Non - Metallic Materials
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Module – 03
Diffusion, phase transformation in non – metallic materials, glass and glass - ceramics
Lecture – 13
Fundamental of diffusion, Fick's laws, their solution and applications (Part – 02)

Welcome to my course, Non Metallic Materials and we are in module number 3, where I am describing, Diffusion, phase transformation in non-metallic materials, glass as well as in glass ceramics. And, today I will deliver lecture number 13 on fundamentals of diffusion Fick's law their solution and application.

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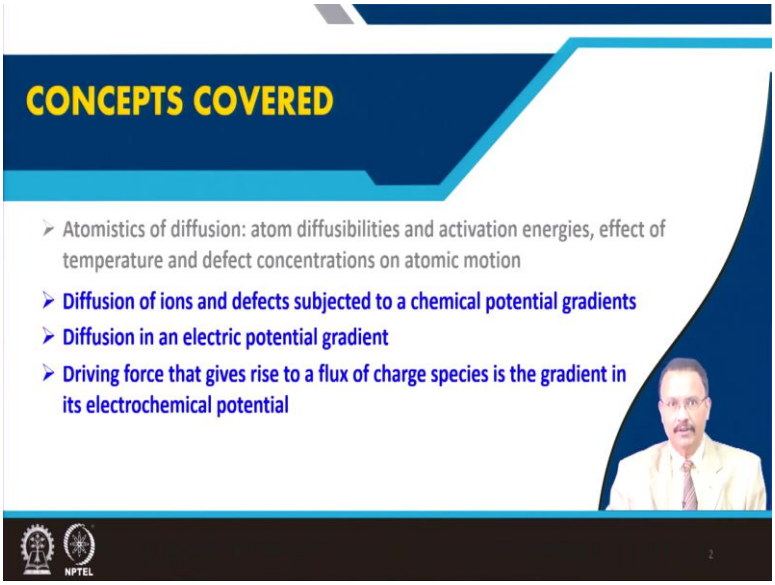

So, the concept that I already covered in part 1 of this lecture is atomistics of diffusion atom diffusibilities and activation energies, and effect of temperature as well as defect concentration on atomic motion. So, that was already covered in part number 1 of this lecture.

Today, we will be examining the diffusion of ions as well as defects in a ceramic material. And, three types of driving force, we will consider. The first one is chemical potential gradients; the next one is the same charge species as well as defects in an electric potential gradient.

And, third one is the driving force which is a combination of these two. That is both chemical potential as well as electric potential; that is eventually electrochemical potential. What is their effect on this charge species that we will consider. Now part of this concepts, I will use well I will talk about the electrical properties of this non-metallic materials and then the connection will be quite apparent.

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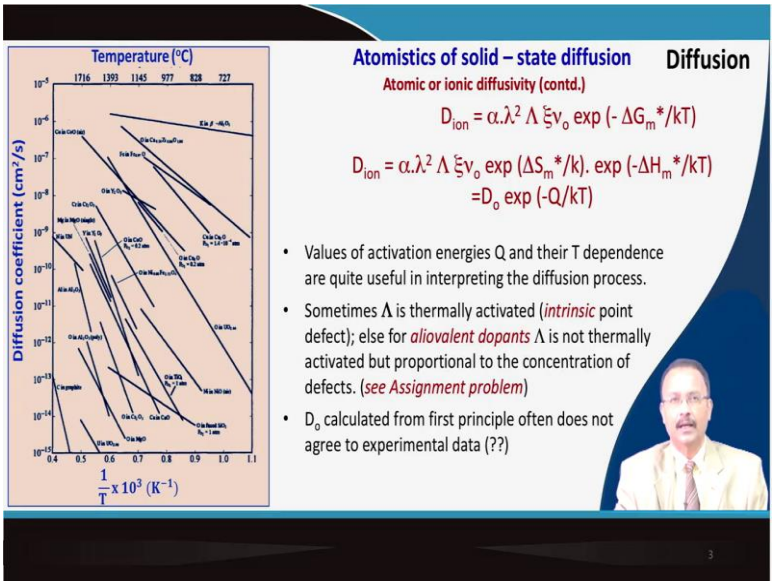

So, I will suggest you who are taking this class to derive these expressions independently, because derivation is very important some of the concepts that I want to convey is only through mathematical formulation. So, you need to understand that well. And, also try to correlate this mathematical concept, the expressions, how it is correlating with the physical behavior of the non-metallic oxide materials. This interconnection is very important for you to understand.

