Defects in Crystalline Solids (Part-I)
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Lecture – 12
Diffusion (Interstitial Diffusion)

So, let us continue our example solving session.

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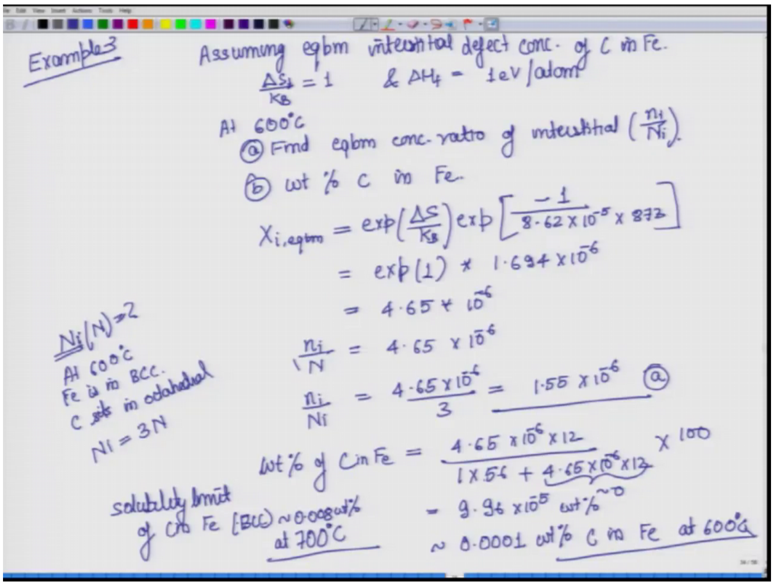

Example 3

Assuming eqbm interstitial defect conc. of C in Fe.

$\frac{\Delta S_f}{K_B} = 1$ & ΔH_f = 1eV/atom

At 600°C

ⓐ Find eqbm conc. ratio of interstitial $\left(\frac{n_i}{N_i}\right)$.

ⓑ wt % C in Fe.

$$X_{i,eqbm} = \exp\left(\frac{\Delta S}{K_B}\right)\exp\left[\frac{-1}{8.62 \times 10^{-5} \times 873}\right]$$

$$= \exp(1) * 1.694 \times 10^{-6}$$

$$= 4.65 \times 10^{-6}$$

$N_i(N) = 2$

At 600°C

Fe is in BCC.

C sits in octahedral

$N_i = 3N$

$$\frac{n_i}{N} = 4.65 \times 10^{-6}$$

$$\frac{n_i}{N_i} = \frac{4.65 \times 10^{-6}}{3} = \underline{1.55 \times 10^{-6}} \text{ ⓐ}$$

$$\text{wt \% of C in Fe} = \frac{4.65 \times 10^{-6} \times 12}{1 \times 56 + \underbrace{4.65 \times 10^{-6} \times 12}_{\sim 0}} \times 100$$

$$= 9.96 \times 10^{-5} \text{ wt\%}$$

$$\sim 0.0001 \text{ wt\% } \underline{\text{C in Fe at 600°C}}$$

solubility limit of C in Fe (BCC) ~ 0.008 wt% at 700°C

So, we will now solve example 3, and here it is related to interstitials. So, you are given that assuming equilibrium interstitial concentration defect concentration of carbon in Fe. So, we are talking about steel and given that delta S f by K B is equal to 2 and delta H f is equal to 1 electron volt per atom; what you need to find is at 600 degree Celsius find equilibrium concentration ratio of interstitial, that is you have to find ni by Ni. And second you have to find weight percent of carbon in Fe. So, basically you are finding same thing, but putting it in a different terms ok.

So, again we start with what we know X i equilibrium can be given as and it is given that H f is 1. So, it is minus 1 and it is in per atom. So, again we will use K B you will just use 62 you can use 6 1 7, it is not a big deal you will end up with very close value. So, this comes out to once you solve it you know delta S by r which is 2.

And when you solve this you would see that this is ok, there is one correction here this is supposed to be 1 not 2. So, I had the earlier written delta S f by K B equal to 2, but that is that was a mistake it should be taken as delta S f by K B equal to 1, otherwise you will not get the final answer same as mine. The x equilibrium when we write x equilibrium we are actually writing x equilibrium in terms of total number of lattice sites. And therefore, this is 4.65 into 10 to the power minus 6.

