Nanomaterials and their Properties

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Lecture - 11
Thermodynamics of Nanomaterials

Students, we are going to start the lecture 11. As I mentioned in the very beginning of the course, the half of the lectures of this course will be on architecture, how nanostructure developed in different kinds of natural and manmade materials followed by thermodynamics and surface energy. So, in the first case for the architecture, we have discussed many such examples of natural materials.

We have not discussed much about the man made materials which we will discuss obviously. Then, I started discussing about surface energy because surface energy and thermodynamics, they are interrelated. So, I have to go back and forth as you know.

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In the last lecture, we have learned some e things Thermodynamics of nanomaterials. We shall learn more ...

Recap:
Thermodynamic derivation

Effect of size

Questions?

So, in the last lecture, we started learning a lot of things about thermodynamics right. As you know thermodynamics is a very basic subject of material science and engineering and its metallurgy also. Lot of things can be explained using thermodynamics in principle. So, in the last lecture, I introduced several important aspects. I introduced what is the change of temperature, change of vapor pressure, then change of in the melting temperature, in fact, chemical potential also.

Today, we are going to continue some more discussions. In fact, we are going to go to basics even because after analyzing the lecture, I understood we should do much basic things for you to understand the subject. Well, the most important aspect when you talk about nanomaterials and thermodynamics of nanomaterials, this is the effect of size; how the small size can affect the thermodynamics of material so that we can understand various kind of properties later on much easily.

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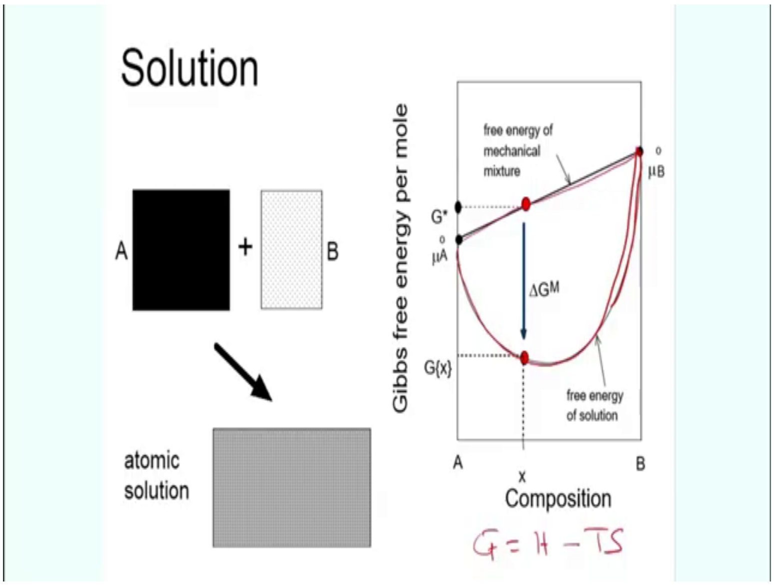

Solution

$G = H - TS$

Well, so, as you know thermodynamics mostly talk about solutions. Well, you know pure metals are not solutions, although there may be dissolved oxygens, nitrogen or maybe some moisture; but we never bother much about that because they will be very small amount like in fraction of a percent weight percentage or maybe in PPO level in many cases.

But they are important for various applications in nano scale like gas sensors. Nonetheless, we will be dealing with various alloys right an alloys means solid solutions. What are the solid solutions? Well, you know liquid solution ok. Liquid solution is what?

If I take glass of water ok, if I take this water ok, this is in a container, this is my water bottle and I pour salt into it, maybe one teaspoon of salt into it and then, do such a kind of a vigorous steering option. So, what will happen? It will form a very nice solution right. Salt water solution which is easily available in sea water ok.

That is why we do not drink sea water because it is salty and its sour, it does not taste good; we always like to have a water which is sweet ok. So, many cases people like to add sugar into it, you can add another teaspoon of sugar, shake it up, it form a solution of sugars and salt in water which is good for many many kinds of you know fatigue or sometimes, you may have stomach upset, you can use it right.

So that is the solution in liquid state, same thing in solid state is also solid solution. There is nothing no difference at all. So, you have to put one into other. Now, here, you have A and B; A is bigger B is smaller. You are adding B into A so that B get dissolved into A just like salt get dissolved in water. Water content was bigger, salt was very very small; one teaspoon (Refer Time: 04:34).

Same thing you are putting small amount of B into large quantity of A, then there is a solid solution of B in A. It can be vice versa like if you have a large quantity of B, then you add small quantity of A. Let us say give example of very common stainless it is steels actually. Steels have very low carbon, less than about 1 weight percentage.

Like in 100 grams, you have less than about a gram of carbon. 100 gram of what? Iron, you have iron as the base material for steels right. Correct? You know that. So, that means, you are adding carbon into iron to make a solid solution, while steel has many many phases like gamma, austenite, alpha, ferrite, delta, ferrite many many solid solutions in physics exist.

So, solid solution is very important concepts. Now, why do they good, the solid solution get stabilized? That is why thermodynamics can be explained easily. Why do I add salt into water and shake it up and it forms liquid solution there must be something happening in the material. Well, so that is the thing actually.

So, by the way, to differentiate between solid solution and a physical mixture, let us compare this situation. You have a suppose, sand; sand is easily obtain (Refer Time: 05:54) to you right. You can go to beach and you can get sand. And, you add a little bit of salt into it and mix them together, they will never mix each other. Pure sand, dry with no water, salt dry with no water will never mix each other. They will remain as a physical mixture.

So, that is if I have to calculate the free energy or the physical mixture, this will follow the straight line. You can see that, that is the line. So, as you keep on adding the salt into the sand, linearly the free energy system will increase ok. Free energy is nothing but $G = H - TS$. This we have discussed many times that is what is free energy is ok.

This is Gibb's free energy. $G = H - TS$ right that is equal to Gibb's free energy; it was given by Gibb's. That is what; so, it is the difference between enthalpy minus T into entropy; T is the temperature. So, that is how it will vary. Now, the moment, I form is atomic scale solution, what is that atomic solution that is what you can here write.

Intermixed like a salt, if you put in water, shake it up, it forms an intermixed liquid solution; something is there in solid also. That means, you cannot separate the atoms from one to from other. If you mix sand and salt, you can separate them out very easily. You know how to do experiments right, I am not talking about. It is then maybe 7th or 8th standard experiments, students do it in the school.

So, that is the thing actually. So, that if you do that, if you form atomic solution; free energy actually goes like this ok. That is a parabola, you can see that.

