Defects in Crystalline Solids (Part-I)
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Lecture - 14
Self-diffusion+Examples

So, to make things simpler we will assume that there is this surface.

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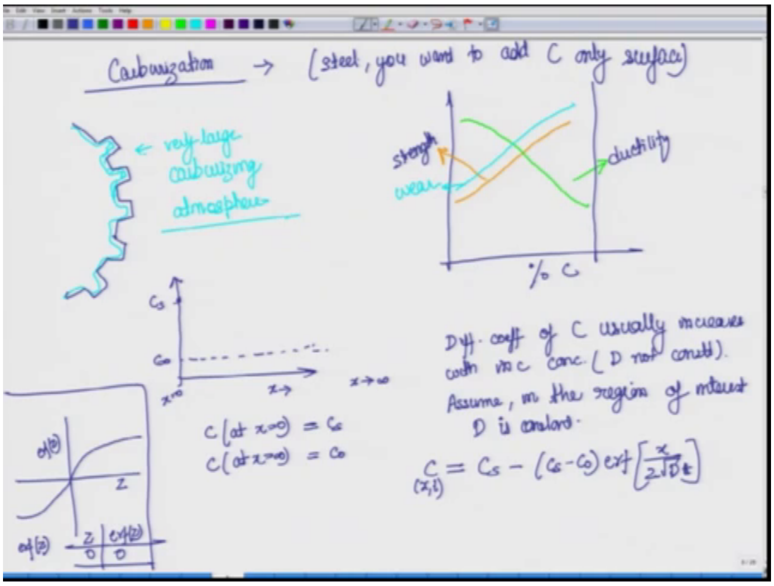

Carburization → (steel, you want to add C only surface)

very large carburizing atmosphere

$C(\text{at } x=0) = C_s$
$C(\text{at } x=\infty) = C_0$

Diff. coeff of C usually increases with inc C conc. (D not const). Assume, in the region of interest D is constant.

$$\underset{(x,t)}{C} = C_s - (C_s - C_0)\,\text{erf}\left[\frac{x}{2\sqrt{Dt}}\right]$$

z	erf(z)
0	0

This is the surface which we will take as x equal to 0, and this is the distance which is going through the depth of the gear. So, this is increasing x and somewhere over here we will have extending to infinity for the matter of diffusion, because in diffusion very large x you can take as extending to infinity.

Now here add the surface, because you have introduced a carburizing surface. You can assume that there is a very large concentration of carbon. Let us call it C as meaning carbon at surface. And there is a background carbon inside the material. So, this is given by this dotted line which will represent by C naught.

Now, what are the boundary condition that we know? C at x equal to 0, what is the value; this is equal to C s that we have already mentioned because this is the atmosphere that we are exposing where this is the carbon concentration. Now carbon at x equal to infinity like we said that this is how you can represent in terms of diffusion, we are not talking about miles and miles of distance. Only if you are talking about few millimetres then in terms of diffusion it becomes infinity, because we are talking about very small time scale. So, at x equal to infinity C is equal to C naught.

Now, here usually if you have some concentration gradient, then diffusivity which is these are the diffusion coefficient of carbon; usually, increases with increasing concentration meaning our D would not be constant. But again we will make a simplifying assumption; assume that, in the region of interest D is constant ok.

So, what you will see is that, if you put these values in the equation that we have derived earlier, then putting these boundary conditions you would get a equation the solution of this form; C which is the concentration as a function of x and t. So, this is the function of s and t is equal to C s minus C s minus C naught erf, I will tell you what this erf is many of you would already know 2 root Dt.

So, this is x meaning how much far you are looking at, this is t, how many how much time later you are looking at, D is the diffusion diffusivity coefficient which we have assumed to be constant. So, this is the relation that you would be able to derive not derive, but the solution for the equation when we use those ficks first and second law, then this is the solution that you would get.

Now, here erf is nothing but a function which so, I will use this corner erf if we are talking about erf z, then this is the function how it looks like. So, this is z this is erf. And usually I will tell you some of the important values what are the; for 0 erf z is equal to 0, for infinity if you go to very large value of z, then erf z becomes 1.

