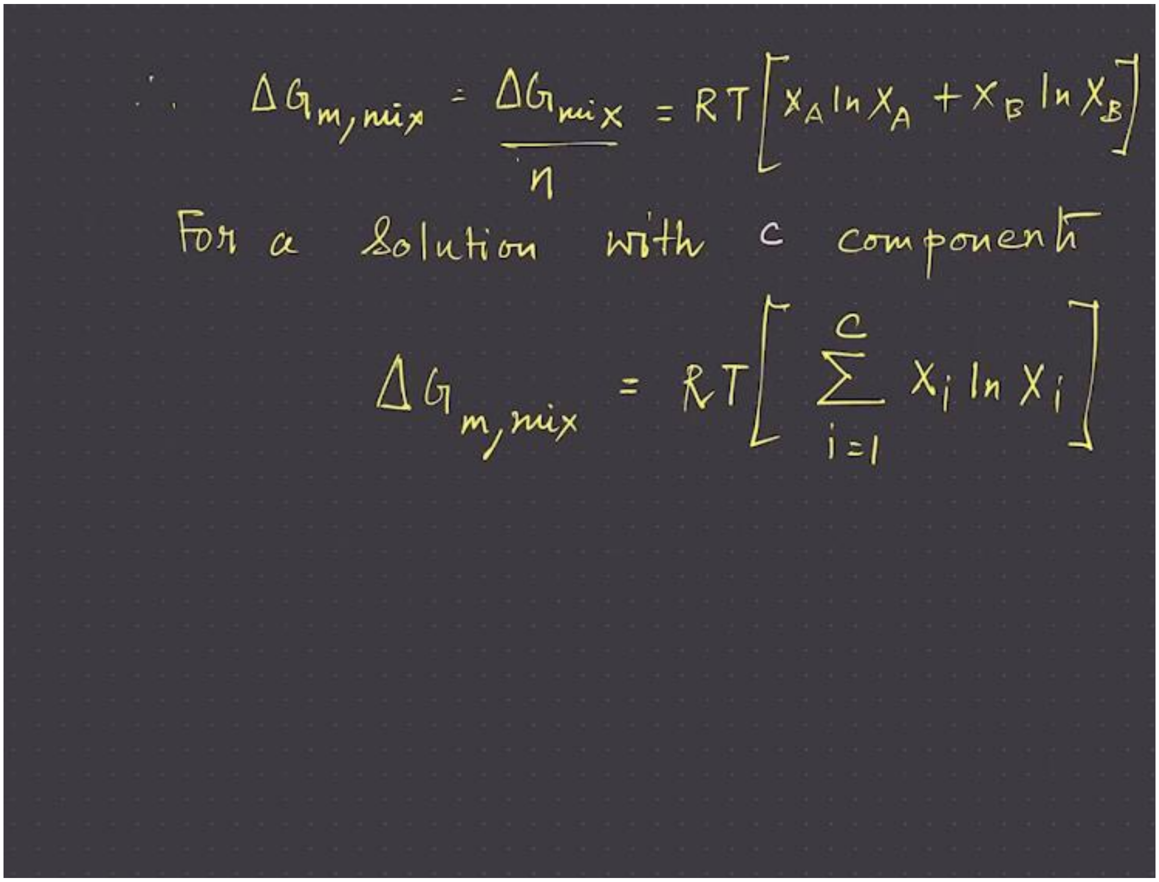
29 so the amount of oxygen dissolved at 25 milli Celsius from what is given we find out to be this 0.29 milli moles per liter right now in an ideal solution all this Raoult's law is followed by ideal solutions and see this is a partial pressure form of Raoult's law but the Raoult's law can also be expressed in terms of activity and we already know that the way it is done we write activity of a component equals to gamma A XA where gamma A is activity coefficient and if gamma A equal to 1 then basically this is nothing but Raoult's law for component right so this is something we know so if gamma A equal to 1 for ideal solutions gamma A should be equal to 1 so if you look at a binary solution



