Nanomaterials and their Properties

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Lecture - 13

Nanophase Diagrams

Today as a part of the lecture 13 you know phase diagrams are very important they found the basis for various phase formation alloying mixing different components to get properties which are much better than the individual components. So, that is why a detailed discussion on the effect of size on this phase diagrams is warranted and it is important that you know these aspects.

So, that using the computational tools available nowadays you one can generate this kind of nanophase diagrams for various applications purposes. Even before you do experiments, you can probe these phase diagrams as a function of size and then understand what might be happening to it that is very important for you to know.

So, now question is how much we can discuss on these aspects right that is something which is very important. What I mean to say is that, how deep I can discuss about it. So, I am not going to discuss very deep. So, that it becomes very you know tangential to your understanding because, this requires quite a bit of fundamentals.

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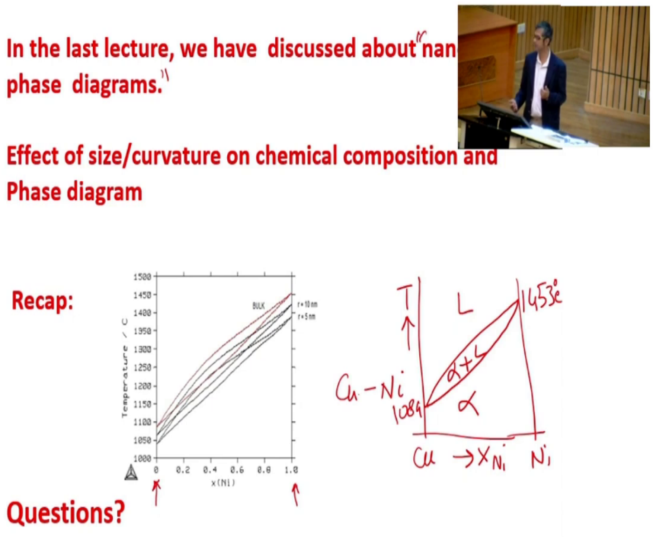

In the last lecture, we have discussed about "nan
phase diagrams."

Effect of size/curvature on chemical composition and
Phase diagram

Recap:

Questions?

So, what did you study in the last lecture? We have discussed about some nano aspects of nanophase diagrams ok; this word nanophase diagram means many things. So, that is why it should be you know quoted as such as because this is widely used in literature, but what does it mean is that effect of size and curvature on the chemical composition temperature and in an effect on the phase diagram itself.

As you see I have shown you this phase diagram again and again this is copper and nickel phase diagram. Copper and nickel actually is very you know the first phase diagram we study in material science and metallurgy that forms an isomorphous type phase diagram, what is the meaning of isomorphous?

Well, if you mix copper and nickel any proportion whatever proportion needs starting from 0.01 percentage of nickel into copper to 99.99 percentage of nickel into copper or vice versa ok. In the sense the phase formation is same, that is you will have a single phase forming that is the FCC solid solution between these two elements.

So, that means, its form continuous series of solid solutions depending on does not matter what is the composition of the alloy is. So, that is why it is called a isomorphous. That means, it looks same iso mean same; morphous means looking; ok. Morphology is what the synonymous word of morph is. So, it looks same for whatever way you look at it its basically lens separate phase diagram all of you know that ok.

Lens separate phase diagram in the literature copper and nickel ok; copper has a melting temperature much less than nickel, this is what is look like. I have drawn it earlier I am drawing it again, copper has a melting temperature of 1084 degree Celsius and so, this is temperature axis 1084 degrees Celsius nickel axis similar temperature 1453 degree Celsius ok and this is the mole fraction of nickel.

So, you add whatever amount of nickel into copper and vice versa. That means, copper into nickel or nickel into copper it forms same phase. So, you can clearly see that phase diagram which is basically representative of this red color thing here the written as a bulk is changing or its depending on the particle size or the diameter or radius of the particle its changing ok.

One thing is very clear for the pure copper or pure nickel lies on the both ends here and there the change is basically melting temperature change because of the size and because of curvature that we have already discussed ok you can go back to lecture previous lecture where I have discussed about this melting temperature change as a function of size or curvature ok.

So, that is understandable, there is no chemistry involved in that there is no chemical composition the pure component the copper or pure nickel, but in between in the center of the phase diagram or maybe in the both sides other than these two pure components you have an effect of chemical compositions, that is why we need to know how it is going to be its affected ok.

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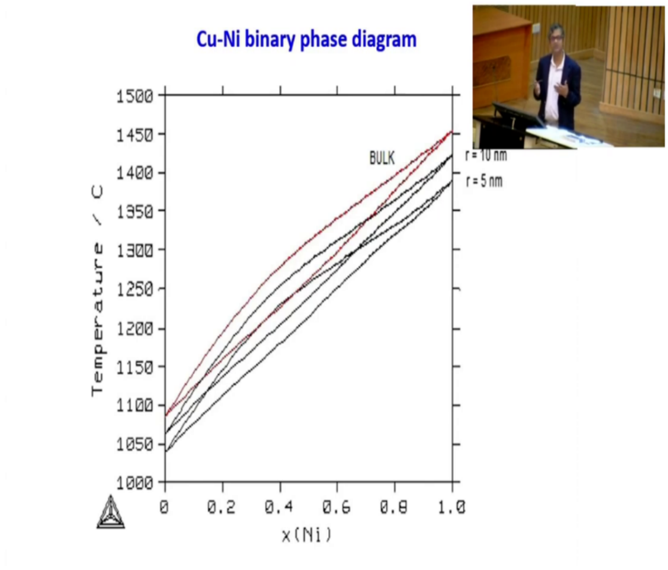
Cu-Ni binary phase diagram

So, while this is in an bigger picture of copper nickel phase diagram as you see the bulk one lies there the red color curves and the black ones are basically one for radius 10 nanometers, other one I said for radius 5 nanometers. So, what is the meaning of this; these diagrams are calculated using computational tools like using a program or maybe on a console platform which even we have in our department which you can do this.

One can write even codes to do that this is all possible, but the basic fundamental how these things are derived, how you make the calculations ok, mathematical background of this is required to be known then only you can do these things very easily and you will be doing in your understanding of research ok while you are doing nanomaterial research on various alloys or maybe various ceramic systems or polymeric systems also ok. So, that is something which is very fundamental which you need to know is at the fundamental level that is the purpose of these lectures.

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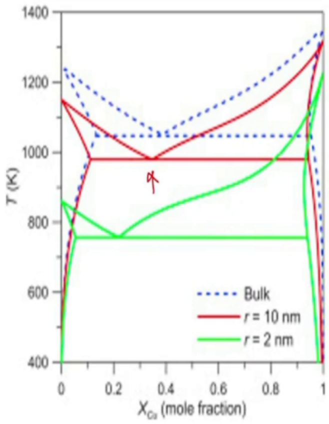
Ag-Cu binary phase diagram



And when you complicate phase diagrams like this one which is an eutectic phase diagram you see there is a eutectic point here right, it is between silver and copper. You know silver copper eutectic is very important material for various purposes think of solders ok little bit higher temperatures obviously.

