Thermodynamics And Kinetics Of Materials

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Lecture 28

Quasichemical Approach and regular solutions

- Volumes of pure A and pure B are assumed to be equal

- Volumes of A and B do not change during mixing

- Interatomic distance and bond energy does not depend on composition

As we were continuing the regular solution model discussion, we basically are considering a A-B solution and we are assuming a quasi-chemical theory that is the A-B solution is like a large molecule and in this large molecule there are several bonds and these bonds are like you know these bonds are like A-A bonds, A-B bonds, B-B bonds right and all types of so basically this is like a it's a large chain so inside lattice you have like A-A-B arrangement in random and as a result if you have A-B arrangement in random for example let us look at this so I have like a box here the box I have lattice sites and you have like say A atoms and say B atoms let us give another B atoms and then you have A atoms, A atoms, A atoms are random and putting some A atoms and think of this as a periodic lattice so that there you have B. So this is like a large molecule this entire thing is like a large molecule and you have all these different types of bonds that are possible so what are the bonds possible you have bonds between two yellows so these yellows are say B atoms, B atoms and this is like A atoms so and this is again a B atoms so you can see A-B bond and you can also see B-B bonds, B-B bonds and you can also see A-A bonds right you can see various A-A-B-B so basically in regular solution model you want to look at the interactions

in such way and you are only looking at so pair wise interactions so for example if you are looking at an A atom then you are looking at its adjacent atoms say for example like simple cubic lattice there will be six adjacent positions right because if you think of a simple cubic lattice if you think of a simple cubic lattice you have these are in name and this is your arrangement so if you look at one atom here so you are basically looking at an atom here, looking at an atom here, you are looking at an atom here, here and also you are looking at here and right so basically you think of that if it is an A atom and let us assume that there is a B atom here so basically I extend it here and I see that there is a B atom here then again I extend it, I extend it this side so I am looking only at the nearest neighbors as you can see this is B atom. So basically if you look at that I am looking at only the simple cubic lattice for example I am looking at the nearest neighbor coordination which is Z equal to 6 right Z is equal to 6 so we are looking at A we are seeing this is B, this is B, this is say A-A-A-A and again say A-A-A so you have so just for this example configuration you have like 6 neighbors right 1, 2, 3, 4, 5 so and this is 6 so the 6th neighbor we can always think of this as so this is also another B atom. So B-B-B-A-A-A and this is your central atom so basically you are now going from atom to B now you go to B again you will look at neighbors so basically now you will have this additional neighbor let us call this a neighbor. So as you can see here whether you look at simple cubic lattice for Z equal to 6 or a BCC lattice if you look at BCC then as you know in BCC you have this in BCC you basically have you can draw BCC cell for example and I put this so excuse my poor drawing skills but what I am trying to say is for BCC lattice say for example you can look at a BCC lattice think of this as an A atom is an A atom say and then you have a B atom here say and a B atom here B atom here and let us assume that again you have A-A-A. Now think of the central atom now if you think of the central atom it has basically the name nearest neighbors are basically these 1, 2, 3, 4, 5, 6, 7 and 8 so there are 8 nearest neighbors so   Z   equals   to   8.
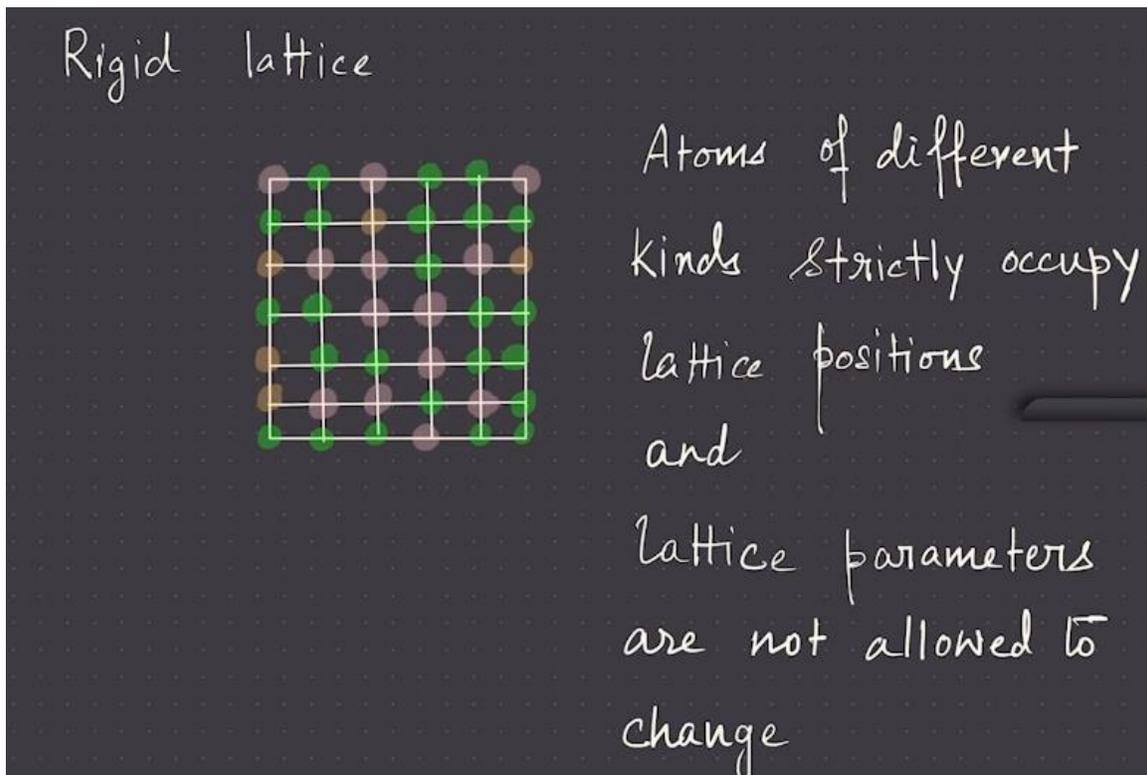
Similarly for FCC where you have this face centered cubic crystal structure then in this case Z equals to 2 but what I am trying to say here is this that you have a B atom you have say a B atom you have again some A atom and again this connectivity continues which is not restricted to one lattice so the BCC is expanding in space so basically as you know this is a periodic lattice structure and in that you have all these A atoms B atoms and every atom you go there are these 8 adjacent neighbors and these 8 adjacent neighbors you are basically counting the number of bonds you are counting the number of bonds. What type of bonds are we counting? We are counting bonds A-A, B-B and A-B and then we are writing E-E or U-U or E because to something like E-A-A which is the bond energy A bond energy times N-A-A which is the number of A-A bonds plus E-B-B which is the number of its B-B bond energy and N-B-B plus E-A-B N-U. Now this is what we are writing and we want to know how to calculate N-A-A, how to calculate N-B-B and how to calculate N-A-B using a mean field approximation means basically you will see that

regular solution model basically gives you a tool to calculate this A-A, B-B and A-B bonds you just do not go to a random lattice and just look at that look at the number of A-B bonds you count by hand it is not so it is a tool there is an idea and this idea comes from some of the assumptions of a regular solution model. One of the assumptions is volume of pure A and pure B are assumed to be equal volumes are assumed to be equal and volume of A and B do not change to be mixing and then inter-atomic distances and bond energies do not depend on composition, inter-atomic distance and bond energy does not depend on composition.

