Non - Metallic Materials

Prof. Subhasish Basu Majumder
Department of Materials Science Centre
Indian Institute of Technology, Kharagpur

Module – 03
Diffusion, phase transformation in non – metallic materials, glass and glass - ceramics
Lecture – 12
Fundamental of diffusion, Fick's laws, their solution and applications (Part - 1)

Welcome, to my course Non-Metallic Materials and this is part of module number 3. Diffusion, phase transformation in non metallic materials, glass and glass ceramics which is Fundamental of diffusions, Fick's law and their solution and applications. So, this is the part 1 of the lecture on diffusion and then we will continue the remaining part in my next lecture.

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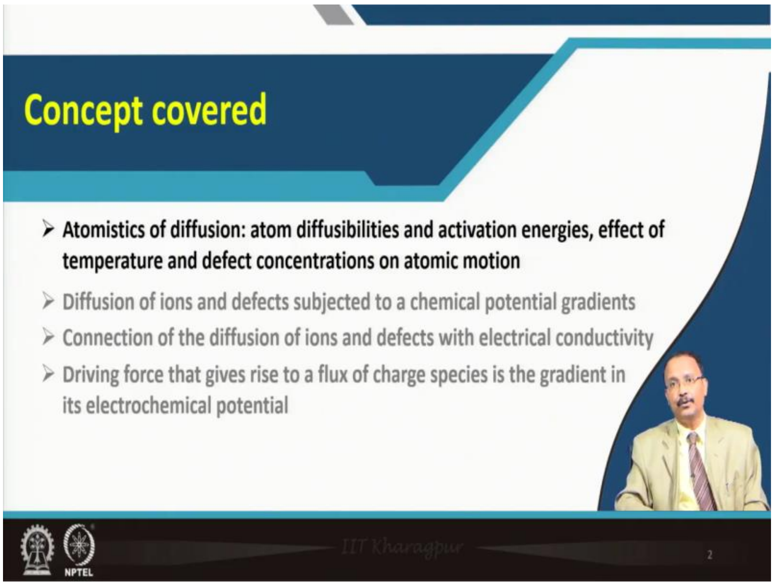

Concept covered

- Atomistics of diffusion: atom diffusibilities and activation energies, effect of temperature and defect concentrations on atomic motion
- Diffusion of ions and defects subjected to a chemical potential gradients
- Connection of the diffusion of ions and defects with electrical conductivity
- Driving force that gives rise to a flux of charge species is the gradient in its electrochemical potential

Now, in this particular lecture basically I will be covering atomistics of the diffusion, and that will include atom diffusibility and activation energies, effect of temperature, and defect concentration on atomic motion. So, I want to develop the concept in the part 1 of this lecture. And, once the concept is built, then we will talk about diffusion of ions and defects subjected to a chemical potential gradient, which is slightly complicated from what I will develop in as a part of this lecture.

And, then we will try to connect the diffusion of ions and defects with the electrical conductivity, which is pretty important. And, this will be continued when I will be talking about the electrical properties separately for this non metallic materials, so this concepts will be applied and you will see the inter elation which is very important for you to understand really.

And, the driving force that gives rise to the flux of charge species is eventually the gradient in its electrochemical potentials. So, we will develop that concept also in the forth coming lectures.

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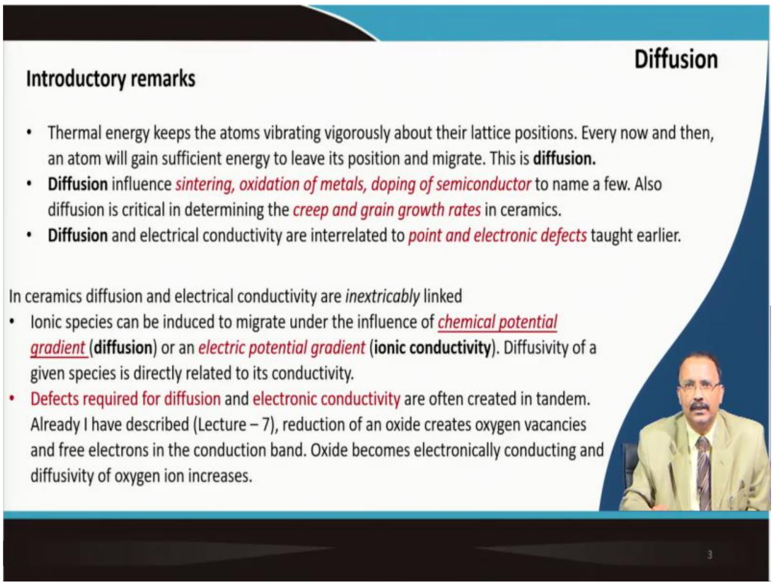

Diffusion

Introductory remarks

- Thermal energy keeps the atoms vibrating vigorously about their lattice positions. Every now and then, an atom will gain sufficient energy to leave its position and migrate. This is **diffusion.**
- **Diffusion** influence *sintering, oxidation of metals, doping of semiconductor* to name a few. Also diffusion is critical in determining the *creep and grain growth rates* in ceramics.
- **Diffusion** and electrical conductivity are interrelated to *point and electronic defects* taught earlier.

In ceramics diffusion and electrical conductivity are *inextricably* linked

- Ionic species can be induced to migrate under the influence of *chemical potential gradient* (**diffusion**) or an *electric potential gradient* (**ionic conductivity**). Diffusivity of a given species is directly related to its conductivity.
- Defects required for diffusion and electronic conductivity are often created in tandem. Already I have described (Lecture – 7), reduction of an oxide creates oxygen vacancies and free electrons in the conduction band. Oxide becomes electronically conducting and diffusivity of oxygen ion increases.

