Phase Transformation in Materials

Prof. Krishanu Biswas
Department of Material Science & Engineering
Indian Institute of Technology, Kanpur

Lecture - 12

Effect of Temperature on Solid Solubility, Influence of Interfaces on Equilibrium

So, in this lecture we are going to derive two expressions, one; what is the effect of temperature on the solubility? We know that solubility of two phases into one into another it depends on the chemical potential equality. And a particular component, but one is to derive the mathematical expression to find out; whether we can actually calculate the solubility as a function of temperature. So, how to do that? To do that let us assume a simple phase diagram ok.

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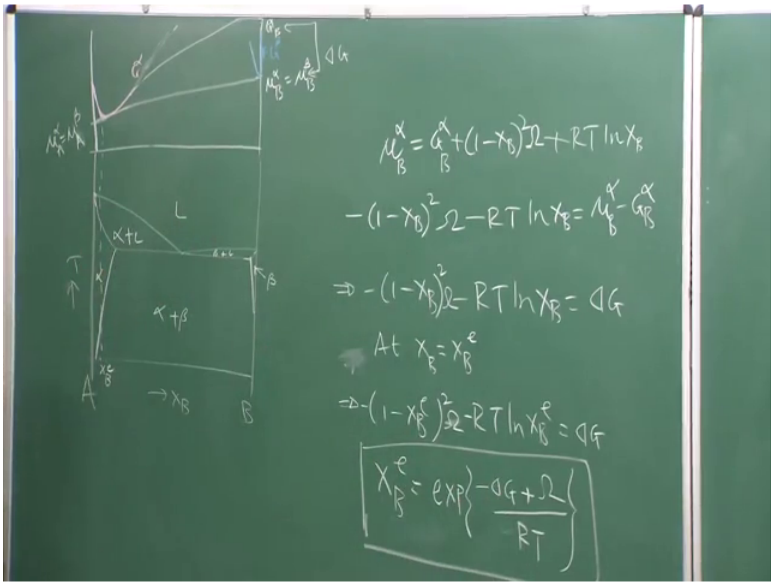

$$\mu_B^\alpha = G_B^\alpha + (1-x_B)^2\Omega + RT\ln x_B$$

$$-(1-x_B)^2\Omega - RT\ln x_B = \mu_B^\alpha - G_B^\alpha$$

$$\Rightarrow -(1-x_B)^2\Omega - RT\ln x_B = \Delta G$$

$$\text{At } x_B = x_B^e$$

$$\Rightarrow -(1-x_B^e)^2\Omega - RT\ln x_B^e = \Delta G$$

$$\boxed{x_B^e = \exp\left\{\frac{-\Delta G + \Omega}{RT}\right\}}$$

Which is as a tangent solid solution on the one side, and another side there is very little solid solution. And on this side we assume that is a very little solid solubility. And you know these two curves; one here one there they indicate how the solid solubility of A in B or B in A changes; as a function of temperature. The question is this can I can have a mathematical expression using thermo dynamics of solid solubility as a function of temperature.

So, let us consider an alloy composition this; which is solidified and then solid solubility elements are slowly changed. As you see beta is basically having very low solid solubility of A in B, but alpha has large correct. So, because of that; because of this they are going to be you have to see how this free energy composition values will look like. So, I am going to draw the free energy composition diagram there, and because beta has very low solid solubility, so beta free energy composition diagram will looks like this it is better to use a colour chalk that is what we have been doing.

On the common tangent between them, just draw a little bit this side; otherwise the phase diagram method will not match isn't that, because this is where the phase diagram, now I draw a common tangent. So, that is what is a equilibrium composition. Now if you see here two things you must see carefully; let me explain one is that this line tells you equality of equability between the chemical potential. Now, this is A end this B end. So, here also it will be A; we can extend this line till further wherever it meets there. So, that mean it tells you that we have a small solid solubility in beta and large solid solubility in alpha and B component and we are going to do that. So, as you know mu is given by this expression.

G let me see whether I have written it properly or not; sometimes I also do mistakes did I write it properly (Refer Time: 05:18) sometimes we here that is the gamma we have seen that right. So, if I write down this is this will be in alpha phase fine. So, that is basically the chemical potential of B in alpha that is equal to the free energy G plus 1 minus X B whole square into gamma sorry sigma is here sorry gamma not sigma gamma is here interaction parameters and plus R T l n X B I have already given you this expression.