$$U \text{ or } E = E_{AA} N_{AA} + E_{BB} N_{BB} + E_{AB} N_{AB}$$

BCC $\quad Z = 8$

FCC $\quad Z = 12$

$Z = 6$
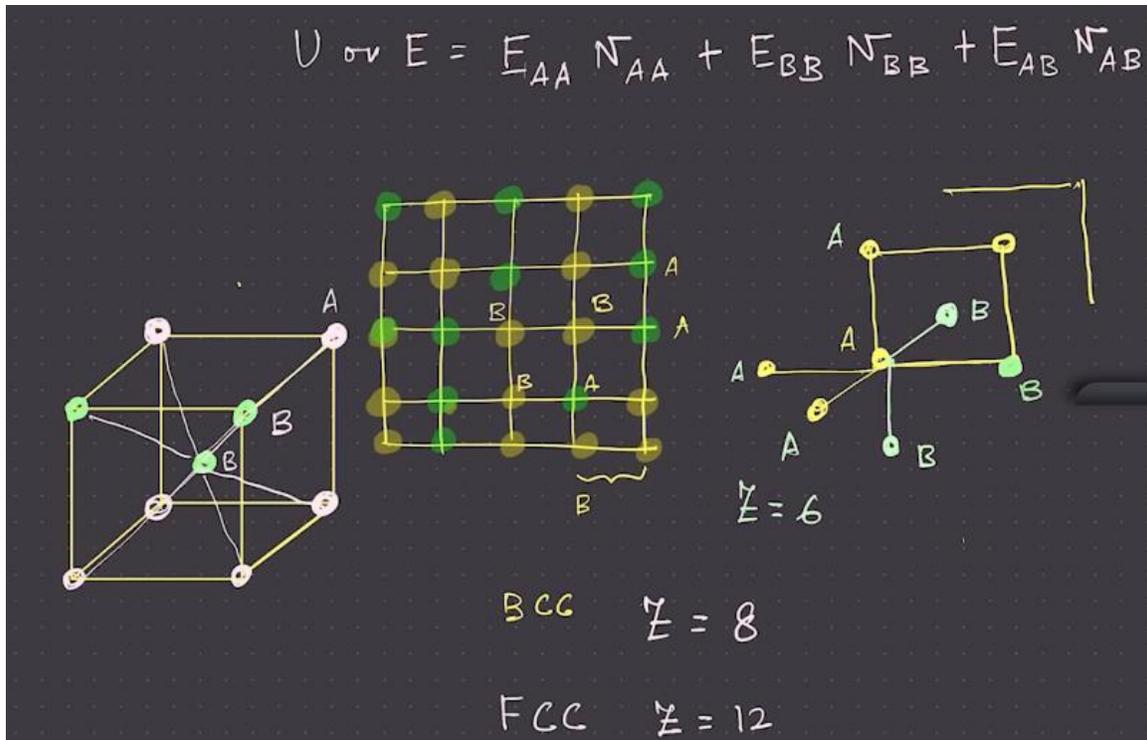
So if you look at that that is this random approximation this is the most important approximation in a regular solution model this is central to regular solution model for a disordered solution so regular solution model the major one of the major assumptions is this random alloy approximation. Now random alloy approximation basically gives you a way to calculate the number of bonds or how do you calculate the number of bonds because you assume the probability of finding a kind one kind of atoms basically one particular kind of atoms one kind of atoms is mole fraction of that type is equal to the mole fraction of that kind that means if you want to find say basically probability of finding one type of one kind of atoms so basically what I am trying to say probability of finding an A atom is equal to the mole fraction of B. Probability of finding a B atom is basically equal to the mole fraction of B so this approximation is called random alloy approximation and also it is also called mean field approximation. So regular solution theory is a mean field theory again we have an atomistic description right you have an atomistic description of A atoms and B atoms they are arranged in random in on the lattice sides and you have this different types of interactions that are possible AABB and AB and basically this random

alloy approximation gives you a way to find the number of A bonds number of B bonds and number of A B bonds and what I told what is the random alloy approximation? Random alloy approximation states that probability of finding an A atom on this on this quasi chemical solution or let us say like a large molecule or you can think of on a lattice where A and B are randomly arranged on a crystal in which A and B are randomly arranged is basically equal to the mole fraction of the probability so basically P of A P of A is the probability of finding an A atom on the lattice is equal to XA. Similarly P of B equal to XB so if I tell that now comes the most important part that now probability of finding an AB bond see because P of A is XA and P of B is XB so probability of finding an AB bond and AB bond is basically equal to XA times XB so this is something that we will use to calculate water NAA water NAA NBB and NAB.

Rigid lattice

Atoms of different kinds strictly occupy lattice positions and lattice parameters are not allowed to change

So, you also we assume a rigid lattice that is the lattice cannot relax there is no displacement of the lattice so the lattice positions do not change the lattice positions are the atoms only occupy rigid lattice means atoms only and strictly occupy lattice positions atoms of different kinds or atoms of different species like A atoms and B atoms in the binary solution strictly occupy lattice positions they cannot occupy positions any of lattice positions atoms of different kinds strictly occupy lattice positions it is called a rigid lattice assumption. So, one important assumption that there is no difference in molar volume of A and B of the species second approximation random approximation probability of finding an A atom is equal to the mole fraction of A probability of finding of B atom is equal to mole fraction of B probability of finding an AB bond is nothing but mole fraction of A times mole fraction of B right and second third assumption is rigid lattice that is the lattice

