Thermodynamics And Kinetics Of Materials

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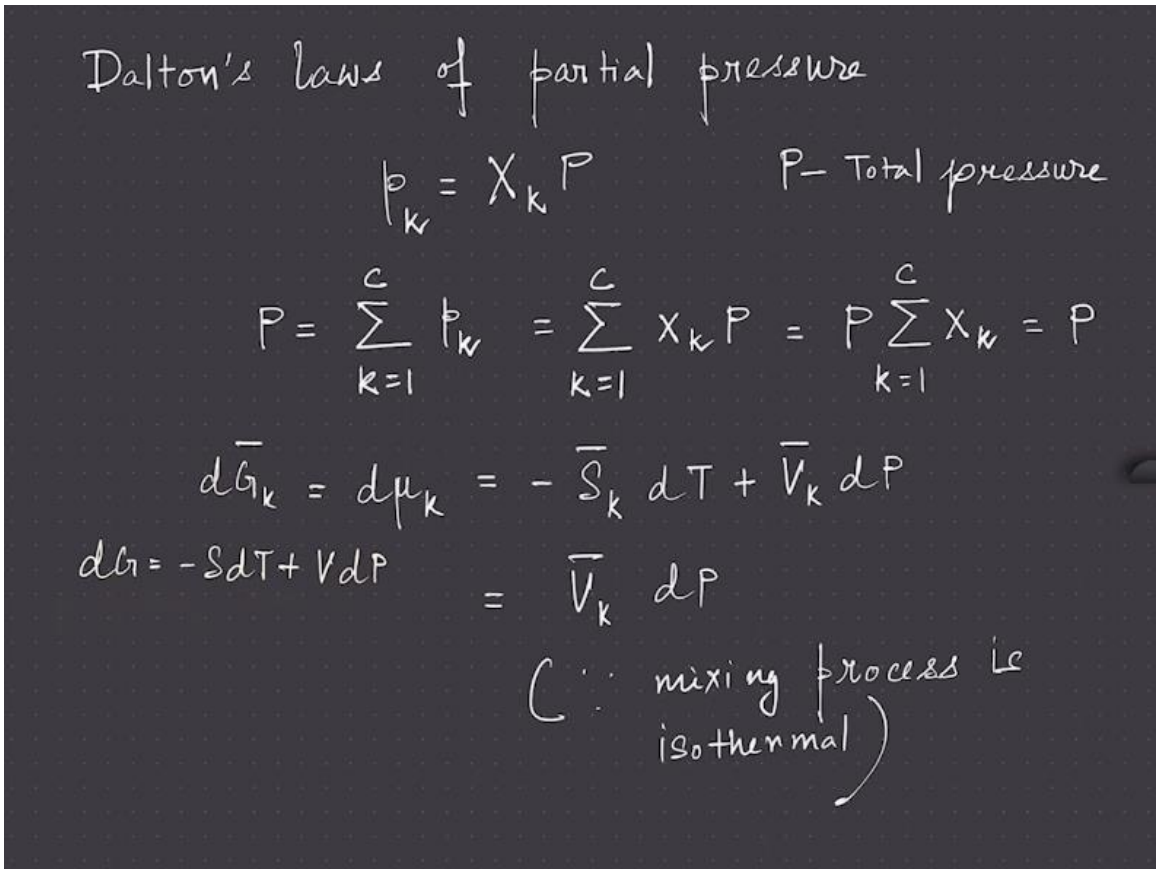
Lecture 25

Ideal and Real Solutions



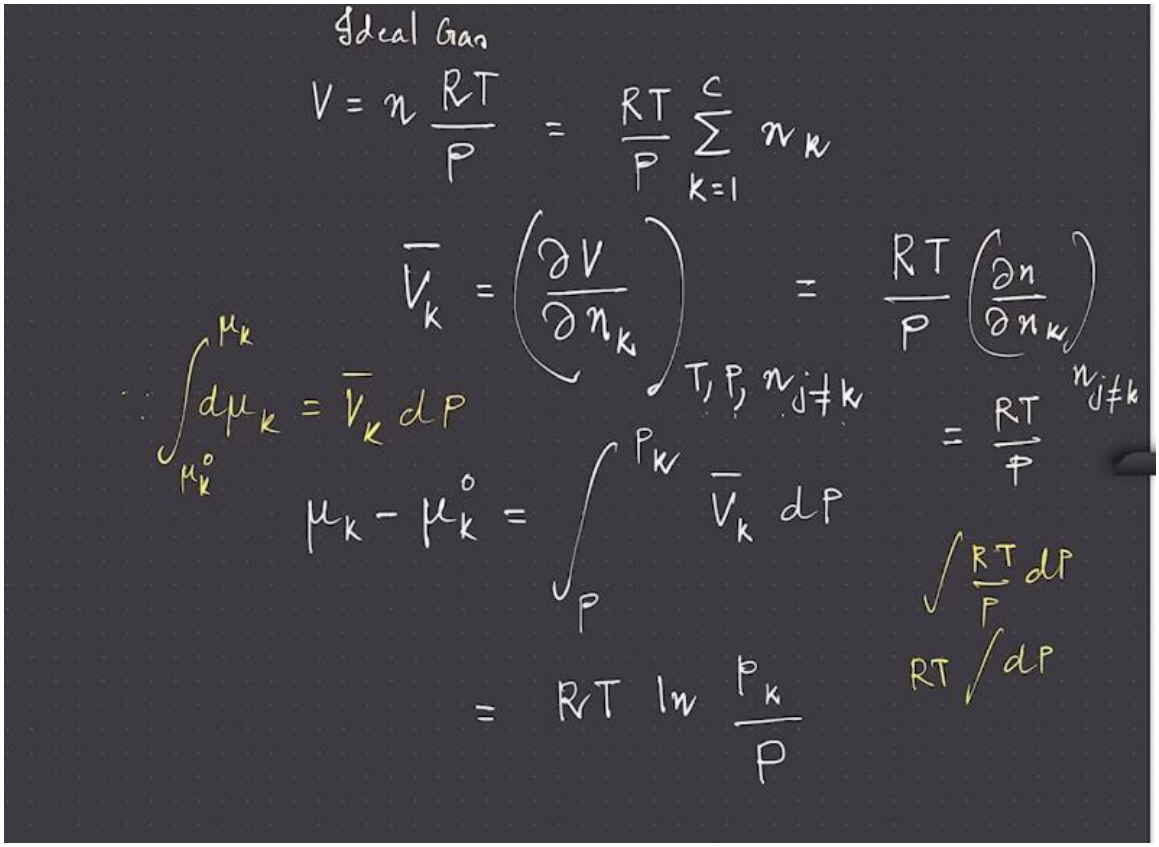
The third part means I want to start with again as I finished. So, we had ideal gas mixture we start with ideal gas mixture and we see that p k there is a partial pressure of component k partial pressure of component k equals to x k times p where x k is the mole fraction of component k. Now, p is summation of p k k equal to 1 to c if you have c components which is summation x k p and as you can see that p summation x k p is the total pressure which is constant. So, you see p equal to p. So, it is a consistent definition in the partial. So, this is a consistent definition partial pressure equal to p.

So, mole fraction is your total pressure. Now, as you know d g equals to minus s d plus v d p again this relation works for extensive property works for also the partial molar

property as we have already told. So, d g k bar is equal to d mu k d g k bar is what the g k bar is the partial molar free energy. So, d of g k bar.

So, d of the k bar means differential of g k bar the change or d mu k the d of mu k that is the differential of the chemical potential of component k. So, chemical potential is nothing, but the partial molar free energy of component k in the mixture which is equals to minus s k bar minus s k bar is the partial molar entropy of component k times d t plus v k bar which is the partial molar volume of component k times d p. Now, we are basically telling the temperature is fixed let us assume that the mixing process is isothermal. Let us assume the mixing process is isothermal. We are telling mixing process occurs at a given temperature and the total pressure is p, but we are basically telling the total pressure is p and, but p is not constant, but the temperature is constant or temperature the mixing process is isothermal.

So, as a result d t will go to d t equal to 0 d t equal to 0. So, this is becoming equal to. So, minus s k bar d t. So, this one goes to 0. So, you still have v k bar d p.



So, v g k bar equals to v k bar d p. Now, v the total volume v equals to n R T by p because it is an ideal gas right it is an ideal gas. So, which is R T by p summation k equal to 1 to c n k. Now, v equals to R T by p n and that is summation n k and v k bar equals to del v del n k which is nothing, but del v del n k keeping p p n j not equal to k and now if

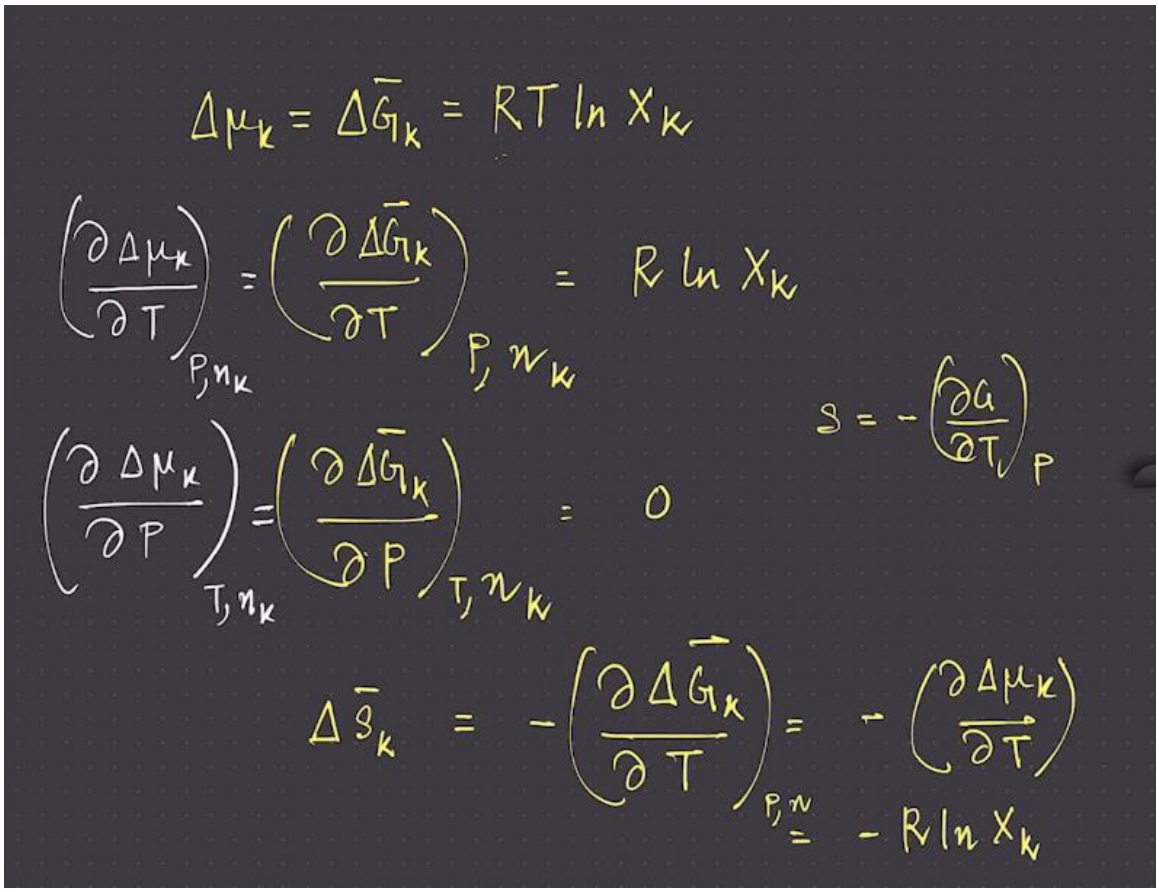
you look at that. So, it is basically v k bar is v is what R T by p times n.

So, del n del n k. So, basically this is basically del n del n k right where now here what does this mean it means that only k is in k component the mole number of k component k is varying and n j for all other components the mole number is fixed. So, and t. So, basically t is fixed say p is fixed then this becomes equals to nothing, but del n del n k is nothing, but 1. So, this becomes nothing, but R T by p right.

So, v k bar is R T by p. Now, since d mu k equals to v k bar d p you can write d mu k if I integrate. So, if I integrate d mu k if I integrate d mu k and I tell that this is pure component. So, if I tell that this is mu k that is the solution and this is the mu k 0 that is component k in the pure form then mu k minus mu k 0 is equals to p to p k. See p is the total pressure right and that was when it was mu k 0 right that was the pressure that right when it is not mixed then the pressure was p when it became mixed then it became partial pressure p k right component k only exerts partial pressure because component k has a mole fraction and mole fraction then partial pressure again becomes total pressure.

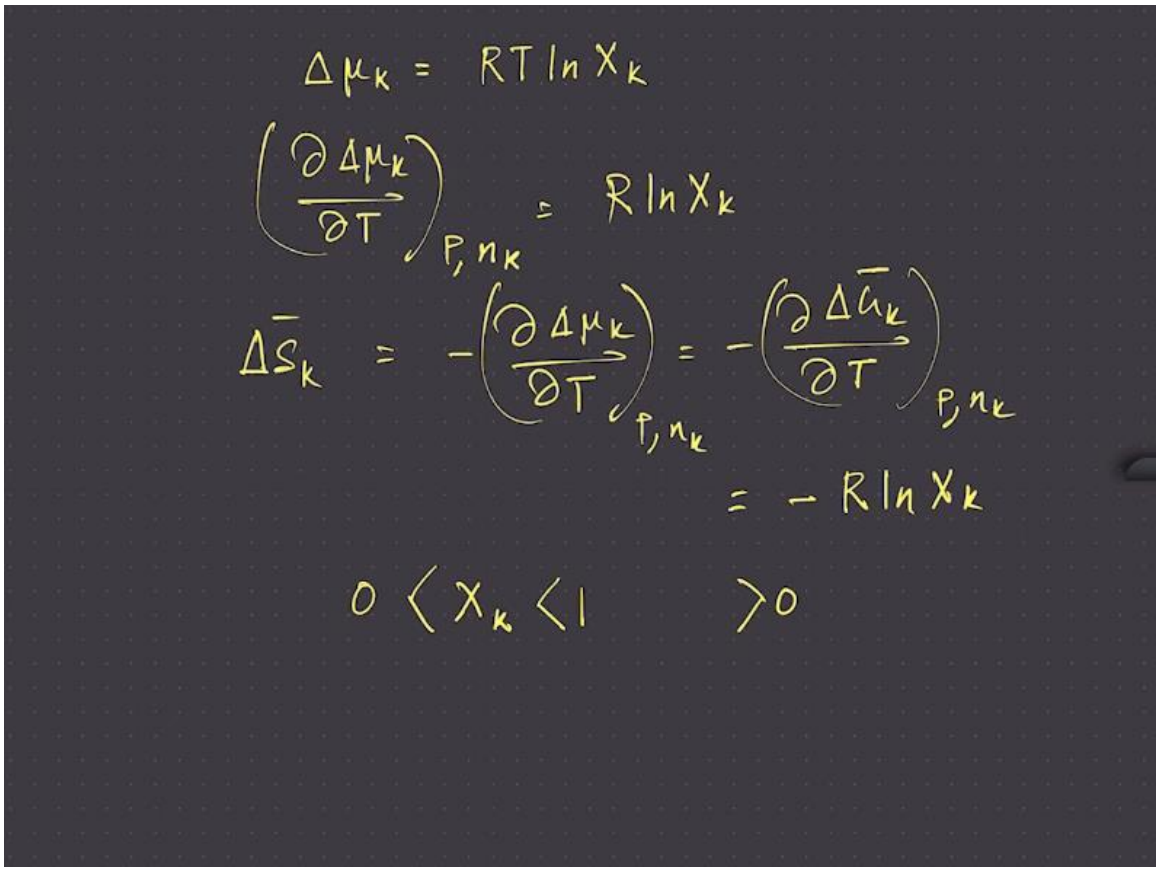
So, this is equals to v k bar d p. So, this becomes R T l n. So, if you do this what is v k bar v k bar is R T by p d p. So, R T by p. So, integral R T by p d p you can take R T out and then because d p by p which is basically R T integral d p by p.

So, this becomes R T l n p because p is fixed isothermal. So, if I do that. So, this is R T l n p plus some integration constant right some integration constant k 1 or k i. Now this R T l n p, but you do not require this integration constant if you have the limits right. So, p when mu k 0 was there when mu k 0 was there that is in the pure state you had the pressure right that was the correspondence when it is mu k now in the mixture your pressure is p k right.



So, p k is the partial pressure of component so this becomes R T l n p k by p right. So, mu k minus mu k 0 becomes R T l n p k by p. Now p k is x k p. So, delta mu k which is mu k minus mu k 0 or which is equal to delta g k bar which is relative partial molar free energy or this is relative change in chemical potential you can call it due to mixing of component k due to mixing which is mu k minus mu k 0 which is equal to delta g k bar is nothing, but R T l n x k because p k by p p k by this implies p k by p equal to x k mole fraction of component k. So, delta mu k which is delta g k bar is R T l n x k.

Now you see del mu k del delta mu k del t at p n k is nothing, but del delta g k bar del t right that is this one right. So, same thing which is now it is like del R T l n x k del t. So, basically if that is so this becomes R l n x k right this becomes because n k is fixed right. So, this becomes R l n x k see. So, from delta mu k I got the derivative with respect to temperature which is nothing, but R l n x k.



Now del delta mu k del p at fixed temperature n k now is nothing, but as you can see there is no p term. So, basically so with respect to p the variation in the partial molar free energy or variation the chemical the change in chemical potential due to mixing is equal to 0 right because delta g k bar is R T l n x k or delta mu k is R T l n x k. So, with respect to p if I take a partial derivative then with respect to p there is no term. So, this becomes equal to 0. So, you have these two terms and what you know delta s k bar if you look at this equation d g goes to V d b.

So, basically del g del t p equal to minus s right del g del t p equal to minus s. So, basically you can if you can write the same thing. So, or s equals to minus del g del t p. So, this means that this relation also follows delta s k bar equals to minus of the negative of the partial derivative of the relative partial molar Gibbs free energy right the negative of the partial derivative of relative of the relative partial molar Gibbs free energy with respect to temperature right. So, this relation follows right because s equals to minus del g del t right.

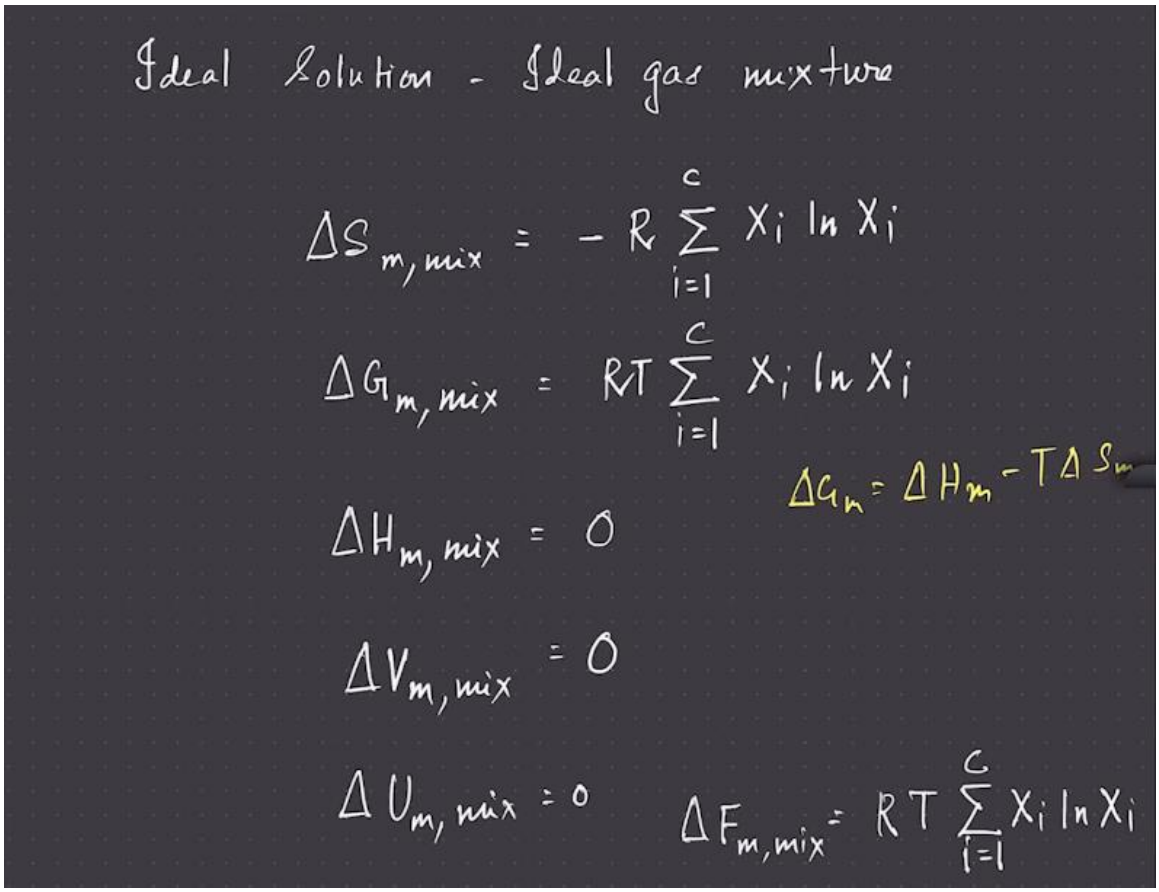
So, this is what exactly we are writing here. So, this is p and we are writing n k. Now if that is so then this becomes minus of. So, this delta g k bar and delta mu k is the same. So, this becomes equals to minus because this we know as since we know that this guy equal to R l n x k.