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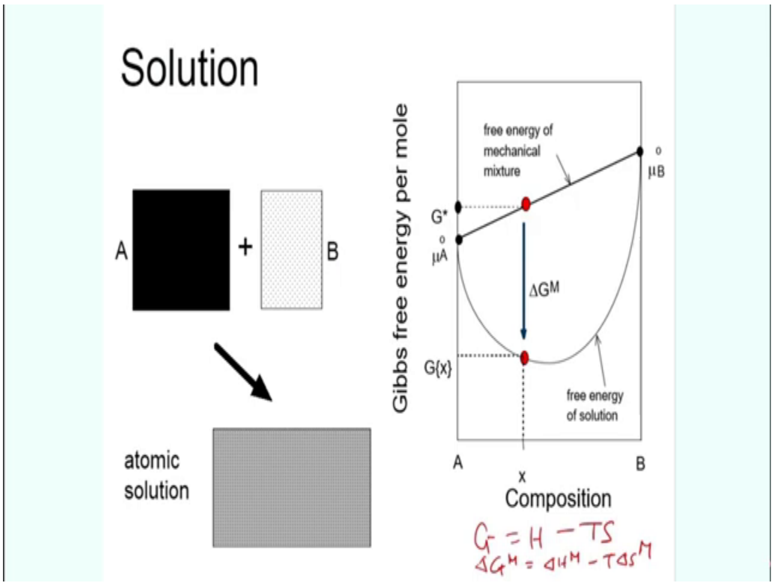

Solution

$G = H - TS$

$\Delta G^M = \Delta H^M - T\Delta S^M$

So, free energy drops drastically if you formatting a solution. Why does it happen? Well, mostly happens because of Boltzmann ok, because of Boltzmann that I have discussed in the last lecture. So, Boltzmann given entropy; when the moment you mix 2 atoms to the entropy increases that is what it is $G - H =- TS$.

This term increases and that is gives you the basically ΔG^M and ΔG^M is mixture actually, M for mixture, is equal to ΔH^M- $T\Delta S^M$. So, now question is how do you calculate ΔH^M and ΔS^M, right? That is something which you need to know very well correct.

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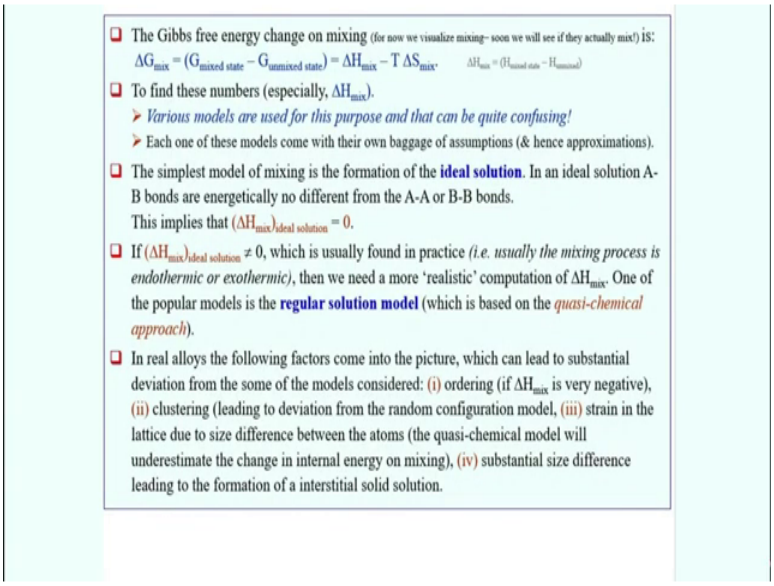

- ☐ The Gibbs free energy change on mixing (for now we visualize mixing– soon we will see if they actually mix!) is:
  $\Delta G_{mix} = (G_{mixed\ state} - G_{unmixed\ state}) = \Delta H_{mix} - T\,\Delta S_{mix}$. $\Delta H_{mix} = (H_{mixed\ state} - H_{unmixed})$
- ☐ To find these numbers (especially, ΔH_{mix}).
  - ➢ *Various models are used for this purpose and that can be quite confusing!*
  - ➢ Each one of these models come with their own baggage of assumptions (& hence approximations).
- ☐ The simplest model of mixing is the formation of the **ideal solution**. In an ideal solution A-B bonds are energetically no different from the A-A or B-B bonds.
  This implies that $(\Delta H_{mix})_{ideal\ solution} = 0$.
- ☐ If $(\Delta H_{mix})_{ideal\ solution} \neq 0$, which is usually found in practice *(i.e. usually the mixing process is endothermic or exothermic)*, then we need a more 'realistic' computation of ΔH_{mix}. One of the popular models is the **regular solution model** (which is based on the *quasi-chemical approach*).
- ☐ In real alloys the following factors come into the picture, which can lead to substantial deviation from the some of the models considered: (i) ordering (if ΔH_{mix} is very negative), (ii) clustering (leading to deviation from the random configuration model, (iii) strain in the lattice due to size difference between the atoms (the quasi-chemical model will underestimate the change in internal energy on mixing), (iv) substantial size difference leading to the formation of a interstitial solid solution.

So, therefore today, we are going to see that. So, as you have see in ΔH_{mix}, a ΔH^{M}; M for mix, I told is $\Delta G_{mix} = G_{mixed\ state} - G_{unmixed\ state}$, when you mix them automatically together; when you compare the unmixed that is your ΔH_{mix} - $T\Delta S_{mix}$ correct. So, to that means, we need to have ways and means to calculate ΔH_{mix} and ΔS_{mix}.

ΔS_{mix} can be easily calculated by using Boltzmann hypothesis that $S = k ln W$ can be used with that; but what about ΔH_{mix}? Well, let us do that ok. So, most important ok thing about ΔH_{mix} is let me do it here ok.

