Electroceramics
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Lecture - 11

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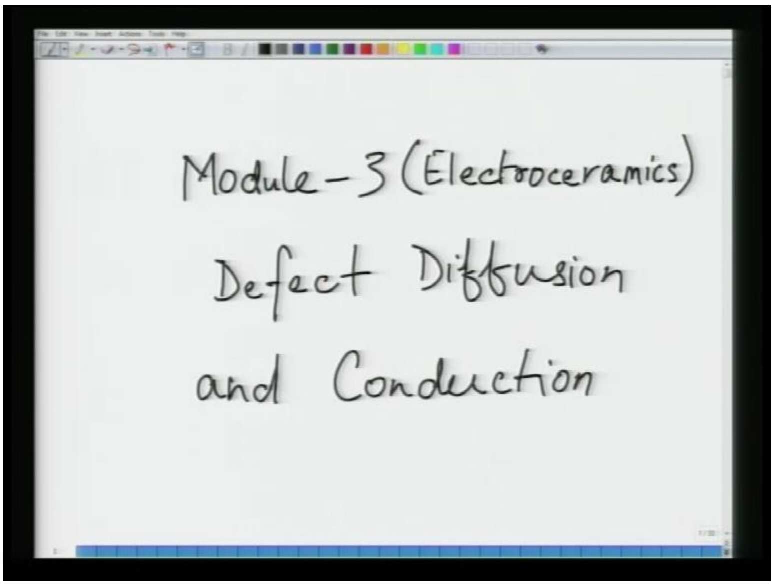

Module - 3 (Electroceramics)
Defect Diffusion
and Conduction

So, welcome to this new class. So, we have completed two modules. In the first module, we looked at the structures of various ceramic materials. So, we started with our discussion on just basic fundamentals of structures and bonding, followed by discussion on the structures. What sort of structures with do ionically bonded solid possess. So, in the category typically you have three kinds of structures; one is you can have cubic close packed structures based on cubic close packing of anions; second is you can have a structures based on hexagonal closed packing of anions and third one is other structures which are typically either cubic packing of anions or you have orthorhombic and tetragonal structures as well such as superconductors.

So, and then we moved on to the defects, and defects are very important part of this course, because movement of formation and movement of defects under various operating conditions is instrumental and tailoring the properties of these materials. So, we looked at the formation of various kind of defects. Point to be noted here is, we discussed we limited our discussion to the point defects because point defects are they play an important role in property determination. So, we discussed the defects in stoichiometric solids and then we discussed the defects in non-stoichiometric solids. What happens when you incorporate an impurity inside and oxide and then we looked at various conditions under which, what is the effect of partial pressure and temperature? How do you determine the concentration?

We established defect equilibria and in that process we also learned we also established a formalism; so that we can express a defect reaction, just like a chemical reaction, by treating a dilute solution kind of model. Then we looked at various conditions of partial pressures of oxygen at a given temperature and finally, came over the diagram which is called as Brouwer’s diagram, where you can plot the concentration of defects versus partial pressure of oxygen. This is something which is very important because when you make conductivity measurements in these materials often you can replicate these, often these are, you can translate from one, you can translate from measurement to the schematic diagram or from the measurement I you can corroborate the conductivity in diagram. So, these are very important things.

And now, what we will look at is the this is the third module. In this module we will learn about how these defects move, which means defective fusion as well as what is their role in conductivity of these ionic solids because ionic solids, many of these ionic solids are used as a conductors in many applications. Although you would find that many of most of these ionic solids they are, they work as insulators, but at the same time materials like for example, glasses and fast ion conductors and some other doped oxides they are very good conductors of electricity or you can say, they are very good conductors. This conductivity could be a mixer of both electronic and ionic conductivity and this is where we will, this is the module in which we will study these aspects.

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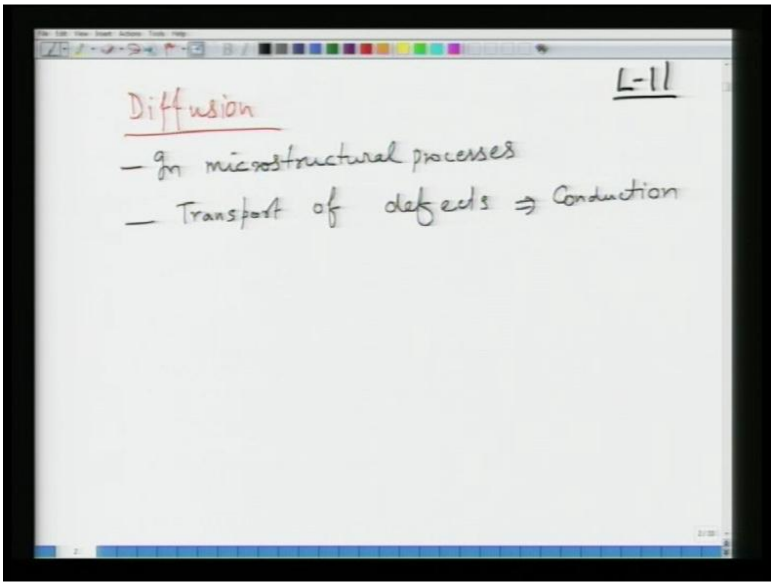

L-11

Diffusion

- In microstructural processes
- Transport of defects ⇒ Conduction

So, this is our new lecture. So, I believe this is a lecture 11 and we will start with our discussion on diffusion. So, first we will just study diffusion in general and then we will extend this to diffusion of ionic diffusion in ionic solids. So, diffusion is a very important process as you might know from your background of material science or metallurgy or even other disciplines, it diffusion is a process which occurs at microscopic level. Where atoms or species they move from one place to another and this movement could be as a result of variety of forces, such as you can have a concentration gradient, you can have a thermodynamic potential gradient, you can have electrical force gradient etcetera.

Diffusion is a process which is very fundamental in nature, but it causes massive changes in for example, microstructure of the materials or it can cause significant changes in the properties of the material. Microstructural changes occur in the processes such as your sintering, here sintering is nothing but a densification process where you mix small particles together and form a bulk, form a form a big chunk which is, which when not heated is nothing but a mixer of, nothing but loosely packed powder particles. They are just mechanically pressed against each other whether you, whether or not using a binder.