For example mu A star say for example you have mu A star mu A star is nothing but the chemical potential of pure A chemical condition of A in pure state okay so there is a star that indicates it's a pure state but this is equal to we can write that this is equal to standard state the pure state can often be taken as the standard state or reference state similarly for B we can take the pure B that is the mu B star to be the reference state or the standard state right now if you think of this the partial molar free energy of A or so basically please note that partial molar free energy of A in the pure state is equal to partial molar so in this case partial molar free energy of A in the pure state is equal partial molar free energy of A in the reference state which is nothing but remember partial molar free energy is nothing but the chemical potential right so that is chemical potential of A in the pure state and that is chemical potential of A in the standard state so the pure state can often be taken as the standard state that's the only thing that I want to tell you so you can also take us choose a standard state that is not the pure state of either A or B but if you it is also convenient to choose the pure state for A or for B to be the standard state. So now let us look at mixing so if you look at mixing what happens so mixing is what we have some rules of A we have some container containing A and we have some container containing B you have A some amount of A and some amount of B and you are mixing them together right that's the idea so you have a container which is like A which contains A molecules A and plus you have another container another container which contains B and you are mixing them together okay to form so now before you mix them together before you mix them together what do you have you practically have say let us consider the atoms of A to be red so you have some A atoms here I will call C there are some A atoms and say consider so this is basically so if we tell this is basically B this is basically A then I am adding them together so the initial state is basically what I have pure A I have pure B and so the initial state before mixing is GI superscript I basically indicates initial is equals to nothing but as we have shown before it is NA times mu S0 this comes from what it comes with the Euler equation it is a standard Euler equation at a given temperature and pressure at a given temperature and pressure at a given PNP at given P comma P you can write GI that is the initial the free energy of the initial state of this mixture of A and B this is just before mixing right we have still A atoms the block of A atoms and then we have the block of B atoms we have not mixed them so you basically have the total energy but we have just taken them together we have just brought them together but we haven't mixed them right it has not mixed it has been just brought together okay then think of this like imagine this like A atoms a block of A atoms and a block of B atoms are coming together to form two sub systems and they are basically subdivided by a partition and this partition is not yet removed so that A and B are basically we are not allowing A and B to mix okay and the partition is basically impermeable to either A or B okay now then GI that is the energy of the mixture the total energy of the mixture will be the free energy of the mixture will be NA mu S0 plus NB mu B0 where mu S0 and mu B0 are basically the partial molar free energies or chemical potentials of A or B in their pure state right however after mixing what happens after mixing you basically get NA mu A so as you can see NA mu A plus ND mu B where mu A is the chemical potential of A after mixing so when it has been mixed so what does what does it mean how does it look like it looks like this so you have some A atoms and then you have some B atoms at random B atoms A atoms at random and say some like that so you basically have made up a mixture a completely random mixture of A and B and what you get is physically so NA times mu A the Euler equation becomes NA times mu A where mu A is the chemical potential of pure component of component A in the solution



so this is basically not the component A in the pure state not mu A0 but mu A and mu A is nothing but the chemical potential of component A in the solution right chemical potential of component A in the solution similarly so because they have formed a solution and NB times mu B where mu B is the chemical potential in the solution now this is after mixing now as you know mu A as you know that mu A can be expressed as mu A0 plus RTLNA A where AA is the activity of A right of component A similarly mu B is mu B0 mu B0 mu A0 are in the pure state or standard state chemical potential and then there is this additional term right there is this additional term so this is something that you please concentrate on like RTLNA A and RTLNA B and this AA and AB we call them activities of A and B respectively now for ideal case AA equals to XA and AB equals to XB that we know now GF is NA mu A right instead of mu A I am writing mu A0 plus RTLNA XA and NB mu B0 plus RTLNA XB and delta G mix is nothing but GF G final minus G initial the free energy of the final configuration minus free energy of the initial configuration which comes out to be NA RTLNA XA plus ND RTLNA XB now I can write NA is nothing but NA is nothing but N times XA and NB is nothing but N times XB where N is the total number of molecules or total number of atoms right so in such a case you get N XA RTLNA XA plus N XB RTLNA XB or you get N RT XA N XA plus XB N XB okay so basically delta G mix becomes N RT XA N XA plus XB N N XB when you have an ideal solution that is what you get so you basically get delta GM mix which is delta G mix by N that is this is a molar free energy of mixing equals to RT right because it is divided by N, N is the total number of molecules or total number of atoms



then basically this becomes RT XA N XA plus XB N XB where N is the total number of molecules or total number of moles of so basically the total energy of mixing is this right and where N is the total mole number of compounds right AN basically is the mole number of mixed is the total mole number of components AN or in other words AN is nothing but NA plus NV where NA is the mole number of A mole number of A and NV the mole number of now so delta GM mix that is the molar right because I am now divided by the total number of moles, total number of moles is N right total number of moles is N so I am dividing by that so I get the molar free energy of mixing which is RT XA plus XB N XB and for a solution with C components I can generalize so this is for binary two components right instead of binary we are talking about C, C is the number of components okay so then if C is the number of components here I equals to basically here I equal to A and B right or 1, 2 so basically it's X1NX1 plus X2NX2 or 1 minus XN 1 minus X plus XNX where X is basically the mole fraction of say B okay but if it's a solution with C components or multi component solution then delta GM mix there is a free energy the molar free energy of mixing goes to RT times I equal to 1 to C XN and XN right this looks very familiar right XN and XI you have already seen