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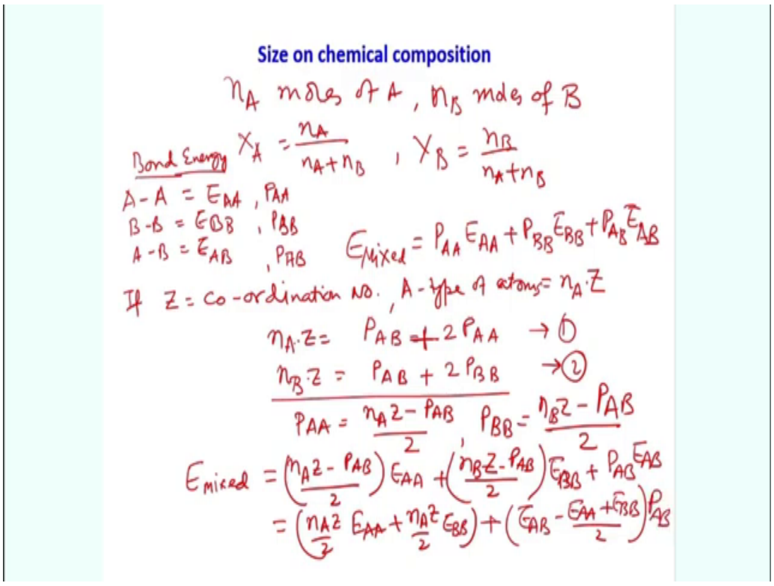

Size on chemical composition

n_A moles of A, n_B moles of B

Bond Energy $X_A = \frac{n_A}{n_A+n_B}$, $X_B = \frac{n_B}{n_A+n_B}$

A-A = E_{AA}, P_{AA}

B-B = E_{BB}, P_{BB}

A-B = E_{AB}, P_{AB} $\quad E_{Mixed} = P_{AA}E_{AA} + P_{BB}E_{BB} + P_{AB}E_{AB}$

If Z = Co-ordination No., A-type of atoms = $n_A \cdot Z$

$$n_A \cdot Z = P_{AB} + 2P_{AA} \rightarrow ①$$

$$n_B \cdot Z = P_{AB} + 2P_{BB} \rightarrow ②$$

$$P_{AA} = \frac{n_A Z - P_{AB}}{2}, \quad P_{BB} = \frac{n_B Z - P_{AB}}{2}$$

$$E_{mixed} = \left(\frac{n_A Z - P_{AB}}{2}\right)E_{AA} + \left(\frac{n_B Z - P_{AB}}{2}\right)E_{BB} + P_{AB}E_{AB}$$

$$= \left(\frac{n_A Z}{2}E_{AA} + \frac{n_A Z}{2}E_{BB}\right) + \left(E_{AB} - \frac{E_{AA}+E_{BB}}{2}\right)P_{AB}$$

Delta H mix is what? Correct? Is the model given by Quasi chemical theory, what is that model? Let us consider ok, I will talk from various sources, mostly from let us consider 1 mole of a solution consisting of 2 components A and B right and there are n_A numbers of A, n_A moles of A and n_B moles of B correct.

So, then, we can calculate the mole fraction of A and B as what? If I have n_A moles of A and n_B moles of B in a solid solution exist, the mole fraction of A, $X_A = \frac{n_A}{n_A+n_B}$. Similarly, $X_B = \frac{n_B}{n_A+n_B}$ right, ok.

Now, so many cases and AB atoms are situated in a solid solution, there will be lattice ok. Is it not? This is solid crystalline solid double lattice. So, therefore, some places A atoms will sit, some places B atoms will sit ok. So, that means, some places AB will form bonds, some cases A will form bonds, some cases BB will form bonds depending on how they are occupying the lattice right. This all probability exists. You agree with it, not? There is these three types of bonds can form.

Let us suppose the bond energies of A-A bond is one energy E_{AA}, these are all bond energies, B-B= E_{BB} and A-B is E_{AB}. So, let us double write that. E_{AA}, E_{BB} and E_{AB} three different bonds and three different energies. Now, what else we need? We need to know also number of bonds A-A type, B-B type, A-B type. Let us suppose number of bonds are A-A type is P_{AA} , B-B type is P_{BB} and A-B type P_{AB}, am I right?

So, therefore, in the when you mix them together, total bond energies, total bond energies, I write E_{Mixed}, when you mix them together automatically is number of bonds of $P_{AA}E_{AA} + P_{BB}E_{BB} + P_{AB}E_{AB}$, am I right?

Now, any crystalline lattice, they are with specific coordination number like in FCC coordination number is 12; that means, one atom is surrounded by 12 atoms; HCP also, BCC remember you can go back to my lectures, its 8, it is a common central atom and surrounded by 8 atoms. So, 8 is the coordination number.

So, nonetheless, if suppose Z is the coordination number, if Z is the coordination number, Z is the coordination number, then there will be how many AA type atoms? A-types atom type of atom, we obviously, will be equal to n_A; n_AZ; Z is a coordination number. Correct?

Now, this is talking about A-types of atoms ok. So, it will also have two types of bonds; A bonds and AB bonds that is possible right. Obviously, both the cases A is common. So, A atom is present in both cases; whereas, AA or AB does not matter, A is common. So, now, we have to calculate how many of these are AA and how many of these are AB.

So, I can write down easily n_AZ total number of A atoms in the one mole of step solution = $P_{AB} + 2P_{AA}$; P_{AB} is the number of AB bonds. It should have been a $P_{AB} + P_{AA}$; but we are adding $2P_{AA}$. Why? Because factor 2 is basically because each AA bond has two A atoms. But on the other hand, each AB bond has one A atoms. So, P_{AA} is number of AA bonds, each bond has two atoms and we are calculating number of A atoms.

So, therefore, this is must be used. Correct? Let us consider write down these as equation number 1. Similarly, I can write down n_BZ that is equal to $P_{AB} + 2P_{BB}$, n_BZ is number of B atoms. I hope this equation is clear to you right. Why the factor 2 is coming? Factor 2 is coming because each BB bonds has 2 atoms. So, you have to double the number of B atoms for one bond that is what.

So, easily you can solve these two equations ok. A and B, 1 and 2 equations that will give you $P_{AA} = \frac{(n_A Z - P_{AB})}{2}$ and $P_{BB} = \frac{(n_B Z - P_{AB})}{2}$. You do yourself right, I am not doing. That is easy basically, you have to subtract, then only you will get very easily.

So, now, let us calculate E_{mixed}. So, now, we know how many AA bonds, how many B bonds; one and this way, AA, BB, AB everything you know. So, what is E_{mixed}? Remember you mixed you have written like this, $P_{AA}E_{AA} + P_{BB}E_{BB} + P_{AB}E_{AB}$ So, ok so now, we are putting these things. So, P_{AA} is what? $\frac{(n_A Z - P_{AB})}{2} E_{AA}$.

Similarly, $\frac{(n_B Z - P_{AB})}{2} E_{BB} + P_{AB}E_{AB}$ right. So, we can always simplify it very easily. What? $\frac{n_A Z}{2} E_{AA} + \frac{n_B Z}{2} E_{BB} + (E_{AB} - \frac{E_{AA} + E_{BB}}{2})P_{AB}$. That is what you will get, correct? So, as usual the like last classes, we will erase the top part keeping some important things on this ok. So, that is the mixed.

