

Thermodynamics And Kinetics Of Materials

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Lecture 30

Quasichemical solution model for ordered phases II

So in my previous recording I was in this slide and then suddenly it stopped because there was some problem with my the storage of my computer so I am really sorry for that I just go back so because I was continuing teaching I was continuing the derivation but somehow abruptly it stopped I did not notice so I will just go back a little bit and I will just tell you so this is the slide where it stopped so as you have seen that based on r_α which is basically the site of fraction of alpha sites that are containing A atoms or the right mounted atoms is r_α so you know the definition of r_α and you know the definition of r_β right so I will just reprise quickly so if you know the definition of r_α and r_β so you know basically r_α and you know r_β and then you also know X_A is the mole fraction of A and X_B is the mole fraction of P and we have taken an alloy composition of X_A equals to $\frac{1}{2}$ and X_B equals to $\frac{1}{2}$ right and we told that r_α is the fraction of alpha sites occupied by A and r_β is the r_β fraction of beta sites occupied by A. Also we define l which is the long range of the parameter as $r_\alpha - X_A$ by $1 - X_A$ which is equals to $r_\beta - X_B$ by $1 - X_B$.

Handwritten derivation on a chalkboard:

r_α - fraction of α sites occupied by A X_A
 r_β - fraction of β sites occupied by B X_B

$X_A = \frac{1}{2}$ $X_B = \frac{1}{2}$

B2 lattice NiAl

$$L = \frac{r_\alpha - X_A}{1 - X_A} = \frac{r_\beta - X_B}{1 - X_B}$$
$$L = \frac{r_\alpha - 1/2}{1 - 1/2}$$
$$L = 2r_\alpha - 1$$

or, $r_\alpha = \frac{1+L}{2}$

If $r_\alpha = 1 = r_\beta$ $L = 1$ (complete order)

If $r_\alpha = X_A$ or $r_\beta = X_B$ $L = 0$ (complete disorder)

Now when r_α equal to 1 then you have w_α equal to r_β like r_β or r_α 1 and this is the mean if r_α equal to 1 right which is complete alpha is also in the right and we also know if r_α equal to X_A or r_α equals to X_A or r_β equals to X_B right then in such a case you get r_α equal to c that is complete right that X_A or X_B as you remember that it is basically coming as a random alloy approximation right that we use in regular solution model right finding the probability of finding an A atom on the lattice site is equal to X_A is a regular solution assumption or a random alloy assumption right or random alloy approximation. So basically if we put r_α equal to X_A or r_β equals to X_B we basically get a long range of parameter of 0 which basically tells complete disorder right however we also started with a 50 atomic percent A 50 atomic percent B which corresponds to a B2 lattice or a B2 lattice right it is a B2 lattice one common B2 lattice example is NiAl right NiAl has a B2 structure nickel iron has a B2 structure. So basically if you look at that you have 50 percent nickel 50 percent aluminum or 50 percent A and 50 percent B now if that is so I can write r_α equals to r_α minus half by one minus half and from there we could do like $2r_\alpha$ right $2r_\alpha$ one minus half is basically let me write this one so one minus half is half so basically what we get is $2r_\alpha$ minus one equal to 1 or r_α equals to one plus 1 right so we basically got r_α equals to one plus 1 right

$$\begin{aligned}
 r_\alpha &= \frac{1+L}{2} & w_\alpha &= 1 - r_\alpha = 1 - \frac{1+L}{2} \\
 & & &= \frac{1-L}{2} \\
 r_\beta &= \frac{1-L}{2} & w_\beta &= 1 - r_\beta = \frac{1+L}{2} \\
 \\
 N &- \text{total} & r_\alpha \cdot \frac{N}{2} &= \# \text{ of A atoms} \\
 \frac{N}{2} & \alpha \text{ sites} & & \text{in } \alpha \text{ sites} \\
 \frac{N}{2} & \beta \text{ sites} & \frac{1+L}{2} \cdot \frac{N}{2} &= \frac{1+L}{4} \cdot N \\
 & & w_\alpha \cdot \frac{N}{2} &= \# \text{ of B atoms} \\
 & & & \text{in } \alpha \text{ sites} \\
 & & \frac{1-L}{4} & N
 \end{aligned}$$