So, now, here this is only a negative sign that is missing. So, this is a negative sign and the same thing that is this comes in. So, this becomes minus R l n x k. Actually this becomes minus R l n x k. So, if you see this, this is actually quite interesting because see x k is mole fraction.

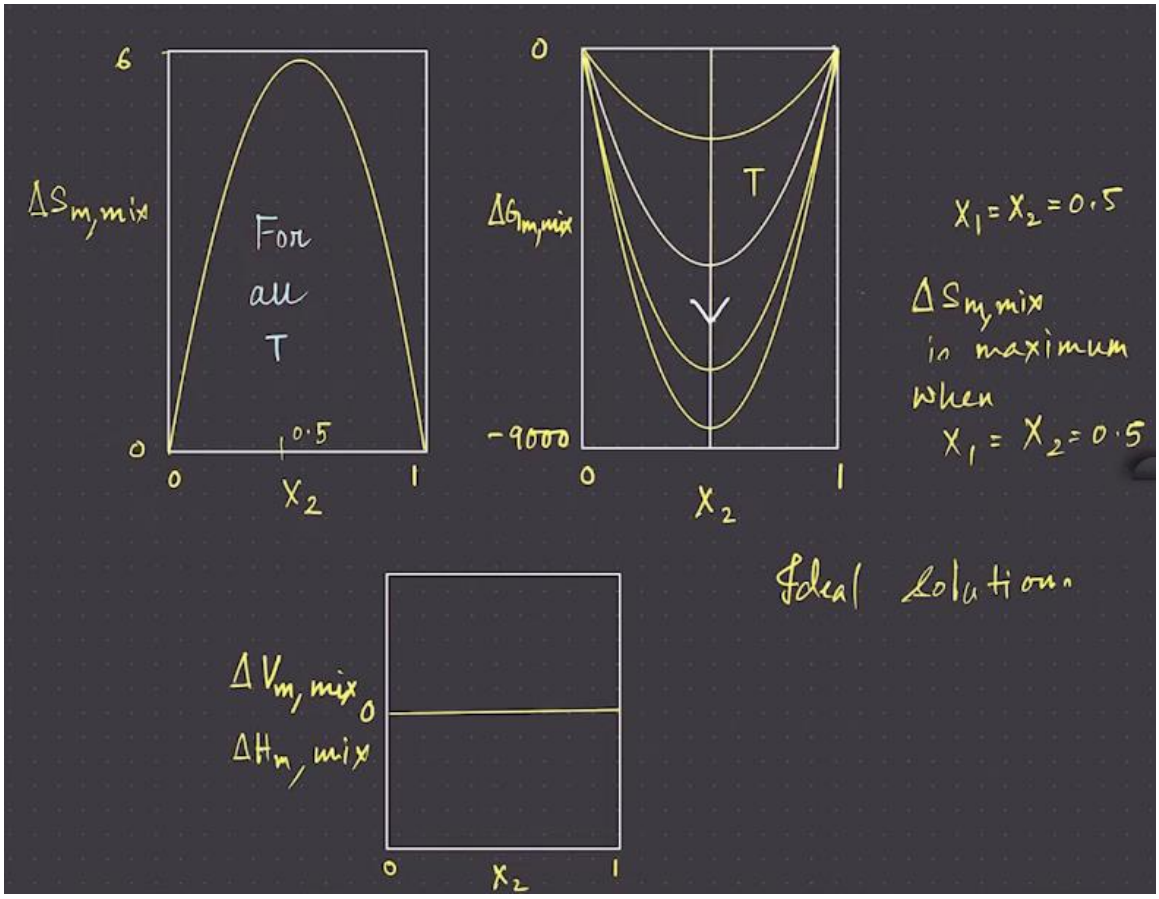
So, x k has to be. So, if you see that what did you get we got delta mu k which is R t l n x k and then del delta mu k del t at constant pressure and n k equals to R l n x k. Then delta s k bar equals to minus of del delta mu k del t right from the definition right because del delta mu k is nothing, but minus del delta g k bar right del t at constant pressure and n k which is equals to minus right because del delta mu k del t is R l n x k. So, this is minus of R l n x k. Now, see x k the maximum value can be 1. Now, if it is 1 then R l n 1 becomes delta s k becomes 0 s k bar becomes 0 right, but x k is not really 1 if you have multi component.

So, if you have multi components s k is always less than 1. So, l n x k when x k is less than 1 x k is between 0 and 1. So, basically x k is between 0 and 1 then l n x k is negative R and there is a minus sign here. So, R is positive R is positive l n x k is negative R is positive and then there is a minus sign. So, this has to be greater than 0 right.

So, this has to be greater than 0. So, this is what you can always check ok. What you are deriving does it make sense? Yes, the entropy of mixing the partial. So, the partial molar the change in partial molar entropy due to mixing the change in partial molar entropy of component k due to mixing has to be greater than 0 right has to be greater than 0 and this is what we are proving because we are getting minus R l n x k right for the this ideal gas mixture.

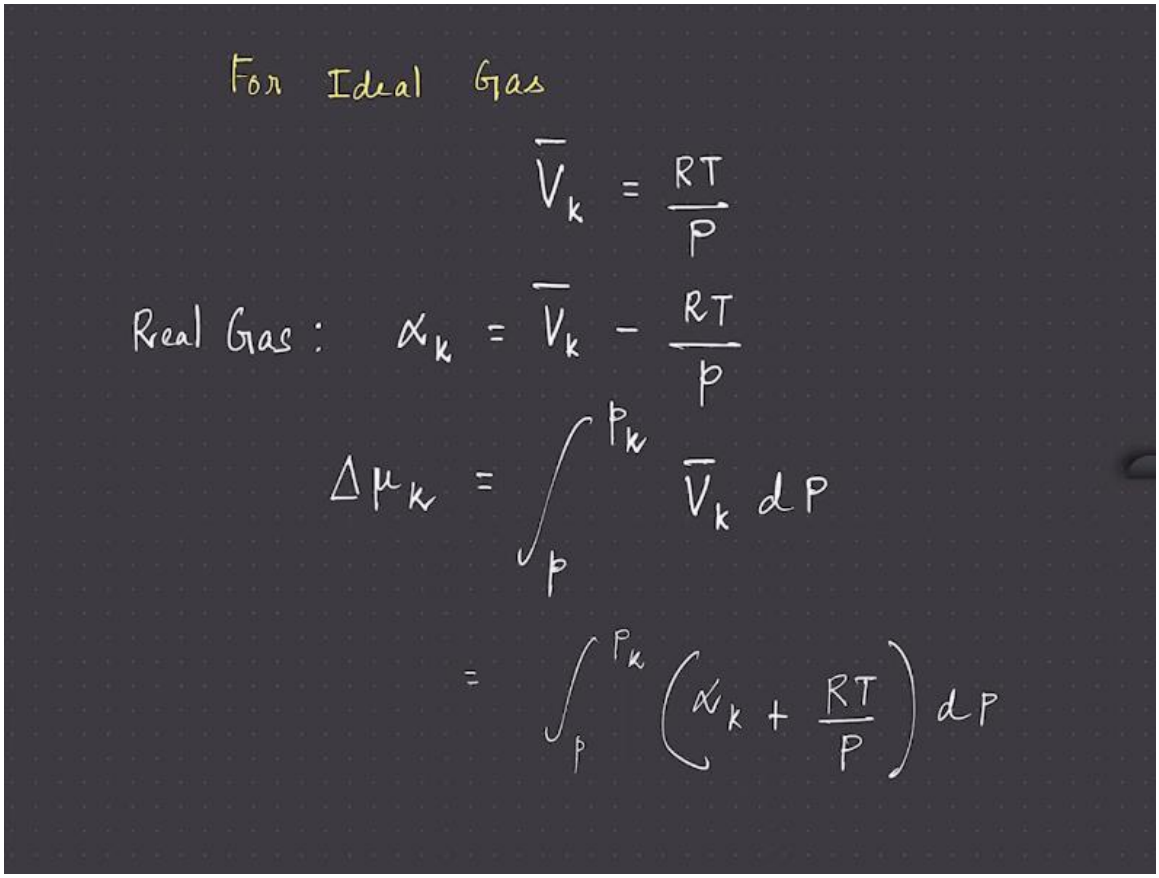


So, that is fine. Now, if you see delta v k bar which is nothing, but del of del del p right del g del p is v right. So, del delta mean k del p at t and k. So, that is what I have written here which is delta same as because delta mu k and these are the same at t and k and we have already seen that this is equal to 0. So, if you see that for ideal gas mixture the change in partial molar volume of component k due to mixing is 0 right. Now, we also know delta g k bar or delta mu k is delta h k bar which is the partial molar enthalpy delta h k bar is partial molar enthalpy of component k due to mixing and the change in partial molar enthalpy of or relative partial molar enthalpy of component k due to mixing minus t delta s k bar which is again relative partial molar entropy of component k due to mixing.

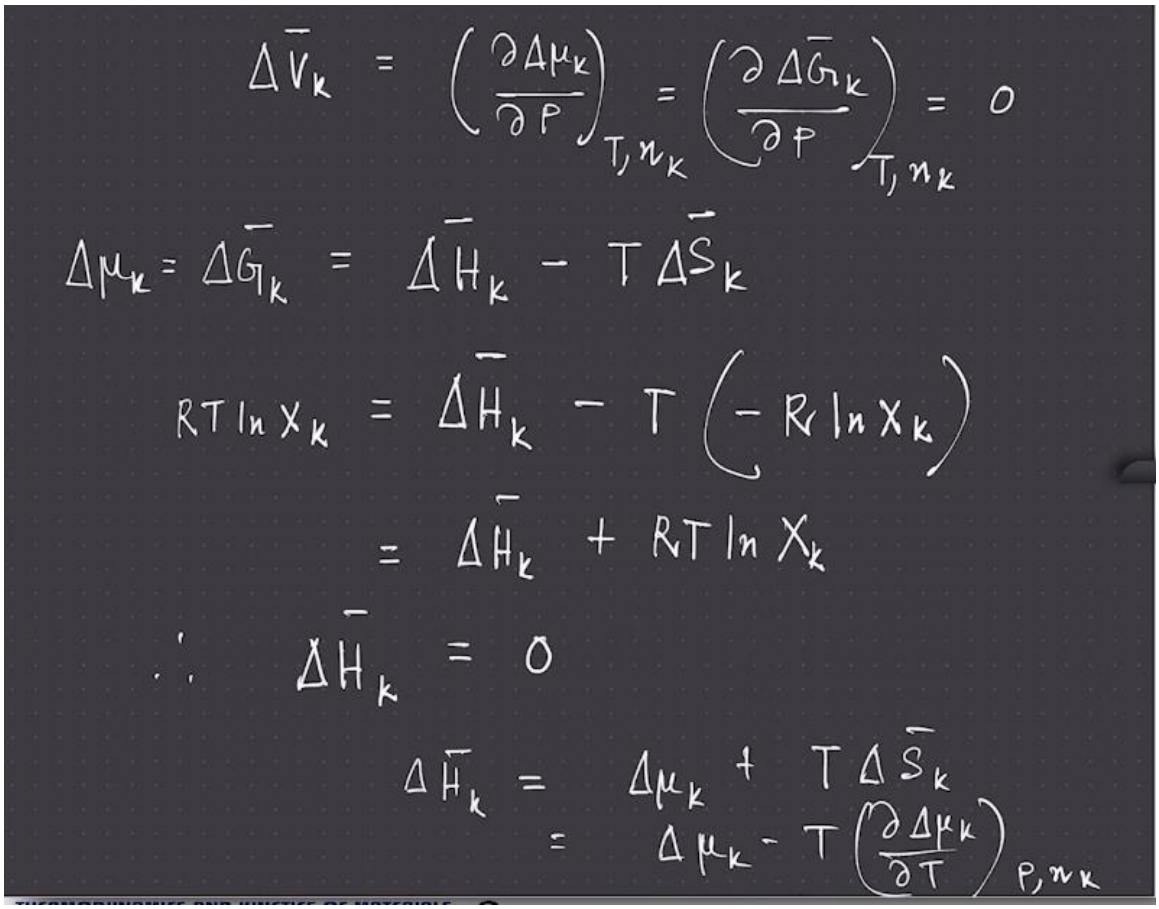


And now, you have delta g k bar which is or delta mu k which is RT ln x k right this is RT ln x k which is delta h k bar minus t minus t and this is delta s k bar is minus R ln x k right we have shown that. So, minus and minus is going plus and you have t. So, this becomes plus RT ln x k and here also RT ln x k. So, delta h k bar which is the partial the relative partial molar enthalpy or change in partial molar enthalpy of component k due to mixing is equal to 0 right. So, delta you can also prove it this way that delta h k bar is delta mu k plus t delta s k which is delta mu k minus t delta delta mu k del t you get the same expression 0.

So, delta h k bar that is the partial the change in partial molar enthalpy due to mixing is 0 right. Now, as you can see here. So, delta mu k also can be written as t del delta mu k del t is this is this possible yes because this is R ln x k. So, this becomes equals to RT ln x k. Now, you can use this term here and you will get the same relation delta h k bar is equal to 0 ok.

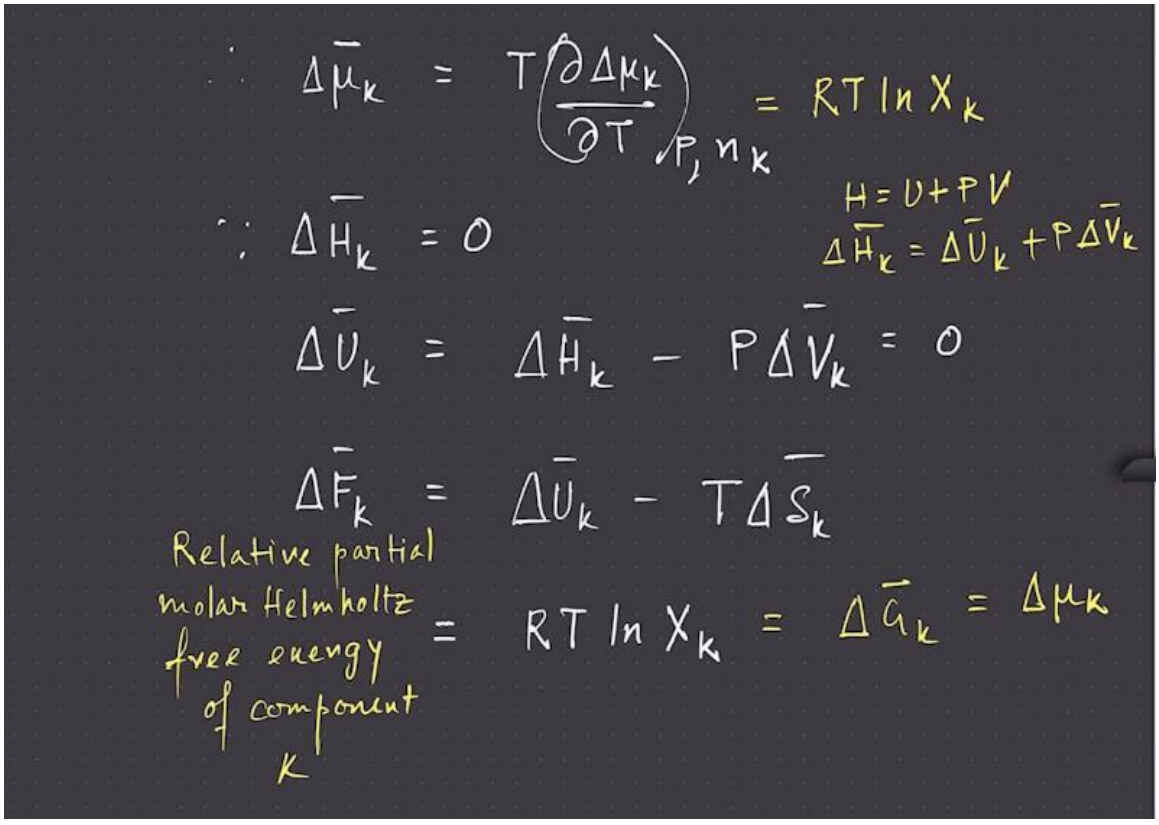


So, delta h k bar equal to 0. So, let us get back. So, let us get back I am sorry for this disturbance that has happened some applications in my computer suddenly popped up and created some issue I am really really apologizing for this. So, as you can see here what we got is delta mu k bar. So, if you look at that we started with this delta mu k or delta which is nothing, but delta g k bar which is nothing, but relative partial molar gives free energy or just free energy of component k due to mixing. Now, from delta mu k once I know delta mu k I can know del delta mu k del t at fixed p and n k and then I can know delta s k bar and that is what I got minus R ln x k and I have proved that it has to be minus R ln x k such that the delta s k bar has to be greater than 0 it is the partial molar and change in partial molar entropy due to mixing of component k.



And then delta v k bar we got 0 delta h k bar also we got 0 for the ideal gas mixture. So, now, since delta h k bar is 0 in 0. So, u k basically h equals to u plus p v u plus p v. So, you can write delta h k bar equals to delta u k bar plus p delta v k bar p is the overall pressure.

So, this becomes. So, therefore, delta u k bar delta u k bar equals to delta h k bar minus p delta v k bar which is equal to 0 right and delta f k bar that is a relative. So, this is the relative partial molar Helmholtz free energy. Helmholtz free energy of component k due to mixing which is delta u k bar which is 0 minus t delta s k bar and then delta s k bar is minus R ln x k. So, minus R ln x k into minus t because R t ln x k which is same as delta g k bar or delta.

