Electroceramics
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Lecture - 12

So, welcome to this new lecture. So, first we will review this last lecture, which where we started the basically defect migration and the impact of this migration on the properties. So, in the context of defect migration, the first important phenomena is diffusion.

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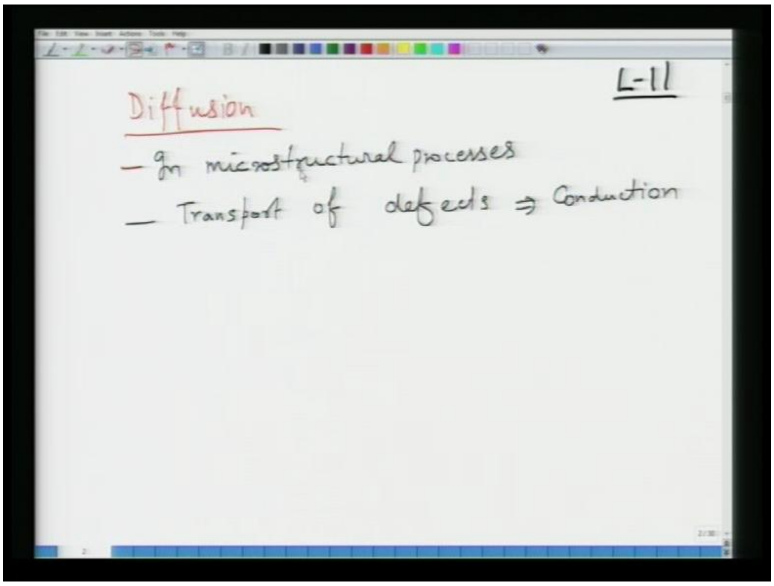

L-11

Diffusion

— In microstructural processes

— Transport of defects ⇒ Conduction

Now, diffusion is a very important phenomena in many micro structural processes such as in sintering, grain growth etcetera, and basically and this here in this context, this means transport of defects, which is related to conduction. So, then we looked at the diffusion kinetics.

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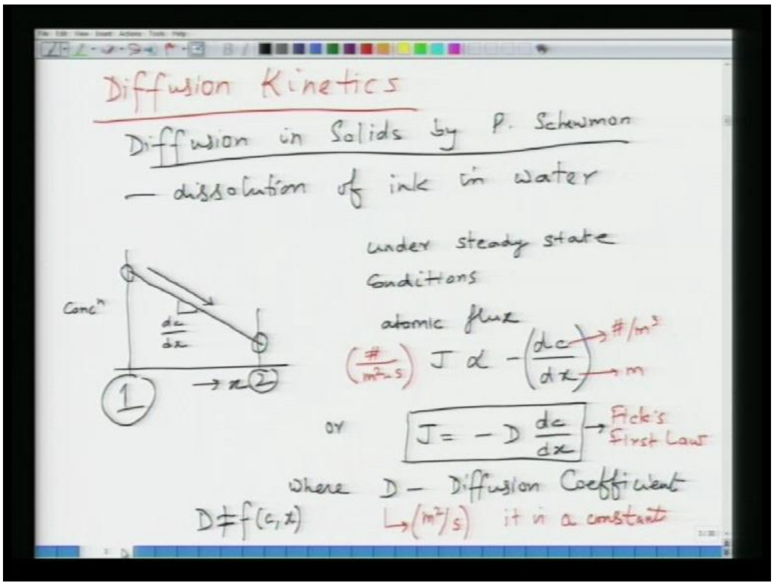

Diffusion Kinetics

Diffusion in Solids by P. Schewmon

— dissolution of ink in water

under steady state conditions

atomic flux

$\left(\frac{\#}{m^2 s}\right) J \propto -\left(\frac{dc}{dx}\right)$ → $\#/m^3$ → m

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

where D – Diffusion Coefficient

$D \neq f(c, x)$ ↳ (m^2/s) it is a constant

So, basically we looked at first the Fick's first law, which says that diffusion flux is proportional to the concentration gradient; and in most circumstances diffusion occurs in the direction from higher concentration to lower concentration.

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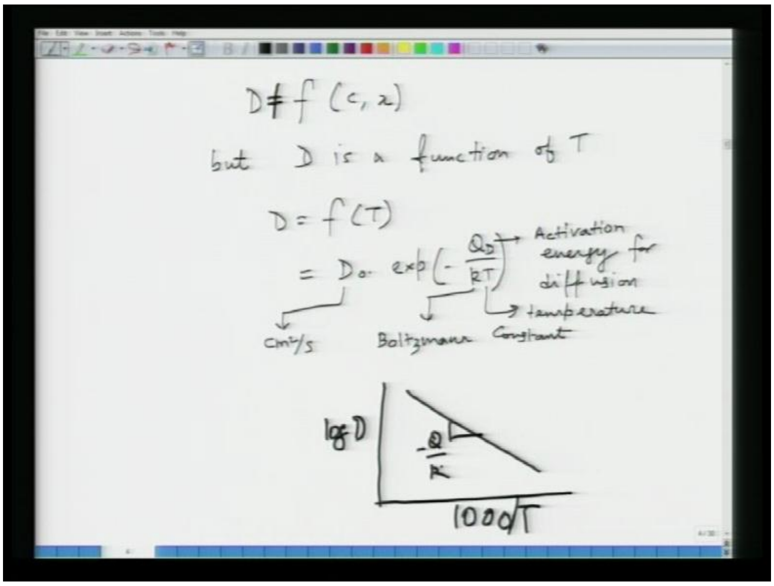