Now, you know the thermal energy that always force the atom to vibrate vigorously about their lattice positions, and very frequently what happens that this atom is part of it they get sufficient energy to leave their original position and start to migrate. And, sometimes they migrate quite randomly and basically this is the diffusion.

And very interestingly this diffusion it influences, lot of ceramic processes, including sintering, oxidation of metals which I have not covering that extent in this particular course, doping of semi conductor is another important area. And also the diffusion is very critical, to determine the creep and grain growth rates in ceramic material, we will be talking about it in the forth coming lectures.

And, you will find that the diffusion and electrical conductivity, they are interrelated to the point defects and electronic defects. Both point defects and electronic defects already I have thought earlier. And this concepts will be very much useful, when you try to understand the diffusion and try to correlate this concept of defects, concepts of diffusion to the respective electrical conductivity of this type of non metallic materials.

So, this two are very intimately related the diffusion and electrical conductivity. So, ionic species can be induced to migrate in the influence of a chemical potential gradient and that we have defined is diffusion, or you can apply electric potential gradient. So, both are important; one is chemical potential gradient; another one is electric potential gradient.

And, here you will find that is related when the ionic species moves under electric potential gradient, then it is conductivity and to be precise ionic conductivity. And diffusivity of the given species particularly in ionic ceramics, ionically bonded ceramics that directly to its conductivity.

So, this diffusion and the electrical conductivity, they are both created simultaneously I mean created in tandem to be precise. So, in lecture number 7 already we talked about when you reduce the oxide, then oxygen vacancies are created. And this oxygen vacancies, they basically form a low level trap.

And in order to maintain the charge neutrality they attract electrons. And, if you that shallow level of defects, they are very small, they are very close to the conduction band as compared to the band gap of this white band gap semi conductor this oxide materials.

So, a slight energy to give when this electrons are de trapped and they goes to the conduction band. So, oxide they basically become electronically conducting not fully, but at least partially the conductivity increases. And also the oxygen vacancy, they also start to diffuse. So, it is basically a complicated phenomenon. So, let us try to understand step by step that what exactly happens in an oxide system.

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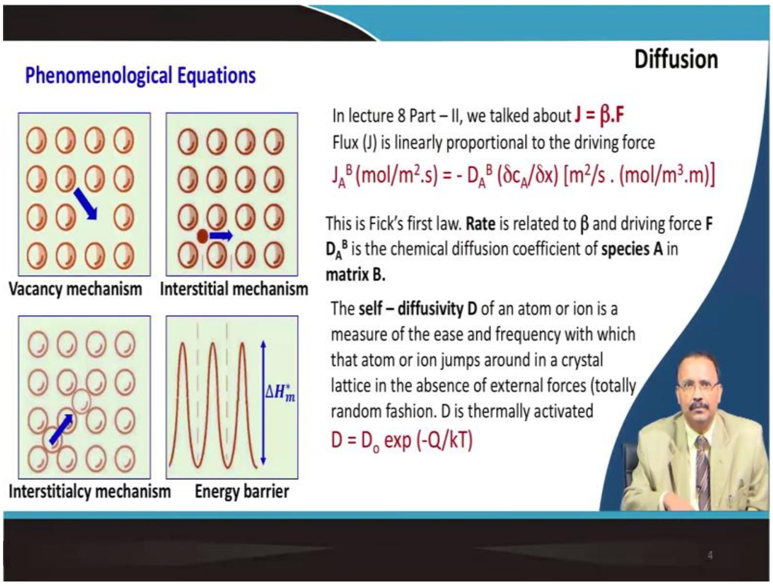

Phenomenological Equations

Diffusion

In lecture 8 Part – II, we talked about **$J = \beta.F$**

Flux (J) is linearly proportional to the driving force

$J_A^B (mol/m^2.s) = - D_A^B (\delta c_A/\delta x)\ [m^2/s\ .\ (mol/m^3.m)]$

This is Fick's first law. **Rate** is related to β and driving force **F**

D_A^B is the chemical diffusion coefficient of **species A** in **matrix B.**

The **self – diffusivity D** of an atom or ion is a measure of the ease and frequency with which that atom or ion jumps around in a crystal lattice in the absence of external forces (totally random fashion. D is thermally activated

$D = D_o \exp(-Q/kT)$

So, let us develop the phenomenological equation related to the defect, but let us first try to understand that what kind of different mechanisms that is prevailing in the diffusion. So, say one situation is something like this, you can see that there is a vacancy here. So, diffusion is related to atomic movement. So, this atom can move and they can come to the vacant lattice position.

So, atomic movement is in this direction and vacancy moves exactly to the opposite direction. So, this is the so called vacancy mechanism. Another one is the interstitial mechanism, were you can see the interstitial cation is there. And, then it is passing through in fact, forcing itself through this bigger anion and goes to the another interstitial site, again the vacancy movement is in the opposite direction then the mass transfer.

So, this is also important in oxide ceramics, this is also important in oxide ceramics, we will see the inter relation. And, there is another mechanism which is not very well described or well known. And, this is also a bit rare which we call interstitialcy mechanism, and where it is just like a carom striker that one atom this is pushing this to go in the interstitial position.

So, a regular atom side which was placed here this is being forced to go to the interstitial side and as I said this is not very common. So, if you see the free energy position here it is the stable position. So, the energy is minima you can see here, and then it will have to force itself to go to this position. So, therefore, there is an energy barrier it will have to cross before it goes to another minimum energy position. So, this is how it works. And this energy is initially we are defining ΔH^{*}_{m}.