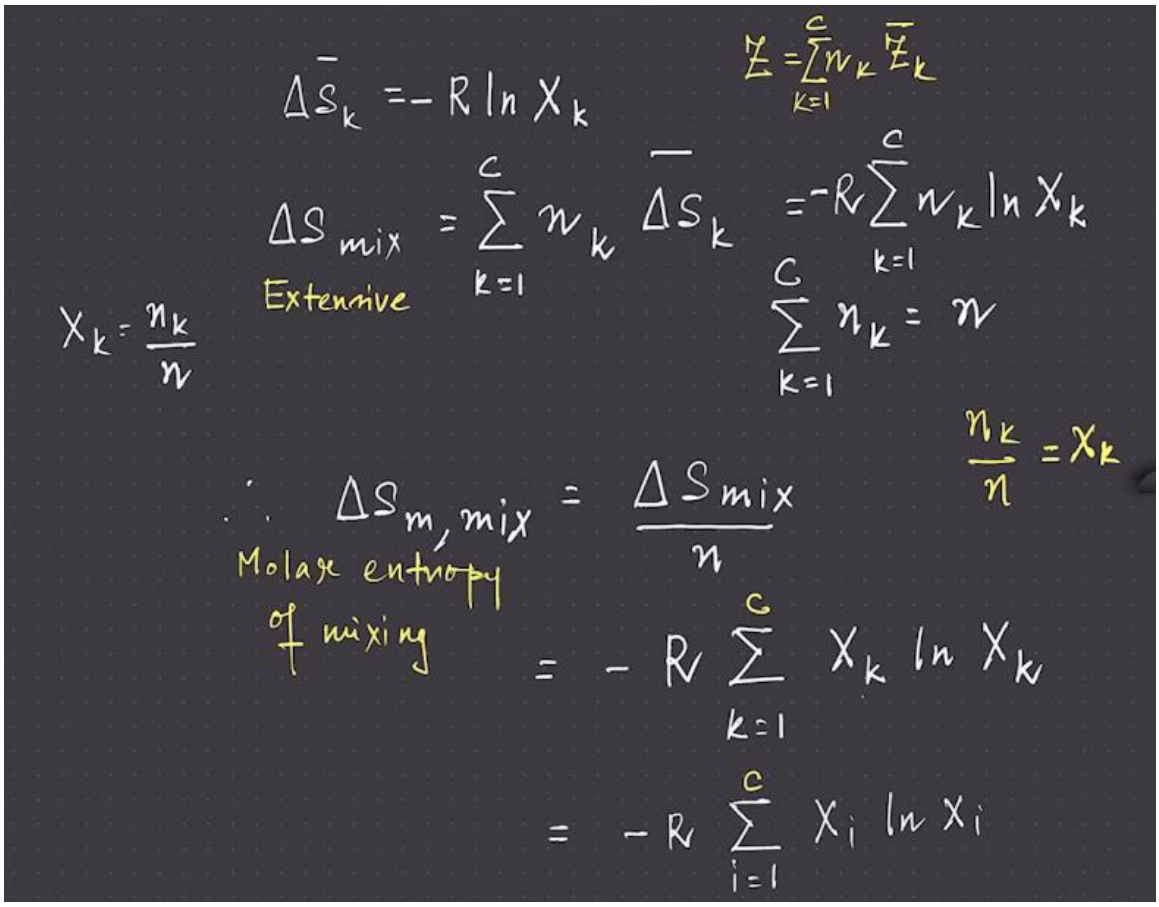


So, this is delta g k bar or delta mu k. So, the advantage of this approach is this that see it is an ideal gas mixture. So, it is like an ideal solution. So, in this ideal solution or ideal mixture where there is no interaction once you got delta mu k bar once you got delta mu k bar as R t ln x k as R t ln x k how did you get R t ln x k from the dalton's law of partial pressure right. You used the integration and you got delta mu k right which is mu k minus mu k 0 which came out to be R t ln x k you got all the other properties all the other properties that you cannot measure directly. So, you cannot measure directly delta h or delta h k bar or delta g k bar even delta v k bar measuring these in this directly is very difficult right this partial mode properties.

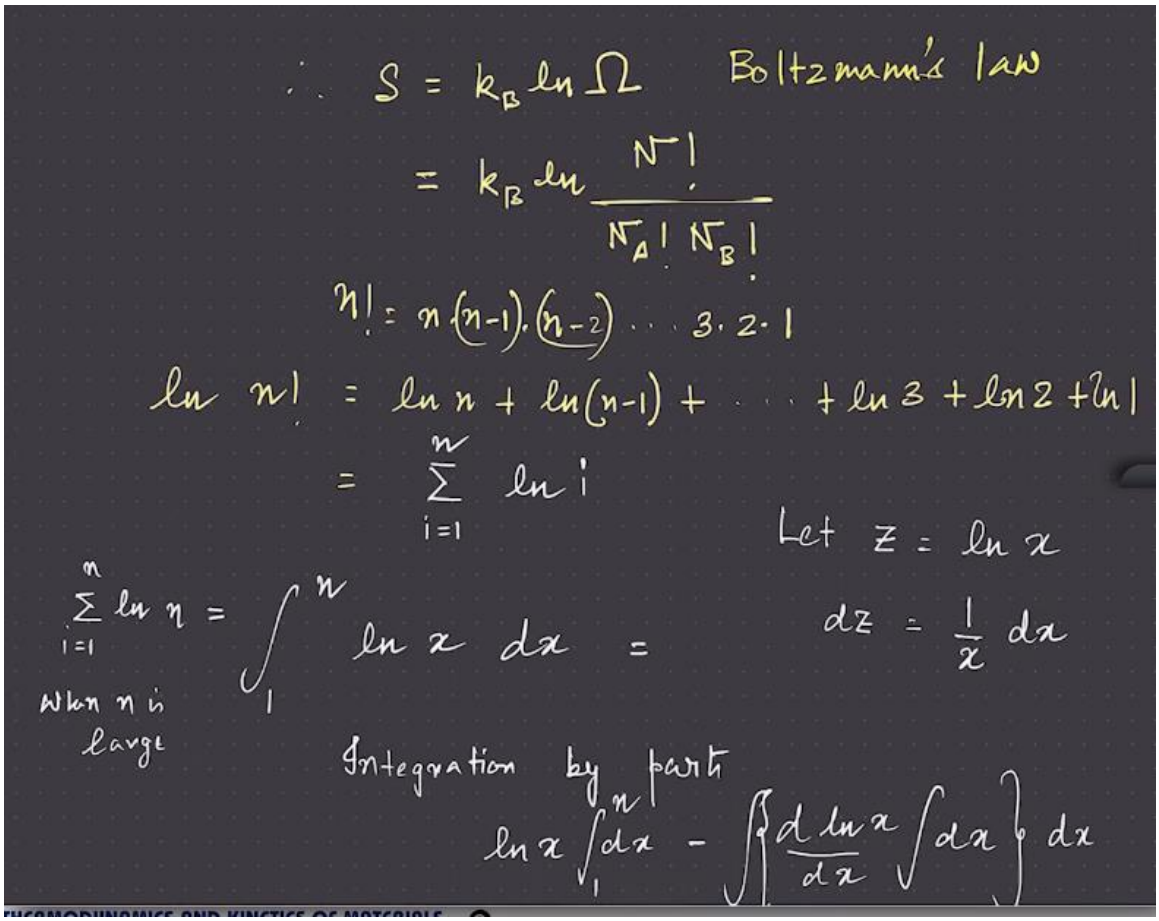
But you can estimate them once you know the change in the change in chemical potential of component k due to mixing right. Once I know that for this ideal mixture or for this ideal gas mixture or this ideal solution ok there where there is no interaction in atoms I could actually get all this indirectly measurable quantities right. So, that is the idea. So, if you now look at this it is a very interesting thing here that you get delta s k bar for this ideals mixing this ideal mixing with delta s k bar equals to minus R ln x k. Now, delta s mix is nothing, but as you know any property any property z this is extensive property z equals to n k z k bar ok.

And summation over k equals to 1 to r where r is the number of components ok small r or 1 to c you can call it 1 to c where c is the number of components. Now, if you see

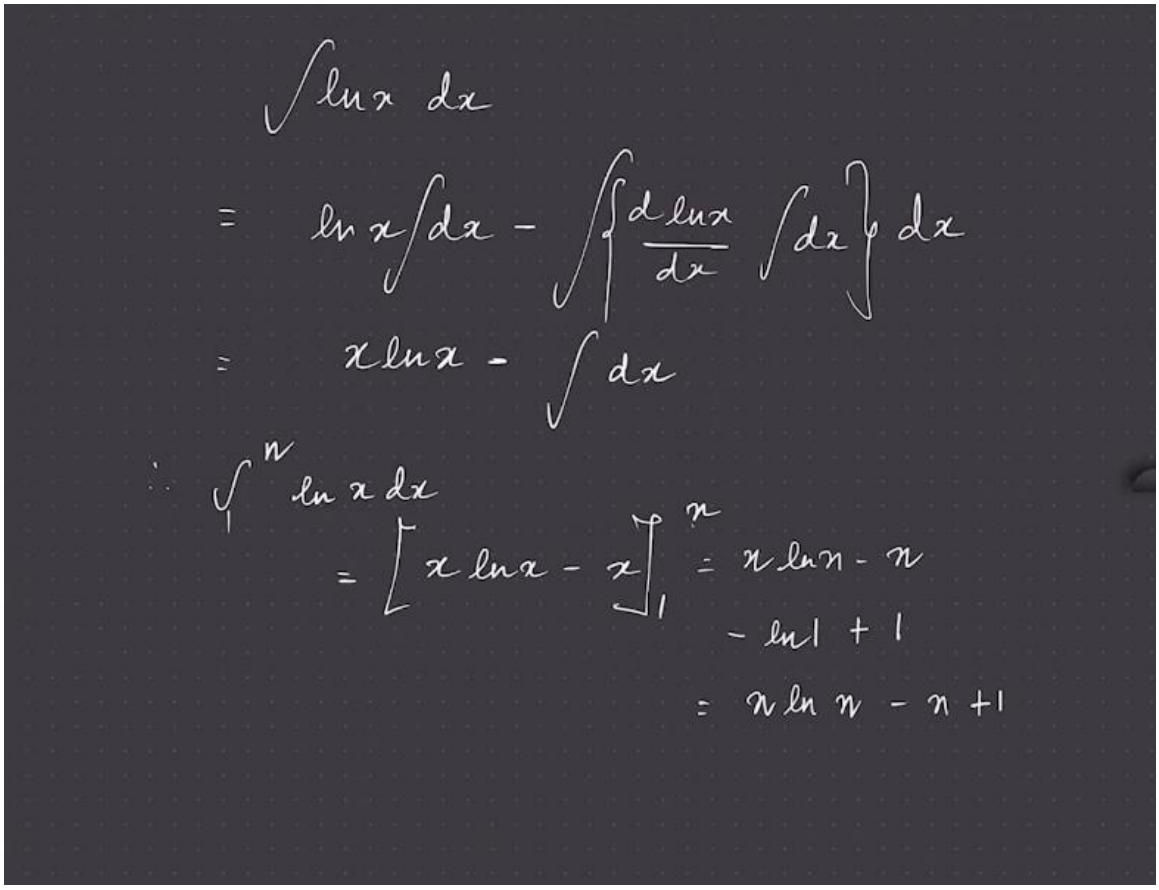
delta s mix is k equal to 1 to c n k delta s k bar right which is minus r n k ln x k. Now, n k summation n k is n right minus r n k ln x k. So, now, this is your delta s mix right this is the total change in entropy right this is the total or extensive this is an extensive parameter right delta s mix is an extensive parameter because it is the total change in entropy or and it depends on the extent of the system right that is the total mole number of the system m. Now, if I tell delta s m mix that is the molar this is the molar entropy is a molar.



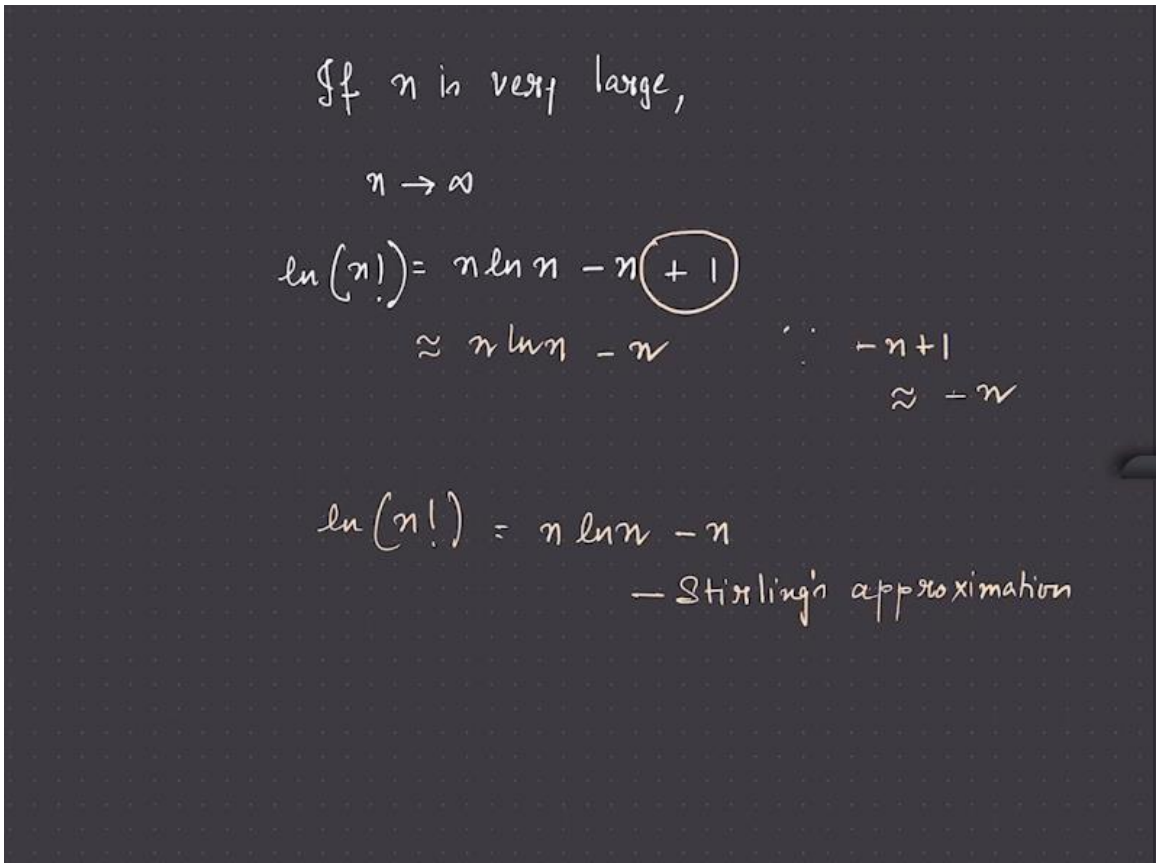
So, let us define this as molar entropy of mixing it is not partial molar right it is overall right, but it is a molar per mole entropy of mixing per mole we can also write that ok which is delta s mix that is the extensive property by n, n is the total number of moles which is basically minus r. Now, n k by n n k by n is nothing, but x k. So, you have minus r summation x k ln x k or since k is of the as you know these are repeated indices k is operating coming twice. So, repeated indices we can use any repeated index right you can make it k k or i i does not matter. So, instead of k equal to 1 to r or k equal to 1 to c let us call it c still just call it c and this there also c ok.



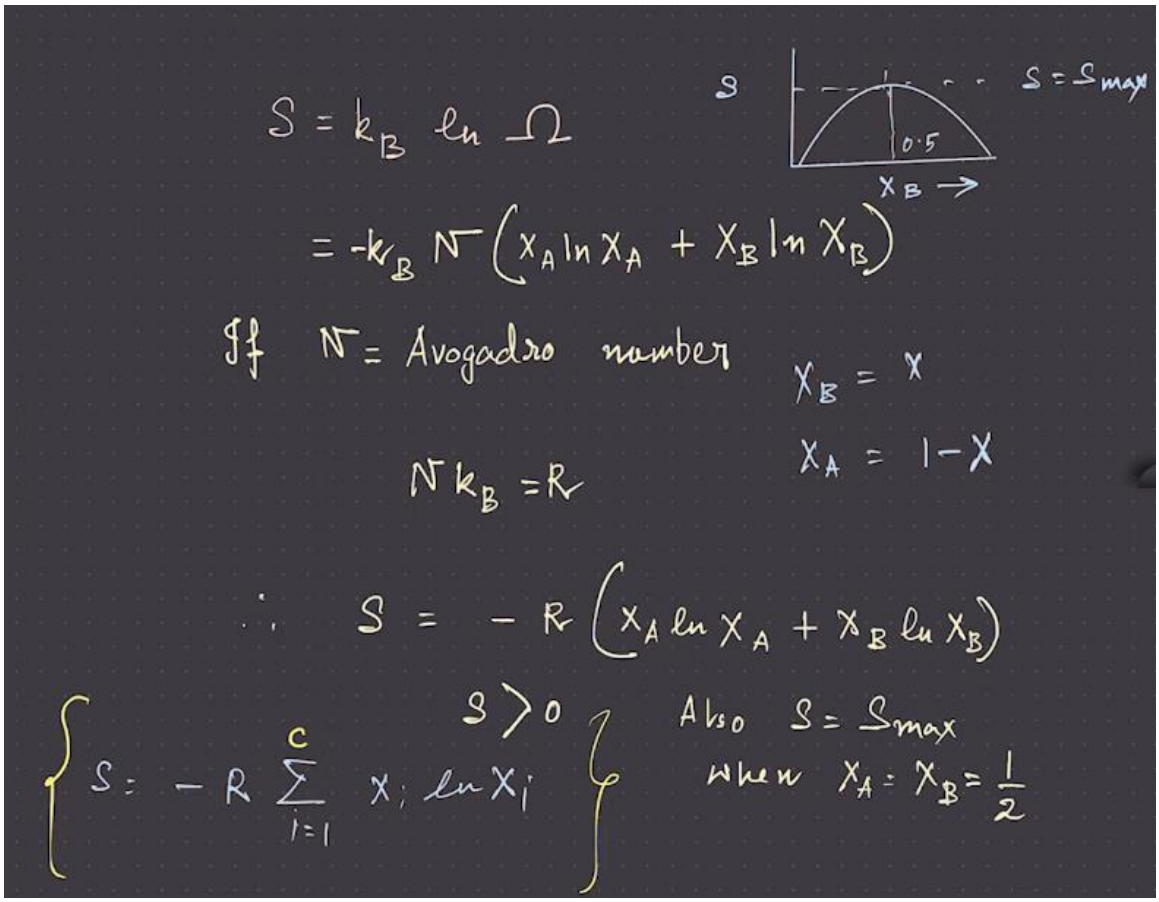
So, that you do not get confused any time. So, this is the number of c c is the number of components. So, basically you get minus r i equal to 1 to c x i ln x i. Now, if you remember when you looked at this statistical interpretation of and made a connection right use this Boltzmann's hypothesis or Boltzmann's law. One statistical mechanical interpretation of entropy and there we wrote k b ln omega, omega is the number of configurations and we looked at a binary solution k b ln n factorial by n a factorial n b factorial. Then we looked at starlings approximation I do not want to go into through this in detail I think in the lecture of week 4 or 5 I think 5 you will get all of these right.



We the statistical mechanical when we looked at the limits of statistical thermodynamics right and then we looked at the starlings approximation and then we went on doing this calculation and then we found that we got into the same random mixing or this number of configurations for this binary lie of a and b or binary solution right. So, binary solution of a and b the components gave me n k b equal to r and we got minus r x ln x a plus x b ln x b then I generalized it and it becomes a is equals to minus r i equal to 1 to k minus r. So, I can again I can write here equal to 1 to c x i ln x i. So, this what I want to say here is that this guy that we obtain here for this for mixing from molecular interpretation right. We are considering number of molecules right in any molecules of a and b molecules of b and in looking at this mole fraction of a mole fraction of b, but we are looking we start from Boltzmann's hypothesis we come to this right from the statistical mechanical version.



But you can see here you can see here that we got the same expression for this ideal gas mixture or ideal mixing where there is no interaction. If we do not consider interaction between atoms what I get is the delta H m mix is 0 right because delta H k bar is 0 therefore the sum of delta H k bar sum of delta H k bar at the overall delta H peaks has to be equal to 0 because delta H k bar for each for any component k the partial model enthalpy of due to mixing is 0 when you have no interactions between the atoms right. So, that is what we assume that it is an ideal mixing. So, ideal mixing means no interaction between the atoms each component acts as if it is occupying the entire volume right.



So, that is the idea and as for ideal mixing. So, if you look at that the entropy of mixing that the molar entropy of mixing comes out to be minus r x i ln x i and from the statistical mechanical interpretation of entropy and looking at the configuration entropy. If we look at the configuration entropy of several components right where the number of components is c we get back the same expression minus r x i ln x i right. So, you can see that there is a very nice connect here ok. So, you can see an exactly same connect here. So, basically ideal solution you get from whatever approach you want whether it is the molecular approach or whether it is or statistical mechanical approach like approach with particles using interaction, but remember in ideal solution no interaction between particles that is what we assumed here ok and we got back minus r x i ln x i and we get the same expression here.