Think of you know conductive materials both are highly electrically conducting materials or if you want to create different kinds of morphologies in nano scale you will this is one of the idle system to study and understand it ok. So, that is severely affected by the size you can clearly see bulk one is sorted dotted blue and then 10 and 2 nanometer size particles are showing red and green respectively. So, you could see that these effects are very-very significant they are not small effects.

So, that is why we need to know how these effects can be understood or how these effects can be easily tabulated using the mathematical formalisms using thermodynamics actually because thermodynamics dictates the equilibrium of (Refer Time: 07:18) ok. That is the thing which is which will be taught to you again and again from various subjects.

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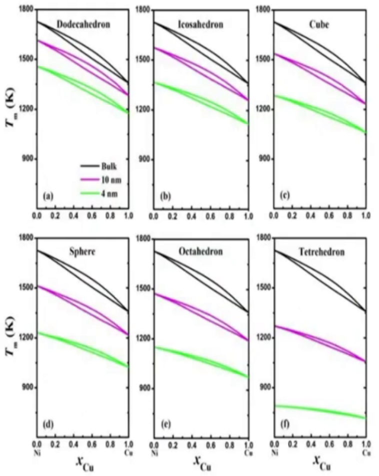

Well not only that I also discussed maybe we will come back 1 or 2 lectures later it is not in the size, but the shape of the particles also change the phase diagrams you can clearly see this is for copper and nickel its plotted in another way ok, nickel on the left side copper on the right side. Nickel has iron melting temperature that is why it is looking lens, but other type of lens ok other type of lens means the orientation of the lens is different ok.

So, now the question is this depending of the particle is dodecahedron; dodecahedron means there are tens face son the solid, icosahedrons 13th faces solid, cube 6 faces solid, sphere I octahedron or tetrahedron there is a significant difference as per the how the phase diagram look ok.

So, size effects are complemented by the shape. So, you know that if shape is a very important aspect because that also dictates the area of the nanoparticles, even it will dictates changes the curvature ok depending on which facets are available on that particular shape. So, that means that you need to know both the effect of size and shape. So, we are only discussing with the effect of size right now.

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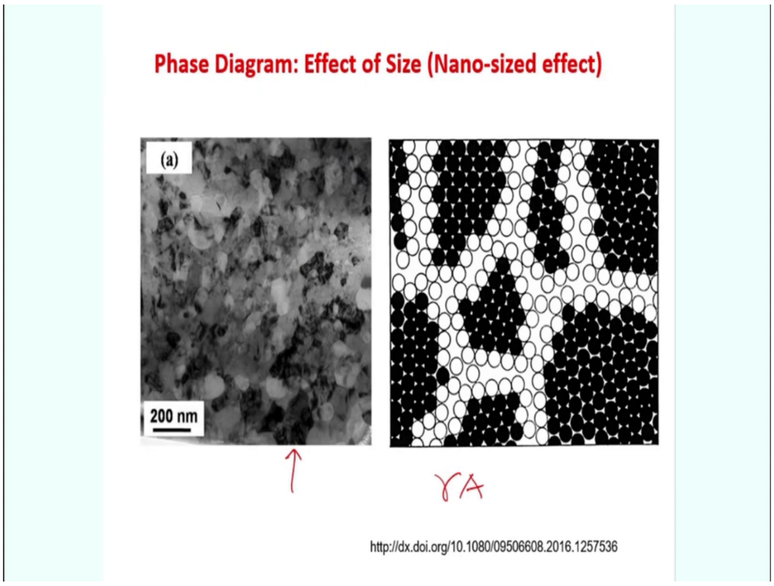

Phase Diagram: Effect of Size (Nano-sized effect)

http://dx.doi.org/10.1080/09506608.2016.1257536

Well you know that is, so most of you will be dealing with free nanoparticle like chemically synthesized or may-be you know thin film deposited in the substrate, but many of you will be dealing with bulk nanomaterials like let us think of a copper a rod of copper a rod basically ok like this kind of rod you see that this is a pen, and this is the shape of a rod, but it consist of nano crystalline grains of copper. That is what is shown here in this picture on the left side; nano crystalline grains of copper.

Now, these grains are separated from each other by boundary that is what we call it grain boundary ok every grain will be separated by the nearest nearby grain by a boundary.

Now have you ever thought the structural difference atomic structural difference between the grain and the grain boundaries there is a distinct difference ok the grains will have well arrangement of atoms and the boundary will have a haphazard or kind of a random or semi random kind of arrangement of atoms right it is nonorder at the boundaries.

So, that is what is the truth then grain boundaries by defect or by defect because of its atomic structure is are going to have a higher energy compared to the grains because atoms are nicely arranged, but in the grains grain boundary it is not. So, this will lead to extra energy.

So, this boundaries are called as like act as interface boundary ok. So, they are not surface, but they are actually interface and these interfaces will have high energy in nano crystalline size of grain this boundary area is pretty large and as you know total energy of system is gamma multiplied by A.

So, therefore, this is the gamma is one aspect, area is another aspect. As you increase area total energy, surface energy will increase and this will have a serious consequence on the stability of these grains and that is dictated by what thermodynamics ok stability is dictated by thermodynamics, whether these grains will be retained in the size or not or they will coercion over the time scale that all will be dictated by the thermo-dynamical aspects or stability aspects of that.

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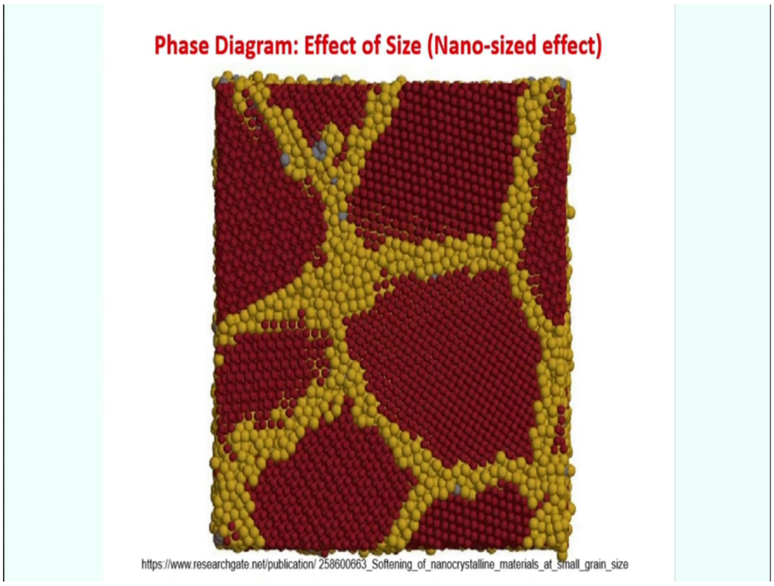

Phase Diagram: Effect of Size (Nano-sized effect)

https://www.researchgate.net/publication/ 258600663_Softening_of_nanocrystalline_materials_at_small_grain_size

So, this is what I have shown you the grain boundary structures are completely different from the grains and the grains will have well arrangement of atoms grain boundaries will have different atoms ok well. So, that is something which is has been discussed from the days of Herbert Gleiterlong back 1980s to now and people have really converged this kind of structures are possible in the nanocrystalline material ok.