You see in the last class, I tried to talk about atomic or ionic diffusibility. So, this is a continuation of the last lecture. And, where I derive this relation, that ionic diffusibility that is dependent on so many factors. Ah. It depends basically on crystal structure, then the distance of atomic jump how much it is jumping from one lattice point to a vacant lattice point. So, that lambda is important. Then, this capital lambda, which is basically the defect fraction, that is important.

A parameter, which is zeta, which is related to the coordination number of the atom in a particular crystal lattice, that is important. And, the frequency of the jump so, it is a

fundamental frequency nu 0 and the barrier, which I defined as del G m star, that is also important.

So, then we just divide or expand this free energy term. And, we got this entropy term, mostly configurational entropy. And the enthalpy the energy barrier which the atom needs to cross, and eventually we showed from first principle, that you can now understand the fundamental diffusion equation D 0 exponential of minus Q by kT, which is very well known.

So, this values of this activation energy Q and their temperature dependence. They are quite useful for inter interpreting various diffusion process. And, sometimes you know that, this defect concentration they are thermally activated. Particularly for intrinsic point defects, you know that this is a thermally activated process. And, when you are considering aliovalent dopant, where the charge is more so, you are doping it in a host lattice then it will create vacancy.

So, then in that case rather than going for this thermal activation, you are more interested in defect concentration. So, some of the assignment problems we will find, based on this concept. Sometimes the defect is dependent on temperature and sometimes the dopant concentration itself is important. Because, that directly affect this capital lambda term.

Now, as I mentioned in my last class as well, that very often the you can estimate the pre-exponential constant that D 0 and that is quite easy. So, if you plot this diffusion coefficient a log plot versus 1 by temperature, then it is a straight line basically.

And, the y axis intercept will give you the value of D 0. So, this value may not match, the experimental value may not match this first principle calculation. If you calculate the value from crystallographic parameters, then jump distance etcetera, if you just put it does not match.

Why it does not match, I have some tentative answer, but I do not have a perfect answer to this question. Probably it is related to the complicacy of the crystal structure or the way we understand the diffusion process, but this is the case that needs to be considered.

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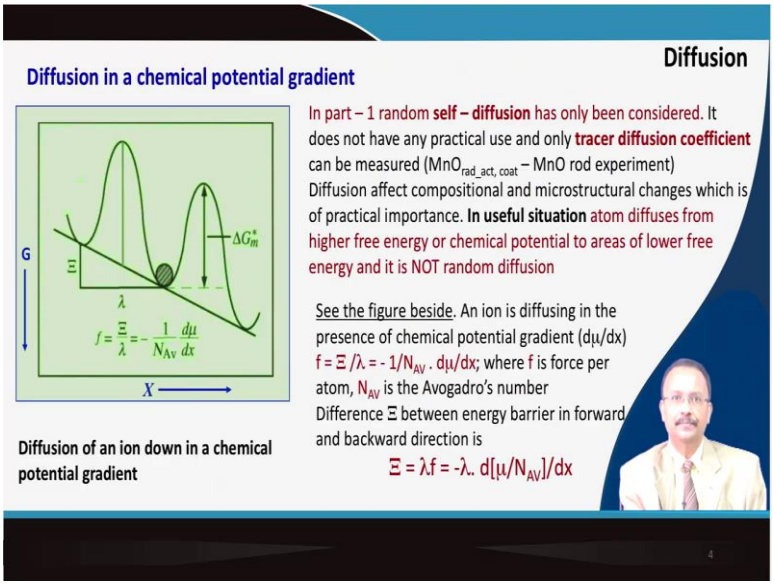

Now, if I now, think you see as compared to the last lecture, where it is a random kind of diffusion. So, diffusion is occurring throughout the system. So, there is no not much utility in it. So, this self-diffusion, which I considered in deriving this relation it does not have any practical use right.

Only tracer diffusion coefficient one can measure, and I told that tracer diffusion coefficient is some way, it is relating the self-diffusion. So, that is there. So, they are interrelated. So, I will explain it later. So, some kind of factor is involved.

So, if you just estimate it and remember I talked about in experiment of manganese oxide rod and a radioactive component there so, atom diffuses from higher energy, chemical potential to lower energy chemical potential. So, if you consider that, if it is a driving force there then exactly it is a useful situation.

So, from one end you will see that the atomic species is moving so, higher energy to lower energy there. So, if you consider that this kind of potential barrier exist between a normal lattice point and a vacant lattice site. Because, that is also equally important, that this site will have to be vacant so, that this can cross this barrier and come to this minimum energy position.

So, this is simultaneously important and actually the vacancy diffusion and the atomic diffusion or ionic diffusion they are coupled. So, if it is going to this side vacancy is going to the opposite side. So, here as you can see that, there is an energy difference between this two energy positions. In fact, that is the driving force.

