Thermodynamics And Kinetics Of Materials

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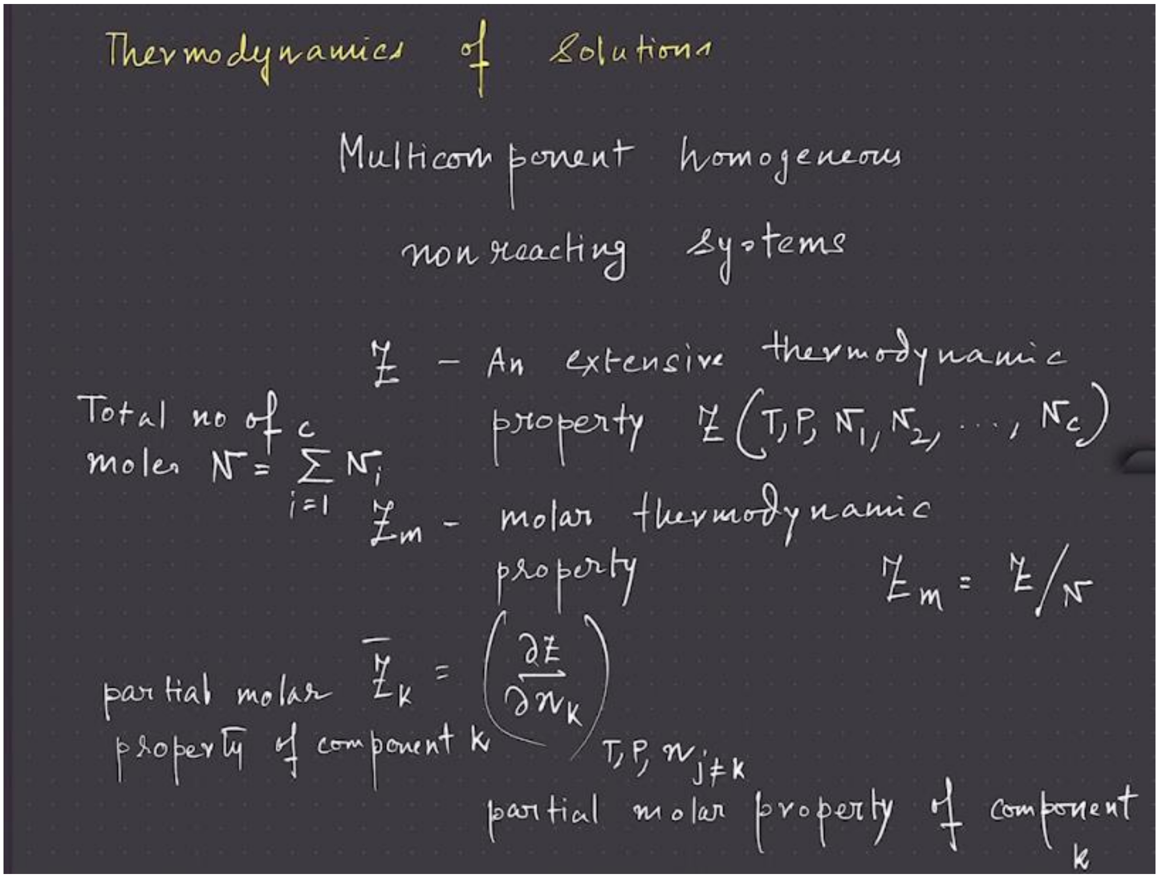
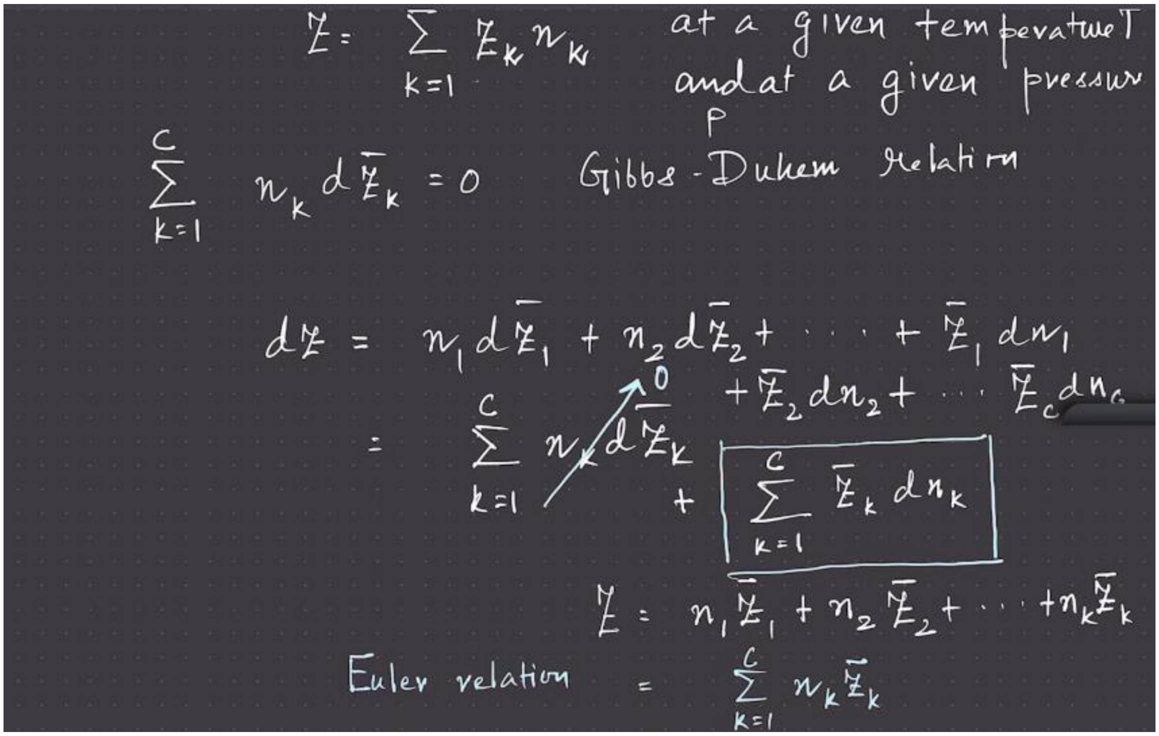
Lecture 23