cannot start there is no possibility that the atoms cannot find so the lattice is fixed it is rigid and atoms strictly atoms of all kinds strictly occupy lattice positions they cannot occupy of lattice sites. And lattice parameters so this is another very important assumption for lattice that is a lattice parameters that is the length between these lengths are not allowed to change this is lattice parameter this is a lattice parameter and these lattice parameters are not allowed to change if the lattice parameters cannot change so it is called a rigid lattice assumption. And also another important thing we can later relax it but now we cannot so basically we are telling that there is no vacancy in the station if that is there the vacancy is there then the model is not just AB model but you can have AB and V right or and if you have interstitials the interstitials are between the lattice sites in between the lattice sites in those positions so these interstitials are also not allowed right or not means we are not taking them in this assumption right so for this regular solution model and we are all only considering pairwise interactions and again to the nearest neighbor only the adjacent atoms are interacting we are not we are neglecting for the time being the next nearest neighbors the second nearest neighbors and so on but you can extend this regular social model to include such interactions you can extend to include vacancies only thing the model becomes more and more complex. Now as you can see since it is a rigid lattice now if you look at the energy it can be called EX or you can call it UX that is the potential energy right now this as a function of R so and this is like Uij or Eij that is like now if you see you have an A atom and you have say a B atom you are taking them together you will see so each atom has this electrons right so that the so electrons and there is a positive charge at the nucleus right so the positive charges will repel the positive charge so if you take them together you have this electrons outer electrons shell and here also you have this outer electrons shell they will repel each other however so think of this the think of this way that say for example this is your outer shell and say this is the outer shell and say this is the positive core of this and this is also this positive core of this one the positive core of atom A and say this is B so positive of A is attracting the negative the electron cloud of B and similarly the electron cloud of so the positive of B is attracted by the electron cloud of A so positive so there is the protons that is the nucleus, the nucleus is attracting the electrons of A right nucleus of B attracting the electrons of A nucleus of A attracting the electrons of B that is possible so there is an attractive force so there is an attractive force and there is also because of this electron-electron interactions there is also a repulsive force right there is a repulsive force so basically you have a force of attraction and a force of repulsion so basically you can think of that there is how do I denote repulsion interaction so basically attraction means A is attracted towards B is attracted towards A another case A is reflected, repelled away from B and B is repelled away from A and this is true not only for AB it is also true for AA or BB now if that is so there is this repulsive part you see I have described late previously also this is the repulsive part and this is the attractive part and as you can see as you move further the interactions become equal to 0 right but this is positive which is repulsive and this is negative and as you can see there is because

of this balance between attractive and repulsive forces between atoms okay because of the interactions of the electrons and the protons that is a positive charged nucleus right positive charged nucleus and the electrons that is the outer shell so because of this interaction between the electrons and of B with the nucleus of A or electrons of B with electrons of A there is this balance between attractive and repulsive forces as a result you basically get energy landscape like this where this D is the equilibrium it gives you an equilibrium inter atomic   spacing.
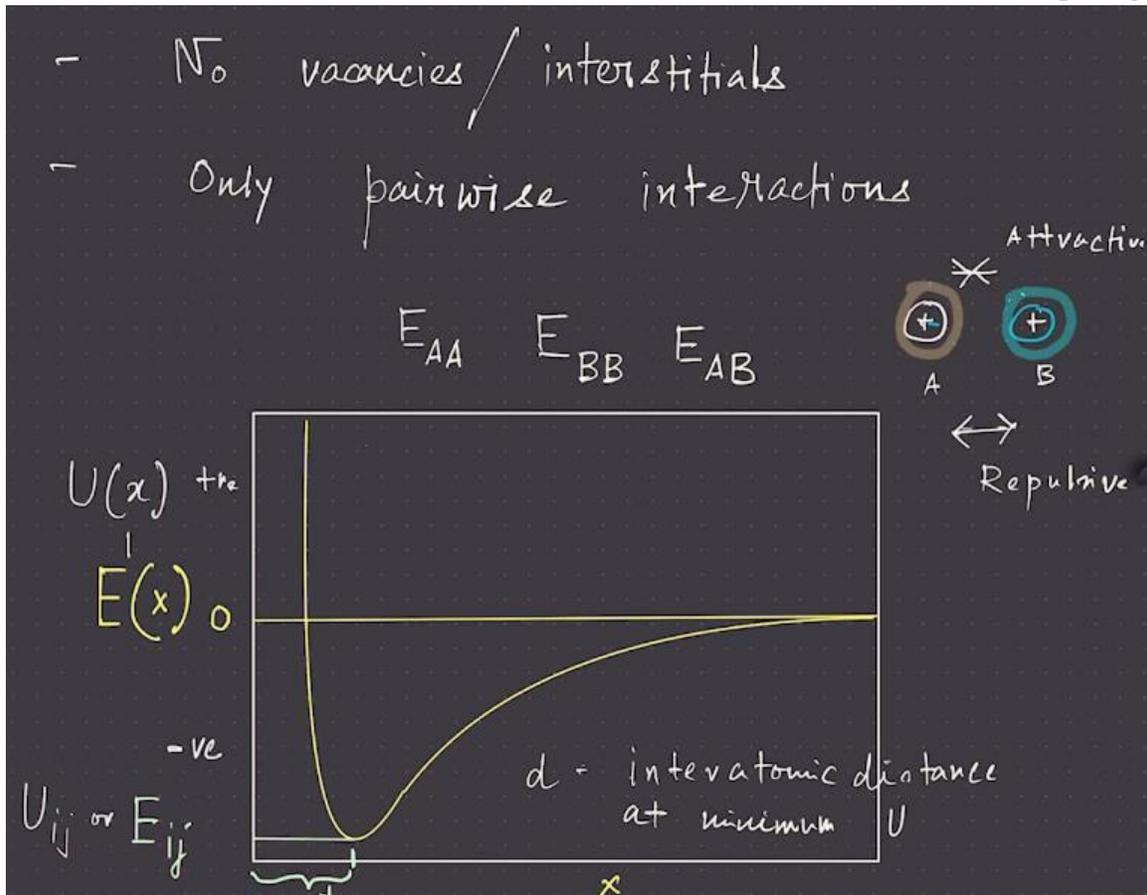
So, this is inter atomic spacing at minimum energy right as you can see there is a minimum here and this minimum corresponds to this distance and this is the inter atomic distance at minimum u okay so basically u D u i at D u i j is u i j again i can be A j can also be A i can be A j can be B or i can be B and j can be B right A A B B and A B again I am looking at only binary solution right we can extend it to further to ternary quaternary and so on but all cases the interactions are pair wise right the interactions are always pair wise and through the adjacent neighbors through the adjacent neighbors and D is the inter atomic distance at minimum u so as you can see here you have this E of D which is minimum so D is the inter atomic distance at minimum u that is basically the distance at equilibrium that is the equilibrium inter atomic separation distance right it is the inter atomic separation at equilibrium and that is what determines lattice parameter right this D is determining the so if you look at this this is your lattice parameter this D right now right this is the inter

width distance right now as you can see there is a minimum here right so there is this repulsive force and iterative force and they balance each other and as you know that negative derivative of potential is force so basically by integrating the forces you can get this we get the energy and plot the energy right you will see there is a minimum and