$D \neq f(c, x)$

but D is a function of T

$D = f(T)$

$= D_0 \exp\left(-\frac{Q_D}{kT}\right)$ → Activation energy for diffusion

D_0 → cm^2/s

k → Boltzmann Constant

T → temperature

And then we looked at the, we assume that the diffusivity is a constant, it is not a, it is independent of concentration and position, but it is a function of temperature. The relation is given as D naught exponential minus Q D by k T, which means it has a exponential dependence. So, what it what happens here is, the if you plot log D versus

1000 by T it varies like this, and the slope of this plot is determines the activation energy, which is minus Q by k.

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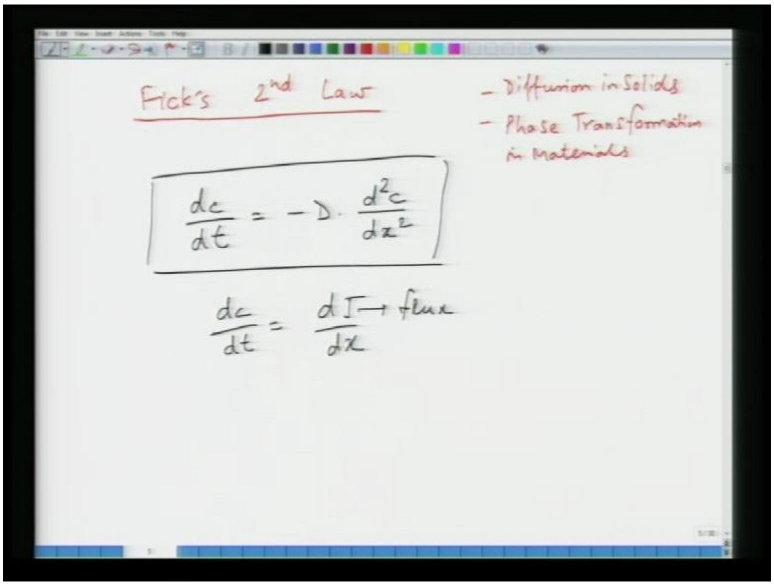

Fick's 2nd Law

- Diffusion in Solids
- Phase Transformation in Materials

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

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

And then we looked at what is the Fick’s second law, which is actually not a law, but a derivation, where we see, what is the rate of change of concentration and related to the basically the flux. And then, we went into what is diffusivity.

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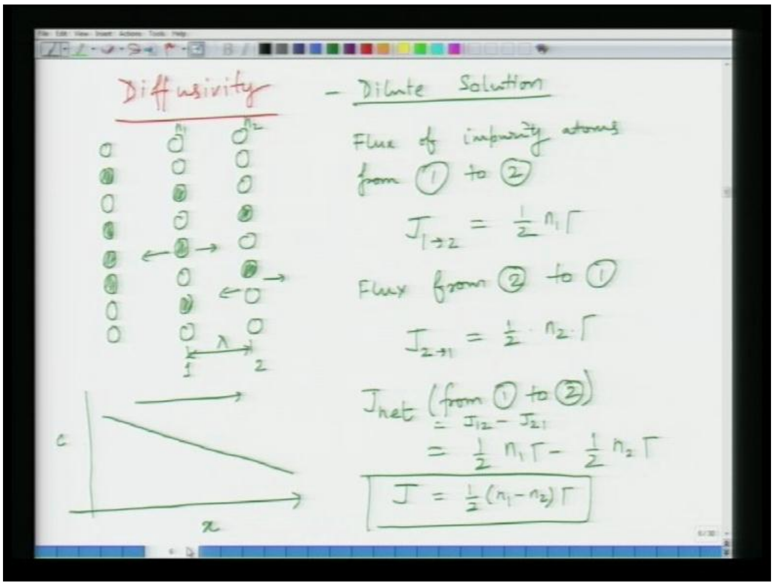

Diffusivity

- Dilute Solution

Flux of impurity atoms from ① to ②

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

Flux from ② to ①

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

J_{net} (from ① to ②)

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

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

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

So, taking the case of dilute solutions took number of for example, we looked at the planes of atoms in a material, and we looked at the flux from one plane to another back and forth, and from that we could find out, what is the net flux.