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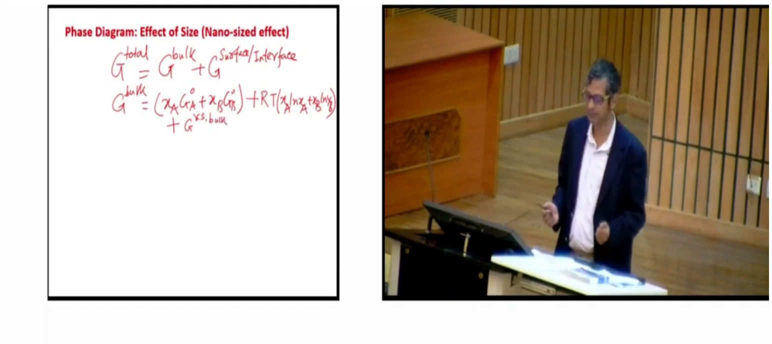

Phase Diagram: Effect of Size (Nano-sized effect)

$$G^{total} = G^{bulk} + G^{Surface/Interface}$$

$$G^{bulk} = (x_A G_A^0 + x_B G_B^0) + RT(x_A \ln x_A + x_B \ln x_B) + G^{xs,bulk}$$

Now, as you know we are talking about effect of size on the phase diagrams. So, what did I do ok? So, very simple thing we did is that, total free energy system has two parts; one is the bulk you know I am writing all G because we talked in metallurgy and material science we use always Gibbs free energy.

Gibbs free energy is predominantly used physics community you say Helmholtz free energy ok that is a different thing not so much different, but there is distinct difference between these two, but we are talking about Gibbs free energy. So, let us focus on that. So, $G^{total} = G^{bulk} + G^{surface/interface}$ right in a nano-crystalline bulk material, you have grain boundaries that is nothing but an interface and what did I do? I did like this, the bulk has three parts, this is known to most of you it is the physical mixture that $x_A G_A^0 + x_B G_B^0$ and because of atomic mixing which leading to solid solution formations. What do you have? You have a entropic change that is dictated by this term RT($x_A$lnx_A+$x_B lnx_B$)+$\Omega x_A x_B$) remember this ln terms are log terms ok, this directly comes from you know Boltzmann's law you can do that. And along with that you have to add an extra term that is known as, $G^{XS,bulk}$ people write XS ok and obviously, because it is bulk let us write this correct. Now, what is this term? This term we have already discussed right because you are mixing them together, the bond characteristics are changing depending on the characteristics of the bonds you are going to have extra term like this remember ok.

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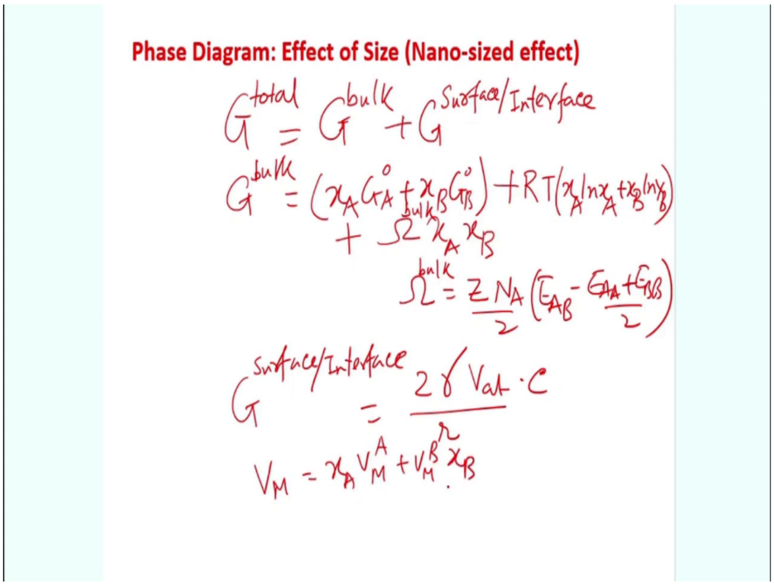

Phase Diagram: Effect of Size (Nano-sized effect)

$$G^{total} = G^{bulk} + G^{Surface/Interface}$$

$$G^{bulk} = (x_A G_A^{o} + x_B G_B^{o}) + RT(x_A \ln x_A + x_B \ln x_B) + \Omega^{bulk} x_A x_B$$

$$\Omega^{bulk} = \frac{Z N_A}{2}\left(E_{AB} - \frac{E_{AA} + E_{BB}}{2}\right)$$

$$G^{Surface/Interface} = \frac{2\gamma V_{at} \cdot C}{r}$$

$$V_M = x_A V_M^A + V_M^B x_B$$

I should write X properly they are not different X remember, this term omega is basically equal to coordination number multiplied by Avogadro number by $2E_{AB}$ minus E_{AA} plus E_{BB} by 2, I do this thing repeatedly. So, that whenever you are studying a lecture it gets backs to.

You do not misunderstands me do not try to misunderstand me these are intentionally done. So, that you can have a slighter feeling of the things as the equations do appear again and again you will have a feeling what are the meaning of physical meaning of this equations ok.

Now, this is G^{bulk} right obviously, you need to write this one also bulk ok better to write then $G^{surface}$ or interface is written very simply for a spherical particle you know that $G^{surface/interface} = \frac{2\gamma V_{at} c}{r}$ where c is a constant depends on the shape ok. Now, other than this you need also the molar volume of the whole thing that is nothing but $V_m = x_A V_m^A + x_B V_m^B$ ok. Let us write it properly there is a systematic of writing things.

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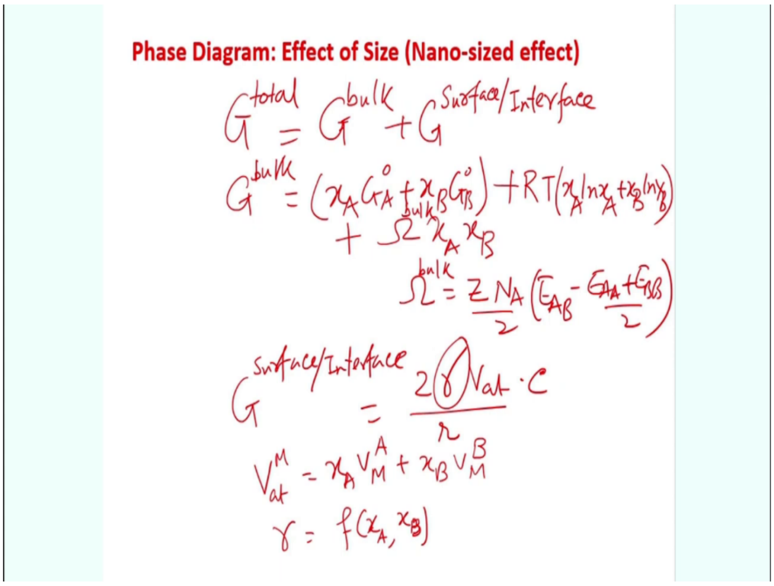

Phase Diagram: Effect of Size (Nano-sized effect)

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$$G^{Surface/Interface} = \frac{2\boxed{\gamma} V_{at}}{r} \cdot C$$

$$V_{at}^{M} = x_A V_M^A + x_B V_M^B$$

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

Because that is you, need in the $G^{interface}$ term this term will go there ok. I understand correct that is what you need the V^{atomic} volume will go because it is molar that is why I am we are writing m correct. So, how do you get it? For V, pure A and pure B you can easily get it you know the mole molecular weight and you know the density then divide molecular weight by density you get molar volume that is easy, then you know the mole fractions X_A and X_B you can do a simple maths to do that. But you know also you need we pointed out γ which is the interfacial energy or the surface energy it is also for an alloy strong function i.e. $\gamma = f(x_A, x_B)$, but in normal calculations if you want to use this methodology which is called CALPHAD methodology very simple one you ignore that you do not consider gamma to be a function of X_A and X_B because that will make the equations nonlinear and difficult to solve, but it is possible to solve ok.