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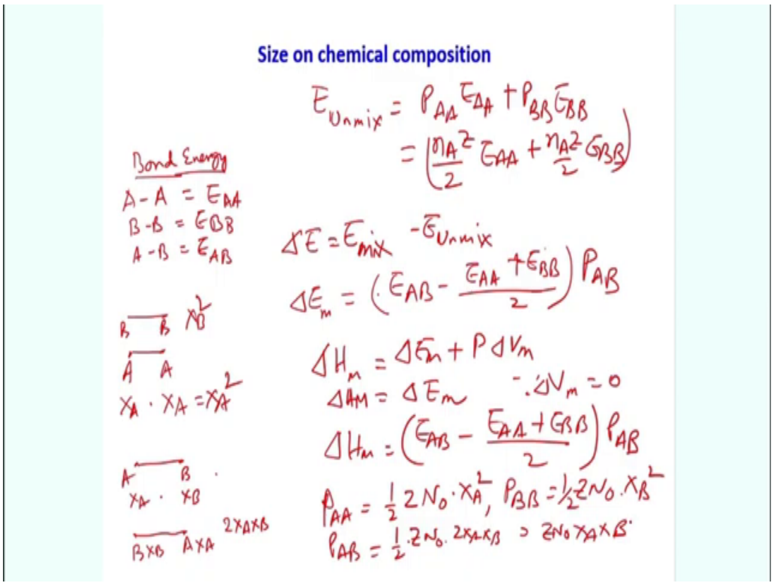

Size on chemical composition

$E_{Unmix} = P_{AA}E_{AA} + P_{BB}E_{BB}$

$= \left(\frac{n_A Z}{2} E_{AA} + \frac{n_A Z}{2} E_{BB}\right)$

Bond Energy

A - A = E_{AA}

B - B = E_{BB}

A - B = E_{AB}

$\Delta E = E_{mix} - E_{Unmix}$

$\Delta E_m = \left(E_{AB} - \frac{E_{AA} + E_{BB}}{2}\right) P_{AB}$

$\overline{B \quad B}$ X_B^2

$\overline{A \quad A}$

$X_A \cdot X_A = X_A^2$

$\Delta H_m = \Delta E_m + P\Delta V_m$

$\Delta H_m = \Delta E_m \quad \because \Delta V_m = 0$

$\Delta H_m = \left(E_{AB} - \frac{E_{AA} + E_{BB}}{2}\right) P_{AB}$

$\overline{A \quad B}$

$X_A \cdot X_B$

$\overline{B X_B \quad A X_A}$ $2X_A X_B$

$P_{AA} = \frac{1}{2} Z N_0 \cdot X_A^2, \; P_{BB} = \frac{1}{2} Z N_0 \cdot X_B^2$

$P_{AB} = \frac{1}{2} Z N_0 \cdot 2X_A X_B = Z N_0 X_A X_B$

What about unmixed states? When if you do not mix them like sand and salt. So, $E_{unmixed}$ that is very simple; $P_{AA}E_{AA} + P_{BB}E_{BB}$, there is no bond between A and B, unmixed right they are stated in separate. So, therefore, this can be written as $\frac{n_A Z}{2} E_{AA} + \frac{n_B Z}{2} E_{BB}$. So, ΔE that is nothing but $E_{Mix} - E_{Unmix}$ ok. This mix, not mixed.

That if you do the mathematics properly, what you will get? You will get simply this equation, $(E_{AB} - \frac{E_{AA}+E_{BB}}{2})P_{AB}$ that is what you will get, correct? Now, in solid solution theories, such a kind of Quasi chemical theory what we are talking about it; it is the Quasi chemical theory.

And Quasi chemical theory of like this, we assume that when you mix A and B together, there is no volume change, mix them that is very unlikely, but it is can be considered. So, in that case, so therefore, ΔH_{mix}, ΔH_{mix} is what? ΔH is ΔE correct. $\Delta H_m = \Delta E_m + P\Delta V_m$.

So, you use ΔV_m as 0; volume change, you have already assumed that is what is the assumption of delta of Quasi chemical theory. So, that means, since $\Delta V_m = 0$, so therefore, ΔH_m is $(E_{AB} - \frac{E_{AA}+E_{BB}}{2})P_{AB}$ that is what it is. So, what does it tells? It depends on the bond energies, differences of this similar bonds minus average of the similar bonds. So, ΔH_m sign will depends on difference of these terms; from E_{AB} and the $\frac{E_{AA}+E_{BB}}{2}$ right.

So, now, basically the problem boils down to how to find out the P_{AB}. Well, problem is now to basically from it find out P_{AB} right. Well, so ok. Now, we know that mole fraction of A, mole fraction of B. Mole fraction of A, mole fraction of B very easily right, we know very easily. So, mole fraction of A is X_A, mole fraction of B is X_B.

So, we can always consider probability of any A atom situated next to A atom as $X_A \times X_A$, probability of A atom sitting in the lattice is X A. So, probability of finding another A atom close to that atom is $X_A \times X_A = X_A^2$. It is very easy. If I have A atom here, so finding this A atom in the solid solution probability is X_A that is a mole fraction.

Now, I want to find another atom from here so that AA form bonds, probability of finding that is X_A. So, this probability of forming this bond is $X_A \times X_A$ that is X_A^2; same thing is true for B. So, now, probability of finding A atom here and then, B atom there is what? X_A and X_B.

But you can also have situation like this, probability of finding B atom here, then A atom here, the bond is same like that is between A and B and B and A is AB bonds. So, that is also $X_A X_B$. So, therefore, probability of finding AB bond is $2X_A X_B$. this is also true, this is also true. But probability of finding AA bond is X_A^2, BB bond is X_B^2 correct.

So, I can write down now knowing these aspects, P_{AB}, P_{AA}, if it is 1 mole. So, $P_{AA} = \frac{1}{2} Z N_0 X_A^2$, $P_{BB} = \frac{1}{2} Z N_0 X_B^2$ and $P_{AB} = \frac{1}{2} Z N_0 2 X_A X_B$ that is nothing but $Z N_0 X_A X_B$ right. This 2 and 2 goes down.

