Introduction to Materials Science and Engineering
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Lecture - 86
Substitutional diffusion revisited

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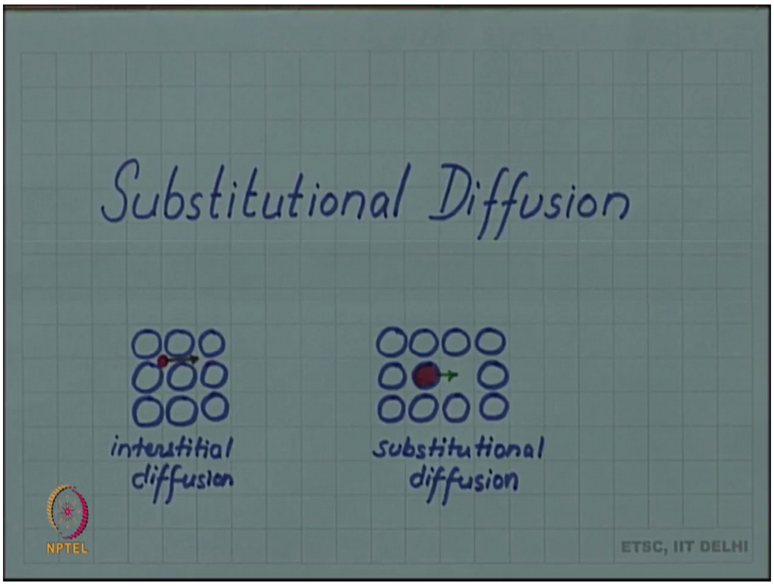

Substitutional Diffusion

We have discussed two kinds of diffusion: interstitial and substitutional. And we saw that in the interstitial diffusion, the solutes are interstitial atoms with jump from one interstitial site to a neighbouring site. So, that was the mechanism for interstitial diffusion, the solute is sitting in one side and then it jumps to a neighbouring vacant site. So, that is the interstitial diffusion and we also saw, there in substitutional diffusion is aided by vacancy. So, if there is a substitutional solute atom, it can move in the lattice only if there is a neighboring vacancy.

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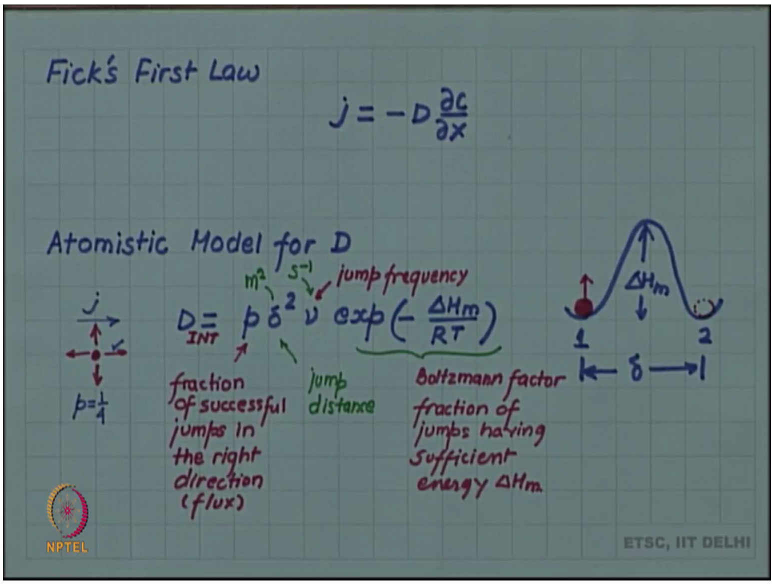

Fick's First Law

$$j = -D\frac{\partial c}{\partial x}$$

Atomistic Model for D

$$D_{INT} = \underset{\nearrow}{p}\,\overset{m^2}{\delta^2}\,\overset{s^{-1}}{\nu}\,\underbrace{\exp\left(-\frac{\Delta H_m}{RT}\right)}$$

jump frequency

fraction of successful jumps in the right direction (flux)

jump distance

Boltzmann factor fraction of jumps having sufficient energy ΔH_m

So, vacancy substitutional diffusion is vacancy a system; we also develop a domestic model for diffusion in the last video. So, for example, we essentially derived Fick's first law on the basis of atomic jumps on the basis of random atomic jumps and then we could show that the diffusivity can be written in terms of atomic parameters, where where this p is the fraction fraction of successful jumps in the right direction or in the diffusion direction or in the direction of the flux in the direction of the flux.

So, that is that is the fraction p, because atoms are jumping randomly in any lattice atoms are jumping randomly and a given solute atom may jump in any of the neighbouring sites. For example, in this example it can jump into any of these four sites, but if I am thinking of diffusion happening in this direction, then only this one, we will give me a movement of atom in the direction of the flux. So, if four possible jumps were there only one out of four possible jumps will be in the right direction. So, p in this example in this 2 D example will become 1 by 4.