$$\Delta S_{m,mix} = -\left(\frac{\partial \Delta G_{m,mix}}{\partial T}\right)_{P,n}$$

$$= -R\sum_{i=1}^{C} X_i \ln X_i > 0$$

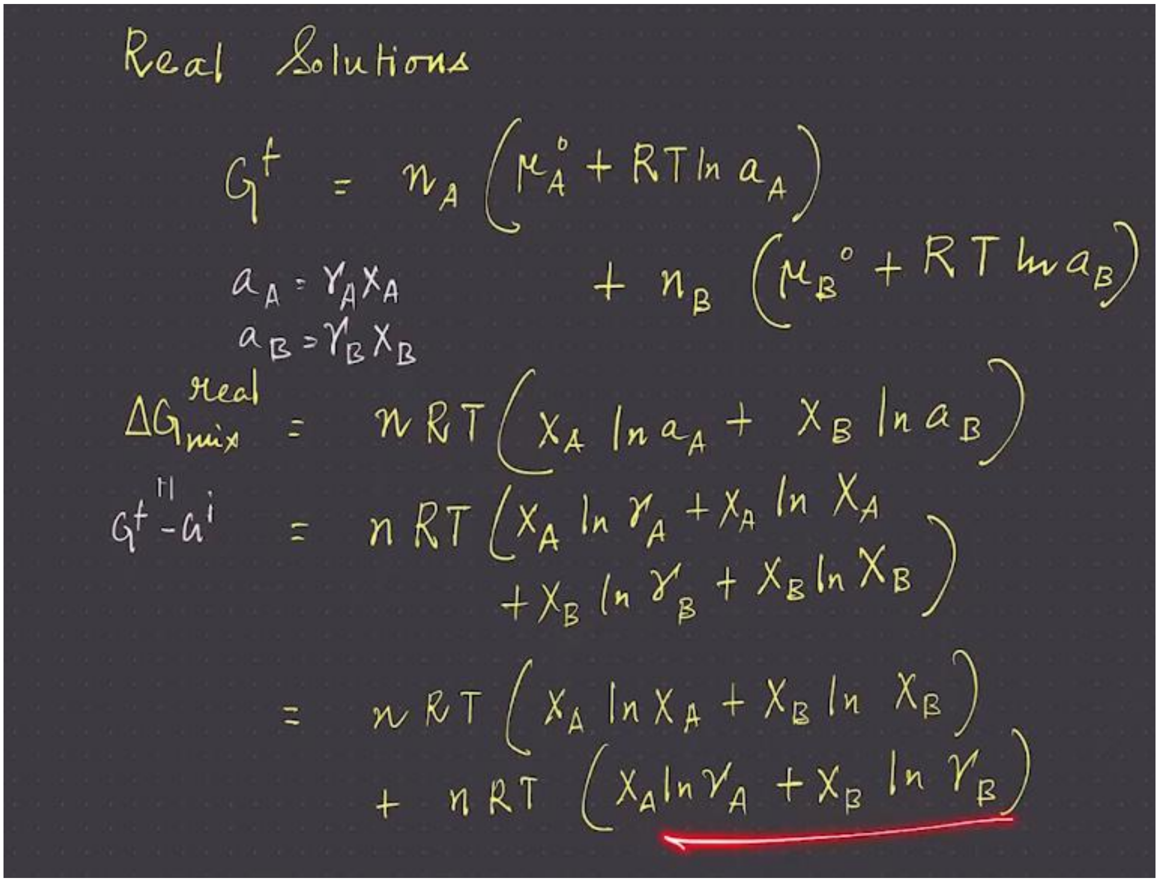
$$\Delta H_{m,mix} = \Delta G_{m,mix} + T\Delta S_{m,mix}$$