So, this driving force is the energy, this energy term, and divided by some kind of distance. So, in this case I am taking this distance as lambda. So, I can always define this force. And, per atom if you consider then you will have to divide it by Avogadro number.

And, the driving force is basically the chemical potential gradient so, d mu by dx. So, f I consider is a force per atom and Avogadro number is involved. And, there is a difference between the energy barrier in forward and backward direction of course, the forward direction it will come ah, but if it wants to go back to the backward direction then you will have to cross an additional barrier.

So, if I consider that, the difference of energy barrier in forward and backward direction, then, I can write this relation. This energy is related to force and distance and a minus term is involved here, because of the gradient. And, then I have this mu term and mu exactly this Avogadro number I have put inside. So, it is d mu by Avogadro number by dx.

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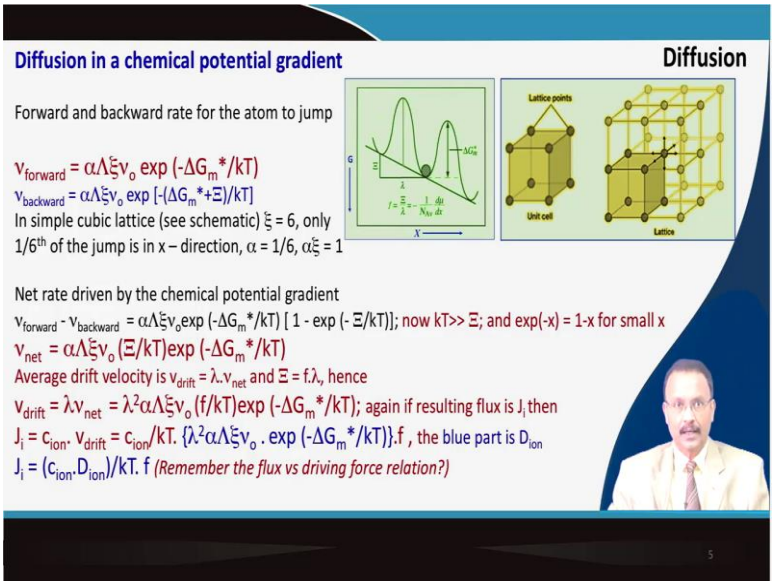

So, now let us consider that diffusion in a chemical potential gradient and consider two different types of jump; one is the forward jump, which is given by this relation. It is a straight forward relation alpha, then fraction of the site that is available, then zeta and frequency and this potential energy barrier. But, when it wants to go to the backward

direction, then you will have to cross an additional energy barrier, which is this e, the e term is additionally added to this.

And, now if you consider a simple cubic lattice, then the usefulness of your alpha and zeta will be clear. Because, there are 6 possible site as you can see, there are 6 possible site it can jump.

So, if you consider only a directional diffusion to the x axis, then certainly it is 1 by 6. So, your alpha is now 1 by 6. So, 6 is the possible coordination, which I defined at zeta. So, zeta is 6. So, this total thing is 1. So, the net rate now you can estimate that the frequency of forward bias and frequency of the backward bias. So, you write these two equations here, and then you make an approximation that the thermal energy for this diffusion that is much larger than the energy.

So, this term is much larger as compared to this term. So, your this total term is very small. So, e to the power minus x, if you expand it is 1 minus x. So, then this 1 and 1 will cut so, you come up with this relation right. So, this is your frequency and if you want to know the drift velocity; so, drift velocity will be this frequency which is having a 1 by second term, and you multiply it with the distance that is traversed.

So, that one will be lambda into v net and energy you know that that will be the force and the distance of diffusion. So, you can always calculate the drift velocity. So, drift velocity, once you calculate, then you can write this relation. So, if I write this relation in terms of the atomic flux, then a concentration will be involved and drift velocity will be there. So, I just do the algebraic part you also do it yourself.

So, you can come up with two part; one part is given this blue term, blue part. So, this blue part already I estimated, this is nothing, but ionic diffusibility. So, then this blue part you replace it by D ion. So, your total flux will be nothing, but concentration of the moving species and the diffusibility of the moving species divided by kT, which is energy term into the force, that is involved.

Now, you remember that we eventually coming to the same old equation, that any rate equation, any flux equation that is linearly proportional to the force. And, the diffusion I mean the constant of proportionality that bears different meaning. So, this also you are doing the same kind of thing you are facing the same kind of thing here.

