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# NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING

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# Phase field modeling; the materials science, mathematics and computational aspects

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**Module No.1**
**Lecture No.1**
## Solution models

Welcome I am going to talk to you about particular model for understanding the thermodynamics of alloy systems. This is known as regular solution model, all of you might know that nickel for example, aluminum for example, copper for example, silver for example, these are metals which crystallize in the cubic crystal structure specifically the phase centered cubic systems. Things like zinc for example crystallize in the hexagonal close packed crystal structure.

Now if you take these two crystals for example, if you take nickel and copper and if you try to put them together they actually form a solid solution. This was not known about 100 years ago for example, people thought that when you take these two materials and put them together, the nickel crystals and the copper crystals are at very small level and they form, they used to think what is known as a mixed crystals.

About 100 years ago it is likely more than 100 years ago people understood that more complicated things can happen if you try to put these different types of atoms together and there is a wide variety of things that you would see when you put them together. For example, nickel and copper forms what is known as an isomorphism system, so it is completely immiscible both in the solid state and in the liquid state and things like copper and silver for example form what is known as a new tactic system.

And things like nickel and aluminum for example, form lots of altered structures we will have a more involved discussion about what this order is all about, and why it comes about, and how it comes about and if you take something like aluminum zinc it phase separates. So there are wide varieties of things, so that all possible, when you take different atoms and put them together. So the regular solution model which we will discuss today is one of the models to understand what happens when you take different types of atoms and put them together.

The bases for this model is the Gibbs free energy, so if you have constant temperature and constant pressure then in those systems, you can understand the equilibrium as one which minimizes the Gibbs free energy. We know that the Gibbs free energy is written as follows.

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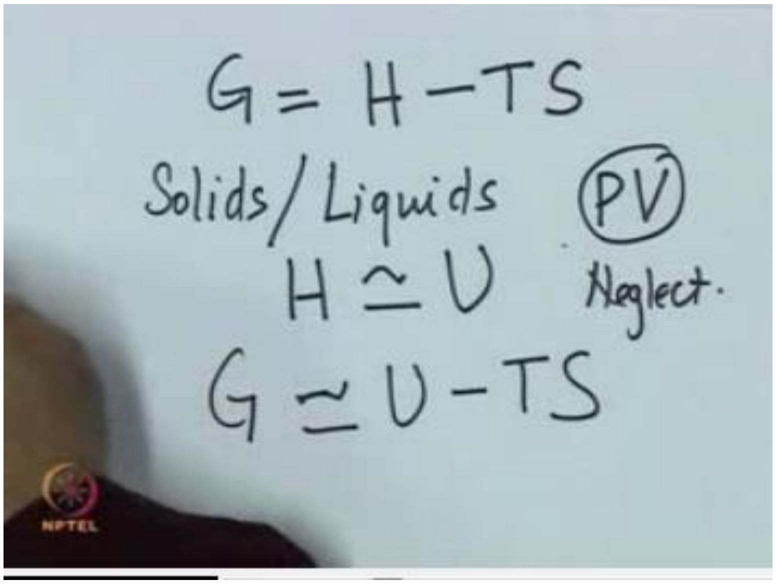

$$G = H - TS$$

Solids/Liquids $\boxed{PV}$

$$H \simeq U$$ Neglect.

$$G \simeq U - TS$$

The Gibbs free energy is nothing but the enthalpy minimum temperature times the entropy. And in condensed system so that is solids and liquids, it is a good approximation that the enthalpy is approximately the same as the internal energy. In other words, the term which is added the PV term which we neglect okay, we will do a short tutorial as to why neglecting this is justified, but we assume.

So the G is approximately equal to U-TS okay. So this is the beginning, so we will look at this free energy and we try to understand the behavior systems in terms of this free energy. We are assuming already that pressure is a constant, we are also thinking about systems most of the times which are at normal atmospheric pressure. In such systems then suppose you have a system which consists of two different types of atoms okay.

One let us call them generically as A type of atoms and B type of atoms okay. One of the simplest models that you can think of is that you put together this A type of atoms and B type of atoms and consider a solid, so we are considering a binary alloy, because it consists of two different types of atoms, one I call as A, the other one I call as B, so A can stand for nickel for example, B can stand for copper for example okay.

It could be any two different species of atoms, and because it is an alloy which is made up of two different types of atoms it is a binary alloy. We are considering this alloy at normal atmospheric pressure and when we put these atoms together then what happens is the question that we are trying to understand. And to do this, to understand what happens when you put them together, B build models, these are thermodynamic models and the most basic thermodynamic model that we build is known as the ideal solution.

In the case of ideal solution, first we define what is known as the free energy of mixing. So what is free energy of mixing, so let me again draw a cartoon to explain what this is.

