Nanomaterials and their Properties
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Lecture - 10
Surfaces and Interfaces-II

Hello students. So, we are going to now, start the lecture number 10 of this course on nanostructure materials characterization and properties. Well, you know I have started discussing about thermodynamics aspects of nanomaterials in the last lecture. And prior to that, I discussed about surface energies and related aspects. We are going to come back to surface energies after we discuss about thermodynamics.

Because some part of the surface energy will be related to the derivations and the equations which I am going to do in the next couple of lectures and including today's one.

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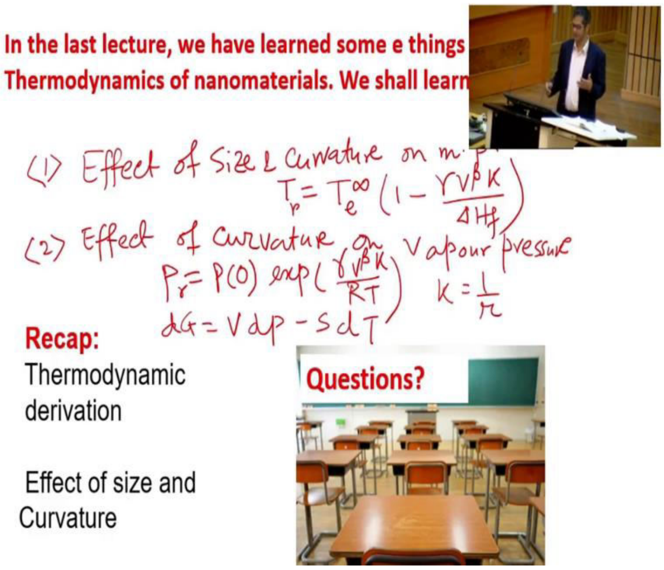

In the last lecture, we have learned some e things
Thermodynamics of nanomaterials. We shall learn

⟨1⟩ Effect of Size & Curvature on m.p.

$$T_r = T_e^{\infty}\left(1 - \frac{\gamma V^{\beta} K}{\Delta H_f}\right)$$

⟨2⟩ Effect of Curvature on Vapour pressure

$$P_r = P(0)\exp\left(\frac{\gamma V^{\beta} K}{RT}\right) \quad K = \frac{1}{r}$$

$$dG = V\,dp - S\,dT$$

Recap:

Thermodynamic derivation

Effect of size and Curvature

Questions?

So, what in the last lecture what we do? We learn some things about Thermodynamics and nanomaterials ok. And we shall learn more, because nano size has basically changed the way we look at thermodynamics.

So, what we did actually in the last lecture. Let us you know kind of recap first. I did two important thermodynamic derivations. First one was what first one was about effect of size and curvature on the temperature basically, melting temperature ok effect of size and curvature and they are related as you know. Curvature is $\frac{1}{r}$ where r is the radius of the particles right.

So, what I derived? Effect of curvature melt and size on temperature basically, melting point. I derive the relationships, where T of the melting temperature of the particle with radius r is equal to T equilibrium temperature, but the particle which is a large size that is what I write superscript in to infinite ok.

And this is $T = T_e(1 - \frac{V^\beta \gamma \kappa}{\Delta H_f})$, γ is surface energy V is the molar volume of beta phase β right; it can be any phase by the way. κ is the curvature and ΔH_f is heat of fusion.

So, you can see that this $\frac{V^\beta \gamma \kappa}{\Delta H_f}$ ok and this; obviously, will be a factor r right which I did not put intentionally. So, you can write down.

So, as the r decreases, this factor actually increases. Rather factor increases $1 - \frac{V^\beta \gamma \kappa}{\Delta H_f}$ decreases and therefore, the melting temperature of a particle of radius r decreases; that is something which you have derived using very simple concepts which we will again do that. That is the first thing I did.

What is the second thing I did? Second thing I did this effect of what? Curvature on vapour pressure right. You know every element at atmospheric pressure is equilibrium with its vapour pressure; that is a liquid solid right. It does not matter what the temperature, but there is a equilibrium between these two that is why they are stable. Well, now this vapour pressure is also a function of size right.

So, we derived a relationship P_r. Again, I am putting r in everywhere which is not there in the previous description to differentiate that this is a vapour pressure of solid with radius r is equal to P_0; that is the vapour pressure of an material with bulk size $\exp(\frac{V^\beta \gamma \kappa}{Rt})$, ok yeah now I can see right. So, the first equation this r will not be there, because kappa is equal to 1 by r right. The kappa is equal to 1 by r that is the radius of curvature ok.

So, let us write $\frac{1}{r}$ the way I have written. So, that right. So, that is our actual. So, vapour pressure increase very rapidly. This is the exponential function. So, this is exactly what I discussed. Now, I want you guys to try these equations from the basic fundamental thermodynamics ok and basic fundamental thermodynamics is what. This is the fundamental equation ok which you should know.

The total differential of Gibbs free energy, $dG = VdP - SdT$ where P is a pressure, T is the temperature, these are all set variables, volume is V and entropy is S right. This is the fundamental equation I used in all the derivations of this nothing else and I derived this equation in the beginning itself of the last lecture. So, please try your hand on this equation to derive it, because these are important for you to know, and you should not forget it.

Obviously, please do collect your questions and whenever we will come back. I would like to answer the questions if you have any ok.

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Welcome to another glorious day!!.

So, now, we are going to switch over and start discussing about something about new things right, that is what I wrote. We will be talking about another glorious day. You can clearly see, the two sea lions are moving in arctic ice water mixture where these are the pieces of ice and this is the water.

And they are wondering how come ice is floating in the water. What is the stability of these two, ok, what dictates the stability and that is something we should be knowing very well, because thermodynamics is something which reserves its opinion about impossibilities, right.

So, here ice pieces of ice are in equilibrium with the water sea water with lot of salts right. And what dictates that equilibrium at the interface between this ice and water. Have you ever asked this question to yourself? I think you should discuss.

In a hot summer day, you may be thirsty you are at home you open your deep freeze and pour little bit of ice from your ice tray into the water. And slowly you will see the ice is getting melted down, because of the temperature in the summer day right, but for few moments, the ice pieces will remain in equilibrium with water. Although, slowly the equilibrium will be getting disturbed and ice will melt to water, but still few moments you will see that

In the Arctic, temperature is sufficiently low enough to have this equilibrium staying long at least, before the dawn of the sun somehow in Arctic right or in Antarctic right. So, what does actually dictate this kind of equilibrium and how this can be interpreted ok?

That is what this guy at the big back is saying speed up in the front or we will miss the lecture of Professor Biswas right ok. They may be stupid enough to ask these questions who wants to listen to lectures of the of a professor right ok, but they are interested some guys are there in the class will be interested always.

Well, the front guy is saying I know I know, but I am trying to figure out how we can describe this two-phase one component system in terms of measurable parameters. And what are the measurable parameters? Temperature and pressure. You cannot measure you can measure other things in terms of that temperature, pressure and volume right, but they are related, but two independent variable temperature or pressure or temperature volume or pressure or volume right.

So, he is saying I am trying to understand it, you know although, we are going to add in the lecture let us go back and ask this question to professor right that is you can keep.

The guy at the back is said what a geek you are geek you are meaning you must sharply move ok these are none of our business ok.

Why you are interested. This is something, which always happens. You know when your students also used to do that things. Before going to the class, we used to think what the professor is going to teach. It may not be understandable to us that is what it is. That is what I say. Welcome to another glorious day of nano materials ok.