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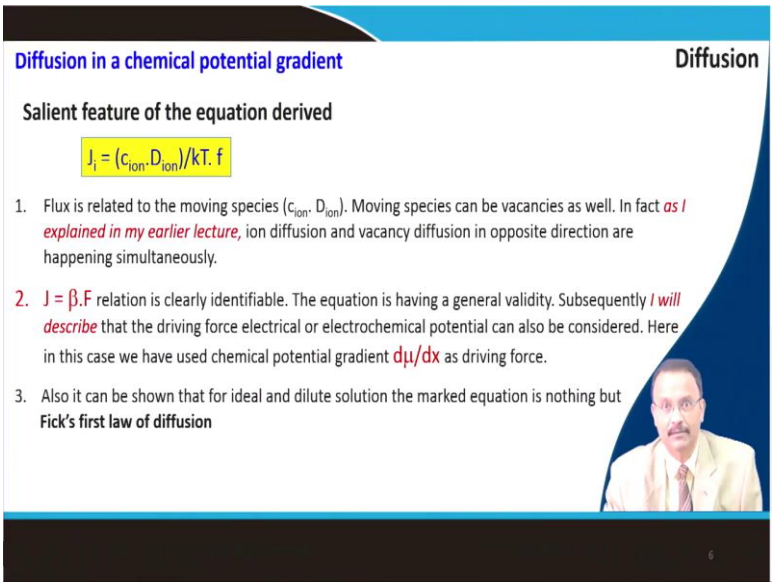

So, let us now have this relation and see what are the salient features of this equation whatever you have derived. So, this flux is related to the moving species. So, that is given by this relation. So, this can be vacancy as well not only the ion or atom that is moving.

So, ion diffusion and vacancy diffusion they will be in opposite direction, but happening simultaneously. The second one is the age old relation that J, the flux is linearly proportional to the force that you are applying. And, here the force is nothing, but chemical potential gradient. And, eventually you can also prove the Fick's first law from this fundamental understanding the first principle calculation.

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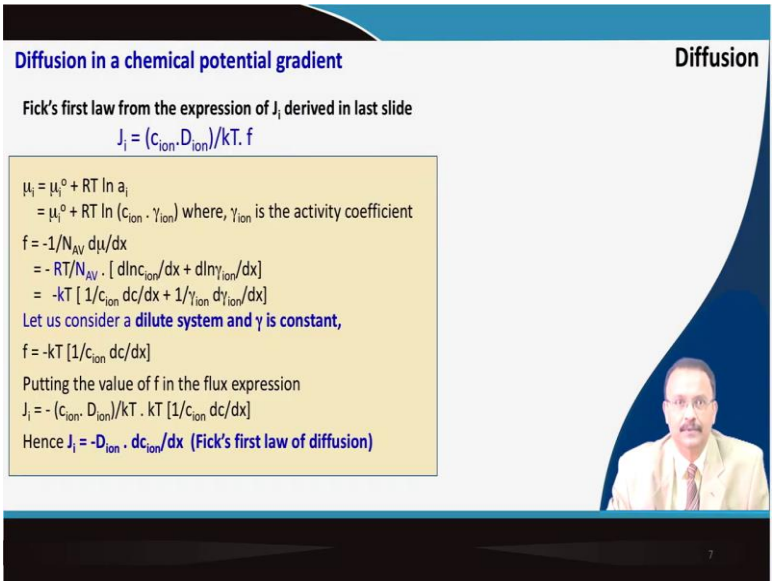

I will just sight you one example. So, this relation already you have derived and you know the chemical potential, I put that this is in the standard state and then gas constant temperature and activity is involved. So, now, the activity, you have concentration and activity coefficient. So, the activity coefficient is gamma.

So, the force is minus 1 by N av and chemical potential gradient. So, you put that value here. So, you put the value of this differential. So, that is the first one is with concentration you are differentiating and second one with the activity coefficient you are differentiating.

Now, if it is a very dilute system then the defect concentration is very low, say in activity coefficient you can take as constant. So, this differential term will vanish. So, your force will be minus kT 1 by concentration of the ionic species, which is diffusing and the concentration gradient.

So, this will come right away like this. Now, you put the value in the flux expression and you come up with this relation. So, eventually you will see that, this concentration, concentration will cut kT and kT will cut. So, you come up with the relation which is nothing, but Fick's first law, which I explained in my last class. So, that is the genesis of Fick's first law from first principle.

