Principles of Physical Metallurgy

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Lecture No. # 16

Diffusion in Solids (Contd.)

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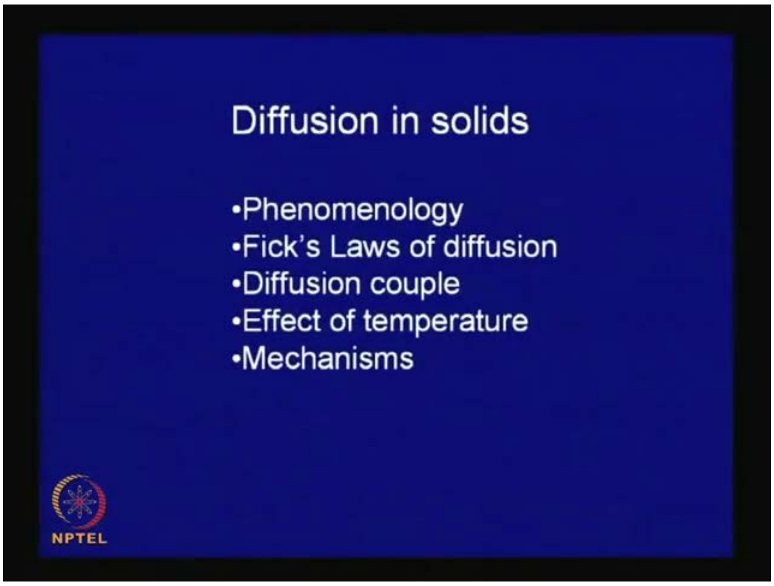

Diffusion in solids

- Phenomenology
- Fick's Laws of diffusion
- Diffusion couple
- Effect of temperature
- Mechanisms

Good morning. We continue our lecture on diffusion in solids, and last class we have learned that diffusion is a process of mixing and we are going to consider particularly this process of mixing in solid state. Now as a we see we have seen last class that and it has been discussed in detail that this moment of atoms they are perceptible, in case of liquid and gases and we can feel or we can see even in certain cases, how the process of mixing continues through a phenomenon of diffusion in liquid and gas.

But the method of diffusion in solid is also exactly same, they atoms in crystals they are not stationary they keep moving and as a result they are will be moment of atoms in a particular direction in solids and this is what we consider last class and we have talked about the phenomenon logic of diffusions the phenomenon. We also looked at the laws of diffusion laws that govern diffusion. We also looked at few problems of diffusion couple how a concentration, if there is a concentration gradient, how does this concentration change with time.

We also looked at the effect of temperature. Today, we shall look at a little more detail about the mechanism of diffusion and what happens, if you have different species you know, whether the both species the move at the same rate or different, and if they are different what effect does it have on the concentration distribution in the solid.

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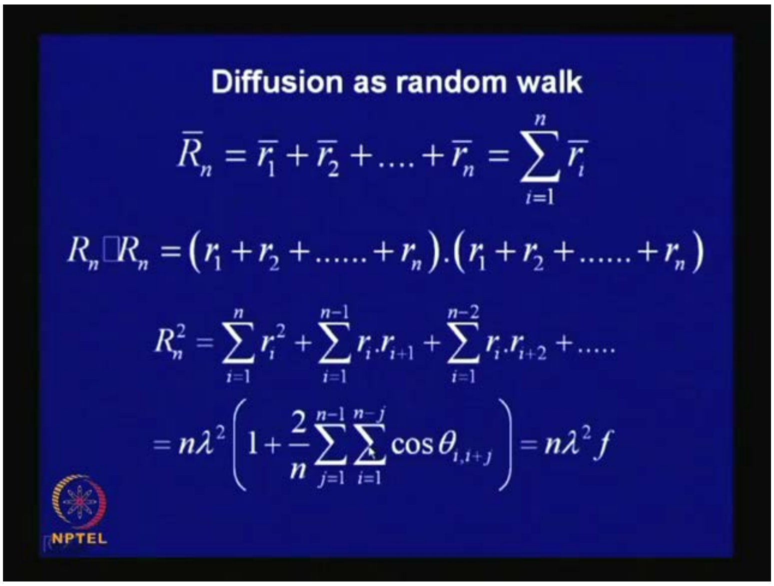

Diffusion as random walk

$$\overline{R}_n = \overline{r}_1 + \overline{r}_2 + ... + \overline{r}_n = \sum_{i=1}^{n} \overline{r}_i$$

$$R_n \cdot R_n = (r_1 + r_2 + ... + r_n).(r_1 + r_2 + ... + r_n)$$

$$R_n^2 = \sum_{i=1}^{n} r_i^2 + \sum_{i=1}^{n-1} r_i.r_{i+1} + \sum_{i=1}^{n-2} r_i.r_{i+2} + ...$$

$$= n\lambda^2 \left(1 + \frac{2}{n} \sum_{j=1}^{n-1} \sum_{i=1}^{n-j} \cos\theta_{i,i+j} \right) = n\lambda^2 f$$

Now, while looking at some of the solutions in the last class, I think what it came out that the process of diffusion can be simulated as one of random walk, and it was at this expression was partly derived up to this. But this also can be you know, you can simplify it, you can add this terms, and then you get a factor like this and here each of these, when you this is at actually a dot products so each of these cases they are a dot product.

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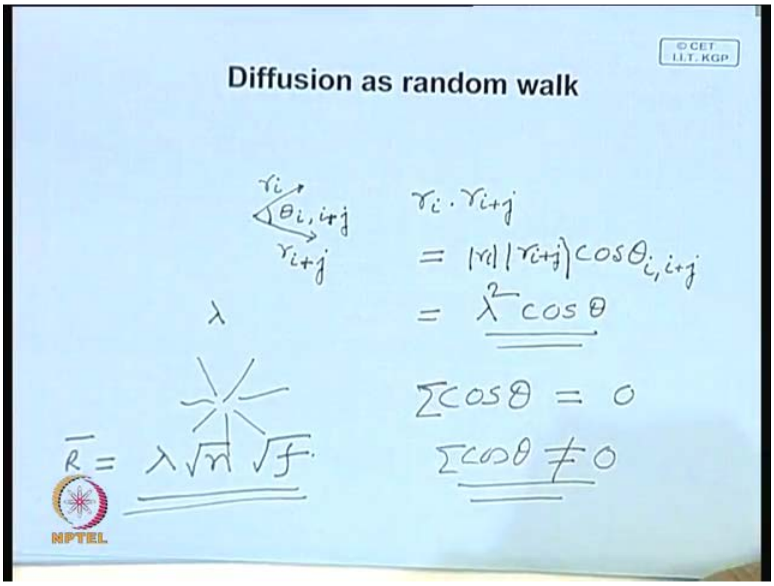

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Diffusion as random walk

$$r_i \cdot r_{i+j} = |r_i|\,|r_{i+j}| \cos\theta_{i,i+j} = \underline{\lambda^2 \cos\theta}$$

$$\Sigma \cos\theta = 0$$

$$\underline{\Sigma \cos\theta} \neq 0$$

$$\underline{\bar{R} = \lambda\sqrt{n}\sqrt{f}}$$

So, here also this is a dot product and what we have done here is a basically, if you have one vector say random walk in this direction, another random walk in this direction. So this is r i this is r. Let us say i plus j. So in that case, there is an angle obtained and we call this angle i i plus j, so this dot product r i dot r i plus j this will be equal to magnitudes of r i, magnitudes of r i plus j times cos theta, that is i i plus j this specific angle. Now, we can always see that the average distance or the step size of the moment, if it is equal to lambda, then we can say this will be equal to lambda square cos theta.

So this is what has been done over here. So clearly, what you see on the slide is this, if you take this common because this some will be n times lambda square. So basically, this you can take common. So you have a factor, which is a function of the direction and this directionality is quite important, if this is totally random. If this materials, this atoms they are free to move in all directions, which is quite possible in certain cases. They can free to move then this sum total of this sum total of cos theta will come out to be zero. Because in certain angle this will be positive in certain direction that cos theta will be negative and therefore, the total sum make come out to be zero.

But in cases, where there is directionality in the moment where there is directionality in the moment in that case, this is some cos theta this may not be equal to zero. So there you can have an orientation factor, which are directionality factor and which is shown here. So, that means that average distance of a random walk average distance of a random walk will be equal to lambda root n, and there will be a concentration factor.