similarly for X_B if I do the same way r_β is one plus 1 by two now we get w_α which is basically one minus one alpha that is the fraction of alpha sites occupied by the wrong atoms that is the B atoms which is basically one minus one plus 1 by two which is basically one minus 1 by two and w_β which is equal to one minus 1 by two right now we have n by two or 50 percent alpha sites if you have total number of sites is n total number of

lattice sites and n by two is alpha sites and n by two beta sites so basically what we are now telling what is n by two so basically if I tell r alpha times n by two what does that mean this is number of number of A atoms in alpha right r alpha times n by two and r alpha is nothing but one plus 1 by two one plus 1 by two into which comes out to be one plus 1 by two

$$\begin{aligned}
 \# \text{ of A atoms on } \alpha\text{-site} &= \left(\frac{1+r}{4}\right) N \\
 \# \text{ of A atoms on } \beta\text{-site} &= \left(\frac{1-r}{4}\right) N & \rho_{\alpha}(r) \\
 \# \text{ of B atoms on } \beta\text{-site} &= \left(\frac{1+r}{4}\right) N & \rho_{\beta}(r) \\
 \# \text{ of B atoms on } \alpha\text{-site} &= \left(\frac{1-r}{4}\right) N \\
 \text{Evaluate } N_{AA}, N_{BB}, N_{AB} \\
 P(\text{A on } \alpha\text{-site}) &= \rho_{\alpha} \\
 P(\text{A on } \beta\text{-site}) &= 1 - \rho_{\beta} = \rho_{\alpha} \\
 z & \text{ is coordination number of sites}
 \end{aligned}$$

similarly we have written number of A atoms on alpha site is one plus 1 by four into n similarly we can write r w alpha into n by two is number of B atoms on alpha in alpha site or in alpha sites so if I look at that which is basically one minus r alpha one minus r alpha is basically one minus 1 by two so basically this will become equal to one minus 1 by four so basically this is where we start here again so this is one plus 1 by four into n which is number of A atoms on alpha site number of A atoms on beta site will be one minus 1 by four into n similarly number of B atoms on beta site is one plus 1 by four into n and number of B atoms on alpha site is one minus 1 by two now you see if I want to know the number of A-A bonds and number of B-B bonds and number of A-B bonds what do I do first I find the probability of finding A on an alpha site which is basically given by r alpha now probability of finding A on beta site is given by one minus r beta r w beta so basically if z is the coordination number of sites basically what we are talking about is like if I am at an alpha site what is the coordination number that we or the nearest coordination so what is the what are the nearest sites that we can go to so basically if you look at that you basically if you have if you look at the BCC where the B2 order lattice then each alpha site which is the body centre this alpha site is nothing but so we have the body centre you can also do it for a corner you just have to draw another extra some extra in itself right so if you look at one body centre if you look at the body centre alpha site if it is a body centre then

it has it is surrounded by z times beta sites where z is the coordination number so B2 again new number is a BCC derivative so z is going to be 8 right so you can actually see that so if you look at the picture that we drew right you have the alpha site is the body centre it is surrounded by eight corners right it is the beta this eight corners of the eight beta sites so it is basically z beta is nothing but 8 into beta then it comes to B2 in itself B2 in itself if you have a B2 this is structure then what will be the B2 in itself you have eight beta sites that are surrounding one alpha site right that is so you have the A probability of finding an A pair is basically z right it basically z times r alpha right r alpha is probability of finding so r alpha is basically A on alpha site right so basically A on alpha site and one minus r beta is A on beta site right one minus r beta is A on beta site so this is A on alpha and this is A on beta and so this exactly that's gives me A pair so this is z r alpha one minus r beta so this has a r alpha is one plus l by two and r one minus r beta is one minus l by two so this becomes one plus l into one minus l by four and there is a z right so this becomes z into one minus l square by four now if I know the probability of finding one A there now I can estimate number of A A bonds only thing always remember if I am at an A and I am counting another A so this is at an alpha site this is at a beta site now from when I am in the beta site