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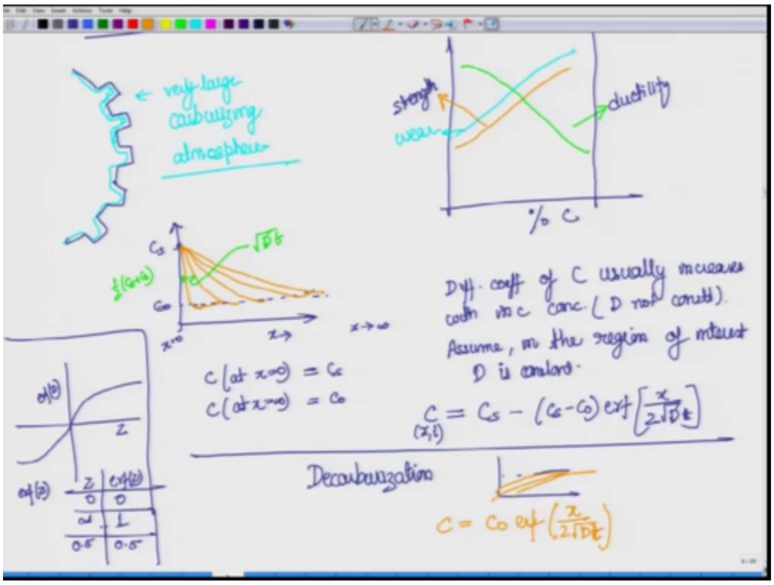

$C(\text{at } x=0) = C_s$
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Diff. coeff of C usually increases with inc conc. (D not constt).
Assume, in the region of interest D is constant.

$$\underset{(x,t)}{C} = C_s - (C_s - C_0)\,\text{erf}\left[\frac{x}{2\sqrt{Dt}}\right]$$

z	erf(z)
0	0
∞	1
0.5	0.5

$$C = C_0\,\text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

If you are talking about 0.5, then erf z is equal to 0.5, and same is in the negative values. So, these are some of the important values, but this is just describing a function and thus so, this is a mathematical function erf is nothing but one mathematical function. And you can find various values for z what should be the erf. And so, accordingly you would be able to solve this or get the concentration of C as a function of x and t.

Now, this is how the concentration would change. And if you want to plot it, this is how it would look like. So, initially it would so, at some very small time, this is how it would look like with increasing time, because we have kept C s as constant; which is already included in our solution. So, we have included in the solution these 2 conditions these 2 boundary conditions remain same throughout the time. And therefore, concentration increases like this. And like I said that this erf 0.5 is equal to 0.5. So, there is a very nice relation that you can obtain at 0.5 of this value which is C s 1 by 2 C s plus C naught, whatever you get this is equal to root Dt. So, this root Dt is a you can say approximate way of finding how much is the depth of carburization.

So, if you know the diffusivity coefficient, and you know for how much time you have let it diffuse, then square root Dt gets the approximate depth of carburization. And at this value this and this root Dt is nothing but the value of concentration at this half midway point. So, this is how the carburization works, and you can predict accurately what will be the depth and what will be how the concentration profile would look like. And just as matter of information there can be carburization so, there can also be decarburization.

So, let us say you have exposed your sample material, particularly steel to atmosphere where carbon concentration is much lower than what you have inside the surface or inside the bulk. And it is at very high temperature where over all diffusivity would be higher then what you can have is also reduction in the concentration or something like this. So, if this is the average concentration then near the surface the concentration would decrease and with time it will becomes a smaller. So, this is decarburization and not approximate and you can also show that the relation for this in terms of x and t would be like this. So, this is the relation for decarburization so, it is just the inverse of carburization.

So, we have looked at 2 examples and what you would later understand is that although we have so far derived only interstitial diffusion, but the overall form of the equation would remain same whether we when we even when we talk about substitutional diffusion. And so, similar type of examples can also be solved and using exactly same methodology, even when we ae talking about substitutional diffusion.

What changes is the q parameter? The delta q that we talked about the enthalpy for activation, and you would see for that interstitial it is much lower and for substitutional it is very much higher. And how what does that lead to? What it leads to is that you will have very high diffusivity when you are talking about interstitial diffusion and very low diffusivity when you are talking about substitutional diffusion.