N_{AA} — number of A-A bonds

N_{BB} — number of B-B bonds

N_{AB} — number of A-B bonds

$$U_{soln} = N_{AA}E_{AA} + N_{BB}E_{BB} + N_{AB}E_{AB}$$

Total number of atoms $N_o = N_A + N_B$

A B C
AA BB CC } ternary
AB BC AC   solution

N_o → total num
N_A → no. of A atom
N_B → no. of B atom

this is what we are talking about that is the inter atomic distance and that does not change right for a digital lattice so that is the thing and as you know I can define NAA as the number of AA bonds NBB number of BV bonds and NAB number of AB bonds now u solution as I told you is NAA plus NBB EBB plus NAB EAB one very important thing to note is the bond energy has to be negative right bond energy has to be negative because the negative bond energy means it is a stable energy right it is a stable bond right so AA bond energy has to be negative so a positive energy has to be input to separate or to break the bond right the bond breaking energy is basically bond formation energy is always negative right because if it is negative then only the bond is stable but bond breaking energy is the opposite right it is basically the energy that is required to break the bond right AA bond has to be broken

so you have to give a positive energy so note that bond energies are negative right bond energies are always negative so you but you have this now you solution where you have this AA bond energy is BB bond energy and AB bond energy and AA bond energy is assumed in NAA that is the number of AA bonds so for each AA bond there is EAA right and for each VB bond there is EBV so the total energy is basically NAA that is number of A bonds times energy per bond right this is the EAA is the bond energy of any AA bond if you have an AA bond then the energy is EAA per bond right EAA is energy per bond and NAA is the number of AA bonds this is number of VB bonds again this is the bond energy of BB right so this is the BB bond energy this AB bond energy and NAB right that you cannot have any other extra term in this equation if you consider a binary solution now if you consider say a ternary solution you will have AA say if you have say three components A, B and C or three atomic species A, B and C then you can have AABB, A and CC and you can also have AB, BC and AC right these are the nearest neighbors interactions pair wise interactions that you can construct right when you have a ternary solution this is for a ternary regular solution. So, binary solution this is a complete expression of U right U the inner solution you have these different types of bonds you are counting the number of bonds and you know how to count the number of bonds and total number of atoms you can consider as NA plus NB which is NO and NA is the number of A atoms and B is the number of B atoms and number of A atoms and total number of atoms is the total number. Now look at this as I told you consider the central atom consider the central atom it has say for example a single cubic lattice has six nearest neighbors for face centered cubic as you know Z equal to 12 and for body centered cubic Z equal to 8 right Z equal to 8. So, for face centered cubic you have the face centers at half 1 1 0 distance if you look at half 1 1 0 is distance the nearest neighbor distance and so if you look at half 1 1 0 then basically you will see 12 nearest neighbors right. So, here it is 6 nearest neighbors right in this case D equals to A right and in the other case D equals to that inter atomic distance is basically D equals to A by root 2 right if it is the lattice for A parameter is A and this is also A then this is root 2 A right you have A here you have A here and so this is a square so diagonal is root 2 A right according to Pythagoras theorem so root 2 A by 2 or   A   by   root   2.
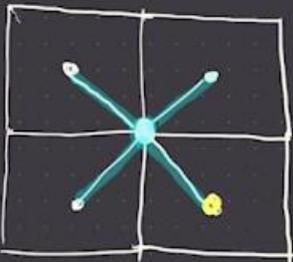
$$X_B = X \qquad X_A = 1 - X$$

face centred cubic
$$Z = 12$$
body centred cubic
$$Z = 8$$

$$Z = 6$$
Cubic

Total number of bonds $\quad N_T = \dfrac{1}{2} N_0 Z$

$$N_{AA} = \dfrac{1}{2} N_A Z X_A$$

$$Z X_A$$
$$\text{o} - \text{A} -$$
$$\text{b}$$

xy

xz

yz

$$= \dfrac{1}{2} N_0 Z X_A^2$$

$$= \dfrac{1}{2} N_0 Z (1-X)^2$$
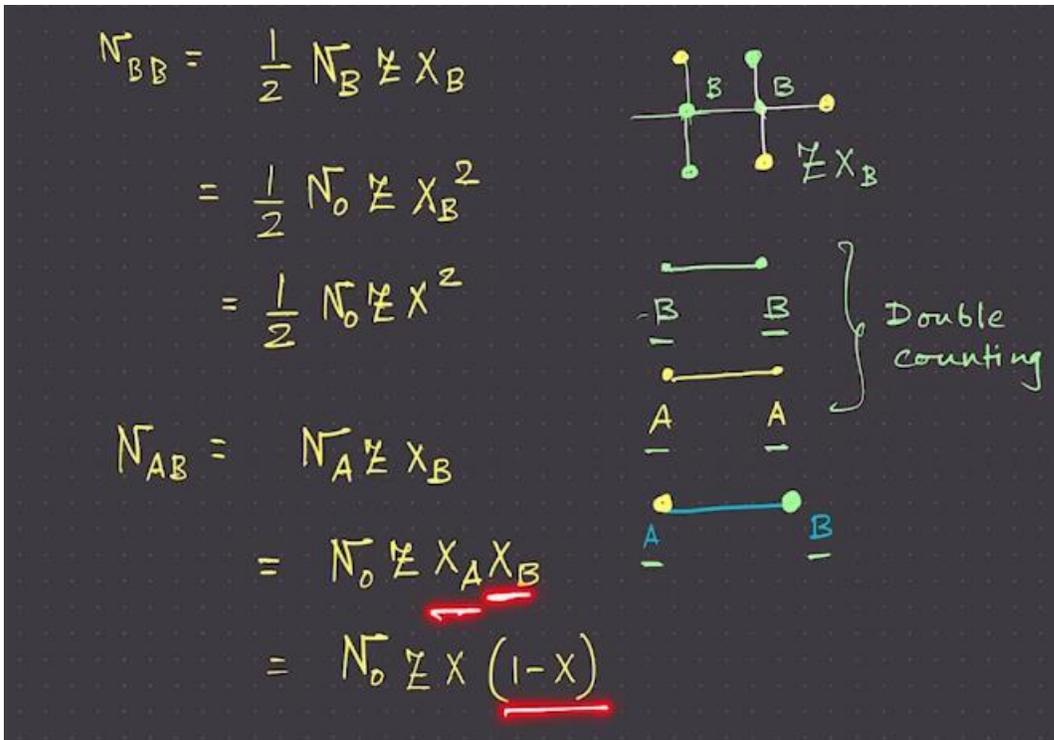
A $\qquad$ A