But then in order to create the strength in this piece you have to heat it to high temperature. So, that you can establish atomic bonding and that is why diffusion is a very important phenomena. You can, this also occurs in for example, creep deformation creep is nothing but high temperature deformation and in high temperature deformation diffusion plays a very important role. This is also important in phenomenas such as grain growth. Grain growth is nothing but coarsening of grains when a when a particular material is heated to high temperatures from room temperature. So, these your microstructural phenomenas, but at the same time diffusion is also related to. So, one role of you can say in, microstructural processes and second is your, it is related to the transport of defects.

So, or charge carriers and this gives rise to you know, conduction for example, in these materials electrical conduction in these materials. We have variety of ionic conductors which are used in many applications such as gas sensors, solid electrolytes or fuel cells batteries and for example, your, one of your, if you want to and sensors as well. So, sensors for example, oxygen sensors work on the basis of conductivity of the defects related to oxygen and one of the material candidate materials for these applications could be your zirconia, which is stabilized with some other stabilizer. This is used for instance in automobiles which can be used to regulate the air to fuel ratio or to optimize the efficiency of convection, combustion. So, so these are some, so you can say transport of defects related to conduction.

So, microstructural processes are related to in the manifestation of increase in density, change in the mechanical properties etcetera and transport of defects is manifested in the electrical behaviour. The transport the movement of these defects or the properties due to movement of this these defects are governed by variety of factors such as type of defects, their concentration, temperature, partial pressure of oxygen or composition etcetera etcetera, etcetera. So, we will look at first the diffusion itself as a phenomena. What diffusion is and then we will and then we will establish formalism for we then we will establish role of diffusion this of is defects.

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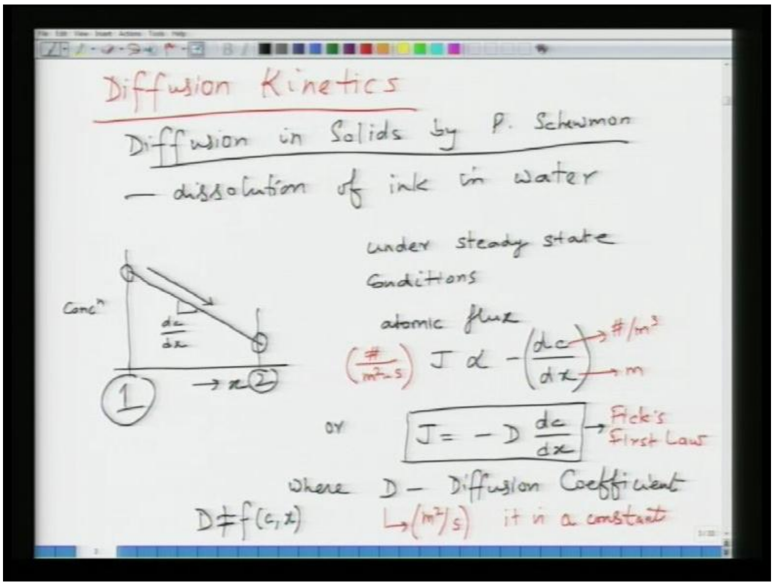

Diffusion Kinetics

Diffusion in Solids by P. Schewmon

— dissolution of ink in water

under steady state Conditions

atomic flux

$$\left(\frac{\#}{m^2\text{-}s}\right) J \propto -\left(\frac{dc}{dx}\right) \begin{matrix}\to \#/m^3 \\ \to m\end{matrix}$$

or

$$\boxed{J = -D\frac{dc}{dx}} \to \text{Fick's First Law}$$

where D – Diffusion Coefficient

$\hookrightarrow (m^2/s)$ it is a constant

$D \neq f(c, x)$

So, first just to learn about the defect kinetics; so or diffusion kinetics I am sorry. So, I am not going to into details of diffusion. If you want to go into details of diffusion, I would recommend this book diffusion in solids by Paul Shewmon, this is a very nice book written by Shewmon on diffusion in materials. So, basically diffusion is nothing but a atomistic atomistical, atomistic process it happens by movement of, let us say atoms in a in a particular material from one place to, typically from regions of higher concentration to lower concentration. And this you can see a very simple demonstration for example, could be your dissolution of ink in water. So, experiment which you can do is that, you take a beaker full of water and then you drop one drop of ink into the water and slowly you watch the phenomena.

Initially, you will see that the place where the ink has dropped that is of ink colour and rest of the water remains of transparent colour, but the moment after a while what you see is that the blue colour or whatever the colour you choose the colour of the ink slowly diffuses into the water and eventually after certain time you see that the whole water, whole of the water has adopted to, the had, a has a has adopted the colour of the ink and this happens by diffusion of ink molecules in water slowly and slowly as a function of time. So, diffusion is basically nothing but movement of atoms or species at atomic scale and it is a time dependent process, it is a temperature dependent process. So, so let us say you have a system; for example, where you have a concentration gradient.

So, let us say this is x which is the distance in that particular system or it could be a metal bar and this is let us say concentration of a particular atom, particular type of atom. So, let us consider the case of for example, a dilute solution. So, in case of dilute solution just concentrate on the diffusion of impurity atoms.

So, let us say you have a concentration gradient. So, like this and this concentration gradient is d c by d x. So, naturally unless there are some other reasons typically diffusion would occur, in the direction of decreasing in the direction of decreasing concentration. So, atoms from the regions of higher concentration will move towards at regions of lower concentration and as a result you will have atomic flux. Let us say under steady state conditions. Steady state conditions mean that this gradient does not change as a function of time, this the gradient remains constant in time.

So, basically under steady state conditions we atomic flux J, let us say we define J is proportional to, we can see it is proportional to concentration gradient because atoms have to move from this place to that place. Let us say this is place 1 this is place 2, so what is it proportional to now? It is proportional to the concentration gradient, but since we are moving down the concentration gradient J is proportional to minus of d c of d c by d x and or I can write J is equal to minus D D c by d x where D is proportional D constant and it is called as diffusion coefficient and this equation is called as Fick's first law of diffusion. So, basically it is a valid under steady state condition, where concentration gradient in a given system does not change as a function of time and in such condition the atomic flux is nothing but number of atoms moving from one place to another per unit area, per unit time.