Multicomponent solutions and mixing process

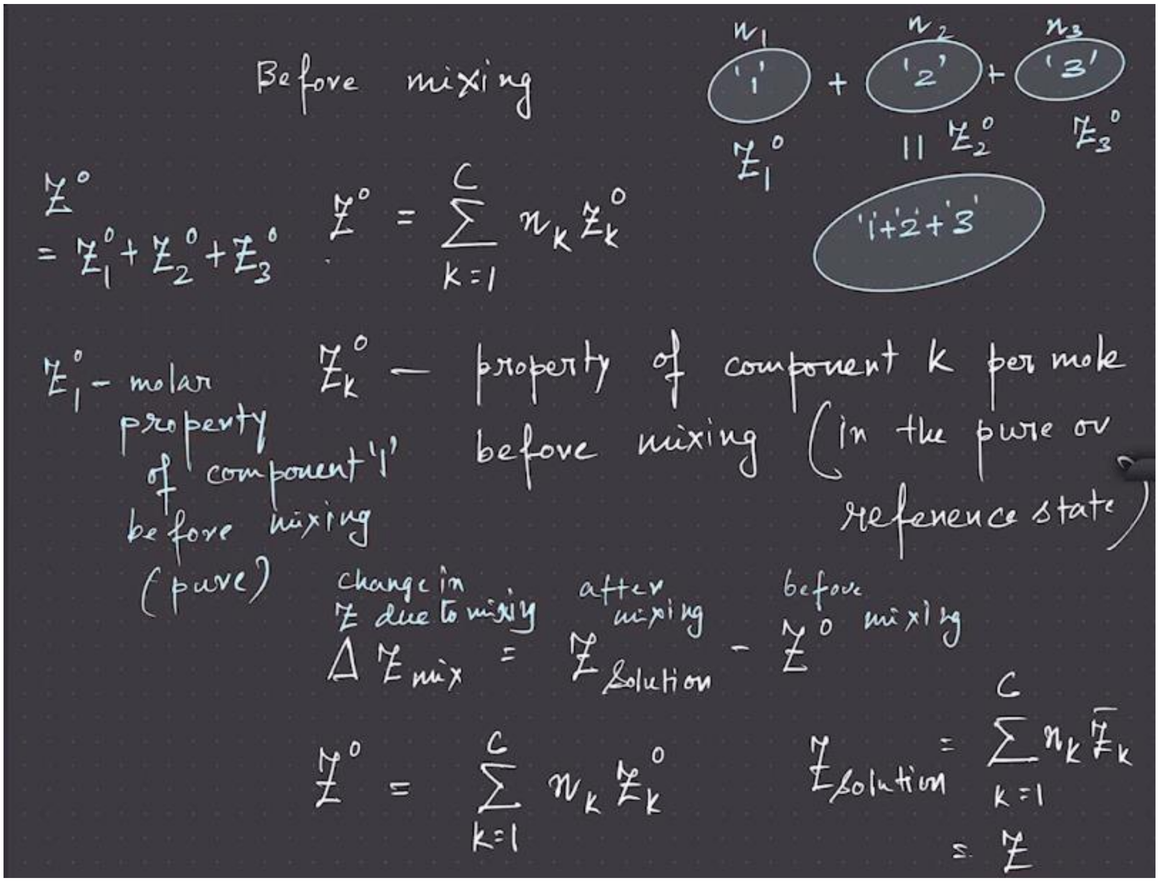
So, I was talking about thermodynamics of solutions, multi component solutions. Multi component solutions means it is basically a mixture of multiple components and the mixture gives rise to a homogeneous non-reacting, it is a homogeneous non-reacting mixture of components where you cannot distinguish one component from the other and they form a solution. So, that is the solution that we define and we will continue with that. Now as you know a little bit of price, so if you think of Z which is an extensive thermodynamic parameter that depends on the extensive thermodynamic parameter, it is a function of Z can be a function of temperature, pressure and mole number of different components like component 1, component 2 and component Z up to C and see n_1 is the number of moles of component 1, n_2 is the number of moles of component 2, n_C is the number of moles of component C, then basically you have total number of moles, if you look at total number of moles, n equals to summation, equal to 1 to n, equal to 1 to C and i. So, Z m is nothing but which is Z_m or Z_m is a molar thermodynamic property and molar thermodynamic property means thermodynamic property per mole, it is per mole, it is an intensive quantity, so it will be defined as Z_m or Z_m equal to Z by m. Now let us look at the partial molar property I have already defined like in the last classes I have already defined, so Z_k bar, so Z_k bar is the partial derivative of Z with respect to n_k that is with respect to species k, the concentration of species k in terms of mole number, so del Z del n_k that means I want to look at the change in the extensive property Z, if I add or remove some amount of k component right, one of the components is k component means the component k, so I am looking at Z_k bar means partial molar property of component k in the solution.



So, remember when I am talking about partial molar property I am already considering a mixture or a solution right, I have considered a mixture I want to look at a contribution of component k to the extensive property, so Z_k bar is defined as the partial derivative of the partial derivative of Z is the property with respect to n_k which is the mole number of species k or component k keeping temperature, pressure and other species mole numbers that is j, j are the other species n_j, j not equal to k, see j not equal to k and this is the other species mole numbers are kept constant. So, only mole number that I am changing or varying is the mole number of component k and as a result I want to see the variation in Z means variation in the extensive parameter remember I am looking at the variation in the extensive parameter not the variation in the molar parameter right, I am not looking at the molar thermodynamic property, but I am looking at so that is the definition of partial molar property. See remember partial molar property is always defined with respect to when I express it in terms of partial derivative then it is with respect, so the quantity that I am basically the quantity of the numerator is basically the extensive thermodynamic property right, is the extensive thermodynamic property. So, it is the partial derivative of the extensive thermodynamic property with respect to the mole number of component k keeping temperature, pressure and mole number of all other components fixed right, keeping mole number of all other components fixed, temperature fixed, pressure fixed we want to see the, so we want to see how the extensive property varies as a function of variation in the mole number of component k, change in mole number of component k.



Now, if that is so Z being an extensive property right, Z is an extensive property, so at a given temperature and pressure if I write at a given temperature say at a given temperature T and at a given pressure at a given pressure P Z there is extensive property, the extensive property is a summation of the partial molar properties of the components k where k can vary from 1 to c right. So, this is the sum of the partial molar properties multiplied with the or weighted with the mole number of each component. So, basically this is nothing but if I expand Z equal to n_1 Z_1 bar plus n_2 Z_2 bar plus. So, this Z_k bar or Z_1 bar, Z_1 bar is the partial molar property associated with component 1 or partial molar contribution of component 1 to the solution ok. And this partial molar the partial molar property of component 1 or associated with component 1 in the solution and the solution has an overall property or extensive property Z right.



Now, if that is so I have also defined the Gibbs Duhem relation right, Gibbs Duhem relation which is basically. So, I did it for Gibbs free energy, I showed it for molar volume, I showed it for the total volume. So, if you look at any extensive property Z then it is n_k d Z_k bar equal to 0. So, basically n_k d Z_k bar again summation from k equal to 1 to c ok. So, if you have repeated indices remember that if you have repeated indices we can also use a Einstein summation convention.

$$\Delta Z_{mix} = \sum_{k=1}^{c} \left(\bar{Z}_k - Z_k^{\circ}\right) n_k$$

For component 'k'

$$\Delta \bar{Z}_k = \bar{Z}_k - Z_k^{\circ} \text{ (pure/standard)}$$

relative partial molar property of 'k'

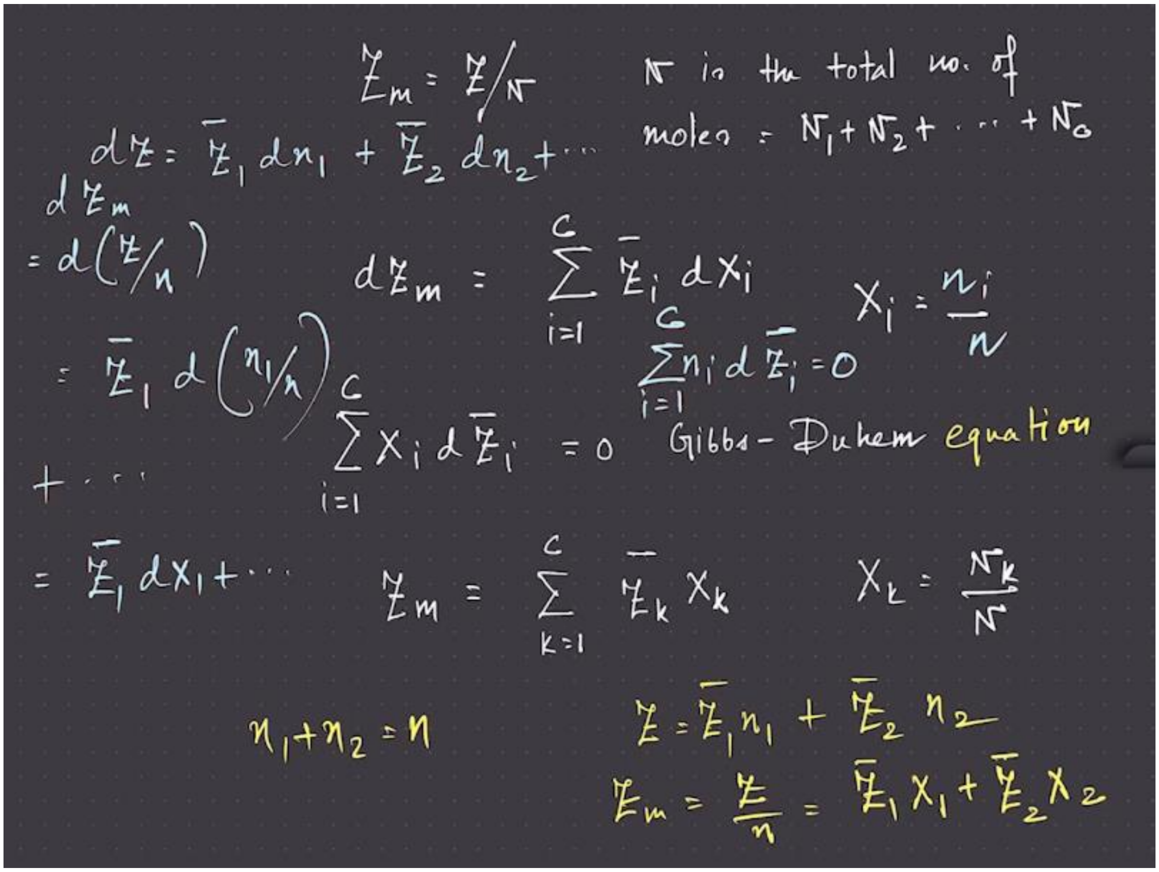
$$\Delta Z_{mix} = \sum_{k=1}^{c} \Delta \bar{Z}_k n_k$$