body centre
Each α -site surrounded by $Z\beta$ sites

$$P(A-A)_{\text{pair}} = Z r_{\alpha} (1 - r_{\beta}) = \frac{Z(1+l)(1-l)}{4}$$

$$= \frac{Z(1-l^2)}{4}$$

$$\therefore N_{AA} = \frac{Z(1-l^2)}{4} \frac{N}{2} = (1-l^2) N$$

$$\therefore Z = 8 \text{ for B2}$$

then I am also again counting the A on the alpha site right so basically there is a double counting so therefore we multiply when I looked at N_{AA} we have P_{AA} times N instead of writing P_{AA} times N I will write P_{AA} times N by two because there is a double counting so you have one terminals to the other terminals so if you have here the alpha site and here beta site you can come to beta site and count this alpha site again so there is a double counting so there is a two here now that actually gives me more simplification because two times four is eight and z is also eight right for B two since z is eight for B two

I can write this N_{AA} there is a number of A bonds is basically right number of A bonds is basically one minus l square right one minus l square into N because z is eight four times two is eight eight and it cancels out so this becomes one minus l square right similarly for N_{BB} it will be equal to z if I look at N_{BB} it will be z r beta one minus r alpha that is equals to P_{BB} right now this P_{BB} times N by two so P_{BB} times N by two again this double counting will come so as a result so if that is so then you have r beta which is one plus l by two and one minus r alpha which is one minus l by two so basically you get N_{BB} to be exactly the same as N_{AA} there is number of B B atoms and number of that is the number of B B bonds and number of A A bonds have the same expression N_{AA} has one minus l square by N N_{BB} also is one minus l square by N right now comes N_{AB} now for N_{AB} look at this so if I have r alpha so probability of P A on alpha and B on beta or you can think of this is basically z equal to z r alpha r beta now P A on so you can write B on alpha say for example I am on B on alpha if B is on alpha

$$\sum w_{\alpha\beta} (1-w_{\alpha}) = P_{(B-B)} \quad N_{BB} = (1-l^2)N \quad A-B$$

$$N_{AB} = \sum [w_{\alpha} w_{\beta} + (1-w_{\alpha})(1-w_{\beta})] \frac{N}{2}$$

$$P(A \text{ on } \alpha) (B \text{ on } \beta) = \sum w_{\alpha} w_{\beta} = \sum \left[\frac{(1+l)^2}{4} + \frac{(1-l)^2}{4} \right] \frac{N}{2}$$

$$P(B \text{ on } \alpha) (A \text{ on } \beta) = \sum w_{\alpha} w_{\beta} = 2(1+l^2)N$$

$$= \sum (1-w_{\alpha})(1-w_{\beta})$$

B	A
A	B
B	A

I have to have A on beta right for an A B bond so this basically becomes z w alpha w beta right so B on alpha is w alpha and A on beta is w beta right so w alpha w beta which is one minus r alpha one minus r beta right which is one minus r alpha into one minus r beta right so basically you have that so you have z again you have this z coordination number right which is for B to this A so r alpha r beta one minus r alpha one minus r beta now again you can see that you are going from A then alpha or A on beta say for example with a B on alpha or you are looking at A on alpha and B on beta now if you are looking at that you have A B as well as B A so there is a N by 2 right there is a double counting right