So, this is the energy component and we call this is an energy barrier. So, in lecture number 8 particularly part 2, we talked about any rate equation that is actually linear equation with the beta parameter and the driving force right. So, something similar here the rate is the molecular flux. So, it is number of mole per unit area per unit second and that is related to the constant and this in this time it is a diffusion constant.

So, it is the concentration sorry this is the diffusion constant of species A in a matrix B and the driving force shears is the concentration gradient. So, since the concentration gradient is there then only atomic flux will move. So, if you put the dimension together, it is meter square per second for these diffusibility and this one is concentration mole per meter cube and there is a gradient so, this meter part is this so, this part and this part is equal.

And this is nothing, but the Fick's first law. And this basically relates according to our formalism relate beta, in this case beta is the diffusibility and driving force F, which is chemical diffusion it is nothing, but the concentration profile, I mean a concentration gradient that is the driving force.

So, the self diffusivity of an atom or ion is the measure of the ease of the frequency at which the atom can jump around the crystal lattice in the absence of any external force. So, it is a total random fashion. So, whenever it process this energy it goes and find the minimum energy position.

And usually D is thermally activated and we will see that how this what is the genesis of this well known relation, most of you know that D is equal to D_0 exponential of minus Q by k T. But, fundamental principles what is involved to get there, I mean how this equations what is the genesis of equation that is part of this lecture.

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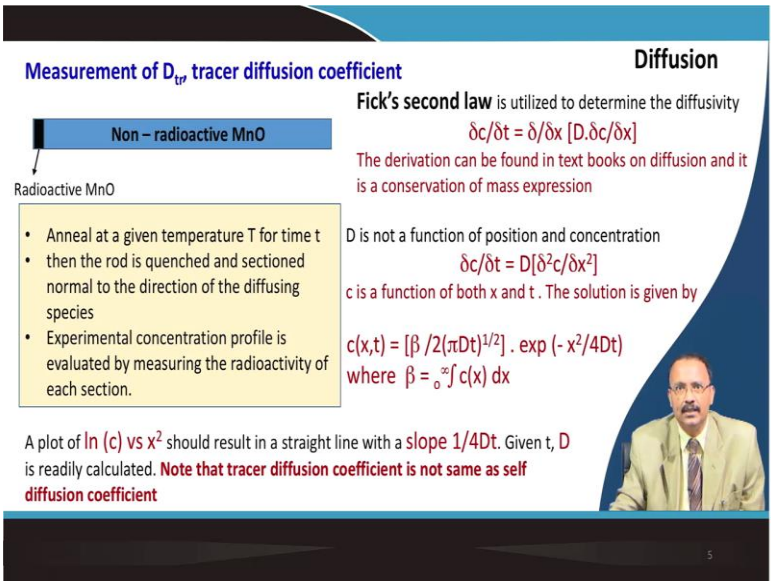

Measurement of D_{tr}, tracer diffusion coefficient

Diffusion

- Anneal at a given temperature T for time t
- then the rod is quenched and sectioned normal to the direction of the diffusing species
- Experimental concentration profile is evaluated by measuring the radioactivity of each section.

Fick's second law is utilized to determine the diffusivity

$$\delta c/\delta t = \delta/\delta x\,[D.\delta c/\delta x]$$

The derivation can be found in text books on diffusion and it is a conservation of mass expression

D is not a function of position and concentration

$$\delta c/\delta t = D[\delta^2 c/\delta x^2]$$

c is a function of both x and t . The solution is given by

$$c(x,t) = [\beta /2(\pi Dt)^{1/2}] . \exp(- x^2/4Dt)$$

where $\beta = {}_0^{\infty}\int c(x)\,dx$

A plot of ln (c) vs x^2 should result in a straight line with a slope 1/4Dt. Given t, D is readily calculated. **Note that tracer diffusion coefficient is not same as self diffusion coefficient**

So, it is important for you to measure the diffusion coefficient. And diffusion coefficient we are particularly interested to measure what we call it tracer diffusion coefficients. So, usually if you want to measure the diffusion of say manganese ion. So, what I will take a big manganese rod and radioactive manganese coating will be given at the end of this rod.

Then, we will anneal it is a given temperature T for time small t, then the rod is quenched at low temperature. And is sectioned normal to the direction of the diffusing species. So, when the temperature is there in allowing time, then this is diffusing this species is diffusing here. So, you just cut it after quenching and the concentration profile you can measure, by measuring the radio activity of each section. So, that is the way the experiment is done.

And Fick's second law that is related to determine the diffusivity, and it says that this concentration del c by del t that is nothing, but del del x of D into del c by del x. So, this derivation is there in various types of textbook and it is related to the conservation of mass. So, this you can just work it out to get this relation. And what it tells? That the concentration with time del c del t is D assuming that D is not a very strong function of time.

And also the gradient then you can take it out so, D del 2 c by del x square and then you can have a solution. And this solution I will explain it in details while we will talk about the assignment problems so, it will be clearer. So, typical solution is this were the concentration is a function of time, as well as the function of the length that is derived by this relation, where beta is the total concentration of this atom c.

So, if you integrate 0 to infinity then you get the beta get this beta value. And this is the expression of the solution for the Fick's second law. So, clearly if you plot the log concentration versus 1 by you can plot this versus log of this versus x square, then you get a slope of a negative slope of minus 1 by 4 D t and D you know because you yourself as annealed it so, the time is known.

And from the slope you can measure the value of D, and this is how the tracer diffusion coefficient is measured and it is not really same as the self diffusion coefficient which I have talked about.