$$N_A = N_0 X_A$$

$$X_B = X$$
$$X_A = 1 - X$$

 So, basically for face centered cubic lattice imagine this face centered cubic when you have a face centered Y 12 is because you have an atom at the face center you have an atom here right and basically if you look at that there is another atom at the face center here this plane and then you have another plane right this is a plane here so this is the adjacent planes if you look at the planes you have this atom. If you look at the adjacent planes I just want to show you quite well so you see in one of the let us say let us consider only the X plane if you consider only the X plane or XY plane if you consider the XY plane so this is for the XY plane let us say so you have this atom 1, 2, 3, 4 now you have also XZ plane which will again have 4 and YZ plane which will again have 4 so basically if you look at this as a central atom this is your central atom this is your let me draw let me highlight the central atom here so if this is your central atom then you have 1, 2, 3, 4 neighbors in the XY plane itself right you have 4 neighbors in the XY plane itself right and now for the XZ plane again you have 4 and for YZ plane again you have 4 so total 12 neighbors and so 12 nearest neighbors so Z equal 12 for the center cube right so that is for FCC for simple cubic it is 6 for body centered cubic is 8 right now total number of bonds if you think of total number of bonds Z is the coordination number N0 is the number of atoms so N0 times Z is the total of bonds but I put a half here why because you have when you are talking about total number of bonds you are considering in pairs so if you are considering in pairs there

will be a double counting and therefore you have to have half right there is a factor of half so NT which is the total number of bonds is equals to half $N_0 Z$ but you need not use NT at all in your calculation you can basically directly see number of AA bonds again the probability of finding an AA is equal to probability of finding an AA bond is equal to X_A times X_A right but now you think of this you have one atom probability of finding the adjacent atom probability of having the adjacent atom to be A is X_A and how many adjacent positions are possible Z so Z times X_A is the probability of finding so if you have one atom of A you have one A atom now you are looking at Z nearest neighbors right Z nearest neighbors okay so if you are looking at Z nearest neighbors and you are telling that what is the probability of finding an A here so whether this guy is an A or not the probability of finding an A is X_A right or probability of finding an A is X_A here also X_A here is also X_A but these four comes from Z right so Z is the coordination number so Z times X_A is the probability of finding an A if you are sitting on an A and now if you are sitting on an A how many times you can sit on an A that is equal to the total number of A atoms right so therefore $N_A Z X_A$ now see this is the point you have one A atom here and one A atom here so basically you are sitting on an A you are trying to find an A right you are trying to find what is the probability of finding an A but you can again sit on this A and you can again count it right if you sit on this terminal A then again you can count this one so there is a double counting right if you have AA because these are two like atoms right this is A this is also A so if I go here then I get an AA if I come here I can so basically if I am placing myself here there is an A here but if I am placing myself here there is another A here but this is the same one so I am double counting therefore I have to put a half here right so half N_A, N_A is the total number of A atoms times $Z X_A$ right $Z X_A$ as you can see for any A you have $Z X_A$ as the possibility of finding an finding a adjacent A so basically for one A there are say $Z X_A$ times Z times X_A AA bonds right Z times for one A there is Z times X_A for N_{AA} there will be N_A times Z times X_A and again it seems there is this double counting as you can as I have demonstrated here that from here you go here this is one terminus so here you have A and you are now finding an adjacent A you are here so you got one bond like this now say you are here then again you get the same AA bond so there is a double counting therefore this half so you get now N_A is nothing but what is N_A? N_A is nothing but N_0, N_0 is the total number of atoms times X_A, X_A is the mole fraction of A. Now N_0 times X_A so basically N_A I am substituting as N_0 times X_A so then this becomes X_A square right this becomes X_A square as you can see here this is X_A square because this is N_0 times X_A and Z times X_A which is N_0 times Z times X_A square which is equal to half of N_0 times Z times 1 minus X whole square so basically what I am telling is X_B so we are assuming X_B equal to X so X_A equal to 1 minus X so then because X_A plus X_B has to be 1 for a binary solution right so this becomes half N_0 Z 1 minus X whole square similarly for N_{BB} so basically again if you look at this I will just demonstrate once so you have a B you are looking at the nearest neighbors you are looking at the nearest neighbors this B atom so this is your B atom you are looking at the

nearest neighbors the nearest neighbors can either be A or B so if this is A then it is a different bond but if it is B again if it is B again then basically how many so how many first of all how many nearest neighbors are there the nearest neighbors are given by Z right Z times now the probability of finding a B atom is X_B so basically Z times X_B so if you are sitting on B the probability of finding an adjacent B is Z times X_B now you have N_{BB} atoms so N_B times Z times X_B and again the point is double counting so you are sitting on this B you are counting this but you go to this B now when you go to this B now say for example I come I have extended it I will just extend it I will just extend it say for example it comes here now I have this B atom and say I have A here and I have B here and I can say B now as you can see here you have B here now say you are sitting on this B now one of the nearest neighbors is this so from here there was a nearest neighbor BB from here also you are counting the same one so you have again a double counting so whenever it comes to BB or AA that is the termination is in the same atom basically if you are looking at BB or we are looking at say AA or BB you are seeing the terminal, terminus is basically the same atom right the terminus is the same atom but if you think of AB if you think of AB so basically let us give it a color where you have one A atom and you have one B atom now you see that the counting here from A you are getting B or from B you are getting so basically if you are looking at that there is also BAM on right there is also a possibility of that right so here again you have to be very very careful but think of this when you count when you are taking this as the central atom if you are taking this as the central atom you are telling if I am on A what is the probability of finding a B if I am on B what is the probability of finding an A so I am going only once then there is no need to basically put the half right so basically if AB if you are considering AB you are not doing a double count of B like you do it in BB or AA right so because you are now sitting on A and finding B you are now not sitting in fact you would have done again N_B and Z X_A then there is a double counting right but if you do not do this if you do not do this if you avoid this then you have only one type counting and so basically you have N_A times Z times X_B so this is what you have right so N_A so here it is this exactly the same only thing X_B is nothing but X so this becomes half N_0 Z X square and this one becomes N_0 Z $X_A X_B$ which is basically X_A is nothing but 1 minus X and X_B is nothing but X right because I am now sitting on A and finding whatever the adjacent atom is B right whether the adjust so I am looking at A I am only looking at B I am not going back to B and looking at A

$$N_{BB} = \frac{1}{2} N_B Z X_B$$

$$= \frac{1}{2} N_0 Z X_B^2$$

$$= \frac{1}{2} N_0 Z X^2$$

$$N_{AB} = N_A Z X_B$$

$$= N_0 Z X_A X_B$$

$$= N_0 Z X (1-X)$$

$$Z X_B$$

Double counting

so I am not double counting in this case right in this case when the termination is in different atoms I am looking at A I am sitting at A I am looking at B or I am sitting at B I am seeking on B and looking at the nearest neighbor A right so if I do not add another term again like NB times Z times XA then there is no double counting when the termination is on different atoms right different atomic species not different atoms but different atomic species or different atomic types or different atomic kinds so if A is one kind of atoms B is another kind of atoms and if you are looking at AB bond then the termination is always on the other atom right other kind of atom right so on the other kind of atom so A is a different one than B remember this is something that I am repeating you may tell why am I repeating so much so that you do not get confused when you are on A and you are looking at A or you are on B and looking at B there is a chance of so in these cases only this double counting becomes an issue but if you are looking at AB then there is no double counting at least in this regular solution model for disordered solutions where the atoms are arranged in random right and that is why you can use the random alloy approximation that probability of finding an A probability of finding an A atom is nothing but the mole fraction of A right this is possible only we are telling that the arrangement of A and B on the lattice is completely random right then only we can use the random alloy approximation and that random alloy approximation basically tells me that the probability of finding an A on the lattice is equal to its mole fraction or probability of finding a B on the lattice is equal to its mole fraction right now if you see that