So, let us try to understand what how is it different the substitutional diffusion.

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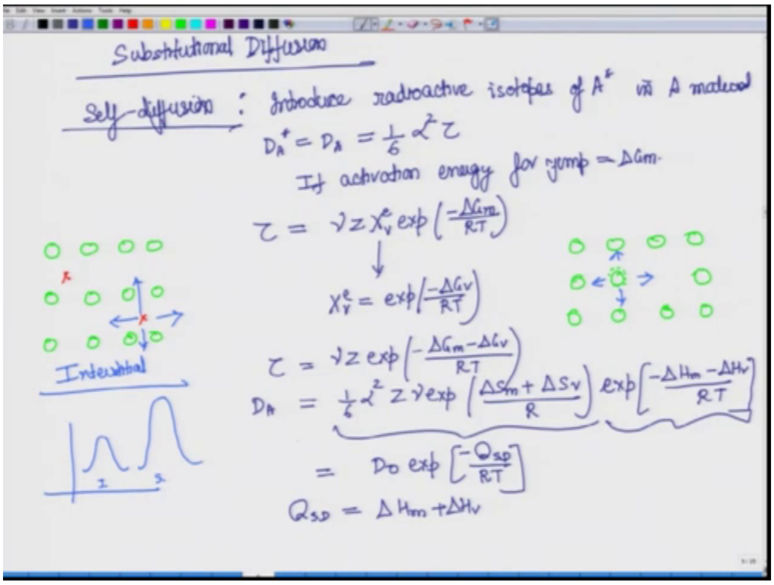

Substitutional Diffusion

Self-diffusion : Introduce radioactive isotopes of A^* in A material

$$D_A^* = D_A = \frac{1}{6}\alpha^2\tau$$

If activation energy for jump = ΔG_m.

$$\tau = \nu z X_v^e \exp\left(\frac{-\Delta G_m}{RT}\right)$$

$$\downarrow$$

$$X_v^e = \exp\left(\frac{-\Delta G_v}{RT}\right)$$

$$\tau = \nu z \exp\left(-\frac{\Delta G_m - \Delta G_v}{RT}\right)$$

$$D_A = \underbrace{\frac{1}{6}\alpha^2 z\nu \exp\left(\frac{\Delta S_m + \Delta S_v}{R}\right)}_{} \underbrace{\exp\left[\frac{-\Delta H_m - \Delta H_v}{RT}\right]}_{}$$

$$= D_0 \exp\left[\frac{-Q_{SD}}{RT}\right]$$

$$Q_{SD} = \Delta H_m + \Delta H_v$$

So, in the substitutional diffusion first thing that we will look at is self-diffusion. Yes, you are so far we talked only about defects, but when we are talking about diffusion than actually even the atoms inside the same or pure material they diffuse. They jump from one side to side one side point to one point, and that is called self-diffusion.

And why we are including here in terms of when we are talking about defects is because the relation that we derive for this one would also be valid for substitutional when we are talking about impurity atoms. And what do we how do we calculate, how do we not calculate? But how do we observe how do we measure in terms of experiments. So, what you what one does is that you introduce radioactive isotopes.

Let us say you are talking about a atom self-diffusivity, then you introduce radioactive isotopes of a atom which will denote as a star in a matical. And then at the other end you can measure or basically taking the slices you can measure the concentration at different points, how many radioactive atoms you are getting and therefore, you will be able to measure it ok.

And since they are isotopes; so, they will have almost same vibrational frequency, and that would mean that D star would be equal to D A. And here also the first part that is the relation for D in terms of tau would remain same; which we had earlier derived as 1 by 6 alpha square tau. Alpha square is the spacing between the atoms, and tau is the jump frequency the successful jump frequency.

Now, if we say if like we said earlier if activation energy for jump is equal to delta G m then now here this is the part that will be little different, we remember we had nu z; where z is the coordination number nu is the vibration frequency, and we had this term exp minus delta G m which is the activation energy by RT. However, now these neighbouring site when you are talking about the substitutional atom are not always available, right. Here when we are talking about interstitial so, let us look at.