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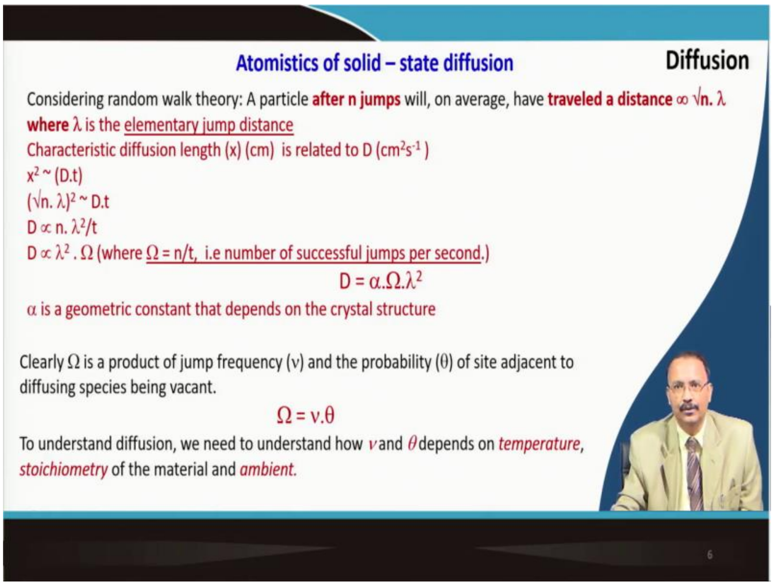

Diffusion

Atomistics of solid – state diffusion

Considering random walk theory: A particle **after n jumps** will, on average, have **traveled a distance $\infty \sqrt{n}.\lambda$**
where λ is the elementary jump distance
Characteristic diffusion length (x) (cm) is related to D (cm^2s^{-1})
$x^2 \sim (D.t)$
$(\sqrt{n}.\lambda)^2 \sim D.t$
$D \propto n.\lambda^2/t$
$D \propto \lambda^2.\Omega$ (where $\Omega = n/t$, i.e number of successful jumps per second.)

$$D = \alpha.\Omega.\lambda^2$$

α is a geometric constant that depends on the crystal structure

Clearly Ω is a product of jump frequency (ν) and the probability (θ) of site adjacent to diffusing species being vacant.

$$\Omega = \nu.\theta$$

To understand diffusion, we need to understand how ν and θ depends on *temperature*, *stoichiometry* of the material and *ambient*.

Now, if you consider a random walk theory, then it tells you that a particle after n jumps n number of jumps, will on an average have travelled a distance which is proportional to the number of jumps root over into distance lambda, which is the elementary jump distance. So, that is from the random walk theory.

So, the characteristic diffusion length is of course, related with the diffusibility you can see that is this is centimeter square per second, and x the characteristic diffusion length of the atom which is x. So, if you square it out so, x square is proportional to D into time. So, this dimension will match centimeter square and centimeter square.

So, if you put the value which is equivalent to root n into lambda. So, have a whole square that is equivalent to D into t. So, actually D is proportional the proportionality is there it is not actually equivalent. So, this proportionality is n into lambda square lambda is elementary jump distance divided by t.

So, here this is proportional to lambda square and this n by t term which is number of successful jump per second, so it is a jump frequency. So, jump frequency I have denoted by omega big omega. So, then this equation comes as alpha, then your jump frequency and the jump distance lambda square. So, this alpha it is a geometric constant proportionality constant and it depends on the crystal structure.

So, we will see its significance when we will proceed in the second part, and also while solving the assignment problems. So, this omega is a product of jump frequency and also the probability of the adjacent site is vacant. Remember that when I talked about the atomic jump into a vacant position, it is also important that whether this position is vacant. So, the probability term is also there.

So, I can have this omega is equal to this jump frequency and as well as the probability. So, in order to understand diffusion well you need to understand separately both of this parameter, both new and theta. And, their dependence on temperature and stoichiometry of the material and also what type of ambient you are talking about.

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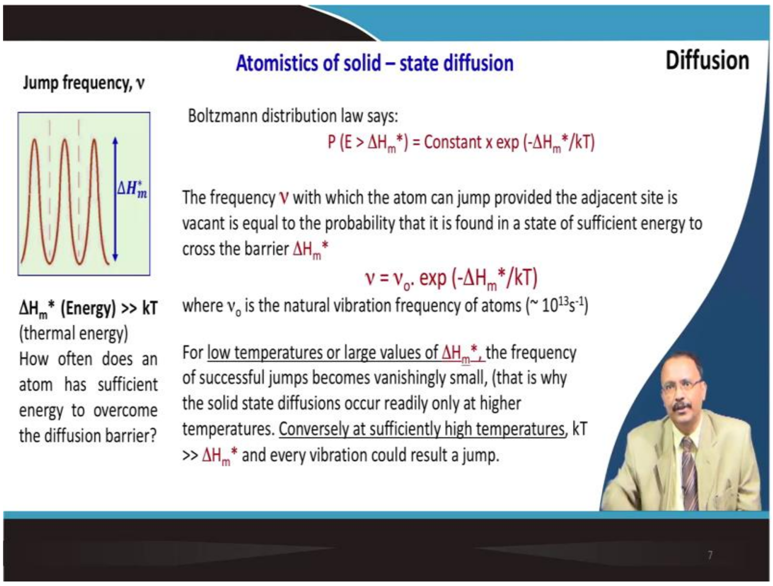

Atomistics of solid – state diffusion

Diffusion

Jump frequency, ν

Boltzmann distribution law says:

$$P\,(E > \Delta H_m^*) = \text{Constant} \times \exp(-\Delta H_m^*/kT)$$

The frequency ν with which the atom can jump provided the adjacent site is vacant is equal to the probability that it is found in a state of sufficient energy to cross the barrier ΔH_m^*

$$\nu = \nu_o.\exp(-\Delta H_m^*/kT)$$

where ν_o is the natural vibration frequency of atoms (~ $10^{13}s^{-1}$)

ΔH_m^* (Energy) >> kT (thermal energy)

How often does an atom has sufficient energy to overcome the diffusion barrier?