$$= RT\sum_{i=1}^{C} X_i \ln X_i - RT\sum_{i=1}^{C} X_i \ln X_i$$

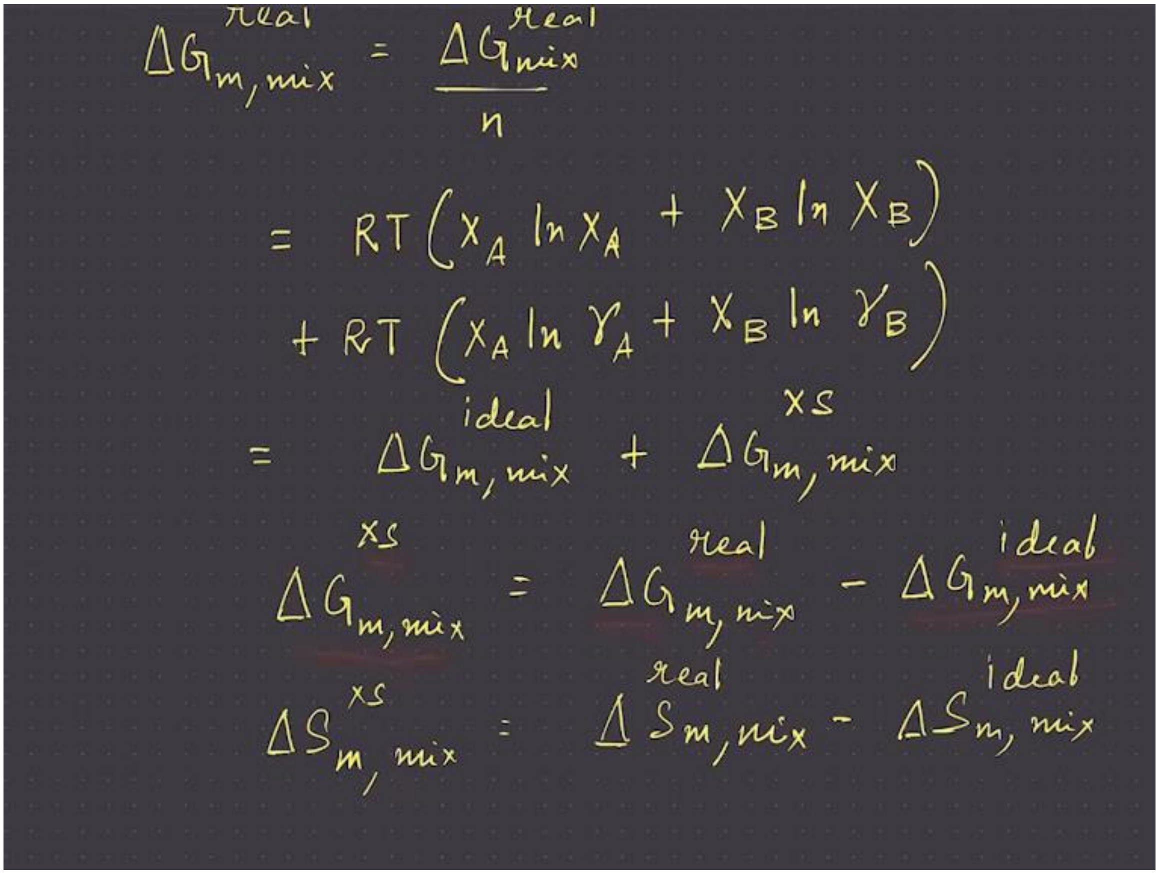
$$= 0$$

$$\Delta V_{m,mix} = \left(\frac{\partial \Delta G_{m,mix}}{\partial P}\right)_{T,n} = 0$$

that right delta SM mix I have told that is nothing but it is minus RXN and XI right I don't want to repeat again but what I am trying to say is that once you know delta GM mix you can basically get delta SM mix you can get delta HM mix which is equal to 0 right for an ideal solution right delta HM mix equal to 0 remember in many books instead of ideal a term perfect is used and sometimes perfect seems more appropriate than ideal because in a perfect solution what we assume is that there is no interaction between the constituent atoms of different kinds so basically if you have A B and C making a solution and the solution is basically perfect then basically A B and C they do not interact it means it seems to A that is occupying the entire volume or it seems to B also it is occupying the entire volume and you see also that it is occupying the entire volume because A B and C they do not actually interact right in a perfect solution however in an ideal solution the interactions balance out I will come to that I will soon come to that but what I am going to say I am just recollecting here delta SM mix ideal is this delta HM mix ideal comes out to be delta GM mix plus T delta SM mix and delta SM mix is minus RXN X I which is basically positive right which is basically positive so now that is so delta HM mix is delta GM mix which is RTXN X I plus T delta SM mix and then delta SM mix is minus RXN X I and we multiply T so delta HM mix as the enthalpy of mixing for an ideal or a perfect solution where there is no interaction between the different kinds of atoms or different kinds of molecules is basically 0 right so the enthalpy of mixing is basically 0 for an ideal solution or a perfect solution even the same goes for molar volume right we have already seen that molar volume mixing right or the molar volume of mixing is basically del delta G del P and del delta G del P in this case is del G