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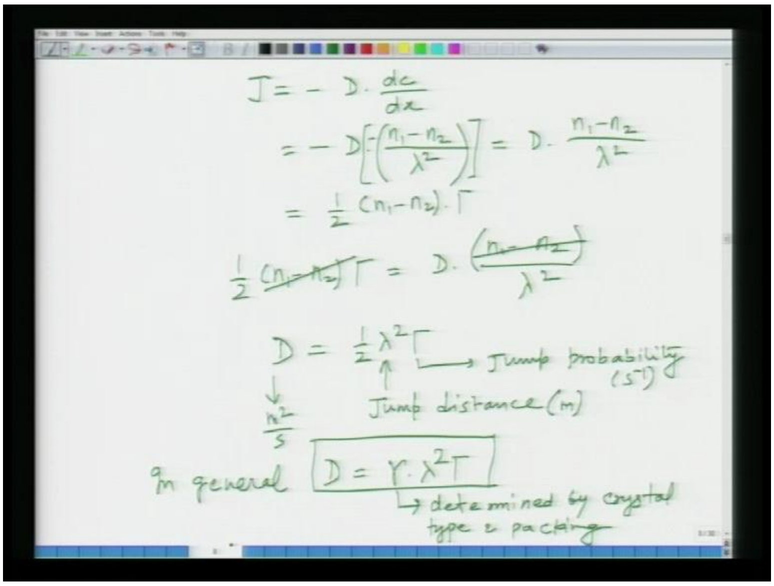

$$J = -D \cdot \frac{dc}{dx}$$

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

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

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

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

Γ → Jump probability (s^{-1})

λ → Jump distance (m)

D → $\frac{m^2}{s}$

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

γ → determined by crystal type & packing

From this we derived what is diffusivity as a function of a constant, which is determined by the crystal type and packing density lambda, which is a jump distance and tau which is the jump frequency.

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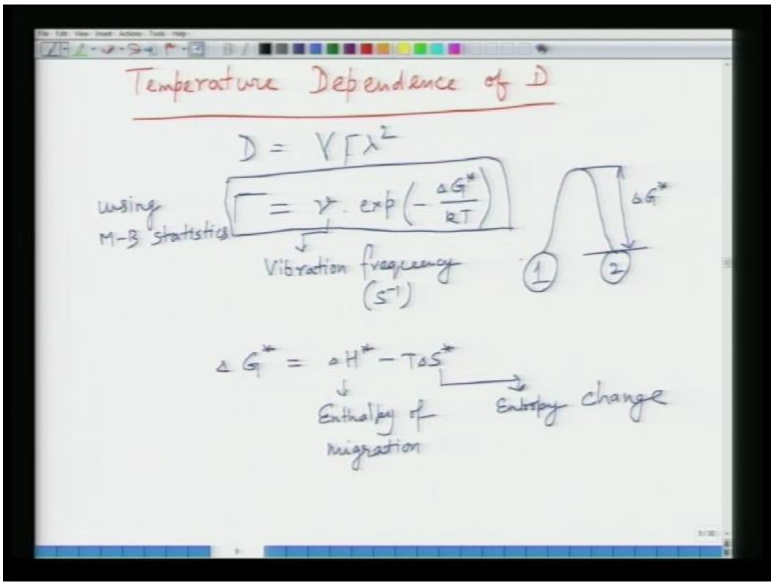

Temperature Dependence of D

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

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

ν → Vibration frequency (s^{-1})

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

ΔH^* → Enthalpy of migration

ΔS^* → Entropy change

From this we went on further to look into, what is tau and tau can be related using Boltzmann statistics to exponential minus of delta G star by k T, where delta G star is nothing but an energy barrier, which has to overcome when an atom moves from one equilibrium state to another equilibrium state.

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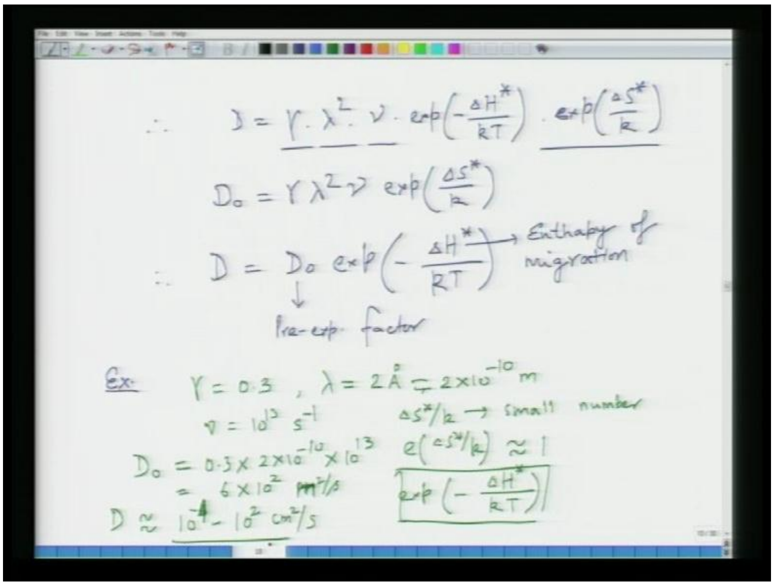

$$\therefore \quad D = \underline{\gamma} \cdot \underline{\lambda^2} \cdot \underline{\nu} \cdot \exp\left(-\frac{\Delta H^*}{kT}\right) \cdot \underline{\exp\left(\frac{\Delta S^*}{k}\right)}$$

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

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

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

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

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

$= 6 \times 10^{2}\,\text{m}^2/\text{s}$ $\boxed{\exp\left(-\frac{\Delta H^*}{RT}\right)}$

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

As a result, we get the temperature dependence of diffusivity and then we looked at various diffusion mechanisms. There are various mechanisms such as vacancy diffusion, interstitial diffusion, substitutional diffusion.