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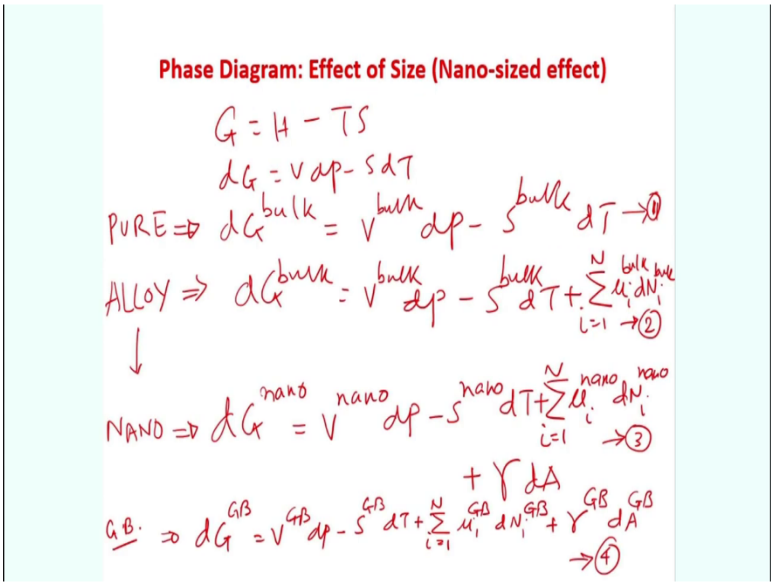

Phase Diagram: Effect of Size (Nano-sized effect)

$G = H - TS$

$dG = Vdp - SdT$

PURE $\Rightarrow dG^{bulk} = V^{bulk}dp - S^{bulk}dT \rightarrow ①$

ALLOY $\Rightarrow dG^{bulk} = V^{bulk}dp - S^{bulk}dT + \sum_{i=1}^{N} \mu_i^{bulk} dN_i^{bulk} \rightarrow ②$

$\downarrow$

NANO $\Rightarrow dG^{nano} = V^{nano}dp - S^{nano}dT + \sum_{i=1}^{N} \mu_i^{nano} dN_i^{nano} \rightarrow ③$

$+ \gamma dA$

GB. $\Rightarrow dG^{GB} = V^{GB}dp - S^{GB}dT + \sum_{i=1}^{N} \mu_i^{GB} dN_i^{GB} + \gamma^{GB} dA^{GB}$

$\rightarrow ④$

So, now you know this aspects. The question is how do I built in the gamma as a functional composition that was something, which we started up, and we discussed. So, you know G, I did something I will repeat it is this and $dG = VdP - SdT$ right this calculus variation we have done. So, therefore, you know for pure dG^{bulk} for pure this is pure suppose pure means without any change of chemical you know other entities actually it is pure A pure B say this $dG^{bulk} = V^{bulk}dP - S^{bulk}dT$ and V^{bulk} you know volume and S^{bulk} is the entropy right. But for an alloy; for an alloy when you have 2 components or 3 components, what do you have? When you have alloy, i.e., $dG^{bulk} = V^{bulk}dP - S^{bulk}dT + \sum_{i=1}^{N} \mu_i^{bulk} dN_i^{bulk}$ you have an additional term $\mu_i^{bulk} dN_i^{bulk}$ i going to 1 to N. Yes, you can have solid solution consisting of Number of components ok, it does not matter whether this N is 1 or N is 2 it can be generalized ok.

So, now correct, but what about same thing for alloy at the nanocrystalline size; nanocrystalline size means very small size. What will happen? You have to add some extra term. So, that is why we write $dG^{nano} = V^{nano}dP - S^{nano}dT + \sum_{i=1}^{N} \mu_i^{nano} dN_i^{nano} + \gamma dA$, where you need to add surface energy term or interfacial energy term that is γdA correct. Size multiplied by γ that ok but γ is independent of anything we always assume, that is why it is otherwise it should have been γdA plus $Ad\gamma$, but because gamma is we are assuming to be constants in all the calculations so far we can use we can ignore $d\gamma$ term ok.

And if you have, if you are considering the bulk nanomaterial, so, you have a grain boundary structure grain boundaries then this will be GB I have to be careful when writing the equation i.e., $dG^{GB} = V^{GB}dP - S^{GB}dT + \sum_{i=1}^{N} \mu_i^{GB} dN_i^{GB} + \gamma^{GB} dA^{GB}$ right that is understandable many times people.

So, this is this gamma is different here for the equation this is suppose let us suppose this is 1 for bulk. This is two for alloy; three for nano alloy and four for nano crystalline material bulk wherever grain boundaries correct, you understand that. Now, we will take up the last equation go to the next slide.

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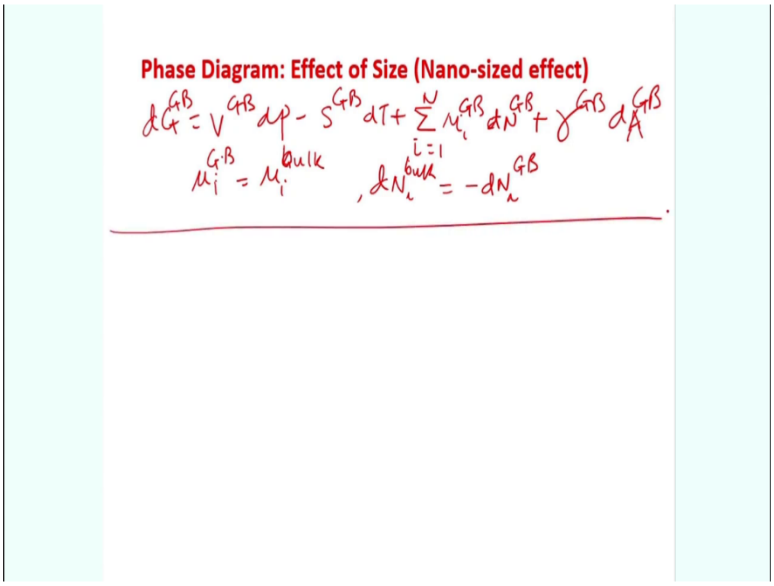

Phase Diagram: Effect of Size (Nano-sized effect)

$$dG^{GB} = V^{GB}dp - S^{GB}dT + \sum_{i=1}^{N} \mu_i^{GB} dN^{GB} + \gamma^{GB} dA^{GB}$$

$$\mu_i^{G.B} = \mu_i^{bulk} \quad , dN_i^{bulk} = -dN_i^{GB}$$

So, you know I have to write it out, you do not have to write. So, if you write out the last equation. So, that it becomes helpful that is the job of a teacher write as many times as possible. So, that it becomes understandable for the student right.