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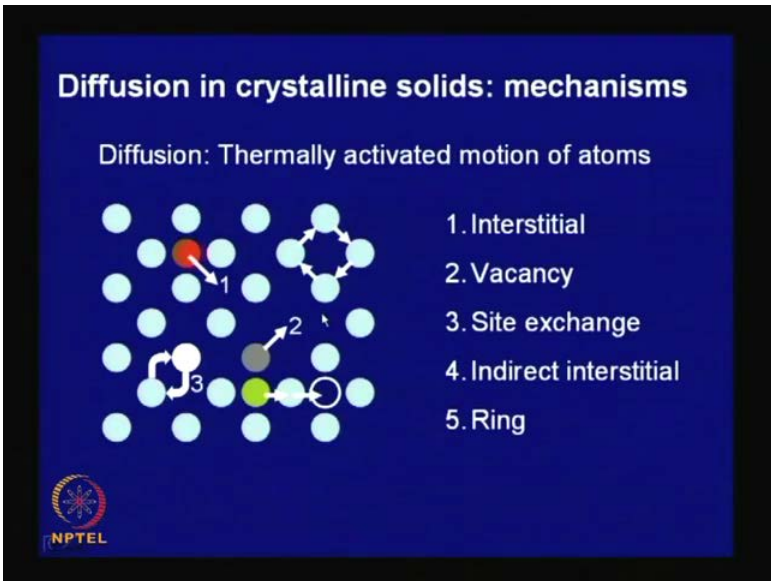

Diffusion in crystalline solids: mechanisms

Diffusion: Thermally activated motion of atoms

1. Interstitial
2. Vacancy
3. Site exchange
4. Indirect interstitial
5. Ring

Now, let us look at the mechanism of diffusion in crystalline solids, mostly that we will be dealing with they are mostly cubic most of the metal majority of the metal may be two-third of the all metals, which are known. They are all they all have cubic structure. Cubic structure as very high symmetric and therefore, for all practical purposes we can assume that diffusivity is same in virtually all direction in most metals, which may not be true in certain metal where they have hexagonal and other with low symmetric. It may be different in different direction but let us not go into that detail and we will look at diffusion mostly in cubic solids and this diagram pictorially represents a systematic array of atoms and here the material of an has some vacancies like some of the places this sites are vacant.

So these are the normal sites. This is 2D and these are the normal site. Now how can atom to move from one place to another. So one mechanism is if there is an atom in the interstitial gap, this is a normal lattice site, this is a normal lattice site and in between there is an interstitial gap if there is an atom here an if it is tries it, if it can move over here possibly, when it moves gap here is smaller may have to push it a little and then come here. So this is one mechanism of thermally activated motion of atoms in solids or diffusion. So basically this is called interstitial mechanism. Another thing which we can think about the atom can exchange position with vacancy sites.

So if there is a lattice vacancy it this lattice site there is no atom here. So an atom which is located here can move to this vacancy. So this is called vacancy driven move motion of atom. We can also think about certain things like site exchange. So this atom is to which are the nearest neighbour sometimes this goes here, this goes there. There is also a mechanism called indirect interstitial moment. So basically if what happens there is atoms here say somehow this of a how happen in a radiation damage an atom is post into interstitial site. So this can push this atom to interstitial and can occupy this lattice site.

This is also through at most moment takes place through interstices. So this we called it indirect interstitial mechanism. There is also a mechanism called ring mechanism that means atoms they can exchange like this, extends of this site exchange and here this moment is like this. But out of this we will see that there have been lot of experiments done and possibly it looks that vacancy an interstitial moment are possibly the mechanism, which can explain many of the phenomenon of diffusion.

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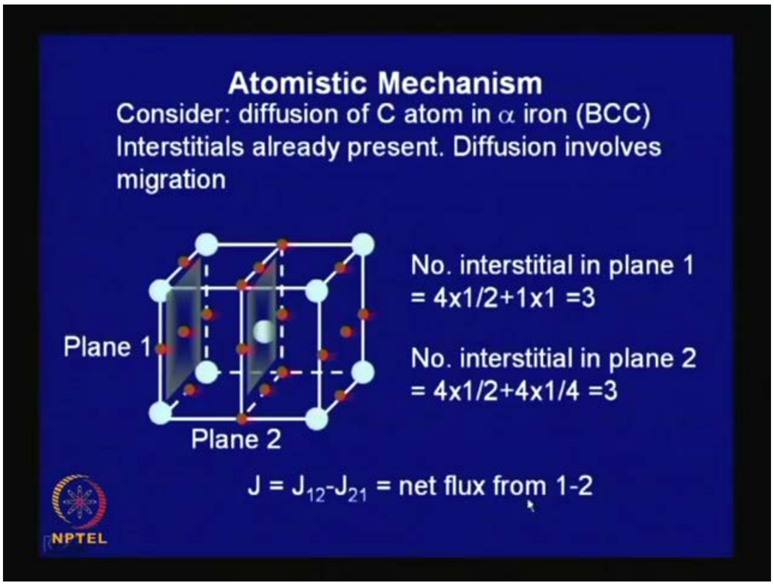

Atomistic Mechanism

Consider: diffusion of C atom in α iron (BCC)
Interstitials already present. Diffusion involves migration

No. interstitial in plane 1 = 4x1/2+1x1 =3

No. interstitial in plane 2 = 4x1/2+4x1/4 =3

$J = J_{12} - J_{21}$ = net flux from 1-2

Now let us look at diffusion of carbon atom in alpha iron. Now we know that alpha iron has BCC structure so BCC structure, which is shown over here and the carbon atoms are present in the interstitials and the lightly there interstitial, which are shown here in the figure with color red. So this one these are the interstitial sites they are called the octahedral sites. Now look at this plane this plane has normal atoms iron atoms located at the corner and we have carbon atoms located these are likely sites, it is not that all of these sites will be occupied and let us consider the next similar plane is this and here also there is an atom over here and these are the interstitial sites.

Now if you look at this atomistic mechanism say, if there is a carbon atom here, if it is has to move to this plane that nearest site here but this is occupied. So this atom is not able to move. But look at this atom over here which is an interstitial atom over here and this can move to this point. So that means not all the interstitial atom on this plane has the ability to diffuse or move to the next plane. So that means, we have to calculate from the atomistic mechanism if you have to calculate or estimate that magnitude of that diffusivity in that case or jump frequency.

We have to look at how many atoms or how many interstitial atoms are likely to move. What is the probability that a particular that this atom of this certain number of atom can move from here to here. For this we have to look at an estimate what is the number of interstitial in a particular plane. Now let us consider the method is described here consider plane A. So plane A apparently it looks one two three four five there are five sites. But they are shade by similar other plane also what it matter is number per unit area. So basically now here say suppose this particular plane if we consider say this one, which is at the center exclusively, belongs to this plane.

So this we can say one atom which exclusively belongs to the plane this is one its contribution to the plane is one. But this corner atoms they are shade by another plane on the next unit cell. Therefore, its contribution to this plane is half. So there is four of this so four times half equal to three. Now similarly, you can calculate this number of atoms in this effective number of interstitial sites on this particular plane. This also will come out to be three. So that means number of atoms interstitial site here and here are same.

Now when the carbon atom moves what is the net flux carbon can jump from here to here it can jump from here to here as well. So this is a random process and so this moment it is both are likely it can go here to here or an interstitial site from here it can go to this plane. So net flux of carbon you if you have to calculate you have to calculate net flux from plane one to two subtract the flux from plane two to one. So this is the net flux from plane one to two.

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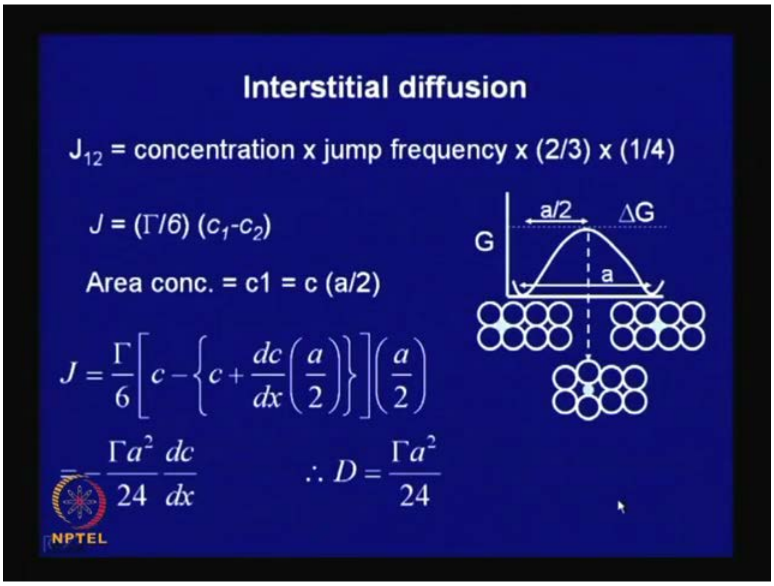

Interstitial diffusion

J_{12} = concentration x jump frequency x (2/3) x (1/4)

$J = (\Gamma/6)\,(c_1 - c_2)$

Area conc. = c1 = c (a/2)

$$J = \frac{\Gamma}{6}\left[c - \left\{c + \frac{dc}{dx}\left(\frac{a}{2}\right)\right\}\right]\left(\frac{a}{2}\right)$$

$$= -\frac{\Gamma a^2}{24}\frac{dc}{dx} \qquad \therefore D = \frac{\Gamma a^2}{24}$$

Let us see how this calculation proceeds does. Now we can visualize that interstitial diffusion like this. So if you have a this is a crystal, this is an interstitial site and see this stability of a structure is determined by its free energy the gives free energy which is shown over here. So if an atom interstitial lies here this gives the structure over here, this is one stable state. Now, if it moves from here to here the arrangement is like this both cases you see that there is little distortion in the lattice both are white stable structure. So this has minimum free energy but for it this atom to migrate from this side to this side, it has to push this to atom a parts something like this and then only it can move to the next site so that means it has to pass through an activation.