Now, we can write down this expression like this minus 1 minus X B whole square. This is equal to mu B, and this may be G B that is; actually G B alpha. G B alpha means the alpha G the value of free energy of alpha phase, when at the B end. So, that is nothing but this difference mu B alpha you can see here G B alpha is somewhere there meeting there. So, that is the difference between these two; that is what is called delta G. So, can write down again that is the difference of free energy of the B alpha phase when it is in equilibrium with, because beta minus when it is not an equilibrium with beta whenever it is present. So, if I extend this free energy curve this is what is going to meet here and that is tells you the free energy of the alpha, when the pure B is at the pure at B end delta G there is a difference of delta G. So, we can write down them very nicely the expression. So, that is actually.

So, therefore, at X B it will be X B e that is at this composition; this can be written 1 minus X B e whole square minus R T l n X B e. So, then what I can do? I can write down X B sorry I have been missing this term always X B e is nothing but exponential minus delta G B delta G plus this divide by R T, because there at X B e equal to X B. So, that is actually solid solubility meet off and that is the solid solubility of X B e as a function of temperature.

So, you must have knowledge of the interaction parameter gamma, and the free energy change between G alphas. And it is equilibrium of between alpha and beta then only you can calculate that and this can be further modified much simpler, because once you know that delta G is dependence on delta h minus T delta s you can little bit modify it, but that does not matter this is what is the expression for the solid solubility as a function of temperature for alpha phase.

So, we only one parameter need to know, because the interaction parameter is always known from the two components; A and B, why do you need to know is a delta G?0 So, that can be only obtained; if I know the free energy function also basically it is the free energy, what is delta G? Delta G is nothing but free energy of alpha phase at the pure B end.

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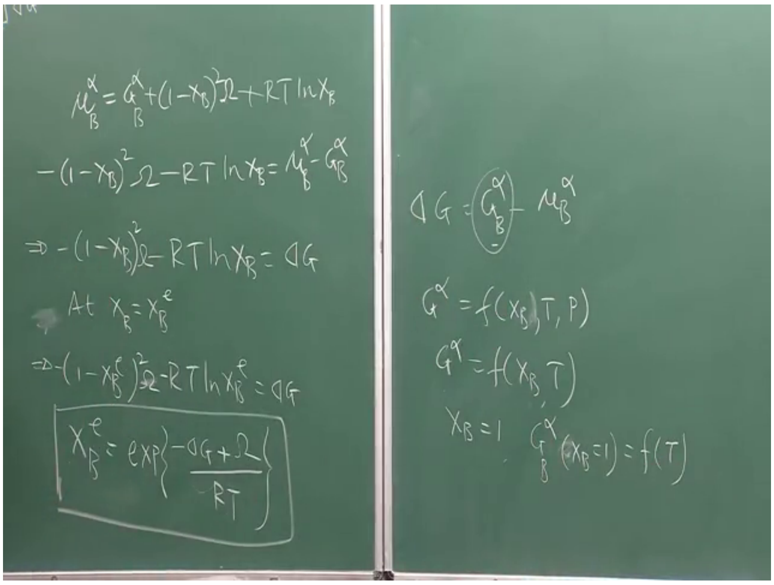

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$$\boxed{X_B^e = \exp\left\{\frac{-\Delta G + \Omega}{RT}\right\}}$$

$$\Delta G = G_B^\alpha - \mu_B^\alpha$$

$$G^\alpha = f(X_B, T, P)$$

$$G^\alpha = f(X_B, T)$$

$X_B = 1$ $\quad G_B^\alpha(X_B = 1) = f(T)$

So, that is can be easily obtained; if I know the free energy expression of the alpha phase minus a chemical potential of B in alpha. So, that chemical potential can be obtained when you draw a common tangent, but this one can be obtained when you know the G alpha; G alpha will be a function X B. Obviously, G alpha is a function of X B temperature and pressure. So, we assume pressure to be constant, then G alpha is a not the function of X B and the temperature. So, then this has obviously to be obtained first. Once you know this functions, then only you can calculate G at pure B end, what is the G alpha; that means, by putting X B equal to 1. X B equal to one you will get G B alpha.