For low temperatures or large values of ΔH_m^*, the frequency of successful jumps becomes vanishingly small, (that is why the solid state diffusions occur readily only at higher temperatures. Conversely at sufficiently high temperatures, kT >> ΔH_m^* and every vibration could result a jump.

Now, the jump frequency let us see that what does it mean. So, this is minimum free energy position. So, you can jump and go here, provided you have sufficient energy. So, if your temperature is say at T at room temperature it is 25 milli electron volt, it may not be sufficient for the jump to occur. So, a certain energy is required which is much more than the k T value. So, that it goes here and the question is that. How often does an atom has a sufficient energy to overcome this diffusion barrier?

So, this is also equally important. What is the probability? And, also whether this site is vacant so, first we talk about the jump frequency then we will talk about the probability. So, then Boltzmann distribution law if you apply here, then the probability of this kind of energy achievement is related by a constant and exponential of minus of this energy this barrier height by k T.

Now, the frequency with which the atom can jump provided the adjacent site is vacant is equal to the probability that it is having a in a state of sufficient energy to cross this barrier. So, here also this is a some kind of probability relationship for this frequency, which is related to the natural frequency, which is typically 10 to the power 13 per second and the relevant energy term.

So, for low temperature or if the value is quite large, the frequency for successful jump its vanishingly small. So, all solid state diffusion process is actually operative at high temperature, at sufficiently high temperature k T is much larger because T if you are increasing k T is much larger than your del H m. So, every vibration that could result a jumps so, that is the basic concept of diffusion.

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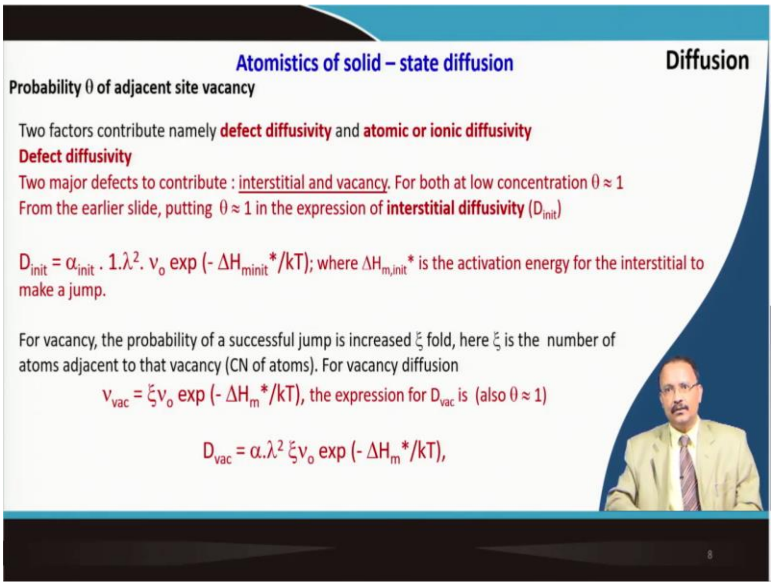

Atomistics of solid – state diffusion

Diffusion

Probability θ of adjacent site vacancy

Two factors contribute namely **defect diffusivity** and **atomic or ionic diffusivity**

Defect diffusivity

Two major defects to contribute : interstitial and vacancy. For both at low concentration $\theta \approx 1$

From the earlier slide, putting $\theta \approx 1$ in the expression of **interstitial diffusivity** (D_{init})

$D_{init} = \alpha_{init} . 1.\lambda^2. \nu_o \exp(-\Delta H_{minit}^*/kT)$; where $\Delta H_{m,init}^*$ is the activation energy for the interstitial to make a jump.

For vacancy, the probability of a successful jump is increased ξ fold, here ξ is the number of atoms adjacent to that vacancy (CN of atoms). For vacancy diffusion

$\nu_{vac} = \xi\nu_o \exp(-\Delta H_m^*/kT)$, the expression for D_{vac} is (also $\theta \approx 1$)

$$D_{vac} = \alpha.\lambda^2 \xi\nu_o \exp(-\Delta H_m^*/kT),$$

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Now, let us talk about the probability which is theta, if the adjacent site is vacant. Now, here two important factors they contribute that is one is defect diffusivity, and another one is atom or ion diffusivity. I already mentioned that once you are talking about diffusion, then what is happening that your atom is moving to the vacant site. And in equally you can consider it, that the vacancy is moving to the opposite direction.

So, first we will talk about defect diffusivity and by the time you know about the defect of the ceramic materials. And usually there are two major defect that contribute to the diffusion one is interstitial, where you find in the interstitial position a cation is sitting there particularly cation. Because, they are smaller size and to less extent it is anion because the size is quite large as compared to the interstitial position.

So, the first kind of defect is interstitial and vacancy. So, both at low temperature sorry at low concentration. The probability is almost equal to 1 so, this is quite natural that you know that once you cross a temperature T, then it is it has to be vacant right.

So, once you consider the defect concentration is low then temperature is sufficiently high, because it is operating at least at room temperature or slightly higher temperature. So, the probability will be very close to 1. So, interstitial diffusivity you can get from the earlier relation whatever I wrote.