$$d\Delta Z_{mix} = \sum_{k=1}^{c} \Delta \bar{Z}_k \, dn_k$$

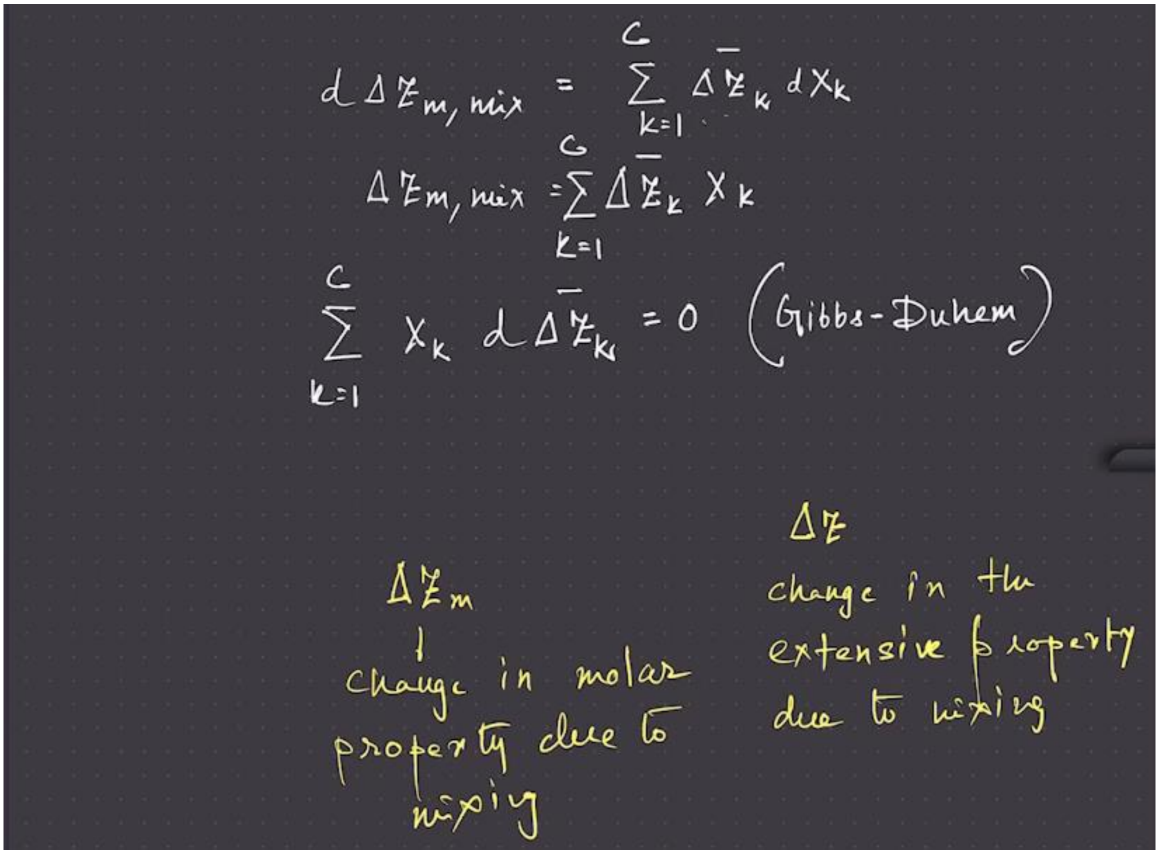
$$\sum_{k=1}^{c} n_k \, d\Delta \bar{Z}_k = 0 \qquad \therefore n_k d\Delta \bar{Z}_k = 0$$

(Gibbs-Duhem equation)

So, basically this means there is always a sum of the repeated indices and the repeated index is k and k denotes the component here, k denotes the component k here. So, number of components here is c and the components are denoted by 1 2 3 up to c ok. So, now if you look at d Z. So, if you look at d Z, d Z is n_1 d Z_1 bar plus n_2 d Z_2 bar plus also you will have now this part you have to remember this is something you have this one and you also have you also have Z_1 bar d n_1 plus Z_2 bar right d n_2 plus Z_c bar d and c right. So, you have this term plus you have another term which is k equal to 1 to c this will be Z_k bar d n_k.



Now, according to Gibbs to him according to Gibbs to him this term n_k d Z_k bar equal to 0 right. So, n_1 d is 1 1 bar plus n_2 d Z_2 bar plus n_c d Z_c bar all of these are 0. So, this term goes to 0 right. So, this term goes to 0. So, this will be 0 according to Gibbs to him, but what is remaining then is this term right.



And this is the Euler relation you see Z equals to Z equals to n_1 Z_1 bar n_1 Z_1 bar plus n_2 Z_2 bar plus n_k Z_k bar or I can write this as summation k equal to 1 to c n_k Z_k bar. See this is the Euler relation right this is Euler equation or Euler relation right. For example, g equals to h minus d_s plus mu_i n_i. Now, if you think of a constant pressure and temperature then g you can basically write as mu_i n_i right mu_i n_i where mu_i is the partial molar free energy of component i or chemical potential of component i. As I told you previously chemical potential of a component basically is nothing, but the partial molar free energy of that component in a solution right.