So, that is the fraction of successful jumps in the right direction, delta is the diffusion distance or is the jump distance jump distance nu is the jump frequency and then finally, this exponential minus delta H m by R T is a Boltzmann factor, which essentially is telling that how many of these jumps will have energy delta H m. So, in the new jump frequency is the number of attempts which the atom is making, but all of these attempts will not be successful only those attempts will be successful, which will have the sufficient energy delta H m.

So, that fraction what is the fraction of jumps having sufficient energy delta H m it call the energy picture we had. So, if this is site 1 and then that amounts we jump to site 2, then we said that there is an energy barrier, because it has to displace surrounding atoms. So, that is; what is delta H m? And the distance from one side to the other side is the jump distance delta.

So, this wall the atomistic model for the diffusivity and we saw that the diffusion coefficient is meter square per second and meter square will come from delta square and per second will come from the jump frequency. So, we can write that; so this gives meter square this gives per second.

Now, in this we tacitly assumed that when an atom wants to jump, so here is an atom trying to jump many times when it will jump it will not have sufficient energy. So, it will not be able to cross the barrier, but when it has sufficient energy it will cross the barrier and will come to site 2, but we are assuming that the site 2 is vacant, if site 2 was not vacant; if site 2 is already occupied, then even if the atom is having the sufficient energy it will not be able to make this move.

So, in this model we have tacitly assumed that the next site is vacant. So, effectively we are assuming that, this is true and we saw that this assumption that the next site is vacant is more or less true for interstitial diffusion, because in interstitial diffusion at least we took one example of carbon, and we saw that even with maximum amount of carbon in austenite the fraction of vacant site is 90 percent.

So, there is a 90 percent probability of finding vacant site. So, the assumption that the next site is vacant is more or less 100 percent true, if the diffusion is interstitial. So, this is true; this model is true for interstitial diffusion. So, what we have written is actually D interstitial; although I did not write it in the previous video, but that is for interstitial diffusion.

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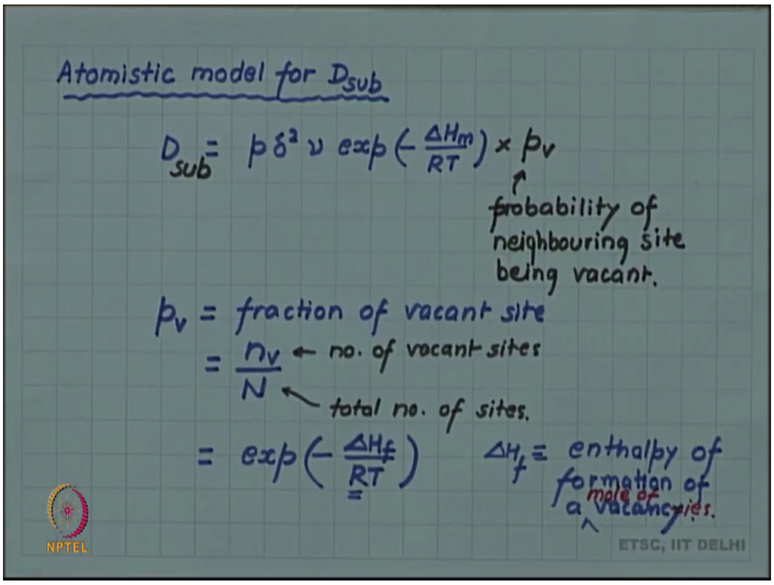

Atomistic model for D_{sub}

$$D_{sub} = p\delta^2 \nu \exp\left(-\frac{\Delta H_m}{RT}\right) \times p_v$$

probability of neighbouring site being vacant.

$$p_v = \text{fraction of vacant site}$$

$$= \frac{n_v}{N}$$

n_v ← no. of vacant sites

N ← total no. of sites.

$$= \exp\left(-\frac{\Delta H_f}{\underline{\underline{RT}}}\right)$$

ΔH_f = enthalpy of formation of a mole of vacancies.

Now, how do I modify this; how do I modify it for substitutional diffusion. So, if I want to write it for substitutional diffusion, all these parameters will still be required p delta square nu and there will be an energy barrier, so exponential minus delta H m by R T, but we have to further multiply this by the probability, because jump will not be successful unless and until the next site is vacant.

So, I have to have next site vacant and the probability of finding next site vacant in a substitutional diffusion is very low, because that is depending on the next site being a vacant site or a vacancy and we have seen that the fraction of vacant sites fraction of vacancies in a crystal is very low it can be as low as 10 to the power minus 10 or even less. So, we have to multiply it by p v, where let this p v is probability, let me write it as probability neighbouring site being vacant.