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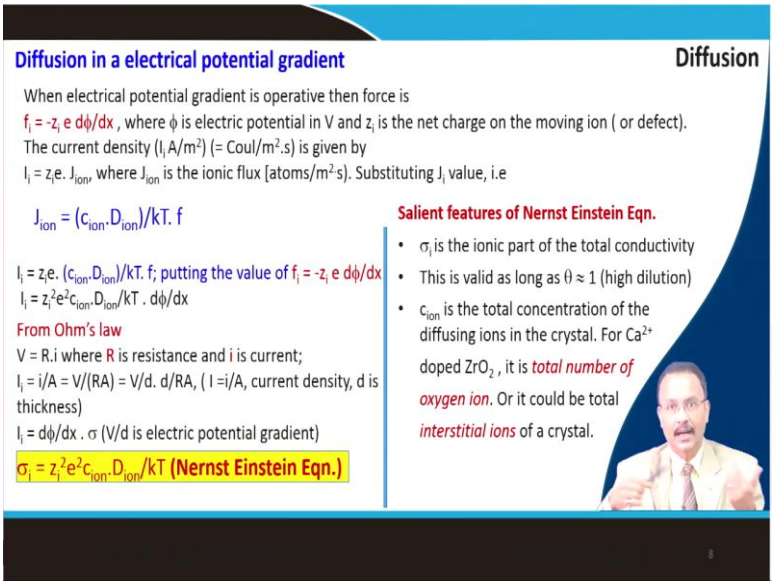

Now, in the electric potential gradient what is happening only the force term that will get changed. So, force term now this is a changing with the potential term. So, phi is the electric potential and Z i is the charge that is involved here. And, current density you can start to correlate, because any moving charge species or any moving species, that will give you the electric current, which is given as ampere per meter square. So, this is nothing, but coulomb per meter square into second.

So, you can have a current component, when you know this diffusion flux. So, you substitute that value here, your force is different now; the force is given by electric potential. So, you come up with this relation and you know that Ohm's law here, I have defined Ohm's law.

So, voltage is proportional to current and R is the proportionality constant. So, here you assume that, you have a sample of thickness D and the area is A. So, from this resistance, you can calculate the resistivity and eventually the conductivity. So, now, you relate your conductivity with the diffusion coefficient from this relation just do it.

And, you will find that, you can have a correlation between the ionic conductivity and the diffusion coefficient of the diffusing species. So, this is Nernst Einstein equation, which relates the ionic conductivity with the diffusion coefficient of ion. And, other terms are also involved, total charge is involved the concentration of the moving species is involved temperature is involved. So, this is the famous Einstein equation.

So, the salient feature of this equation is the sigma is a part of ionic part of the total conductivity. You may have ionic conductivity and electronic conductivity both in an oxide material, a non-metallic ceramic material.

So, this is valid as long as theta is almost 1; that means, it is having a very high dilution of the defects. And, C ion is the total concentration of the diffusing species. Now, remember that when you are talking about an aliovalent dopant say, calcium you are doping in zirconium oxide, then oxygen vacancy will be created. So, in that case oxygen ion will be the moving species.

So, in other case, if interstitial ion is moving then that is the moving species. So, that should be kept in mind sometimes it should be vacancy diffusion as well. So, what exactly you are doing, whether it is an intrinsic defect or extrinsic defect that you should be clear of.

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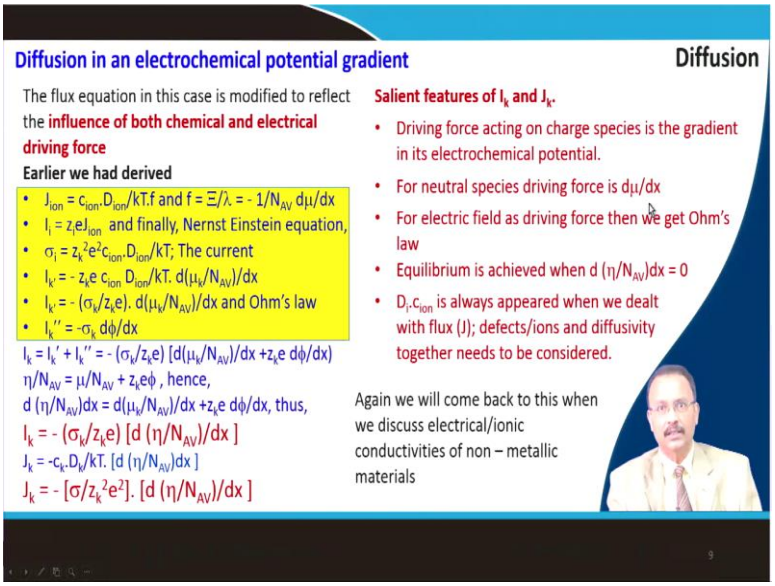

Now, let us see the addition of these two forces. The first one is a chemical force, which is a chemical potential gradient and second one is an electric force. So, now, you combined it, that is your electrochemical potential. The marked equations they are all derived including the Ohm's law the Nernst Einstein equation.