$$\Delta Z_{m,mix} = \Delta Z_m$$

$$\Delta Z = n \Delta Z_m$$

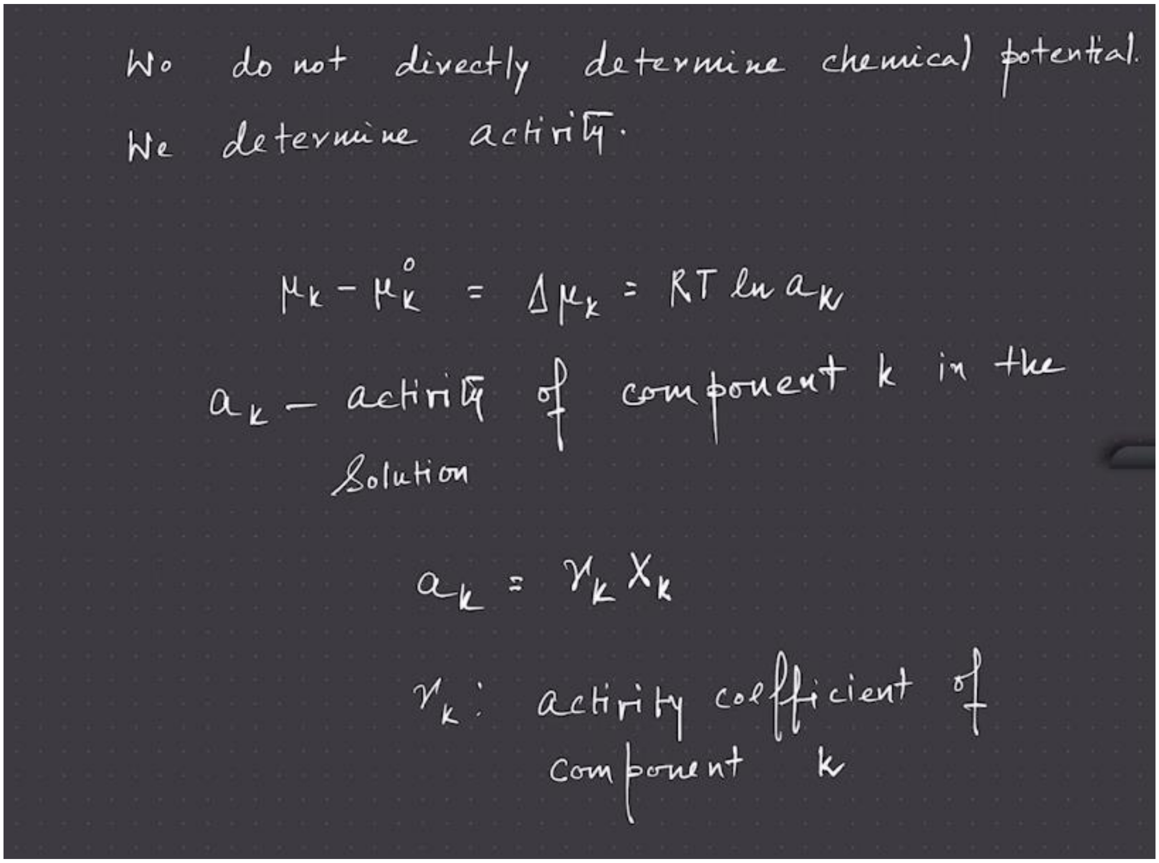
$$\Delta \bar{Z}_1 = \left(\frac{\partial \Delta Z}{\partial N_1}\right)_{T, P, N_{k \neq 1}}$$

$$= \Delta Z_m + (1 - X_1) \frac{d \Delta Z_m}{d X_1}$$

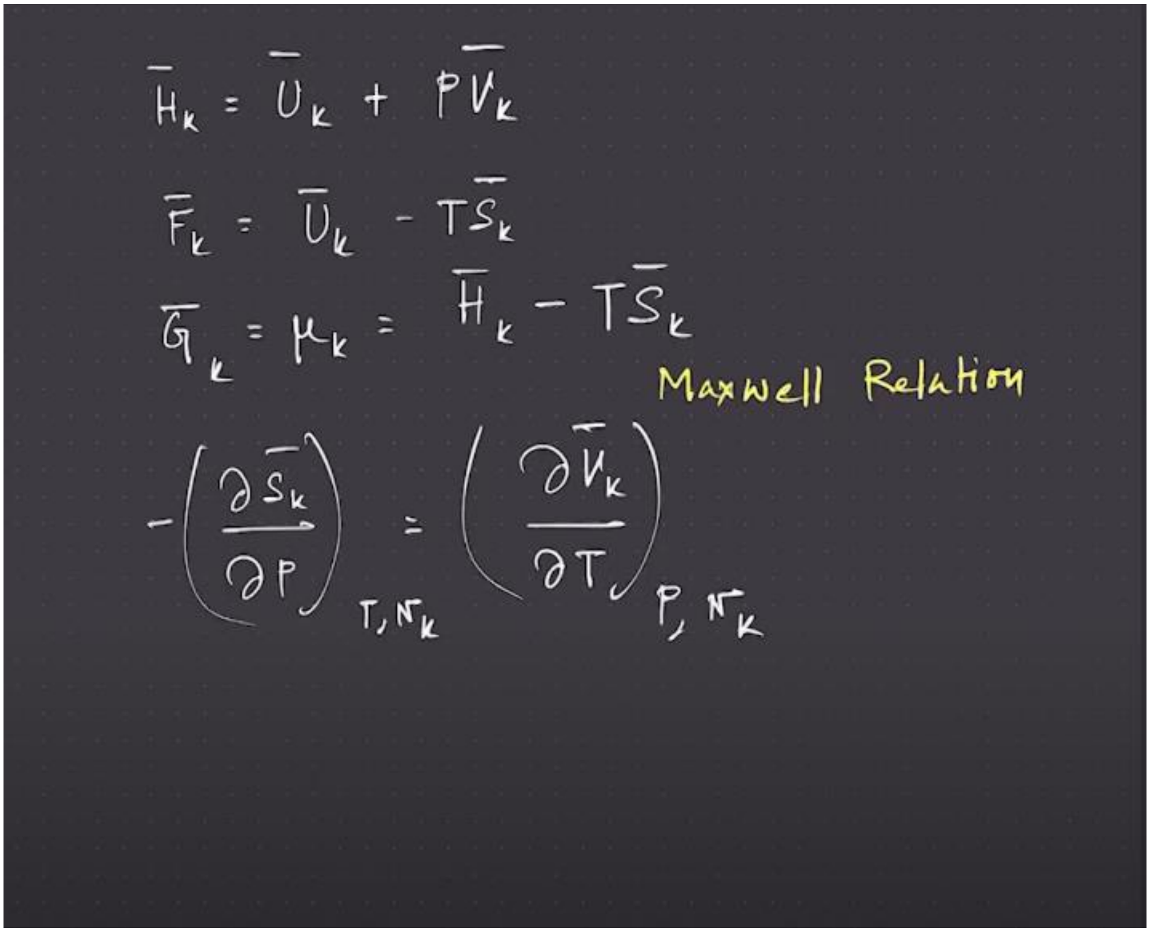
$$\Delta \bar{Z}_2 = \Delta Z_m + (1 - X_2) \frac{d \Delta Z_m}{d X_2}$$

$$\frac{d \Delta Z_m}{d X_2} = - \frac{d \Delta Z_m}{d X_1} \quad \left[\because X_1 + X_2 = 1 \text{ or, } dX_2 = -dX_1 \right.$$