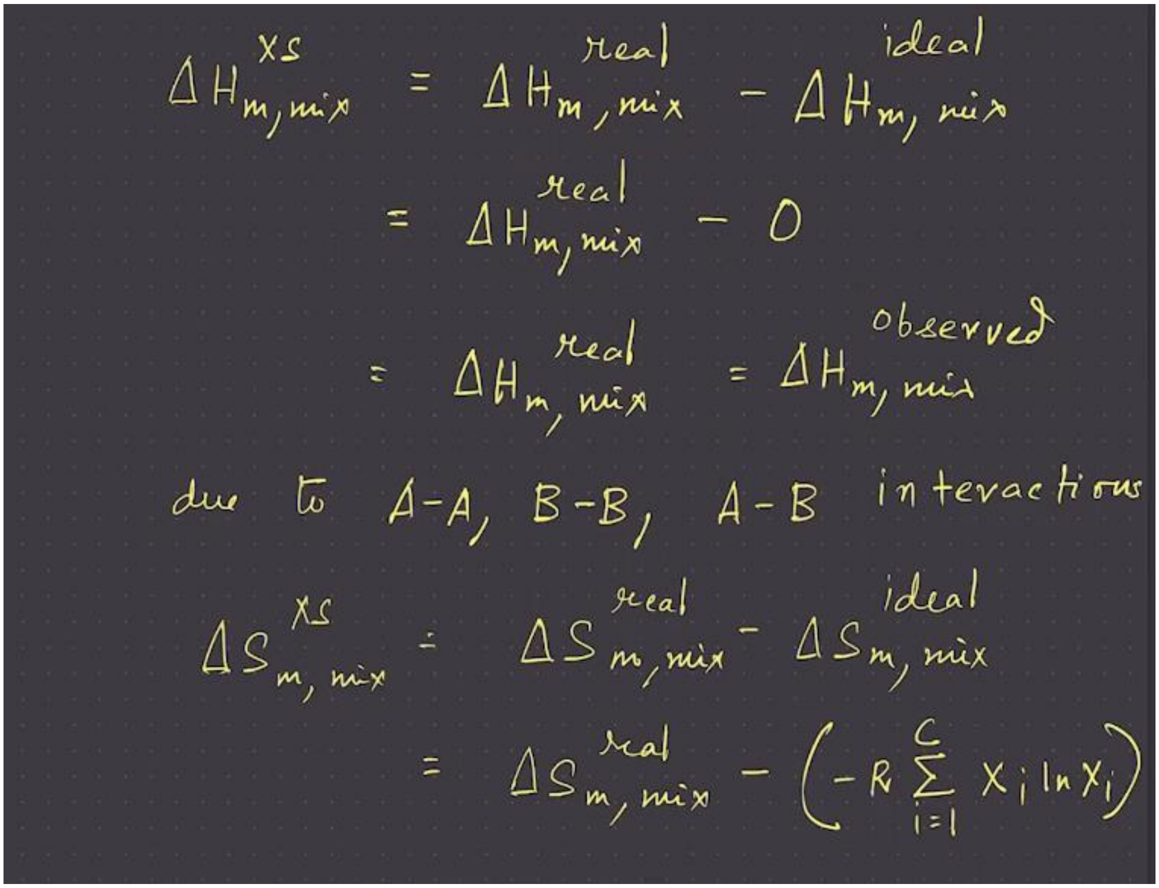


now comes real solution so this is where the difference is now look at the initial form the initial form does not change the initial part does not change these does not change however the final part look at the final part now instead of writing XA instead of writing XA I am writing activity of A and here also I am writing activity of P but as we know that AA goes to gamma AXA and AB goes to gamma BXA where gamma A is the activity coefficient of A and gamma B is the activity coefficient of P and they are not equal to 1 now in that case you have nRT that the delta G delta G is nothing