So, they are all derived, now what I am doing I am taking the two part of this current, whatever the resulting current, that is having two parts. And, one is driven by the

chemical potential force and another one is driven by the electric potential force. So, that gives rise to the total current.

And, eventually once I get the total current, I can get the total flux density also of the moving species. And, the relation is this one, that if you consider both this driving force are there, then the total moving species this relation will be valid.

So, here chemical electrochemical potential is a driving force. Now, if it is a neutral kind of sample, like metal, then it is only chemical potential. And, for electric field driven force, when that is the driving force, then Ohm's law is valid. And, of course, the equilibrium will be there, when this differentiation of this chemical potential gradient will be 0.

And, this term that diffusion coefficient and your concentration of defect that will always appear, when we usually deal with any flux of diffusivity. So, together it needs to be considered. So, not only the diffusibility of the moving species.

But, also the concentration of the moving species, it can be interstitial, it can be a atomic jump, it can be vacancy diffusion. So, together it must be considered. So, this equation are extremely important in all these equation, whatever I have derived.

Having different types of driving force; chemical potential, electric potential, electrochemical potential, they are extremely important in order to understand the conductivity. Effect of this material, ionic conductivity of this materials, for fuel cell, for battery nowadays they are so, important for you to understand. So, we will again come back to this. And, how this relations one can use for any practical purpose we will just revisit it, when I talk about this.

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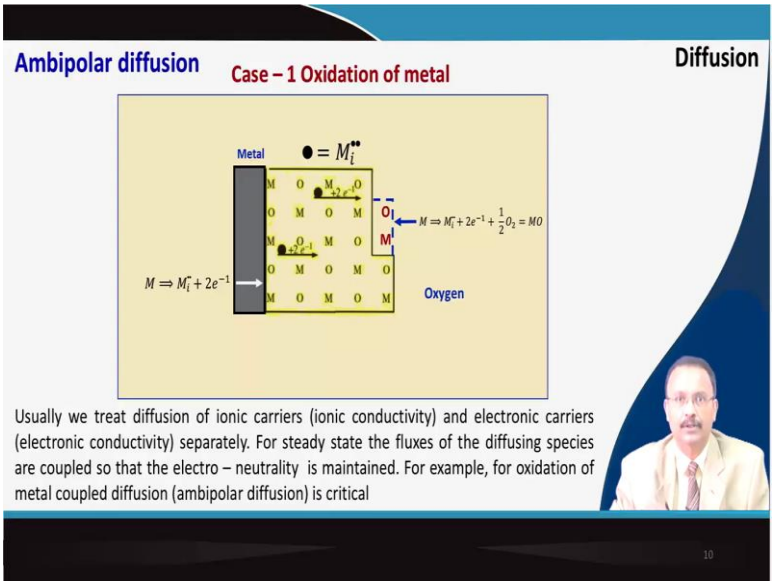

Now, another interesting thing that you must consider, that usually we treat diffusion either when ion carrier ions are moving. So, we get ionic conductivity or electrons can also move in certain condition, because as you know that the band gap of this material is very large.

So, as such the band to band transition rarely happens an electron goes to the conduction band and delocalized. So, that problem is always there, because the band gap is very high, but there are various defect state. For example, oxygen vacancy would be there metal vacancy can be there.

So, the first one can entrap electron, the next one can entrap hole and they create defect levels near to the conduction band in case of oxygen vacancy, or in case of metal vacancy a band near the valence band. So, they will start to conduct the energy difference is very small.

So, you will have to consider for in the steady state, somewhere the diffusing species are coupled with the other charge carrier species like electron. And, this is the case for many practical applications. I will sight some of the examples, the first one is metal oxidation a metal is simply being oxidized.

So, you have a metal interstitial and metal interstitial is positively charged. So, in order to maintain local charge neutrality you have electron entrapped. So, both of them are moving together. So, when both of these things moves together, then we call this is a ambipolar diffusion. And, in case of this ambipolar diffusion it goes through this lattice

this is the oxide lattice, this is the metal part here is the oxygen. So, metal oxide films are growing, which is the ceramic part you can consider.

And, then eventually it comes in the proximity of oxygen and then there is a reaction takes place and slowly metal oxide grows. So, that is the mechanism that you need to have for this ambipolar diffusion.