So, I can write this as number of atoms moving per unit area, let us say meter square per unit time. d c by d x the concentration gradient, if c has a unit of number per meter cube and x has a unit of meter. So, d c by d x will have a unit of number per meter to the power 4. So, as a result if you if you now, balance the units D will have unit of meter square per second. So, so diffusivity or diffusion coefficient is nothing but proportionality constant and as you can see now higher the diffusivity, higher the flux will be of course, higher the concentration gradient, higher the flux would be. But this D is an important parameter as we will see here, we are assuming that D is a it is a constant. Which means D does not depend upon x it is not a function of x.

So, I can write assuming D is not a function of c or x. So, it is independent of both concentration, as well as temperature. So, this is the famous Fick's first law. Now, if you if you look at the, you just remember that, this equation minus sign is because the diffusion is taking place from regions of higher concentration to lower concentrations.

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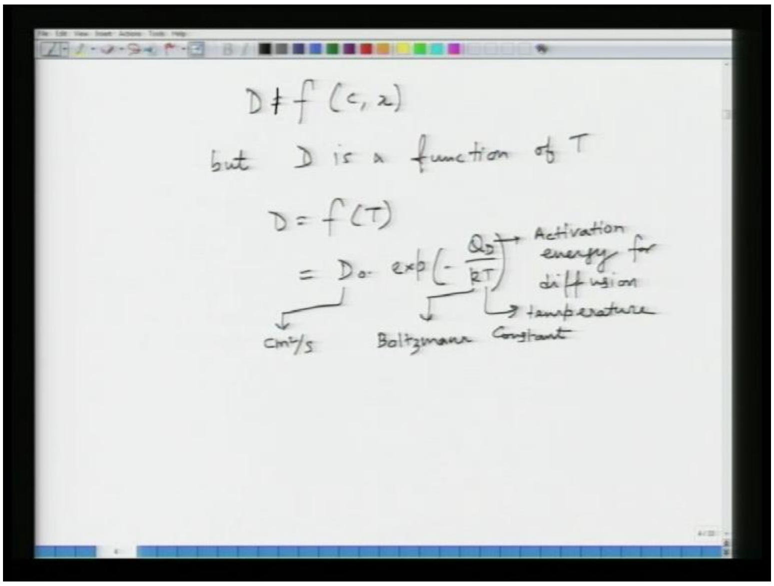

$D \neq f(c, x)$

but D is a function of T

$D = f(T)$

$= D_0 \exp\left(-\frac{Q_D}{kT}\right)$

Q_D → Activation energy for diffusion

T → temperature

k → Boltzmann Constant

D_0 → cm^2/s

However, this D; so we have said that D is not a function of concentration or temperature, but D is a function of as we will see of temperature. So, D is function of temperature and it is given as D naught exponential minus. Let us say Q by Q D by k T right. Q D is the activation energy for diffusion, T is your temperature and k is nothing but your Boltzmann constant. Of course, you can write Q D by r T as well depending upon the units of Q D, you can you can denote Q D in terms of electron bolt per atom or you can also denote Q D as kilo joule per mole or kilocalorie per mole. So, in that case it will become r which is gas constant. So, these are interchangeable and D naught is the diffusivity pre-exponent and whose units are again in centimetre square per second

So, later on as we go into the module we will establish a basis for this relation which is D is equal to D naught exponential minus Q D by k T. Why, what is the reason for temperature dependence of diffusivity? So, at the moment you just note down you just keep in your mind that diffusivity, as it as it is taken in the first Fick's law is a constant independent of concentration and distance and D naught is here is pre-exponential factor.

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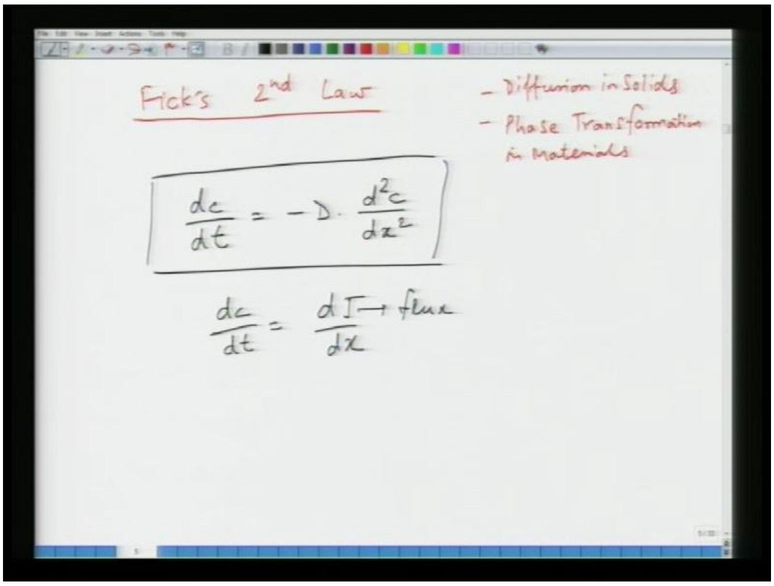

Fick's 2nd Law

- Diffusion in Solids
- Phase Transformation in Materials

$$\boxed{\frac{dc}{dt} = -D \cdot \frac{d^2c}{dx^2}}$$

$$\frac{dc}{dt} = \frac{dJ}{dx} \rightarrow \text{flux}$$

Now, another of Fick's law is Fick's second law. Now, Fick's second law is it predicts how the concentration changes are the function of time. So, actually it is not law rather it is a derivation. How you move, how you graduate from steady state condition to the condition when concentration changes as a function of time. So, it can be derived there is a very simple derivation from the Fick's first law, leading to Fick's second law we are not going in, going to go into details of that derivation. If you want to go into that derivation you can follow the book that I have suggested or you can go you can go through many books for example, you can go through diffusion in solids, you can through to the, go to the book phase transformations in materials materials or solids by porter and easterling.

So, they have very good formalism on diffusion. So, what Fick's second law say is that, under non-steady state condition how the concentration varies as a function of time. This expression is given as d c d t which is a rate of change of concentration with time is equal to minus of D into d 2 c by d x square, this is called as Fick's second law. Although it is actually not a law it is more like a derivation from the first for itself. So, or alternatively you can express it as d c by d t is equal to d by d x excuse me d J by D x where J is nothing but the flux. All the terms are defined except time which is in seconds. So, I have not gone through the derivation of this, but you just derivation is fairly simple and you can through these two books which I have listed here.