if you have now you have now NAA you have now NAA you have now NBB and you have NAB right so you have all of these right so NA times Z times XB which is N0 Z XA is B and XA is 1 minus X, XB is equal to X so you have this and here you have N0 Z X square with a half and here also half N0 Z minus X whole square now put them together so N0 divided by 2 Z 1 minus X whole square EA N0 by 2 Z X square EB plus N0 Z X 1 minus X into EA B right this is what you get now you can rearrange it a little bit why because 1 minus X whole square is 1 minus X times 1 minus X which is basically 1 minus X minus so if you write this this also is possible right 1 minus X into minus X 1 minus X right so basically you are taking 1 minus X as common right so 1 minus X so you can write this this way so 1 minus X minus X into 1 minus X is the same as this right so because 1 minus X is if you take 1 minus X common here then you get nothing but 1 minus X so these and these are equivalent right please look at this very carefully 1 minus X times 1 minus X can also be equal to this similarly X square which is X times X can be written as X in minus X times 1 minus X this is very clear X minus X plus X square so this is the X minus X cancels out so basically 1 minus X minus X into 1 minus X again if you look at this if you expand this or if you don't expand this also you take 1 minus X common you can see this is nothing but 1 minus X whole square and this X square again this is also X square right so basically these and these are equivalent these and these are equivalent are the same means these and these are the same and these and these are the same and we will substitute those right so basically what I am telling is I have this 2 X 1 minus X so basically here if I take n 0 Z by 2 as common n 0 Z by 2 as common then there should be a 2 here right

$$U_{soln} = \frac{N_0}{2} Z (1-x)^2 E_{AA} + \frac{N_0}{2} Z x^2 E_{BB}$$

$$+ N_0 Z x(1-x) E_{AB}$$

$(1-x)^2$

$= (1-x)(1-x)$

$= (1-x) - x(1-x)$

$= (1-x)$

$$= \frac{N_0 Z}{2} \left[(1-x)^2 E_{AA} + x^2 E_{BB} + 2x(1-x) E_{AB} \right]$$

x^2

$= x \cdot x - x(1-x)$

$= x$

$$= \frac{N_0 Z}{2} \left[2 E_{AB} \, x(1-x) - E_{AA} \, x(1-x) - E_{BB} \, x(1-x) + (1-x) E_{AA} + x E_{BB} \right]$$

if I take n 0 by Z by 2 here you have only n 0 Z then there should be a 2 here so you have a 2 so n 0 Z by 2 I have taken as common I have 1 minus X whole square EA A square E B plus 2 X 1 minus X EA B now we have this term 2 EA B X 1 minus X minus EA A right minus EA A X 1 minus X minus EA B X 1 minus X plus you have this term right this term has to be there right plus 1 minus X times EA A so I am using this to use instead of using 1 minus X whole square directly I am using this term so that I can split into X 1 minus X so that is what I have done I have split into X 1 minus X and here also X 1 minus X with a negative sign remember there is a negative sign in front of X times 1 minus X right and there is a positive sign in terms of X sorry in front of X or 1 minus X right so basically that is what I have done 1 minus X EA A 1 minus X EA A is nothing but X A 1 minus X EA A is nothing but X A EA A and this is X B E BB you see X is nothing but X B so this is X A EA A I have separated out X B E BB I have separated out but I have now put 2 EA B this X 1 minus X is now common for 2 EA B minus EA A minus EA B and this 2 EA B minus EA A minus EA E BB is called the regular solution this is called the regular solution parameter see the regular solution parameter multiplies with X and 1 minus X so basically which is nothing but X A sorry X B times X A so X is nothing but X B 1 minus X is nothing but X A which is same as X A times X B correct and you have now N 0 Z by 2 1 minus X now you see this is the mole fraction of A right 1 minus X is

nothing but the mole fraction of A which is nothing but X A and this is nothing but X B right now you see this is almost like the energy before mixing you have only AA right if you if you have only A atoms if you have only A atoms so A atoms I am defecting in general as yellow say if you have only A atoms in the box then you can only have one type of bonds which are the EA A that is pure A and similarly for pure B if you have only B atoms then you will have only BB bonds now the number of BB bonds obviously will be will come from X B and see there is a by 2 so N 0 Z by 2 X B EB B and N 0 Z by 2 X A EA A that is basically coming from something that is before mixing this is something that is basically before mixing

$$U_{soln} = \frac{N_0 z}{2}\left(2E_{AB} - E_{AA} - E_{BB}\right) \underset{x_B x_A}{x(1-x)}$$

$$+ \frac{N_0 z}{2}\underset{x_A}{(1-x)} E_{AA} + \frac{N_0 z}{2} \underset{x_B}{x} E_{BB}$$

regular soln parameter

$$S_{soln} = -R\left[x_A \ln x_A + x_B \ln x_B\right]$$

$$= -R\left[(1-x)\ln(1-x) + x \ln x\right]$$

$$G_{soln} = H_{soln} - TS_{soln}$$

so if you have that but you have this after mixing term right we have X 1 minus X as common or X B X A or X A X B as common and you have 2 A B minus EA A minus EB B with the N 0 Z by 2 now A solution I have already told right it is basically the same as the ideal solution the configuration entropy of mixing for ideal solution is the same as the configuration entropy mixing for a real solution that is what we have assumed right for a regular solution we have assumed that there is no change in the entropy of mixing or the configuration entropy for an ideal solution or a regular solution right so then this becomes I have derived it in multiple ways from the statistical mechanical from an atomistic standpoint we have derived it using Boltzmann's law and we have also derived it from this ideal solution model right we have derived by defining delta G we could define delta S or by defining G we can define S for an ideal solution right because S is nothing but a derivative of the negative of the partial derivative of G with respect to T right negative of basically S T T yeah at a constant pressure right so basically that is what we have so as

you can see here you have the same expression here as in ideal solution and G solution is H minus TS remember it is not U minus TS so H solution is nothing but U solution plus PV solution now as or you can tell that if you think of that final minus initial that is like the delta H mix and then it is nothing but delta U mix plus delta P delta V mix the point is P delta V mix for condensed phases is negligible or PV solution is negligible