So, this is the delta s m mix like molar entropy of mixing. Now, if you look at the molar free energy of mixing this becomes r t x i ln x i because delta h g mix is delta h m mix minus t times delta s m mix. So, therefore, there is a t and minus is there. So, minus and minus it becomes plus. So, this comes because of this because delta g m the idea is delta g m because delta h m minus t delta s m. Now, if you see that for mixing ideal mixing for ideal mixing when there is no interaction between particles this guy is 0 right as a result this is 0 and this is minus r x i ln x i and then there is a t and there is a minus sign.

So, this becomes plus r t x i ln x i. Obviously, you can see from here that at any temperature it has to be negative right. So, ideal for an ideal solution right and if you look at that delta h m mix is 0 delta v m mix is 0 delta f m mix is same as delta g m mix it is what the this is the Helmholtz free energy of mixing and if you look at the delta u m which is the internal energy of mixing again it becomes 0 because there is no interaction between the particles between the constituents. Now, delta s m mix as for all t it is independent of temperature because it is minus r x i it is basically minus r x i ln x i right minus r x i ln x i and basically it has a maximum value at 0.5 for a binary system right when x 1 equals to x 2 x 1 equals to x 2 equal to 0.

5 then delta s m mix the maximum we get the maximum. So, is maximum when x 1 equals to x 2 0.5 you can easily show that I have shown that before right and if you plot it then you can see the delta s m mix for all temperature because delta s m mix is having minus r x i ln x i it is independent of temperature. So, you can see that this has this nice curve and you see if you look at binary solution the maximum value is for x 1 equal to x 2 equal to 0.5 and that comes out to be very near 6.

If you multiply you can easily see 8.314.67 I think and you will get very close to 6 and if you look at now delta g m mix it is 0 it is negative for all temperatures right for all apart from t equal to 0 t equal to 0. Obviously, t equal to 0 kelvin this will be r t x i ln x i summation over all i s all over all components. So, if t equal to 0 then delta g m mix equal to 0 otherwise it is negative right and it goes to negative and as a function of temperature. So, temperature is increasing this way downward temperature increases downward temperature increases this way. So, this is at a lower temperature this is at a have even higher temperature higher temperature higher temperature the higher the temperature the more negativities right.

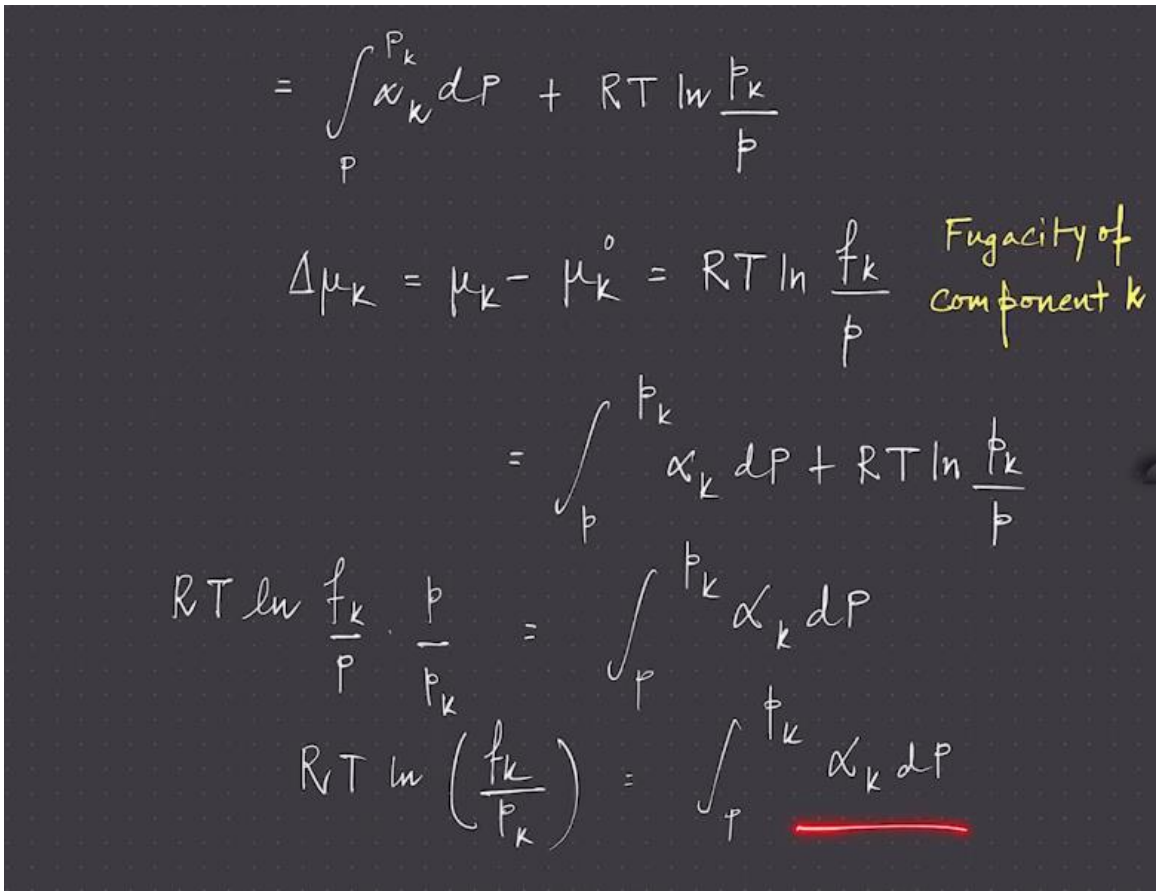
But remember delta h m mix or delta v m mix these are all 0 and if it is 0 then you can just draw it using a horizon. So, there is no variation over the entire composition range there is no variation with temperature it is all 0. So, you can draw it by using a horizontal line about the y axis value of 0 right. So, delta v m mix or delta h m mix has the same. So, if you look at delta h m mix it also has the same nature this is for ideal solutions that is solutions with no interactions between particles ok.

So, now, this is for ideal gas right v k bar equals to R T by P. Now, in real gas v k bar is not equal to R T by P it is that there is a difference which is called alpha k there is a difference alpha k which is v k bar minus R T by P. Now, if you look at delta mu k and you integrate you get v k bar d P which is nothing, but alpha k plus right because if I take this side then this is alpha k plus R T by P d P. So, this is alpha k d P from P to P k

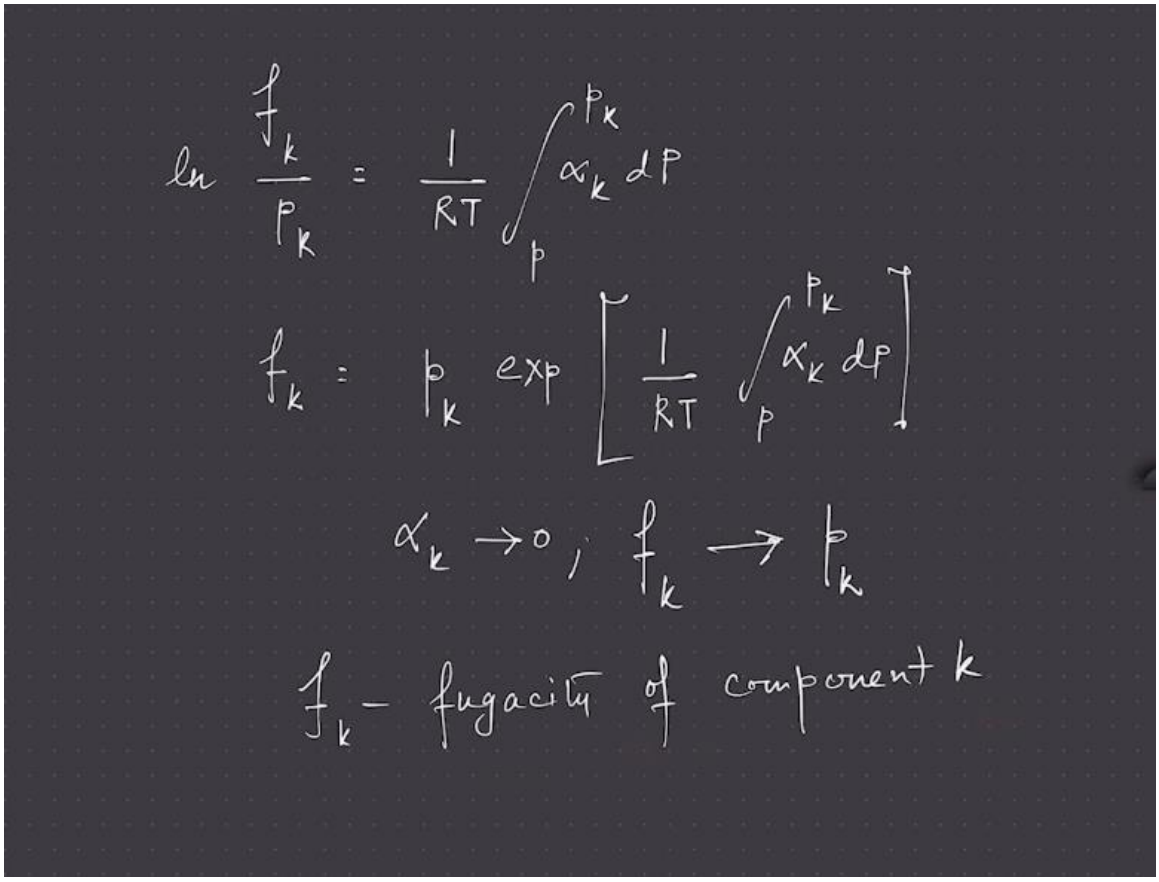
because P is for P is when P is when there is no mixing right there is no mixing right. So, P is for the pure component and P k is the partial pressure after mixing right in the real solution. So, delta mu k comes out to mu k minus mu k naught which is equals to we can write R T ln f k by P where f k is the fugacity we call it fugacity of component k ok.

So, this is called fugacity of component k ok. So, now you have P to P k alpha k d P plus R T ln P k by P. So, which is R T ln f k by P into P by P k which is basically. So, if you just do a little bit of algebraic manipulation if you do a little bit of algebraic manipulation you get this term you get this term which is R T ln f k by P k equals to P to P k alpha k d P. Now ln f k by P k that means basically comes equal to. So, if you have this delta mu k you have this term and you have R T ln P k by P.

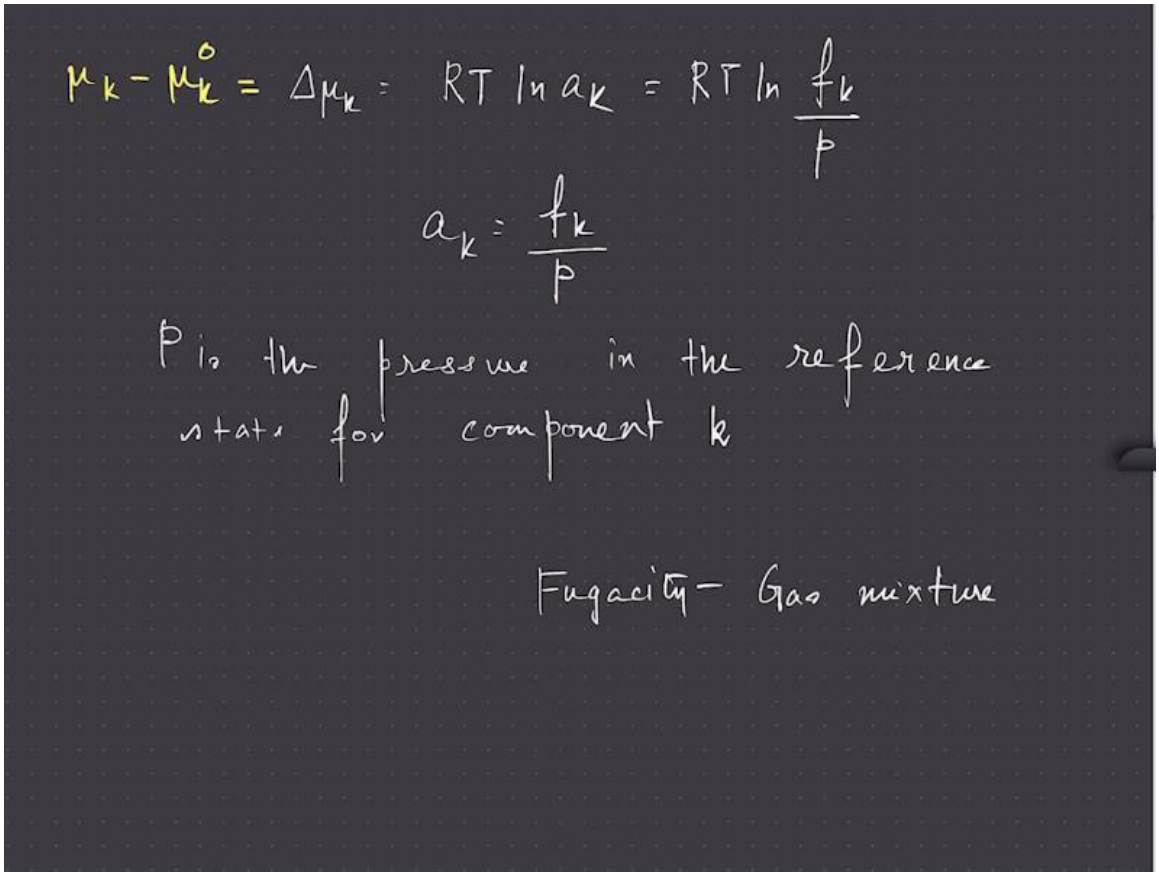
Now you are telling that this guy is the same as this guy and that is why you can write this term ok. You can do a little bit of algebraic manipulation to show. So, basically R T ln f k by P is this integral plus R T ln P k by P now I am taking it on the other side. So, it becomes R T ln f k by P minus R T ln P k by P which is R T ln f k by P into P by P k which becomes R T ln f k by P k right which is equal to integral alpha k d P. Now, if you see ln f k by P k equals to 1 by R T integral alpha k d P from P P again is for the no mixing case right and P k is becomes the partial pressure after mixing this is P is before mixing right total pressure right when each component has a pressure of P right.



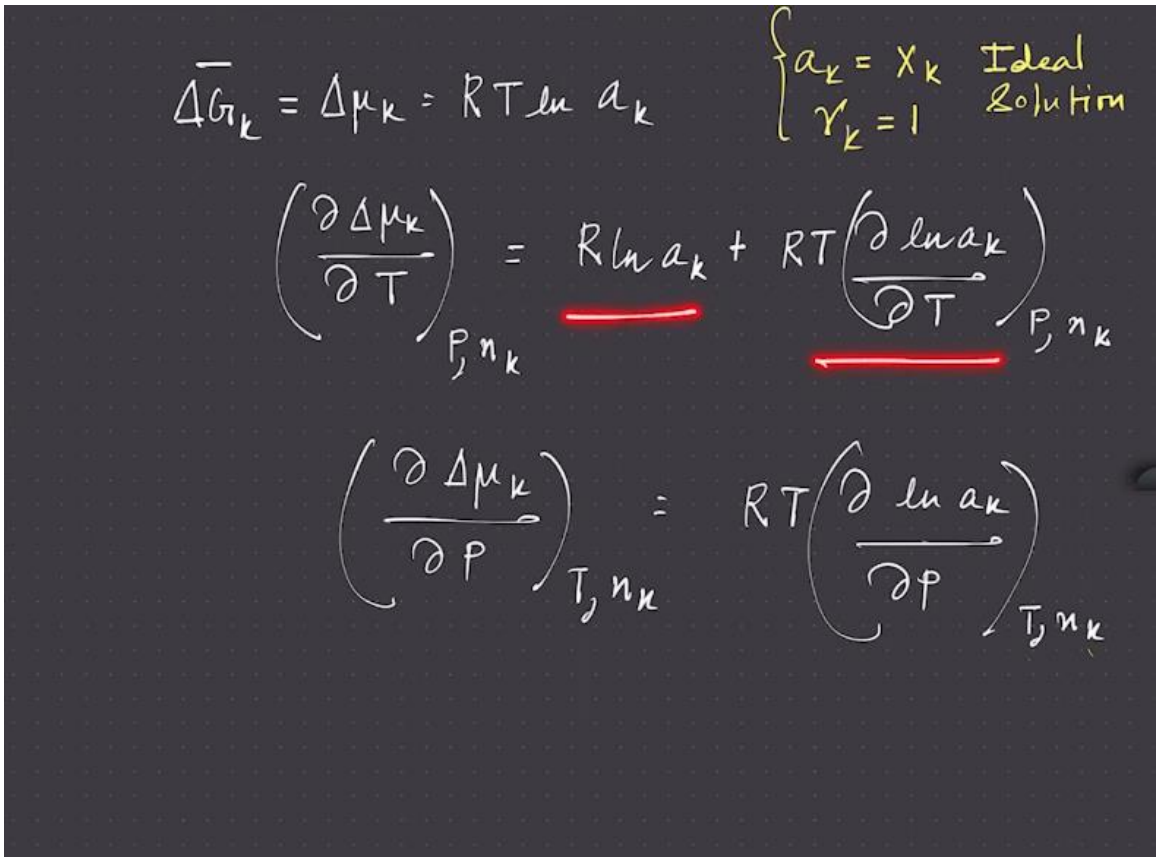
So, because this is before mixing and this is each component now exerts a partial pressure P ok. Now, f k now becomes P k times exponential 1 by R T P to P k alpha k d P. Now, alpha k tends to 0 when alpha k tends to 0 say for example, when real solution behaves ideally then alpha k tends to 0 if that is so if alpha k tends to 0 then this term tends to 0 and so overall x P to the power 0 is 1. So, f k tends to P k right f k the fugacity tends to the fugacity of component k now basically becomes equal to the partial pressure of component k right.



So, f k is as I told you is a fugacity of component k. Now, as I as you know from the definition of activity of component k that delta mu k which is mu k minus mu k 0 mu k minus mu k 0 equals to delta mu k which is RTLN a k which is RTLN f k by P right and therefore, the relation between activity and fugacity is given by a k equals to f k by P right. Now, P is the pressure in the reference state right for component k right that is the that is the pressure all components will have right will experience. So, that is the pressure in the reference state right when there is no mixing now a k equals to f k by P right and fugacity is generally remember activities are more generalized term right activity for any type of solution we can use, but fugacity is specially for gas mixture because we bring in pressure here in the definition right. So, as I told you delta mu k is RTLN a k and you know that del now if I do for this generalized form this is a generalized solution right we are not approximating any ideality we are not approximating anything. So, we are telling a k we deal with a k we tell gamma k is not equal to 1 right in the ideal case a k equals to x k is not it.