Now, we will go through first a very simple model to establish the basis for diffusivity because it is not, it is not these two laws which are very important from the point of view of first law. Of course, is important, but second law is something which is more useful in condition such as metallurgical process like carburising or nitriding or any surface treatment process. That is where the second law becomes solution of second law becomes important. For our purposes we will mostly restricted, restrict our self to first law, but what is more important is to understand the diffusivity because diffusivity is a parameter which is, which is of great importance to the physical properties as we will see later in this course of ion ceramics.

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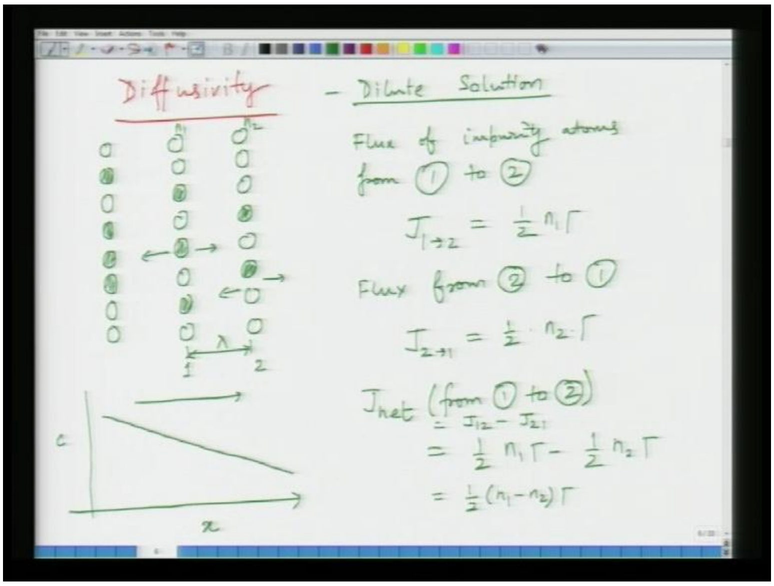

Diffusivity – Dilute Solution

Flux of impurity atoms from ① to ②

$$J_{1\to 2} = \frac{1}{2} n_1 \Gamma$$

Flux from ② to ①

$$J_{2\to 1} = \frac{1}{2} \cdot n_2 \cdot \Gamma$$

J_{net} (from ① to ②)

$$= J_{12} - J_{21}$$

$$= \frac{1}{2} n_1 \Gamma - \frac{1}{2} n_2 \Gamma$$

$$= \frac{1}{2} (n_1 - n_2) \Gamma$$

So, we will take first a very simple model for diffusivity. Now, here scenario is like this. You have you have these plane of atoms. So, let us say this is plane one, this is plane two and I have deliberately not listed this plane, but you can make this one, two and three so on so forth. And now, the thing is here, let us say this is, the these are the atoms of host lattice and some of these atoms are atoms impurity atoms. So, we consider the case of dilute solution, where by enlarged impurity atoms diffuse from one place to another. Since, host atoms are like so let us say, we have a concentration gradient here. So, these dark, these shaded atoms are let us say, the impurity atoms and these number of these atoms changes as we progressively go from left to right.

So, as a result, if you plot the concentration gradient, as a function of distance, so this is distance x, let us say the distance between these two planes is lambda and as you go from left to right, the concentration changes like this. So, this is your concentration versus x. So and, so what we are saying is that now diffusion is process, which is atomistic process. One of the models explain of to, explain the diffusion phenomena is the random walk model which means, in which an atom or species has equal probability of jumping to any of its side given that the sides are available. So, let us say and it is of course, depending upon the availability, it will have certain probability of jump as well. So, let us say, we have we consider this as plane one and plane two.

Let us say the atoms now, we are considering dilute solution, we will consider only the diffusion of impurity atoms. So, let say impurity atom from plane one, they can move to this side, they can move to that side similarly, from plane two they can move to this side. this side Although I am saying that diffusion happens only in one direction, as a result of concentration gradient. But essentially diffusion is random walk process. So, probability of diffusion is equal in all the directions. It is just that there is a net diffusion, net diffusive flux in one particular direction. So, that is what we are going to do now. So, so first we will see what is the flux from, flux of these impurity atoms? Atoms from plane 1 to 2 so, flux of atoms from 1 to 2 can be written as J, let us say J 1 to 2 and this will be written as half number of atoms.

Let us say plane one contains n 1 number of atoms plane two contains n 2 number of atoms and all these planes have are of unit area. So, the cross sectional area of these planes will be unit area. So, half is the factor which will come because the atoms have equal probability to move either on left or right. So, half multiplied by number of atoms, what is missing here is the jump probability. What is the probability of jump, which can be defined as half n 1 tau. So, tau is the jump probability and of course, I have taken since this as unit area, so area will remain unit area. So, we will take that as a one. So, this is let us say the flux from 1 to 2 similarly, flux from 2 to 1 is J 2 to 1 and that is given as half.

If number of atoms on plane two are tau n 2 sorry and if tau is the again the jump probability, it should be half into tau. Now, only difference in these two equations is number of atoms on each plane n 1 and n 2 and we are saying that n 1 is larger than n 2. So, as a result you will have, since n 1 is larger than n 2 as a result you will have net flux of atoms from 1 to 2. So, what is J net? J net from 1 to 2 is equal to half of n 1 tau minus half of n 2 tau, which is nothing but difference of J 1 2 minus J 2 1. So, this is given as half n 1 minus n 2 multiplied by tau.