So, we wrote diffusion D is related to this alpha value interstitial probability is 1 and this jump distance typically is lambda square. And the frequency that is nu 0 exponential and this is the relevant energy to cross for the interstitial cation.

So, this is the activation energy of the interstitial cation to make a jump. So, you can write this relation. Now, think about the vacancy the probability of a successful jump that is increase this zeta time. And what is this zeta? That is the atom which is present adjacent to the vacancy because, it is a simple crystal lattice so, lot of atoms are there and suddenly one atom is missing. So, that is the point vacancy.

Now, the coordination number of this atom is important right, because the vacancy can jump at any position. So, atom is movement is there towards vacancy means vacancy is jumped into that. So, any position I mean any kind of jump is possible so, the coordination number of the surrounding atom that is important for the vacancy diffusion.

So, the vacancy diffusion is multiplied this expression is multiplied by zeta and here also your probability is 1. So, the vacancy diffusion coefficient that give rise to the alpha value that is for the vacancy lambda square will be there zeta term will be there, and then this relation for the vacancy is also there to consider.

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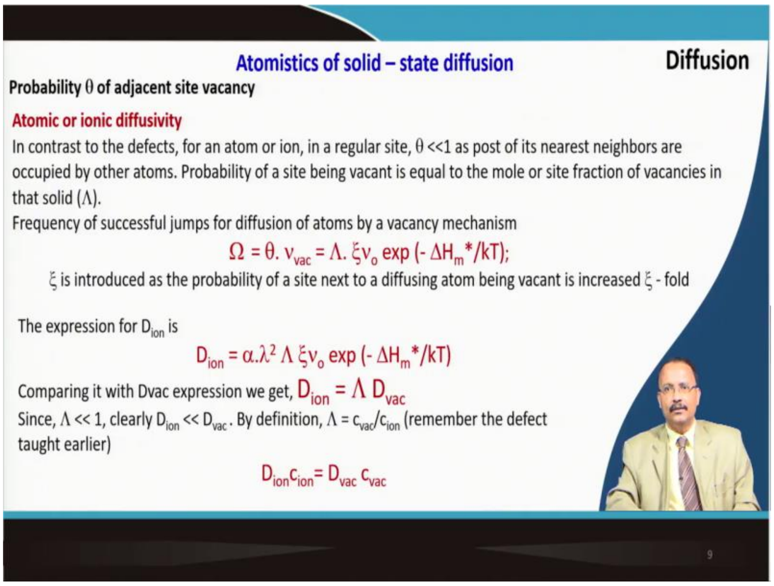

Atomistics of solid – state diffusion

Diffusion

Probability θ of adjacent site vacancy

Atomic or ionic diffusivity

In contrast to the defects, for an atom or ion, in a regular site, $\theta << 1$ as post of its nearest neighbors are occupied by other atoms. Probability of a site being vacant is equal to the mole or site fraction of vacancies in that solid (Λ).

Frequency of successful jumps for diffusion of atoms by a vacancy mechanism

$$\Omega = \theta.\ \nu_{vac} = \Lambda.\ \xi \nu_o \exp(-\Delta H_m^*/kT);$$

ξ is introduced as the probability of a site next to a diffusing atom being vacant is increased ξ - fold

The expression for D_{ion} is

$$D_{ion} = \alpha.\lambda^2 \Lambda \xi \nu_o \exp(-\Delta H_m^*/kT)$$

Comparing it with Dvac expression we get, $D_{ion} = \Lambda D_{vac}$

Since, $\Lambda << 1$, clearly $D_{ion} << D_{vac}$. By definition, $\Lambda = c_{vac}/c_{ion}$ (remember the defect taught earlier)

$$D_{ion} c_{ion} = D_{vac}\ c_{vac}$$

Now, let us now consider the atom or ionic diffusibility you talked about the vacancy 1 and now it is the atomic 1 to consider. Now, you see the in contrast to the defect for an atom or ion in a regular lattice site, it will remain there. So, the probability term it is not having smaller concentration like vacuum like the vacancies.

So, the probability term is much less than 1 of its nearest neighbor to occupied by the other atom. So, probability of the site being vacant is equal actually the mold fraction of the site of vacancy in the solid. Because, of course, the vacancy and the probability term is interrelated and that is interrelated the vacancy concentration will basically decide about the probability.

So, that parameter we have defined as the capital lambda. So, frequency of this successful jump for a diffusion of atom by the vacancy mechanism that now again you can define by this which is probability into this frequency term for, the vacancy. And, now the probability you cannot ignore. So, the probability term is also there and the atomic coordination number is also there.

So, you can write this equations. So, in the same similar concept for the vacancy also we have introduced. So, zeta parameter will also be there. So, now, you write the diffusion expression for the ionic diffusion. So, here it is alpha lambda square the probability term capital lambda will be there, the coordination term zeta will be there. And nu 0 exponential this energy term exponential term will also there.

So, if you compare the vacancy expression with this diffusion of ion expression, they are almost similar they are very similar, except you are introducing one probability term which is lambda. So, diffusion coefficient diffusibility of ion is related to the probability factor of and the diffusibility of vacancy.

Now, usually the probability is far less because, you do not expect that in your crystal like lattice there are lot of vacancy will be there so, it is far less than 1. So, eventually your ionic diffusion coefficient ionic diffusibility is far less than the vacancy diffusibility. So, we have already defined this in fact, this definition of the fraction of the vacancy that already we have described in our defect lecture.

So, if you remember that then this capital lambda is the concentration of the vacancy with respect to the concentration of all the ions. So, if you just replace this by this simple relation, then you end with D ion into c ion is equal to D vacancy into concentration of vacancy.