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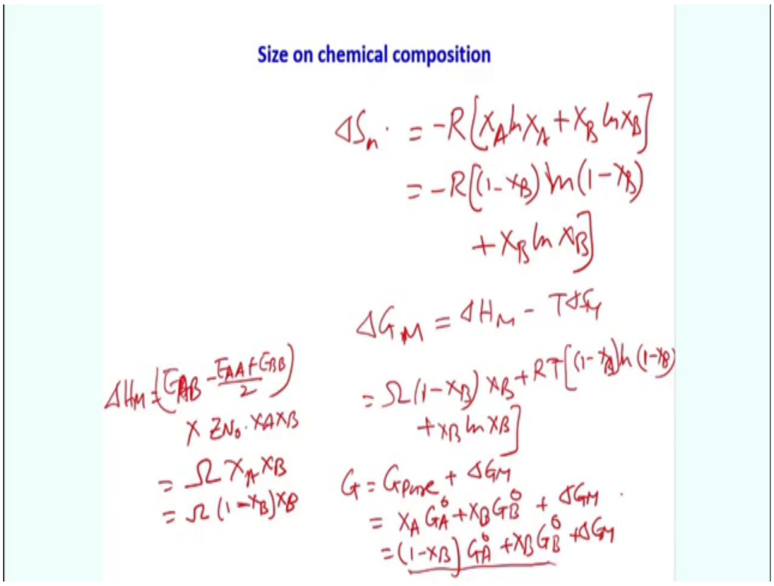

Size on chemical composition

$$\Delta S_m = -R\left[X_A \ln X_A + X_B \ln X_B\right]$$
$$= -R\left[(1-X_B)\ln(1-X_B) + X_B \ln X_B\right]$$

$$\Delta H_m = \left(E_{AB} - \frac{E_{AA} + E_{BB}}{2}\right) \times Z N_0 \cdot X_A X_B$$
$$= \Omega X_A X_B$$
$$= \Omega (1-X_B) X_B$$

$$\Delta G_M = \Delta H_M - T\Delta S_M$$
$$= \Omega (1-X_B) X_B + RT\left[(1-X_B)\ln(1-X_B) + X_B \ln X_B\right]$$

$$G = G_{pure} + \Delta G_M$$
$$= X_A G_A^0 + X_B G_B^0 + \Delta G_M$$
$$= \underline{(1-X_B) G_A^0 + X_B G_B^0} + \Delta G_M$$

So, now, let me erase some part to come to the conclusion of this Quasi-chemical theory. The conclusion of this Quasi chemical theory is that ΔH_m is nothing but $\Delta H_m = \left(E_{AB} - \frac{E_{AA}+E_{BB}}{2}\right)ZN_0X_AX_B$ and you know E_{AB}, E_{BB}, E_{AA}, Z and N_0 all are constant for a particular system.

When it comes to AB type system, two between two elements it is fixed, bond energy between AB, bond energy between 2 A-A atom, bond energy between 2 B-B atoms, Z coordination number and Avogadro number all are constant. So, that is plug in into a sigma. ΩX_AX_B and many times, it is written $\Omega(1 - X_B)X_B$ plus what it is ΔH_m.

So, you understood now how to get the ΔH_m. So, I am not going to do it how to get ΔH_m ok right. We are not going to do that. That is coming from the early Boltzmann, you should do yourself ok. There might be some homework for you also. So, what is that ok? What is that? Ok, let me erase it completely, leaving this part and I will let you know this is actually our elementary thermodynamics.

I will do it because many of you may not understand or many of you may be finding it out of the things. So, $\Delta S_m = - R(X_A lnX_A + X_B lnX_B) = - R((1 - X_B)ln(1 - X_B) + X_B lnX_B)$. So, now, you know the ΔG_M. Ok, I should not use mix, I should use M only because we have been using M.

So, ΔG_M is what? $\Delta H_M - T\Delta S_M$. So, that is becomes $\Omega(1 - X_B)X_B + RT$. This minus and minus sign will become + $RT((1 - X_B)ln(1 - X_B) + X_B lnX_B)$. that is my ΔG_M and this is Quasi chemical theory. This is something like a regular solution ok.

But there will be other models available, we are not going to that and what is G? G is basically $G_{pure} + \Delta G_M$ and what is G_{pure}? $X_AG_A^0$. X_A is the mole fraction of A. Pure A has a free energy of $X_AG_A^0 + X_BG_B^0 + \Delta G_M$ and this can be again written $(1 - X_B)G_A^0 + X_BG_B^0 + \Delta G_M$.

So, now, if you look at carefully, this equation, this is straight line ok. That is what you see in the earlier plot that is a straight line. This one, the first two terms. The last term shows is a parabola with $(1 - X_B)$; $1X_B$ is X_B^2, $(1 - X_B X_A)$ X_B^2, X_B $X_B - X_B^2$. Nonetheless, this is X_B^2 right that is why you are getting a parabola.

This is the reason origin for such a kind of shapes correct. So, now, so I have spoken about 20 minutes or so. So, therefore, this is something which you have been taught in thermodynamics of materials right.

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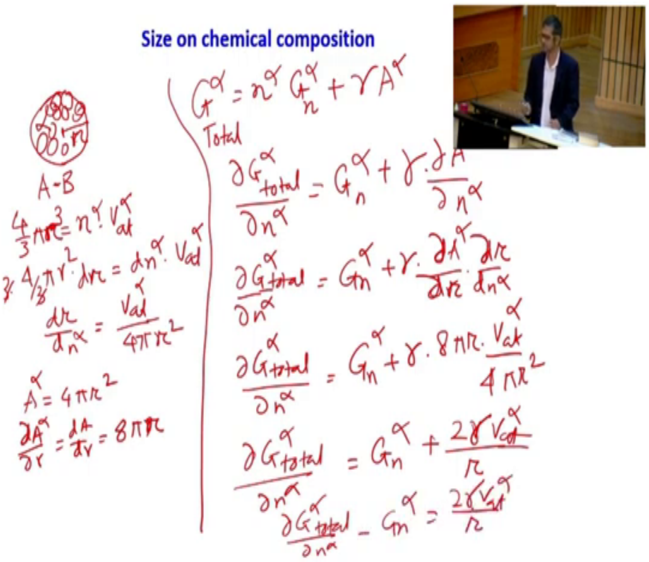

Size on chemical composition

A-B

$\frac{4}{3}\pi r^3 = n^\alpha V_{at}^\alpha$

$3 \cdot \frac{4}{3}\pi r^2 \cdot dr = dn^\alpha \cdot V_{at}^\alpha$

$\frac{dr}{dn^\alpha} = \frac{V_{at}^\alpha}{4\pi r^2}$

$A^\alpha = 4\pi r^2$

$\frac{\partial A^\alpha}{\partial r} = \frac{dA}{dr} = 8\pi r$

$G_{Total}^\alpha = n^\alpha G_n^\alpha + \gamma A^\alpha$

$\frac{\partial G_{total}^\alpha}{\partial n^\alpha} = G_n^\alpha + \gamma \cdot \frac{\partial A}{\partial n^\alpha}$