there is a double counting so if it is so you have this N by 2 here or if you have N by 2 here and r alpha times r beta is one plus l square by four this is one minus l square by four and this is N by 2 and there is a z here so basically if you see two times four is eight eight and z cancels out so you have one plus l square one plus so this is basically going to be one plus two l plus l square plus one minus two l plus l square so two l minus two l cross two goes out so you get two into one so basically you take what is equal to right so basically I do one thing this is the r alpha that I have done right and so if you see that this comes so there is a N by 2 factor right so it is N by 2 factor because why N by 2 because it cannot be N simply because if it is N simply then you are doing a double counting right so N by 2 so it is eight and there is eight so this is basically this and so this one plus l whole square plus one minus l whole square basically becomes one plus l square but there is a two right because one plus l square and again here is one plus l square which is two plus two l square is two into one plus l square times N now if you look at that the enthalpy of mixing is nothing but $N_{AA} e_{AA}$ right it is $N_{AA} e_{AA}$ plus $N_{BB} e_{BB}$ plus $N_{AB} e_{AB}$ right we are only looking at the nearest neighbors

Enthalpy of mixing $H_{\text{ord}} = N(1-l^2)(E_{AA} + E_{BB}) + 2N(1+l^2)E_{AB}$

$N_{AA}E_{AA} + N_{BB}E_{BB} + N_{AB}E_{AB}$

$S_{\text{conf}} = k \ln W$ - Boltzmann's law

$W = \left\{ \frac{\left(\frac{N}{2}\right)!}{\left(\text{No. of A atoms on } \alpha\right)! \left(\text{No. of B atoms on } \alpha\right)!} \right\}$ ← α -sublattice

$X = \left\{ \frac{\left(\frac{N}{2}\right)!}{\left(\text{No. of A atoms on } \beta\right)! \left(\text{No. of B atoms on } \beta\right)!} \right\}$

now if it is so N_{AA} and N_{BB} has the same expression so basically N_{AA} and N_{BB} have the same expression which is N into one minus l square right so basically that is what is right you have N_{AA} or N_{BB} which is one minus l square into N so one minus l square into N is taken into common and you have e_{AA} plus e_{BB} e_{AA} and e_{BB} are the bond energies right AA bond energies and BB bond energies remember that a can be so here when I am looking at AA on this ordered lattice it is like a on an alpha side and a on the beta side right so now for e_{AB} which is two N one plus l square just we have two N one plus l square so that is

what I am doing two N one plus l square into a now you have that is the N ab e ab now if you have that you already got what is called the enthalpy of mixing for the ordered lattice right for the ordered lattice now you will use Boltzmann's law S conv equal to k N omega to basically or k N N w to get the configuration of entropy right so w equals to now if you look at that the first part is for the alpha side right this is alpha sub lattice in fact it is called the alpha sub lattice so and then there is a multiplication

$$\begin{aligned}
 &= N \ln \frac{N}{2} - \left(\frac{1+L}{2}\right) N \ln \left(\frac{1+L}{4}\right) N \\
 &\quad - \left(\frac{1-L}{2}\right) N \ln \left(\frac{1-L}{4}\right) N \\
 &= N \ln N - N \ln 2 - \left(\frac{1+L}{2}\right) N \ln \left(\frac{1+L}{4}\right) \\
 &\quad - \left(\frac{1+L}{2}\right) N \ln N \\
 &\quad - \left(\frac{1-L}{2}\right) N \ln N - \left(\frac{1-L}{2}\right) N \ln \left(\frac{1-L}{4}\right) \\
 &= \ln N \left\{ N - \left(\frac{1+L}{2}\right) N - \left(\frac{1-L}{2}\right) N \right\} + \dots
 \end{aligned}$$