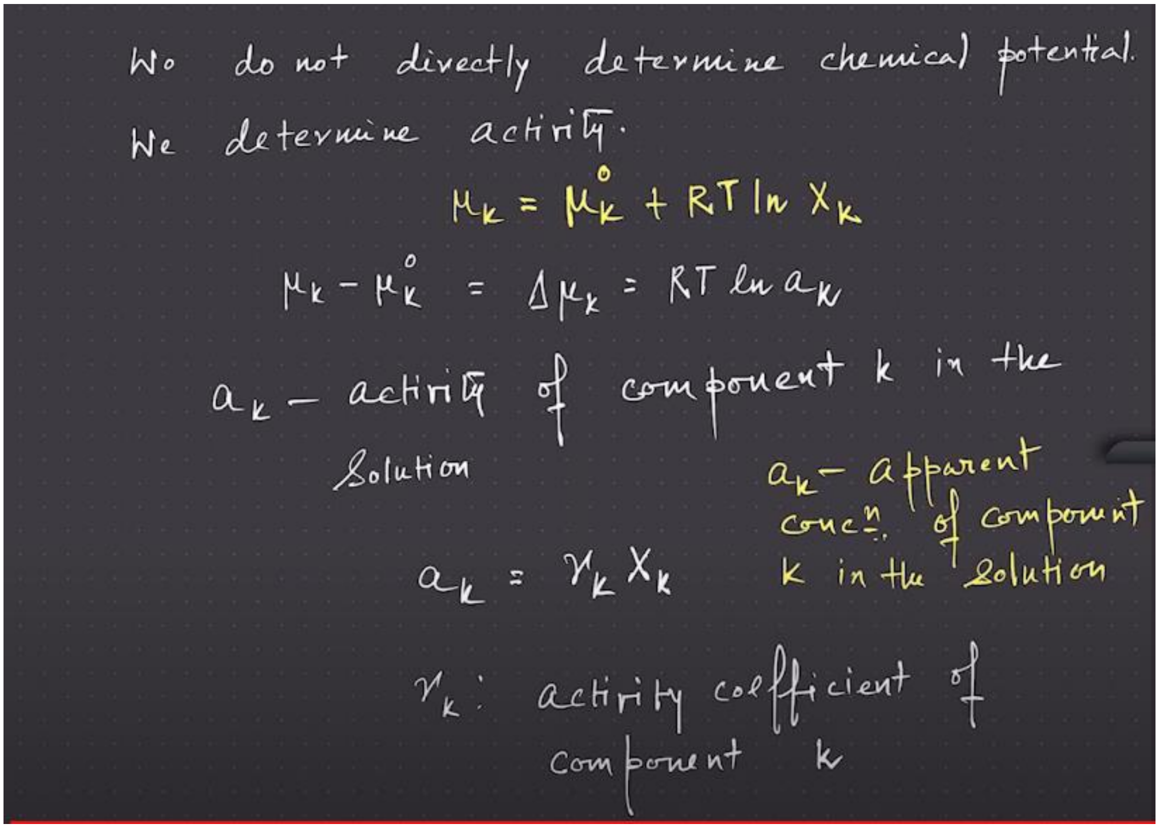
Now, what types of solutions are possible solid in liquid, solid in solid, liquid in solid mixture of gases. So, any type of solution is possible. Now, comes an interesting part which is basically again I am reprising I have already defined it previously, but please listen because this part is very very important when you want to understand solutions or thermodynamics of solutions right. When you want to understand thermodynamics of solutions you do have to remember the Gibbs-Duhem relation which is n_k d Z_k bar. So, basically what it tells is that this d Z_k bar means if you have a partial molar property if you do a differential of that partial molar property and weight it with the mole number then basically the sum of these will always go to 0 that is the Gibbs-Duhem relation right.



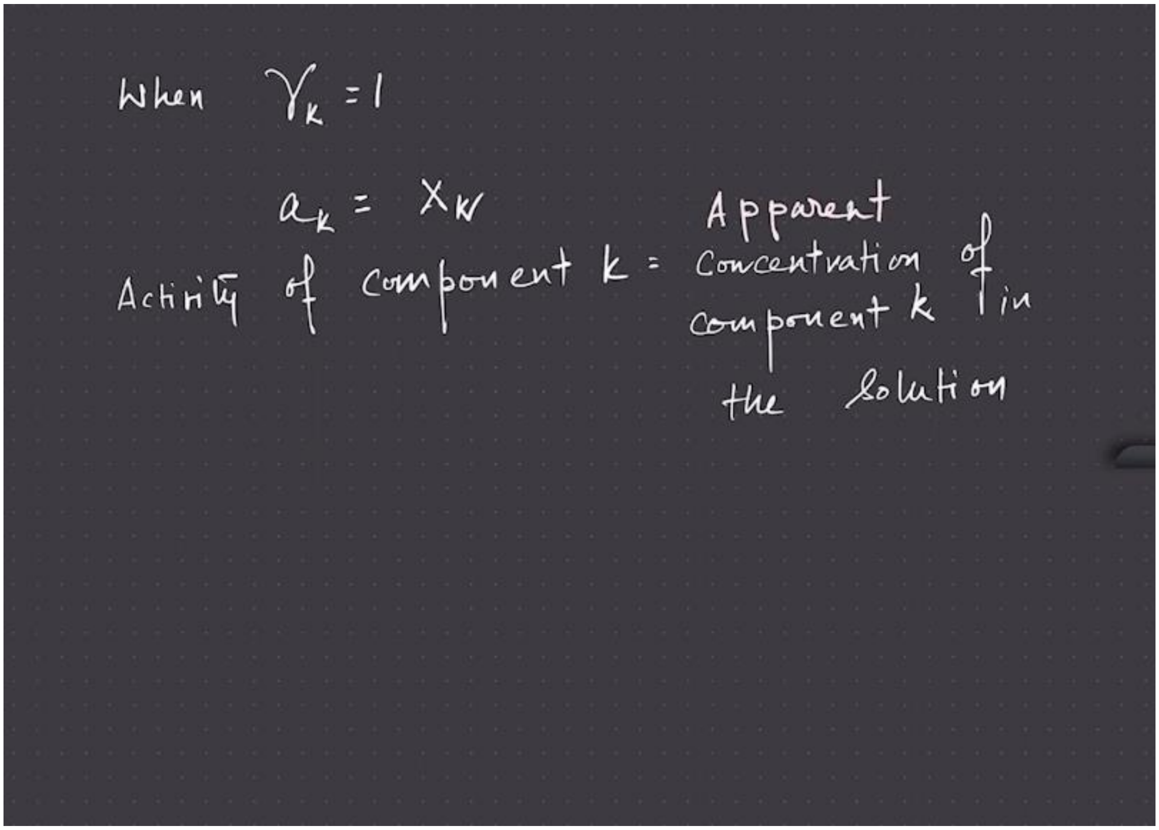
And also as a result we can tell from this equation means that this is the equation this is the Euler equation from this equation and this equation we can tell d Z is nothing, but sum over all components Z_k bar that is the partial molar property times the differential of the mole number right the differential of the total differential of the mole number d n_k right. Now, look at this say for example, you have these components you have these components like 1, 2 and 3 you are adding them once you add them you get this guy which is this guy which is basically a mixture or if it is a homogeneous mixture then it becomes a solution. So, 1 plus 2 plus 3 so all these components have to be right. So, this is component 1, this is component 2 and this is component 3 right. Now, if that is so the property that it had is Z_1^0 Z and the property here would be Z_2^0 and here it is Z_3^0.



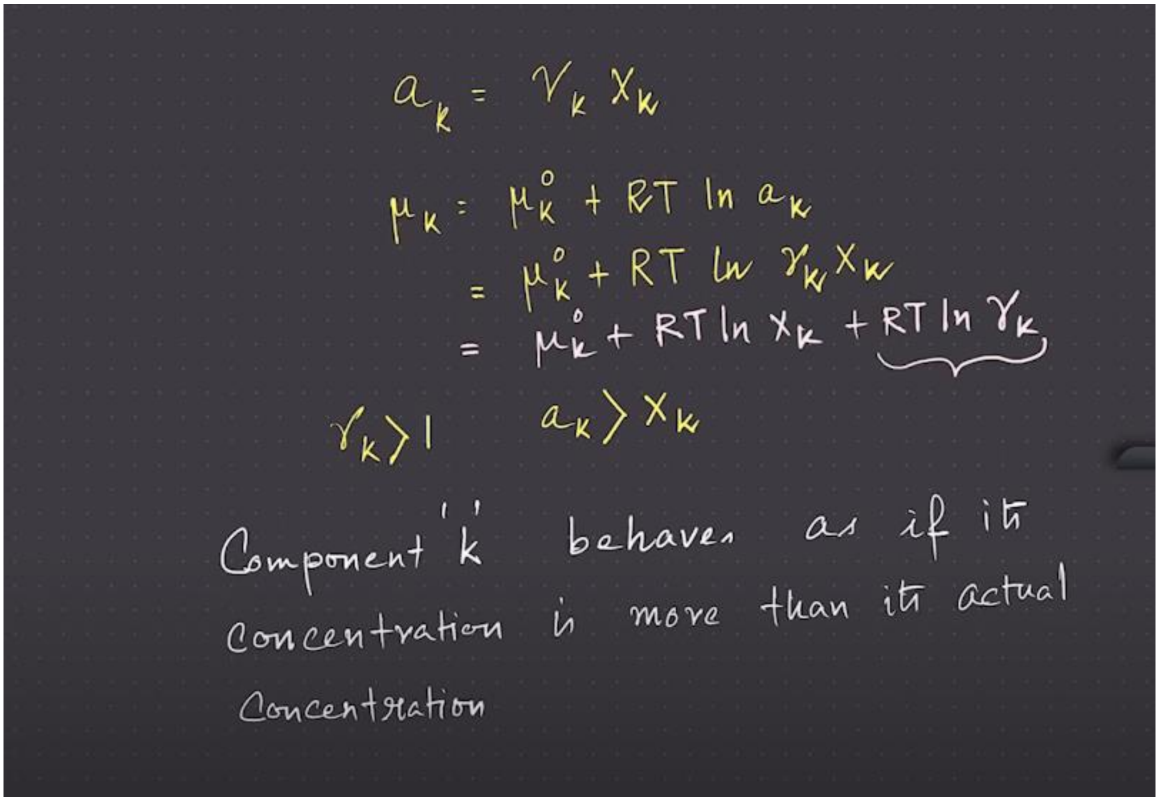
Now, if it is a 3 component system then Z_0 in this case equal to Z_1^0 plus Z_2^0 plus Z_3^0. See this is before mixing see these are before mixing we put them together. So, before mixing that total the Z_0 is basically now remember Z_1^0 is basically molar property or property of component k. So, Z_1^0 is molar property or property of component 1 per mole before mixing. So, this is property of component 1 per mole or molar property of component 1 before mixing before mixing means it is in the component is in the pure state right it is a pure component.