$\frac{\partial G_{total}^\alpha}{\partial n^\alpha} = G_n^\alpha + \gamma \cdot \frac{\partial A^\alpha}{\partial r} \cdot \frac{\partial r}{dn^\alpha}$

$\frac{\partial G_{total}^\alpha}{\partial n^\alpha} = G_n^\alpha + \gamma \cdot 8\pi r \cdot \frac{V_{at}^\alpha}{4\pi r^2}$

$\frac{\partial G_{total}^\alpha}{\partial n^\alpha} = G_n^\alpha + \frac{2\gamma V_{at}^\alpha}{r}$

$\frac{\partial G_{total}^\alpha}{\partial n^\alpha} - G_n^\alpha = \frac{2\gamma V_{at}^\alpha}{r}$

So, now we are going to discuss few important aspect. First, we are going to discuss about size effect on chemical compositions. That is why do we need this section, what is this? Well, that is very not difficult things to understand. I have already explained you various things. So, now, it is easy for me to do that.

It tells you that if I have a spherical particle of an alloy, this is spherical particle ok of radius R of an alloy component A and B. The composition of B or A, suppose composition is B whether it will remain same here the surface and center or there will be change of composition of B because of the curvature at on the circle. What do you think? Obviously, it will not be same and this will be scaling with $\frac{1}{r}$.

So, as the particle size will decrease, this will decrease that is the derivations, we are doing it in the last lecture right and now, you know it is a little bit tricky ok. So, let us consider this as a alpha phase correct. So, obviously, free energy of the alpha phase can be written like this.

Number of moles of alpha multiplied by G of 1 mole right. If its number of moles of alpha is n^{α} and alpha per mole as free energy is G_{n}^{α}, this is the free energy of alpha. Well here, we have considered this phase to be perfectly order. So, entropy change is compact. You can do it, this will make things complicated only correct ok.

Nonetheless, so, this is basically free energy of the bulk, we are not considered spherical particle or not. This is a free energy of the bulk big material alpha. So, if you want to know the total because of bulk and the surface, then you have to add γA^{α} that is obvious right. This is a free energy of alpha and the bulk, there is a free energy of the surface because it small size actually.

This bulk means very big, where you can surface area is very small, you can ignore that term second term; but in a nano, you cannot. You have to consider this term very seriously correct. Now, if you look at this construction obviously, this will be consisting a lot of atoms; A and B ok.

So, I can always write down $\frac{4}{3}\pi r^{3}$ is equal to this r is the radius. So, this is the volume that is equal to $n^{\alpha}V_{at}^{\alpha}$, what is that atomic volume? Volume of each atom, the volume of each atom is V_{at}^{α} that you multiply number of atoms in this shell which you have done actually that is equal to the total volume. That is nothing but $\frac{4}{3}\pi r^{3}$.

So, I can write down, if I differentiate these equations with respect to an alpha; $3\times\frac{4}{3}\pi r^{2}dr$; 3, 3 will get cancelled, dr, ok I think I should write this way; otherwise you will get confused gamma n r.

So, $dn^{\alpha}V_{at}^{\alpha}$. Why V_{at}^{α} will not change? It is a constant number, it will not change like γ. For a particular atomic species, the volume of the atom is fixed. So, what do you do? $\frac{dr}{dn^{\alpha}} = \frac{V_{at}^{\alpha}}{4\pi r^{2}}$;

right. This is understandable to you. It is easy correct. So, this is something which we will keep at the background here.

Now, we will work on this equation. So, I can always do the same thing, differentiation with respect to n^{α}. What does it give? This one at constant temperature, this is the chemical potential. If you look at carefully, this gives you chemical potential. $\frac{\partial G^{\alpha}_{Total}}{\partial n^{\alpha}}$ is basically chemical potential of alpha in the solid solution of A and B that is nothing but $G^{\alpha}_{n} + \frac{\gamma \partial A}{\partial n^{\alpha}}$ is always remain constant; γ we should assume constant isotropic.

Obviously, it will not be $\frac{\gamma \partial A}{\partial n^{\alpha}}$ right. It will be different, it will be partial. Am I clear? Well, I can write this equation like this $\frac{\gamma \partial A^{\alpha} \partial r}{\partial r \partial n^{\alpha}}$. Now, you understand why I derive this term $\frac{dr}{\partial r}$ right; $\frac{\partial r}{\partial n^{\alpha}}$, ok, the second term. Why did I do? So, you understand now right. Well, what is A? What is the surface area of this particle?

That is basically $4\pi r^{2}$. So, what is dA? That is a $\frac{\partial A^{\alpha}}{\partial r}$, this is nothing but here $\frac{dA}{dr}$, this is equal to $8\pi r$. So, I get this term. First, I write down this term $8\pi r \frac{V^{\alpha}_{at}}{4\pi r^{2}}$ by mistake. So, finally, that is what you get.

So, because of small size, you get an extra term called $\frac{2\gamma V^{\alpha}_{at}}{r}$. So, you can see that the chemical potential is too much dependent on that right. So, this then, further can be equated with the equations which I gave you earlier or not this ok, difference of these two; difference of these two means this term can be equated with the one which I derived in the last slide correct. Nonetheless, we will not prolong at these mathematical derivations to make you bore too much.

We come back to the actual thing right. That is can be done, anybody we can do that ok because I have given you the equations, we can always discuss when you are having questions or so, right. So, we could nonetheless what you can do? You can write down when you have a particle.