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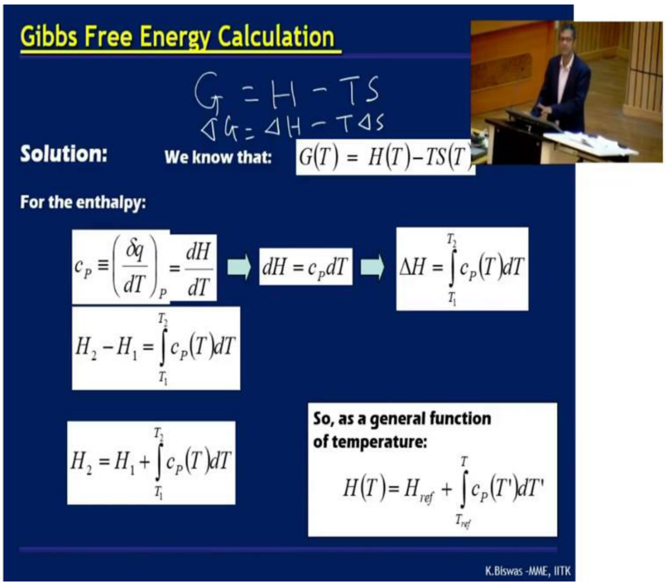

Gibbs Free Energy Calculation

$G = H - TS$

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

Solution: We know that: $G(T) = H(T) - TS(T)$

For the enthalpy:

$c_P \equiv \left(\frac{\delta q}{dT}\right)_P = \frac{dH}{dT}$ ⇨ $dH = c_p dT$ ⇨ $\Delta H = \int_{T_1}^{T_2} c_p(T)dT$

$H_2 - H_1 = \int_{T_1}^{T_2} c_P(T)dT$

$H_2 = H_1 + \int_{T_1}^{T_2} c_P(T)dT$

So, as a general function of temperature:

$H(T) = H_{ref} + \int_{T_{ref}}^{T} c_P(T')dT'$

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You know Gibbs free energy calculations right. What is Gibbs free energy? This energy freely available to you to do the work; if you are a system that is what it is. For any system, energy freely available to the work and we know that Gibbs gives this fundamental equation $G = H - TS$

This is a fundamental equation please do not forget it even at the end of the semester also ok. G is the Gibbs free energy, $G = H - TS$ right. This is very easy to do that ok. Many people define in many ways, but I am not going to those things.

There are many ways you can remember it ok, but best to remember is $H - TS$. H is the total enthalpy total energy of the system, enthalpy is the bond energy of the system minus the thing which is not recoverable; that is the entropic part, because entropy is 1 by temperature; that is what you make the units ok on the both side you have to multiply by temperature right that is what it is. So, this part he knew long back that this part is not usable. This part is gone in the system you cannot retrieve it.

So, that is why you have to subtract it. Well, that is the very fundamental law fundamental equation actually, which is dictated which can which will dictates almost everything in the world ok. It is this aspect of this can be used in the stars to oceans to rain cycle to carbon dioxide cycle everything you can discuss with this.

This is a very fundamental equation. So, we know that G is a function of temperature pressure both. If we consider pressure to be one atmospheric pressure, that is what ion metallurgy ok sorry about others.

So, then it is (Refer Time: 12:18) temperature is equal to $H(T)$. This is also comes from temperature minus TS(T). So, this looks like a equation related to temperatures right. Now, H, H is related to c_p actually, c_p is heat capacity. You already studied in second year of bachelors or maybe, if you have not, please go to any books of thermodynamics like Gaskell G Gaskell or maybe, in other thermodynamics the lipids ok correct that is equal to $c_p = \frac{dH}{dT}$.

So, that is if you know c_p. You can calculate the change of enthalpy that is dH and then if you integrate that, you get a enthalpy of the system, $\Delta H = c_p dT$.

So, what you need? You need basically, that is give change of enthalpy. So, you need a standard state to get the actual value of enthalpy, but we are not interested we are interested in change right. You have seen that most of the equation what you interested is this $\Delta G = \Delta H - T\Delta S$ changes you are interested we can change our dictates which way the system is moving.

So, c_p if you know, heat capacity of any material solid, liquid, gas. You can calculate $\Delta H = \int_{T_1}^{T_2} c_p(T) dT$; that is what you know fundamentally need to know. What about that is the thing and then; obviously, if you know one you can calculate other H_1 is known and H_2 can be calculated; that is what you need a standard state ok.

I am not going to teach you those are things. This will be taking a lot of time for me, but if you are done these courses, you will be knowing it ok. This is not the class for this kind of aspects.

So, therefore, general term if it is this $H(T) = H_{ref} + \int_{T_{ref}}^{T} c_p(T')dT'$ that is what you need to do. It is very easy to do computational way right and calculate in computer. So, why did not you know all these thing ok.

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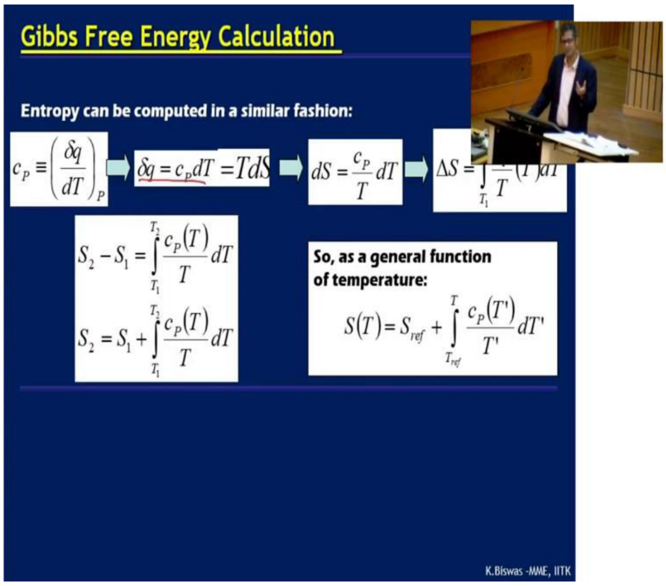

Gibbs Free Energy Calculation

Entropy can be computed in a similar fashion:

$$c_P \equiv \left(\frac{\delta q}{dT}\right)_P \Rightarrow \delta q = c_p dT = TdS \Rightarrow dS = \frac{c_P}{T}dT \Rightarrow \Delta S = \int_{T_1} \frac{\quad}{T}(T)dT$$

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{c_P(T)}{T}dT$$

$$S_2 = S_1 + \int_{T_1}^{T_2} \frac{c_P(T)}{T}dT$$

So, as a general function of temperature:

$$S(T) = S_{ref} + \int_{T_{ref}}^{T} \frac{c_P(T')}{T'}dT'$$

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Now, nearly entropy is also related to c_p correct as a constant pressure you see $c_p = \left(\frac{\delta q}{dT}\right)_P$ and that is $\delta q = c_p dT,$ ok. And that is equal to second law of thermodynamics still that is δq =TdS, right. This is basic basically heat $\delta q = c_p dT$ that is equal to heat right oops that is my white color chalk that is why it cannot visible and then, we see principle of thermodynamics still this is TdS.

So, now you can write down $dS = \frac{c_p dT}{T}$ straight forward right. There is nothing in it. Integration of that gives you change of an entropy, $\Delta S = \int_{T_1}^{T_2} \frac{c_p(T)dT}{T}$. In enthalpy, it is $\int_{T_1}^{T_2} \frac{c_p(T)dT}{T}$. This is the mistake, many student does. They always try to forget distribution terms ok. Then, you can do all these things.