But what we need is ni by Ni so, what we need to find here is what is the number of interstitial sites, for that what we need is to understand how many ni how many Ni are there with respect to N. So, what is ni as N equal 2? So, let us see what are the information we have it is iron it is at 600 degree Celsius and we are talking about carbon. So, at 600 degree Celsius carbon is in BCC form, Fe is in BCC form and carbon in this sits in octahedral that is something that we showed you in the earlier lecture.

So, now that carbon sets in the octahedral sites, then it would mean that ni is equal to 3 N. And therefore, over here if you want you will have to divide it by 3 so, this solves our first part this is the equilibrium concentration ratio of interstitial in these terms ni by Ni. So, you see that here we need to know how many interstitial sites are there with respect to the lattice sites, and that information is given because we know it is iron. So, it is BCC at 600 degree Celsius and we are talking about carbon-carbon sits in the octahedral site.

So, you remember that when we derived we said that ni will have to be will depend upon what is the structure, and which particular interstitial site we are talking about. So, this is the informant this is now you see how to use this information.

Next what we need is to solve weight percent weight percent of carbon in Fe. Now, we see that this is a very small quantity ni by N. Therefore, it means that the number of the total number of the in the denominator the total number we can take as 1. And they have one meaning for each 1 atom, there are so many carbon atoms, and there is so, for each 1 atom of total units there is so many of carbon atoms and 1 Fe atom.

And therefore, here we will multiply it with 12 and 1 with 56, because that is the weight of iron. And therefore, this will relation will look like this. So, this is the number of carbon atoms with its weight and, if we had added iron then we will get the total weight, but what we need is the weight percent of carbon. So, on the denominator we will divide it by 1 into 56. So, this is the total number of atoms and we will assume that this is 1 atom of 51 atom of iron so, it is 56 plus.

Now, as you can see this is a very small quantity so, with respect to this. So, we can neglect this and what we need what we will calculate is this and we need percentage. So, we will multiply it with 100 and what you get 0.0001 weight percent carbon in Fe at 600 degree Celsius. So, this is the equilibrium interstitial concentration that will exist and these numbers are not the exact values that number that you have been given delta S f by K B and delta and delta H f.

But they give us very close to what is the real concentration value, we know that in Fe the concentration of Fe is very the; in sorry at 600 degree Celsius in the ferrite form the concentration of carbon in Fe is very very small. And which is also what we get over here, if you remember the solubility limit itself is in the BCC form is approximately equal to 0.008 weight percent and that is at close to 700 degree Celsius.

So, this is itself a very small quantity and at lower temperature the equilibrium concentration, we are not talking about doping or not talking about allowing it has to be much smaller. So, these values are plausible I would not say realistic, but plausible. So, now, we have solved three examples in different kinds or in the; or different types of problems to understand defect concentration. Now, what we will do is we will move on to one important property or phenomena exhibited because of point defects.

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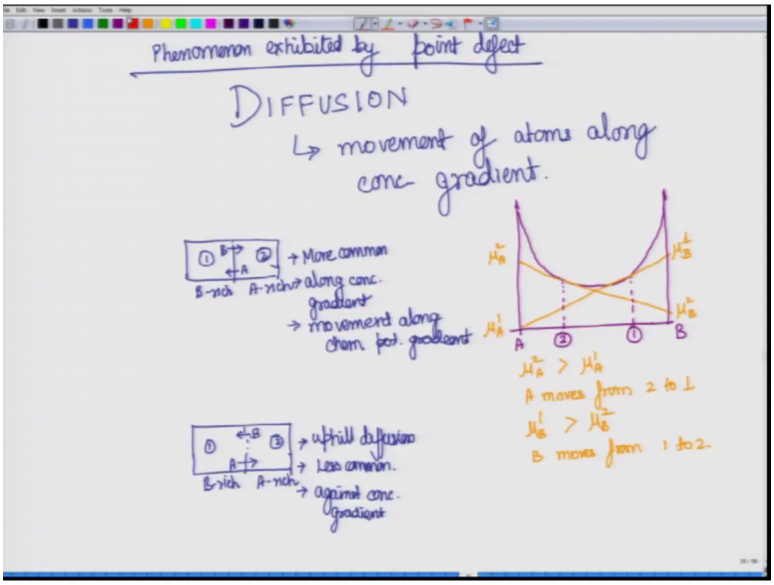

Phenomenon exhibited by point defect

DIFFUSION

↳ movement of atoms along conc gradient.