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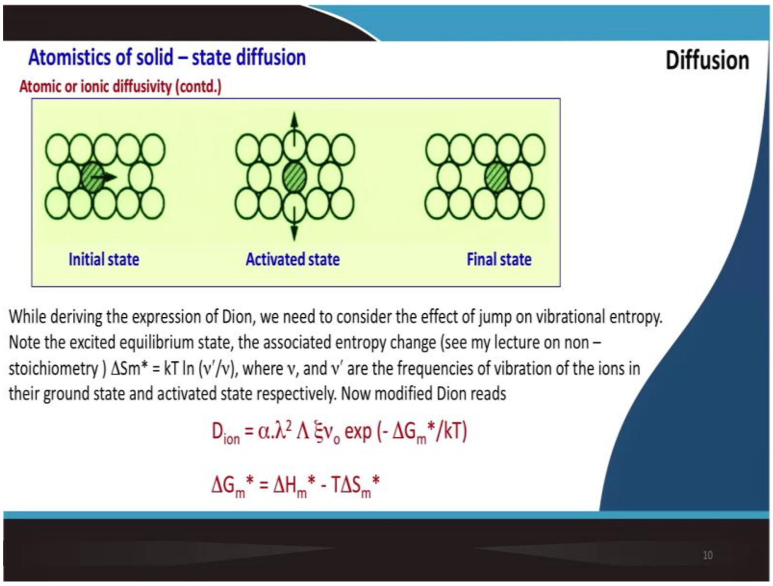

Atomistics of solid – state diffusion

Atomic or ionic diffusivity (contd.)

While deriving the expression of Dion, we need to consider the effect of jump on vibrational entropy. Note the excited equilibrium state, the associated entropy change (see my lecture on non – stoichiometry) $\Delta Sm^* = kT \ln (\nu'/\nu)$, where ν, and ν' are the frequencies of vibration of the ions in their ground state and activated state respectively. Now modified Dion reads

$$D_{ion} = \alpha.\lambda^2 \Lambda \xi \nu_o \exp(-\Delta G_m^*/kT)$$

$$\Delta G_m^* = \Delta H_m^* - T\Delta S_m^*$$

Now, you consider the situation schematically that in the initial state your atom is diffusing into these vacancy so, it will have to cross this two atom it will have to squeeze it. So, it will go here momentarily it remains here, and then it goes to the vacant lattice position. So, the final state is here intermediate state is here and initial state is here. So, this intermediate state where it is squeeze pass this two atom. So, this is a activated state.

So, while we derive this diffusion coefficient for the ionic diffusion, we need to consider this that the effect of jump on the vibrational entropy, because it is a disorder kind of structure. So, of course, the vibrational entropy term also needs to be included, which we did not include while we derive from first principle the earlier equations.

Now, in the excited equilibrium state it is related to the entropy change, and you remember my lecture on non stoichiometry, where we derived that this entropy change is related to the two frequencies that Einstein relation two vibrational frequency. One is at their ground state and another one is the activated state.

So, this is the ground state and this one is the activated state so, this relation is valid. And, now your energy term which was only enthalpy so far. Now, I replace it with a free energy term. So, you know that G is related to enthalpy and entropy.

So, entropy term I am putting it here and rewrite this relation. So, alpha is there jump distance is there probability factor is there. And, then xi this coordination number is there and also your frequency term with the energy nu 0 exponential this term is there. So, now, you replace this value g with enthalpy and entropy.

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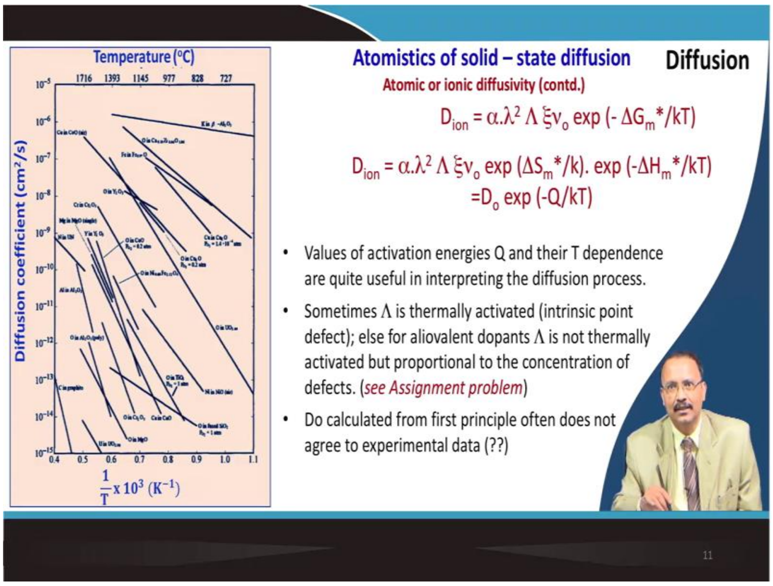

Atomistics of solid – state diffusion

Diffusion

Atomic or ionic diffusivity (contd.)

$$D_{ion} = \alpha.\lambda^2 \Lambda \xi \nu_o \exp(-\Delta G_m^*/kT)$$

$$D_{ion} = \alpha.\lambda^2 \Lambda \xi \nu_o \exp(\Delta S_m^*/k).\exp(-\Delta H_m^*/kT)$$
$$= D_o \exp(-Q/kT)$$

- Values of activation energies Q and their T dependence are quite useful in interpreting the diffusion process.
- Sometimes Λ is thermally activated (intrinsic point defect); else for aliovalent dopants Λ is not thermally activated but proportional to the concentration of defects. (*see Assignment problem*)
- Do calculated from first principle often does not agree to experimental data (??)