So, basically finally, it boils down $S(T) = S_{ref} + \int_{T_{ref}}^{T} \frac{c_p(T')}{T} dT$. So, you can get c_p always from any solid liquid grass. Then, you can calculate H(T) and S(T) and that is all then you can calculate G(T).

Once you know for every phase every material G(T) then you are done, but that is about the bulk thermodynamics. Bulk thermodynamic means, thermodynamics of big materials, but size does not matter. Why? Because in big materials surface area is very very small as compared to the volume or compared to the bulk atoms surface atoms are very very small. So, you can ignore them. It is a hardly 2 to 3 percent is the total number of atoms sitting in the surface.

So, you said I do not need them. I do not need them to be considered for my calculation. I can ignore, that is will be only 1 percent of my calculation. So, I do not need right. So, that is what it is. So, but in nano materials that is the subject of today's lecture or maybe our semester; that is not the way. There surface area is very very large.

Number of atoms in the surface is pretty large and it is a function of the size of material and that is why that must be considered right it is a must be considered, because if you ignore that, you are engineering almost 25 to 30 percent or sometimes 40 to 50 percent of the total energy system. It is not at all advisable to ignore that.

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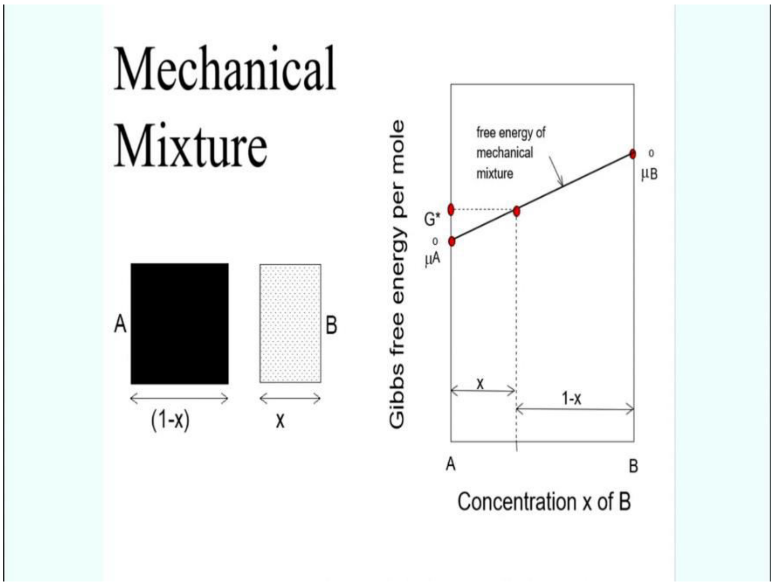

Mechanical Mixture

Correct; that is what you must remember which I have been telling you again. Now, let us come back to the concept of entropy a little bit, before you move into various other aspects. You know if I take sand and salt. So, (1-x) part of sand, x part of salt, x can be anything.1.2.3 or (1-x) is basically the other one.

So, if I mix them together physically, the free energy system which I have given you H - T S will be behaving like a straight line. As a function of x as you keep on adding salt (1-x) is sand and x is salt.

So, these will keep on increase in a straight-line way because they are physically mixed. Put a sand and salt just rub it off and mix it together. It will never be mixed automatically correct. They will be mixed physically. You can even separate them out after some time correct.

You can pour water sand will remain on a filter vapour and salt will go into the water then, water will boil it up you can get sand salt back; that is a classic experiment the school students always do to retrieve sand salt from the sand and salt mixture. So, they are physically mixed. They are not mechanically, but they are not sorry they are not automatically mixed.

They are not mixed in atomic levels so that, we cannot separate them out ok. So, that is the aspect of physical or mechanical mixture in which if we mix them together, (Refer Time: 19:01) system will increase in a linear fashion as a function of the fraction of the secondary that is it correct.

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http://hobbieroth.blogspot.com/2015/09/boltzmanns-tomb.html

But you know, there is a guy long back ok sometime in 1870’s to 1880’s. He is known as Ludwig Boltzmann many of you heard about him and this is his tombstone ok. Let me just share a story about it.

He was a Austrian he is from Austria. He worked with gases and developed Maxwell Boltzmann theory. He worked with Stefan’s law Stefan Boltzmann’s law 604 law, but he was one of the finest brains in the world, ok. He said entropy is related to probability. And then, he attracts lot of criticism and sometime, at the age of 70 or so, he committed suicide.

So, but this law $S = kln(W)$; ln is log right. This law is a very fundamental law. It is a fundamental to everything in this world; whether you talk about biology to physics to chemistry to material science to mechanical engineering, any field of science and engineering this is a fundamental law, and it is so important; that is why in tombstone it is written ok.

He lived in Vienna. He was born in Vienna. He lived there and he died. You know this law changes changed everything ok, because it is a probabilistic law it is we know that it is very fundamental law. Now, it is almost 115 years ok probably death of Boltzmann, but that is ok correct.

And his father was a civil servant and he was a brilliant scientist. He did many things, but finally, he accrued lot of criticism and he could not take it up anymore; that is what happens in science. In science, you attract if you want to do something new, you will be suicide. You will be kind of you know attacked again and again. This has happened many times in history of science. This happens here also we also do the same thing.

This is not true, or this is true for every aspects of science section engineering, but that does not mean that you will not do anything new ok. Human nature is too obvious. So, he was one of these classic examples you know.

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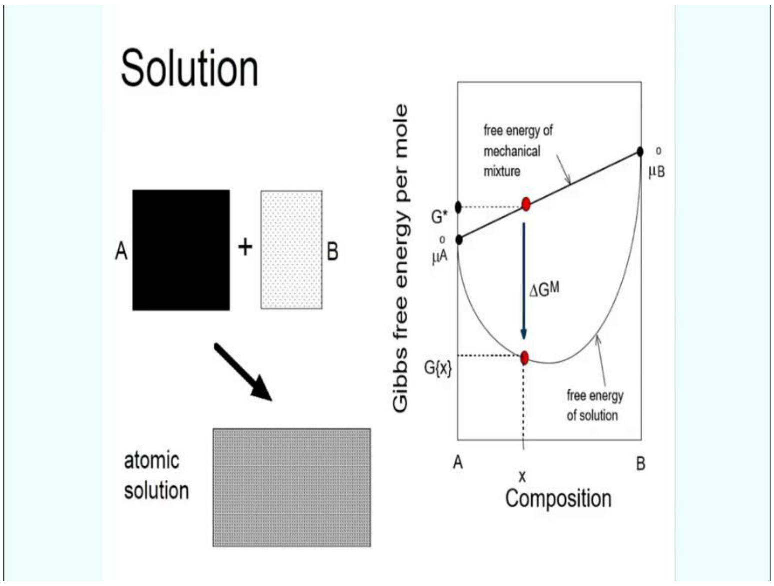

Solution

So, if you mix two things together; like, if I take salt and water, mix them together there will be solution right. Or if you take sugar and water mix them together, stir it up many times you drink that right sugar syrup ok. So, that is the solution.

Solution is automatically mixed between the two pieces, atomic mixture. So, if you do that then, free energy will not behave like this straight line here. It will behave like a parabola going down; that is very funny right. That is mainly, because of entropy ok.

Just imagine if Boltzmann equation was not derived, we could have followed that one. I am not saying that one. Somebody else could have come, but Boltzmann was that big discovery he made. Atomic solution means, it is completely mixed nothing is separable completely mixed with the atomic level ok.