→ More common
→ along conc. gradient
→ movement along chem pot. gradient

→ uphill diffusion
→ Less common.
→ against conc. gradient

$\mu_A^2 > \mu_A^1$
A moves from 2 to 1
$\mu_B^1 > \mu_B^2$
B moves from 1 to 2.

And what is that it is diffusion so, most of you would know that what is diffusion, diffusion is movement of atoms along or against actually against meaning in the negative direction of the concentration gradient. But this is not really the fundamental definition let me tell you why.

Let us take two different systems, in the first system we have here is a B rich system B rich material and here is a rich material. This is one material, this is two material. Now here because we have the system is such let us say that B atoms are moving from here to over here. And, A atoms are moving from over here to here. So, you would say yes this is not the big deal this is what we are expected, but that is not really true you may also get a situation like this, where you still have it need not be the same when I say B rich I do not mean that this is the same element this is the same element we are talking about two systems.

And it is possible that in this system what the interaction are such that, A goes from over 1 to 2 and B goes from B to 2 from 2 to sorry B goes from 2 to 1. So, this will this is something that you are not very familiar with probably and you would sink that this is not really diffusion, this is what is called as uphill diffusion, this is more common, this is less common, this is a long concentration gradient, this is against concentration gradient.

So, what is the fundamental? So now, if I now tell you that this is something really happens and this is also diffusion, then what is the more fundamental principle behind it let us look at it. So, if we draw the free energy diagram for the two systems this will look more or less like this. So, this is a pure A this is pure B, and in this particular system, we have free energy something like this. And most likely your system two which is A rich is somewhere over here system one which is B rich is somewhere over here.

Now, if you take the slope which will give you the chemical potential at this concentration. So, this will give you chemical potential of B in system two this will give you chemical potential of a in system two. Similarly let us look at the concentration gradient for concern for chemical potential in for A and B in system one so, for this we will have in system in the system one A will have chemical potential mu A 1 in this will have 1.

Now, here what you see is that mu A 2 is greater than mu A 1 and that would mean that a must flow because this is the higher chemical potential. So, we know that to get to lower energy the system must attain or try to achieve lower chemical potential. And therefore, the elements were the A component will diffuse from 2 to 1, over here what we see is that mu B 1 is greater than mu B 2 so, for the same reasoning B moves from 1 to 2. So, this is also this also happens to be along the concentration gradient. Now, let us look at the other case, since I do not have space let me go to the next page.

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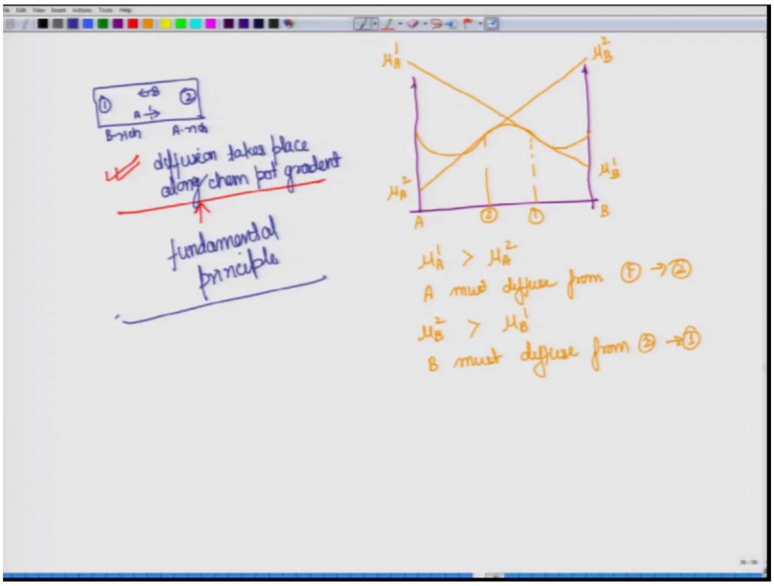

diffusion takes place along chem pot gradient

fundamental principle

$\mu_A^1 > \mu_A^2$

A must diffuse from ① → ②

$\mu_B^2 > \mu_B^1$

B must diffuse from ② → ①

And here let me draw for the second system and I will have to replot this one quickly let me draw this. So, this is 1, this is 2, this is B rich and this is a rich and we have said that B moves from 2 to 1 a moves from 1 to 2 that is against concentration gradient. So, over here how would how is actually the free energy plot look how does the free energy plot look like it probably looks something schematically something like this. And here most likely your system two which is sorry let so, this is a pure A this is pure B. So, system one which is B rich is somewhere over here system two which is a rich is somewhere over here.