So this is the thermal activation which has to be provided for this atom to move one atomic distance or one particular one atomic distance from here to here. Now so the case is basically so this is the so effectively what we can say that if it moves this distance a by 2, the other part is quite easy and this is spontaneous. So effective distance this atom must move with a by 2. So with that let us look at how we calculate this net flux from plane one to two. This will depend on how many atoms are there that is concentration number atoms per unit area.

Then there will be a jump frequency jump frequency times the how many of these atoms can move and there is also a geometrical factor one-fourth we discussed last time. For an atom to move in a particular direction this probability in 3D in a moving in a particular direction comes out to be one-fourth. So with this you can calculate that flux will be equal to this is the jump frequency and this is the jump frequency capital gamma is the jump frequency and this product is one over six and then this concentration different. Now this concentration is number of atoms that in that particular area.

So basically if we go to the previous site so number of atom over here, so that means we can take a thin slice a by 2 that distance from here to here that a by 2 is the distance over here and in that case how do you calculate this we go back to this. So this will be that volume will be if you say that a plane area is unity then this is the volume unit area times a by 2. This is the volume we have to consider and then times this is the volume concentration c 1 is this. Now there is a similarly, you can calculate c 2 also will be because number of in atom their similar.

So they you can say the concentration that also will be similar but point is there is different if we know the concentration here there is likely to be a different in the concentration nearby, which is done by this is the tailor series you consider the first step, and then if you solve this then it comes you get this and then this gamma a square by 24, this comes out to be the diffusivity. So that means from this atomic concept mechanism also you can find out an expression for diffusivity and which is over listed over here. Now what is a?

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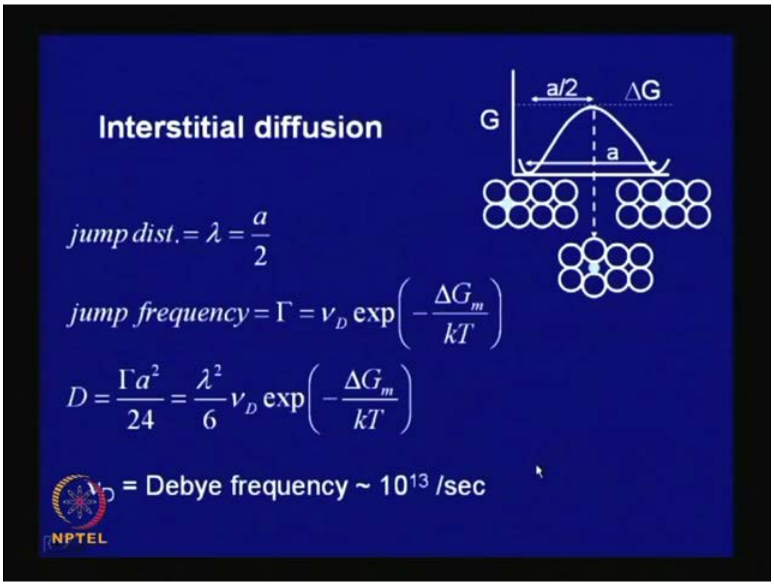

Interstitial diffusion

$$jump\ dist. = \lambda = \frac{a}{2}$$

$$jump\ frequency = \Gamma = \nu_D \exp\left(-\frac{\Delta G_m}{kT}\right)$$

$$D = \frac{\Gamma a^2}{24} = \frac{\lambda^2}{6}\nu_D \exp\left(-\frac{\Delta G_m}{kT}\right)$$

ν_D = Debye frequency ~ 10^{13} /sec

Now that is a jump distance average jump distance we talked about is lambda and here we find at average jump distance is a by 2 in the crystal lattice if we go previous here this is the distance a jump distance is a by 2. So basically so this is the jump distance and what is the jump frequency? Jump frequency is given by this is a frequency which is of the order of 10 to the power 13 per second and exponential minus this is the gives free energy so similar that activation held over k T. So this is the jump frequency therefore, the diffusivity expression is this.

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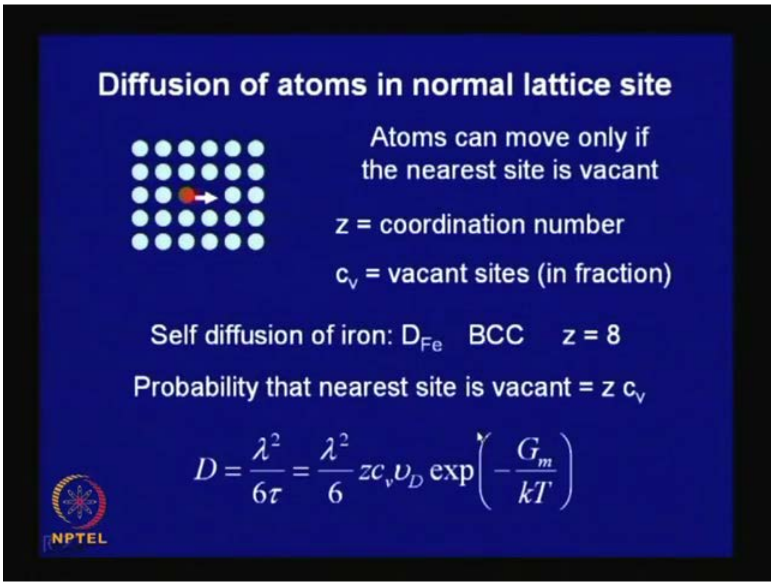

Diffusion of atoms in normal lattice site

Atoms can move only if the nearest site is vacant

z = coordination number

c_v = vacant sites (in fraction)

Self diffusion of iron: D_{Fe} BCC z = 8

Probability that nearest site is vacant = z c_v

$$D = \frac{\lambda^2}{6\tau} = \frac{\lambda^2}{6} z c_v \upsilon_D \exp\left(-\frac{G_m}{kT}\right)$$

Now, let us look at diffusion of atom in a normal lattice. In a normal lattice also we just talked about the interstitial diffusion and we have seen that from the atomistic mechanism it is possible to find an expression for diffusivity coefficient. Now can similar thing we done in case of a substitutional atom or that self diffusion say something which is shown over here. Now, in case of interstitial a large fraction like carbon, when we were considering carbon in alpha iron large number of this sites are vacant but there number of vacancies here most of these sites will be occupied.

So which is shown here there is a vacancy over here. So that means an atom can move if there does a vacancy exist. Otherwise if it has to move it has to create another vacancy if it has to move a push if this atom is moves here this has to prove and then a vacancy has to be created at another site. So this is so basically the two states will be involved. Now atom is so this is what is return here? Now, we have learned about a factor called coordination number z is the number of atoms the nearest neighbor atom. So like here in the 2D whatever is shown here so which is the nearest atoms this is one two three four.

So there is this plane the nearest neighbor is four so but in 3D this nearest neighbor where is from crystal structure to structure. So like if you have a face centered cubic structure where you have maximum coordination number z is twelve. In body centered cubic structure coordination number is eight and let us says that c v represents that number of vacancies that is in fraction this is the vacant sites in fractions. Now let us try and find out the self diffusion of iron in BCC lattice where this coordination number is eight. So here is the probability that a site is vacant a particular site out of this eight how many are vacant this will be z times c v and then go we can back to the previous expression that in a general any lattice say diffusivity is equal to that lambda square this distance over six tau.