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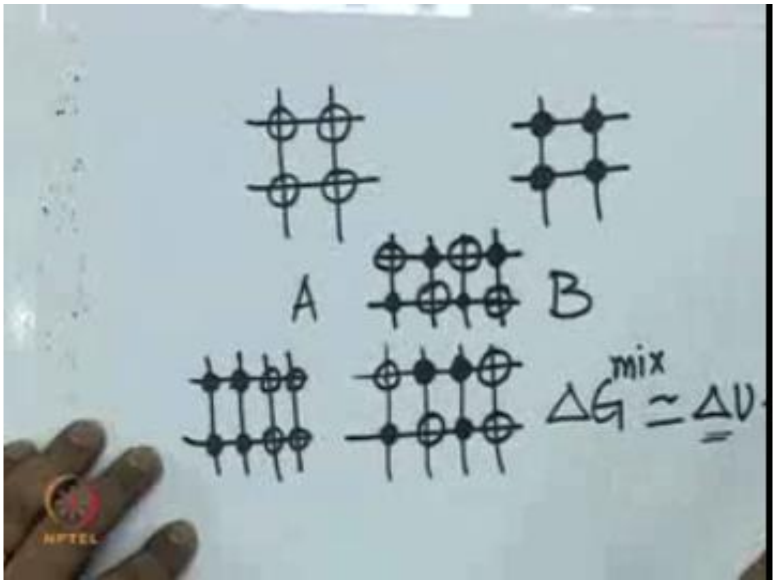

Suppose you have some A type of atoms, so let me represent A type of atoms by open circles, so these are the A type of atoms, so this can be standing for nickel for example, and then you have the B type of atoms. So let them be represented by filled circles, so these are B type of atoms okay. And so there is free energy associated with this A type of atoms and with this B type of atoms and suppose if I take them together and now I need more number of lattice points, so there are four, there are four.

So I atleast need 8 lattice points, and on this 8 lattice points I try to put these A and B type of atoms right. So I try to put, maybe this is a B atom, maybe this is another B atom, maybe there is A atom, maybe another B atom here, A atom here, B atom here and A atom here. So I have now taken the same number of lattice points and I have put them together, so let us say that this has some free energy okay.

Now the difference between this free energy and the free energy of these two is what is known as the free energy of mixing okay, so it is called $\Delta G^{mix}$. Obviously, because G is U-TS so this is equal to $\Delta U-T\Delta S$. So if we can calculate this $\Delta U$ and this $\Delta S$ then we can estimate how much is the $\Delta G^{mix}$, and the idea is, because systems try to optimize the Gibbs free energy. If this $\Delta G^{mix}$ is negative in other words by doing something right, it can so happen that if the system is such that, suppose when you have these 8 sides okay it is preferable to have all B like this, all A like this.

It is possible that the system can prefer like this or it is also possible that the system would prefer to have alternate A and B right, you will start with A, you will have a B, you will have another A, you will have a B, and here you will have a B, you will have an A, you will have a B, you will have an A and so on. So there are several different ways in which this mixing can happen at your atomistic level.

And depending on whichever is the one which is going to give the maximum reduction in free energy whichever one which gives you the ΔG mixer to be negative and as large negative as possible that is the one that would be preferred out of this okay. So for the simplest of the approximations let us do that, this is known as the ideal solution.

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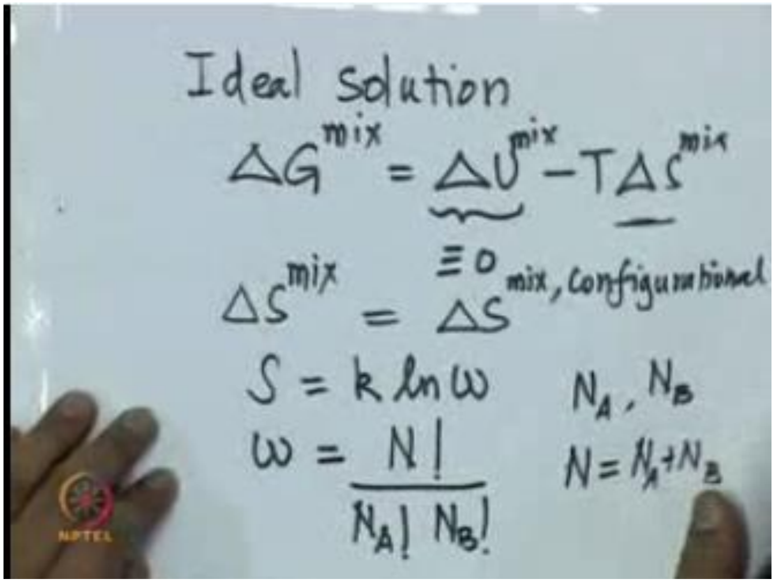

Ideal solution

$$\Delta G^{mix} = \underbrace{\Delta U^{mix}}_{\equiv 0} - T\underline{\Delta S^{mix}}$$

$$\Delta S^{mix} = \Delta S^{mix,\,configurational}$$

$$S = k \ln \omega \qquad N_A,\ N_B$$

$$\omega = \frac{N!}{N_A!\,N_B!} \qquad N = N_A + N_B$$

In the case of ideal solution okay, we know that $\Delta G^{mix} = \Delta U^{mix} - T\Delta S^{mix}$. We assume that this quantity $\Delta U^{mix} = 0$ okay. So we will later explain why for an ideal solution this $\Delta U^{mix}$ is 0, for now let us assume that it is not there. And now we want, also want to know what is the change in entropy, so that, that can be multiplied with the absolute temperature in which the system is kept and then we will know how much is the free energy of mixing. We make an assumption in majority of the cases that we will discuss for these kind of alloy models, that the only contribution to the entropy comes from the configuration entropy.

In other words like we were discussing in the earlier slide, whenever you are distributing the A and B atoms on the lattice you are generating different configurations for example, you had a configuration at which they were randomly distributed, you had another configuration in which all A was on one side, all B was another side, you had another configuration where A and B were alternating.