Now, here also let us try to get the chemical potential of the two components. Now here so, this is for system 1 and here we will have mu A 2 sorry in system 2 the chemical potential for A is this, and in system one chemical potential for A is this, over here chemical potential of B in 1 is this and chemical potential of B in 2 is this.

So, now what do we see here we see that mu A 1 is greater than mu A 2 and now like I said that this is the higher and this is lower. So, A must diffuse from 1 to 2 this is what is happening for B mu B two is greater than mu B 1; therefore, B must diffuse from 2 to 1. So now, we see that indeed what is predicted by chemical potential is what is happening over here, it means that in both the cases movement or diffusion takes place along chemical potential gradient. So, here also this is more fundamental principle is what I am trying to come to the conclusion. So, the diffusion takes place along chemical potential gradient.

So, now let us look at this diffusion in a more detailed manner.

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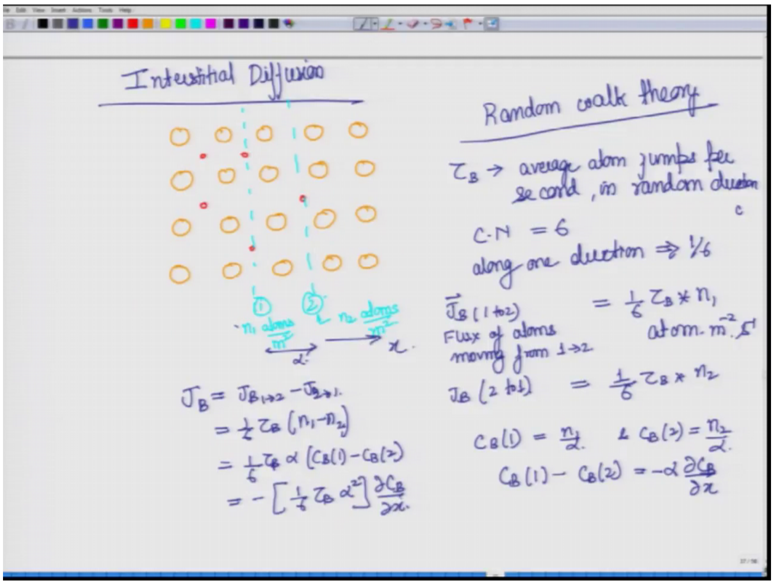

Interstitial Diffusion

$$J_B = J_{B\,1\to2} - J_{B\,2\to1}$$
$$= \frac{1}{6}\tau_B (n_1 - n_2)$$
$$= \frac{1}{6}\tau_B\,\alpha\,(C_B(1) - C_B(2))$$
$$= -\left[\frac{1}{6}\tau_B\,\alpha^2\right]\frac{\partial C_B}{\partial x}$$

Random walk theory

$\tau_B \to$ average atom jumps per second, in random direction

C.N = 6

along one direction $\Rightarrow 1/6$

$\vec{J}_B(1\to2) = \frac{1}{6}\tau_B * n_1$

Flux of atoms moving from 1→2

atom. $m^{-2}.s^{-1}$

$J_B(2\to1) = \frac{1}{6}\tau_B * n_2$

$C_B(1) = \frac{n_1}{\alpha}$ & $C_B(2) = \frac{n_2}{\alpha}$

$C_B(1) - C_B(2) = -\alpha\frac{\partial C_B}{\partial x}$

So, let us first look at what is called as inter stitial diffusion and I would refer you to the book by (Refer Time: 20:16), because it explains this concept in a very lucid manner ok. So, we are talking about interstitial diffusion meaning inside the matrix inside the material that we are talking about there are some interstitial defects, or interstitial impurity which diffuse so, we are talking about how they diffuse.

So, we let us draw it let us draw this schematically. So, let us say these are the lattice atoms and let us say these are our interstitials. So, it is not everywhere they are at some places and what I am trying to show you here are that there are two planes, that we are talking about this is plane one this is plane two, and the way we are showing is that concentration is higher on this side and lower on this side. So, this has n 1 atoms per meter square and this has n 2 atoms per meter square.

Now, diffusion why does the diffusion take place what is the fundamental theory behind it is called the random walk theory. So, the atoms or in this case the interstitials they are moving randomly in some direction, because of the inherent vibration they move keep hopping from one side to another side. And in the process they see lower energy to the side, where the concentration is lower or in fact, where the chemical potential is lower for. Now, we will assume that the chemical potential gradient is along the same direction as the concentration gradient.