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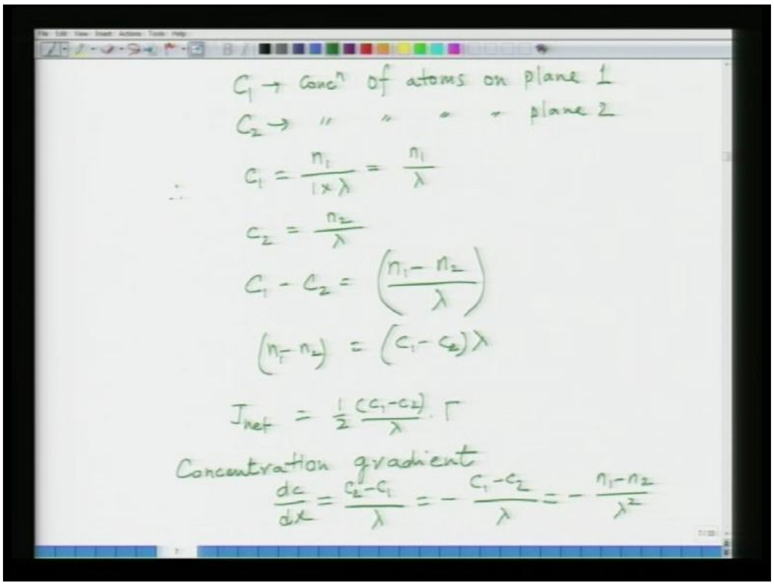

$C_1 \rightarrow$ Conc^n of atoms on plane 1

$C_2 \rightarrow$ " " " " plane 2

$$C_1 = \frac{n_1}{1 \times \lambda} = \frac{n_1}{\lambda}$$

$$C_2 = \frac{n_2}{\lambda}$$

$$C_1 - C_2 = \left(\frac{n_1 - n_2}{\lambda}\right)$$

$$(n_1 - n_2) = (C_1 - C_2)\lambda$$

$$J_{net} = \frac{1}{2}\frac{(C_1 - C_2)}{\lambda} \cdot \Gamma$$

Concentration gradient

$$\frac{dc}{dx} = \frac{C_2 - C_1}{\lambda} = -\frac{C_1 - C_2}{\lambda} = -\frac{n_1 - n_2}{\lambda^2}$$

So, now we define what is concentration? Concentration let us say on each plane is equal to C 1 concentration of atoms. When I say atoms it is mean the shaded atoms and concentration of not C 1, it should be plane one and similarly this could be plane two. So, concentration is given in terms of number of atoms per unit volume whereas, n 1 and n 2 were just number of atoms. So, in that case C 1 would be equal to number of atoms n 1 divided by volume. I have taken unit area. So, 1 multiplied by the distance that is lambda. So, this would be n 1 divided by lambda. What would be C 2? C 2 would be n 2 divided by lambda. So, n 1 minus n 2 would be equal to sorry excuse me. So, C 1 minus C 2 will be equal to n 1 minus n 2 divided by lambda.

Now, so I can just, so, n 1 minus n 2 will be C 1 minus C 2 into lambda as a result J net will be equal to half C 1 minus C 2 divided by lambda into tau. So, this is your J net. Now, we can also workout what is the concentration gradient. Concentration gradient is d c by d x and that is equal to number of the concentration at plane two C 2 minus concentration on plane one divided by lambda. And if I now, replace this with C 1 minus or this would be minus of C 1 minus C 2 divided by lambda, all right? This would be equal to minus of n 1 minus n 2 divided by lambda square, if I replace C 1 minus C 2 as n 1 minus n 2 divided by lambda. So, this is your concentration gradient.

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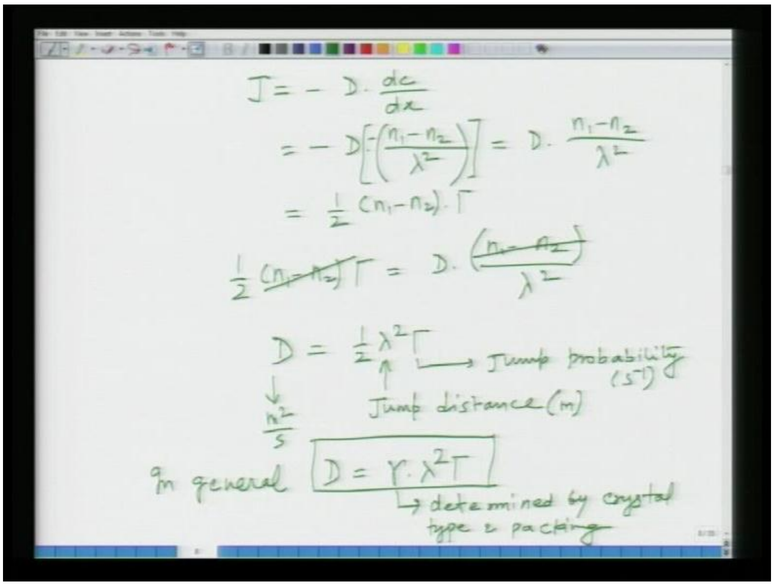

$$J = -D \cdot \frac{dc}{dx}$$

$$= -D\left[-\left(\frac{n_1 - n_2}{\lambda^2}\right)\right] = D \cdot \frac{n_1 - n_2}{\lambda^2}$$

$$= \frac{1}{2}(n_1 - n_2) \cdot \Gamma$$

$$\frac{1}{2}\cancel{(n_1 - n_2)}\,\Gamma = D \cdot \frac{\cancel{(n_1 - n_2)}}{\lambda^2}$$

$$D = \frac{1}{2}\lambda^2\Gamma$$

$\Gamma \rightarrow$ Jump probability (s^{-1})

$\lambda \uparrow$ Jump distance (m)

$D \downarrow \frac{m^2}{s}$

In general $\boxed{D = \gamma \cdot \lambda^2 \Gamma}$

$\gamma \rightarrow$ determined by crystal type & packing

Now, you know that from Fick’s first law, J is equal to minus D d c by d x. So, this becomes J is equal to minus D into n 1 minus n 2 divided by lambda square and if I now, equate this to previous equation then what we get, here that was equal to that was equal to J was equal to half n 1 minus n 2 into tau half n 1 minus n 2 into tau. So, what do you get now here? You get an expression for diffusivity which is, so you get an expression for diffusivity. Excuse me there is a certain mistake here. I think yes, there is a minus sign missing here, so this would be minus of n 1 minus n 2 divided by lambda square. So, this would become D into n 1 minus n 2 divided by lambda square.

So, if you equate these two sides what you get here is half n 1 minus n 2 tau is equal to D into n 1 minus n 2 divided by lambda square, n 1 minus n 2 cancel each other. And what you get an expression for D which is half lambda square tau? So, what is lambda here? Lambda is nothing but your jump distance, the distance between two planes is equal to jump distance and tau is nothing but your jump probability and jump probability will be in per unit time and this would be in meter. So, the units of D would be in meter square per second.