Now this one over tau you can say you can say that this is that diffusivity. Now here how do you calculate this? Now here you have to multiply this by so here one over tau is equal to this is the diffusion distance so you have to multiply this by this probability that site is vacant and times this you go to the previous one. You see this diffusivity is given over here.

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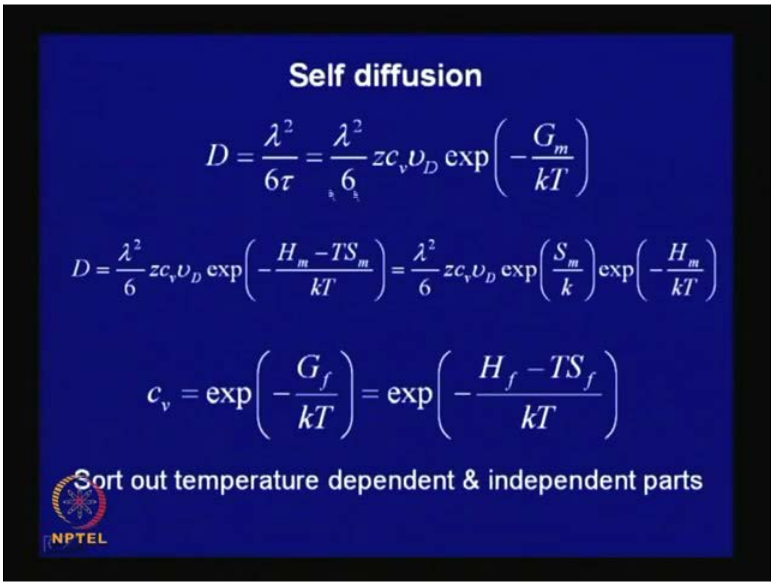

Self diffusion

$$D = \frac{\lambda^2}{6\tau} = \frac{\lambda^2}{6} z c_v \upsilon_D \exp\left(-\frac{G_m}{kT}\right)$$

$$D = \frac{\lambda^2}{6} z c_v \upsilon_D \exp\left(-\frac{H_m - TS_m}{kT}\right) = \frac{\lambda^2}{6} z c_v \upsilon_D \exp\left(\frac{S_m}{k}\right) \exp\left(-\frac{H_m}{kT}\right)$$

$$c_v = \exp\left(-\frac{G_f}{kT}\right) = \exp\left(-\frac{H_f - TS_f}{kT}\right)$$

Sort out temperature dependent & independent parts

If you build up on this is equal to say there are one term you know, this is a free energy term over here. Now this free energy also you can this has two parts one is that enthalpy another is the entropy. So free energy means this end part of that energy is not free so if you substitute this and then you try and take out the part, which is not depended on temperature, so which is shown here if you substitute this is simple algebraic simplification. Now this part is dependent on the temperature. Now the question comes there is a how what is this vacancy concentration, how do you determine?

This is given by this expression exponential that number of sites which are vacant is given by that Boltzmann statics so or a this is exponential this is the energy, which is needed to create a vacancy over k t, k is a Boltzmann constant and here also capital G this is the free energy and which is as also the two parts. This is the enthalpy to create a vacancy and this is the entropy terms the t times this is entropy which is associated with a vacancy creation. Now here also then you sort out the temperature dependent and independent parts if you do it which is shown over here.

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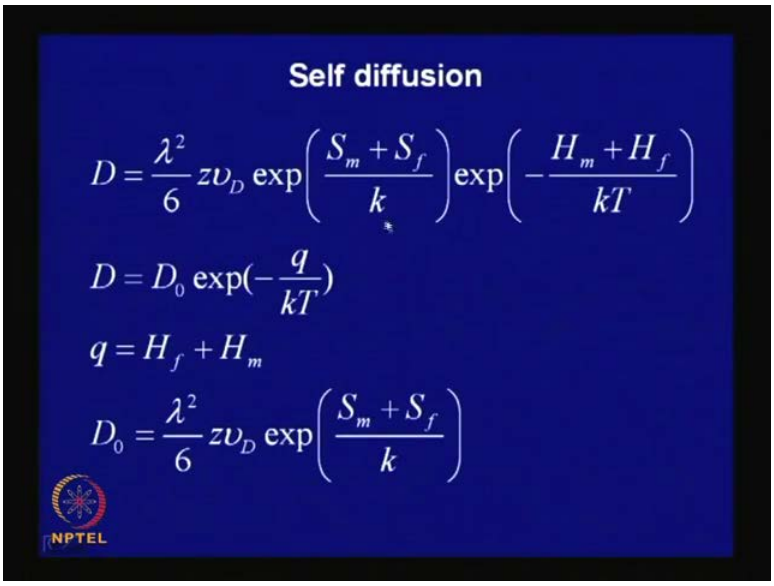

Self diffusion

$$D = \frac{\lambda^2}{6} z\upsilon_D \exp\left(\frac{S_m + S_f}{k}\right) \exp\left(-\frac{H_m + H_f}{kT}\right)$$

$$D = D_0 \exp(-\frac{q}{kT})$$

$$q = H_f + H_m$$

$$D_0 = \frac{\lambda^2}{6} z\upsilon_D \exp\left(\frac{S_m + S_f}{k}\right)$$

Now, this part is temperature independent and we have seen earlier that diffusivity can be return as D is equal to D naught exponential this activation energy for diffusion over k T. Now here this q which is that activation energy, which is equals to these two. So that means for self diffusion, you have the two enthalpy terms are involved one is the enthalpy for migration another is enthalpy for formation of basically, a vacancy that means this is vacancy assisted.

Now, a question can come that what is the diffusivity the vacancy diffusion and self diffusion which is higher now obviously a here you have two component; so in case of self diffusion that activation energy is higher therefore, obviously self diffusion will be slower then vacancy diffusion and D naught part which is basically frequency dependent which is called which is called which is equal to this.

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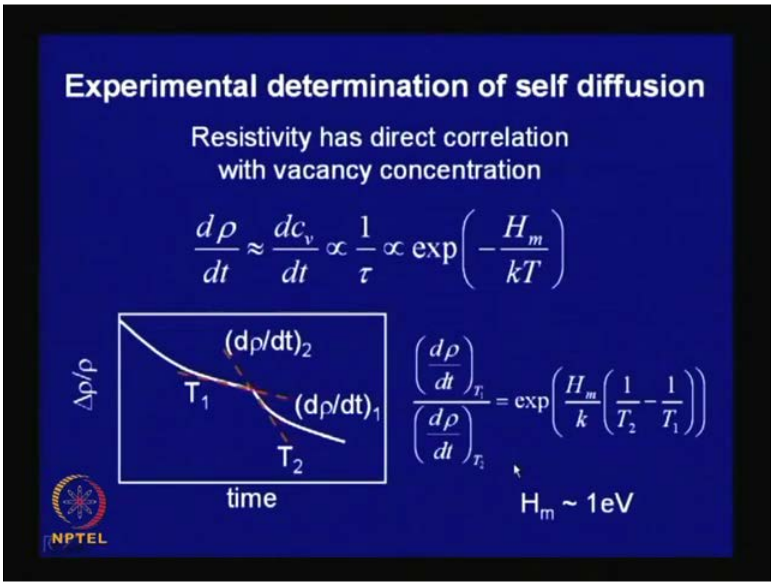

Experimental determination of self diffusion

Resistivity has direct correlation
with vacancy concentration

$$\frac{d\rho}{dt} \approx \frac{dc_v}{dt} \propto \frac{1}{\tau} \propto \exp\left(-\frac{H_m}{kT}\right)$$

$$\frac{\left(\frac{d\rho}{dt}\right)_{T_1}}{\left(\frac{d\rho}{dt}\right)_{T_2}} = \exp\left(\frac{H_m}{k}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right)$$

$H_m \sim 1$eV

So this explains how from the concept of atomistic mechanism, it is possible to derive and have some idea about the factors on which the diffusivity will depend and one thump rule is diffusivity of any atom or any self diffusion of coefficient of any metal at room temperature will be a function of its melting point. The materials which is low melting point at room temperature they have higher diffusivity. So this is the general thump rule and in fact many cases where diffusion data or not available there are simple methods expression by which from the melting point it is possible to estimate self diffusion.

Now let us look at we talked about diffusion phenomenon self diffusion how are there any experimental method of determining self diffusion. Now, we have talked about well considering the measurement of vacancy and we have seen the resistivity has a direct correlation with a vacancy concentration. So, resistivity measurement is a good technique to measure or determined the coefficient of self diffusion. Now, this changes resistivity say what we try and monitor if you take a piece of metal say suppose silver or any metal copper heat it to a high temperature and then quench then at room temperature you have arrested that higher number of vacancy so this is in a meta stable state.