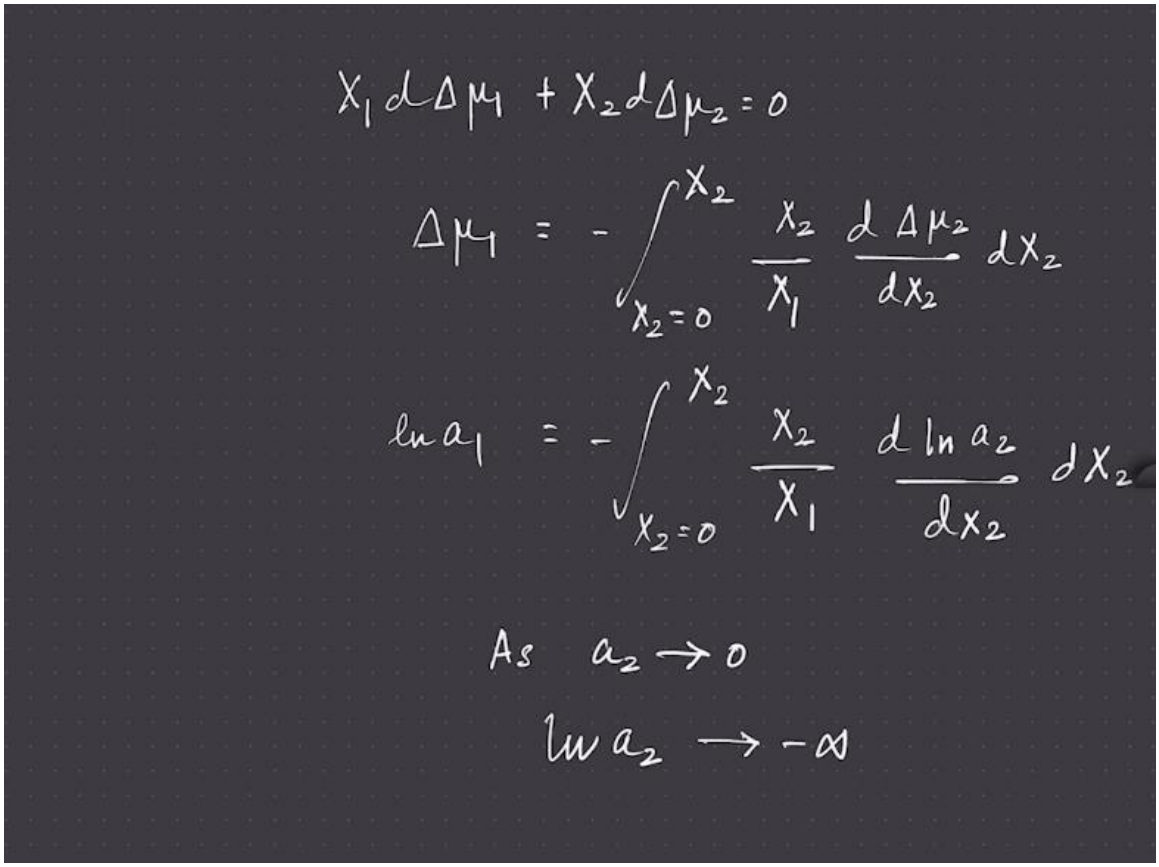


So, a k equals to x k that means gamma k that is the activity coefficient is equal to 1 correct that is the ideal case this is the ideal case ideal solution. But in general you have del delta mu k del t which is RLN a k plus RT del LN a k del t and or you can write this way because delta mu k del t right this is RLN a k plus RT del LN a k del t because I do not know how a k changes with temperature right. So, I am del delta mu k del p is RT del LN a k del p at t and k. So, fixed is t and k. So, these terms are additional terms that you are seeing right this becomes equal to 0 right this becomes equal to 0 and here it becomes RLN x because a equals to x.

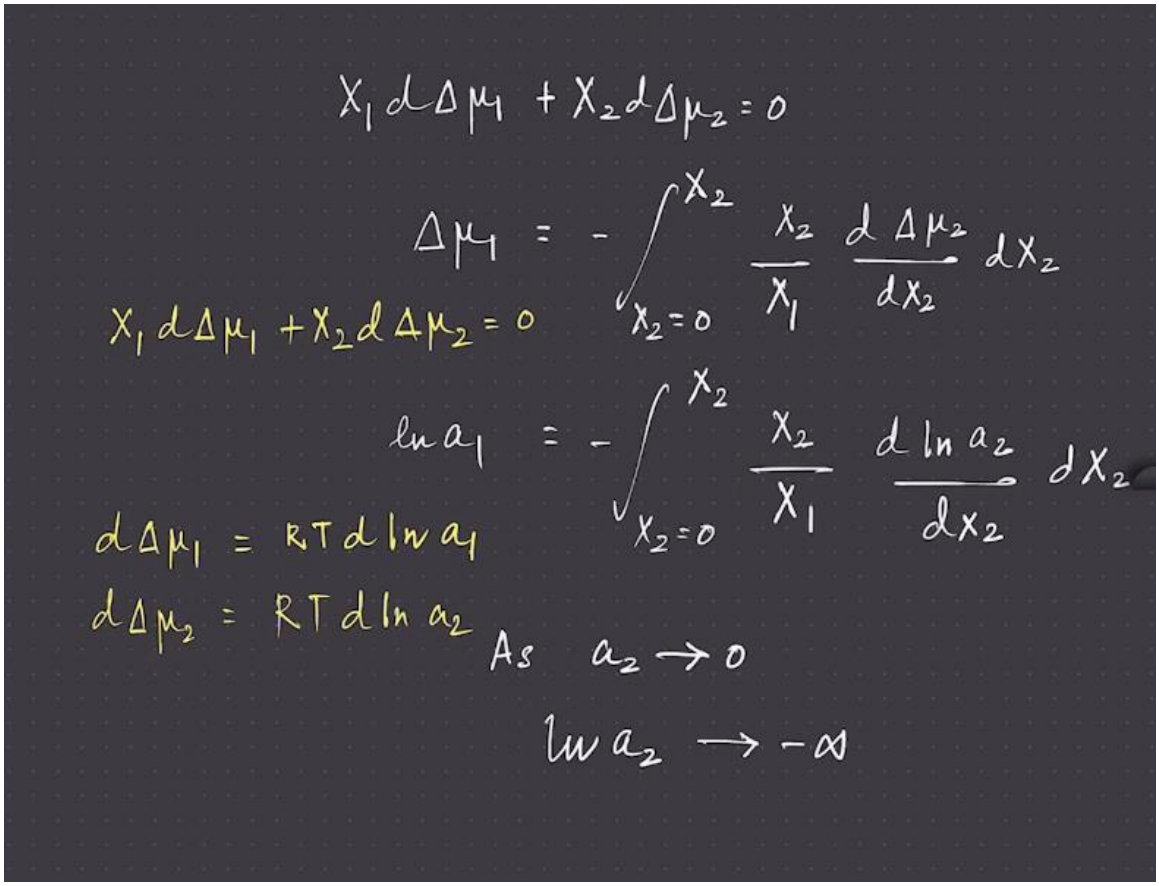


So, it becomes RLN x k right in general. So, del mu delta mu k del t because RLN x k when it is an ideal solution, but now it is RLN a k plus RT times this term. So, this term becomes very very important this term becomes important this term also becomes important. Now you have again if you know activity of one component you can get the activity of other component how again using the Gist-Wen integration that we have done previously in the in the seventh week. So, you have x 1 d delta mu 1 plus x 2 d delta mu 2 equal to 0. Now delta mu 1 if I do which is equals to minus of right delta mu 1 is if I do it is minus of because d delta mu 1 equals to x 2 by x 1 minus of x 2 by x 1 d delta mu 2.

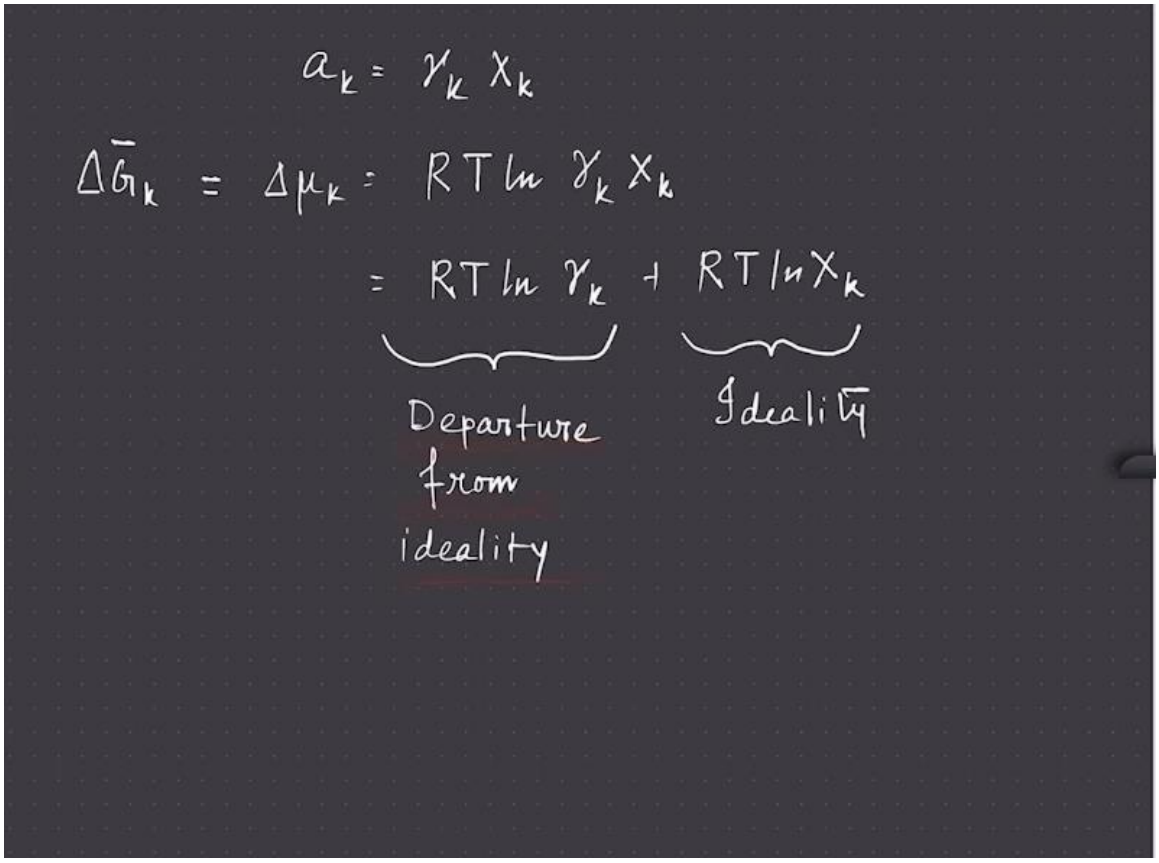
Now d delta mu 2 dx 2 if I do. So, d delta mu 2 dx 2 if I do you get because this is delta mu 1. So, and so this becomes x 2 equal to 0 right x 2 equal to 0 is the pure component right x 2 equal to 0 means is pure x 1 right. So, basically there x 1 equal to 1 x 2 equal to 0 means x 1 equal to 1 right to x 2 x 2 is where you have some contribution of component 2 right which is and then there is x 2 by x 1 d delta mu 2.



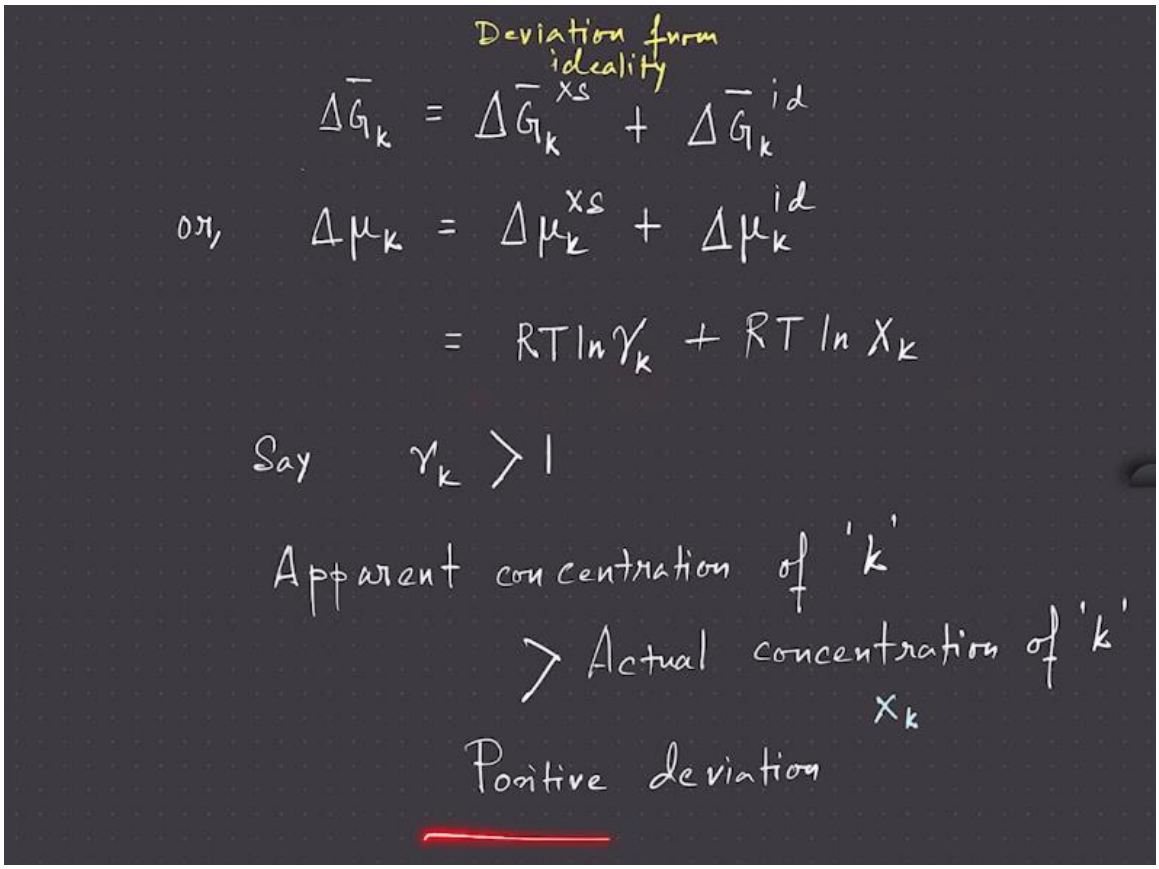
So, this becomes d delta mu 2 dx 2 dx 2 right. So, this is dx 2. So, dx 2 I am taking the limit. So, basically if I take dx 2 here the limit is this x 2 equal to 0 which is the pure solvent or pure component 1 and to some value x 2 ok that is added. So, if you have that delta mu 1 is nothing, but so if I look at this you have delta mu 1. So, if you see delta mu k equals to RT ln a k right.



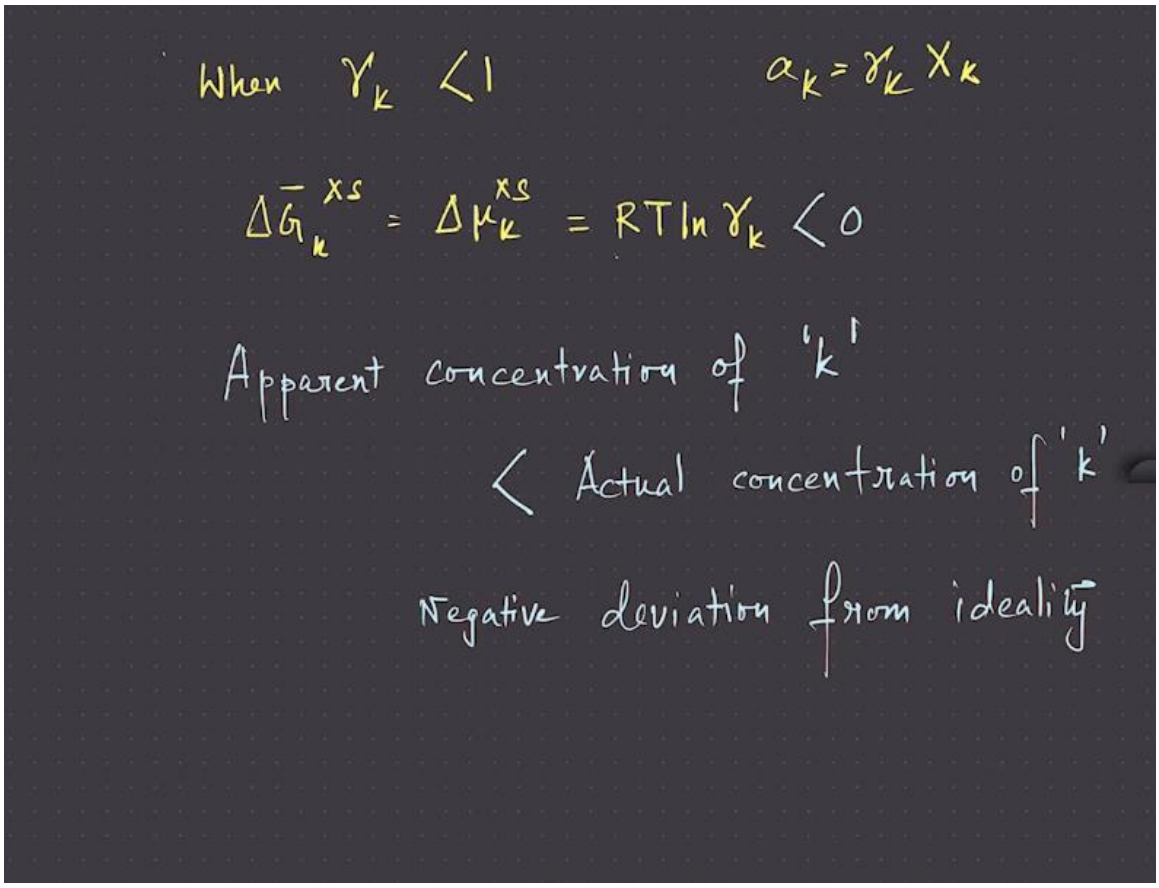
So, delta mu 1 is so there should be an so if you look at that delta mu 1. So, if you look at that you have x 1 d delta mu 1 plus x 2 d delta mu 2 equal to 0 and d delta mu 1 equals to see if you look at this d delta mu 1 is RT d ln a 1 right and d delta mu 2 equals to RT d ln a 2. Now if you do this so you have x 1 RT d ln a 1 x 2 RT d ln a 2 R equal to 0 RT cannot be 0 because t is not equal to 0. So, RT you can remove. So, what you get back is the same integration.



So, you have get here ln a 1 and you get x 2 to x 1 d ln a 2 d x 2. So, if I know the activity of 2 I basically can get the activity of 1 right and again x 2 goes from x 2 equal to 0 that is the pure x 1 means pure 1 your component 1 to the mixture composition which is the x 2 ok. So, as a 2 tends to 0 say for example, as a 2 tends to 0 ln a 2. So, ln a 2 will tend to see if a 2 tends to 0 then ln a 2 will tend to minus infinity correct. Now as you know that a k goes to gamma k x k and delta g k bar equals to RT ln gamma k x k. Now you have RT ln x k right you already know delta g k bar equals to RT ln x k for ideal solution.



So, RT ln gamma k denotes the departure from identity right because RT ln x k is already for the ideal solution delta g k bar equals to RT ln x k you have defined for ideal solution where there is no interaction in particles. So, this RT ln gamma k is the defines the departure from identity right. Though now you can define this as 2 parts one is the ideal contribution and another is the excess over ideal right which is like the deviation from idealities. So, this is called delta g k bar excess which basically I call it as deviation from ideality ok.



So, basically you can write this also as the same way. So, instead of delta g k bar I am using here delta mu k if I use delta mu k there is a delta mu k excess which is deviation from identity and then there is a delta mu k accesses with the ideal or ideal solution. And delta mu k is nothing, but there RT ln x k right this one is this and this is RT ln gamma k, but I do not know gamma k. Now if I tell gamma k is greater than 1 now if you look at that if gamma k is greater than 1 then this is a positive contribution right if it is a RT ln gamma k is positive right. So, basically we can tell the apparent concentration of component k the apparent concentration of component k is greater than the actual concentration of component k that is x k right.

Apparent concentration has to be greater than. So, if gamma k is greater than 1 the apparent concentration of component k that is say you can think of a k which is gamma k x k and gamma k is greater than 1. So, obviously apparent concentration of component k is greater than the actual concentration of component k and that gives a positive deviation. So, gamma k greater than 1 basically gives a positive deviation from identity and gamma k less than 1. Now if you see delta g k bar excess which delta mu k excess or delta mu k excess is basically RT ln gamma k.