So the entropy associated with these different configurations is known as configurational entropy and most of the times, majority of the times we will concentrate only on the configurational entropy differences. So the $\Delta S^{mix}$ becomes nothing but the $\Delta S^{mix}$ of configurational entropy okay. So what is this configurational how do we calculate it is then the next question so we are considering a binary a lie which consist of A and B type of atoms and by definition we know that entropy is nothing but the k ln $\omega$ where $\omega$ is the number of micro states as they are called k in the case of configuration entropy $\omega$ is nothing but the number of ways in which you can distribute suppose you had $N_A$ number of A atoms and $N_B$ number of B atoms.

And you are trying to distribute them on N number of size obviously $N = N_A + N_B$ if you assume that this a binary alone and there are no defects like vacancies okay so you have N number of sites which is $= N_A + N_B$ and where $N_A$ and $N_B$ are the number of A and B atoms respectively so you are trying to distribute $N_A$ number of A atoms and $N_B$ number of B atoms on N number of sites then the total number of configurations that you can generate if you assume that you cannot distinguish A and B type of atoms happens to be $N!/ N_A! N_B!$ Okay.

Now why is the number of configurations given by $N! / N_A! N_B!$ let us try to do a little bit of algebra okay.

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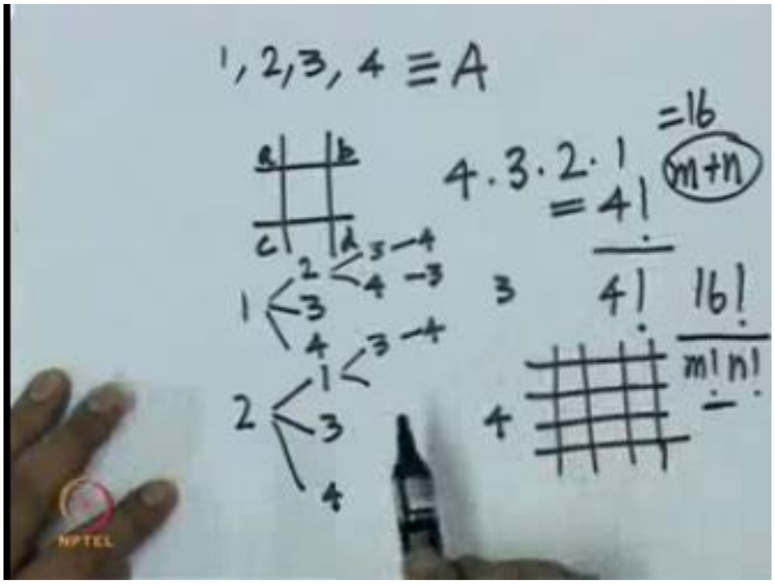

So let me say that I have 4 distingue atoms okay let us call them as 1, 2, 3 and 4 and let me say that I have 4 sides okay let me also label these sides as say a, b, c and d okay so the total number of ways in which I can put this 1, 2,3, 4 on a, b, c, d is as follows for example for a I can choose 1 or I can choose 2 or I can choose 3 or I can choose 4 once I have chosen 1 for the A side for the B side either I can choose 2 or I can choose 3 or I can choose 4 if suppose I have chosen 1 for a and 2 for b then c and d there are 2 possibilities.

So 1 is where I choose this to be 3 and the other 1 is 4 the other 1 where I choose this to be 4 the other 1 is 3 so in other words it happens to be 4 of this choose for the 1st one and then there are 3 chooses for each one because for when I have 2 for example I can the choose 1, 3 and 4 so for each one of these then I have 3 chooses and each one of these then I have 2 chooses and once I have exhausted for example 2, 1, 3 if chosen this as to be necessarily 4 so there is only 1 choose in other words so this is equal to 4 !.

That is if I have 4 distingue atoms and if I have 4 distingue sides if I can distinguish between those atoms that is nothing but 4! if I have 4 atoms it is 4! If I want to distribute it on 4 sides suppose if I cannot distinguish 1, 2, 3, 4 they all are identical that I can only name them as so A then I do not know which is 1, which is 2, which is 3, which is 4 that means then I have to that there is only 1 way because all a and you have 4 sides you will just but a atom on all side so 4! / 4!

So if suppose you have say let us say you had some 16 sides okay so you will have 16! Ways provided they are all destining entities but if suppose out of which some m of them are in distinguishable and some n of them are distinguishable which give together this is equal to 16 say then the number of ways in which you can distribute is the 16! / m!/ n! okay if you have this m + n , m among themselves in distinguishable n among themselves been distinguishable you can think of it as a total number of balls for example is 16 m can stand for red balls and n can stand for black balls.

So you have to say some 7 red balls and 9 black balls so what is the total number of ways in which you can arrange them the total number of different configurations you can have where you are not going to be able to distinguish the red balls among themselves and the black balls among themselves is this.

So we will again do a small tutorial to understand where this division by m!n! Comes but you can see for example if they are all the same then it will be 16! Divided because there is only one way in which you can arrange okay now we consider given this information we consider the following case what do we consider we say that I have total number of sides.