So, just by taking a very simple model two dimensional model sorry one dimensional model, we have established that D is equal to half lambda square tau. In general for a for a general system D can be gamma lambda square tau, where gamma is determined by possible number of jumps that can happen in a given system. So, in this case I have taken only two neighbours, so it can only jump to two sides. If you take for example, is a simple cubic material, it has each atom which is the corner of the cubic has six nearest neighbour. So, it can move to, it can it can jump to any of those six sides. So, depending upon what is the crystal structure you have, what is the packing of atoms you have, this gamma will be determined by those things. So, gamma is nothing but it it is governed by possible number of jumps.

So, determined by crystal type and packing; so what is the basically atomic configuration of the material? So, this is the general expression D is equal to gamma lambda square tau. So, now if you look at this expression carefully, gamma is a factor which is determined by crystal type and packing lambda is fixed because for a given system lambda would be fixed as well. How about tau? Is there anything in tau which is nothing but jump probability that will be variable of anything because if lambda if tau is constant then D is always constant.

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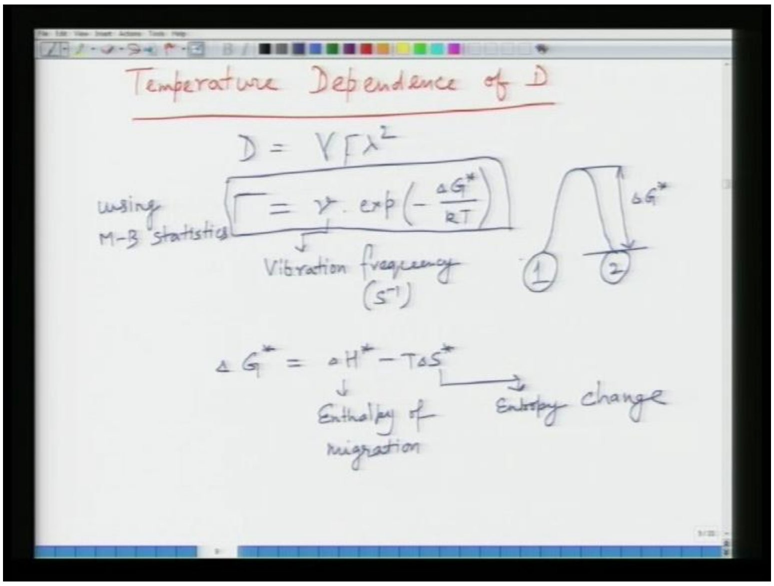

Temperature Dependence of D

$D = \gamma \Gamma \lambda^2$

using M-B statistics $\boxed{\Gamma = \nu . \exp\left(-\frac{\Delta G^*}{RT}\right)}$

ν → Vibration frequency (s^{-1})

$\Delta G^* = \Delta H^* - T\Delta S^*$

ΔH^* → Enthalpy of migration

ΔS^* → Entropy change

So, let us see how this expression develops further. So, what we are going to develop now is from this expression, what is the temperature dependence of D? So, if I look at the temperature dependence at D, so you, just now we said that D is equal to half tau lambda square, lambda is constant in. I will take a general case, so in that case I will replace this half by gamma and gamma is a constant. So, the only thing which can vary is now tau. So, tau is jump frequency; and this jump frequency, if you now recall Maxwell Boltzmann statistics, it is defined as, so using Maxwell Boltzmann statistics, this jump frequency tau can be defined as frequency of vibration in a solid, which is nu multiplied by exponential of minus of sum energy barrier G star divided by k T, where G star is an activation energy, which is a smaller than the thermal energy that is k T available.

So, the if the atom is moving from one, so what it basically means is that you have atoms in a system which have a natural frequency of vibration which is given as mu, but they cannot jump to any random side just like that, they have to overcome a certain barrier because they have to move from one place to another, which means the bonds have to be broken and again they have to be re-established. There is an expense of energy, this expense of energy is, so if it wants to move from position one to position two, it has to cross this energy barrier, which would be delta G star. So, this is free energy that has to be overcome to allow this atom to allow the atoms to move from their position. So, here k again is Boltzmann constant T is temperature and nu is the vibration frequency. Frequency of vibration, vibration frequency and this is given in per second, so the units are maintained.

Now, further we know delta G star just from the basic thermodynamics, I can I can expand it into delta H star minus delta T delta S star, where delta H star is nothing but your enthalpy of migration and delta S star is nothing but your associated entropy change that happens upon migration. So, upon migration now what I do is that now, I will substitute this delta G star into expression of tau, but the first thing from that you must notice from this expression is that now, the tau is which was looking like a constant is no longer a constant. You have a vibration frequency which is constant, but you have this temperature T which is a variable. So, what it shows is that the jump probability for a given material will depend upon the temperature. So, that should ring the bell that diffusivity is a function of temperature. Although we are going to do it further now.

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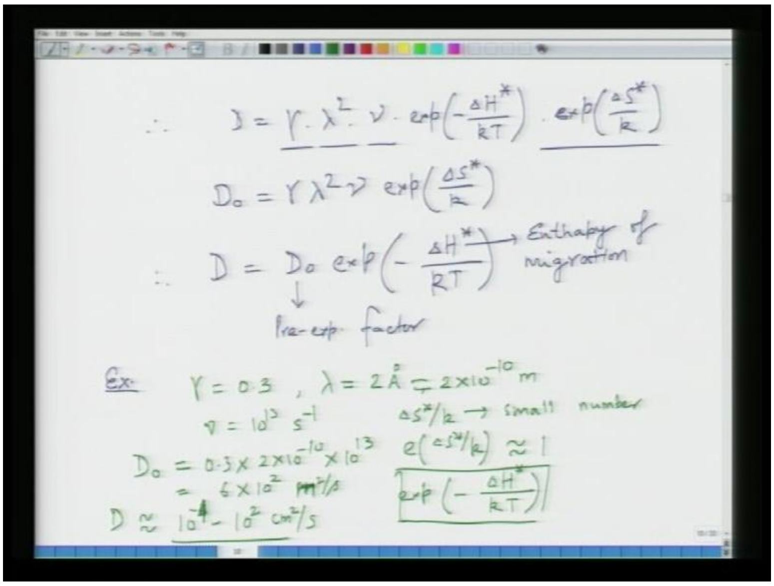

$$\therefore \quad D = \underline{\gamma} \cdot \underline{\lambda^2} \cdot \underline{\nu} \cdot \exp\left(-\frac{\Delta H^*}{kT}\right) \cdot \underline{\exp\left(\frac{\Delta S^*}{k}\right)}$$

$$D_0 = \gamma \lambda^2 \nu \exp\left(\frac{\Delta S^*}{k}\right)$$

$$\therefore \quad D = \underset{\substack{\downarrow \\ \text{Pre-exp. factor}}}{D_0} \exp\left(-\frac{\Delta H^*}{RT}\right) \rightarrow \text{Enthalpy of migration}$$