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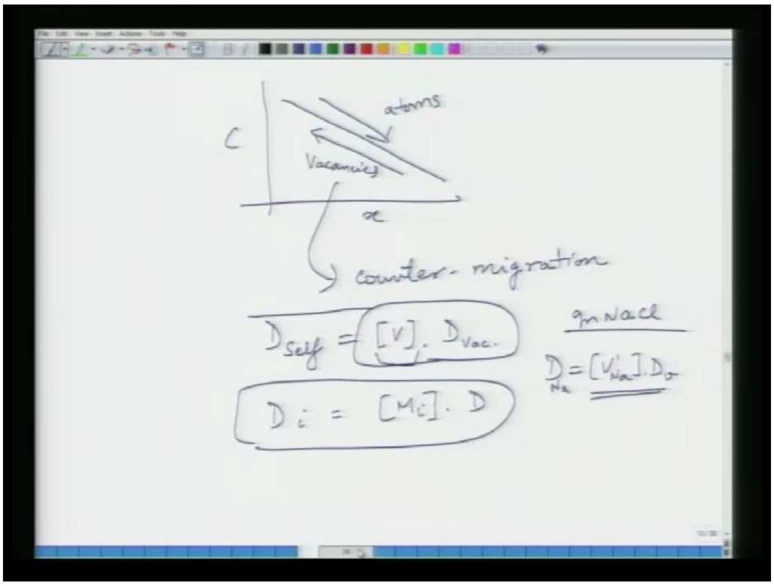

$$D_{Self} = \boxed{[V] \cdot D_{Vac.}}$$

$$\boxed{D_i = [M_i] \cdot D}$$

In NaCl

$$D_{Na} = \underline{\underline{[V'_{Na}] \cdot D_v}}$$

And it turns out that the diffusion mechanisms, basically among all these diffusion mechanisms vacancy diffusion and interstitial diffusion have lower activation energy, because of least resistance offered by the lattice in the movement. We also saw that, since there is a countermovement of vacancies in atoms, the self diffusion coefficient or the interstitial diffusion coefficient can be related to the proportion or the concentration of vacancies or the interstitials.

So, for example, in NaCl this would be, sodium diffusion would be proportional to, would be equal to vacancy diffusion coefficient multiplied by concentration of sodium vacancies. Now, in this lecture here we will start. So, what we will now do is, we will take a take a look at the example of diffusion and for example, sodium chloride. And we will see what happens when sodium chloride is in pure form, and what happens when sodium chloride is not in pure form.

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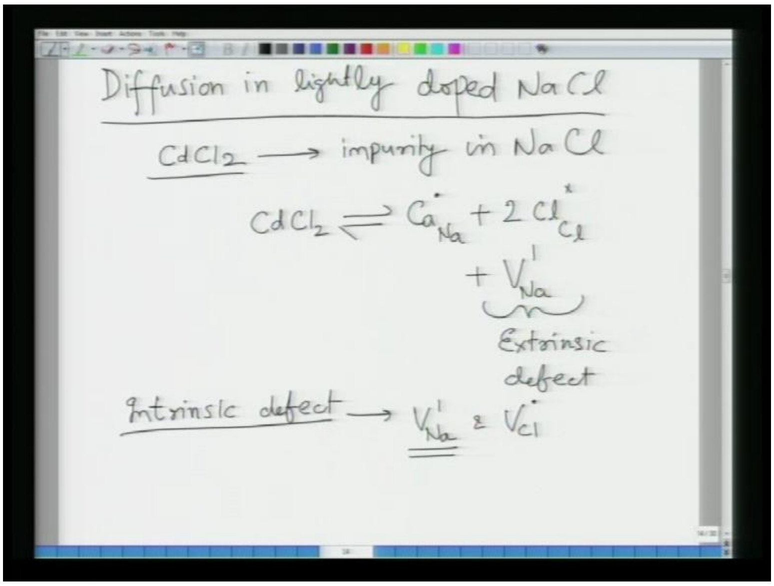

Diffusion in lightly doped NaCl

$\underline{CdCl_2} \longrightarrow$ impurity in NaCl

$$CdCl_2 \rightleftharpoons Ca^{\bullet}_{Na} + 2\,Cl^{x}_{Cl} + \underbrace{V'_{Na}}_{\text{Extrinsic defect}}$$

$\underline{\text{Intrinsic defect}} \longrightarrow \underline{\underline{V'_{Na}}}$ & $V^{\bullet}_{Cl}$

So, sodium chloride, so basically we will say diffusion in lightly doped NaCl. So, sodium chloride is an important material; it is used in electrolyte and many applications and that is why it is a good example for providing a picture of diffusion. So, sodium chloride contains cadmium chloride, is a common impurity in sodium chloride and it is present in very small quantities.

So, when you dope cadmium sodium chloride with cadmium chloride what happens is; your cadmium goes to sodium site. Now, when cadmium goes to sodium site it will give one extra positive charge. So, C d Na dot plus, let us say if both the chlorines go to chlorine chlorine sites, so they these will be charge less.

So, now we do not have the charge balance and also we do not have the site balance, because both the chlorines have gone to chlorine sites, which means for two of these chlorine sites I should have two of these sodium sites. One of those sodium sites is occupied by calcium and another one must be empty. So, V Na and this will carry 1 negative charge, this will be the defect reaction.