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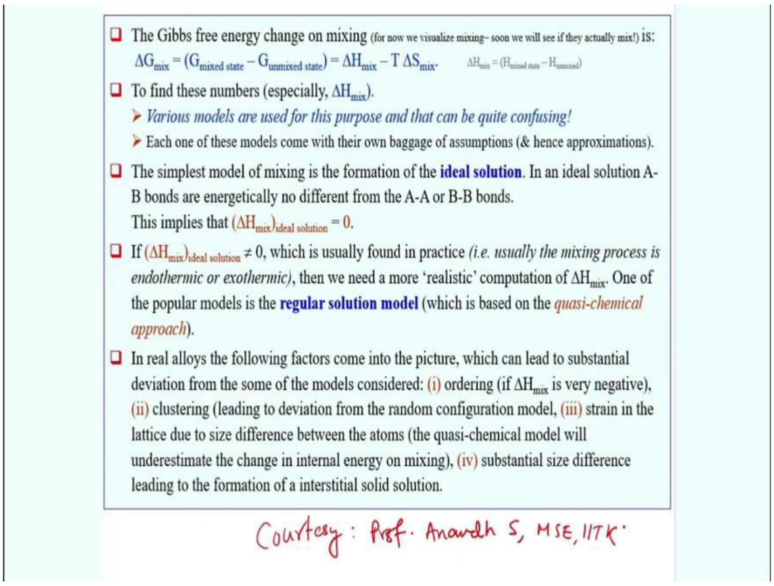

- The Gibbs free energy change on mixing (for now we visualize mixing– soon we will see if they actually mix!) is: $\Delta G_{mix} = (G_{mixed\ state} - G_{unmixed\ state}) = \Delta H_{mix} - T\,\Delta S_{mix}$. $\Delta H_{mix} = (H_{mixed\ state} - H_{unmixed})$
- To find these numbers (especially, 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.

Courtesy : Prof. Anandh S, MSE, IITK.

Now, ok these are the slides I am using from my colleague Professor Anand Subramaniam ok. So, I should you know Gibbs free energy mixed difference is basically mixed state minus unmixed state that we have already done ok.

Now, depending on the values of ΔH_{mix}, there are different kinds of solution is possible. First one is that, obviously, there is a relative to bond right bond. If you have two pieces A and B like, salt and the water. Salt is one thing, water is another thing. They are molecules. Salt is Nacl, water is H_2O, ok. So, A and B. Now, if the bonds are same.

Bonds are just same for A-B B-B A-B A-A then, ΔH_{mix}= 0. Let us call ideal solutions. Ideal means something which never happens in life. It is very difficult to perceive this situation the two guys will mix at the bond before the mixing and after mixing will remain same ok. This really happens.

ΔH_{mix} will always be not equal to 0, which is the usually found in the practice ok; that means, mixing part is either endothermic or exothermic. There will be heat producing or heat absorption. Then, you need a more realistic composition of delta is mixed; that is why different models are available, because it is non-zero, you need to then use different concept.

So, I am not going to discuss about that, as most is used more or less quasi chemical approach, in which you can calculate difference of bond energies after the mixing and before the mixing.

In real materials, real solutions always following factors comes into picture, which can lead to substantial deviation ok. First is that some cases these atoms can be ordered this can, if they can be clustered, they can be strain in the materials then, they can be substantial difference of size like, interstitial solid solution iron carbon right.

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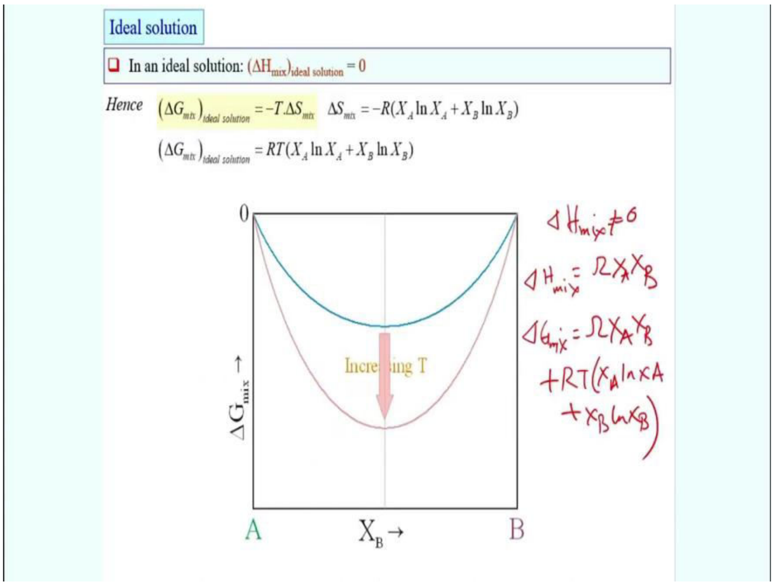

Ideal solution

❑ In an ideal solution: $(\Delta H_{mix})_{ideal\ solution} = 0$

Hence $(\Delta G_{mix})_{ideal\ solution} = -T.\Delta S_{mix}$ $\Delta S_{mix} = -R(X_A \ln X_A + X_B \ln X_B)$

$(\Delta G_{mix})_{ideal\ solution} = RT(X_A \ln X_A + X_B \ln X_B)$

$\Delta H_{mix} \neq 0$

$\Delta H_{mix} = \Omega X_A X_B$

$\Delta G_{mix} = \Omega X_A X_B + RT(X_A \ln XA + X_B \ln X_B)$

So, there are different models right. Now, as you know in case of ideal solutions, ΔH_{mix} is 0. So, therefore, ΔG_{mix} mix is $-T\Delta S_{mix}$, where ΔS_{mix} is given by Boltzmann law, ok. You can derive ok, that is going to $\Delta S_{mix} = -R(X_A lnX_A + X_B lnX_B)$ plus this log term is coming from this fundamental equation S $= kln(W)$, where X_A and X_B are the mole fraction of A and B correct. So, therefore, if you put together $-T\Delta S_{mix} = RT(X_A lnX_A + X_B lnX_B)$ right.

So, then if you look at calculus, this becomes a negative term right, because X_A is a fraction X_B is also a fraction. So, log operating fraction is negative. So, this value will make the energy system more negative so; that means, ΔG_{mix} will go down from 0 and that is why stability will increase.

Correct, but you know most of the cases this does not happen del, because ΔH_{mix} will not be 0. And many models like regular solution model quasi chemical model says $\Delta H_{mix} = \Omega X_A X_B$ mix is equal to this right, where sigma is basically interaction parameter.

How strongly these atoms are bonded ok how strong you are bonded with your friends same thing; that is what it is. So, then $\Delta G_{mix} = RT(X_A ln X_A + X_B ln X_B)$ that is it. So, if you; that means, the ΔG_{mix} value will depend on the relative values of this term the $\Omega X_A X_B$ and the relative values of the entropic term. So, that is there are lot of many situations possible right.

Let us not discuss about that. This is the brief introductions of the solutions, free energies and how they are related ok.