Now if you a annihilate at a certain temperature say may be fifty little higher than room temperature may be eighty degree or hundred degree if you keep annealing and as a function at a particular temperature T 1. Then we will find its resistivity will go on decreasing and which is shown over here and this rate of decrease is actually proportional to the change in vacancy concentration and vacancy concentration, which is shown over here. This is proportional to that one over that relaxation time. So basically this will be proportional to exponential H over k T this H m is you can see that this is the enthalpy of or activation energy for migration of or moment of this migration of atoms.

Now here if you look at this plot what plot and then you do you change the temperature suddenly. Now, this resistivity that of available which are automated and if you change the temperature suddenly if you increase it this rate of decrease this will increase. Now then what you draw is a tangent over here and tangent over here. So these are this d row over dt to find out at two different temperatures and it is quite easy to show from this, if you the ratio of these two tangent will be equal to this factor. I leave it to you to derive and by this several experiment have been done and in fact a in the on the same sample you can repeat it number of time.

Like here you can increase it again then decrease increase decrease so that way you can find out get as several readings between T 1 and T 2 an average of that will give you a measure of that activation energy for migration and usually this comes about for materials for self diffusion, it comes about one electron volt.

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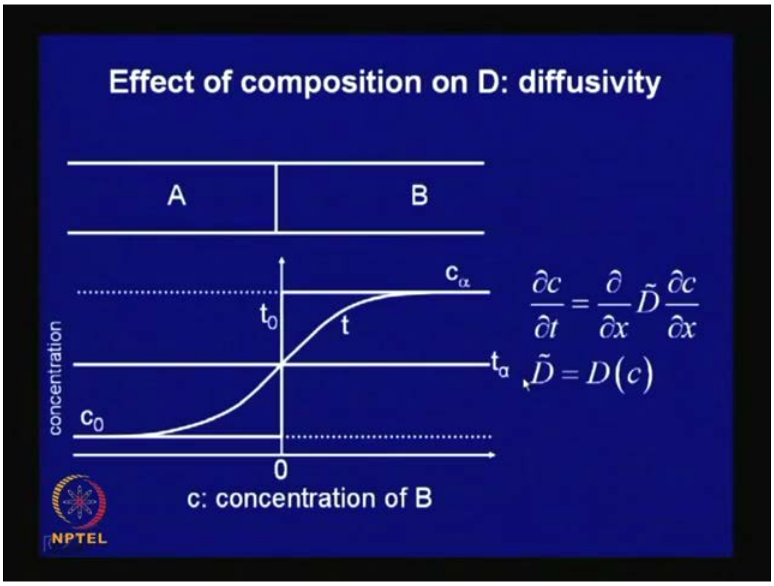

Effect of composition on D: diffusivity

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\tilde{D}\frac{\partial c}{\partial x}$$

$$\tilde{D} = D(c)$$

c: concentration of B

Now let us see is composition if diffusivity is this a function of a composition, so for we did not look at it or ignore that we assume that diffusivity is not a function of composition and therefore, that in that diffusivity equation we took out I mean the D so basically in this diffusivity expression we use to take the outside and will use to write it dc dt d to dx square. Now what happens if this is a function of composition then you cannot take this out. So basically this is because this will be a function of concentration and we know that from our some of these types of plot that this concentration keeps on changing with the distance the concentration here is different, here it is different.

So that means D if this diffusivity is a function of concentration in a way an concentration changes with distance, so this two is the function of x. Therefore, you cannot take it outside therefore it is need to there is a necessity to know how this diffusivity depends on concentration. Now here are two a diffusion couple to metal A and B and this is the interface.

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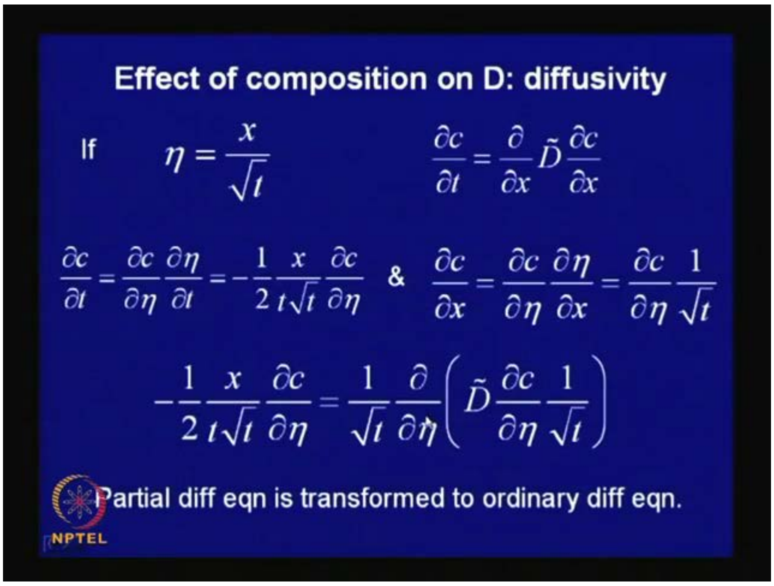

Effect of composition on D: diffusivity

If $\eta = \frac{x}{\sqrt{t}}$

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\tilde{D}\frac{\partial c}{\partial x}$$

$$\frac{\partial c}{\partial t} = \frac{\partial c}{\partial \eta}\frac{\partial \eta}{\partial t} = -\frac{1}{2}\frac{x}{t\sqrt{t}}\frac{\partial c}{\partial \eta} \quad \& \quad \frac{\partial c}{\partial x} = \frac{\partial c}{\partial \eta}\frac{\partial \eta}{\partial x} = \frac{\partial c}{\partial \eta}\frac{1}{\sqrt{t}}$$

$$-\frac{1}{2}\frac{x}{t\sqrt{t}}\frac{\partial c}{\partial \eta} = \frac{1}{\sqrt{t}}\frac{\partial}{\partial \eta}\left(\tilde{D}\frac{\partial c}{\partial \eta}\frac{1}{\sqrt{t}}\right)$$

Partial diff eqn is transformed to ordinary diff eqn.

Now this problem that comes up is can you how do you solve this is there a way we can solve this equation. Now in differential equation, often we do some amount of transformation.

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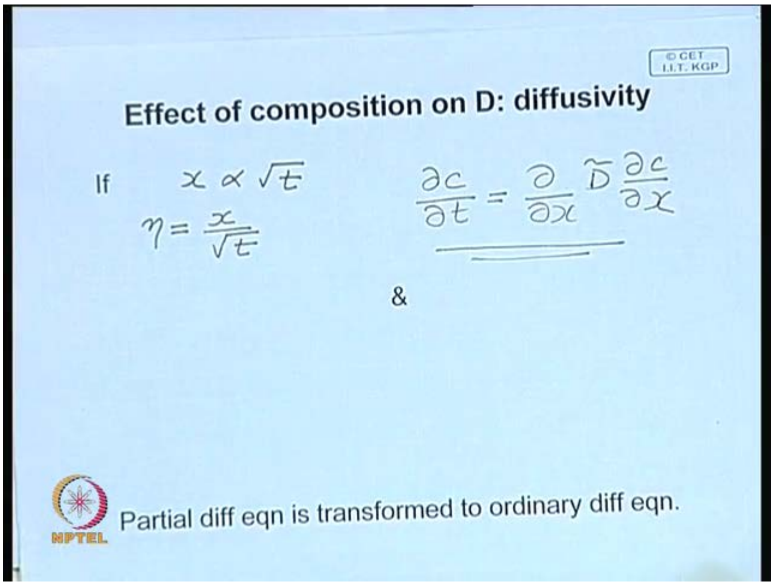

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Effect of composition on D: diffusivity

If $x \propto \sqrt{t}$

$\eta = \frac{x}{\sqrt{t}}$

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\tilde{D}\frac{\partial c}{\partial x}$$

&

Partial diff eqn is transformed to ordinary diff eqn.

Now here is we talk about a particular transformation where particular transformation, which is based on we have seen the diffusion distance is actually proportional to route over t. So basic therefore, if we make a substitution that a variable we think about a variable which is x as eta which is we put route over t and if we substitute this in the diffusivity equation that dc dt equal to d dx, if we make this substitution then we will find out that this partial differential equation gets converted in to an ordinary differential equation.

Therefore, which is shown over here what has been done is dc dt this is how you can convert and once you substitute it here then it becomes it is transformed into a ordinary differential equation. So which is possible you can to integrate it is find out the solution.