So, this is $dG^{GB} = V^{GB}dP - S^{GB}dT + \sum_{i=1}^{N} \mu_i^{GB} dN_i^{GB} + \gamma^{GB} dA^{GB}$ GB is superscript GB is always a superscript because it is talking about grain boundaries right. Now, when you do this when you have a such a kind of structures when you have grain boundaries and grains just now I have shown you.

So, two other conditions to be made out, so, this is the system right grain and grain boundaries. Obviously, the first condition to be met is $\mu_i^{GB} = \mu_i^{bulk}$ or $dN_i^{GB} =- dN_i^{bulk}$ rather bulk, inside the grain its atoms are in a like a bulk state all the bounds satisfied only the boundaries they are not right because haphazard arrangement of atoms are present just like we have discussed in case of surface.

So, interfaces also similar types they are dangling bonds or wrong bonds all kinds of things are possible because of that you have energy increase correct. But this condition which is the Gibbs conditions that interfacial energy across the interface grain and grain boundary must be same otherwise thermodynamic stability will not be valid, this is very fundamental, you can derive it.

In fact, this is what you can find in many of lectures myself on phase diagrams or may be thermodynamics of materials or phase transformation materials this equation is derived. The conditions of equality of chemical potentials of any component in both the phases must be equal at equilibrium.

And secondly, you need also to follow this condition also. For any component i, $dN_i^{GB} =- dN_i^{bulk}$. What does it mean? That means if you have a transport of mass from the grain-to-grain boundaries opposite is true, loss of mass to the grain boundary grain and grain of the mass to the grain boundaries. So, this total mass should be conserved. So, $dN_i^{GB} + dN_i^{bulk} = 0$ there is no gain no loss.

If you transfer from one place to other what the place from where you are transferring that place loses and the place where it is getting transferred that place gains. So, if it is transferred from grain to grain boundary that is what happens it can also happen from grain boundary to grain correct. If a grain boundary is consumed then this will not happen, if the grain boundary is accreted then other things will happen nonetheless this vital conditions to this mass transfer condition is to be satisfied.

So, now as you know if you consider only for a bulk material that is we have written ok this is these are all 3, 4, 5 equations ok. So, now, I go back here ok. I erase this part that is what I have did I will go back there erase some part of it, why did I do it ok let us while write it down. So, I am just size effects I am erasing now, we will go back to bulk and then start deriving some equations so that you understand.

You know our basic purpose is to calculate the gamma as a function of chemical composition that is what our basic job is. In order to do that, I am explaining many fundamental concepts. So, that you do not forget it and nothing you know is lost correct.

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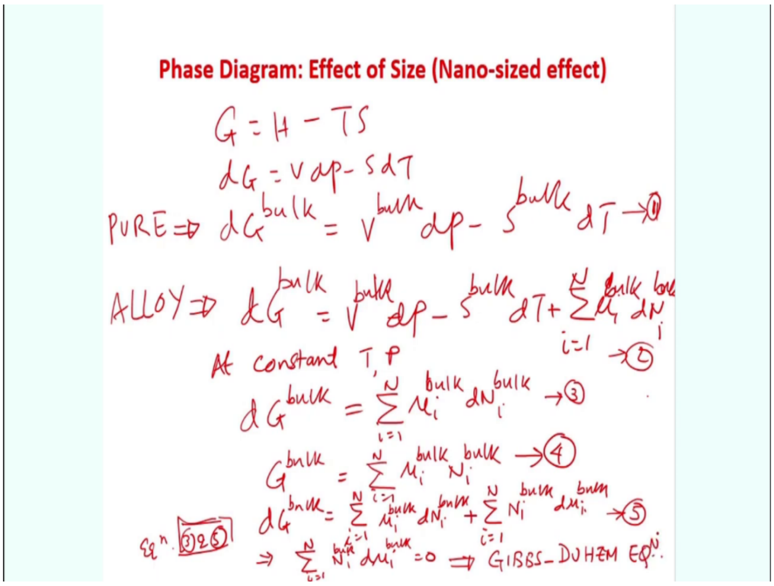

Phase Diagram: Effect of Size (Nano-sized effect)

$G = H - TS$

$dG = Vdp - SdT$

PURE ⇒ $dG^{bulk} = V^{bulk} dp - S^{bulk} dT \rightarrow ①$

ALLOY ⇒ $dG^{bulk} = V^{bulk} dp - S^{bulk} dT + \sum_{i=1}^{N} \mu_i^{bulk} dN_i^{bulk} \rightarrow ②$

At constant T, P

$dG^{bulk} = \sum_{i=1}^{N} \mu_i^{bulk} dN_i^{bulk} \rightarrow ③$

$G^{bulk} = \sum_{i=1}^{N} \mu_i^{bulk} N_i^{bulk} \rightarrow ④$

$dG^{bulk} = \sum_{i=1}^{N} \mu_i^{bulk} dN_i^{bulk} + \sum_{i=1}^{N} N_i^{bulk} d\mu_i^{bulk} \rightarrow ⑤$

$Eq^n.\ \boxed{③ \,\&\, ⑤}$ $\Rightarrow \sum_{i=1}^{N} N_i^{bulk} d\mu_i^{bulk} = 0 \Rightarrow$ GIBBS-DUHEM EQN.

So, what was this equation for alloy which I mistaken $dG^{bulk} = V^{bulk} dP - S^{bulk} dT$ right. So, at constant pressure and temperature, what is the meaning of that? dP is 0, dT is 0 because temperature and pressure are constant. So, therefore, differentiation differential of those two are, dP=0, dT=0.

So, dG^{bulk} become only dependent on composition correct. So, if I integrate that I get $G^{bulk} = \sum_{i=1}^{N} \mu_i^{bulk} N_i^{bulk}$. So, this was I write down 2, this is 3, this is 4 right. So, if you differentiate now totally ok this term, what do you get? dG^{bulk} is total differentiation is $\sum_{i=1}^{N} \mu_i^{bulk} dN_i^{bulk} + \sum_{i=1}^{N} N_i^{bulk} d\mu_i^{bulk}$ correct. So, this equation I term as 5.

Now, if you compare equation 3 and equation 5 these two, if you compare equation 3 and 5 ok, these two equations especially what do you get? Compare means, you suppose subtract, you will freely simply you will get $\sum_{i=1}^{N} N_i^{bulk} d\mu_i^{bulk}=0$, this one this is known as Gibbs-Duhem equation for bulk many of you have studied that it's nothing about it ok.

So, now because I am doing this calculation again I erase some part of it at the top and bring there because we can finish it up in one slide. So, that you can understand, so that means, so this is for the bulk ok, everything is bulk you see. So, what will happen to nanoscale; same thing analogically.