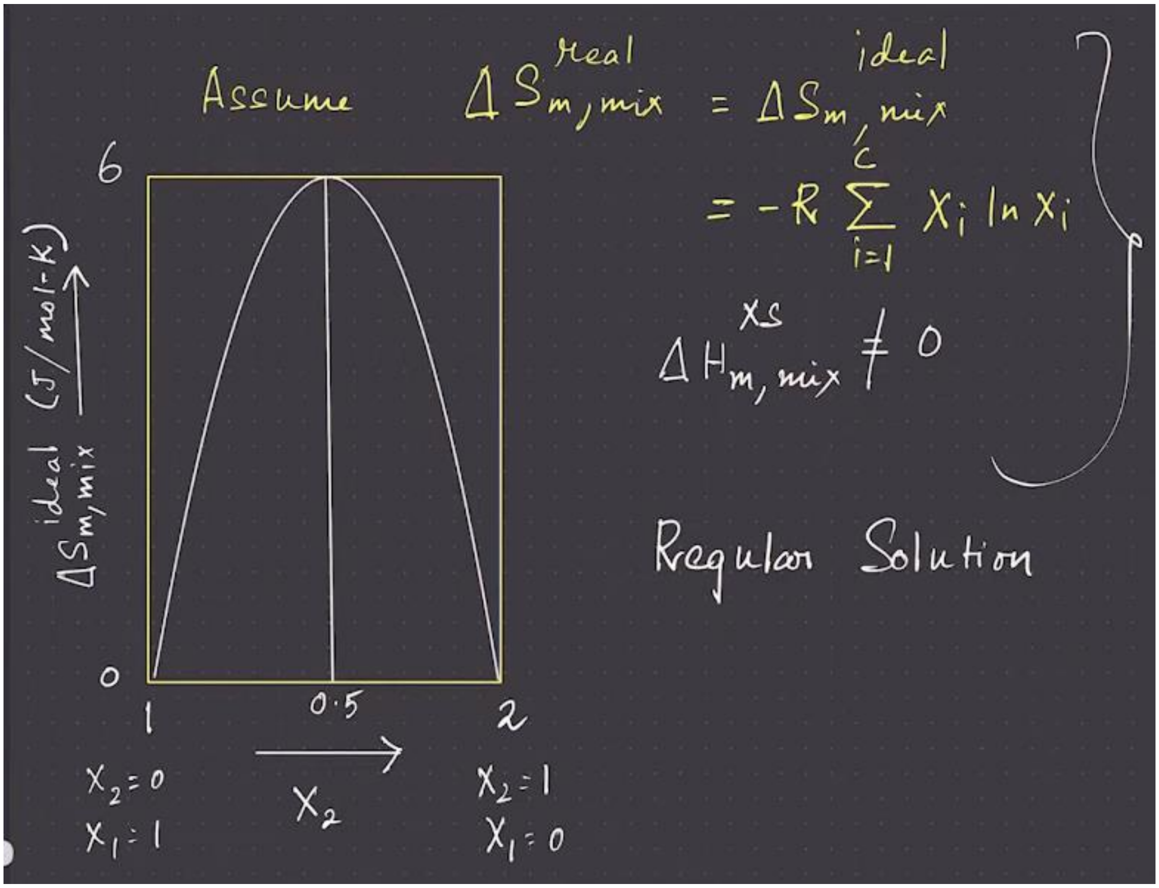


but again GF minus GI which is equal to GF minus G. Now GI is nothing but NA so in GI what is what are the terms involved NA mu S0 and NB mu Z0 okay now all of these are gone so you have NA RTLNA A plus ND RTLNA B or we can write n common nRT XA then AA plus XB then AB and then you can write it is as nRT XN gamma A because AA is gamma XA write XN gamma A plus XN XA and X and again XB times so it is all within the bracket so basically I will just tell you this is all with the bracket so basically XN gamma A so basically this what I am writing here is XA and gamma A I am writing XA sorry XA ln AA I am writing XA ln gamma A which is equals to XA ln XA plus XA ln gamma A right so that is what I am doing so XA ln XA gamma A XA ln XA XB ln gamma B is the nR mix right multiplied with NA. So if you do that so nRT this term XN XA plus XB ln XB comes and then there is this term right this additional term