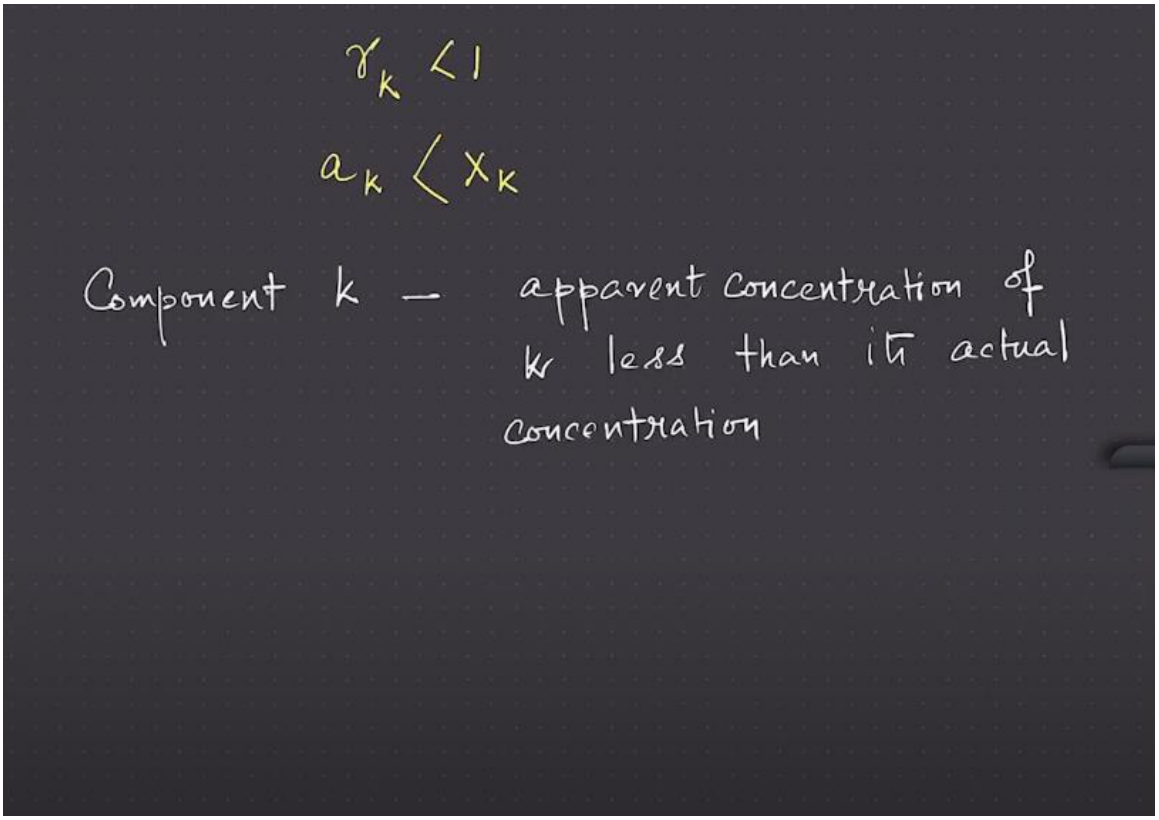
So, then so basically Z_k^0 is property of component k per mole before mixing in the pure or in the reference or in the standard state. When you have a superscript of 0 I am denoting what is called a standard state. Now, if I have this standard state and then the delta Z mix is equal to so delta Z mix is basically the change in the molar property or relative change in the property change in the property. So, you can call it like change in property due to mixing change in property due to mixing is delta. So, that is why there is a delta sign.



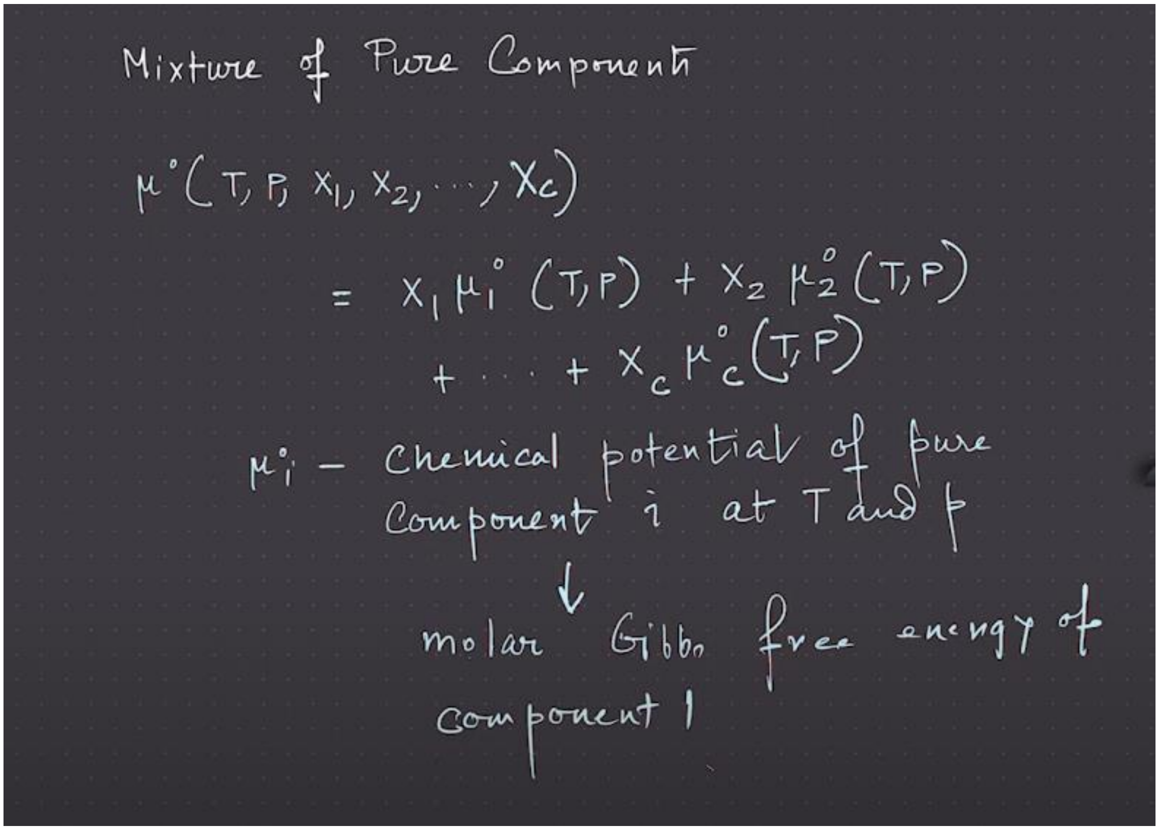
So, it is change in property due to mixing. So, that is equal to Z solution Z of the solution minus Z_0 where Z_0 is the sum of the sum of the molar properties of pure components weighted by the mole number. Sum of the molar properties of pure components weighted by the mole number. If you sum it up then what you get is Z_0 and Z_0 is an extensive property, but that is an extensive property of the mixture when we are not taking into account any mixing. So, it is like Z_0 is the sum of properties of pure components 1, 2, 3 and so on and weighted by weighted by the mole number of each component right.