Ex. $\gamma = 0.3$, $\lambda = 2\text{Å} \simeq 2\times10^{-10}$ m

$\nu = 10^{13}\ s^{-1}$ $\quad \Delta S^*/k \rightarrow$ small number

$D_0 = 0.3\times 2\times10^{-10}\times10^{13}$ $\quad e^{(\Delta S^*/k)} \approx 1$

$= 6\times10^{2}\ m^2/s$ $\quad \boxed{\exp\left(-\frac{\Delta H^*}{kT}\right)}$

$D \approx \underline{10^{-4} - 10^{-2}\ cm^2/s}$

So, now if you make the proper substitutions I can write D is equal to gamma lambda square multiplied by nu multiplied by exponential minus delta H star divided by k T into delta exponential of delta S star divided by plus k. If you now rearrange these, this is a constant, this is a constant, this is a constant and this is a constant, there is no temperature dependence here. So, all these things make, will make D naught which will be gamma lambda square nu exponential of delta S star divided by k. So, D will be given as now D naught exponential minus delta H star divided by k T. Now, this expression is similar to expression that we developed earlier, that I wrote earlier. So, this will be your enthalpy of migration, the energy which needs to be overcome in order to, in order for diffusion to occur and this is your pre-exponential factor. So, this establishes the basis for temperature dependence of diffusion.

Now, what you can do is that you can verify yourself by putting in some numbers just to work out the value of D. For instance if you take for example, let us say gamma as some arbitrary value of 0.3 example lambda in a typical crystal system would be. Now, we will take an example and just to see how the numbers turn out to be? So, example let us say assume gamma is some small value of 0.3 lambda for a typical crystal system would be of the order of atomic distances, let us say one angstrom or two angstrom. So, let us say let us say typical two angstrom, if the lattice parameter is about four angstrom and which is equal to your 2 into 10 to power minus 10 meter and nu is approximately 10 to power

13 per second, which is the frequency of vibration and let us say this delta S star divided by k is some small positive number.

If entropy change will always be positive, but since it is a diffusion is a slow process this delta S will also be not be very large. So, delta some small number as a result exponential of delta S star by k will be almost equal to 1. So, in that case I can write D naught as 0.3 multiplied by 2 into 10 to power minus 10 multiplied by 10 to power 13. What this looks like is 6 multiplied by 10 to the power 2 centimetre square per meter square per second. Now, all it depends upon what is now the value of exponential minus delta H star divided by k T? So, typical values which are therefore, interstitial diffusion where you have interstitial impurities which diffuse.

So, these values are typically depending upon the magnitude of this factor D varies between 10 to the power minus 3 to roughly 10 to the power 2 centimetre square per second 10 to the power minus 3 minus 4 to 10 to the power 2 centimetre square per second. These are the magnitudes of value, if you put in the values for delta H star delta H star will of course, be few electron volt per atom and very very not very a large depending upon the system whether it can be large or small and you know whether k or T. So, choose for various systems, so this sort of these numbers give you an idea of the order of diffusivity values for most systems.

So, now what we will do is that we will take the example of diffusion in ceramics; one of the examples of diffusion in ceramics, one thing which you need to be. So, so now we are saying that diffusion is random walk phenomena and diffusion takes place as a result of random walk movement of atoms in various sides and which covers a jump probability and the and the gamma factor and so on and so forth. So, now we will look at what are the diffusion mechanisms?

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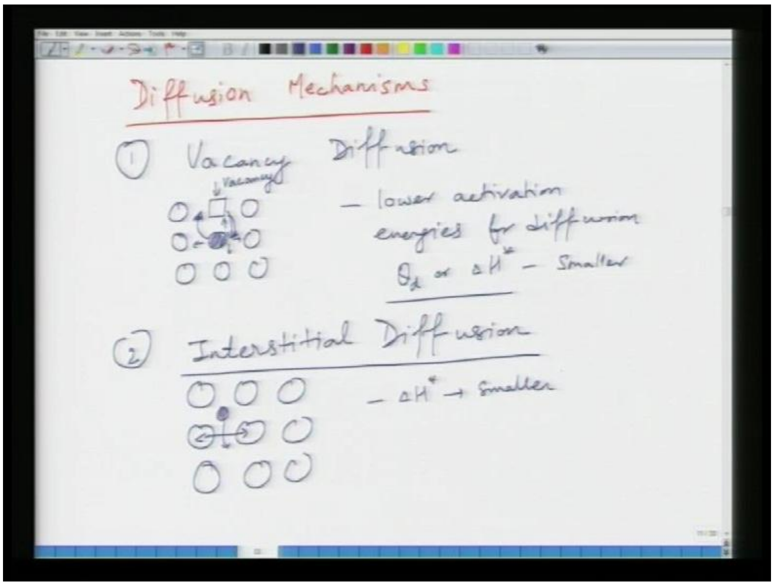

Diffusion Mechanisms

① Vacancy Diffusion

– lower activation energies for diffusion

Q_d or ΔH^* – Smaller

② Interstitial Diffusion

– ΔH^* → Smaller

Now, diffusion mechanisms the first common mechanism is your vacancy diffusion or vacancy assisted diffusion. Now, what basically it means is that you have this kind of lattice or atomic configuration. So, if you want in such a system where there are no vacancies, if you want these for example, this atom to this atom to move somewhere here or here or here or here it has to expand the whole lattice because it does not lattice is a close packed lattice. So, in order for this atom to move to another position it has to expand the lattice, which because it has to break its bonds and it has to go through the small a small channels, which are present in any lattice and then it has to occupy other position.

At the same time since it is moving from one position to another, this guy also has to move here which means massive dilation of lattice will occur. Now, so this is this is a very energetically demanding process. Now, suppose what happened, instead of having this atom here you had a vacancy. So, this is let us say a vacancy so now, the process is much more simpler. Whole thing has does not need to be dilated only this vacancy has to move here and this atom has to move there. Of course, the bond breaking of for this atom has to occur, but the overall energy expense goes down. So, as a result this vacancy assisted diffusion is typically has lower activation energies for diffusion, which means I said Q d or delta H star depending upon how you write it are typically smaller.