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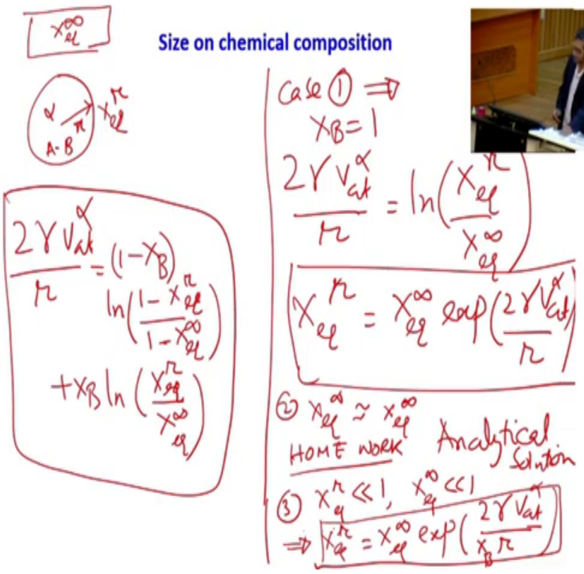

Size on chemical composition

$\boxed{X_{eq}^{\infty}}$

α

A-B

r

X_{eq}^{r}

$$\boxed{\frac{2\gamma V_{at}^{\alpha}}{r} = (1-X_B)\ln\left(\frac{1-X_{eq}^{r}}{1-X_{eq}^{\infty}}\right) + X_B \ln\left(\frac{X_{eq}^{r}}{X_{eq}^{\infty}}\right)}$$

Case ① ⟹

$X_B = 1$

$$\frac{2\gamma V_{at}^{\alpha}}{r} = \ln\left(\frac{X_{eq}^{r}}{X_{eq}^{\infty}}\right)$$

$$\boxed{X_{eq}^{r} = X_{eq}^{\infty} \exp\left(\frac{2\gamma V_{at}^{\alpha}}{r}\right)}$$

② $X_{eq}^{\alpha} \simeq X_{eq}^{\infty}$

HOME WORK Analytical Solution

③ $X_{eq}^{r} \ll 1$, $X_{eq}^{\infty} \ll 1$

$$\Rightarrow \boxed{X_{eq}^{r} = X_{eq}^{\infty} \exp\left(\frac{2\gamma V_{at}}{X_B r}\right)}$$

Let me; let us now remove it from a particle, the original problem ok and suppose, this is the composition equilibrium composition because of radius r and if you have bulk material, very very big the composition is infinity. We can always write down $\frac{2\gamma V_{at}^{\alpha}}{r} = 1-X_B$. Remember this is r, there is an alloy of AB of alpha phase, X B log of this is nothing but what?

The entropic terms right ok. So, $ln\left(\frac{1-X_{eq}^{r}}{1-X_{eq}^{\infty}}\right) + X_B \ln ln\left(\frac{X_{eq}^{r}}{X_{eq}^{\infty}}\right)$. You must be wondering, I am taking It is just compared to bulk right. Remember this is total free energy and we are subtracting total free energy minus G_n per mole action like what is this? This differentiation is basically per mole ok.

So, per mole basis, we are doing that; difference of total free energy minus free energy of the bulk. So, this is equal to $\frac{2\gamma V_{at}^{\alpha}}{r}$. This must be equal to the entropic term. So, this is equation whatever I have written here this has nontrivial solution, very difficult to solve. It is a possible logarithmic equation, it has two unknown terms, one unknown term although, that is no yes one unknown term that is X equilibrium at the surface for the radius of the particle r.

For the bulk, it may be known for a given value of X_B. But for the nano, it will not be known right. So, you need to find out that, but because the logarithmic equation, you may not be able to find the solutions. That is why you have to make a lot of simplifications for that and various simplifications are available various ok.

And if I keep on discussing, then it will take lot of time all the things. But I will tell you the different ways of you know kind of simplify these equations correct. So, how do you simplify first? First and easiest way of simplifying this is to assume a funny assumption, what is that?

Is to assume the case 1, case 1 it says that if I consider X_B to be equal to 1, the moment if you consider X_B equal to 1, basically it tells you it is a pure, it B; it is not A is there at all, mole fraction of B is 1 means mole fraction of a is 0 right. But funny, interestingly, if you do that, then it gives you what it gives you? It gives you these things, this term goes vanish.

So, I can write down $\frac{2\gamma V^{\alpha}_{at}}{r}$ is equal to first term (Refer Time: 43:12) vanishes, $X_B \ln ln\left(\frac{X^{r}_{eq}}{X^{\infty}_{eq}}\right)$. So, that means, $X^{r}_{eq} = X^{\infty}_{eq}\, exp(\frac{2\gamma V^{\alpha}_{at}}{r})$. This is something which is widely used ok. But you know that the assumption involved is very peculiar, X_B to be equal to 1.

Second assumptions and third assumption which is homework for you is that you can always assume $X^{r}_{eq} \sim X^{\infty}_{eq}$, that is nothing but a bulk right, you can try it out, it will lead to analytical solutions ok and I would like to know, what is analytical solutions. Please do your homework and submit.

And third one is you can always write down $X^{r}_{eq} \ll 1$ and $X^{\infty}_{eq} \ll 1$. If you do that, what does it happen? This term goes to close to 1, log 1 is 0. Then, you will get the same thing ok. No, you will not get the same thing, what we will get? Because this is spherically less than 1, this is very lesser 1.

So, this this becomes what? 1 minus this also become 1, 1 minus also become 1; 1 by 1 is 1, log of 1 is 0, first term vanishes. So, that is gives you X_B. X_B of what? $X^{r}_{eq} = X^{\infty}_{eq}\, exp(\frac{2\gamma V^{\alpha}_{at}}{X_B r})$, but along with, you will have X_B.

This tells me when the composition of X_B equilibrium composition is bulk and this nanoparticle is very small, I mean dilute alloys, this condition 3 is for dilute alloys, very dilute alloys. So, on the corners of the phase diagrams that is true, correct. So, this is more logically correct. That is why this equation is much better to be adopted, when you do these calculations ok.

Now, so, that is about the size on the chemical composition. So, you can see the r in nano materials distinctly affect the composition. So, whenever you are doing research, never accept the composition of the particle, when you put measure totality. You have to always measure compositions of the surface and a bulk of a center in the surface, then you can consider.

Center is obviously bulk because atoms are coordinated in the center of the particle; surface atoms are not coordinated, there are a lot of dangling bonds, the compositions must (Refer Time: 46:43) and that is how it should change. This is what is the analytical formulae is are talking about it. So, please remember this and let you also do this as a home assignments ok. Let us see how many of you do the maths properly. So, that is something which I wanted to discuss and finish of today ok.

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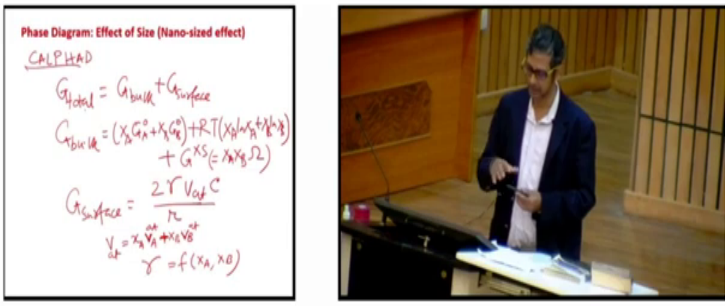

Phase Diagram: Effect of Size (Nano-sized effect)

CALPHAD

$$G_{total} = G_{bulk} + G_{surface}$$

$$G_{bulk} = (X_A G_A^o + X_B G_B^o) + RT(X_A \ln X_A + X_B \ln X_B) + G^{XS} (= X_A X_B \Omega)$$

$$G_{surface} = \frac{2 \gamma V_{at} C}{r}$$

$$V_{at} = x_A V_A^{at} + x_B V_B^{at}$$

$$\gamma = f(x_A, x_B)$$

Now, I am going to discuss something new today. You know we metallurgists and many of the ceramic engineers are interested in phase diagrams. Phase diagrams are very important, you can understand ok, very very important. Why? Because they carry information on various aspects right. Phase stability, temperature compositions ok, let us see that ok.