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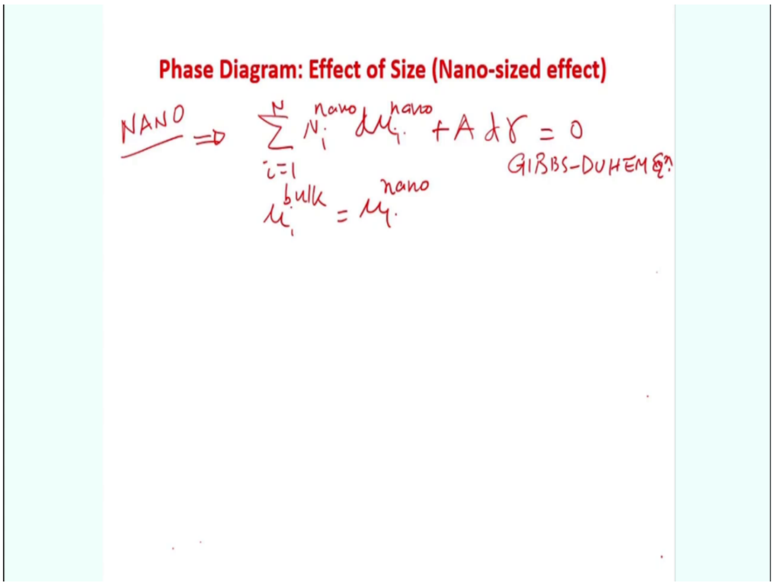

Phase Diagram: Effect of Size (Nano-sized effect)

NANO $\Rightarrow \sum_{i=1}^{N} N_i^{nano} d\mu_i^{nano} + A\,d\gamma = 0$ GIBBS-DUHEM Eq^n

$\mu_i^{bulk} = \mu_i^{nano}$

You can write down same things for nano, what will happen this is $\sum_{i=1}^{N} N_i^{nano} d\mu_i^{nano} + A d\gamma$ =0. So, that is the difference between of Gibbs-Duheme equation for the bulk and this is also Gibbs-Duhem bulk and nano. So, nano you are adding a term Adγ gamma correct. So, that is the difference between bulk and nano right.

So, now let us go forward and with this equation, correct. We will apply some constraint or constraints rather which I have already discussed for this equation and try to derive the γ as a function of composition right, that is what we will do that is why you have a $d\gamma$ term right. So, you those who are smart guys, smart girls they will understand why you have $d\gamma$ term there because we all like to know we would like to know gamma as a function of composition, then our job is done then you can plug in that equation into the model which we have done ok.

If you do that; we can plug in there this gamma and do the calculation right. So, ok you must be looking at this gamma right, this G interface term gamma is there. So, gamma we can plug in there as a functional composition make the equation much more reliable ok. So, as you know $\mu_i^{nano} = \mu_i^{bulk}$ ok or let us simple change to grain and grain boundaries that becomes very easy right that is much easier. So, I am putting this say all say grain boundary ok.

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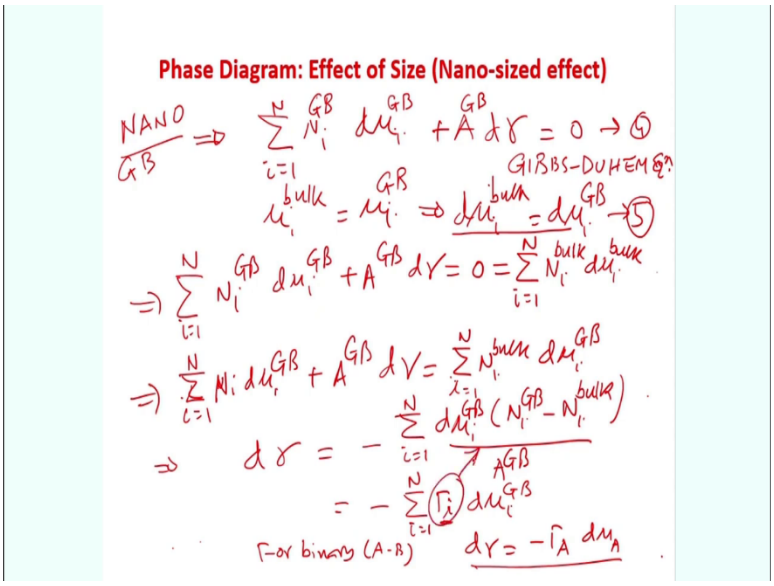

Phase Diagram: Effect of Size (Nano-sized effect)

$$\frac{NANO}{GB} \Rightarrow \sum_{i=1}^{N} N_i^{GB}\, d\mu_i^{GB} + A^{GB}\, d\gamma = 0 \rightarrow ④$$

GIBBS-DUHEM Eq^n

$$\mu_i^{bulk} = \mu_i^{GB} \Rightarrow \underline{d\mu_i^{bulk} = d\mu_i^{GB}} \rightarrow ⑤$$

$$\Rightarrow \sum_{i=1}^{N} N_i^{GB}\, d\mu_i^{GB} + A^{GB}\, d\gamma = 0 = \sum_{i=1}^{N} N_i^{bulk}\, d\mu_i^{bulk}$$

$$\Rightarrow \sum_{i=1}^{N} N_i\, d\mu_i^{GB} + A^{GB}\, d\gamma = \sum_{i=1}^{N} N_i^{bulk}\, d\mu_i^{GB}$$

$$\Rightarrow \quad d\gamma = -\sum_{i=1}^{N} \frac{d\mu_i^{GB}\left(N_i^{GB} - N_i^{bulk}\right)}{A^{GB}}$$

$$= -\sum_{i=1}^{N} \Gamma_i\, d\mu_i^{GB}$$

For binary (A-B) $\quad \underline{d\gamma = -\Gamma_A\, d\mu_A}$

Why I am doing that you must be thinking, why sir is doing this? Because that thing the analysis will be same, but because we are discussing about grain and grain boundaries this will be making our life much easier for you to understand that is the only purpose you can always write down nano and keep on doing the calculation, am I right?

So, this gives used $\mu_i^{GB} = \mu_i^{bulk}$ you can always differentiate correct. So, then I can use this equation which is $\sum_{i=1}^{N} N_i^{GB} d\mu_i^{GB} + A^{GB} d\gamma = 0$. So, what will happen? Well, this means $N_i^{GB} \mu_i^{GB}$,there is an additional step which I am missing $A^{GB} d\gamma$ is equal to 0 right this also can be written as less you are thinking why I am doing this.

Because this is also equal to zero, this is the Gibbs-Duheme equation; Gibbs-Duheme equation for bulk $\sum_{i=1}^{N} N_i^{GB} d\mu_i^{GB} + A^{GB} d\gamma = 0 = \sum_{i=1}^{N} N_i^{bulk} dN_i^{bulk}$. So, you can always equate right and there is nothing in wrong about it, this term is also 0 this term is also 0. So, you can always equate these two terms. Mathematically this is nothing wrong about it ok, physically there may be some problem, and mathematically we can do this.