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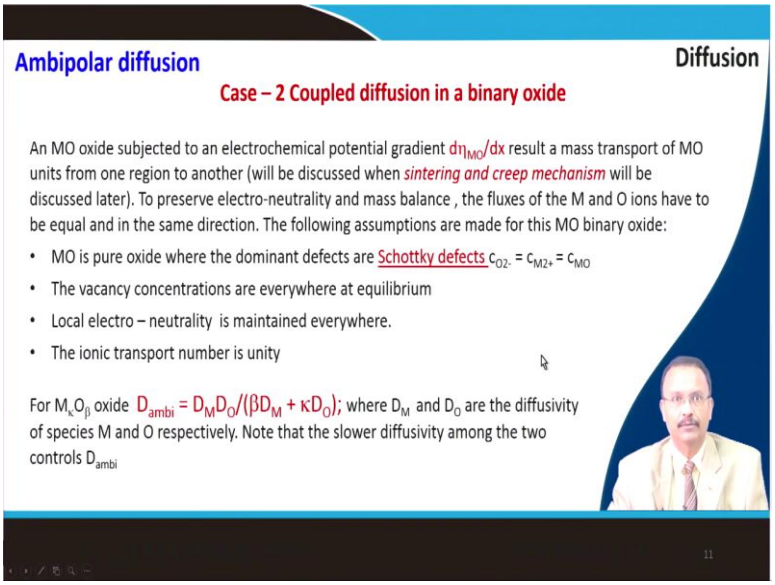

Second one is something similar, which is coupled in a binary oxide. In binary oxide you know that you can have a Schottky defect. So, you have a metal vacancy and you have a anion vacancy as well and both of them can move together.

So, for this ambipolar oxide this diffusion, coefficient, you can write through this simple relation, where individual diffusibility of metal and oxygen you need to consider. So, this is a typical example for the Schottky defect.

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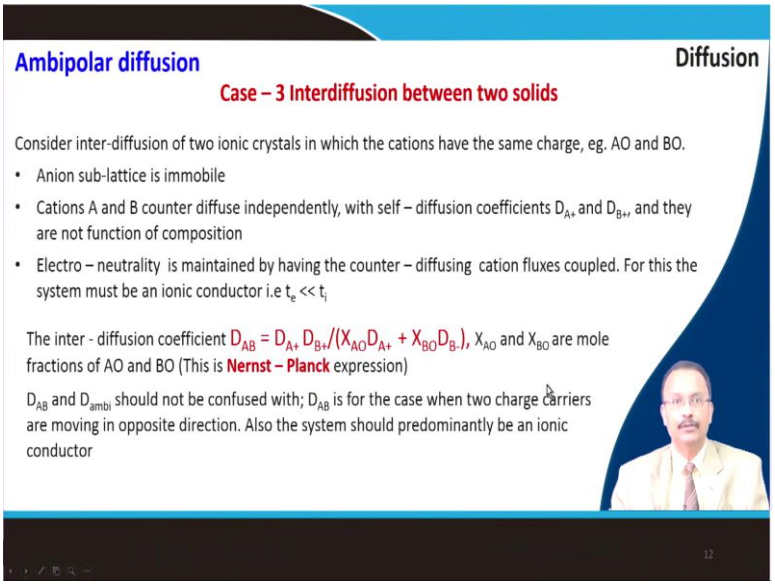

When solid solution forms, then it is similar, but in that case two diffusing species they are moving towards each other. And, they eventually form a solid solution. In earlier cases cation vacancy, anion vacancy are moving in the same direction towards the crystal lattice surface, but in this case they are reacting forming a solid solution.

And, this ambipolar diffusion coefficient can be given by this simple equation where the individual molar fraction is important. So, this is nothing, but Nernst Planck expression of this ambipolar diffusion.

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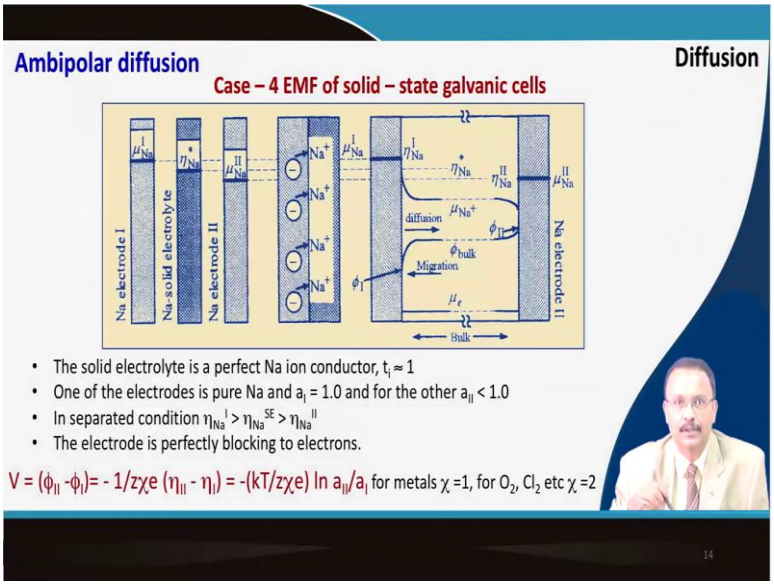

The fourth one, which is important I will consider this in details when I will talk about the battery rechargeable battery. So, that is the EMF in a solid state galvanic cell, where the electrode is having different chemical potential than the electrolyte.