And in that case G B alpha is X B equal to 1, will be only a function of temperature, because you assume that X B is a constant here. So, that is what I am saying. So, once you know this parameter by the way you have derived and you know the interaction parameter gamma, then actually you can easily calculate what is the effect of temperature on the solid solubility of B in A alpha phase.

So, that is the first thing you should know this is important in many of the calculation using your nucleation kinetics. So, now, let just whatever time I have in this lecture let us first derive; let us derive another important expression. You know interfaces will have a strong effect on the phase transformations. Interfaces means between two phases suppose you have a one solid one liquid phase or one solid in another solid interface will be allow and these interfaces will have a strong effect on the phase transformation. So, how do I do that so; that means, what we are going to do is as is written in this book the influence of interface and equilibrium. So, let us suppose.

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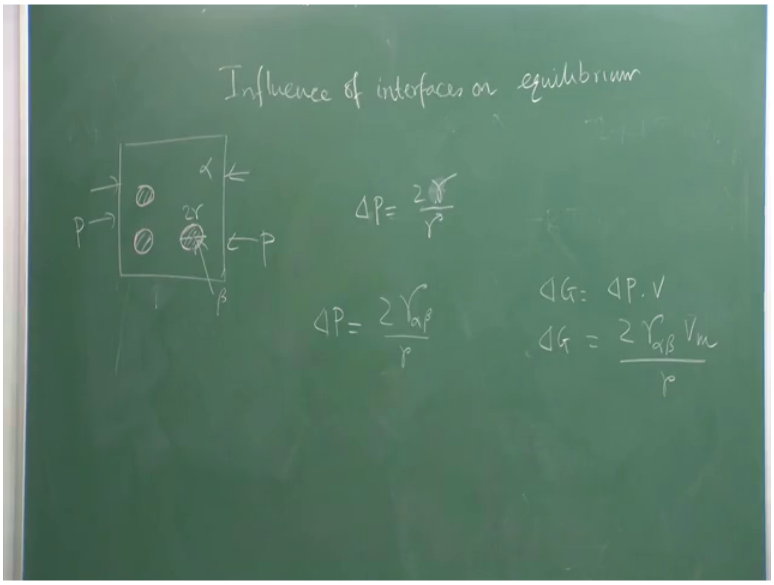

Influence of interfaces on equilibrium

$\Delta P = \frac{2\gamma}{r}$

$\Delta P = \frac{2\gamma_{\alpha\beta}}{r}$

$\Delta G = \Delta P . V$

$\Delta G = \frac{2\gamma_{\alpha\beta} V_m}{r}$

Therefore influence: remember I will discuss interfaces in detail manner; that is why we are starting of now interfaces. Basic idea is that whatever derivations I have done. So, far for the free energy we will assume that an interface has no effect, basically on the equilibrium, why, because we assumed the interfaces to be very small in number or small actually in to affect the equilibrium.

But that is not the case. Why? Because let us assume I have alpha phase and any small amount of beta phases are formed here; these are all beta phases correct. So, what are the effect of interface between alpha and beta this interface on the equilibrium. If we assume that the beta is very large in the sense is that the surface area interface area between beta and alpha are very large then there is a strong effect on the equilibrium. So, that must be bought in how we can do that it is very simple case like here you know; soap bubble in a soap solution. We know that if I have a soap bubble in a solution the pressure will increase; pressure inside the soap bubble is nothing but this is gamma and this is the radius of the bubble.

So, similar analysis we can apply here. How we can do? That we can always assume that both alpha and beta phases are subjected to atmospheric pressure p. But you know because beta is a small and within alpha just like a soap bubble in a bucket of soap of mixture water mixture. So, therefore, there is a extra pressure within the beta phase just like a soap bubble; in a soap bubble we always assume extra pressure. So, because of these because this beta phase is well inside the alpha anyway small in size, there is an extra pressure on the beta phase, because of that aspects and that is exactly same as what happens in a soap bubble and this extra pressure is nothing but 2 into gamma divide by r. So, we can write down this extra pressure here; in this case is 2 gamma alpha beta divide by radius of the beta. If this is twice r then you can write an r is the radius of the beta phase particle average radius.