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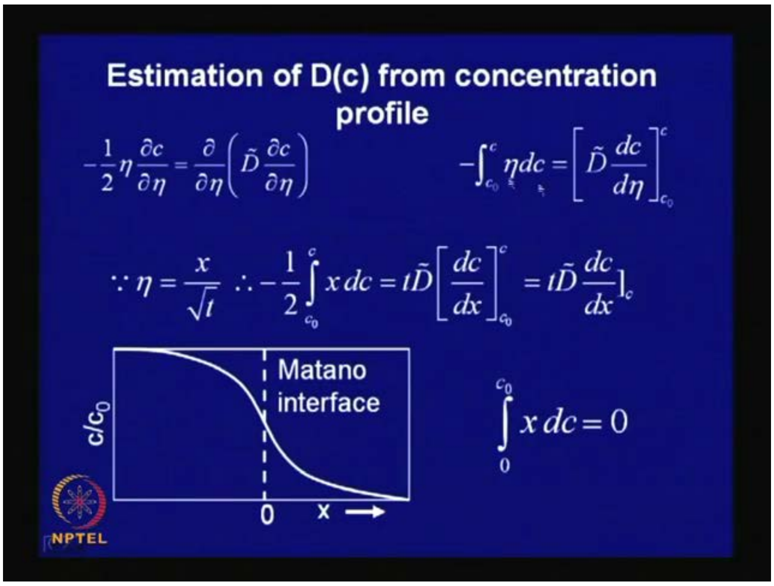

Estimation of D(c) from concentration profile

$$-\frac{1}{2}\eta\frac{\partial c}{\partial \eta} = \frac{\partial}{\partial \eta}\left(\tilde{D}\frac{\partial c}{\partial \eta}\right) \qquad -\int_{c_0}^{c}\eta\,dc = \left[\tilde{D}\frac{dc}{d\eta}\right]_{c_0}^{c}$$

$$\because \eta = \frac{x}{\sqrt{t}} \quad \therefore -\frac{1}{2}\int_{c_0}^{c} x\,dc = t\tilde{D}\left[\frac{dc}{dx}\right]_{c_0}^{c} = t\tilde{D}\frac{dc}{dx}\Big]_{c}$$

$$\int_{0}^{c_0} x\,dc = 0$$

Now this is shown over here. So this is the expression and here if you now integrated this integration is possible because if you integrate so this goes out. So this is the solution that is d dc d eta then you have to substitute the limit that is concentration c zero at a time t zero or c and this is the concentration at a particular point and when you do it so. Now this question comes how do you find out this now for this you have to carry out an experiment that means you make a diffusion couple and often when such a couple is made people should put some marker here.

So markers are nothing but a different metal which is not soluble in either. So whenever and whereas, this two A and B they are soluble in each other. Therefore, this markers will not get effected B will move from this end to this end A will move from this end to this end and ultimately A concentration profile will be set of initially this is c zero and here this is the concentration of B in A and this is the concentration of B in B. So this is how a concentration profile will certain at any time t. Now any time t if you know this plot then it is possible to integrate that expression and find out this effective the diffusion coefficient diffusion coefficient as a function of concentration and this is what is shown over here.

So this is the concentration profile and often we can normalize it write it c over that initial that composition c naught c over c naught and this starts from zero so let us say this is one. Now look at this expression here this eta you can substitute back x over root t if you do that then this get converted this is integral x dc c zero to c so this is the part and this part becomes this. Now look at this gradient now at c zero so basically where is this c equal to zero. So if the concentration is c zero you find that this is concentration is c zero in that case and both this ends this slope is zero.

Therefore, here you can say that it is necessary you can substitute one of these concentrations this is the solution. Now the question comes what is that concentration any c any c is over here, so which let me c this one.

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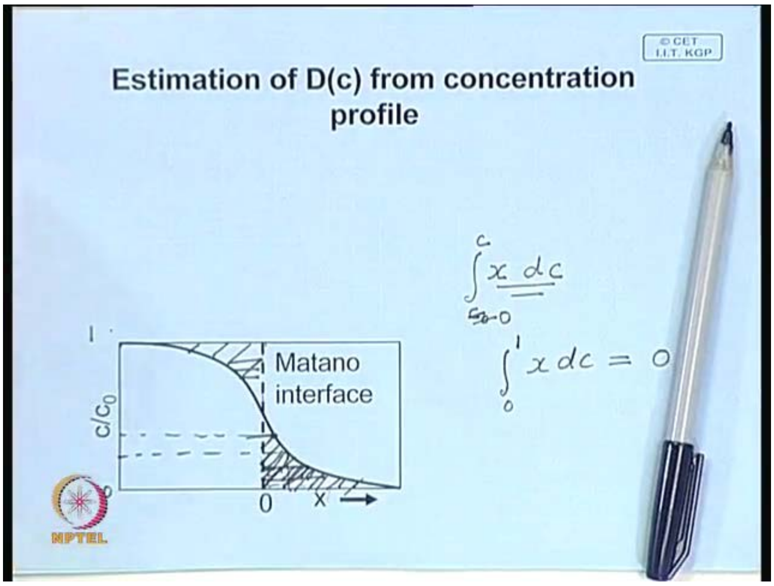

Estimation of D(c) from concentration profile

$$\int_{c=0}^{c} \underline{x\,dc}$$

$$\int_{0}^{1} x\,dc = 0$$

So any c say suppose this is the one any c in that case that integration is refers to this area x and from where do you measure x? So it is quite important to find out that interface from where you will measure the x. Now this is defined as a line which is called the matano interface or matano plane and what does this signify? This is a plane or a line over here where this two area they are equal see this integration when you say that integration x dc if you find this out so x is actually a small element here. This is the small element and you can find out this area and this is the change in concentration dc.

So this is the area then you integrated from particular concentration that is say c zero to c or you say in this particular case is initially this concentration is zero it is normalize with c zero as another atom. So basically you can say that from zero to c from zero this is zero this is final concentration one and in fact if you substitute it from zero to one x dc this area will come out to be zero. In this part this area this is negative so total area so that means this defines this matano plane or matano interface.

So first take us to find out this matano interface and then for each concentration you find out this area, if this is the concentration you find out this area, if you say next is up to this then you find out area up to this particular area and that is how it is possible to find out in that case once you do it then it is a real it just substitution so basically its simple substitution and then you can calculate this once this is known and then you can also find out this particular concentration you draw this tangent this tangent will give you this and usually this plot is for a fix time t which is known.

This is for a fix time which is known therefore, in this expression this area you have found out you substitute it here and this t is known this tangent at particular concentration can be determine by drawing a tangent on that particular point. So having done this it is possible to find out this effective diffusion coefficient.

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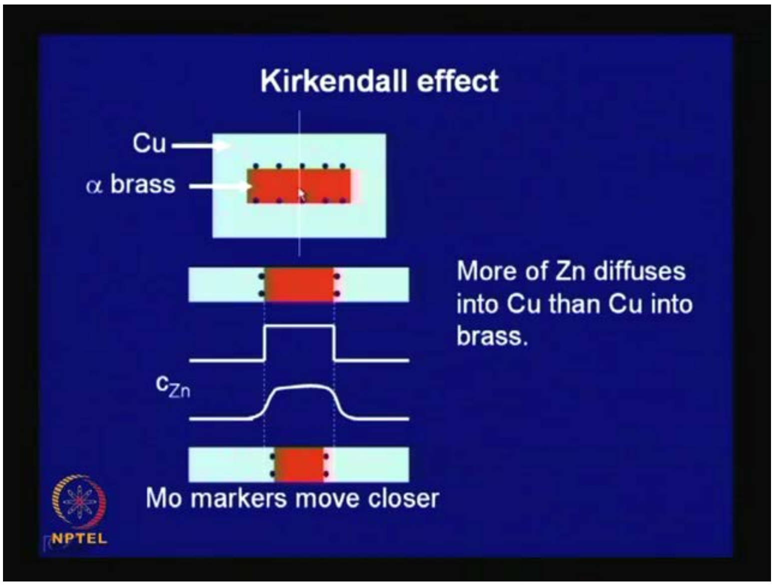
Kirkendall effect

More of Zn diffuses into Cu than Cu into brass.

Mo markers move closer

Now let us look at that there is excellent experiment it was conducted by Kirkendall that is a way by this effect is known after his name is known as Kirkendall effect. Here taken a piece of copper which surrounding and put it surrounding an alpha brass and molybdenum markers which as shown over here and if you heat it and then take a section and this section diagram it looks like this and then one can do chemical analysis and find out the concentration. So initially you can see the concentration alpha brass it is an alloy it has about thirty percent zinc dissolved in copper.