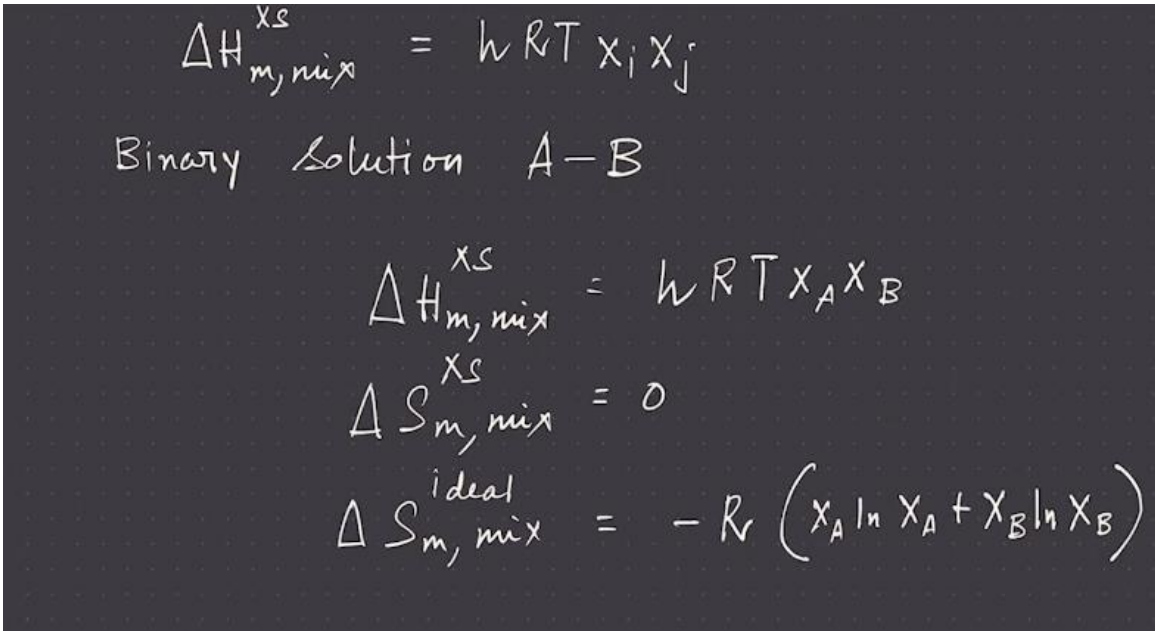
comes now as you know delta Gm mix is real is equal to so again the molar free energy of mixing for a real solution is nothing but the delta G mixer is a total free energy of mixing for the real solution divided by the total mole number right so now this becomes RT XN XA plus XB ln XB plus RT so as you can see there is this additional term right in the real solution XA ln gamma A plus XB ln gamma B so basically if I now just look at this part this is the ideal part so delta Gm mix for a real solution is a sum delta Gm mix of the ideal solution plus delta Gm mix XS so this is the most important concept that you learnt in solution so basically as you can see here when you are looking at a real solution there is a part which is also the ideal means that we have proved that RT XN XA plus XB ln B is nothing but the that the free energy of mixing for ideal solution right free energy of mixing for ideal solution however this term okay are RT equal to XN gamma A plus XB ln gamma B this is basically as you can see here this is basically delta Gm mix XS please note the superscript so delta Gm mix XS is delta Gm mix real minus delta Gm mix ideal and delta XM mix XS is delta XM mix real minus delta XM mix ideal now comes delta Hm mix XS which is delta Hm mix real minus delta Hm mix ideal this part as you have seen is 0 so this delta Hm mix XS is nothing but delta Hm mix real and this delta Hm mix real is nothing but the delta Hm or the change in molar enthalpy of mixing that is observed okay due to why do you observe this this non-zero value this is due to A-A B-B and A-B interactions in a binary solution if you consider a binary solution then there are A-A B-B and A-B interactions if this is a ternary solution you have A-A B-B C-C A-C B-C and A-B interactions right