We will write some numbers later on and another mechanism which is, common is interstitial diffusion. A interstitial diffusion is you have lattice and you have some atoms let us say sitting here. This is a small interstitial atom it can diffuse through just by little bit expansion of neighbours, it can go from this side to that side another vacant side. This is again in dilute solutions, where impurities are present in smaller numbers. So, again interstitial diffusion. So, so for this case delta H star will be smaller as well not very large values few kilojoules per mole or.

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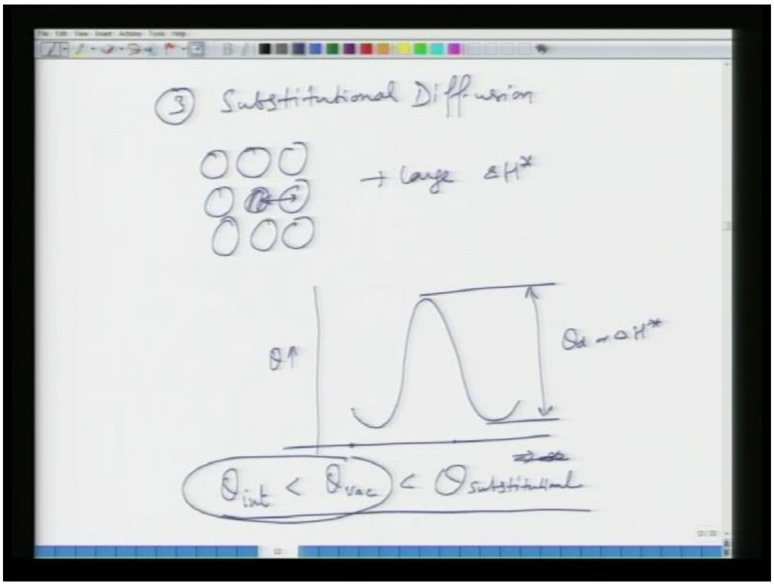

So, on the other hand if you have substitutional diffusion, where this guy replaces replaces with this demands large delta H star so massive expense of energy is required because the, then the whole lattice has to be dilated in the in the surrounding of these two diffusing atoms. So, these are the common mechanisms of diffusion and as you can see vacancy and interstitial mechanisms are more dominant mechanisms because they require least expense of the energy because of less, because of significantly reduced requirement of dilation of surroundings for atoms to move. So, if you plot for example, the distance versus sorry the activation energy plot. So, let say this is the activation energy.

So, so this is your Q d or delta H star. So, Q for interstitial is typically smaller as compared to vacancy as compared to substitutional. These two although can be of almost similar magnitude for some cases, depend on the type of lattice, but substitutional diffusion typically requires larger the energies for movement to occur.

Now, another thing which is of importance in dilute solutions is that where the diffusion takes place by vacancy assisted diffusion. So, for example, you take a system in which you impose a concentration gradient, that concentration gradient can be imposed either by chemical means or mechanical means. You impose a concentration gradient as a result you have diffusion of atoms on one side and diffusion of vacancy in on other side. So, which means you have counter migration of.

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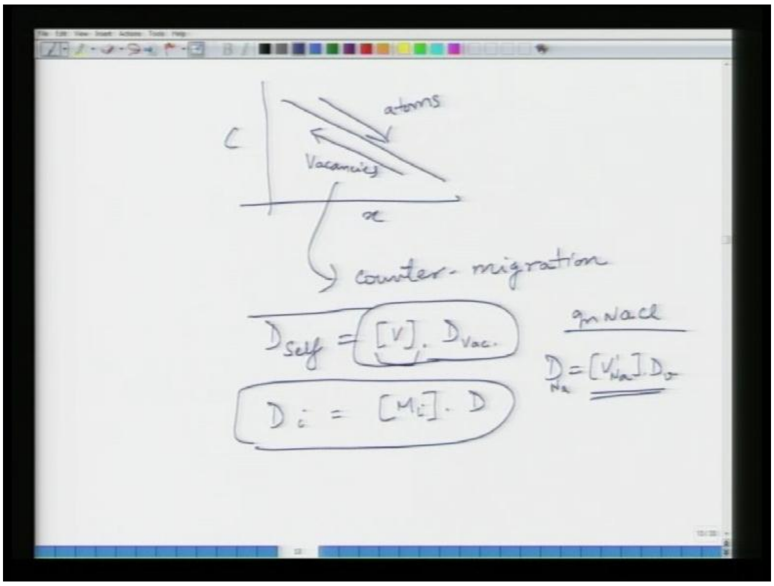

So, your atoms, so you have a concentration gradient let us say this is your C by x. So, your atoms will move on this side, and if it was vacancy assisted mechanism, your vacancies will move on other side. So, this is your counter migration. So, in such cases what happens is that the diffusion, the diffusion coefficient is also is also depends upon the number of vacancies, which are available. So, in such case in if you, if you take number of vacancies being relatively much smaller than number as compared to number of atoms. So, diffusion of these atoms D self can be thought of as D the proportion of vacancy or number of vacancies multiplied by diffusivity of vacancy diffusion coefficient.

So, this is your atomic self diffusion coefficient. In case of interstitials, it would be D i multiplied by whatever the interstitial concentration multiplied by diffusion, diffusivity coefficient. So, now what we will do is that, so this is just a small change which happens. So basically, you can write the diffusion coefficient and the effective diffusion coefficient for that particular ion, let us say sodium ion and sodium chloride. So, in sodium chloride, so D N a will be equal to sodium chloride is a material with Schottky defects, so where you have vacancies of sodium which move, so this will be equal to V N a multiplied by D D v. So, this will be for example, for diffusion coefficient.

So, now we are, what we will do is that in the next class, we will take some diffusion examples for example, in sodium chloride and magnesium oxide, what happens in these systems, and what is the temperature dependent? How does the diffusion coefficient varies in a pure ceramic as a function of temperature and in a impure ceramic containing impurities as a function of temperature? So, we will do that in the next class and then we will establish some formalisms for for the, for electrical properties based on these analysis.

Thank you.