So, this is your extrinsic defect formation. So, this is your extrinsic defect, extrinsic defect means that defect, which is formed due to impurities. Now, what is the intrinsic defect? Intrinsic defect we know in NaCl, NaCl is very prone to having Schottky defects. So, intrinsic defects is V Na and V Cl. Now, V Cl, V Na in NaCl is more mobile as compared to V Cl. So, we will compare this formation of V Na and its impact on diffusion. So, in whatever the scenario is now; whether it is extrinsic scenario, intrinsic scenario the diffusivity of sodium D Na is governed by vacancy concentration.

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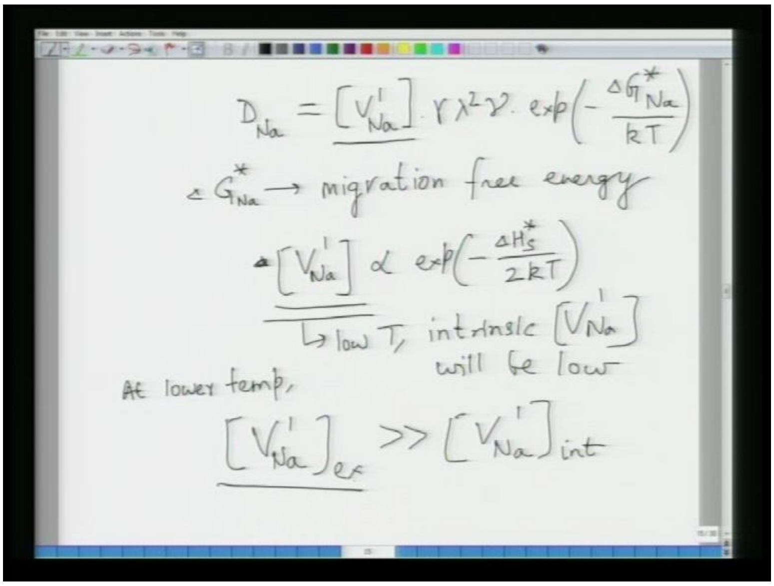

$$D_{Na} = \underline{[V'_{Na}]} \cdot \gamma \lambda^2 \nu \cdot \exp\left(-\frac{\Delta G^*_{Na}}{kT}\right)$$

$\Delta G^*_{Na} \rightarrow$ migration free energy

$$\underline{\underline{[V'_{Na}]}} \propto \exp\left(-\frac{\Delta H^*_s}{2kT}\right)$$

↳ low T, intrinsic $[V'_{Na}]$ will be low

At lower temp,

$$\underline{[V'_{Na}]_{ex}} >> [V'_{Na}]_{int}$$

So, we will have D Na is equal to V Na multiplied by gamma lambda square nu into exponential of minus delta H star Na divided by k T. In fact, it should be delta G star because we will break it down little later. So, if this is the expression for diffusivity, where delta G star Na is nothing but free energy, migration free energy associated with sodium vacancies, the sodium vacancies, where V Na is the sodium vacancy concentration.

So, now what happens at that, at lower temperatures your Cd Cl 2, let us say if it is present in PPM quantities. Now, you know from the defect reaction that for each cadmium ion you have one sodium vacancy. So, basically the number of sodium vacancies in sodium chloride is going to be equal to number of cadmium ions or cadmium chloride concentration. So, at lower temperatures when Schottky defect formation does not give rise to large number of vacancies because we know that, intrinsic defect concentration V Na is proportional to exponential of minus delta H s star divided by 2 k T.

So, at lower temperatures the intrinsic, lower temperature means, intrinsic V Na concentration will be low. So, what happens is that at lower temperatures, the concentration of V Na is determined by presence of impurities. If you have Cd Cl 2 present in larger quantities than those than, let us say that number of vacancies, which are created by intrinsic ionization, in that case the vacancy is. So, at lower temperatures V Na extrinsic, which is due to presence of Cd Cl 2 in moderate quantities will be much larger than V Na intrinsic. So, what will now is this extrinsic concentration temperature dependent? It is not temperature dependent because it is solely dependent upon the concentration of vacancies.

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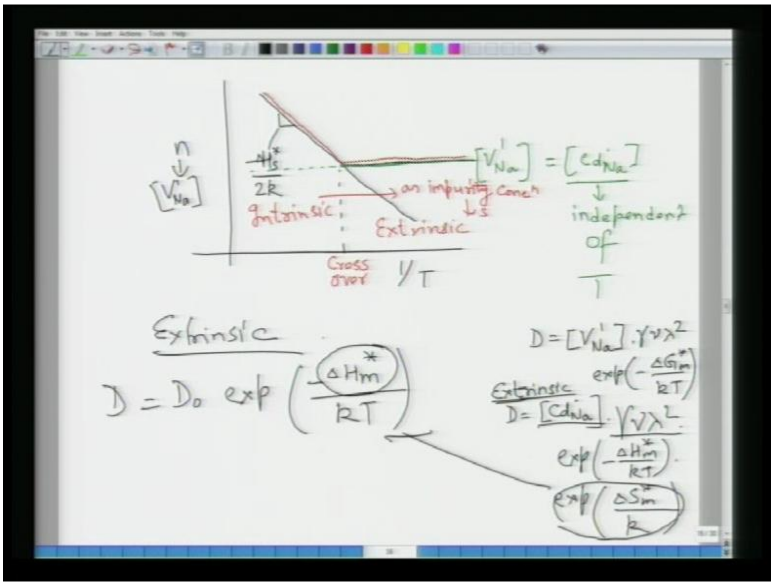