Now gamma k is less than 1. So, RT ln gamma k is less than 0. So, that this part becomes negative. So, the apparent concentration of k is less than the actual

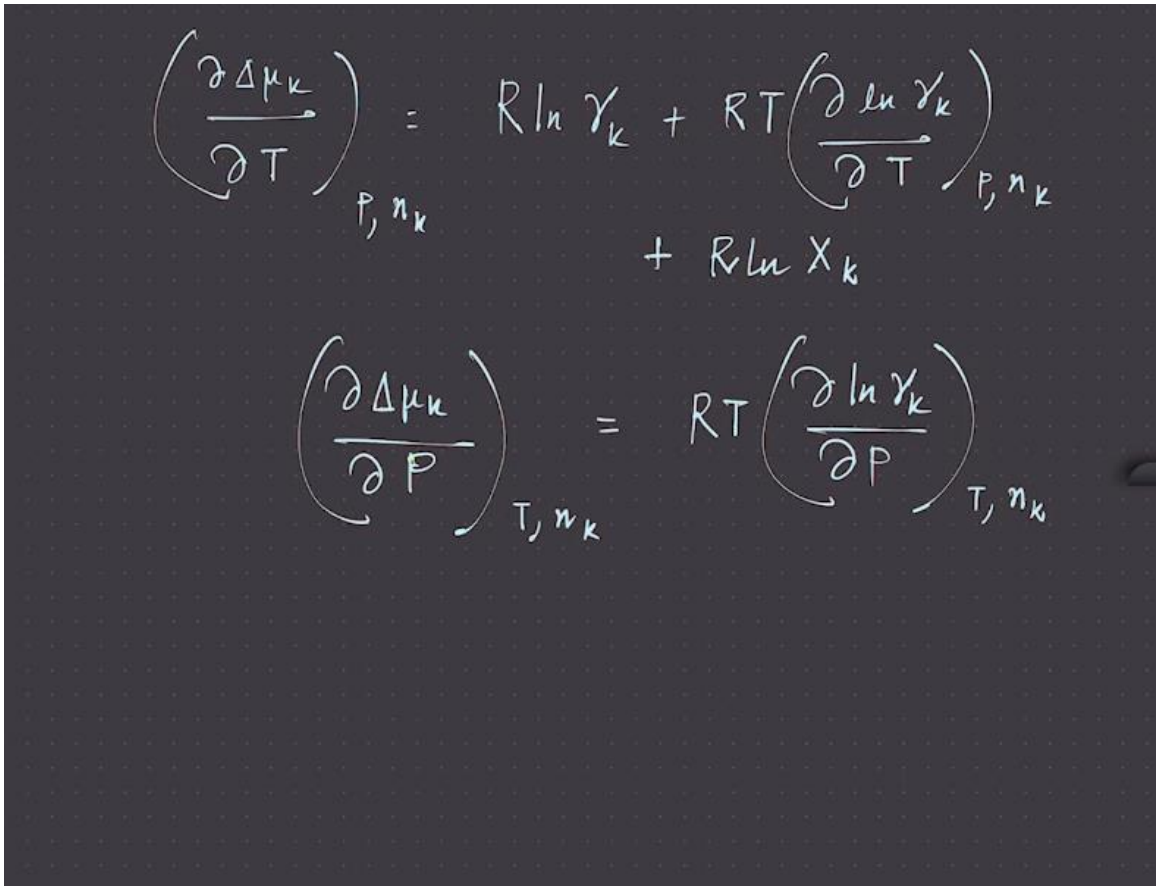
concentration of k correct because right if you have this. So, gamma k is less than 0 sorry gamma k is less than 1 remember gamma k is less than 1.

So, RT ln gamma k. So, ln RT ln gamma k is less than 0 or it becomes negative. So, RT ln gamma k is negative. So, it adds to the total delta g which is delta g k bar total which is delta g k bar excess plus delta g k bar ideal which is RT ln x k right. So, RT ln x k and there is a negative term. So, it comes out. So, basically what does it means the gamma k x k or the apparent concentration a k is ultimately gamma k times x k right.

Now gamma k is less than 1. So, a k basically now that you can immediately see the apparent concentration of k now is less than the actual concentration of k. So, basically you have a component k in the solution if there is a deviation from ideality that means there is a positive or negative gamma k when it is a not positive or negative you have a gamma k which can be greater than 1 or less than 1. If you have a gamma k less than 1 then then ln gamma k is less than 0 right ln gamma k is less than 0 RT ln gamma k is less than 0 because r is positive right r is positive T is positive. So, ln gamma k is less than 0 means gamma n has to be less than 1 gamma k does not have to be negative gamma k is not negative gamma k is less than 1.

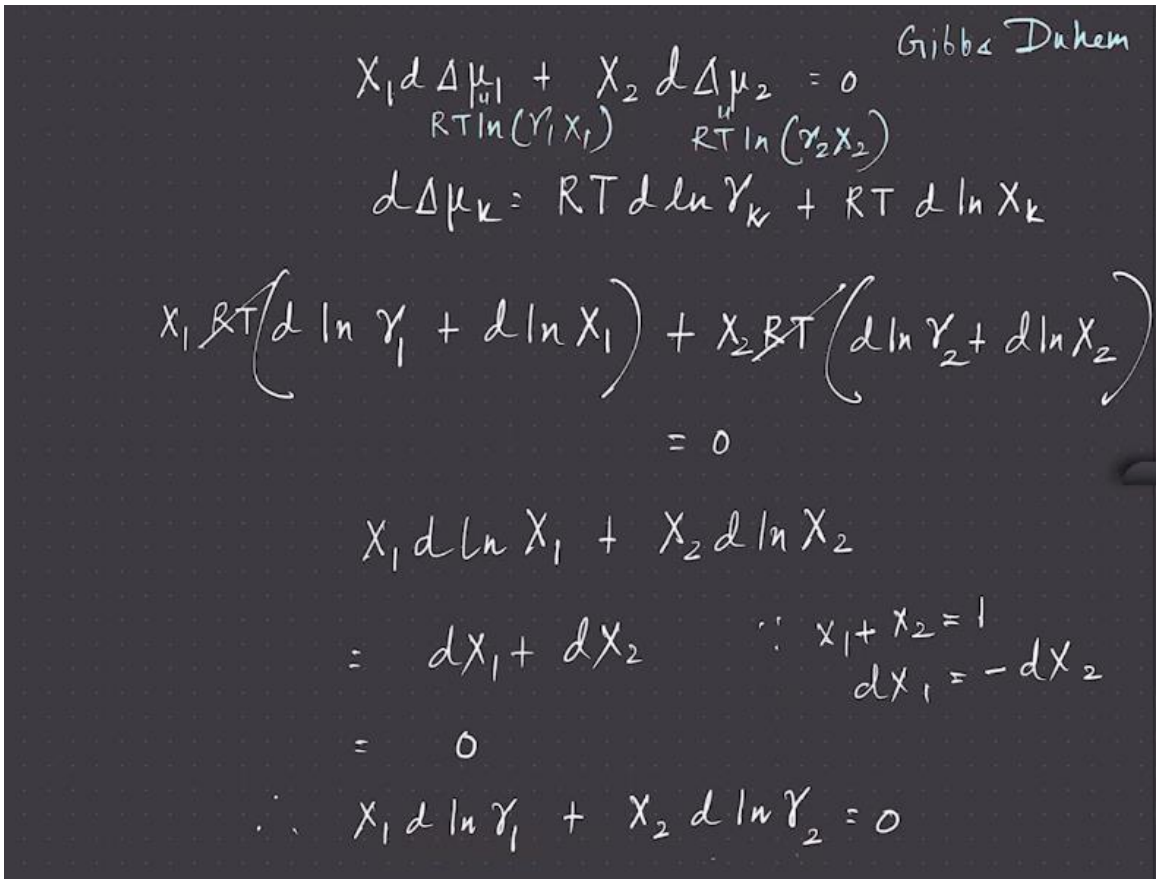
So, gamma k is less than 1. So, a k equals to say 0.9 x k. So, that means, the apparent concentration or the activity of component k in the solution is less than the actual concentration of k which is x k. So, that gives me negative deviation from identity ok. So, identity means a k equals to x k if a k equals to 0.9 x k then it is a or gamma k can be some expression which is a function of temperature composition pressure right.

So, we will come to that we will come to this different real solutions ok. So, what I am trying to say here is that depending on the value of the coefficient because remember this RT ln gamma k is what gives you that this is the excess part RT ln gamma k. Now, if gamma k is greater than 1 this is positive. So, there is a positive deviation from ideality. So, this is your ideality and there is a if this is positive RT ln gamma k is greater than 0 if it is greater than 0 then this adds to this.



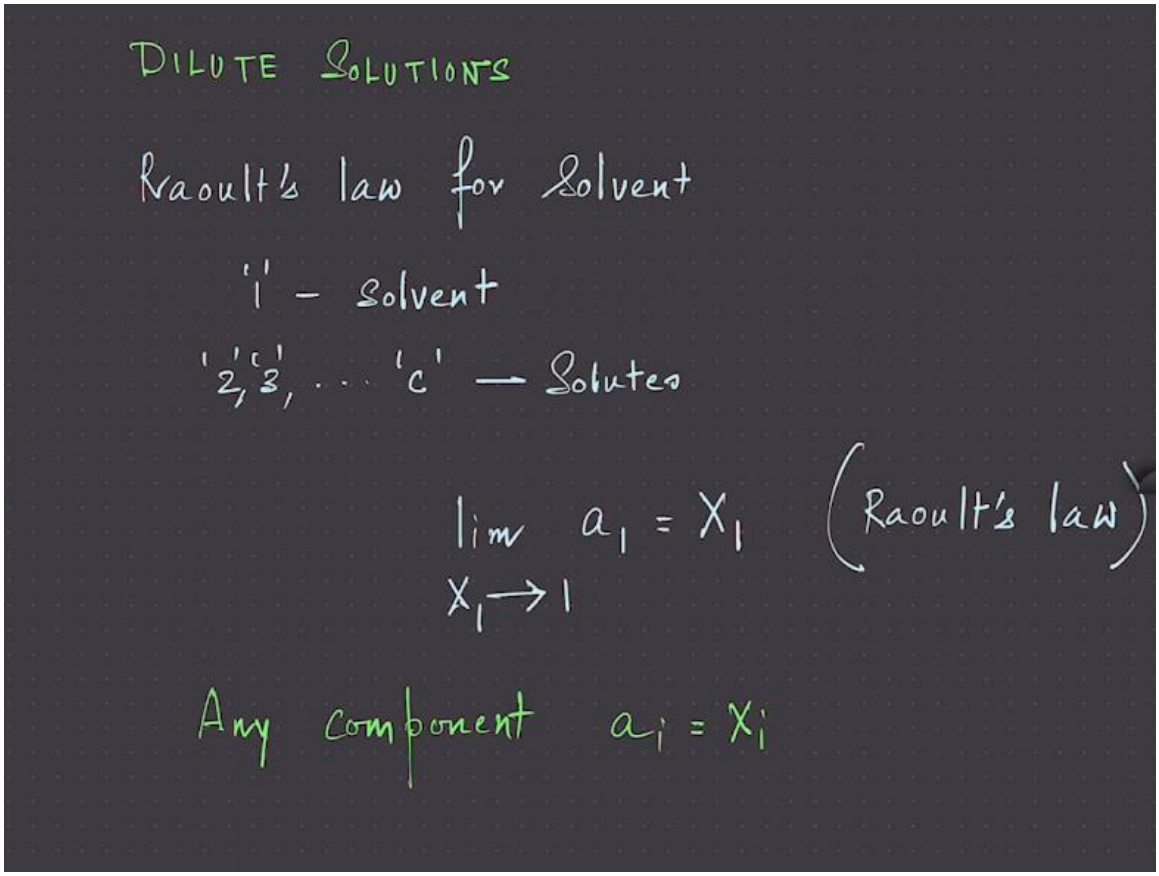
So, delta mu k for the real solution has a positive deviation from ideality ok. There is a positive deviation from ideality and here it is a negative when gamma k is less than 1 then you have a negative deviation from ideality ok. So, now, you can write down this there is this R ln gamma k you can have this ln ln gamma k del T right because now see gamma k can be a function of temperature gamma k can be a function of pressure right gamma k can be a function of pressure. So, if you look at this partial derivatives by the way this is if I do this then this is not correct this has to be this has to be del delta mu k del T which is RT del ln gamma k del T at fixed temperature and m k ok. So, another thing if you have this is again gives to him relation right this is gives to him. You can write this way T delta mu k is RT d ln gamma k plus RT d ln x k right because the other part what about.

So, you have this right d ln gamma k right you have mu delta mu is RT ln. So, delta mu is nothing, but RT ln a k or RT ln gamma k x k or here it will be RT ln gamma 1. So, you are taking a binary solution this is gamma 1 x 1 and this is this is equal to this guy only this guy this guy is equal to that and this guy is equals to RT ln gamma 2 x 2. Now, you do a chain rule. So, d delta mu 1 is RT d ln gamma k plus RT d ln x k. So, now, you have x 1 RT d ln gamma 1 plus d ln x 1 plus x 2 RT because x 1 is there already right this is gives to him.



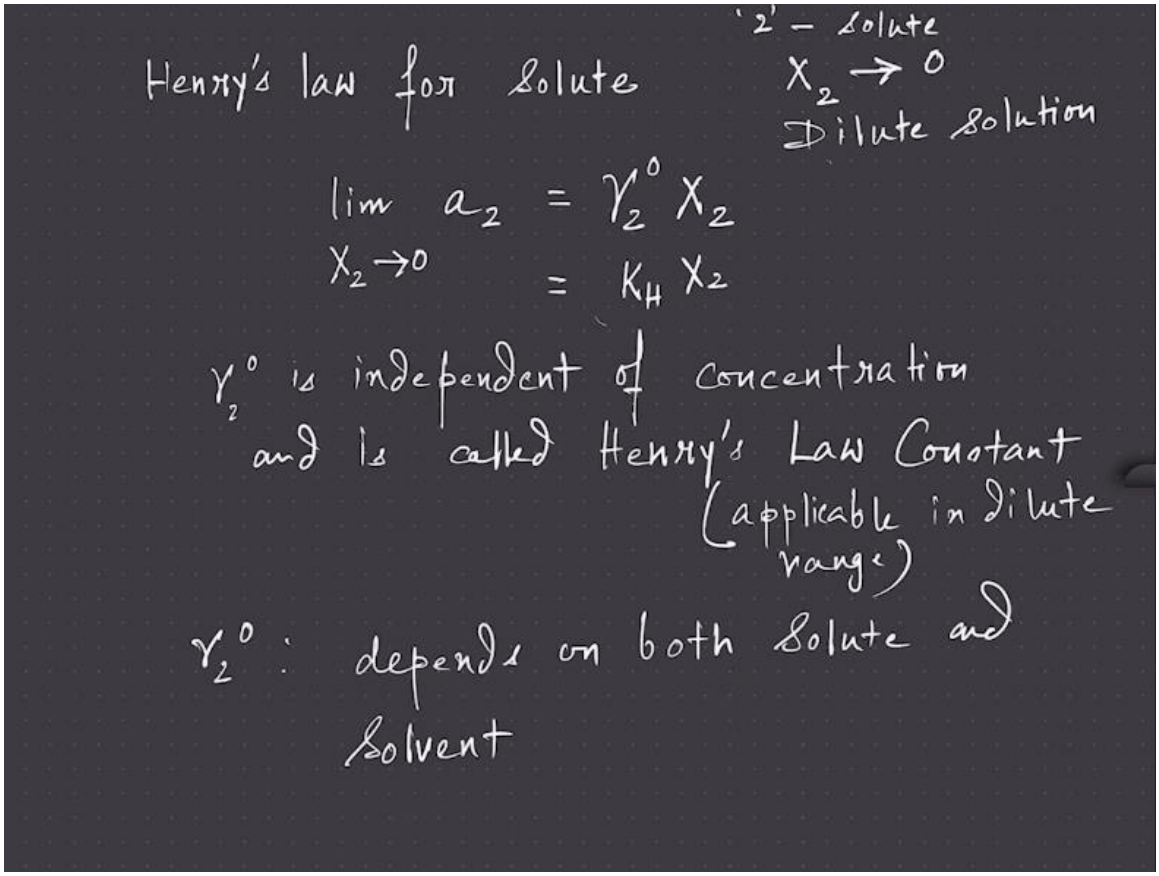
So, x 1 times RT times d ln gamma 1 plus d ln x 1 plus x 2 times RT plus d ln gamma 1 x 2 times RT plus d ln gamma 1 this has to be d ln gamma 2 d ln x 2 right because this is RT ln gamma 2 x 2 right. So, x 2 RT d ln gamma 2 d ln x 2 and there is d ln gamma 1 plus d ln x 1 this is d ln gamma 2 plus d ln x 2 equal to 0. Now, x 1 d ln x 1 so RT RT you can cancel out RT and RT you can cancel out because it is equal to 0 RT is a constant. Now, x 1 d ln x 1 plus x 2 d ln x 2 is nothing, but d ln x 1 is x 1 by x 1 d x 1 plus x 2 by x 2 d x 2 which is d x 1 plus d x 2 which has to be equal to 0 because x 1 plus x 2 equal to 1 and d x 1 equal to minus d x 2 right since therefore this is equal to 0.

So, x 1 d ln gamma 1 plus x 2 d ln gamma 2 we can show using gives to m to be equal to 0 right. So, basically we can tell that if I know gamma 1 I can get gamma 2 again by the gives to m integration right. See ln gamma 1 I can get now ln gamma 1 if I want to do that x 2 equal to 0 again is a pure solvent right x 2 equal to 0 is the pure solvent or pure component 1 and x 2 is the composition so any composition in the mixture. So, we can again use the same gives to m integration. Now, I will just come to a very interesting point here which is called dilute solutions right dilute solutions.

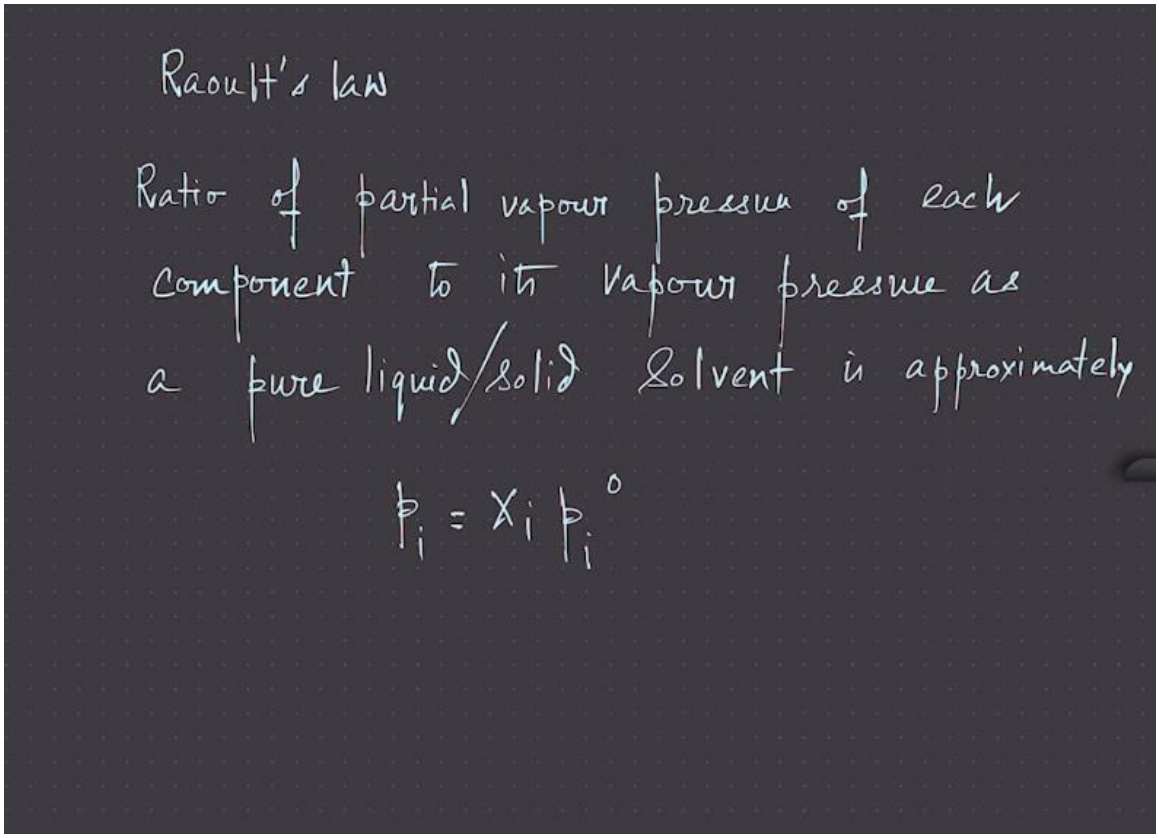


So, for example, here are these different laws that you can get Raoult's law. So, this is Raoult's law for solvent ok for dilute solutions if I have a solvent 1 say I have a multi component system where 1 is solvent ok which because the amount and 2, 3, C all of these are solvents. Now, if x 1 tends to 1 that means the solvent is very very large compared to 2, 3 and all the other solvents. So, that solute concentration is very small.