So, now because we have done this the top equation now we can always write down, $\sum_{i=1}^{N} N_i^{GB} d\mu_i^{GB} + A^{GB} d\gamma = \sum_{i=1}^{N} N_i^{bulk} dN_i^{bulk}$ this term because of this equality I can change over. So, finally, what do you get? Finally, if you do a maths carefully you will get $d\gamma = -\sum_{i=1}^{N} \frac{d\mu_i^{GB} N_i^{GB} - N_i^{bulk}}{A^{GB}}$ So, you could see that finally, after doing. So, much of maths you must be thinking I could relate $d\gamma$ as a function of composition and the change of chemical potential or the grain boundary. Now, my task will be to convert this change of chemical potential into composition then I am done actually, then I can relate integrate this equation and get gamma as a function of composition, how do we do that right. Well, that is not very difficult to do ok, why? Well, first of all this is always written as summation this term divide by A^{GB} is written as $d\gamma = -\sum_{i=1}^{N} \frac{d\mu_i^{GB} N_i^{GB} - N_i^{bulk}}{A^{GB}} = -\sum_{i=1}^{N} {}_{i} d\mu_i^{GB}$. So, for binary system binary means, AB, $d\gamma = - {}_{A} d\mu_A$ all right, this is what we can write. So, we will use this one from now onwards because binary is easy, forget about summation size you can use the binary. So, now, in order to convert this you know this why do you use this kind of capital gamma because of isothermal effects ok that is why sorry absorption effects.

So, whenever you have a nano crystalline grain composition of grain boundaries may will be different because of the chemical potential, equality and many other transport effects correct. So, now I am going to erase this part which we kept it.

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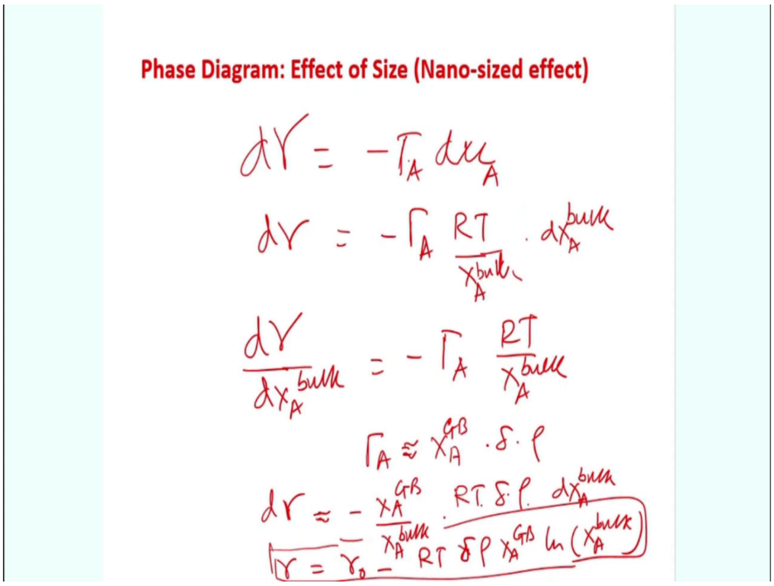

Phase Diagram: Effect of Size (Nano-sized effect)

$$d\gamma = -\Gamma_A \, d\mu_A$$

$$d\gamma = -\Gamma_A \frac{RT}{X_A^{bulk}} \cdot dX_A^{bulk}$$

$$\frac{d\gamma}{dX_A^{bulk}} = -\Gamma_A \frac{RT}{X_A^{bulk}}$$

$$\Gamma_A \approx X_A^{GB} \cdot \delta \cdot \rho$$

$$d\gamma \approx -\frac{X_A^{GB}}{X_A^{bulk}} \cdot RT \cdot \delta \cdot \rho \cdot dX_A^{bulk}$$

$$\boxed{\gamma = \gamma_0 - RT\,\delta\,\rho\,X_A^{GB} \ln\left(X_A^{bulk}\right)}$$

So, here as you have seen d gamma has become very simple equation for binary that is minus ok this is what is d gamma is, now to over simplify it that is what we will do. We can apply Henry’s law, why? What is Henry’s law by the way? Henry’s law many of you may not know it, let us let me explain it and we will come back. We will apply Henry’s law to this ok, so let, me just discuss.

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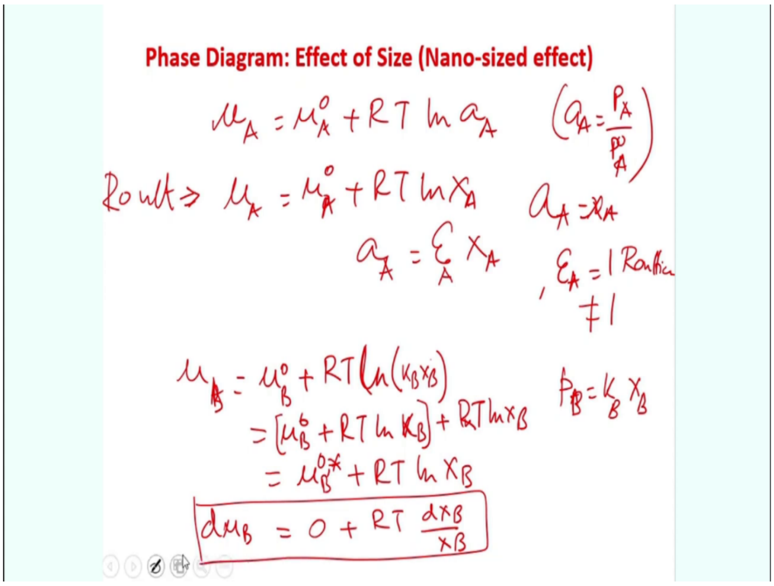

Phase Diagram: Effect of Size (Nano-sized effect)

$$\mu_A = \mu_A^0 + RT \ln a_A \quad \left(a_A = \frac{P_A}{P_A^0}\right)$$

Rault ⇒ $\mu_A = \mu_A^0 + RT \ln x_A$ $\quad a_A = x_A$

$$a_A = \varepsilon_A x_A \quad , \varepsilon_A = 1 \text{ Raultia}$$
$$\neq 1$$

$$\mu_B = \mu_B^0 + RT \ln(k_B x_B) \quad p_B = k_B x_B$$
$$= [\mu_B^0 + RT \ln k_B] + RT \ln x_B$$
$$= \mu_B^{0*} + RT \ln x_B$$
$$\boxed{d\mu_B = 0 + RT \frac{dx_B}{x_B}}$$

You know general and what is general form of chemical potential. General form of chemical potential is $\mu_A = \mu_A^0 + RT\ln a_A$ ok activity a_A and activity for gas it is written as a $a_A = \frac{P_A}{P_A^0}$ in a gas mixture partial pressure P divided by the pressure of pure A that is what it is ok.

So, if it is 1 atmospheric pressure in air partial pressure of oxygen is 0.2 or 20 percent oxygen. So, 0.2 is divided by 1 that is what your activity of oxygen in the air, you understand that? So, in a gas mixture if you have two gases hydrogen and helium 40, 60, so, if you want to calculate the activity of hydrogen that is 40 that is 0.4 divided by the total pressure that is equal to 1 atmospheric ok so; that means, 0.4 right that is what it is. So, now Rault law says well you know to understand the solvent and solute effects in solid solutions Rault came into picture and he says why to you use such a kind of complex things he said Rault $\mu_A = \mu_A^0 + RTlnk_A X_A$ simply you write in the mole fractions. That means, according to Rault law $a_A = x_A$ mole fraction ok, that is what it is quantity A is activity. Now, well, so that is what it is so, but to generalize these things one can write down $a_A = \varepsilon_A X_A$. So, $\varepsilon_A = 1$ that is for Raultian and $\varepsilon_A \neq 1$for others correct it can be less than 1 actually, most likely. So, for Raultian for the Rault's law this will be equal to 1 then its activity become mole fraction.