and again if you look at this this is for so this is for the so the top one is for so top one is alpha sub lattice so in alpha sub lattice okay you have N by two sides now in N by two sides you are arranging okay in the N by two sides that N by two alphas over the sides you are arranging A and B so you have number of atoms in alpha factorial and so in the denominator of any number of a atoms in alpha factorial Airbnb alpha factorial 71 and b on a proud factorial electorate c on alpha factorial and b on alpha factorial so if you think of that a on alpha we have already written right we have already written yeah a on alpha is one plus alpha is one to n and b on alpha is one minus alpha is one to n so basically that is what we are writing in factorial now this is for the beta sub lattice this term is for the beta sub lattice remember it is a product of two a product of arrangement in the alpha sub lattice and beta sub lattice because the entire ordered of the star is made up of two sub lattices one is alpha another is beta so this is for the beta sub lattice this is for the beta now if that is so again for beta sub lattice we it is 50 50 right alpha number of alpha sides are 50 percent and number of beta sides are 50 percent this is the N by two and N by two so you have N by two factorial in the numerator in both and you have only in the denominator you have the the the a atoms on alpha factorial means how to arrange a so basically you are arranging this N by two atoms on this N by two sides on this N by two alpha sides and

how are you arranging you are arranging a atoms and b atoms and as you know that number of a atoms on alpha they are basically in distribution between one another and again number of b atoms so so basically a atoms are in distribution right they cannot you cannot you can distinguish a from b but a from a would not so basically you have to write this formula

$$\begin{aligned}
 &= \ln N! - N \left\{ \ln 2 + \left(\frac{1+L}{2}\right) \ln \left(\frac{1+L}{4}\right) + \left(\frac{1-L}{2}\right) \ln \left(\frac{1-L}{4}\right) \right\} \\
 &= -N \left\{ \ln 2 + \left(\frac{1+L}{2}\right) \ln(1+L) - \left(\frac{1+L}{2}\right) \ln 4 + \left(\frac{1-L}{2}\right) \ln(1-L) - \left(\frac{1-L}{2}\right) \ln 4 \right\} \\
 &= -N \left\{ \ln 2 - \left(\frac{1+L}{2}\right) \ln 2 - \left(\frac{1-L}{2}\right) \ln 2 + \frac{1}{2} \left[(1+L) \ln(1+L) + (1-L) \ln(1-L) \right] \right\} \\
 &= N \left[\ln 2 - \frac{1}{2} \left\{ (1+L) \ln(1+L) + (1-L) \ln(1-L) \right\} \right] \\
 &\qquad\qquad\qquad R = k N
 \end{aligned}$$

right we wrote previously N factorial by N a factorial and b factorial for example for regular solution model right so you have now because N a factorial why because N a was a number of a atoms and N b was a number of b atoms now in this case we are looking at number of a atoms but on alpha so which is one plus L by four into N and this is one minus L by four into N and this is one plus L by four into N and this is one minus L by four into N and this is one plus L by four right and it is just factorial so if you look at that you have L n w right a six k L n w so we found out w now if you so I am looking at k, k is the Boltzmann constant so k L n w or k B L n w and if you look at that L n w which is L n N by two factorial one plus L by four into N factorial right this term and this term again you have a product of N by two factorial by the same terms like one plus L by four factorial into N factorial one minus L by four into N factorial right now if you have that what you can do you can basically now take L n N by two factorial minus L n one plus L by four into N factorial minus L n one minus L by four into N factorial but you see which is the same here as well as here so this becomes so this is N by two factorial and again here N by two factorial so this becomes two N by two factorial two L n N by two factorial this is two L n minus two L n one plus L by four into N factorial it is minus two L n one minus L by four into N factorial and that is so you can write now further you can simplify say for example now you can use starlings approximation what is starlings