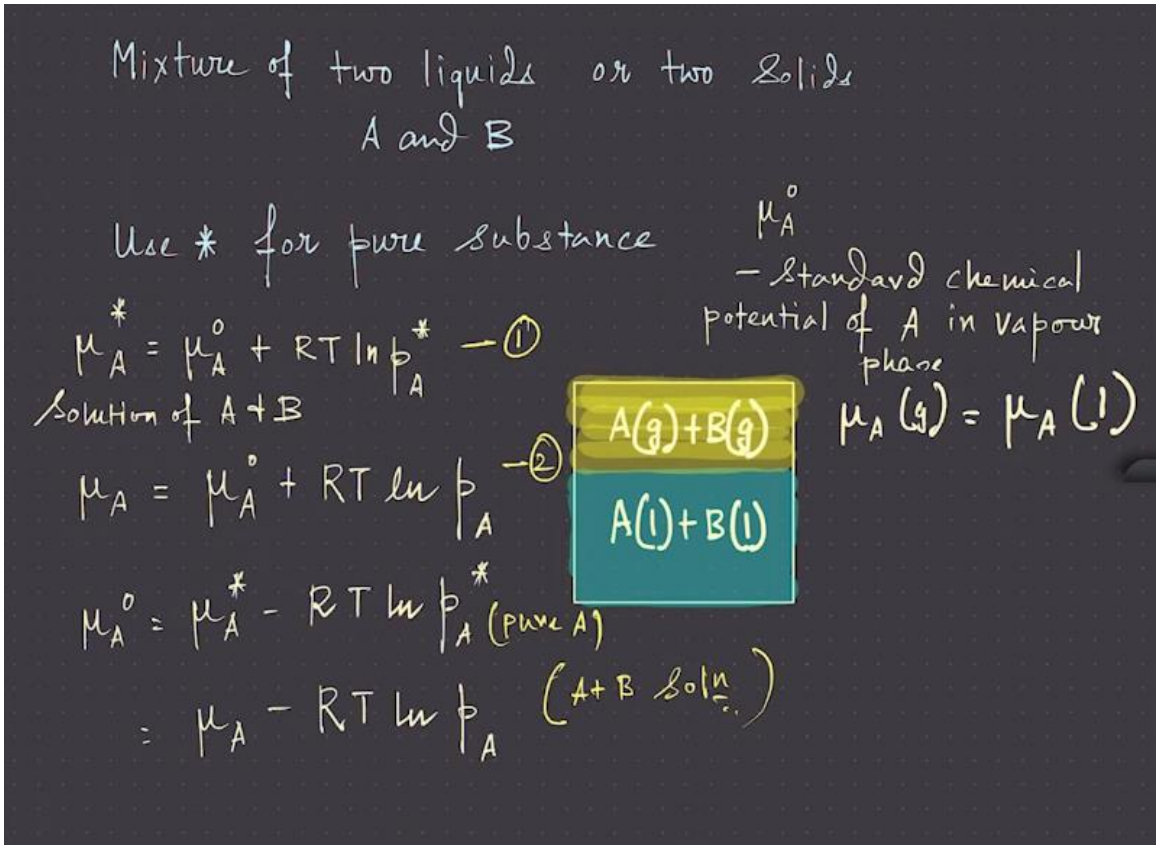
So, x 1 tends to 1. So, then Raoult's law states A 1 that is the activity of 1 is equal to x 1. That means when x 1 tends to 1 it becomes pure solvent for a pure solvent the activity of 1 is the same as the if it becomes a pure solvent 1 the activity is equal to mole fraction right that is what Raoult's law tells. Actually for any component if that component is large enough right compared to the other components right for any component A i equal to x i is basically Raoult's law right. So, for any component we can write and if A i equal to x i we are basically telling that for the other. So, A i equal to x i is basically an ideal right it is an ideal definition.



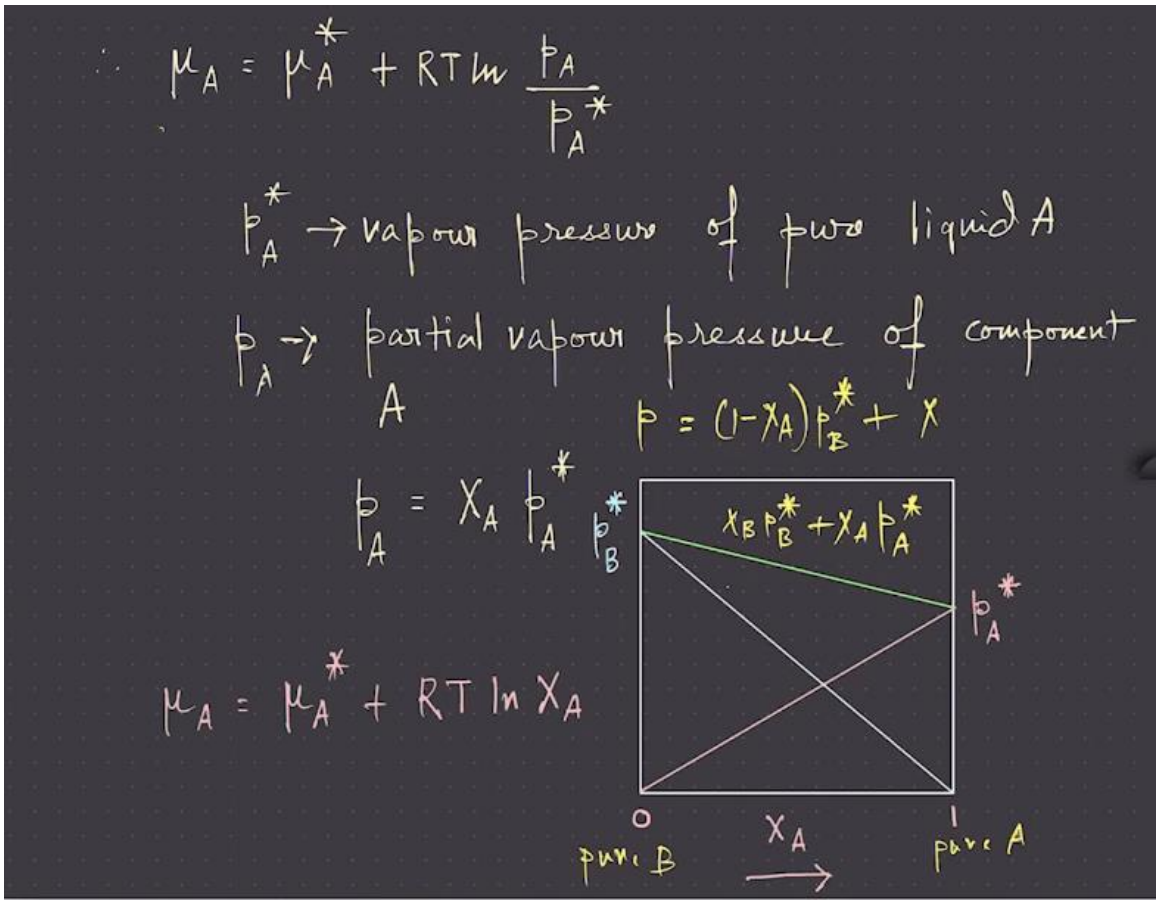
So, Raoult's law is basically for ideal solutions and again in the limit x 1 tends to 1 A 1 goes to x 1. Now, there is some other very interesting law that comes in which is called now this is the thing. So, when I talk about dilute solutions Raoult's law is for ideal solution. Raoult's law is more about ideal solutions.



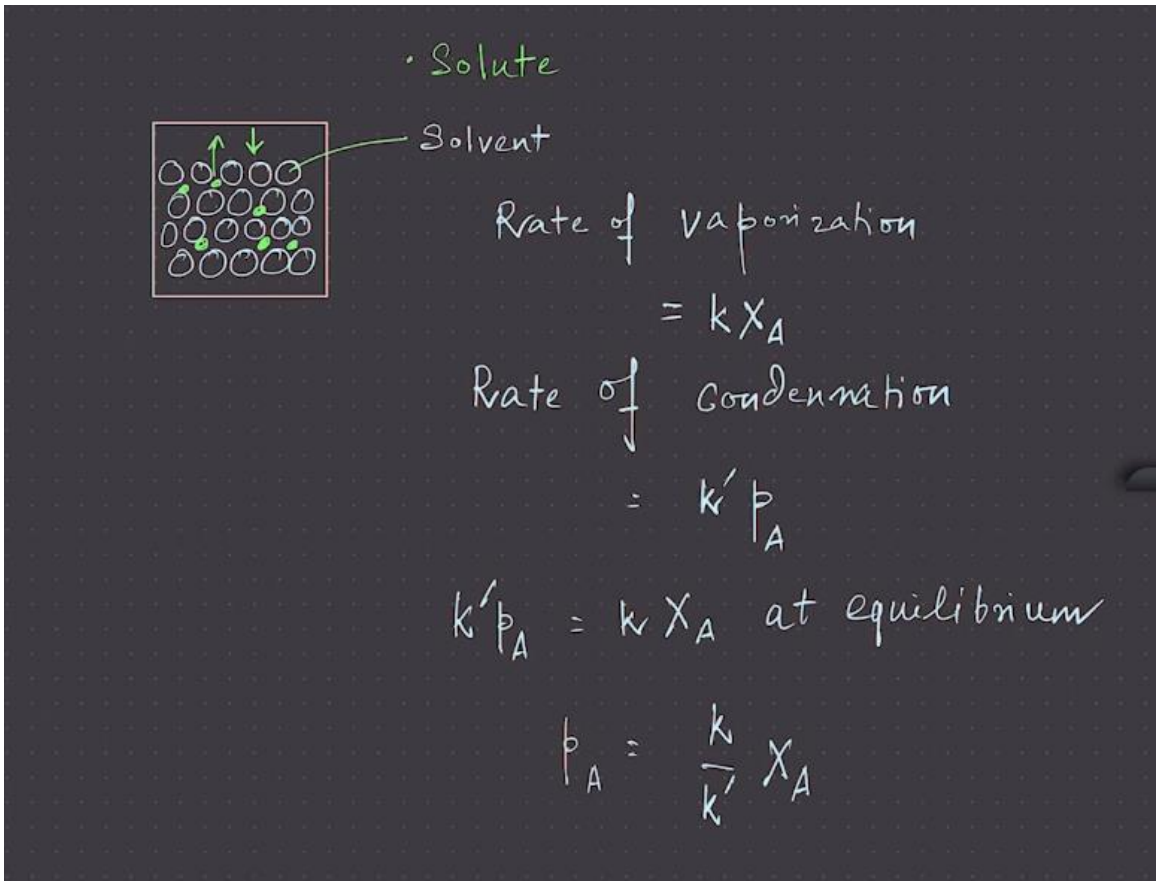
It is not really dilute solution. Dilute solution means A k equals to x k because gamma k equal to 1 right. So, for any component right we can write, but if you see even it follows for dilute solutions because if x 1 tends to 1 when 1 is solvent then basically A 1 will become equal to x 1. So, basically if you have more solute for example, if you have more solute there is a deviation from Raoult's law, but as soon as the amount of solute decreases it becomes so dilute that the solvent is like pure solvent then again you come go back get back the Raoult's law that is correct, but for Henry's law is for solute. So, when x 2 tends to 0 so this is for solute. So, x 2 tends to 0 is the dilute solution limit. So, this is called x 2, x 2 is your solute say 2 is your solute, 2 is solute and x 2 tends to 0 is called dilute solution limit or dilute solution.



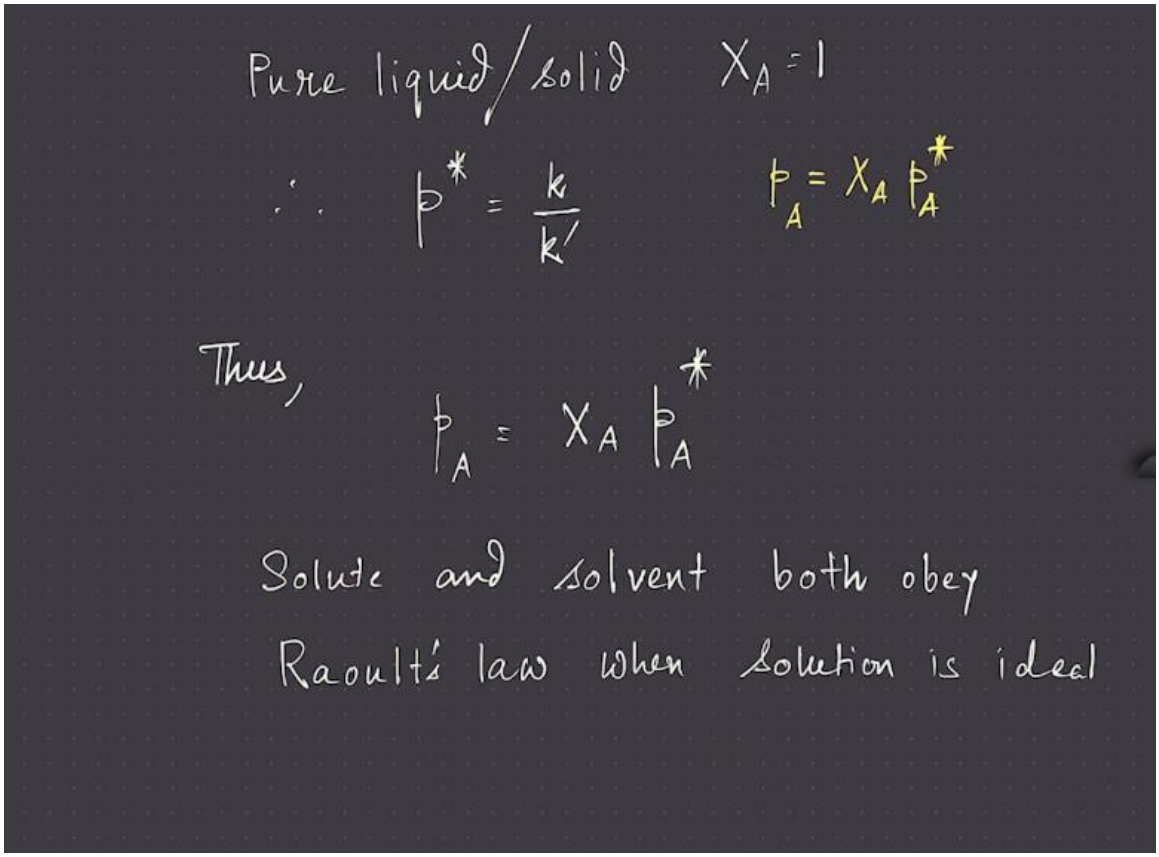
When you define dilute solution we are telling that the concentration of solute tends to 0. Now, in such a case A 2 can be written as gamma 2 0 times x 2 or sometimes it is also called k h x 2 or this is the Henry's law coefficient and gamma 2 0 is independent of concentration, gamma 2 0 is independent of concentration and is called Henry's law first and it depends however gamma 2 0 depends on both the solute and the solvent. So Raoult's law can also be written this way when you look at this gas dissolved in vapor the gas dissolved in a liquid solution or a solid solution or basically if you have a solvent which is a liquid or a solid and then you have a gas that is dissolving in this liquid or solid then we can write that the ratio of partial pressure partial vapor pressure of each component to its vapor pressure as a pure liquid solid solvent is approximately 0. So basically P i is 0 so basically what we are telling is this is the vapor pressure of component i when it is a pure solvent or pure solvent. So basically i pure solvent then there is a partial vapor pressure which is in there is a vapor pressure of component i for a pure solvent which is stated as P i is 0 this vapor pressure this vapor is in equilibrium with the solvent when i is a pure solvent. So when pure then again we are using this superscript of 0 and then we are telling now the partial vapor pressure when these components are mixed is equal to again proportional equal to mole fraction of component i times the vapor pressure exerted by component the vapor of component i when i is a pure solvent.



So you have a solvent if you have a solvent if you have a solvent then there is always a gas phase. So if you have a solvent right there then there is always so you have solved component i and this is component i in gas phase and this is in the liquid phase. Now in the pure form the vapor pressure exerted by i in the gaseous state is P 0 i. However when you have a mixture of different components then basically you have again i is there but then there are other components and here also i is there in the liquid phase but what we are telling now this is P i and that is equals to now what is the relation between P i and P i naught that is related to the mole fraction of component i that is what Raoult's law steps right that is what Raoult's law steps. So this is another alternate definition of Raoult's law. So if you look at this you have say for example, instead of two liquids or two solids like a L b L or a S b S we could have written.



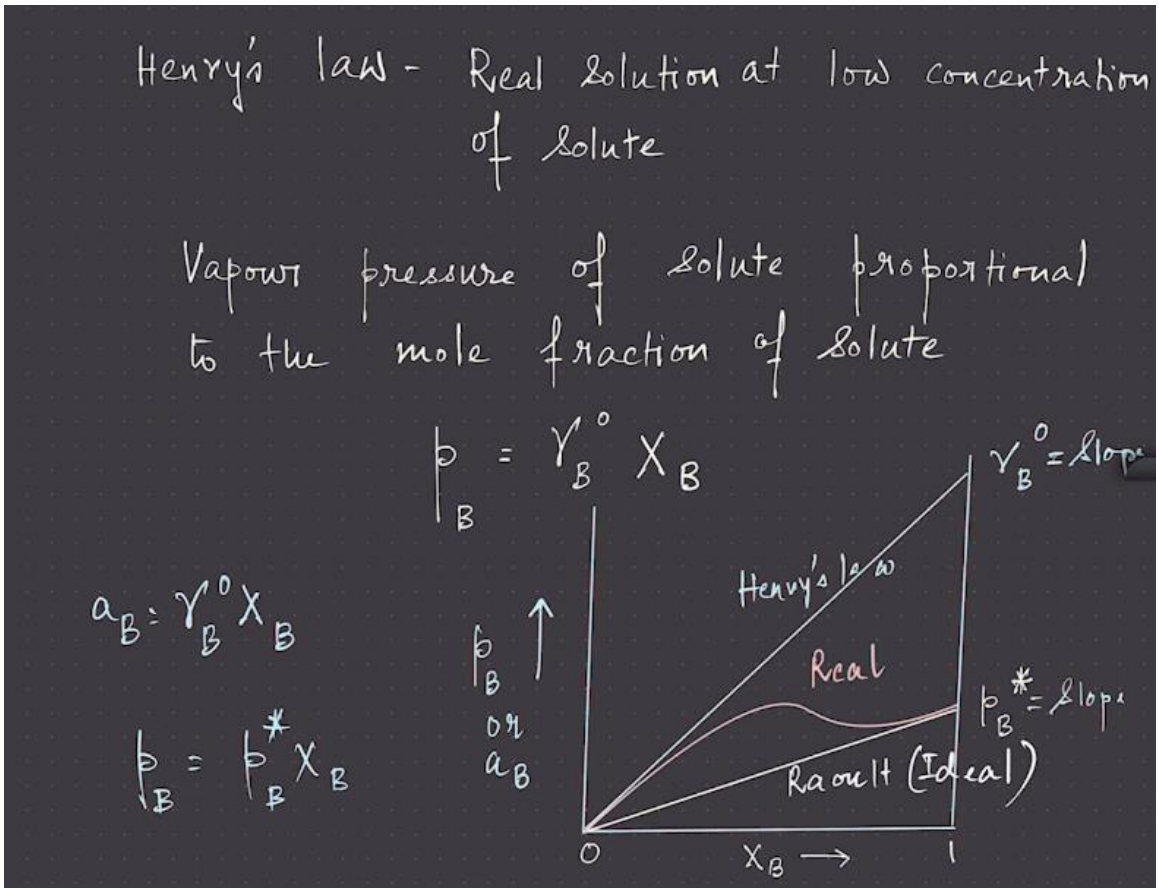
So there are two solids a and b or two liquids a and b and they are mixed and you have this here a liquid plus b liquid and also for a liquid there is a gas and for b liquid there is a b gas. So basically there is a vapor vapor so this a this is a vapor this is b vapor and if you look at that you can use star for pure substance. So if it can have been only a there is no b there is no b then mu a star that is in the pure state equals to mu a 0 that is some standard state plus RT ln P a star and the solution of a and b again mu a equals to mu a 0 see now this is what we are trying to distinguish. So star is for pure substance but a is 0 is some standard state some standard state where this standard state can be some very small amount of b or whichever we want to. So mu a 0 is a standard state mu a star is that of the pure substance so there is a chemical potential of component a when a is completely pure and this is again related to P a star which is the vapor pressure of component a the of the vapor pressure exerted by the vapor that is in equilibrium with the pure liquid a.