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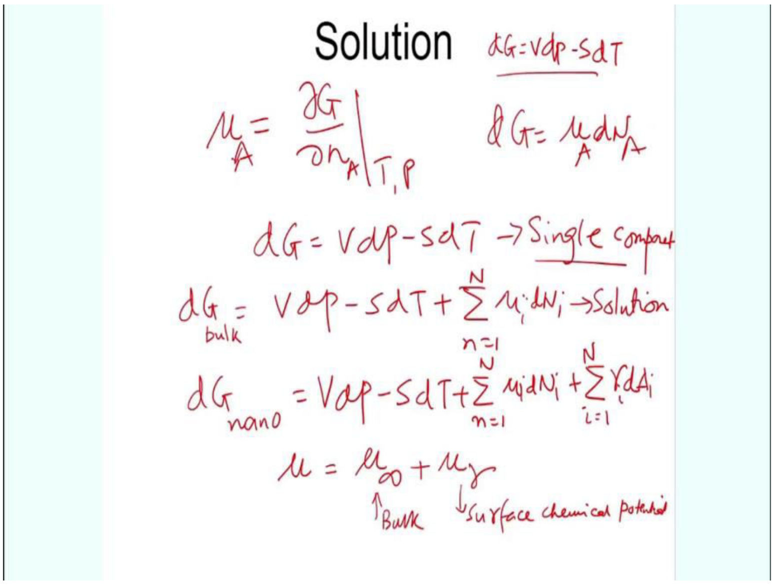

Solution $dG = Vdp - SdT$

$$\mu_A = \frac{\partial G}{\partial n_A}\Big|_{T,P} \qquad dG = \mu_A dN_A$$

$$dG = Vdp - SdT \rightarrow \text{Single compound}$$

$$dG_{bulk} = Vdp - SdT + \sum_{n=1}^{N} \mu_i dN_i \rightarrow \text{Solution}$$

$$dG_{nano} = Vdp - SdT + \sum_{n=1}^{N} \mu_i dN_i + \sum_{i=1}^{N} \gamma_i dA_i$$

$$\mu = \underset{\uparrow \text{Bulk}}{\mu_\infty} + \underset{\downarrow \text{Surface chemical potential}}{\mu_\gamma}$$

Now, I am going to discuss few important things about solutions right what? First thing, I am going to discuss about is chemical potential right ok. You know when you talk about solutions most important aspect coming into picture is mind yes.

So, the that is what we started with right ice water mixture. What dictates the stable the equilibrium between ice and water mixture with the interface? It is the chemical potential. So, you must be wondering what is this let us go back ok.

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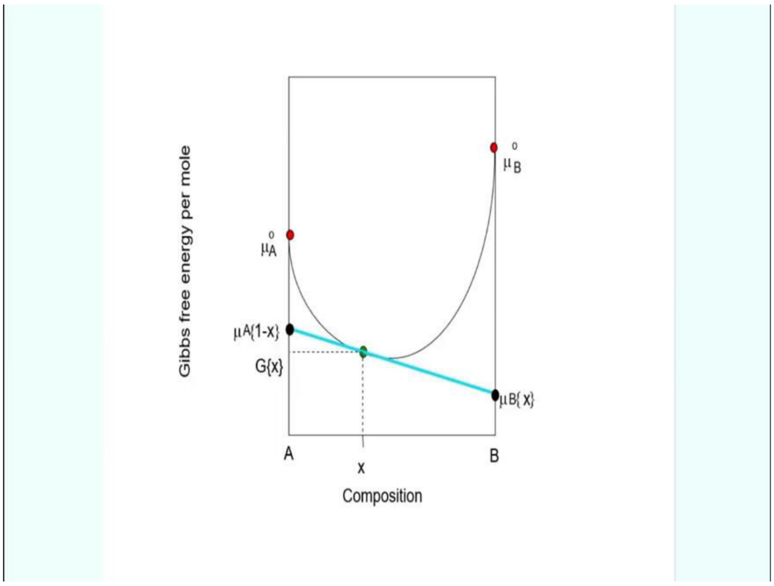

Let us go back there. You know what is chemical potential? Well, when you know chemical potential any thermodynamic system chemical potential is nothing but amount of energy absorbed or released per unit mole that is it. What is that? Let us come back.

You know the way chemical potential is defined as this μ, μ is defined is used as a chemical potential. Well, let me just start with that you know. When I say I you suppose if I say your potential with to become prime minister of this country.

What does it mean; that means, you have all the abilities to become a prime minister of the countries. We do not talk about potential of any atom in a solution, that means, ability of that atom to react with the other species in the solution. If the species A yes ability to react with species B the this ability is defined as a chemical potential remember that forget about all the mathematic. This is the physical meaning of that.

So, chemical potential has the same meaning as you see here. It is chemical, because they are related to reaction that is why. So, μ is basically defined as $\frac{\partial G}{\partial N_a}$ right at constant temperature and pressure; that is why it is defined so; that means, if I take a huge solution, I add only one mole of A into its change of free energy per unit mole is known as chemical potential. You take it is big room ok and add only one mole molecule of oxygen atom.

The change of the free energy first mole of this mixture it does everything. It is carbon monoxide, carbon dioxide, oxygen, nitrogen, moisture, argon. I am adding one molecule of oxygen a change of this free energy that is very small right; obviously, that is why at a constant temperature and pressure that is what is known as the chemical potential ok now. So, you have to do a process called addition and subtraction of molecule.

Then you can measure the change; that is what it is defined. Now, if you assume a fixed entropy and volume of volume actually, then we can always write down we can always write down $dG = \mu_A dN_a$ right; this is nothing, but same thing here alright.

This should not be G_A it should be only G, because free energy system right not A that is what it is. So, now, as you know we have already written what we have already derived actually not written dG for single component system: dG = VdP - SdT right.

So, in a solution, this must be, this is for single component like water vapor right, but when a solution this has to be modified, because we need a chemical potential change and that is written like this $n = 1\ to\ N, \mu_i$, oops. There are many components a b c d e f g h in a solution. They are like in this gas mixture you have so many components like you have oxygen, nitrogen I showed you.

So, you have to consider everything here. The changes of chemical potential, the changes of the free energy; that is related to all effect of all this aspect like $\mu_i dN_i, \mu_1 dN_1, \mu_2 dN_2, \mu_3 dN_3$ like that correct; that is the difference between the single component system and a solution right. Single component is N_i is 0 there is only one component. There is no solution, pure water. So, there is nothing in it other than water.

So, water mole fraction of water, 1; there is nothing. So, therefore, this term goes to 0 dN_i term and we can ignore it, but in a solution between this gaseous mixture or suppose salt and water or sugar and water, this term cannot go to 0. This is the final value of dN_i. So, that is why you need to consider this aspect right that is good. So far so good for bulk system, in which size is surface size is not important ok.

So, I write down this as a bulk. What about nano? Clearly discuss right you cannot ignore the surface area. This has to be modified there. How it is has to be modified? Very simple what is this term $\gamma_i dA_i$ that is the surface energy the real γA. So, if you have suppose, many many surfaces, then each surface have different energies it is a different areas actually. So, you have to multiply with that.

So, and each surface can also have different energies. Suppose in a cubic crystalline material 111 facets its one energy, 100 facets it is another energy,, 110 facets is the different of energy you have add it up. So, this is going to be this equation. Now, remember that we started with in at the last lecture with dG =VdP - SdT right that is what this equation is and then, we will end it up a new equation.

We have added chemical terms we have added surface energy terms. That is what this is it is not difficult to understand very easy to understand right. So, therefore, what I can do? So, I can write down chemical potential and nanoscale has two parts; one, this is for the bulk at the moment, I write infinite, that means, bulk, bulk means, size is very big and surface energy right surface energy term to be written in gamma right ok. Let us erase it and write properly right.

So, you can see that that is the fundamental law correct. So, this is the bulk chemical potential. This is known as surface potential bulk chemical potential surface potential right correct and thus, gamma is surface energy.

So, now, we can always ok let us erase it up some of the things. We can always. Just like in the last lecture, we can always do a simple math by using a spherical size. You must be thinking some of them is a spherical size, because spherical size is something which helps us to do the mathematics very clean and understandable.