So here you have zinc in solution in copper and here it is pure copper. So there is concentration gradient zinc will try and diffuse copper also will try and also move across the interface. Now, the mobility of these two atoms is different. Therefore and we know that zinc diffuses faster because its melting point is much lower than that of copper. So zinc moves from this to this copper moves from this to this so there is a difference in their diffusivity therefore, a concentration gradient something like this is setup and when this experiment this section was taken and found out then they found that this markers keep moving they are not stationary, the markers move.

In fact the number of zinc atoms the move then the copper through that interface therefore, this marker shifts. So molybdenum a marker the move closer in that case because more zinc from here goes to copper then number of copper atom which comes this side therefore, the marker moves. So this is a clear indication of a vacancy assisted basically we will see later this is a clear case that vacancy mechanism or direct evidence how vacancy plays an important role in diffusion.

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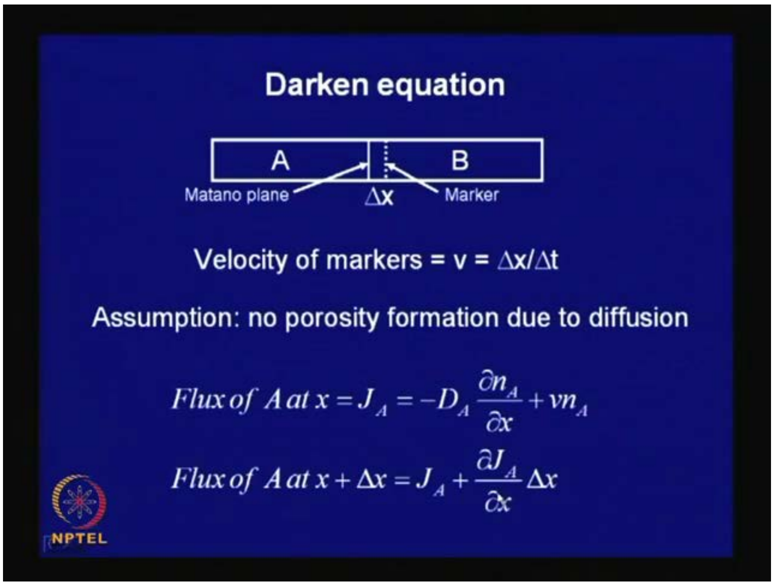

Darken equation

Velocity of markers = $v = \Delta x/\Delta t$

Assumption: no porosity formation due to diffusion

$$Flux\ of\ A\ at\ x = J_A = -D_A\frac{\partial n_A}{\partial x} + vn_A$$

$$Flux\ of\ A\ at\ x+\Delta x = J_A + \frac{\partial J_A}{\partial x}\Delta x$$

Now with this concept it is possible to derive an expression that see this effective the diffusivity this D whether the question that comes true this D it is a function of composition. But how does it depend the two atoms A and B they may not have same diffusivity and in fact the kirkendall effect shows that the A and B they are not equal and if they are not equal then the marker will move. Now question comes is it possible to find out diffusivity of the D A and D B individually. Now for that, we have to look at we have to derive on expression and this is the famous equation goes by the name of darken who was the first derive it and you visualize this is the diffusion couple of two metal A and B and there was a marker here and after some time whatever we find that marker has move one side and this is the matano plane.

So what we can say with respect to that means matano plane is the one which represents that is you can say the diffusion flux between that concentration the profile the center point of the concentration profile is the matano interface. So this distance it is measurable this marker moment is measurable and you can do it as a function of time and if you do that marker moment the distance between the matano face a matano interface and distance between matano this plane and this x you will find that x is proportional to route over t. So in that case you can write that x square by t will be a constant this. What it means this is a constant not Boltzmann constant some constant.

So this is measurable so that means B can be measure by experiment. Now question comes how we do estimate D A and D B and this is shown over here and this derivation is based on the assumption that there is no porosity formation due to diffusion. One may wonder if the two the diffusivity are different it may leave behind some voids. Now which are known as they it actually forms in certain material they are known as kirkendall void but we make that the assumption that no such void formation is there. So with that assumption in that case the net flux has to balance.

Now let us see how do you calculate net flux of A at this place this x A atom moving from here to this side. This is given by this equation D A and this is the concentration gradient. So number of A atom per unit volume and n is the number of free atom so this is basically the Ficks law and here you can see that number of this atoms they keep moving through the marker. Now here at unit time that marker moves a distance v. So number of atom which moves through the marker it has move from here to here so this is the volume basically unit distance this will be v. So v times this area if you assume this cross section area is one. So this volume is v times n A. So this is the flux so similarly the flux of A at x plus dx will be this.

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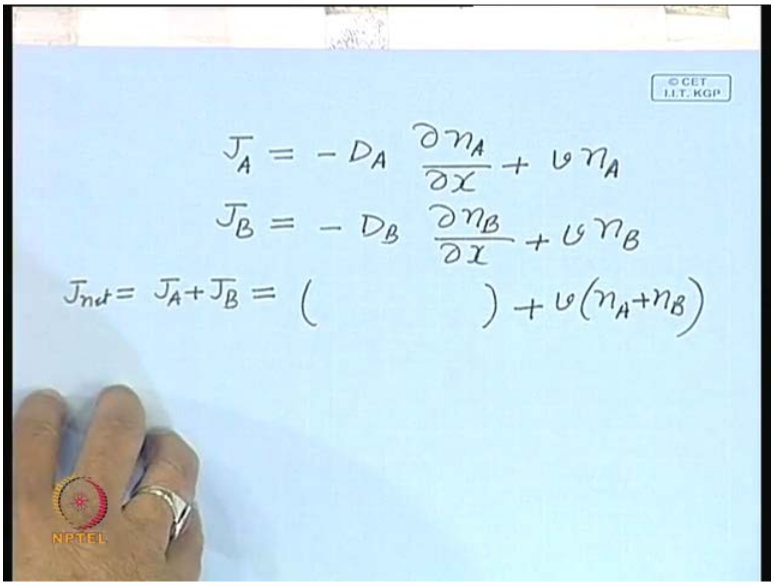

$$J_A = -D_A \frac{\partial n_A}{\partial x} + v n_A$$

$$J_B = -D_B \frac{\partial n_B}{\partial x} + v n_B$$

$$J_{net} = J_A + J_B = (\qquad\qquad) + v(n_A + n_B)$$

Now let us see that now if you look at here the flux of A this is equal to minus D A d n A dx plus velocity times similarly, B also you can write out in the same way, v this is number of B atoms per unit volume and if you add that two which is the net flux through the marker this is the j net and then if you add the two you will have this plus v n A plus n B. Now which is shown over here so if you do a little algebraic simplification.

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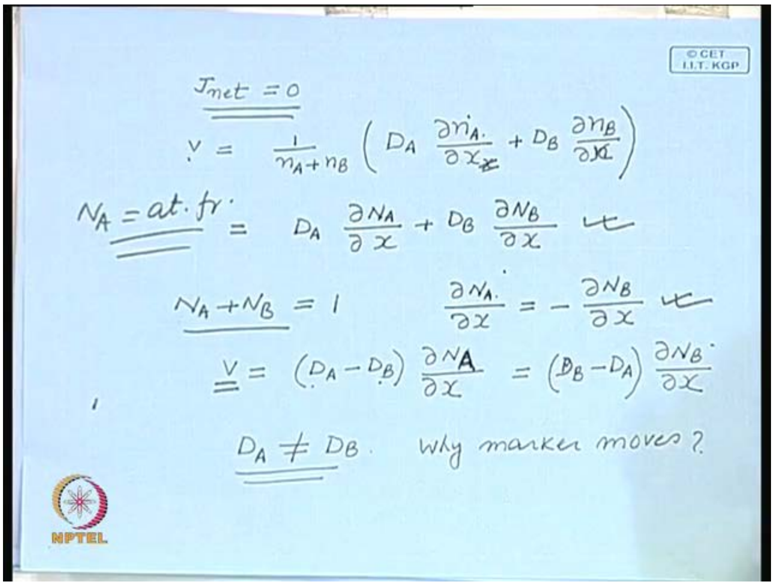

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$$J_{net} = 0$$

$$v = \frac{1}{n_A + n_B}\left(D_A \frac{\partial n_A}{\partial x} + D_B \frac{\partial n_B}{\partial x}\right)$$

N_A = at. fr.

$$= D_A \frac{\partial N_A}{\partial x} + D_B \frac{\partial N_B}{\partial x}$$

$$N_A + N_B = 1 \qquad \frac{\partial N_A}{\partial x} = -\frac{\partial N_B}{\partial x}$$

$$v = (D_A - D_B)\frac{\partial N_A}{\partial x} = (D_B - D_A)\frac{\partial N_B}{\partial x}$$

$D_A \neq D_B$. Why marker moves?