And basically you come up with this relation, and then you put it here and just little bit algebraic terminology just simple replacement. And you get this relation one whole constant term and then exponential of this G term right. This H term is there and this one is also there, but here only the G term is there.

So, this is basically the activation energy and all this part this proportionality constant which is related to the crystal structure, atomic jump, probability, then coordination number of the surrounding atom all are included in this D 0 and also 10 to the power 13 1 this standard frequency.

So, this is the relation that you are familiar with always you write in the terms. So, values of the activation energy Q and their temperature dependence are quite useful, you can use this relation you take log into different site and plot it with 1 by T l n of D with 1 by T you get this activation energy. So, their temperature dependence are quite useful for interpreting different types of diffusion process.

Sometimes for example, your this probability it is intrinsic point effect. So, that is thermally activated we already understood it that in is a thermally activated process. Sometimes when you are adding dopant, then it is not a thermally activated process it is actually dependent on the concentration of the dopant that you are adding.

So, unfortunately in many of the problem we have found that from first principle calculation, if you all use this values. Then, this value whenever from experiment you determine the D 0, they do not match and actually this reason I also do not know why they do not match; when you solve certain problem you will see that it is something like this. So, that remains a open question and if you know the answer just share with me.

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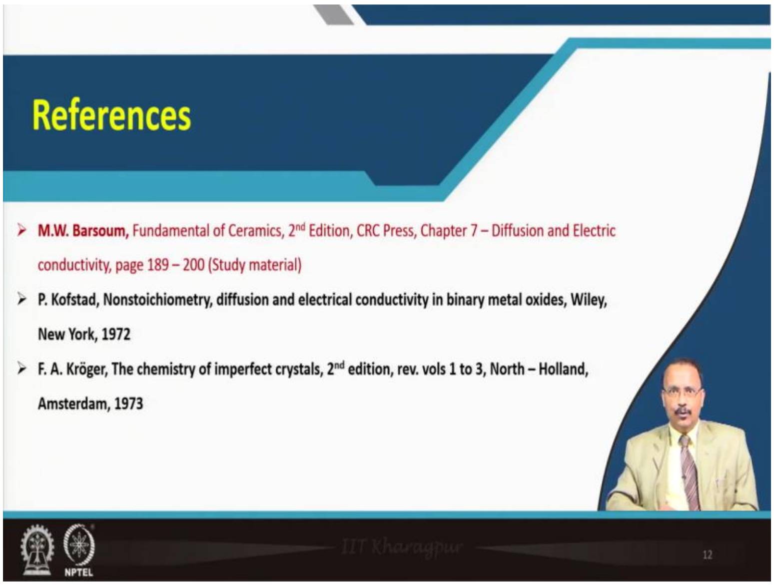

References

- **M.W. Barsoum**, Fundamental of Ceramics, 2nd Edition, CRC Press, Chapter 7 – Diffusion and Electric conductivity, page 189 – 200 (Study material)
- P. Kofstad, Nonstoichiometry, diffusion and electrical conductivity in binary metal oxides, Wiley, New York, 1972
- F. A. Kröger, The chemistry of imperfect crystals, 2nd edition, rev. vols 1 to 3, North – Holland, Amsterdam, 1973

So, this is the reference of the Barsoum book, again chapter number 7 diffusion of electrical conductivity. And, this you will have to read thoroughly and there are two reference books.

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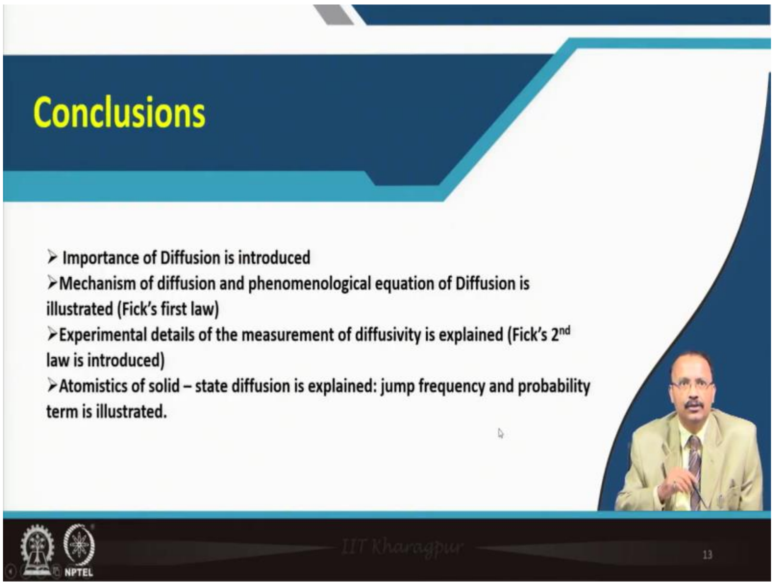

Conclusions

- Importance of Diffusion is introduced
- Mechanism of diffusion and phenomenological equation of Diffusion is illustrated (Fick's first law)
- Experimental details of the measurement of diffusivity is explained (Fick's 2nd law is introduced)
- Atomistics of solid – state diffusion is explained: jump frequency and probability term is illustrated.

So, in this particular lecture importance of diffusion is introduced and Fick's first law and second law the concept. And the derivation of Fick's second law is important and atomistic model of solid state diffusion for the first principle, we basically evaluate it the very well known diffusion equation, but in a much systematic order, so that each step now you understand that what is the genesis of this D 0. And we will continue in the next part of this lecture with some other important topic.

So, thank you so much for your attention.