$$H_{soln} = U_{soln} + PV_{soln} \simeq U_{soln}$$

$$\text{or,} \quad \Delta H_{mix} = \Delta U_{mix} + \underbrace{P\Delta V_{mix}}_{} \simeq \Delta U_{mix}$$

negligible for condensed phases

$$\therefore \quad G_{soln} = U_{soln} - TS_{soln}$$

$$= (1-x)G_A(T) + xG_B(T)$$
$$+ \omega_{AB}x(1-x) + RT\left[x\ln x + (1-x)\ln(1-x)\right]$$

so basically delta H is approximately equal to delta U or H solution is approximately equal to U solution now if I do that then G solution is nothing but U solution minus TS solution which is basically again you have omega okay so sometimes please do not get confused this omega is not like the Boltzmann's omega this we can actually for simplicity we can call it like you know omega okay so this is like omega A B let us call it omega A B which is a regular solution parameter so this is omega A B so instead of so this one you can substitute as delta A B and so that you do not get confused with the omega that is in the Boltzmann's hypothesis because we can often call it sometimes we call it W that is why so basically that is basically the maximum number of microstates so the number of configurations that can be achieved right there is a number of total number of configurations that can be achieved for the most probable microstate right so basically so the number of configurations that are possible right for the most probable or number of microstates right the microstates are possible for the most probable microstate or that

number of ways of arranging Na atoms of A and Nb atoms of B on N lattice sites right Na
so basically it comes from this N factorial by Na factorial Nb factorial is omega and then
you have this ln of that and then you take a Stirling's approximation and finally you end
up with the same expression as we have shown here as we have shown here so I am again
and again emphasizing this so this part is the regular solution parameter this part is coming
from the entropy so this is the entropy part this is the interactions part or the enthalpy part
but as you can see there is also this additional terms now these terms are nothing but like
1 minus XGA and XGB this is nothing but this corresponds to this guy and the next one
corresponds to this guy so I have written that in the next page

$$(1-x)\, G_A(T) = (1-x)\, \frac{N_0 Z}{2}\, E_{AA}(T)$$

$$X\, G_B(T) = X\, \frac{N_0 Z}{2}\, E_{BB}(T) \qquad A\ B\ A\ B \cdots$$

$$\omega_{AB} = \frac{N_0 Z}{2}\left(2E_{AB} - E_{AA} - E_{BB}\right)$$

$$\omega_{AB} = 0 \qquad \text{Ideal Sol}^n \quad E_{AB} = \frac{1}{2}\left(E_{AA} + E_{BB}\right)$$

$-ve$ departure $\omega_{AB} < 0$ Increase in no. of A-B bonds,
                                              ordering

$+ve$ departure $\omega_{AB} > 0$ Increase in no. of A-A and
                                              B-B bonds, clustering
                                              A-A-A-B-B-B

so 1 minus XGA t is nothing but 1 minus X n0z EAA and EAA can change with
temperature right EAA itself that atomic the bond energy can change with temperature so
EAA is a function of temperature so XGBt is nothing but X n0z by 2 EBB to gain a
function of temperature omega Ib that is the regular solution parameter is n0z by 2 EAB
minus EAA 2 EAB so if you take the common you have this term 2 EAB minus EAA
minus EBB so 2 EAB minus EAA minus EBB is the major parameter which and then you
have this coordination number Z and n0 is the total number of atoms and there is a factor
of 1 by 2 and this gives you the regular solution parameter but see it is a function of this

interaction right regular solution parameter is a function of this interaction so a balance between these interactions now as you can see when omega Ib equal to 0 2 EAB equals to EAA plus EBB or EAB in this case EAB equal to half of EAA plus EBB or see there is a balance between the interactions exact balance right they are exactly balancing out so that omega Ib comes out to be 0 right but if you have negative departure say think of this you have negative departure that means omega Ib is less than 0 you have omega Ib less than 0 there is an increase in number of AB bonds right there is a negative departure means increase in the number of AB bonds or Rd and positive departure means omega Ib greater than 0 that is increase in number of AAM to be bonds or cluster right positive departure indicates omega Ib is greater than 0 that means the increase in number of AAM to be bonds and that means basically there is a clustering of A atoms of like atoms like clustering of like   atoms   right

$$\therefore \quad \mu_i = G_m + \sum_{j=2}^{n} \left(\delta_{ij} - x_j \right) \frac{\partial G_m}{\partial x_j} \left. \right\} \text{ Generalized formula}$$

Binary system

$$\begin{cases} \mu_A = G_{soln} - x \dfrac{dG_{soln}}{dx} \\[4mm] \mu_B = G_{soln} + (1-x) \dfrac{dG_{soln}}{dx} \qquad x_1 + x_2 + x_3 = 1 \end{cases}$$

$$\delta_{12} = 0$$
$$\delta_{22} = 1$$

$$\mu_A = \mu_A^o + RT \ln \gamma_A + RT \ln x_A$$

$$\mu_B = \mu_B^o + RT \ln \gamma_B + RT \ln x_B$$

$$G_{soln} = x_A G_A + x_B G_B + \omega_{AB} x_A x_B + RT \left(x_A \ln x_A + x_B \ln x_B \right)$$

so that is why you call it clustering because A atoms want to be surrounded by A atoms and B atoms want to be surrounded by B atoms but when there is a negative departure A atoms want to be surrounded by B atoms and B atoms want to be surrounded by A atoms so there is an order right A atoms want to be surrounded like so if you have A which is surrounded by B and then B again surrounded by A so basically as you can see that there

is an ordering so basically there is a like like the ordering means you have A and then you have B and then again A then there is A so there is some order in the randomness right B and again you have A so basically I can write it the simpler way like A then you have B then A and then B and so on right that is basically the ordering and here you have like A A A and then suddenly if you have B then you have like B and so on right so this is just an example. Now as you know in a binary system you can find see this is something that I have derived in week 7 or in week 8 I have derived this expression generalized formula for n components right for chemical potential right for a solution we have derived the generalized formula where delta ij is kronecker's delta when i equal to j delta is equal to 1 if i not equal to j delta is equal to 0 and if you use this formula or you can also use the graphical method you will get mu A that is the chemical potential of A in the solution chemical potential of A in the solution can derive as G solution so you have G solution which you have derived now for the regular solution model including interactions minus X dG solution dx right and mu B is G solution plus 1 minus X dG solution dx right. Now but you also know that mu A equals to mu A 0 plus RTL gamma A plus RTL x A and mu B is mu B 0 mu B A 0 and mu B 0 are the pure state right it is you can call it mu A star also there is no problem because we are assuming that mu A 0 or mu B 0 are basically the chemical potentials of pure A or pure B right so basically these are like the the the molar frequencies of A and this is like the molar free energy of B right it because this is why molar not partial because it is 0 at 0 we are telling the standard state here is basically the pure   state.