So, that is Z_0. Now, Z solution is after mixing Z solution comes. So, this is after mixing all components and this is before mixing right. This is before mixing this is after mixing. Now, once you have after mixing minus before mixing this is the change right change in the property due to mixing. So, change in property change in property Z extensive property Z due to mixing.



So, change in Z due to mixing is basically the extensive property of the solution that is after mixing minus the extensive property of all the pure components weighted by the mole number of each component, because these are the components these are the boxes that you are mixing or these are the containers that you are mixing. So, 1 basically say for example, 1 the number of components is n the mole number is n 1 for 2 it is n_2 for 3 it is n_3. So, n_3 of $Z^0{}_3$ is coming n_2 of $Z^0{}_2$ is coming n_1 of $Z^0{}_1$ is coming and they give us 1 2 and 3. But however, the atoms of or molecules of 1 2 and 3 will mix right the atoms molecules will mix to form a mixture and that mixture if the homogeneous mixture is nothing, but the solution. Now, the solution will form and solution will have some property right which is Z solution and this is before mixing.



So, the difference between them is the change due to mixing right. Now, Z 0 equals to this sum right sum of n_k Z_k^0 where Z_k0 is the property molar property of the pure component k right and molar property of pure component k and n_k is the mole number of component k and Z solution when I am writing this also can be explained as a summation, but the summation is over now n_k times Z_k bar Z_k bar is the partial molar contribution of component k to the overall property of the solution partial molar property of component k or contribution of component k to the overall molar property of the solution and it is weighted by again the mole number of that component right and summed over all components. So, that Z solution is nothing, but Z for us right there is a Z that you measure for a solution and Z minus Z_0 gives me delta Z. So, delta Z mix as you can see here is again Z_k bar Z_k bar is the partial molar property of component k minus again this is a partial molar property and this is the molar property of the pure component k right. The difference between them is multiplied or weighted by n k gives me that delta Z mix or summed over all components it gives me the delta Z mix or delta Z mix.

So, if I look at delta Z_k bar that is for each component. So, for each component so here for example, I am considering only component k I can substitute k by 1 2 3 and so on. So, or a b c and so on. So, delta Z_k bar is the change or this is called relative partial molar property of component k or change in partial molar property of component k due to mixing. So, delta Z_k bar is basically Z_k bar minus Z_k^0 again this is nothing, but the pure slat standard.

Now, therefore, delta Z mix which is basically sum of this which is delta Z_k bar. So, if you can see here I am having this guy delta Z_k bar and instead of this I am writing this directly as delta Z_k bar. So, delta Z mix is delta Z_k bar multiplied by n_k and summed over all components. Now, if I want to do an exact differential if I want to find the differential of that. So, d delta Z mix because to k equal to 1 to c delta Z_k bar d n_k why because since n_k d delta Z_k bar will be equal to 0 because of again gives to him relation.

So, as you can see Gies-Lemme equation is not only valid for the partial molar property mu the partial molar property, but also for the relative partial molar property that is a delta mu right it is the or the relative partial molar property is the difference in the partial molar property after mixing difference often from that before mixing right. This is the partial molar property before mixing this is the partial molar property before mixing this partial molar problem the after mixing the difference between then gives me the relative partial molar property of component k. And n, so, basically if I extend Gibbs-Lemme I can write n k d delta z k bar equal to 0. Now, if it is so as we know that the molar property Z m equal to Z by n where a n is the total number of moles right and d Z_m is Z_i bar d x_i. Now, why is dx_i because d Z, so, as you see d Z equals to Z_1 bar d n_1 plus Z_2 bar d n_2.

Now, right. So, now, I am dividing I am dividing. So, d Z by n equal to Z_1 bar d n_1 by n plus which is n_1 by n is nothing, but x_1. So, this will become. So, this becomes the d Z by n or d Z_m is equal to this right. So, this is nothing, but Z_1 bar dx_1 right.

So, Z_y bar dx_i is d Z_m right. So, that we know right. So, now, it has become x i remember this has become mole fraction and previously it was mole number mole number is an extensive property, but mole fraction which is the ratio of n i and n right n is a total mole number total mole total number of moles of all components in the mixture on the solution and n i is the mole number of component i. So, x i is a ratio of these and so x i is an intensive property and we also know gives to n for example was n d mu. So, n_i d mu_i equal to 0. So, we had n_i d mu_i summation over i equal to C equal to C.

Now, if I again divide by n right we will get x i d mu i equal to 0 or d x i d let me call it here d Z_i bar. So, x_i d Z bar equal to 0 is a Gibbs-Dewine equation, but using molar molar mole fraction right. So, we are looking at mole fraction. So, this is again a Gibbs-Dewine equation this is Gibbs-Dewine equation, but uses mole fraction instead of mole number right. So, and again Z_m can be written as Z_k bar.

So, you have n_1 Z_1 bar plus n_2 Z_2 bar plus so on and if I divide by n again. So, if I divide so Z equals to this right Z equals to n_1 Z_1 bar n_1 plus Z_2 bar. So, if I take binary say n_2 now n_1 plus n_2 to n. So, Z_m which is equal to Z by n equal to Z_1 bar see it is already partial molar property right it is partial molar part mole right and this will be n_1 by n which is basically X plus this will be Z_2 bar right. These are very very important relations ok when we talk about molar free energy right we have already shown it in the tangent construction I am just surprising.

So, that you are clear with all these important concepts ok. Now, as you can see that if you do it for the change in the molar free energy right we looked at our molar property we looked at change in property right due to mixing change in the total property or change in the extensive property is given by d delta Z. So, delta Z sorry just given by delta Z. So, delta Z is the change in the extensive property ok due to mixing. So, therefore, just taking that Q we can also write something called delta Z_m which is change in molar property due to mixing ok.

So, if you do that then the Gibbs relation you can see here d delta Z m X equals to k equal to 1 to c delta Z_k bar d X_k instead of instead of writing d n_k that we wrote previously now you can use d X_k right. And d X_k basically basically means it is the differential of the mole fraction of the composition of component k in terms of mole fraction. So, delta Z_m mix for example, is delta Z_k bar X_k right and therefore, Gibbs duema also we can write as X_k times d delta Z_k bar which is equal to c. So, n_1 d mu_1 equal to 0 n_1 d mu_1 plus n_2 d mu_2 equal to 0 is equivalent to X_1 d mu_1 plus X_2 d mu_2 equal to 0 ok. So, delta Z_m mix if I call it as delta Z_m I just denote it as delta Z_m for convenience otherwise you have to always put a comma and all.

So, basically if that is so, this is the overall right now, but for each of these what about delta Z_1 bar the delta Z_1 bar is the relative partial molar property of component 1 which is again d delta Z d n_1 and keeping t_p and n_k which is not equal to 1 constant. So, delta Z 1 bar can be written as so, now you can see you have already done this ok this can be written as delta Z_m plus 1 minus X_1 d delta Z_m d X_1 right. How does it work you please refer to the last week's class and then you can easily find it is very important otherwise you can also do this way like this and delta Z you can write this way like delta Z_m equals to n delta Z_m and then you can carry out the partial derivative where you will use a chain rule then basically what you will get and this is something that I have shown in the previous class is this plus this right. So, delta Z_m plus 1 minus X_1 d delta Z_m d X_1. Now, if you look at this delta Z_2 bar also can be written as delta Z_m plus 1 minus X_2 d delta Z_m d X_2 right.