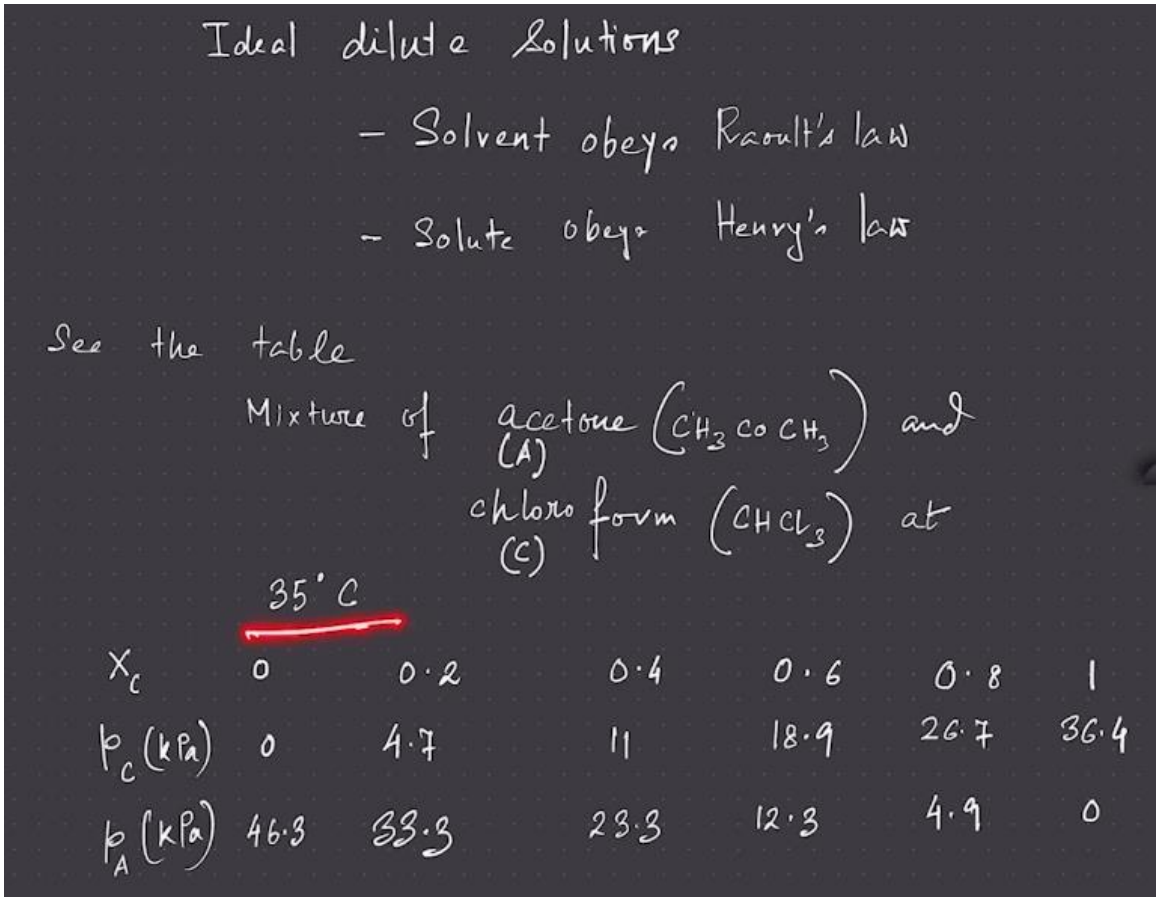
That is the ln that is RT ln P a star. Now if you have solution of a and b then it is mu a and this is P a which is the partial pressure partial vapor pressure of component a when you have a solution of a and b. Again you can write now if you but the mu a 0 is standard now if you look at that you can equate mu a 0 in these two equations let this be equation 1 let this be equation 2 if I have 1 and 2 now I have mu a 0 which is from 1 it is mu a star minus RT ln P a star and which is equal to mu a minus RT ln P a. Now in this case I am considering a plus b solution and in this case I am considering pure a okay I am considering pure a right here I am considering pure a. Now if you see this is both mu a 0 so I can equate this so what I get mu a now you see mu a 0 is eliminated and now you get mu a star which is again the pure form the chemical potential of a in the pure form and which is equal to mu a which is the chemical potential of a in this mixture plus RT ln P a by P a star and P a star is that of pure liquid a okay the vapor pressure of the vapor phase which is in equilibrium with the pure liquid a and this is the partial vapor pressure of component a that is in equilibrium with the liquid solution okay. So in that case you have P a by P a star and P a by P a star basically you can write this as mu a star plus RT ln X a and so P a equals to X a P a star right we can write P a by P a star is nothing but X a so mu a equals to mu a star plus RT ln X a and if you look at that this is P a star which is for now this is X a equal to 1 that is pure a this is pure a right so this is pure and this is pure so there you have P b star right so if you have pure b you have P b star you have P a star here and this is the X a how it is changing so as you can see you have if you look at

this pure a it starts from 0 it starts from 0 and moves to P a star again if you look at P b star so it is pure b and this is if it is so basically pure b means X b equal to 1 and here X b equal to 0 so it starts from here and then goes down and comes here now the total pressure is coming around this line because it is X a P b X b P b star so this is basically the line of X b P b star plus X a P a star or we can also write it as 1 minus X a P b star plus X so P is equals to that right so basically you have a P that is changing P a or P b that is changing according to this equation okay so this is for an ideal setting okay now think of this why is this Raoult's law what is the physical meaning what's the molecular interpretation again every time we look at that right so we have this blue colored or blue bordered solvent molecules here as you can see and you have this green solutes here some green solutes some solute here now if you have rate of evaporation which is basically proportional to the mole fraction of component a now and rate of condensation is proportional to the partial pressure of component a now if you see K prime P a so if you see at the steady state or at equilibrium these rates are equal right K X a equals to K prime P right rate of evaporation so solvent can vaporize solvent can also condense because there is always if you have a solvent in a liquid state it's in the liquid state it is also there this is like a in liquid state then there is also a in the gas state right which is a the gas state which is in equilibrium right so there is a liquid vapor equilibrium that's what I am considering so if I consider liquid vapor equilibrium that means that it in that equilibrium rate of the creation of the solvent from liquid to vapor is equal to rate of condensation of the solvent molecules from vapor phase to the liquid phase okay so K X a equal to K prime P a or P a equals to K by K prime X a now pure liquid or solid if you think of pure liquid or solid X a equal to 1 so P star so basically if it is pure liquid or solid P star is K by K prime right because if you remember Raoult's law P equals P a equals to X a P a star right X a P a star so basically P star equals to K by K prime thus P a equals to X a into P a star so solvent and solute both if both obey Raoult's law then the solution is called ideal okay Henry's law basically does not care about ideality it is for a real solution part with a very low concentration of solid right very low concentration of solid now in that case the vapor pressure of the solute okay vapor pressure of the solute is P b right when X b equals to 0 see P b okay this is the this is this is called this is Henry's law now if you see Henry's law very carefully you can see this line is drawn at X b tends to 0 see this is the tangent that I have drawn to this curve this is a real solution so there is a deviation from Raoult Raoult's but is what that P b equals to X b P b star right or P a equals to write P b so if you have 0 to P b star 0 to 1 so this is basically X b the slope is basically P b star right so 0 to X b so the slope here so P b star is the slope for Raoult's law but here the slope is so this is the slope for Henry's law right so Henry's law is for a real solution with very low concentration of solute now if you have higher concentration of solute then there is obviously deviation as you can see here from the red line so so this part this is where I draw the tangent and that is giving me the Henry's law and Raoult's law is basically telling me P b P b so this is P b is the partial pressure of P

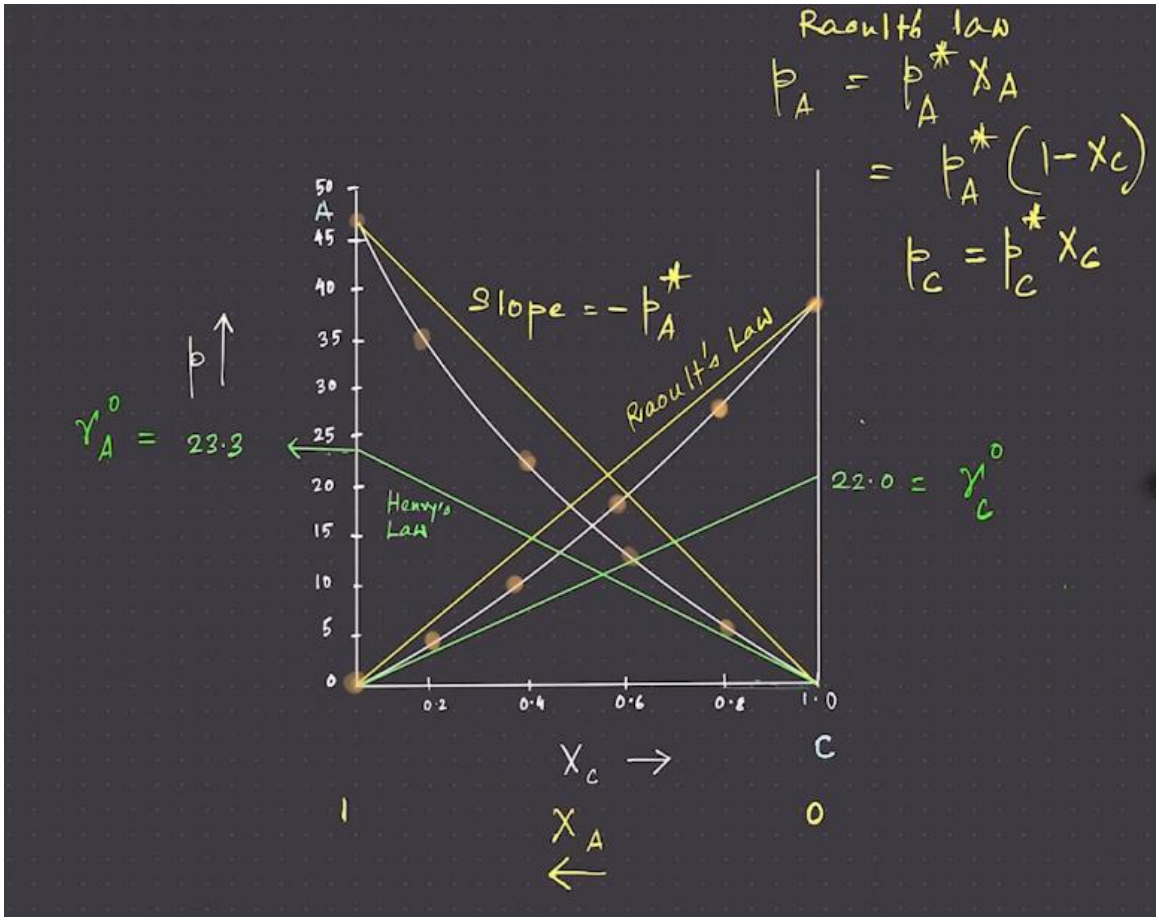
so basically P b equals to X b P b goes to P b star P b equals to P b star X b and X b is the x-axis right X b is the x-axis P b is the y-axis and P b star is the slope right P b star is the slope other way Henry's law for a real solution but at dilute concentrations of solute okay so basically you can call some solutions which are called ideal dilute solutions okay



Ideal dilute solutions where solvent obeys Raoult's law while solute obeys Henry's law okay so look at this mixture of acetone and chloroform okay and you have this so basically chloroform is denoted by C chloroform is denoted by C and acetone is denoted by A so this is a mixture or a solution at 35 degrees Celsius at 35 degrees Celsius now if I look at that there is a P C okay that is the partial pressure of component C as a function of composition right you can see the composition of chloroform is increasing from 0 to 1 as a result and there is a also a corresponding increase in the partial pressure of component C from 4.



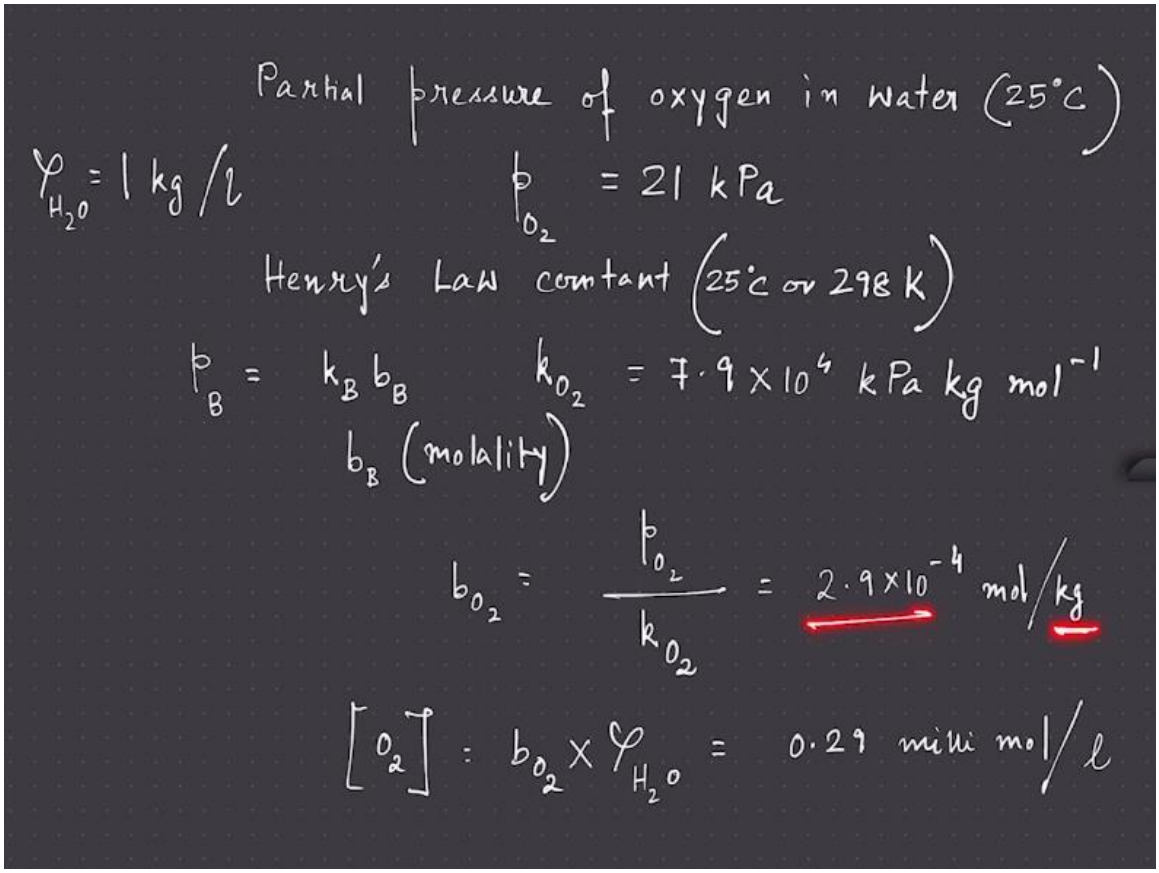
7 11 18.9 and all this and again as the solute that the concentration of C increases there is P A that changes from 46.3 then 33 and then it goes to 0 when X equal to 1 right so it falls right that is falls right is acetone so acetone initially when X equal to 0 that means it is pure acetone the vapor pressure was 46.



3 pure acetone vapor pressure 46.3 then it became 33.3 when you have 0.2 chloroform or 0.8 acetone this is 0.6 acetone this is 0.4 acetone and 0.2 acetone and 0 acetone then basically the partial pressure goes to 0 if you look at this these are your experimental data points these are your experimental data points for this is component C. component C increases from 0 to 1 right so this is for component C right these are the points for corresponding component C and these are the grains corresponding to component A right this is the point called corresponding to component A so this is for pure A and this is for pure C right so pure C now if you look at that you can see that the Raoult's law basically tells that the partial pressure of this component say for example partial pressure of component C because Xt Xc times P star right so basically P equals to P star Xc when I tell you Pc is Pc star so Pc star is where Pc star is somewhere here right so basically Raoult's law basically gives me the yellow lines right that's the yellow line similarly I can write if I look at Raoult's law for so for component C or component A I can write Pa star Xa Pa or equal to Pa star to 1 minus Xc right so you can see that there is a minus Pa star slope right so this has a slope of slope is minus Pa star and Pa star is here Pa star is here right the slope is minus Pa star and Pc so I can also write Pc so these are all Raoult's law Raoult's law I am drawing using that's why I am using yellow pen right Raoult's law and Pc because Pc star C right so now but Henry's law look at Henry's law Henry's law is

drawn at the concentration of the solute which is negligible right so if we look at C the concentration of solute means A

A equal to 1 here and A equal to 0 here right if I look at Xa Xa increases this way now if you look at that when Xc is basically very small that is where you have to draw the tangent right that green tangent so the green tangent basically gives me a partial pressure value of that the activity that's gamma 2 value so that is basically gamma so let us look at this line the green line is basically here or here say so this is basically equal to gamma C 0 right so this is the constant and this is basically gamma A 0 right because when I am looking at A as the solvent then basically when basic A as the solute the limit of A so C is the solvent A is a solute then we have to draw the tangent at C equal to 1 right so at C equal to 1 so this gives me the gamma A 0 so this is basically called this is the these are the constants from Henry's law so this is something that is often used in liquid solutions in liquid solutions or solid solutions and we look at that but remember the data points show deviation from ideality the data points show deviation from ideality right so the data points here are showing so if you look at this white curve it is deviated right it is either showing a positive it is showing a deviation from ideality it can be positive deviation here it is it may be a negative deviation from ideality right here it is showing a negative deviation from ideality so that's the idea so partial pressure of oxygen in water for example is 21 kPa and Henry's law constant say for example is given by 7.9 10 power 4 kPa kg per mole and PB equals to kB B B where B B is the molality of B or so basically B here is O2 so B equal to you can take B equal to O2 then B O2 is P O2 by k O2 where k O2 is already given Henry's law constant that is how much of oxygen is dissolving in water so we can basically see it is 2.



9 10 power 4 moles per kg so the concentration of O2 we can write we can see that it is millimoles 0.29 millimoles per liter okay so basically what I am trying to say is that say for example this is one example of dissolution of oxygen in water and you have very little amount of oxygen right millimoles 0.29 millimoles of oxygen in water okay per liter and so basically you can apply right the the the the the Henry's law but here we are using so the Henry's law can be written also in terms of molality so here this is the molality of solute B okay molality means per kg right per kg so B B yeah so B O2 for example is these many moles per kg of the solvent right per kg of the solvent, solvent here is what okay so there is another property which is called collective property or colligative properties right these are called colligative properties colligative means it does not depend on the nature of the particle but it only depends on the collection of particles colligative comes from this spot collection because of the solvent because of solute dissolving the solution right say for example sodium chloride dissolving in water you have now two moles of means if one mole of water you consider and you have one mole of sodium chloride you have added to say one liter of water say let us consider one liter of water and you have added one mole of sodium chloride one mole of sodium chloride means two one mole of Na plus one mole of chloride ions one mole of those two moles of Na plus ions and chloride ions and these are the particles we do not care about whether it is sodium ions or chloride ions but we only care about the collection of these particles that are added to water okay and they are dissolving in water so in that

case what generally happens is if you look at the phase diagram of water this is pure water phase diagram right which has say at one bar pressure it has a zero degree Celsius as the freezing point or the melting point and 100 degrees Celsius is the boiling point so we will continue this discussion of corrugative properties in the next week in the next week and we will go into how to define quasi-chemical models for real solutions okay