$$\Delta G_{mix} = \omega_{AB} X (1-X) + RT \left[(1-X) \ln(1-X) + X \ln X \right]$$
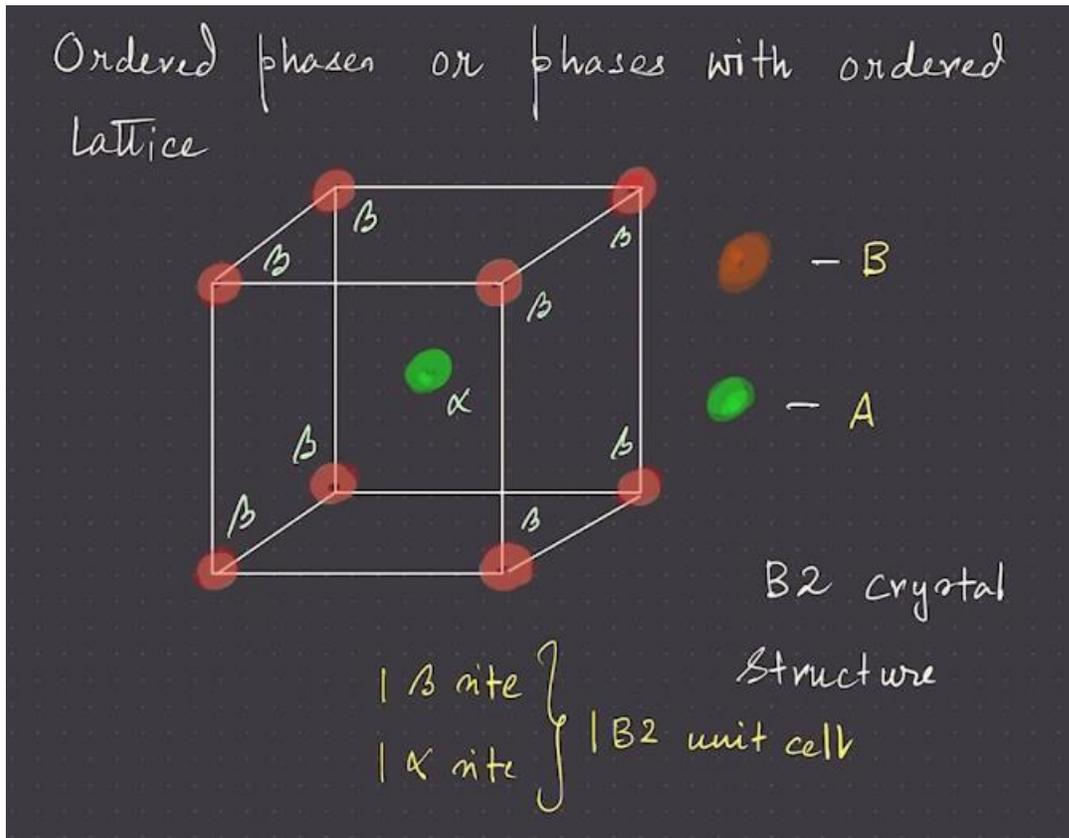
Prove that

$$\ln \gamma_A = \frac{(1-X_A)^2 \omega_{AB}}{RT}$$

$$\ln \gamma_B = \frac{(1-X_B)^2 \omega_{AB}}{RT}$$

Now you have this additional terms like RTL and gamma A is the excess term and now you can also derive from here right using this expression for G solution there is a G solution expression the G solution expression is here so 1 minus X GAT plus X GBT plus omega AB X 1 minus X plus this right so if you take this or you can write this simply so you know G solution equals to X A GA plus X B G V plus omega AB X A X B plus RT X A ln X A plus X B ln X A. Now as you know depending on the omega B formula your G solution will change I have also shown you how to get this graphically right in using this simple python script right so basically if you look at this this term this first two terms are basically before mixing terms right where you have only A atoms and where you have so you have a box of A atoms and you have a box of B atoms and they have mixed so just before mixing is these two terms. So, basically if you think of this after mixing the total term is this so basically delta G is nothing but if you can if you take subtraction from G if you take the subtraction GF minus GI so basically before mixing and after mixing so you have after mixing minus before mixing so after mixing you have G solution is this and before mixing G solution is only this right and after mixing it is the entire term right the entire term comes after mixing and before mixing it is just this. So, if you take a subtraction so final minus initial so if you subtract then what you get is delta G mix okay which is equal to this regular solution parameter again you can call it omega AB and this is nothing but X1 minus X is nothing but XA XB and then RT XA XA plus XB XB right. Now in

such a case you can prove the coefficient is definitely not 1 and the coefficient becomes ln gamma A is 1 minus XA whole square omega so this is like omega AB so in this case this is ln gamma AB and here this I mean omega AB by RT so you can see gamma A and gamma B varies as a function of XB or XA and it has it also has this parameter omega AB so definitely it is not equal to 1 right like in an ideal solution right gamma A gamma B are equal to 1 for ideal solution but now since there is an interaction C now look at this if omega AB equal to 0 then ln gamma A equal to 0 and gamma is equal to 0 which is not right when omega AB is 0 omega AB is 0 corresponds to ideal solution right omega AB equal to 0 corresponds to ideal solution but if omega AB is non-zero then you basically have now gamma A which is dependent on XA or XB right or the concentration of the solution right.

Ordered phases or phases with ordered Lattice

B — B

α — A

B2 crystal Structure

| B site
| α site } | B2 unit cell

 Now when you have ordered phase okay so we will quickly understand this when you have ordered phase you cannot use this regular solution model which is for a disordered solution where A disordered solid or liquid solution where A and B can randomly occupy any lattice side these ordered phases are more common in solids and in solids for example this ordered phase for example this is a BCC derivative this structure that I have shown is a BCC derivative so you have two distinct a very distinct arrangement here see B atoms are occupying this side the same body center side while the A atoms are all at corners right these are called beta side say and this is the alpha side so in alpha side you have A or in the beta side you have A so in fact I can do the other way in fact I can put like this is B

beta side you have B and alpha side you have A it just for conventional conventionally it becomes easy to look at that so A is so alpha side is occupied by A atom and beta side but the beta sides are the corners beta sides are the corners of the lattice right that is occupied so now each corner if you look at a periodic arrangement each corner is occupied by eight such cubes right each corner so basically one eighth so basically you have one eighth of so there are eight corner atoms but each corner is shared by eight eight eight lattices so basically one eighth into eight so you have like one beta side so in this B2 crystal you have one beta side B2 crystal you have one beta side if you just look at one unit cell then you have one beta side at one alpha side in one unit cell one B2 unit cell see if you have a disordered BCC B2 unit cell okay so we will continue this ordered phase discussion okay in the in the next lecture so thanks for your attention thank you you