Now, this net moment that flux should balanced through that is amount material moving through the marker since no vacancies have been created this is equal to zero. If you do it then it is possible to show that velocity of the marker is given by this equation. Now here, if you substitute this is the total number of atom, then N A the capital N A is the atom fraction N A this is atom fraction. Now, this total capital N A plus N B equal to one therefore, you can say that this is the relationship between N A and N B if you substitute it is possible to show that velocity of the marker it is equal to D A minus D B and del capital N A del x. It can be return in terms of N B as well. So clearly you see that if the D A is not equal to D B this will have a finite value so this is why the marker moves.

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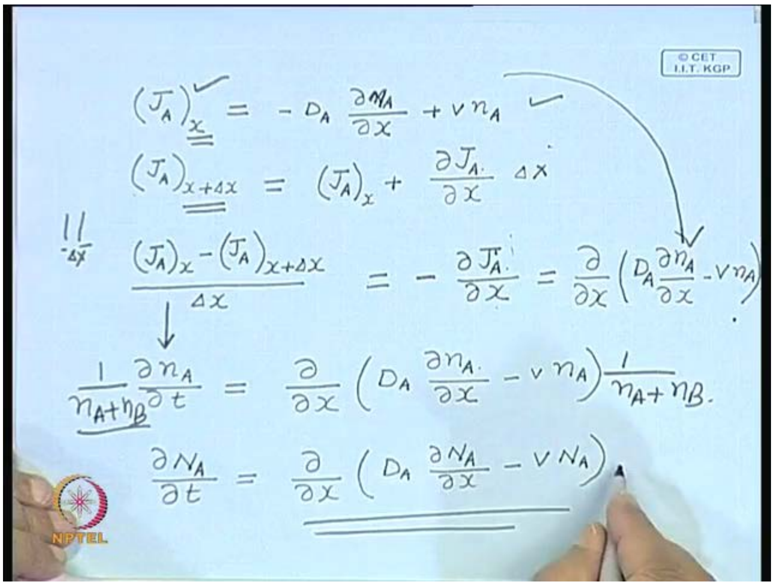

$$(J_A)_{\underline{\underline{x}}} = -D_A \frac{\partial n_A}{\partial x} + v n_A$$

$$(J_A)_{\underline{\underline{x+\Delta x}}} = (J_A)_x + \frac{\partial J_A}{\partial x}\Delta x$$

$$\frac{(J_A)_x - (J_A)_{x+\Delta x}}{\Delta x} = -\frac{\partial J_A}{\partial x} = \frac{\partial}{\partial x}\left(D_A \frac{\partial n_A}{\partial x} - v n_A\right)$$

$$\downarrow$$

$$\underline{\frac{1}{n_A+n_B}}\frac{\partial n_A}{\partial t} = \frac{\partial}{\partial x}\left(D_A \frac{\partial n_A}{\partial x} - v n_A\right)\frac{1}{n_A+n_B}$$

$$\frac{\partial N_A}{\partial t} = \underline{\underline{\frac{\partial}{\partial x}\left(D_A \frac{\partial N_A}{\partial x} - v N_A\right)}}$$

Now, the question comes in that case is it possible to find out and expression how you find both together. So for this you find this say let us now look at that flux of A at an interface x which is given here. Similarly, you can write the same flux at x plus dx. So basically you have to differentiate it and this is the incremental flux. In that case, this is the buildup of the concentration in that thin cell this is the delta x thin cell, this is the buildup of the concentration and which is equal to this you can say the minus J A del x and then you can from here itself you can substitute this term over here.

This J A is over here you substitute you get this and this is the concentration buildup therefore, you can say this is del n A dt therefore, this is one expression and you can also convert it you divide both by n A plus n B the total number of atom this side and this side then you get this expression.

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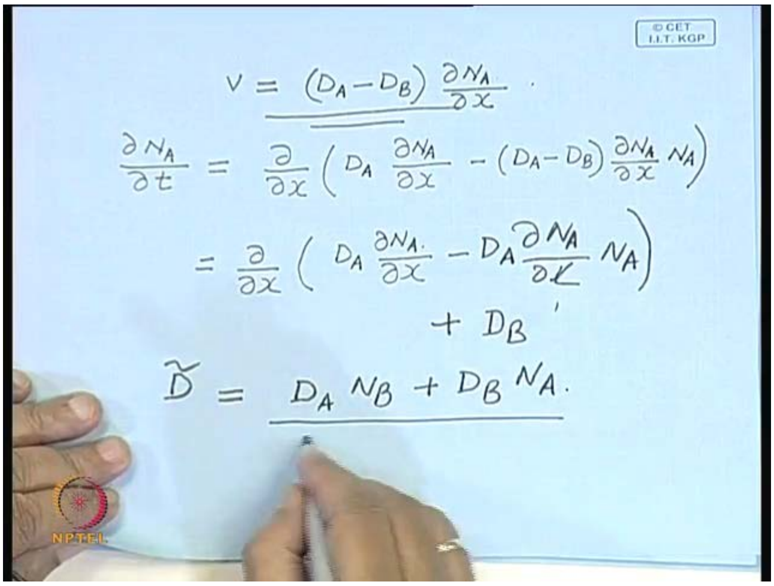

$$v = (D_A - D_B)\frac{\partial N_A}{\partial x} .$$

$$\frac{\partial N_A}{\partial t} = \frac{\partial}{\partial x}\left(D_A \frac{\partial N_A}{\partial x} - (D_A - D_B)\frac{\partial N_A}{\partial x} N_A\right)$$

$$= \frac{\partial}{\partial x}\left(D_A \frac{\partial N_A}{\partial x} - D_A \frac{\partial N_A}{\partial x} N_A\right)$$

$$+ D_B$$

$$\tilde{D} = D_A N_B + D_B N_A .$$

Now here if you substitute previous one if you substitute a expression for v which has been derived and then you get this expression and then what you get this is equal to this minus D A similarly plus D B you can write this and ultimately it is possible to show that this is equal to N B plus so this is one expression.

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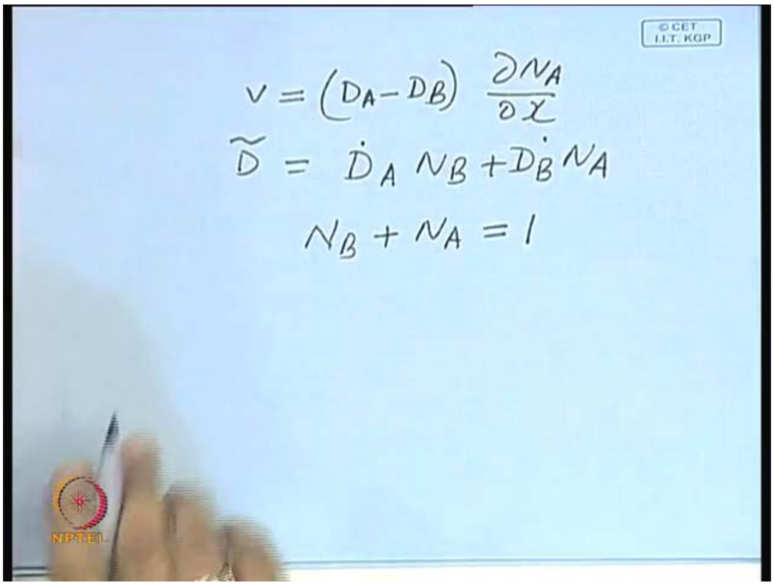

$$v = (D_A - D_B)\frac{\partial N_A}{\partial x}$$

$$\tilde{D} = D_A N_B + D_B N_A$$

$$N_B + N_A = 1$$

So to sum up what you can see here you have one expression which is velocity which is determinable so D A minus D B del N A del x. So this is we can be experimental determine then we also have this expression this is also determinable in that case and another relation you have N B plus N A equal to 1. So we have two unknown this is one and two and the concentrations unknown therefore, which can be determined. So it is possible to determine D A and D B individually.

So today we looked at that atomicity mechanism we also seen that if this species are different there is a different in a moment it can lead to a moment of concept of that kirkendall effect we have looked at and assuming with some assumption that there is no void we derived on expression for the individuals or intrinsic diffuse diffusion coefficient that D A and D B they are called intrinsic diffusion coefficient. Now almost of and this is our importance subject and maybe I think two our it was difficult to cover it fully but later on from time to time will be referring to this concept and it will be further illustrated in subsequent lectures. Thank you.