And, here you can define this the voltage, which is generating out of this electrochemical potential difference and that is useful for you to make eventually the battery. So, here also the ambipolar diffusion, that is taking place in this case also.

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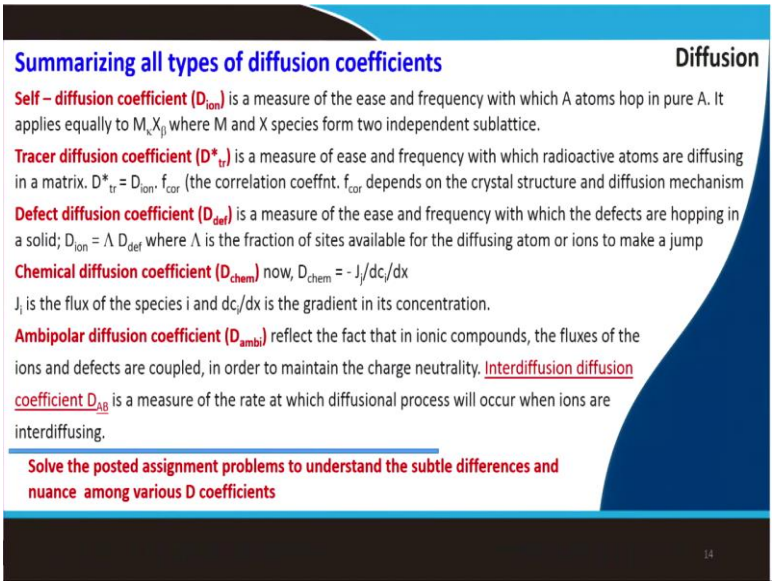

So, if you now summarize all types of diffusion coefficient, then you will be comfortable to know that we talked about self-diffusion coefficient. We talked about tracer diffusion coefficient and tracer diffusion coefficient is related to the self-diffusion coefficient.

So, there is a correlation coefficient is involved. We talked about defect diffusion coefficients, we talked about chemical diffusion coefficient and to understand the Fick's Law, and various types of ambipolar diffusion coefficients. So, some of the problems I have set where the subtle differences between amongst this kind of diffusion coefficients are well understood.

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And, these are the reference from the book by Barsoum and there are other excellent references are available.

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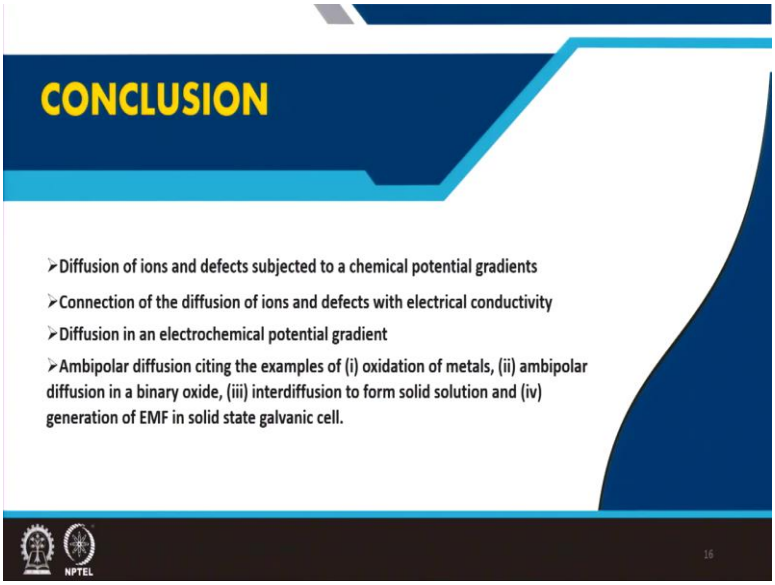

And, we now talked about the diffusion as a whole for the diffusion without any kind of gradient and then three different types of gradient, and that helped us to identify various types of diffusion coefficient.

Thank you for your attention.