So, now what happens is, so when you plot the vacancy concentration, now let us say concentration as a function of temperature, let us say 1 by T. Now, in the lower temperature site let me just. So, your, this is n would mean basically V Na concentration. So, intrinsic vacancy concentration varies like this as a function of temperature and this slope will be equal to delta H s star divided by 2 k. If you start coming now, if the sodium chloride was impure and if you start coming from low to high temperature, up to certain temperature the concentration of sodium vacancies due to extrinsic impurities is constant, because extrinsic impurities concentration does not change as a function of temperature. So, this V Na is basically equal to Cd Na and this is independent of temperature, which means concentration of V Na over certain temperature range is going to be remain, going to be basically a constant.

Now, however there is going to be a point when thermally created vacancies, due to Schottky defect are going to take over this. So, now what happens? After a certain temperature the concentration of, so this curve will follow like this. Now, after a certain temperature the thermally created vacancies start creeping in. So, those starts dominating, what happens is that up to after this point the V Na is now governed by temperature. So, you have two regions here, if I now draw these two regions.

So, this will be overall concentration, intrinsic region followed by extrinsic region. So, this will be your intrinsic vacancy creation region and this will be your extrinsic vacancy creation region. What it basically means is that, in the extrinsic region the concentration of vacancies is going to be determined by concentration of impurities; in the intrinsic region concentration of vacancies is going to be determined by temperature.

Now, this crossover temperature, so this crossover what will this depend upon? Now, crossover will naturally shift to right if the impurity concentration was low. So, as impurity concentration decreases this crossover will shift towards right, which means the behaviour will become more and more intrinsic in nature. So, basically now when you plot diffusivity, so in case of diffusivity your intrinsic diffusivity will be like this because intrinsic you know that, diffusivity is equal to V Na into gamma nu lambda square exponential minus delta G star divided by k T.

Now, if you break this up, what this means is that D is equal to, if you just take an intrinsic region then V Na is governed by Cd Na, which is a constant. Just sorry extrinsic region, it is not intrinsic region, if I said intrinsic region. So, extrinsic region D C d will be equal to gamma nu lambda square into exponential of minus delta H star, H m star divided by k T into exponential of delta s m star divided by k. So, what is the activation energy in this case? In this case the activation energy, if I just if I just rub this out I will plot this on the next slide. So, in this case, extrinsic case D will become, this is a constant for a given temperature, these are constant and this is a constant. So, this will become D naught exponential minus of delta H m star divided by k T. So, the slope of the curve in the extrinsic region will be this.

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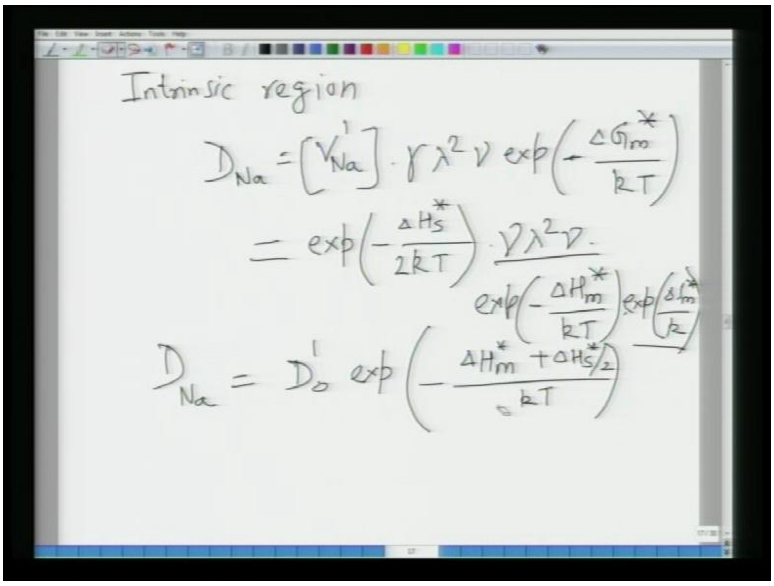

Intrinsic region

$$D_{Na} = \left[V'_{Na}\right] \cdot \gamma \lambda^2 \nu \exp\left(-\frac{\Delta G_m^*}{kT}\right)$$

$$= \exp\left(-\frac{\Delta H_s^*}{2kT}\right) \cdot \gamma \lambda^2 \nu \cdot \exp\left(-\frac{\Delta H_m^*}{kT}\right) \exp\left(\frac{\Delta S_m^*}{k}\right)$$

$$D_{Na} = D_0' \exp\left(-\frac{\Delta H_m^* + \Delta H_s^*/2}{kT}\right)$$

Now, let us examine the intrinsic region. We know that D Na is again equal to again V Na into gamma lambda square nu exponential minus of delta G m star divided by k T. Now, in the intrinsic region V Na is equal to exponential of, minus of delta H s star or you can say H Na star, H s star divided by 2 k T gamma lambda square nu into exponential of minus delta H m star divided by k T, into exponential of delta s m star divided by k. So, now what is constant here, this is a constant, this is a constant.