So, if that is so, you can see that d delta Z_m d delta Z_m d X_2 is equal to minus d delta Z_m d X_1 right. Why because X_1 plus X_2 equals to 1 so, d X_2 equals to minus d X_1 right. So, d delta Z_m d X_1 or d delta Z_m d X_2 d delta Z_m d X_2 equal to minus d delta Z_m d X_1. Another important thing that I want to mention is that all the partial molar properties can also be written using the same definitions of founding potentials that we have derived previously right. So, basically this is the partial molar enthalpy.

So, if you look at the partial molar enthalpy of component K which is equal to the partial molar internal energy of component K plus P times partial molar volume of component K. Similarly, the Helmholtz free energy F k right, if the partial molar Helmholtz free energy of component K equals to partial molar internal energy of component K minus T times partial molar entropy of component K. Similarly, we can write g K bar which is nothing, but mu K which is that the chemical potential of component K which is equal to h K bar again h K bar is the partial molar enthalpy of component K and S K bar is partial molar entropy of component K right. And we can also write something like Maxwell's relations for this partial molar quantities all of these are valid. So, this is one Maxwell relation right which is basically minus del S K bar del P right del S K bar del P equals to del V K bar del T at fixed pressure and mole number.

If the mole numbers are fixed and pressure is fixed and here it is temperature and mole number. So, del S K del P minus del S K bar del P equals to del V K bar del T this transform the equality of the secondary activities ok. So, one thing you have to understand is that we define something called activity instead of. So, instead of the mole fraction of components in the solution we define something called activity of component K in solution ok. And we generally never determine the chemical potential of components in a solution we generally determine something called activity.

So, activity of components in solution somehow should be related to the chemical potential, but remember this is what we determine experimentally we determine activity we do not determine chemical potential. Now, look at this relation mu K minus mu K 0 equals to delta mu K equals to R T and then A K ok this is the definition of activity you might have recognized this equation this is equation was written as mu K equal to mu K 0 plus minus right. So, it was previously now it is instead of X K. So, here I have given X K mu K equals to mu K 0 mu K 0 is a chemical potential of component K in the pure form or in the standard form plus R times R is the universal gas constant times T times logarithm of ln of X K right. So, something like this right instead of X K we will now use something called A K because we can directly determine activity, but we cannot directly determine chemical potential right.

Chemical potential is basically partial molar free energy and as with different types of energies that we have experienced energies cannot be evaluated directly, but activity can be determined ok. So, activity of component K in the solution is nothing, but the apparent concentration apparent concentration. So, as I told you activity is basically let it the composition of the component in a solution. So, activity if you look at the definition here A K equals to gamma K X K is basically this gamma K term which is an activity coefficient that comes in and this X K is nothing, but the actual composition of component K in the solution. So, as you can see for different gamma K's other than 1 A K is related to X K, but X A K gives the apparent concentration A K gives the.

So, basically what I want to say is that A K is the apparent it is a measure of apparent concentration of component K in the solution ok and A K equals to gamma K times X K ok and gamma K is again written as activity coefficient of component K. When gamma K equal to 1 as I told you when gamma K equal to 1 A K and X K are same right gamma K to 1 basically means A K equal to X K and activity of component K is concentration is basically the apparent so, remember to use about apparent concentration of component K in the solution that is A K. Now, as you know A K equals to gamma K X K and mu K I can write as mu K 0 plus RT and A K and that is basically nothing, but mu K 0 plus RT and then gamma K X K. Now, if gamma K is greater than 1 obviously if gamma K is greater than 1 then this can be written as by the way this can be written as mu K 0 plus RT ln X K plus RT ln gamma K.

Now, this is the part you can see that comes as X S. So, come now this part if gamma K for example, is greater than 1 this part will be positive right if gamma K is greater than 1. So, this part is positive activity which is X K times gamma K activity becomes greater than the movement fraction of component K and component K behaves as if the concentration of it of its concentration is more than its actual concentration X K. So, as if its concentration is more than its actual concentration which is nothing, but X K. So, that is how we define activity of a component in a solution. Similarly, if gamma K is less than 1 then RT ln gamma K is going to be negative right if gamma K is less than 1.

So, A K becomes less than X K and in that case the apparent concentration of component K is less than its actual concentration right. So, now we can also look at the mixture of pure components various pure components and that mixture of pure components means you have just put them together you have just added them together they are not yet mixing right they have just been added together and these are like pure components from 1 to n. Say for example, from 1 to n you have n clear components or you can think of instead of making any confusion you can tell up to this term. So, mu 0 basically is what I am trying to say. So, this is X c and this is mu c 0 at a constant temperature and pressure.

So, let me just use the same color. So, this becomes X c mu c 0 at the same temperature and pressure right. So, this is the mixture of pure components. So, this is the mixture of pure components up to X c where mu I 0 mu I 0 or mu K 0 is the chemical potential of pure component I in at temperature and pressure and that is nothing but the stand the reference or you can think of like a pure the it is like the partial molar Gibbs free energy of partial molar Gibbs free energy of component 1 in the pure form which is nothing but the molar is nothing but the molar. So, molar is the molar of component 1 right. So, now if you look at condensed mixture that is condensed mixture means mixture of liquids or mixture of solids in general for mixture of liquids or mixture of solids we consider the p v work and we have already seen some examples of p v work is negligent.

So, basically we keep p equals to 1 bar or 1 goes there on only when the p is of the order of some few kilobars or some giga like 10 giga Pascal or more that we have also shown you will see that in such cases p v work becomes important for the condensed mixture. So, if it is a condensed mixture of pure components. So, basically you have a mixture of pure components say for example copper and nickel you have mixed together and you have formed a solution a solid solution or you have taken say some acetone and water and you have formed a solution or some ethanol and water and you have formed the solution. So, in such a case the pressure is assumed to be 1 bar or 1 atmosphere and until very high pressure is applied this is because in such a case the p v work will be really really negligible right. If it is a solid solid solid liquid liquid solid type of or liquid liquid type of mixture.

So, in that case you have to remember that we have to keep pressure fixed at 1 bar or 1 atmosphere and we have to basically once you keep pressure fixed once you keep pressure fixed you can define properties molar properties or partial molar properties of a partial molar properties of the components in terms of only temperature because pressure is fixed right for condensed mixture we are taking the pressure fixed. So, basically as you see that you can express the molar free energy in terms of partial molar free energies or chemical potentials again here we are telling by if I take a binary mixture and before mixing this is before mixing has started because the mixing process is what you have collection of A atoms which is basically your species A and you have collection of B atoms your species B put them together unless the mix unless the mix they are still in that pure form the blocks are in that pure form right they have to mix and once they mix then basically you have found a solution before that it is like you have placed 1 block of A atoms 1 block of B atoms ok and so. So, basically if you look at the molar free energy as a function of temperature and so again pressure is fixed remember for once phases because pressure does not do much ok the PV work is negligible ok. So, basically g m is a function is equals to. So, g m is basically nothing but mu 0 and mu 0 is nothing but the molar partial molar free energy or chemical potential in the standard state which is equals to x A mu A 0 plus x B mu B 0 right x A mu A 0 plus x B mu B 0.

Now as you can see here you have this mu A 0 you have this mu B 0 there is nothing much has changed. So, this point is mu A 0 and this point is mu B 0 ok. So, in the next class I will start from here and I will tell how activity modifies the property of the solution ok how this definition or how all this that you have learnt basically why this before mixing and after mixing although I have given up an small atomistic picture before mixing after mixing how does this property how does this properties get modified is what I will do in the next lecture. Thank you.