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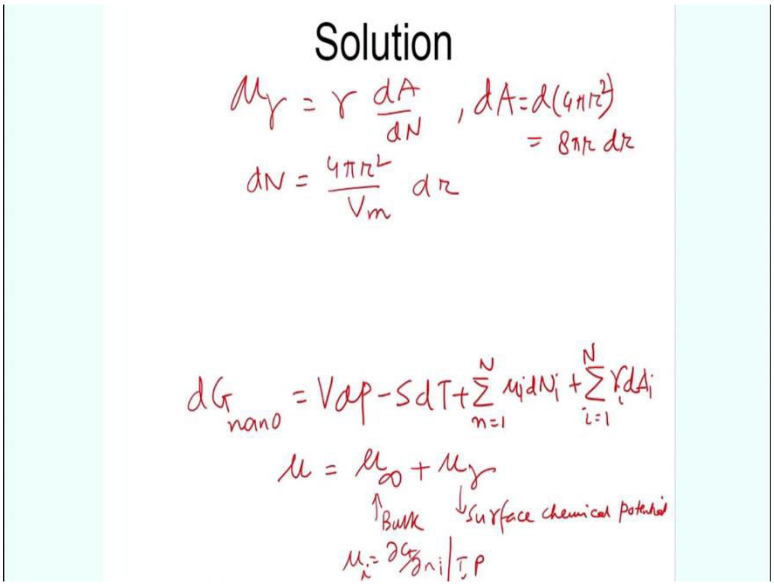

Solution

$\mu_\gamma = \gamma \frac{dA}{dN}$, $dA = d(4\pi r^2)$

$= 8\pi r\, dr$

$dN = \frac{4\pi r^2}{V_m} dr$

$dG_{nano} = Vdp - SdT + \sum_{n=1}^{N} \mu_i dN_i + \sum_{i=1}^{N} \gamma_i dA_i$

$\mu = \mu_\infty + \mu_\gamma$

↑Bulk ↓Surface chemical potential

$\mu_i = \partial G/\partial n_i |_{T,P}$

So, μ_γ is what? $\mu_\gamma = \frac{\gamma dA}{dN}$; that is obvious it is coming from this equation right coming from that equation which I derived this equation ok. You can see that if I take $\frac{\gamma dA}{dN}$, the $\frac{\partial G}{\partial N_a}$ is nothing, but $\frac{\gamma dA}{dN}$ ok you remember no μ is defined as $\frac{\partial G}{\partial N_i}$ temperature pressure; i is any component.

So, therefore, if I take that for nanoscale, this becomes $\frac{\gamma dA}{dN}$ remain constant right thus, remember that. And dA, dA is for a spherical particle is what $d(4\pi r^2)$ it was nothing, but $8\pi r dr$. I think we should be careful about that i and γ. I should write it properly, otherwise oh this also right am I clear.

So, now then what is $dN, dN = \frac{4\pi r^2}{V_m} \times dr$, V_m is the molar volume, volume of one mole ok; that is the number of atoms change of number of atoms ok, $4\pi r^2 dr$ and dA is that right am I clear not clear. Well, what is N ok?

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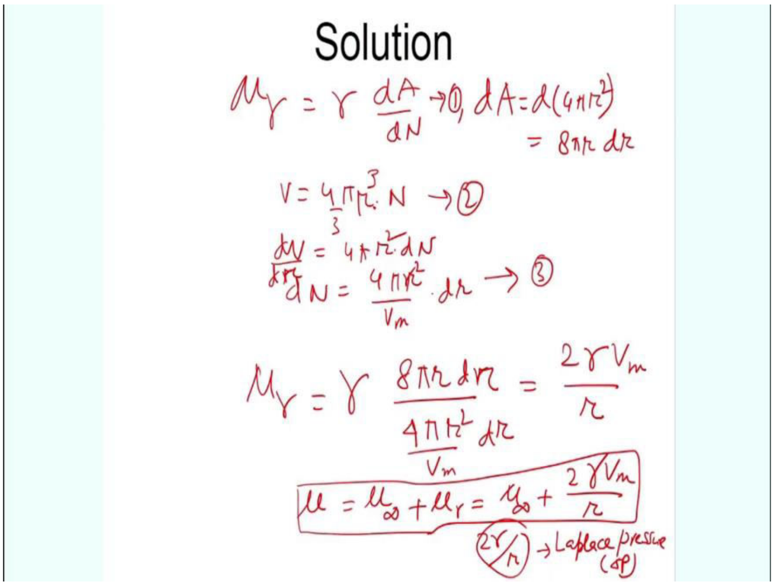

Solution

$$\mu_\gamma = \gamma \frac{dA}{dN} \rightarrow ①, \quad dA = d(4\pi r^2) = 8\pi r\, dr$$

$$V = \frac{4}{3}\pi r^3 N \rightarrow ②$$

$$\frac{dV}{dr} = 4\pi r^2 dN$$

$$dN = \frac{4\pi r^2}{V_m} dr \rightarrow ③$$

$$\mu_\gamma = \gamma \frac{8\pi r\, dr}{\frac{4\pi r^2}{V_m} dr} = \frac{2\gamma V_m}{r}$$

$$\boxed{\mu = \mu_\infty + \mu_\gamma = \mu_\infty + \frac{2\gamma V_m}{r}}$$

$$\frac{2\gamma}{r} \rightarrow \text{Laplace pressure } (\Delta P)$$

Let us erase this equation you must be confused. What is N? Ok, let us not write N. $V = \frac{4}{3}\pi r^3$ is a volume of one atom multiplied by the number of atoms ok that is the total volume correct. So, then $\frac{dV}{dr} = 4\pi r^2 dN$, correct.

So, dN is $\frac{dV}{4\pi r^2} \times dr$, which I have written in a smaller volume into dr correct right. So, then find upon knowing this. Let us do to complete the maths, I like to do this. This gives me feeling of erasing the board right correct.

So, by doing some kind of mathematical operation, which is very easy actually you can put γ here, dA is known, dA, dN is known. So, μ_γ is equal sorry μ yes, $\mu_\gamma = \frac{\frac{\gamma 8\pi r dr}{4\pi r^2 dr}}{V_m}$

So, you can see this becomes $\frac{2\gamma V_m}{r}$, this is very good for a sphere actually ok. So, this is. So, μ_r is basically $\frac{\gamma dA}{dN}$. And dA is for a spherical particle is $8\pi r dr$. You know volume of the particle is basically $\frac{4}{3}\pi r^3 N$, ok. Now, you can write down $\frac{dV}{dr}$, yes $\frac{dV}{dr}$, that is equal to $4\pi r^2 dN$

So, d N is equal to $4\pi r^2$. So, this is r^2, yeah $\frac{4\pi r^2 dr}{V_m}$ that is. Then, I plug in all these things I plug in this. Let us write down 3, this is 2, this is 1. So, I plug in you know in one the dA term and dN term I get this correct. So, therefore, total $\mu = \mu_\infty + \mu_\gamma$, so, $\mu_\infty + \frac{2\gamma V_m}{r}$, right.

This is a fundamental equation you must remember that ok always remember you do not forget at all. This will be used in our future description many of these future descriptions. So, therefore, by increasing the spherical radius, chemical potential of small systems can be increased; that means, my reactivity can be increased. Potential can be increased; that means, reactivity can be increased. And you know this term $\frac{2\gamma}{r}$ is known as a Laplace pressure term. This is exist in Sobolev experiment also.

This can be converted into Laplace pressure the pressure and volume you see $\mu = \mu_\infty + \mu_\gamma = \mu_\infty + \Delta P V_m$; that is how it can be treated. This is done by Laplace actually. So, this is one derivations which I thought I you should know very well ok.