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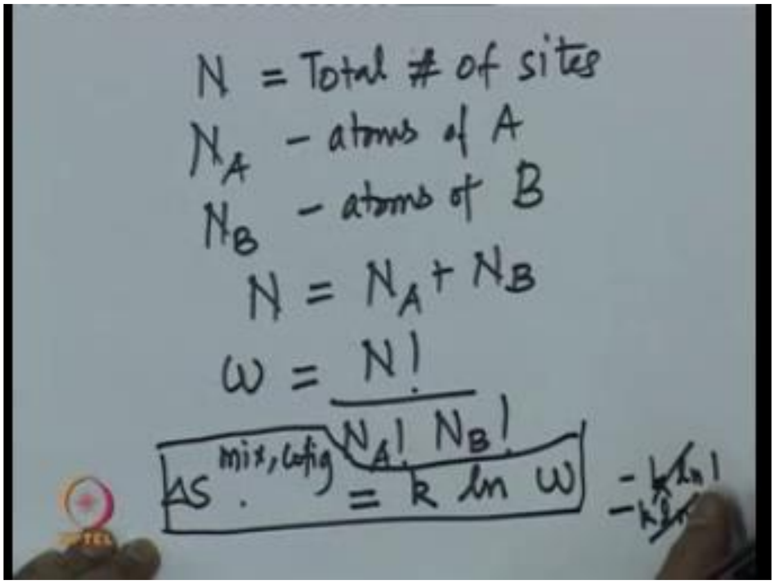

N = Total # of sites

$N_A$ - atoms of A

$N_B$ - atoms of B

$$N = N_A + N_B$$

$$\omega = \frac{N!}{N_A!\, N_B!}$$

$$\boxed{\Delta S^{mix, config} = k \ln \omega}$$

$-k \ln 1$

$-k \ln$

As N and I have $N_A$ atoms of A and $N_B$ atoms of B and the total number of sides is nothing but $N_A + N_B$ and initially the initial configuration entropy because I had only A atoms and $N_A$ side so there is only one way logarithm 1 is 0 so the initial configurational entropy is 0 similarly the initial configuration entropy for B atoms is also 0 but the moment I put them together on a lattice I get this number of configurations that is possible as $N!/ N_A!\ N_B!$ okay because the initial configuration gives 0.

So the $\Delta S^{mixing}$ of the configuration entropy is nothing but besides which is k ln ω okay because the other quantity the ω is 1 so ln 1 is 0 so there is some –k ln 1 kind of terms okay another –k ln 1, 1 is for A types of atom another one for B type atoms this is all 0 so this is all we have as the $\Delta S^{mix}$ of configurational entropy now let us so the algebra in a little bit more of detail so this is the configurational entropy I have.

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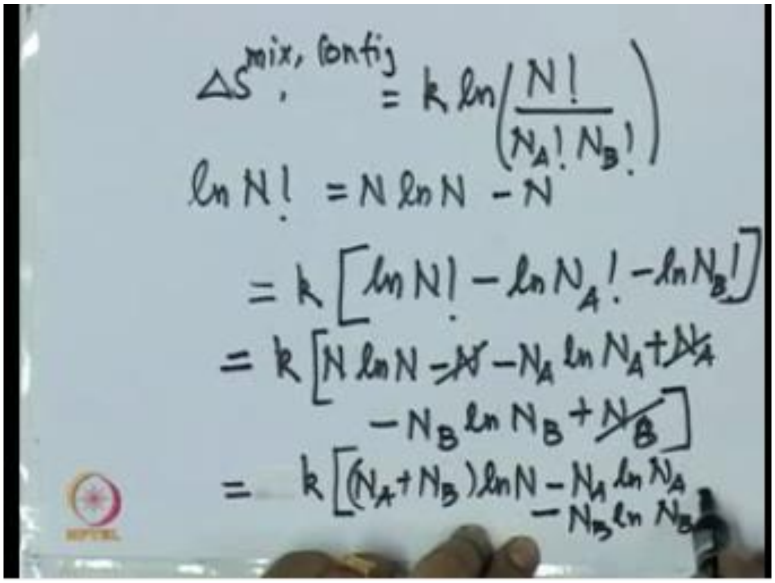

$$\Delta S^{mix,\ config} = k \ln\left(\frac{N!}{N_A!\, N_B!}\right)$$

$$\ln N! = N \ln N - N$$

$$= k\left[\ln N! - \ln N_A! - \ln N_B!\right]$$

$$= k\left[N \ln N - \cancel{N} - N_A \ln N_A + \cancel{N_A} - N_B \ln N_B + \cancel{N_B}\right]$$

$$= k\left[(N_A + N_B) \ln N - N_A \ln N_A - N_B \ln N_B\right.$$

$\Delta S^{mix}$ of configurational entropy that is nothing but k ln N! / $N_A$! $N_B$! Now we use an approximation called the starlings approximations starlings approximation say ln N! is Nln N-m N okay this is very good approximation for large N in fact we will do another tutorial to find out or what value of N this approximation is good okay but for now let us say that this approximation is good remember if you take one mole for example this N is really a large number it is like a number of order of $10^{23}$ so sterling approximation is very good for such large numbers but for now let us assume that this approximation is okay.