approximation? N factorial L n of N factorial equals to $N L$ n minus N actually there is also plus one but that plus one is empty because N is very large so if that is so you have two N by two L n N by two minus two N by two right so basically and here again you have two L n two one plus L by four into $N L$ n one plus N by four into N minus so here there is a minus sign so it should be plus now if you see this plus two one plus L by four into N again here also there is a so here also you look at this guy so again if you look at the starlings approximation here so you have one minus L by four into $N L$ n one minus L by four into N minus and this minus and here there is a minus so this is the here there is a minus sign here there is a minus sign so I can put the minus sign properly minus signs here so as you can see and so you have two L n one minus L by four in factorial so this is the minus two this thing but there is a $N L$ n minus N right so minus N means it becomes plus so plus two one minus L by four into N now if you look at that two one plus L by four into N this term this term is like this term right two into an N by two factorial is two N by two N by two minus two N by two so this term and this term and this term if you combine you get basically N here and here you basically get one plus L by two into N and here you get one minus L by two into N you add them up so basically you get here N minus N by two minus N minus N plus N by two plus N by two so basically this can cancel so this this and this cancel out. Now if you see you can further simplify you have this term you have now this term now in this term you have L n this term plus into N so if you think of log of $A B$ this is what I used is log of A plus log of B or L n of A plus L n of B if it is L n A now what I am doing now here is so you have two N by two L n N by two right so basically I am writing as $N L$ n N by two minus one by one plus L by two into $N L$ n one plus L by four into N and again so basically I have just rewritten that for clarity right because this terms have gone right this term this term and this term have become zero right they have cancelled out.

$$S_{\text{conf}} = R \left[\ln 2 - \frac{1}{2} \left\{ (1+L) \ln(1+L) + (1-L) \ln(1-L) \right\} \right]$$

$$L=0 \quad S_{\text{conf}} = R \ln 2$$

$$\text{In the limit of } L=1 \quad S_{\text{conf}} = 0 \text{ (complete order)}$$

$$G = H - TS$$

$$= N(1-L^2)(E_{AA} + E_{BB}) + 2N_s(1+L^2)E_{AB} + RT \left\{ \ln 2 - \frac{1}{2} \left[(1+L) \ln(1+L) + (1-L) \ln(1-L) \right] \right\} + N S_v^0$$

Now if that is so now if I write this this guy I am writing as $L \ln L + (1-L) \ln(1-L)$ right and here also minus one plus L by two N now this I am writing as a product right $\ln(A \cdot B) = \ln A + \ln B$ so $L \ln(1+L) = L \ln 1 + L \ln 2$ and then again you have the same minus one plus L by two into N so this is exactly what I am writing here so minus one plus L by two into N $L \ln N$ right there is an $L \ln N$. Similarly if I expand here also one minus L by two into $L \ln L + (1-L) \ln(1-L)$ and then again minus one by L one minus L by two into N $L \ln(1-L)$ right so now you have this term you have this term right this has $L \ln N$ this has $L \ln N$ there should be another term yeah there is one more term there $L \ln N$ you have now N has come minus one plus L by two into N minus one minus L by two into N so if you look at that this becomes basically N minus so if you have so if this is one plus L and this is one minus L and there is by two so it is minus N by two minus N by two and this is plus N so this becomes zero right this term becomes zero. Now you have minus N and now if you simplify further you have $L \ln 2$ and you have having like one plus L by two and N you can take as common right you can take N as common now you can take N as common now here and here and here right so if you take that as common I have taken that I have taken minus N as common in fact