But you know Henry says, very dilute solid solutions ok only in the you know ends of the phase diagram. So, solid solutions are very dilute like 2 percent,3 percent, 5 percent concentration of the solute Henry says μ_A is equal to or basically Henry says much easier way, Henry says partial pressure I can use $p_B = K_B X_B$.

KB is a constant that is what is not (Refer Time: 41:12) constant that is Henry's constant ok you should remember that $p_A = K_B X_B$.. So, if you put back that. So, mu A sorry no, why it is B, it should not be B right it should be A ok B is solute that is why A is a solvent dilute solutions.

So, A is applied A is solvent basically Rault's law is mostly applied to solvents and Henry's law is applied for dilute solutes ok solids solution, but (Refer Time: 41:46) solute is dilute; dilute means very small concentrations. So, $\mu_B=\mu_B^0 + RTlnK_B X_B$ right. You are not here that is why you are not able to point out. So, these can be added together because K_B is a constant that is the Rault's sorry Henry's constant. So, that is why it can be written $\mu_B^{0*} + RTlnX_B$ right. So, what is $d\mu_B$? This is a constant. So, this becomes $0 + RT(\frac{dX_B}{X_B})$ got it. So, this is what it is.

So, now I go back here plug in that. So, $d\gamma=\mu_A.RT/X_A$ correct bulk multiplied by dX_A bulk right, am I clear? Remember we are not using surface energies here that is why. So, I can write down $d\gamma=-\ {}_A\left(\frac{RT}{X_A^{bulk}}\right)dX_A^{bulk}$ right.

Well, since we have to bring in the effect of grain boundaries what you do? Very simple ok, we are almost done actually. So, we can always assume this gamma if this absorption thing which that is why the nano effects are there ok you remember that you know, why, you see, this A^{GB} is there μ^{GB} all GB's are there grain boundary terms are there in this term, this is equal to this right.

So, this can be simplified to make life very not very complicated this can be simplified ok where delta is the thickness and rho is the density of grain boundaries these are all very difficult terms. So, thickness of grain boundaries can be obtained, density of grain boundaries.

Well it will be less than the grains because it has more random grain atomic structures, but one can actually measure by looking at the grain boundary structure very easily. You know the grain boundary volume then you can know the number of atoms presents then mass by volume can be obtained as a density *i.e.* ${}_A \approx X_A^{GB}\delta\rho$.

So, if you plug in there. So, $d\gamma$ become what? $d\gamma= - \frac{X_A^{GB}}{X_A^{bulk}}$ RTδρdX_A^{bulk} correct. So, that is why gamma can be written as $\gamma = \gamma_0 - RT\delta\rho X_A^{GB} ln(X_A^{bulk})$ that is it. So, if you, you can get an expression like this after doing so much of mathematical calculation last half an hour or so, then you can use this expression and put it here in this gamma term.

So, as you see here because it is a function of X_A or virtually it is a function of X_B; X_B X_A are related $X_A+X_B=1$. So, that means, this is a nonlinear functions now gamma and that is what something which you should remember. So, by these by doing this you can simplistically you can actually put a relationship between gamma and compositions and do it.

And for nanostructure materials it is rapid it is widely done; it is widely done nanostructural materials ok remember this is very easily done.

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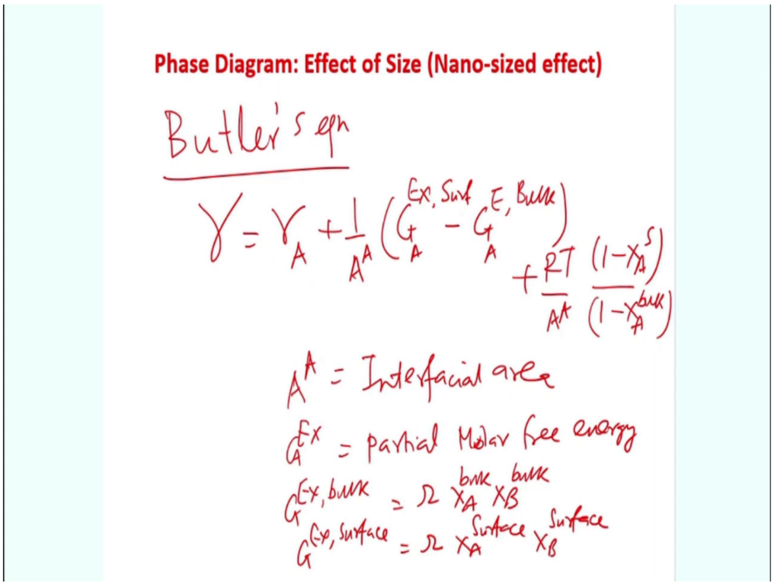

Phase Diagram: Effect of Size (Nano-sized effect)

Butler's eqn

$$\gamma = \gamma_A + \frac{1}{A^A}\left(G_A^{Ex,Surf} - G_A^{E,Bulk}\right) + \frac{RT}{A^A}\frac{(1-X_A^S)}{(1-X_A^{bulk})}$$

A^A = Interfacial area

G_A^{Ex} = partial Molar free energy

$G^{Ex,bulk} = \Omega X_A^{bulk} X_B^{bulk}$

$G^{Ex,Surface} = \Omega X_A^{Surface} X_B^{Surface}$

Now, before I wind up this lecture let me tell you this is a very simplistic thing. One can even use little more rigorous analysis and derive this equation these are known as a Butler's equation which you know actually there is nothing in knowing, but this will not be part of your exam Butler's equation. Where this γ is related as $\gamma = \gamma_A + \frac{1}{A^A}(G_A^{Ex,Surf} - G_A^{Ex,Bulk}) + \frac{RT}{A^A}(\frac{1-X_A^{Surface}}{1-X_A^{Bulk}})$ ok. And then what is A^A? A^A is interfacial area right and these excess terms surface and bulk they are partial molar free energy of surface or bulk yeah. For bulk you understand no, for $G^{\text{excess bulk}} = \Omega X_A^{Bulk} X_B^{Bulk}$. So, these are all bulk composition. So, $G^{\text{excess surface}} = \Omega X_A^{surface} X_B^{surface}$. So, one can use this also straightforward. So, either of these two equations, but this one is very simple ok which you have done that and you can plug in there.

So, that is something which you should know that is why. So, then if you do a if you put these things into a model and do a better computational work you can easily get you know effect of composition on the surface energies and this is very important for many of these alloys. Without doing that you will be doing a huge mistake, the accuracy of your calculations will be pretty low.

So, that is why one has to do know this mathematical formalisms and plug in this equations and that is the purpose what I took so much of time to write that correct, that is the main reason why I spent so much of time to derive this ok. So, in the next lecture which is lecture number 14, I will be talking about the generalized equations ok I know you are getting quite a bit you know loaded with mathematical things.

But that is this last thing which I will do, generalized equations for a free energy for a nanomaterials, which can be used for anything you can use one equation to solve mathematically or computationally the phase diagram problems ok. So, let us stop here.Thank you. We will come back to it in the next lecture that is lecture 14 and discuss about those.

Thank you.