So then you can calculate the $\Delta S^{mix}$ configuration which is nothing but k right so ln something by something so it becomes ln N! – ln $N_A$! - ln $N_B$ ! now if we do then it becomes k / this approximation N ln N – N there is – sign so it becomes $N_A$ ln $N_A$ – $N_A$ + because there is a – sign and similarly it becomes $N_B$ ln $N_B$ + $N_B$ but remember N is nothing but $N_A$ + $N_B$ so – N $N_A$ $N_B$ will go away so we are left with N ln N – $N_A$ ln NA – $N_B$ ln $N_A$ k and you have N let me write that N as $N_A$+ $N_B$ ln N – $N_A$ ln $N_A$ – $N_B$ ln N this is what we have so let is expand and so a little bit of algebra so what do we get we get $\Delta S^{mix}$

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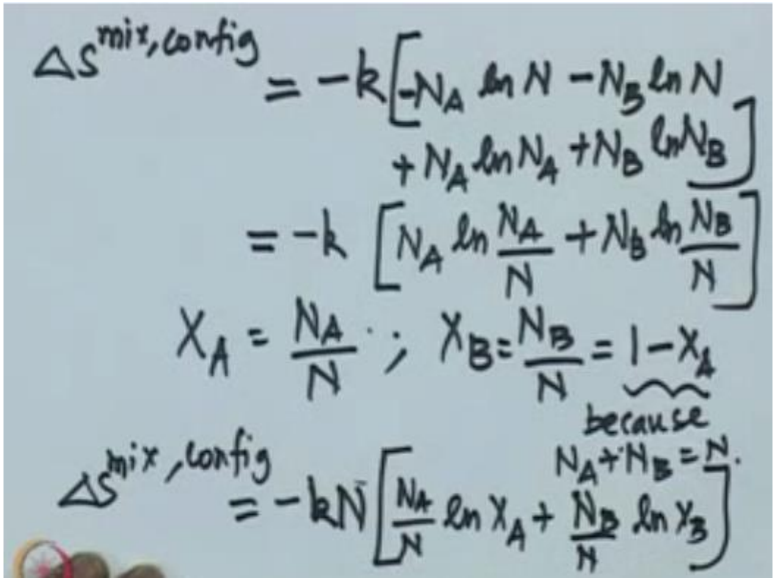

$$\Delta S^{mix,config} = -k\left[-N_A \ln N - N_B \ln N + N_A \ln N_A + N_B \ln N_B\right]$$

$$= -k\left[N_A \ln \frac{N_A}{N} + N_B \ln \frac{N_B}{N}\right]$$

$$X_A = \frac{N_A}{N} \; ; \; X_B = \frac{N_B}{N} = \underbrace{1 - X_A}_{\text{because } N_A + N_B = N.}$$

$$\Delta S^{mix,config} = -kN\left[\frac{N_A}{N} \ln X_A + \frac{N_B}{N} \ln X_B\right]$$

Configurational is nothing but –k $N_A$ ln sorry – pulled so this is – $N_A$ so –$N_B$ ln N + $N_A$ ln $N_A$ + $N_B$ ln $N_B$ this is what we have now let me also okay so – k let us do B so NA you can take as common so it is ln $N_A$ – ln N so that becomes $N_A$ ln $N_A$/ N + $N_B$ similar fashion ln $N_B$ / N right because $N_B$ you can pull out it is ln $N_{B\,-}$ ln N so that is nothing nut ln $N_B$/N so $N_A$/ N let us call it as so these are the automatic fraction so number of the atoms to the total number size, number of the atoms to the total number size.

So let us call $X_A$ as $N_A$/N and $X_B$ as $N_B$/N because $N_A + N_B = N$, $X_B$ is nothing but 1 – $X_A$, so this is because why is this, this is because $N_A + N_B = N$ so if $N_A$/N is $X_A$ then $N_B$/N will be 1 – $X_A$ because we are dividing N on both sides, okay. So this becomes so we have $\Delta s^{mix}$ configurational as –k let me also multiply by N here and divide by N here so I have [$N_A$/N ln $X_A$ + $N_B$/N ln $X_B$] but again $N_A$/N is XA so we get the expression –kN[$X_A$ ln $X_A$ + $X_B$ ln $X_B$].

So this is the configuration entropy so you can now calculate the configurational the free energy of mixing because we said that for the ideal solution there is no contribution from the internal energy of mixing or entropy of mixing. In the case of condense systems like solids and liquids these two are assumed to be the same and is a very good approximation.

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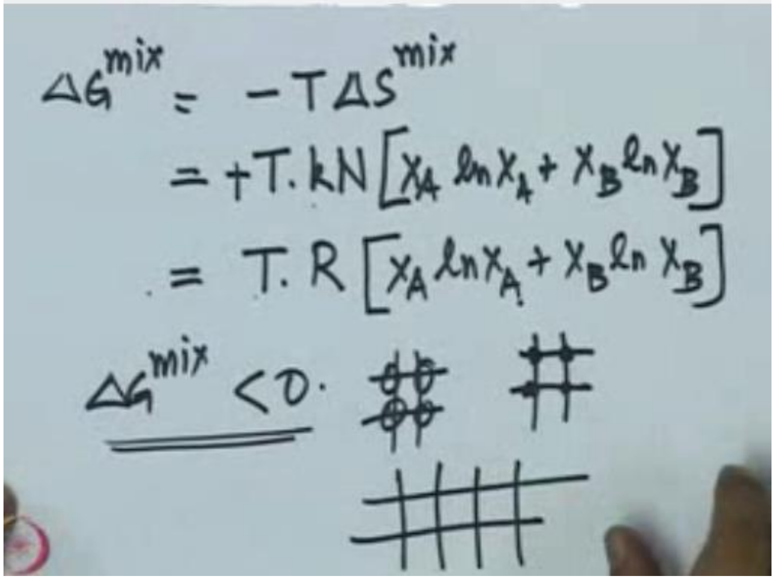

$$\Delta G^{mix} = -T\Delta S^{mix}$$
$$= +T.kN\left[X_A \ln X_A + X_B \ln X_B\right]$$
$$= T.R\left[X_A \ln X_A + X_B \ln X_B\right]$$
$$\underline{\underline{\Delta G^{mix} < 0.}}$$

So we have $\Delta G^{mix}$ which is the free energy of mixing has nothing but the $-T\Delta S^{mix}$ and we assume that this ΔS mixes only the configuration entropy, there could be vibration entropy configuration for example which we are not considering which means you have $-T.kN[X_A \ln X_A + X_B \ln X_B]$ remember there was a negative sign so this is, if you assume that this N is the Avogadro number, k is the Boltzmann constant.