So, somewhere one atom here one atom is over here in interstitial. So, in this particular case all these neighbouring sides are available. But when we talk about substitutional or even self-diffusion, let us say this is and this is our radioactive atom. So, let us say there is 1 vacancy on side of it.

So now you can clearly see that only this particular site there is a vacancy, at in this particular case that we have drawn other sides are not available. Even this side would not have been may not be available for jumping. So, the jump would depend on how many sites are available, and will the how will we know that? That is simply fraction of vacancies and if you are talking about equilibrium condition then x vacancy equilibrium.

So, this factor this factor alone is able to solve this, but you must remember that this is a very very small factor. If equilibrium we are talking about 10 to the power minus 4, that is the fraction of equilibrium vacancy. So, it is a very small factor and therefore, the number of successful jumps actually reduces by a long margin. So, that is where it becomes very different. And now we can expand this relation which we know X v equilibrium if you remember is equal to exp minus delta gv by RT.

So now we put it over here, both of them are RT. So, they will get this multiplication would lead to addition of this these 2 terms and therefore, you will have; and if we look at diffusivity A if you are calling at D A then this becomes, and we will also expand delta g to delta h minus t delta s therefore, this becomes delta s to components for delta s also. So, this is enthalpy now. Now you can clearly see this is the thermal component, this is a thermal component. And therefore, this will be your relation D naught exp minus q substitutional diffusion by RT. What is the difference? That major difference is in Q sd.

So now Q sd is earlier if you remember Q sd was just delta delta. Now Q sd is equal to delta plus delta hv; when we have increased the barrier. So, the barrier is now higher. If the barrier is higher what does that mean that number of successful jumps have become much smaller. So, if we compare over here and here; so, this is let us say so, this is for interstitial, and if you are talking about substitutional then this is substitutional.

So, you can see that the jump the activation energy barrier has become larger and therefore, the number of successful jumps would become smaller. That is the biggest implication, but as far as the formal equation or the formalism is concerned, you see that it is still the same formalism. And that is the best part about it whether you are talking about interstitial diffusion or you are talking about substitutional diffusion, the form of the equation remains same.

And you can just you have to just measure it to understand that there will be a big difference between the Q sd and the Q id which is the interstitial diffusion versus the substitutional diffusion. Or the diffusivity if you look at diffusivity of interstitial atoms could be much faster may be orders of magnitude higher than diffusivity of substitutional atoms.

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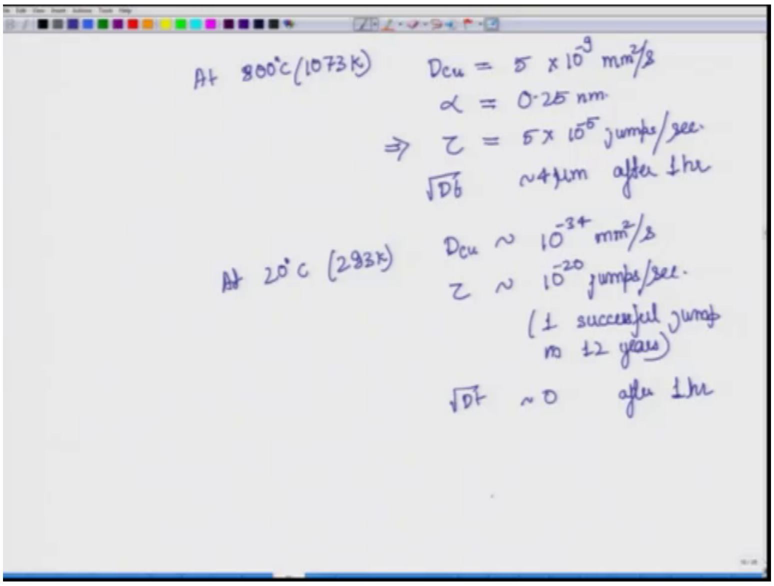

At 800°C (1073 K)

$D_{Cu} = 5 \times 10^{-9}\ mm^2/s$

$\alpha = 0.25\ nm$

$\Rightarrow \tau = 5 \times 10^{5}$ jumps/sec.