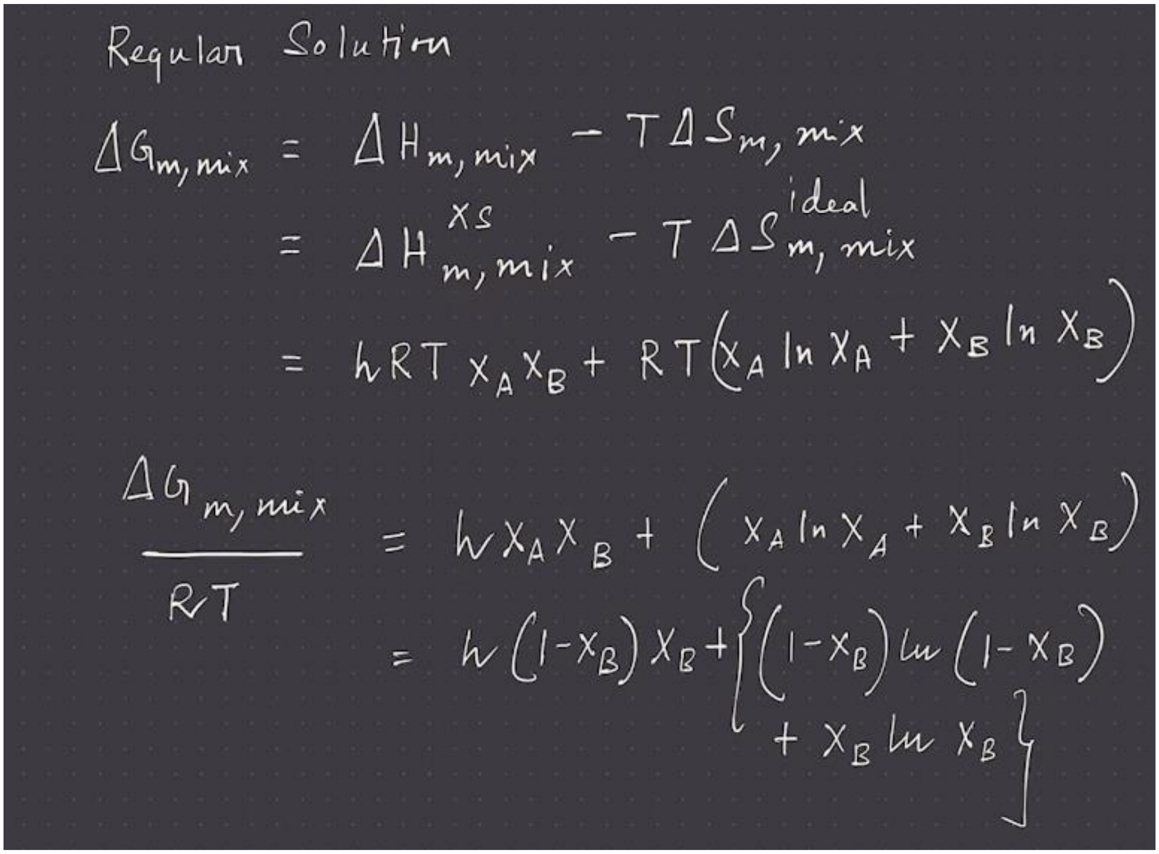
that's the ideal again for delta Hm mix XS I can do that delta Hm mix real minus delta Hm mix ideal and delta Hm mix real minus of minus R XI and Xi and then basically we can assume that delta Hm mix real is nothing but delta Hm mix ideal so that means delta Hm mix XS is equal to 0 now if you tell that delta Hm mix real is the same as delta Hm mix ideal then basically what you are getting is minus R XI and Xi right minus R XI and Xi and if you plot this for a binary solution you will see that it will have the highest it will be highest it will have the highest value at 0.



5 right at 0.5 axis and this highest value corresponds to nearly 6 right so this the highest value corresponds to ln it comes out to be ln 2 multiplied by R right so 8.314 multiplied by ln 2 which is like 0.693 and basically what you get is very close to very value very close to 6 so yeah 8.314 and ln 2 is you please check so you will get a value very close to 6 and this is basically delta Hm mix ideal which is basically in joules formula and as you can see the ideal entropy of mixing has a peak corresponding to it's equal to 0.5 right it's equal to 0.



5 now we'll go to one kind of real solution is called a regular solution now in that case for a regular solution we basically use a form given by this delta Hm mix Xs is nothing but H this is small h R T X i X j now this small h R T X j basically comes here so this is not equal to 0 right that was there for ideal solutions so for real solutions in particular for regular solutions it is assumed pair wise interactions and you can easily write the excess entropy of mixing to be h the small h R T X i X j right now if you look at this a binary solution it is first condition binary solution



so as you can see delta Hm mix is already given as H T X i X j but delta S m mix Xs as we saw in the previous slide that delta S m mix real is nothing but the delta S m mix ideal and as a result delta S m mix X s goes to 0 but delta S m mix ideal is basically minus R X i X j now if that is so now you have delta G m mix you have delta G m mix and you have delta H m mix you have delta Hm mix so delta G is nothing but delta H minus T delta H so you have this delta H m mix and you have T delta S m mix and now this is nothing but so as you can see this is delta H m mix X s minus T delta S m mix ideal right this is the regular solution model where the X s is only in the mixing enthalpy but not in the mixing entropy to do that then basically you get H R T X S B small h m because that is what we started with and plus R T X S B that is basically what you are telling is this guy is the same as this one and this part is same right now if I just divide by R T in this case we get H times X S B plus X S A plus X B R X B which is H minus X B and plus so if you just do this manipulation here so basically I am taking X B as the independent variable and X A plus X B remember 2 1 okay now if I want to plot this for different values of H this is what I get so I will discuss further in the next lecture okay we will continue from here in the next lecture