So, what we need to know is the interfacial energy between alpha and beta that is the effect. Now how does it happens in the free energy; as you know free energy has a pressure temperature term right pressure volume term and (Refer Time: 15:22) affects is like this change of free energy will be equal to change of pressure multiplied by volume multiplied by the basically molar volume; that is obvious G is nothing but E plus P V minus T S; so this effect of pressure.

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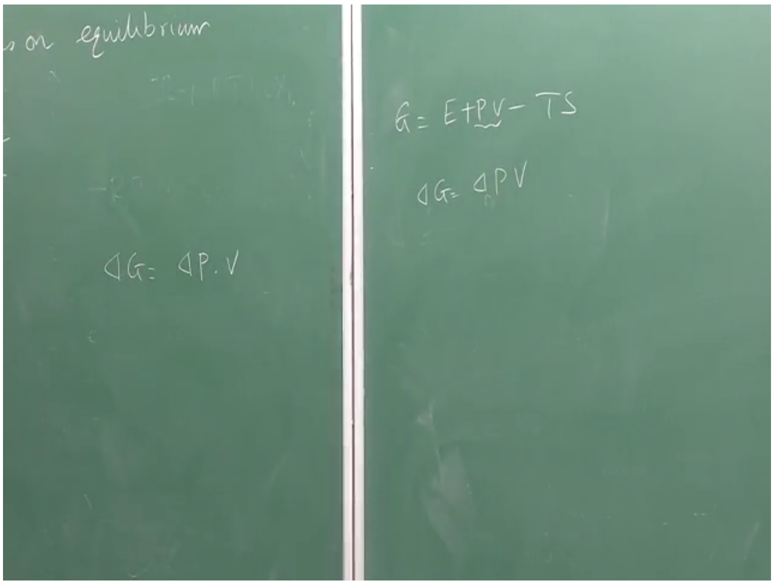

Because of change of pressure if everything else is constant temperature and all things are constant the change of free energy, because of pressure change will be equal to this; because we assume volume is not changing much.

Therefore, we can write down delta G is nothing but twice gamma alpha beta multiplied by V m divide by r. So, that is the change of free energy, because of the interface; because we have a finite interface between alpha and beta this is what the effect which will happen is. This equation you have seen many many times, but probably we have never thought, how it is to be derived? This derivation of delta P equal to twice gamma by r is available even in 12th standard books.

So, there is no point of doing it the pressure difference can be easily calculated; from this expression we can easily get down into G equal to twice gamma alpha beta multiplied by molar volume of the beta phase divide by the radii radius of the beta phase. So, smaller is the r value higher is the delta G change smaller say larger is the alpha beta interfacial energy higher is the delta G so; that means, what this change in free energy because of the pressure because of this interface basically is directly proportional to the interfacial energy inversely proportional to the radius of the particle; that is why smaller the particle that is why precipitates actually you will see the precipitation case they are nano size.

Therefore effect of the interfacial energy on the free energy will be more. So, now, you understand whatever; calculation of free energy and derivations you have done so far has to be connected with this effect which we have not done so far because I was only talking about the cases where interface was very you know negligible effect. In fact, in bulk thermo dynamics you always ignore the effect of interfaces, dislocation defects all you ignore, because that is helps us making the things understandable easily handle able. Now that you know how to add it so for every G expression every G expression means every G free energy expression which you have derived in order to taking the concentration effect of the interfaces we have to add this term.

What will happen if you add this term graphically let us see what will happen? What will happen if basically the compositions which are equilibrium composition interface will change? So, let me draw it here.