Now, let us be let me go back you know chemical potential can be derived or can be obtained very easily by knowing this free energy composition curve, which is a parabola. And then, drawing a tangent at any point where we want to know the chemical potential.

So, here is x and if the wherever if you draw a straight line or a tangent to this curve at this point, it will hit the vertical axis and wherever hits, you get μ_A chemical potential of A and chemical potential of μ_B you can get that is.

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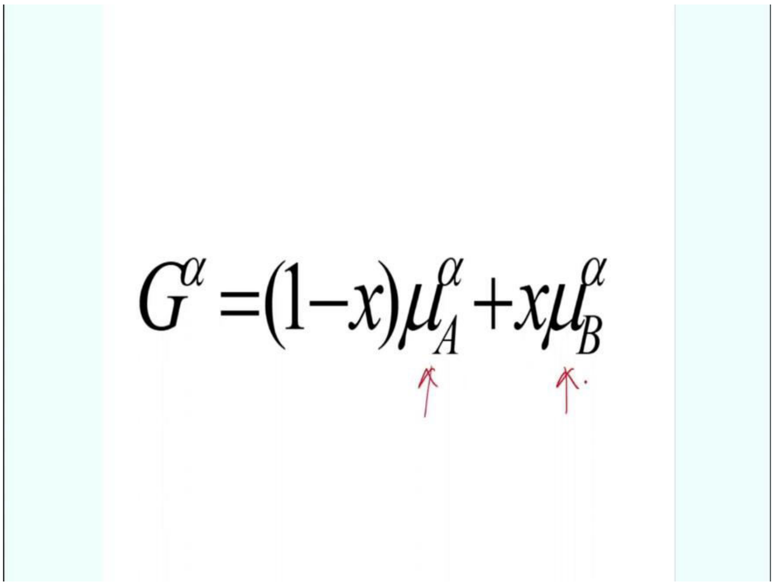

$$G^\alpha = (1-x)\underset{\uparrow}{\mu_A^\alpha} + x\underset{\uparrow}{\mu_B^\alpha}$$

Something which is done in typical thermodynamics and then, you once you know mu A mu B, you can measure $G = (1 - x)\mu_A + x\mu_B$, right. This is also very standard, because the two chemical potentials of A and B components for phase alpha you can do that.

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$$\mu_A^{\alpha} = \mu_B^{\alpha}$$

$$\mu_B^{\cancel{\alpha}} = \mu_B^{\beta}$$

Well, why it is so, important? Because it tells you the stability conditions so, in ice water mixture. So, for the water, chemical potential in ice must be the chemical potential with salt in the ice right. Similarly for water also ok. This should be beta right that is it ok.

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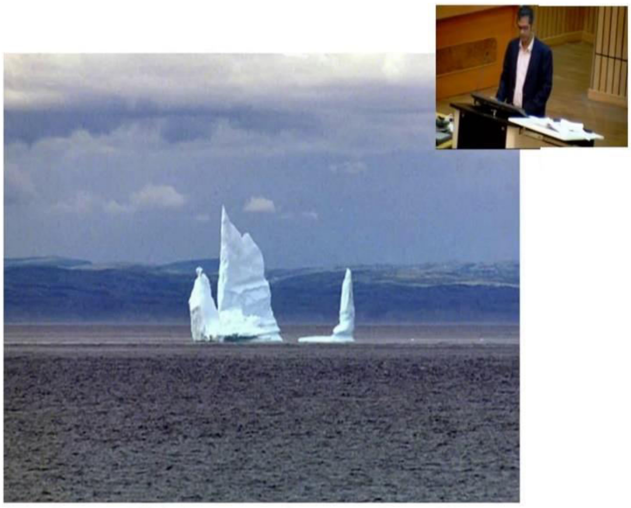

So, I will not discuss further except that we will show you a picture of ice water mixture. Now, question is this for the last whatever time I have let me come back here. You know not only that this is the something which chemical potential modification is done.

So, for a nanostructure system, you can clearly see how it is modified. This is also, in fact, are the compositions of the solutions you know solid solution right. So, you can have nano particles of alloys; the chemical compositions of the two species A and B will also, depends on the curvature or the size of particle.

And this can be easily derived how? Well, let us do that. That is very easy to do. I think it can be done in 10 minutes or so I have.

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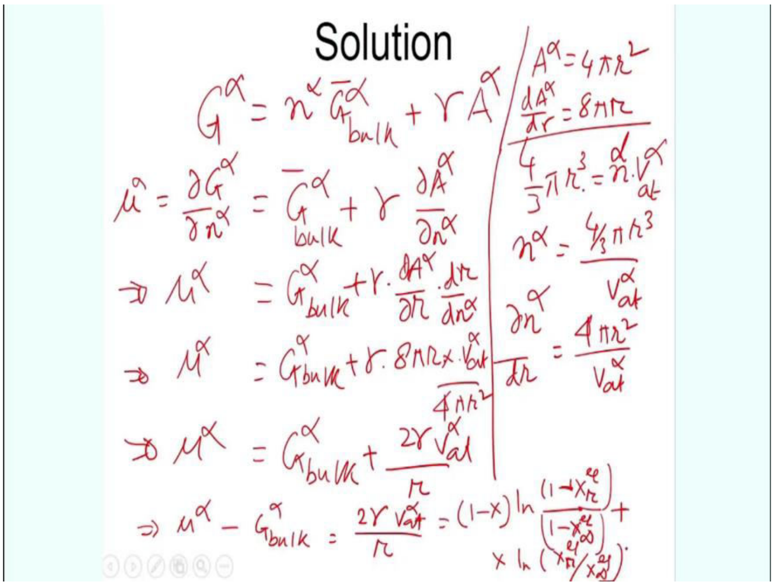

Solution

$$G^{\alpha} = n^{\alpha}\bar{G}^{\alpha}_{bulk} + \gamma A^{\alpha}$$

$$\mu^{\alpha} = \frac{\partial G^{\alpha}}{\partial n^{\alpha}} = \bar{G}^{\alpha}_{bulk} + \gamma\frac{\partial A^{\alpha}}{\partial n^{\alpha}}$$

$$\Rightarrow \mu^{\alpha} = G^{\alpha}_{bulk} + \gamma\cdot\frac{\partial A^{\alpha}}{\partial r}\cdot\frac{dr}{dn^{\alpha}}$$

$$\Rightarrow \mu^{\alpha} = G^{\alpha}_{bulk} + \gamma\cdot\frac{8\pi r \times V^{\alpha}_{at}}{4\pi r^2}$$

$$\Rightarrow \mu^{\alpha} = G^{\alpha}_{bulk} + \frac{2\gamma V^{\alpha}_{at}}{r}$$

$$\Rightarrow \mu^{\alpha} - G^{\alpha}_{bulk} = \frac{2\gamma V^{\alpha}_{at}}{r} = (1-x)\ln\frac{(1-x^{\alpha}_{r})}{(1-x^{\alpha}_{\infty})} + x\ln\left(x^{\alpha}_{r}/x^{\alpha}_{\infty}\right)$$

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

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

$$\frac{4}{3}\pi r^3 = n^{\alpha}\cdot V^{\alpha}_{at}$$

$$n^{\alpha} = \frac{4/3\,\pi r^3}{V^{\alpha}_{at}}$$

$$\frac{\partial n^{\alpha}}{dr} = \frac{4\pi r^2}{V^{\alpha}_{at}}$$

So, G suppose any phase alpha G is, obviously, n^{α} and then, this is for the bulk ok oops why I always end in surface energy term and this is what it is am I right.