S_v^0 - Vibrational entropy per atom

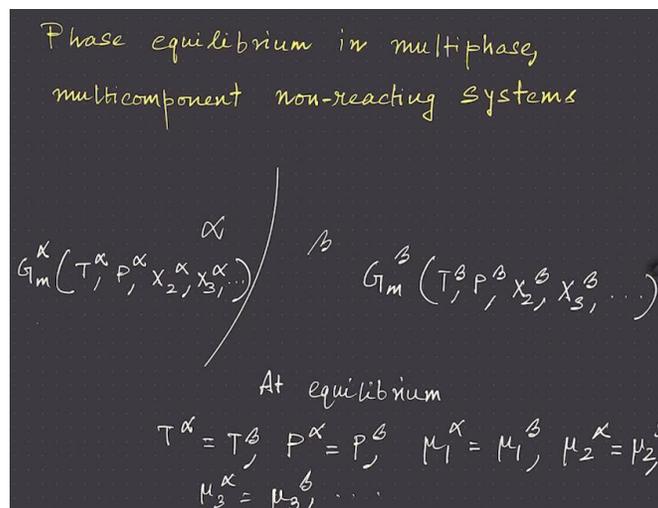
3N independent oscillators

$$S_v = k_B \sum_{i=1}^{3N} \left[-\ln(1 - e^{-\beta \epsilon_i}) + \frac{\beta \epsilon_i}{e^{\beta \epsilon_i} - 1} \right]$$

$$\beta = (k_B T)^{-1} = \frac{1}{k_B T}$$

so I have $L \ln 2$ but since minus N I have taken as common minus N so this becomes plus $L \ln 2$ right so minus N is common so this is $L \ln 2$ and if I now look at N again here so now you have minus I have taken as common so this becomes plus right so this is really becomes one plus L by two and then one plus L by four and one minus L by two and then one minus L by four now you have minus N common $L \ln 2$ and this is one plus L by two $L \ln 1$ plus L right $L \ln 1$ plus L by two and this is again this is like $L \ln A$ by B goes to $L \ln A$ minus $L \ln B$ exactly that is what I am using so $L \ln 1$ plus L by four I am writing as $L \ln 1$ plus L minus L by four and you have also this coefficient which is one plus L by two right one plus L by two. Similarly for this term you have one minus L by two as coefficient and this is written as $L \ln 1$ minus L minus L by four now if you see so you have a minus sign and four here also minus sign four right so basically if I take this common because $L \ln 4$ is nothing but two $L \ln 2$ right two $L \ln 2$ because $L \ln 2$ square because two $L \ln 2$ so you have $L \ln 2$ minus one plus L $L \ln 2$ right you have $L \ln 1$ minus one plus $L \ln 2$ because two and two cancels out right if I put out two here and two $L \ln 2$ and two and two cancels out so you have one plus $L \ln 2$ plus one minus $L \ln 2$ and then plus half right there is a half remain one plus $L \ln 1$ plus $L \ln 1$ minus $L \ln 1$ minus L and basically if you now rearrange you get $L \ln 2$ here now if you see here there is a minus sign there is a $L \ln 2$ here and see if you look at this if you add them up one plus $L \ln 1$ minus $L \ln 1$ $L \ln 2$ cancels out so this becomes $L \ln 2$ minus two $L \ln 2$ which is minus $L \ln 2$ and there is a minus sign absorb the minus sign so this becomes $L \ln 2$ and this guy becomes plus becomes minus right so $L \ln 2$ minus half one plus $L \ln 1$ plus L plus one minus $L \ln 1$ minus L and if you see n if I take assume n number of lattice size n is basically equal to Avogadro number for one mole of atoms right one mole of material or one mole of the ordered phase one for one mole of the order phase n is nothing but the Avogadro number then R is the universal gas constant is equal to both ones constant times n and so if you get this you get the contribution entropy as $R L \ln 2$ minus half one plus $L \ln 1$ plus $L \ln 1$ minus $L \ln 1$ minus L so S_{cons} is a function of the long range order parameter and now if it is so let us put L equal to zero I get S_{cons}