So, D Na is equal to D naught some constant, let us say in this case D naught prime, exponential of, minus of delta H m star, 2 H m star plus delta H s star divided by 2 k Tor you can write it as delta H s by 2 divided by k T. So, this will be D naught prime exponential delta H m star plus delta H s by 2 divided by k T.

So, naturally you can see that in this case the activation energy has gone up by the amount delta H s star divided by 2. So, when you plot this.

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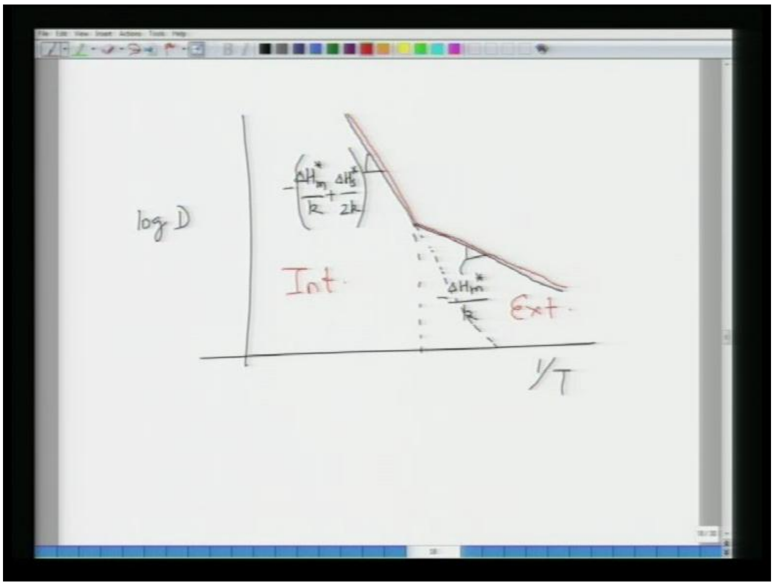

So, let us say this is log D and this is 1 by T and let us say this is the crossover point for composition, at a particular composition of impurities. So, up to this point my, I can plot this in this manner. So, this is low temperature to the cross over point, the activation energy in this case is going to be delta H m star divided by k, minus of delta H m star divided by k. Now, what is the behaviour going to be after this point? After this point I know that the activation energy has increased as a result the slope will become like this.

So, this will become minus of delta H m star, H m delta H m star divided by k plus delta H s star divided by 2 k. This will be the activation energy and if you just extrapolate this curve somewhere here, this will be the intrinsic line and this is your extrinsic line. So, what you see here is, so if I now represent the overall behaviour, the overall behaviour would be like this, this is the overall behaviour. So, this is your this is your intrinsic region and this is your extrinsic region. So, in a normal ceramic which contains some impurities as a result of whatever be the reason, is it may be because of processing, it may be because of intention, but whatever be the reason in a normal ceramic, which contains the impurities, typically the diffusion or diffusivity has two regions as a function of temperature. First region, from low temperature to a crossover temperature which is determined by the impurity concentration will be extrinsic region.

In this region since the vacancy concentration is solely determined by the impurity concentration, which is independent of temperature. The only activation energy which needs to be overcome or the energy which needs to be supply, supplied has to be equivalent to only the migration energy. However, at higher temperatures when thermally created defects start dominating in that case the activation energy becomes sum of migration energy as well as the defect formation energy. So, what it means is that basically you need to provide much more energy in order of diffusion to occur.

However, since higher thermal energy supports the formation of more defects, the thermally created defects dominate at these temperatures and as a result diffuse, intrinsic diffusion dominates. So, I hope that this point is clear that there are two regions in most of the ceramics, one is extrinsic region and one is intrinsic and this is also reflected in the in the in the conductivity plot as well, as we will see later on that conductivity is proportional to diffusivity.

So, now what we will do is that we will discuss. So, we have discussed what diffusivity is that and what diffusivity is in ionic systems or in ceramics. Now, we will discuss some of the electrical properties and then we will establish a relation between electrical and properties and diffusivity. So, now, we will take what is called as mobility.

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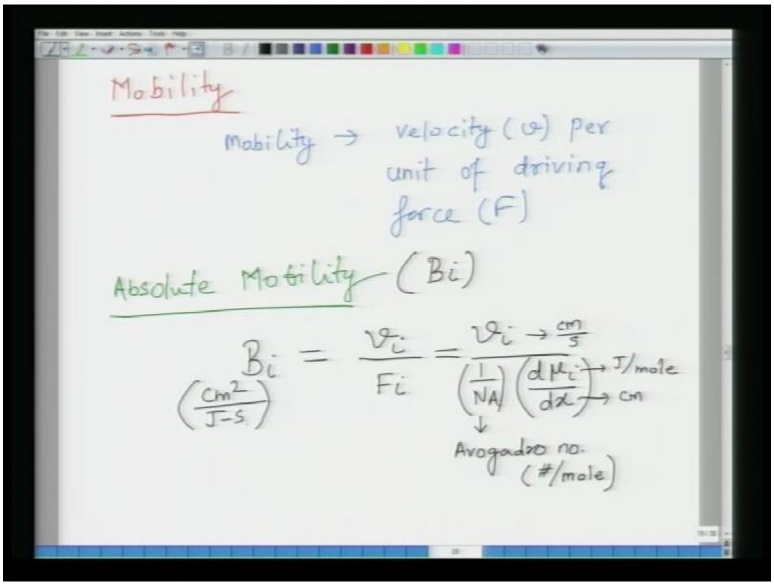