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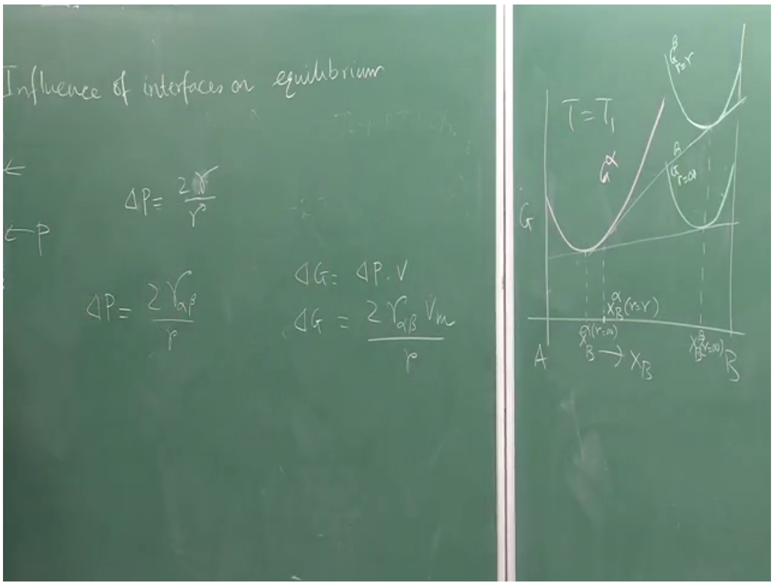

I will just draw a free energy composition diagram; for two phases alpha and beta. In one case the r is infinity; see if r is infinity then delta G is change is 0, because 1 infinity is 0; other case r is finite; that means, r is having a specific value. So, this is my suppose alpha free energy curve. Now I am going to draw two free energy curves of beta; one for which this is G beta let us write down properly this is G beta r is equal to infinity; that means, very large value of r very large value of r means what this interfaces are basically will not have any effect onto that. Here my this is delta G is inversely proportional to r the smaller the r larger the effect on G delta G. Now if I have a finite value of; so, therefore, yes what is the what is this equilibrium? Two equilibrium; we need to draw a common tangent. And you see this is what the X B alpha is when r is equal to infinity and this is X B beta when r is equal to infinity.

Now so therefore, if I now consider when r is not infinity r is having definite value; that means, this term has to be added to the free energy curve this is the free energy curve. So, if I add this will go up this is addition. So, therefore, it will go up. So, let me just draw it. So, this is G beta where r is equal to r some finite value of r. Now, if you clearly see the common tangent oops common tangent; we have to change colour of the systems every time. So, then the equilibrium between alpha and beta phase get shifted this is the composition X B alpha at r is equal to r. So, the equilibrium composition between alpha and beta get shifted to the higher value; that is the effect of change in, because of the influence of the interface. So, if I have a finite diameter or the particles or the phases of beta in alpha that equilibrium compositions will shift.

So, therefore, effect is always observing channel change in change in equilibrium concentrations. So, the phase diagram boundaries whatever drawn they are drawn actually at a when r is equal to infinity. So, for r equal to any other finite value we have to redraw the phase diagrams; actually we have to calculate it everything to calculate you need gamma alpha beta and this gamma alpha beta is very rarely you know measured normally so that is where the problem is atom volume can be obtained very easily. So, this diagrams actually now drawn for an beta for an nano size particles suppose if r becomes 100 nanometres or r become 50 nanometres. We can actually draw this diagrams separately on the same phase diagrams or on separate also possible, because composition are changing and this is a separate temperature T equal to T 1. So, similarly for other temperature also this effectively variable, ok

Now, I know actually we are assume that particles is spherical, but it may not be the case if it is non spherical particle this can be also derived and can be shown the same formula actually applies, there is no problem. We can always assume sorry we can always assume the radius of a non spherical particles as a you know equilibrium sorry you cannot equate that the surface areas of a sphere surface and the surface area of the non spherical particles, and find out what is the similar r values and we can do the calculations if possible. It is there in the book or you can also actually do as a part of your homework that is not a big problem you can do that, otherwise we can I can explain you later.

So, in a Nutshell with all these descriptions, we have completed the discussions on the thermodynamics of the solution thermodynamics order phase inter metallic’s effect of pressure, temperature even interfaces we have started that also. So, in the next class we are going to start discussion about the diffusion. Diffusion will have a and diffusion actually controls many of the nucleation and other dynamics of the phase diagram; so the phase transformations.

So, we are going to discuss about that and then after diffusion we will discuss detail about the interfaces. What kind of interfaces will be there and how they are going to affect? Because this value alpha beta (Refer Time: 24:15) G will be depend upon type of interface. And the type of interface has to be then discussed then we will start different types of phase diagrams.