So, what is the effect of size on the phase diagram? How do you dealt with it? How can you deal with effect of size on the phase diagram? Can you do it or you cannot do it ok? So, you can do it many ways; normally, it is done by a technique known as CALPHAD ok. What is CALPHAD?

Calculation of phase diagram; CAL is for calculations, FAD phase and D is for diagram. Very simple thing is this CALPHAD uses the concept minimization of free energy, G which you have used in all the calculation that is what is they do, you minimize G. For a particular temperature, pressure composition whatever variables you have, they minimize. It is basically multivariable minimization problem.

Mathematically, you have a pressure, constant obviously one atmosphere metallurgical phase diagrams, temperature is not constant and they are composition are variable. So, it is a multivariable minimization of free energy is done by the CALPHAD. It is a routine program which is installed in many computers, it is available in our department and many others also. It does its very simple, you do not need to write a code or so.

But if interested, you can do that. What is the basic philosophy of that? So, it minimizes free energy G right. So, as you know G_{Total}, I have already done just now. $G_{Total} = G_{bulk} + G_{surface}$. G_{bulk} is the free energy of the bulk alloys and $G_{surface}$ is the surface energy or excess energy which is because of the surface right.

So, as you know I have already done G_{bulk} is first is your for a binary alloy, free energy of individual elements multiplied by the mole fractions in a binary alloy $X_A G_A^0 + X_B G_B^0$. What is G_B^0? 0 superscript means free energy of B to your state, when it is pure ok.

Because its mole fraction of X_B that is factor has to be multiplied. Then, you have a entropic term. Just now we have done that right. This is because of entropic change plus we have G^{XS} and what is this G^{XS}? G^{XS} is nothing but this G^{XS} is nothing but the one I wrote $X_A X_B \Omega$. This derivation has been shown and done for the Quasi-chemical theory right. So, that is the G_{bulk}. Now, what is $G_{surface}$? $G_{surface}$ is you know that $\frac{2\gamma V^{\alpha}_{at} C}{r}$, but this assumes spherical particle right.

If I want to do it for any particle, any shaped particle, you can multiply their factor C; C is a factor which will take care of the shape, shape change correct. So, now, you have the total free energy, G_{Bulk}, $G_{surface}$, then you minimize; but when you minimize this, you also need some more informations.

What you need is the $V_{at} = X_A V^{at}_A + X_B V^{at}_B$. Why you need that? Because you see this atomic volume that is what is required ok and what else you need? If you want you can or may not, you can basically use this gamma which is a surface energy also as a function of composition.

There are various models available, I am not discussing about that will complicate the situation ok. So, once, you have all this information with you, you have free energies and the atomic volume, what do you do? You can simply do a write a code in computer or you can basically use this platform available and calculate the this phase diagram that is a function of size. Today, let us see how a few of this looks like, then we will stop.

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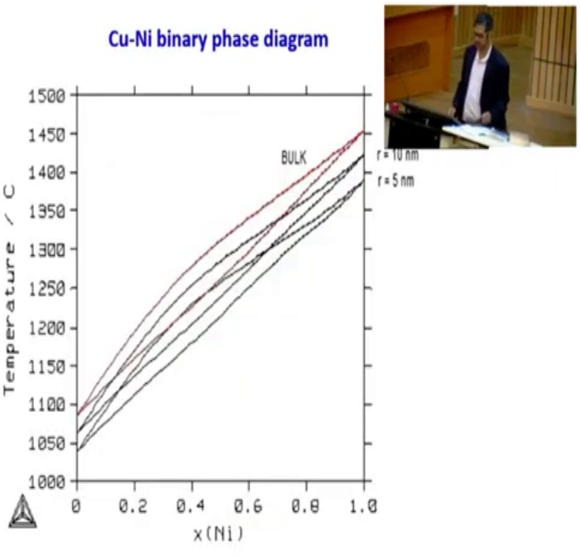

Cu-Ni binary phase diagram

So, this is the copper-nickel binary phase diagram; pure copper, pure nickel that is the mole fraction of a in a nice one. Mole fraction of C is 1. This is temperature on the y axis. Now, you see the bulk phase diagram is shown by red and for radius 5 and 10 nanometers shown, you can clearly see the phase diagram has gone down right. We will discuss maybe next class in detail manner.

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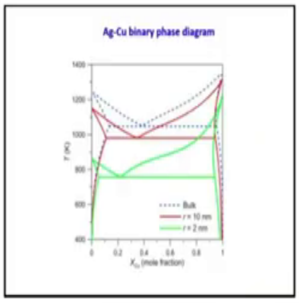

Ag-Cu binary phase diagram

This is for the silver copper eutectic phase diagram. You can clearly see the whole phase diagram has gone down. The bulk is shown by dotted blue and the size aspect is shown by red and the green in solid.

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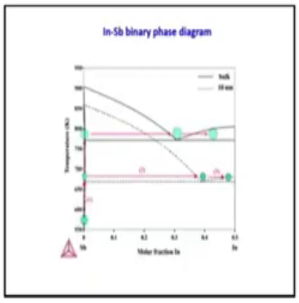

In-Sb binary phase diagram

Indium antimony phase diagram very funny ok, it shows eutectic; but no solid solubility on both sides. It also gets affected. We will discuss for this next class in detail about that.

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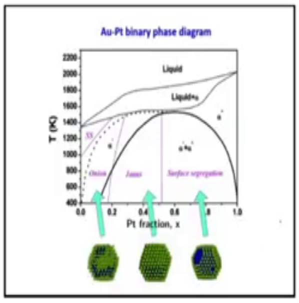

Au-Pt binary phase diagram

And also gold and platinum. So, every phase diagram does get affected by the size and this methodology, I have given. Now, we will discuss a bit some of these things in the next lecture to wind it up so that phase diagram aspect is known to you ok.

Thank you.