Boltzmann constant time the Avogadro number so if you consider this quantity as N as a one mole right, so then you have T.R which is the universal gas constant times $X_A \ln X_A + X_B \ln X_B$ okay, so this is the positive quantity this is the positive quantity logarithm of some fractions so this is going to be a negative number so $\Delta G^{mix} < 0$, in other words ideal solution this is called ideal solution.

Because the configurational entropy is always going to reduce the overall free energy so if you take a system in which you have all these A atoms and you have these B atoms and if you try to put them together in the absence of entropy of mixing or internal energy of mixing then it is always favorable for the system at any temperature above 0 to have mixing because mixing then reduces the overall free energy, that is the reason why it is called ideal solution.

Because it will always mix very homogenous because the perfect mixing randomly arranging the A and B atom on the given lattice this is what we have assumed by arriving this is the one that is also going to have the lowest free energy so the system is going to choose it in such a way that it is going to randomly arrange this A and B atoms, it is also ideal solution in another sense, in the sense that it is not you are thinking that you are putting A atoms and B atoms.

As per the system is concerned it is not showing any enthalpy change or internal energy that means it is not distinguishing between A atoms and B atoms in that sense also it is an ideal solution because it is not distinguishing between A type of bond, B type of bond is treating all of them to be equal that is the reason why the enthalpy of mixing or the internal energy of mixing is 0 and that automatically also results from entropy concentrations to complete this, okay.

So this is known as an ideal solution so ideal solution always gives the free energy of mixing this is negative so because the free energy of mixing is negative ideal solution is always have this actual solution isolated, it will take the atom it will take on a lattice and it will distribute that random, now let us discuss the next model which is slightly more complicated than the ideal solution model that we have discussed till now.

But we are going to introduce some approximation which can sometimes be questioned, I am going to tell you what this consequence are and I am also going to show you how the expression is there in the case what is known as a regular solution model, okay.

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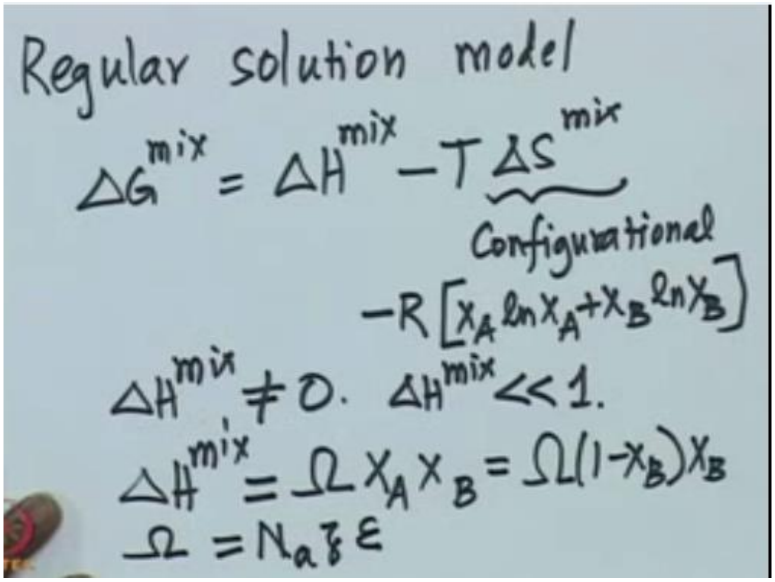

Regular solution model

$$\Delta G^{mix} = \Delta H^{mix} - T\underbrace{\Delta S^{mix}}_{\text{Configurational}}$$

$$-R\left[X_A \ln X_A + X_B \ln X_B\right]$$

$$\Delta H^{mix} \neq 0. \quad \Delta H^{mix} << 1.$$

$$\Delta H^{mix} = \Omega X_A X_B = \Omega(1-X_B)X_B$$

$$\Omega = N_a z \varepsilon$$

We assume that in $\Delta G^{mix}$ remember you had two terms one was $\Delta H^{mix}$ - T $\Delta S^{mix}$ we are going to assume that this $\Delta S^{mix}$ is still given only by the configurational entropy and what is mole, the expression that we derive by assuming that the AA and B atoms are randomly distributed all the given number of lattice we assume that, that approximation is also valid and we use the same expression that we derived in the ideal solution namely.

That this is a noting but $R[X_A \ln X_A + X_B \ln X_B]$ this is what we are going to assume for the configuration, in addition we are going to assume that this $\Delta H^{mix}$ which was assumed to be 0 in the ideal solution K is not equal to 0 that is what makes it this regular solution model that and we are also going to assume that even though the $\Delta H^{mix}$ is not equal to 0 it is still a small number, okay.