$\sqrt{Dt}$ ~4 μm after 1 hr

At 20°C (293 K)

$D_{Cu} \sim 10^{-34}\ mm^2/s$

$\tau \sim 10^{-20}$ jumps/sec.

(1 successful jump in 12 years)

$\sqrt{Dt}$ ~0 after 1 hr

And to give you a or rough numbers to be able to appreciate diffusivity in let us say in copper. So, we are talking about now substitutional diffusion. So, let us look at 800-degree C, D copper and alpha which is a spacing is given as 0.25 nano metre. So, from this you would be able to derive that tau which is the successful jump is equal to 5 into 10 to the power minus 5 jumps per second. And hence, you can also calculate root Dt is approximately equal to 4 micro metre after one hour, this is a self-diffusion of copper.

Now, if you extend the data given the thermal and a thermal component to 20 degree Celsius which is room temperature; so 293 k you know, that it will it should reduce, but how much let us look at it, you would see the first thing that becomes very small is this diffusivity coefficient, D cu because there were the a thermal and the thermal components. Because of the thermal components, this has reduced and how much it is of the order of minus 34, it is very very small quantity.

And accordingly tau which is the frequency of successful jump becomes 10 to the power minus 20; this is also very very small quantity. If you want to understand it, what it means is one successful jump in 12 years. So, obviously, if you look at root Dt, it will be approximately 0 after one hour. And that is why you do not observe so much diffusivity at room temperature. Because this tau which is the jump a successful jump frequency becomes very small. And D cu in effect becomes very small. So, this is the one aspect of substitutional diffusion which is the diffusion of thus same species also called as self-diffusion.

Next what we can look at inside the material, you have even in a pure material, you will have the material and also the vacancy. Now when if the atoms are moving so can the vacancies move? So, we can also talk about vacancy diffusion.

So, next we will look at vacancy diffusion.

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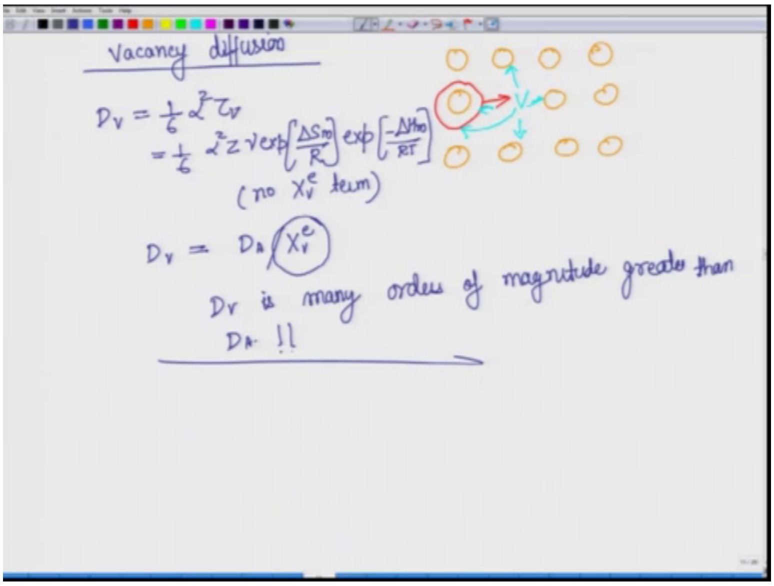

Vacancy diffusion

$$D_v = \frac{1}{6}\alpha^2\tau_v$$

$$= \frac{1}{6}\alpha^2 z \nu \exp\left[\frac{\Delta S_m}{R}\right]\exp\left[\frac{-\Delta H_m}{RT}\right]$$

(no X_v^e term)

$$D_v = D_A / \boxed{X_v^e}$$

D_v is many orders of magnitude greater than D_A !!

Which is again a important phenomena with respect to defects. But you would see that is this particular case would be much much easier to understand or to extrapolate the relation. Why? Because now let us look at what we have looked at earlier. So, we said that these are some atoms ok.