into R one two remember regular solution S cons is R one two right if it is affected with the solution you have minus R xi L n xi right minus sign and i is repeated so it is summed over so you have i equal to one to two so it is basically have and now if I tell x one equals to x two equals to point five then you basically have minus R half L n half plus half L n half basically L n half so minus R L n one minus L n two which is basically L n one is zero so which is basically R right the other term goes cancels out only equal to zero why because if I put L equal to zero this is one and this is L n one and L equal to zero this is also L n one so L n one is zero so this term vanishes right and so you can only get R L n two which is exactly for the disorder right if it is a disorder solution or disorder liquid solution I get the same R L n two however in the limit of L equal to one if you look at that this is L n two this is half minus half and this is two L n two right L equal to one so minus half into two L n two is basically minus L n two so L n two minus L n two but there is one more term now in this term what happens if I put L equal to one then one minus one is zero but I cannot really do that directly that is why in the limit that is why we write in the limit of because if I do not use in the limit of that put L equal to one directly then one minus L is zero and log zeros undefined or L n zeros undefined as a result it is important to tell that when I put L equal to one in the limit of L equal to one like L coming and L is going as close to one as possible so then one minus L is supposed to be zero and L n one minus L is supposed to be basically the L n one minus L is supposed to even be finite but it is multiplied by zero so this is zero and this is minus L n two this is plus L n two so basically when in the limit of L equal to one the configuration entropy is going to be fine if it is complete order there is no configuration but there should be something else and that part you can do something like vibrational entropies.



Now if you have that you have the you have H you have the order for the order that is you have the entropy of mixing or molar entropy of mixing and you have now the molar

entropy of mixing molar entropy R is there so it is molar entropy of mixing and G which is basically molar free energy of the ordered phase is H minus TS which I am now writing as H we already know H is nothing but the H order and S is nothing but so now S is basically configuration plus vibration I can include vibration entropy also but if you see H order has n one minus L square E_a plus E_a plus two n so basically this is one plus L square E_a and then $RTLn$ two so the temperature dependence is there you get the temperature dependence so by that if you do the second derivative of G and put it to zero you basically get that P_c you can try that you can find the P_c I will discuss it in week 11 about stability so basically now you have G equals to these terms which is the interaction term this part and then this term which is basically the configuration entropy part is $RTLn$ two minus half one plus L n one plus L plus one minus L n one minus L but you have also an additional term which you can use it is like n times S_d0 where S_d0 is the vibration entropy of atom right and n is the number of atoms so it is vibration entropy of atom and if you have $3n$ independent oscillations using the statistical mechanical concepts that I have been taught in the statistical thermodynamics classes you can basically arrive at so I am not going to do the entire derivation here but I am just writing it you will come out with this $3n$ if you assume $3n$ independent oscillations then the vibration entropy comes out to be k_B and this all this $\beta \epsilon_i$ where β is one by $k_B T$ right so β is basically one by $k_B T$ so if you look at that you have this E to power $\beta \epsilon_i$ and ϵ_i are the basically the energy levels right these are basically the $3n$ energy levels that we have right i equal to one to three n so you have $3n$ oscillations that means there are $3n$ energy levels right if you have $3n$ oscillations so you have $h \nu_i$ so ϵ_i equals to $h \nu_i$ right ν is the frequency ν is the frequency now this is something that I want to give and this will be merged with the earlier lectures so basically it becomes a continuous lecture you just listen to it in a merged form and then in the next lecture I will basically discuss the phase equilibrium in multi phase multi component non reacting systems basically I will look at now the same concept that I have taught before of phase equilibrium across subsystems right phase equilibrium across subsystems now the subsystems are nothing but in this case phases right across subsystems and also I will look at something like called phase diagram right or phase stability map so phase diagram or phase stability map right this is something that I will do ok so in the just wait for the next lecture so in the next lecture I will discuss all these different phase equilibria the interesting phase equilibria that you can see in multi phase multi component and non reacting so basically although I am talking of multi component most of the discussion that I will do here is basically focused on binary alloys but yeah you can also look at ternary alloys or ternary systems it may not be alloys it may be ternary oxides or ternary carbides right or you can go beyond ternary but remember when it comes to phase diagram if you go beyond ternary it becomes very difficult to visualize because even in ternary you require basically a 3D model now you can take sections of a 3D model again if you go beyond ternary again you have to start with taking

sections right that is something that you have to do and I will discuss that in the next lecture.