Why is this important you will see that the $\Delta H^{mix}$ is related to the differences in the bond energies between A-A, B-B and A-B kind forms so if you assume that this $\Delta H^{mix}$ is a considerable number, then this assumption that we are using when we are writing this configurational entropy is not quite correct, okay. IF suppose the system for example preferred A-A B-B bonds or A-B bonds.

Then a random distribution of A and B atoms on the given lattices is not going to happen, so this configurational entropy calculation then becomes not quite correct to make sure that this is still valid we are saying that okay this $\Delta H^{mix}$ is not 0 but it is still not very considerable quantity so at higher temperatures this is still dominate and at very low temperature this where this term is not so dominating this will dominate.

So if you can find systems where such a neat distinction exits between at low temperature where it is mostly controlled by the $\Delta H^{mix}$ and at high temperatures it is mostly controlled by $\Delta H^{mix}$ then for those systems this model called regular solution model words that really nicely, so in the regular solution model we assume that the $\Delta H^{mix}$ is not equal to 0 on top of it we actually assume that this $\Delta H^{mix} = \Omega$.

This is known as the regular solution parameter times $X_A$ and $X_B$ remember because $X_A$ is $1 - X_B$ it is also $1 - X_B$ times $X_B$ and so it is a kind of parabolic relation $\Omega$ ids know as a regular solution parameter and $\Omega$ we will do another tutorial to show that this in details so is a nothing but the Avogadro number times Z which is the number of nearest neighbors and the crystal structure that you are assuming. Times a quantity called $\varepsilon$ and $\varepsilon$ is nothing but the difference in the bond energy.

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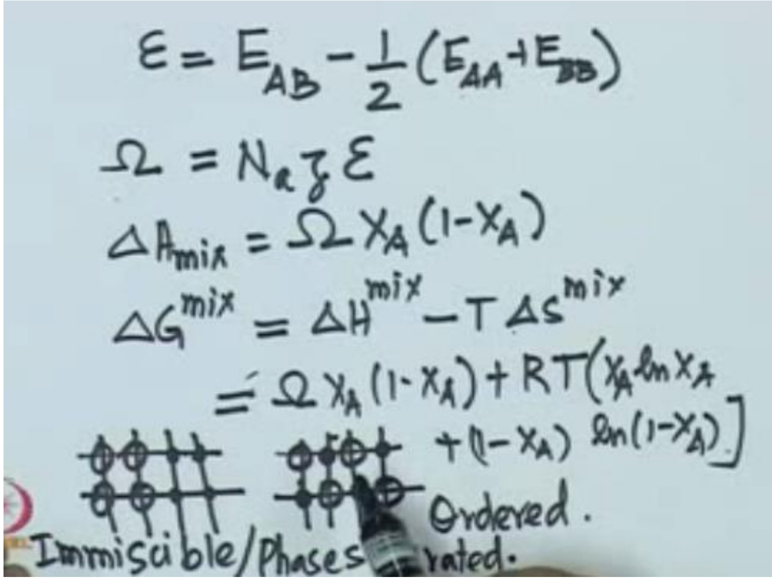

$$\varepsilon = E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})$$

$$\Omega = N_a z \varepsilon$$

$$\Delta H_{mix} = \Omega X_A(1-X_A)$$

$$\Delta G^{mix} = \Delta H^{mix} - T\Delta S^{mix}$$

$$= \Omega X_A(1-X_A) + RT(X_A \ln X_A + (1-X_A)\ln(1-X_A)]$$

So ε is nothing but $E_{AB} - ½(E_{AA} + E_{BB})$ in other words ε is a quantity which tells suppose if I take two AA and BB bonds break them make A-B bonds what is the difference in energy, okay. So ω which is nothing but the others are by the geometric factors are numbers so number of total number sides that you have the number of nearest neighbors in the crystal structure that you are assuming which is for example 12 if it is FCC, 8 it is BCC and so on, 6 it is simple cubic and so on.

So this ω basically the sign of ωs depends only on this quantity because likely said this is nothing but z times ε, so ε is positive that means a AB bonds have higher energy than AA BB bonds ε is negative which means this $E_{AB}$ is less than this quantity that is AA BB, okay so this Ω picks up the sign according to what the sign of ε is going to be, so the $\Delta H_{mix}$ which you can see is dependent on $\Omega X_A(1-X_A)$ again so the $\Delta H_{mix}$ sign is dependent on the sign of.

So in this case now the free energy $\Delta G^{mix}$ okay, which is given by $\Delta H_{mix}$ minus of the T times $\Delta S^{mix}$ was $\Delta S^{mix}$ is nothing but –R times XL on its A , X will be on XB so let us write down the full expression it is $\Omega X_A(1-X_A)$+RT times it multiplies $X_A$ ln $X_A$ +1-$X_A$ln(1-$X_A$). so in this case now, the sign of $\Delta G^{mix}$ so this quantity like we discussed earlier is always negative because logarithm of a fraction logarithm of fraction so this is going to be less than 1 so this quantity is always going to be negative, okay and it is also parabolic.

Now this quantity if suppose this is negative, then everything is negative so there is no problem, but if suppose this quantity is positive then this can swamp this quantity sometimes and that leads to interesting micro solutions. But in all cases suppose if the temperature is very high, then this Ω parameter because we have also assumed it to be very small because we assumed that this ε that makes part of this Ω is very small, so this quantity is negligible so at higher temperatures the system is still driven by the entropy contribution.