So, let us say this is one pure atom, and over here the one particular atom moves from here to here. But this also means that this place which was actually vacancy, it has moved from over here to here. So, the vacancy diffusion is similar to the self-diffusion. The only difference being that for this vacancy if you look all these sites are available, all these sites are available.

On the other hand, for this particular site or the selfdiffusion as you remember we said that, the we have to calculate what is the fraction of available sites. And for that we multiplied it by that factor x 1 v. But in this particular case you can realise that you do not need to multiply that factor and therefore, D v which is equal to 1 by 6 alpha square tau v can be given as 1 by 6 alpha square z mu; so for vacancy diffusion no X v equilibrium term.

And therefore, again the energy barrier as come down. So, it means that vacancy can diffuse much faster. And therefore, what we have is that D v is D A D A you remember we talked we called as the self-interstitial so, D A by X v equilibrium. So, in the same material let us say we are talking about copper whatever is the diffusivity of that self-diffusion.

You divide it by the fraction equilibrium fraction of vacancies at that concentration and you get the diffusivity of vacancy. So, this is a very strong (Refer Time: 22:38) or the very important information regarding diffusivity of vacancy. And at the same time it tells you how these 2 are related. You do not need to do any extra derivation; all you need to know is this particular quantity X v; which is the concentration of vacancy at equilibrium.

Therefore, D v is many orders of magnitude greater than D A. So, this is something that you that we have shown over here. So now, next we will look at is a little bit more complex. Do you remember we said that A and B can go and or b a can go in terms of impurity? So, a can act as a impurity on b or b can act as a impurity on a.

And therefore, according to that there will be different diffusivities this will not be self-diffusion; this will be what is called as inter diffusion. So, a is diffusing b and b is diffusing a. And this would be of you can say the most important in terms of diffusion. And also in terms of understanding how these defects would behave.

So, what we are talking now?

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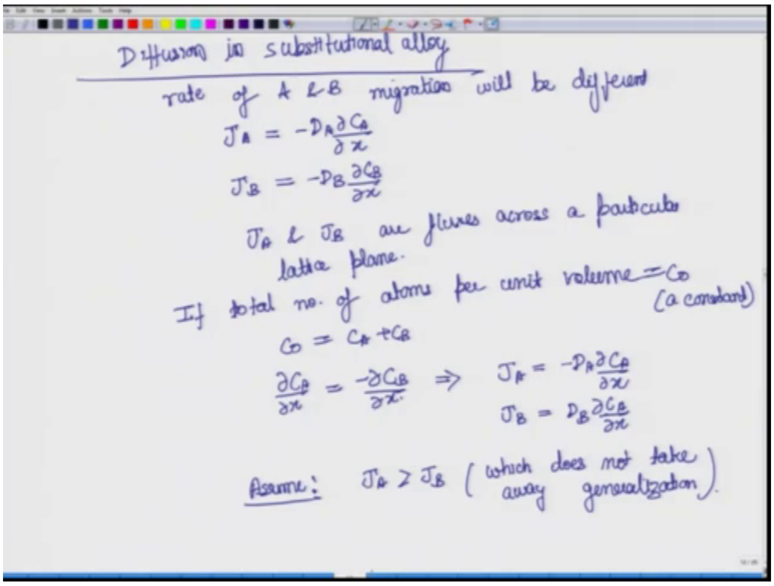

Diffusion in substitutional alloy

rate of A & B migration will be different

$$J_A = -D_A \frac{\partial C_A}{\partial x}$$

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

J_A & J_B are fluxes across a particular lattice plane.

If total no. of atoms per unit volume $= C_0$ (a constant)

$$C_0 = C_A + C_B$$

$$\frac{\partial C_A}{\partial x} = \frac{-\partial C_B}{\partial x} \Rightarrow \begin{aligned} J_A &= -D_A \frac{\partial C_A}{\partial x} \\ J_B &= D_B \frac{\partial C_A}{\partial x} \end{aligned}$$

Assume: $J_A > J_B$ (which does not take away generalization).

About is diffusion in substitutional alloy. So, we have more than one type of atom, and that is what we will make it a little bit more complex rate of A and B migration, what should be the relation between these 2. We are talking about A on B and B on A should they be same? Of course not, so they will not be same they will be different.