Now, we can see that this probability; probability of neighboring site being vacant will be equal to the fraction of vacant site, so p v will be equal to fraction of vacant site, that is if I am having n v vacancies vacant sites out of N total number of sites, n v number of vacant sites and N is total number of sites, then this fraction will be the probability by which I will find a vacant site.

So, n v by N, but we have already developed a formulation for this when we were discussing the defects and we considered vacancy we showed that this fraction is nothing, but exponential minus delta H f by R T, where delta H f is enthalpy of formation of a vacancy. So, it is an enthalpy of formation of a vacancy.

In fact, since I am using R it is not for a vacancy for a mole of vacancy; for Avogadro number of vacancies, enthalpy of formation of a mole of vacancy. So, we have this probability, so if we want to convert our expression. So now, if we want to make it for substitutional diffusion, so now, I write it for D sub; so if in interstitial diffusion was there this probability fact there also this probability factor you can assume to be present, but this was close to 1.

So, we did not write it explicitly, but now since it is such a small number like 10 to the power minus 10 or so; so we have to write this probability and that will control the diffusivity of the material and this diffusivity will depend upon this probability, which is nothing, but the fraction of vacant site which turns out to be simply exponential minus delta H f by R T.

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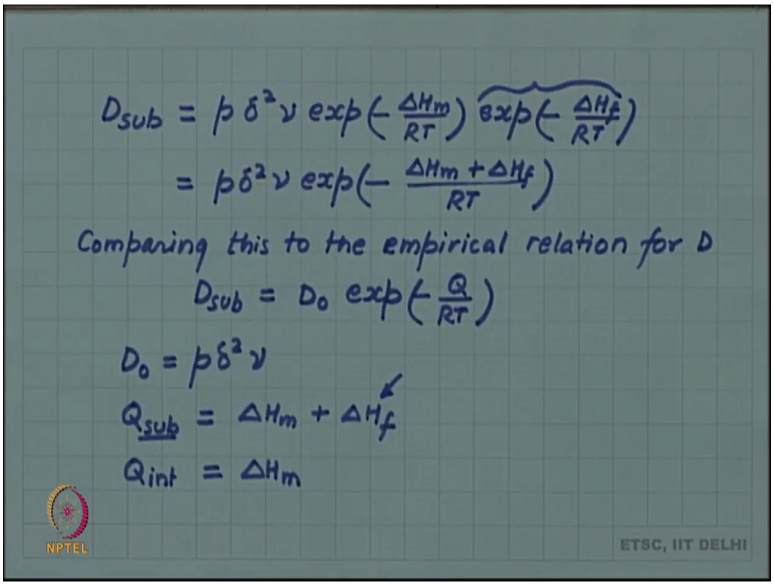

$$D_{sub} = p\delta^2\nu \exp\left(-\frac{\Delta H_m}{RT}\right)\overbrace{\exp\left(-\frac{\Delta H_f}{RT}\right)}$$

$$= p\delta^2\nu \exp\left(-\frac{\Delta H_m + \Delta H_f}{RT}\right)$$

Comparing this to the empirical relation for D

$$D_{sub} = D_0 \exp\left(-\frac{Q}{RT}\right)$$

$$D_0 = p\delta^2\nu$$

$$Q_{\underline{sub}} = \Delta H_m + \overset{\swarrow}{\Delta H_f}$$

$$Q_{int} = \Delta H_m$$

So, if we now write this. So, we will we can complete our expression for the substitutional diffusion, that D sub will become p delta square nu exponential minus delta H m by R T up to this it was fine and it was also true for interstitial diffusion. We multiplied this by another factor p v, which turns out to be exponential minus delta H f by R T; or if you saw this you can combine these two exponential factor into 1, you can write delta H m plus delta H f by R T.

And if you compare this comparing this to the empirical relation relation for D, you now see that D naught is p delta square nu, but Q Q for substitutional diffusion now becomes delta H m plus delta H f whereas, Q for interstitial was only delta H m for comparison.

So, this delta H f, because substitutional diffusion requires vacancy, so you need an enthalpy of formation of vacancy for Q sub, but there is no such requirement for interstitial diffusion. So, activation energy for substitution of diffusion is higher and is higher by delta H f. This is what will generally try to tend to make substitutional diffusion slower, because you have this very small factor multiplying the diffusivity, which was not there in interstitial diffusion.

So, we have already noted that that substitutional diffusion is usually slower much slower than interstitial diffusion. And we now see that that is coming from this fraction of vacant site, which also contributes to the activation energy for substitutional diffusion.