Only at lower temperatures depending on the sign of Ω whether it is positive or negative then either it is going to go the same way as the entropy or it is going to go against entropy. In either case it is going to have important effects to understand this let us assume that we are at absolute 0, the T0 so there is no configuration entropy at all, entropy contribution is completely now there. In which case the system behavior is completely determined by the regular solution parameter, and what is the regular solution parameter say, it says that it depend on whether suppose if you take AA bonds, BB bonds you break them and you make AB bonds and making those AB bonds is going to be costlier, right.

In which case the system would preferred to have AA and BB bonds, that is the system will phase separate, the system will get a configuration like I showed you earlier time in which it will have all A atoms here, all B atoms here. Please notice even if it does that it still has to make some AB bonds which are costlier, okay which are relatively costly if possible it would like to have all A bonds and all BB bonds.

On the other hand, suppose making AA and BB bonds is costlier and if it breaks them and if it makes AB bonds on the average if AB bonds are cheaper that is when it is going to make the other configuration that I tried to show you, what is that configuration it will try to have only AB bonds, right it will try to have only AB bonds so you can see AB, AB, AB, AB, AB, AB, right AB, AB so this kind of mixing that happens at the atomic level leads to what is known as ordered crystals structures we will look at more details and this is known as ordering system.

This kind of separation is known as either immiscible, right because they have not mixing or phase separated, right because the two phases are separated. So in other words and in either case if this is prove only at absolute 0 at any temperature above absolute 0 the entropy is always trying to make the system go to a more random configuration it neither prefers this nor prefers this, this is two ordered this is also two ordered on the entropy point of view. Entropy would like to mix them as randomly as possible and all systems at higher temperatures where entropy contribution becomes the dominant factor will anyway go through this more mixed completely solution kind of structures, okay.

Only at low temperatures depending on the sign of ε and in turned which decides the sign of Ω, so the sign of Ω decides whether the system is going to phase separate or the system is going to order. The models that we are going to talk about in this course which is known as phase fill models or basically models meant to study this kind of phase separation by a specific mechanism known as spinodal decomposition and order.

Basically all phase will models can be taught of as models build from these two basic components model 1 which is known as Cahn Hilliard model which was returned to explain this phase separation behavior through a specific mechanism and another model which is known as Alan Cahn model which was returned to describe this ordering behavior and all phase will models at least as far as this courses concerned can be taught of as combinations of these kind of Cahn Hilliard like and Alan Cahn like models.

So that is the reason why we are starting from this regular solution model and we are trying to see, so remember regular solution model is a thermodynamic model it is talking about the free energies from free energies it is trying to predict at equilibrium what is going to be the structure of the material in question whether it is going to form an uniform solid solution where all the atoms will be randomly distributed or it is going to from an ordered crystal structure where over and above the crystalline order you will have specific occupancy preferences for specific type of atoms like if I have nickel for example I would like to have only surrounding aluminum atoms no nickel should be next to another nickel.

If I have aluminum atoms I should have only nickel surrounding it, no aluminum should be next to it. So this kind of ordered structures or if I have some aluminum, zinc kind of system where I have aluminum rich regions and zinc regions, so this is the kind of problems which are tackled using the phase fill models and so it is always a good starting point to understand phase fill models we start from solution models so what we have discussed today is two different types of solution models, one is known as the ideal solution model the other one is known as the regular solution model. In the ideal solution model we said that $\Delta H_{mix}$ is 0.

So the configuration entropy which is the only contributing factor we have assumed in this kind of binary alloys then shows that the system will always have random occupancy for A and B atoms. So in that sense it is an ideal solution, okay so it is going to be have, going to be having a very complete mix, okay. But it is also ideal in the other sense of the word namely that $\Delta H_{mix}$ which we assumed to be 0 is nothing but representation of the cost associated with making an AB bond by baking AA BB bonds.

So when we are assuming it to be 0 we are saying that on the average breaking and AA bond and breaking an AB bond and making two AB bonds is going to be the same in terms of energy cost associated with this process which means the system in other words is not distinguishing between A and B type of atoms so in that sense also it is an ideal solution because it is not distinguishing between the type atoms it considers them almost like this same spices of atoms and it distribution of atoms on the given lattice.

So that is the ideal solution, of course that is a very ideal case which means it never really happens practically and for the other case where we look at a slightly improved version which is known as the regular solution model it is still is bad in terms of some of the approximation that it means the most important bad approximation that we have made is that we have assume that the distribution of atoms is still random as far as the entropy calculation is considered. But we have also said that the enthalpy of mixing is not 0 which means AA BB bonds and AB bonds there is a preference for one or the other which means assuming random distribution is really not that correct.

But it is okay, in some approximate cases where the $\Delta H_{mix}$ is not 0 but it is also a number which is not too different from 0 okay, it is a very small number. In such cases regular solution approximation is good, so we are going to use this regular solution model and at high temperatures anyway all models are going to give you more ideal solution like behavior because the $\Delta H_{mix}$ becomes not so dominant the T $\Delta S^{mix}$ term becomes dominant and that will always prefer a random substitutional solid solution, okay.

So we will start from this point as the starting point for the next module that we will have in which we will talk about deriving phase diagrams from regular solution like models and what do they tell us about the kind of phases that can excess in binary alloys, so I am going to stop it here we will discuss it in the next module.

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