And if you want to talk about just a then we can use the self-diffusion coefficient and you can write something like this, ok. Now this is the starting point as you would realise, because we want to finally, understand when A is in B and B is in A. And of course, J A and J B are fluxes across a particular plain. So, I will sorry this is so, what are J A and J B? That we have already something similar to self-diffusion and interstitial diffusion; J and J B are fluxes across a particular lattice plain.

Now, if total number of atoms you are already given. Now here we will need to introduce some additional concepts as you will see. If total number of atoms per unit volume is equal to C naught. Then you would realise that C naught should be a constant. So, C naught will have to be constant, you cannot it would not be changing with time even if diffusion is taking place.

So, C naught must be constant, but C naught is what C naught is equal to C A plus C B it has either A or B. So, that concentration of A plus B would give you C naught and therefore, if we have this if we take the differential C naught is a constant therefore, this becomes del C A by del x is equal to; again we are looking in only one dimensional form, minus del C B by del x; which implies that J A, so we are now we have this relation.

So, we can extend the earlier relations that we have obtained, and write this in terms of only one concentration gradient which is del C A by del x. So, J A and J B can now both be written in terms of; so, here this is remains the same, but this one the minus sign goes away, and we are now instead of del C B we are writing it as del C A by del x, because the concentration gradient of one is the inverse of the other.

Now, here we are we have to assume that one of these are of course, one of them will be diffusing faster than the other; and therefore, for that let us assume that will just be a matter of for matter of simplification, nothing more it is not going to in general terms it is not going to change the final outcome of the solution. So, we will one of them is larger and we are assuming that J A is greater than J B. So, this is assumption which does not change generalization; which does not take away generalization. So, if now we are we have assumed that J A is greater than J B ok.

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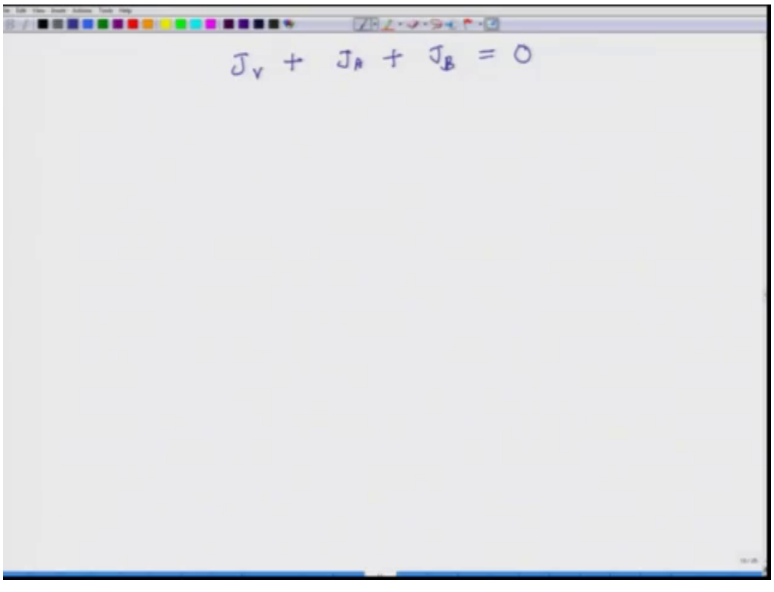

$$J_v + J_A + J_B = 0$$

So now let us look at this derivation. Now we will have also vacancies there. We will also have A atoms moving we will also have B atoms moving. So, what should be the relation between the J v J A and J B? There are 3 basically 3 entities now in terms of flux. So, what should be the relation between these 2? And the simple relation that you have is that J A plus J B plus J v is equal to 0; which means that if a 1 and 2 are moving in one direction, the third is moving in the opposite direction.

That is what it means, and this is again coming from the principal of conservation of concentration. So, these whole things remain same, and at the same time another assumption that we have over here is that the concentration of vacancy remains constant throughout; which also leads to another fact, that we will see later on. But we will leave you leave you with this relation for now. And we will come back and extend this to extend our understanding about inter diffusion, when you are talking about A moving in B or B moving in A.

So, we will see you in the next class.