So, if I consider a spherical particle correct. If I consider spherical particle, $\frac{4}{3}\pi r^3$, volume of each atom ok, whose spherical particle size is this, number of atom is A and each atom has volume atomic volume. Suppose this has atomic volume of V_{α} correct. So, then oh this will be n^{α} correct which I have written. So, $n^{\alpha} = \frac{\frac{4}{3}\pi r^3}{V^{\alpha}_{at}}$, the atomic volume of alpha atomic volume of a single atom ok.

Then number of atoms is equal to volume of this spherical particle; that is understandable right. This is polymer sphere, and each sphere contains n number of atoms of alpha and then, volume of each atom is V^{α}, but this multiplication must be equal to this. So, now, we can write down $\frac{\partial n^{\alpha}}{dr} = \frac{4\pi r^2}{V_{at}^{\alpha}}$ right that is easy. Now, let us take up this is let us take up this equation right.

So, we can always write down μ^{β} that is equal to $\frac{\partial G^{\alpha}}{\partial n^{\alpha}}$ oh sorry μ^{α} why beta. I must be careful enough this should be our α why; it will be β correct. So, that is equal to $\bar{G}^{\alpha} + \frac{\gamma \partial A^{\alpha}}{\partial n^{\alpha}}$ come on that of. Now, α phase writing β phase correct.

We can write down this assuming γ to be constant. γ is not depending on number of atoms here with anything right γ to be constant. This is nothing but if I derive this equation ok take a derivative of this equation with respect to n^{α}.

So, you can see n^{α} and are will get constant ok cancel this becomes $G_{bulk}^{\alpha} + \gamma \frac{dA^{\alpha}}{dn^{\alpha}}$, right. So, you can write down this, because very simply, $G_{bulk}^{\alpha} + \gamma \frac{dA^{\alpha} \partial r}{\partial r dn^{\alpha}}$, I can do that or I cannot do that, you can do that actually, ok. So, this can be written γ. What is $\frac{dA^{\alpha}}{dr}$ what is dA^{α} by the way? dA^{α} is where the sphere is $4\pi r^2$.

So, what is $\frac{dA^{\alpha}}{dr}$ ok? You want me to do it and what is this? $\frac{dr}{dn^{\alpha}}$; that is opposite of this term $\frac{dn^{\alpha}}{dr}$; So, V there is a mistake here, right you could see that that is what I want you to point it out. This will be 4, 3 3 would get cancel this will be four right. So, these mistakes I would like you to point it out. So, this becomes G_{bulk}+ $\frac{2\gamma V_{at}^{\alpha}}{r}$; ok that is clear to you. This is the thing which we already derived.

So, now, then I can write down $\mu^{\alpha} - G_{bulk}^{\alpha} = \frac{2\gamma V_{at}^{\alpha}}{r}$, this is atomic volume of alpha right that you should know right. So, that is; obviously, will be equal to. Remember this is the difference we have taken that is; obviously, will be equal to entropic term entropy change term (1-X) right X_1 and x_A.

So, if I write down x_B as X, then (1-X)$ln(1-X_r^{eq})/(1-X_\infty^{eq})+\ln(\frac{X_r^{eq}}{X_\infty^{eq}})$, ok. I think we should be doing this carefully, because we are talking about the surface composition versus this the bulk composition. So, this is ok let me write down better away.

So, what did I write; that is equal to (1-X)$ln(1-X_r^{eq})/(1-X_\infty^{eq})+\ln(\frac{X_r^{eq}}{X_\infty^{eq}})$, this is the surface composition with the particle size r the equilibrium means thermodynamically equilibrium; obviously, otherwise everything will be invalidated and divide by 1 minus X equilibrium infinity. This is for the bulk ok.

So, surface with respect to the bulk that is what we are doing in a bulk on surface right. And then, (1-X)$ln(1-X_r^{eq})/(1-X_\infty^{eq})+\ln(\frac{X_r^{eq}}{X_\infty^{eq}})$ this is nothing, but entropic term.

Because of the variation in the compositional surface and the bulk ok. Now, if you simply consider X to be 1, then single phase basically X to be 1, then the mathematics will be very simple. Why? X to be 1, because you are considering single . X= 1 means what? Pure right. So, when X equal to 1, X.

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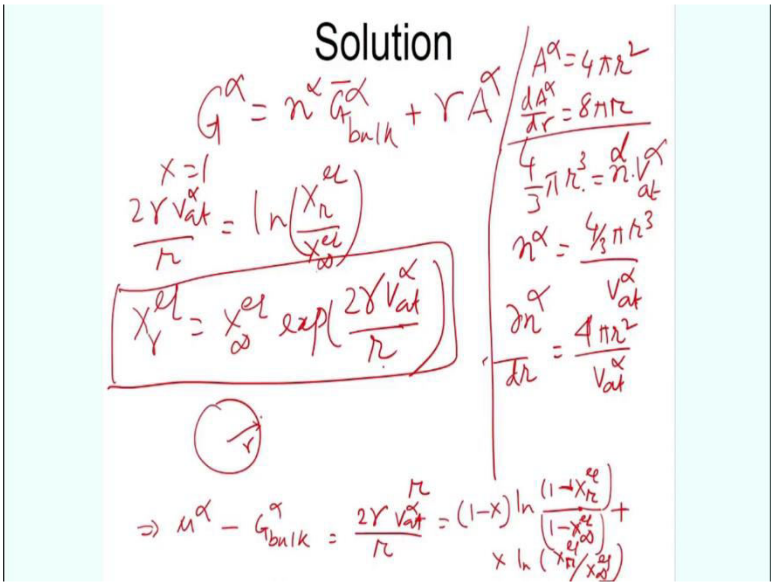

Solution

$G^\alpha = n^\alpha \bar{G}^\alpha_{bulk} + \gamma A^\alpha$

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

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

$\frac{4}{3}\pi r^3 = n^\alpha \cdot V^\alpha_{at}$

$n^\alpha = \frac{4/3\,\pi r^3}{V^\alpha_{at}}$

$\frac{\partial n^\alpha}{dr} = \frac{4\pi r^2}{V^\alpha_{at}}$

$X = 1$

$\frac{2\gamma V^\alpha_{at}}{r} = \ln\left(\frac{X^{eq}_r}{X^{eq}_\infty}\right)$

$\boxed{X^{eq}_r = X^{eq}_\infty \exp\left(\frac{2\gamma V^\alpha_{at}}{r}\right)}$

$\Rightarrow \mu^\alpha - G^\alpha_{bulk} = \frac{2\gamma V^{\alpha\, r}_{at}}{r} = (1-X)\ln\frac{(1-X^{eq}_r)}{(1-X^{eq}_\infty)} + X\ln(X^{eq}_r/X^{eq}_\infty)$

Become 1 then, this becomes this $\frac{2\gamma V_{at}^r}{r}$; this becomes what. This becomes this term becomes goes to 0 X is 1. So, this become goes to 0. So, X is 1. So, that is also goes to 1 right $\ln(\frac{X_r^{eq}}{X_\infty^{eq}})$ ok; why you assume X equal to 1? That is easy, because X equal to 1 gives you pure phase right that is why.

So, then you can see X_r^{eq} = to X_∞^{eq} ×exp($\frac{2\gamma V_{at}^{\alpha}}{r}$). So, this is the composition variation as a function of particle size r from the surface to the center ok.

Let us stop here. We will come back in the next lecture. I think I have discussed enough. We will again discuss this part again.

Thank you.