And now, let us consider these two atoms to derive the relation for that consider these two planes and let us say that tau B is the quantity which talks about average atom jumps per second, but this is in random direction. But this random direction is not in 4 pi direction meaning in the solid 4 pi direction. These atoms have some coordination number and in the configuration given here, we can assume that this coordination number is equal to 6. Therefore, if we are talking about movement along only one particular direction, what we are looking at is 1 by 6, we are looking at 1 by 6th of this atomic jump.

So, now the flux of atoms that is moving from 1 to 2 can be given the given as so, this is flux of atoms from 1 to 2, this will be equal to 1 by 6 tau B number of atomic jumps into the density of atoms that is present there. So, this will be equal to n 1 and the units would be atoms per meter square per second.

Similarly, there will be flux of atoms from 2 to 1 and this will be similar except density on the other side will be different which is n 2. And therefore, we will as you can see this is a lower quantity this is a higher quantity. So, less number of atoms are going from 2 to 1 and more number of atoms are going from 1 to 2. And therefore, there will be a net movement of atoms from 1 to 2 which can be represented as J B equal to J B 1 to 2 minus J B 2 to 1 which is equal to 1 by 6.

Now, if we assume that the separation between the planes is equal to alpha then it can be easily shown that C B 1 that is concentration of atoms at 1 is equal to n by 1 alpha. This will be in per meter cube and C B 2 concentration of atom, at this line two at this plane 2 is equal to n 2 by alpha. And therefore, we can convert it to but this change in concentration from 1 to 2 can also be written as minus alpha, because concentration is changing is decreasing when we go from 1 to 2 so, C B 1 minus C B 2 is decrease, which is represented by minus sign del C B by del alpha sorry del x, that is assuming this is the x direction. So, we can again replace it over here and what we get is a quantity like this. Now, at this point you would start to see that this looks like a familiar equation.

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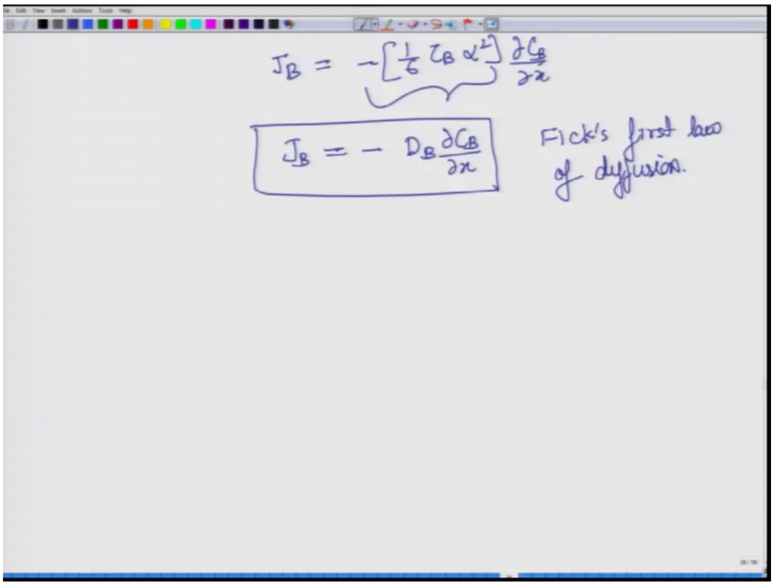

$$J_B = -\underbrace{\left[\frac{1}{6}\tau_B \alpha^2\right]}\frac{\partial C_B}{\partial x}$$

$$\boxed{J_B = -D_B \frac{\partial C_B}{\partial x}}$$

Fick's first law of diffusion.

So, what is this equation J B equal to minus 1 by 6 tau B alpha square del C B by del x. And if you replace this by the quantity called as D B, then now you would be completely convinced that this is the equation that you already know, which is also called as Fick's first law of diffusion.

So, the phenomena that is represented by this vacancy, which is the diffusion can be represented by this equation which is flux of atoms flux of displacement of atoms can be in this particular case we are talking about one direction. So, this flux of atoms can be given by J B equal to minus D B del C B by del x. So, this is a very useful relation and we will look at more and you can also add complexity that is you can talk about three dimensions and all the three dimensions. So, this relation this equation would become a little bit more general, but now you understand how do we derive this equation based on the interstitial impurity.

So, we will come back to this, and we will talk more about diffusion in the next class which is a important phenomena related to point defects. So see you next time.