Mobility

Mobility → velocity (v) per unit of driving force (F)

Absolute Mobility (B_i)

$$\underset{\left(\frac{cm^2}{J\text{-}s}\right)}{B_i} = \frac{v_i}{F_i} = \frac{v_i \rightarrow \frac{cm}{s}}{\underset{\substack{\downarrow \\ \text{Avogadro no.} \\ (\#/\text{mole})}}{\left(\frac{1}{N_A}\right)}\left(\frac{d\mu_i \rightarrow J/\text{mole}}{dx \rightarrow cm}\right)}$$

So, mobility as the name itself suggests it is ability to move, it is a very important term to define conduction in ionic solids and basically mobility is defined as, basically velocity of any species or any entity, velocity v per unit of driving driving force F. So, this is mobility is defined as velocity per unit driving force. This driving force could be a thermodynamic force, it could be a chemical force, it could be a electrochemical force, it could be electrical force any kind of force, but as a result of this force the velocity which is achieved, the ratio of this velocity to force is called as mobility. So, there are various forms of mobilities.

So, first form is called as absolute mobility. So, absolute mobility is defined as B i, i means ith species, v i into v i is equal to v. So, capital B i, B for boy is equal to v i this v is v means velocity divided by some force and this force can be determined as, which can be. So, v i divided by 1 by NA, NA is the Avogadro's number into d mu i by d x.

So, here you can see the units, this is your Avogadro number and mu i is the chemical potential of a species i, the unit of this is centimetre per second and you know what is the unit of this, unit of Avogadro number is, number per mole x is in, let us say centimetre and mu i would be in joule per mole. So, now you can see what the units are going to be the units will be in centimetre square because this centimetre will go up, yes. So, these mole, mole will cancel each other. So, this will become centimetre square per joule second.

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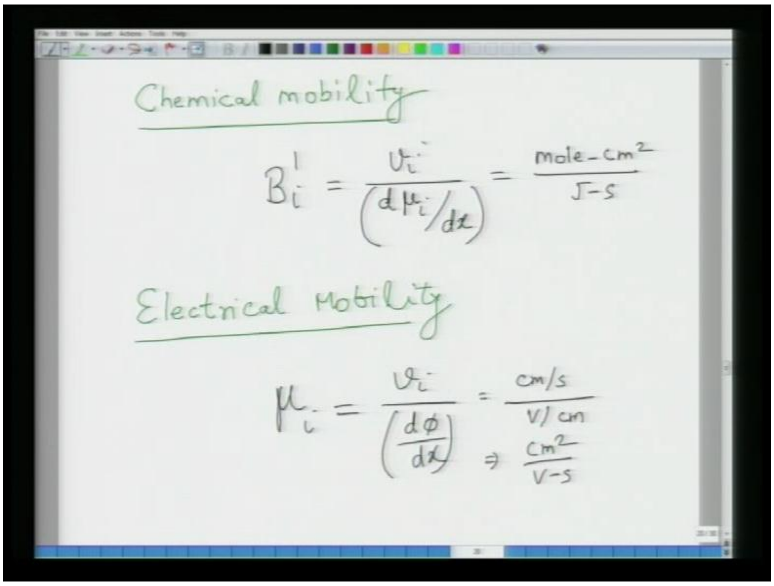

Chemical mobility

$$B_i' = \frac{v_i}{\left(d\mu_i/dx\right)} = \frac{\text{mole-cm}^2}{\text{J-s}}$$

Electrical Mobility

$$\mu_i = \frac{v_i}{\left(\frac{d\phi}{dx}\right)} = \frac{\text{cm/s}}{\text{V/cm}} \Rightarrow \frac{\text{cm}^2}{\text{V-s}}$$

So, this will be your absolute mobility. You can also define what is called as chemical mobility and chemical mobility is defined as B i, let us say prime and this is equal to v i divided by d mu i by d x. This is in units of mole centimetre square per joule second, in case of electrical mobility. So, basically this is the velocity and this is the chemical force.

Electrical mobility is defined as mu, mu i this is equal to v i divided by d phi by d x, which is the force due to applied voltage or the electrical force and the units of this are basically centimetre per second divided by volt per centimetre or centimetre square per volt second.

So, these will be the units of electrical mobility. Now, in from the context of atomic transport, it was first Albert Einstein who pointed out that the one of the most general driving force for the atomic movement, which acts in the diffusion of species in a system is a virtual force. This virtual force is due to basically negative gradient of chemical potential or chemical potential as you know from the thermodynamic fundamentals is nothing but partial molar free energy.

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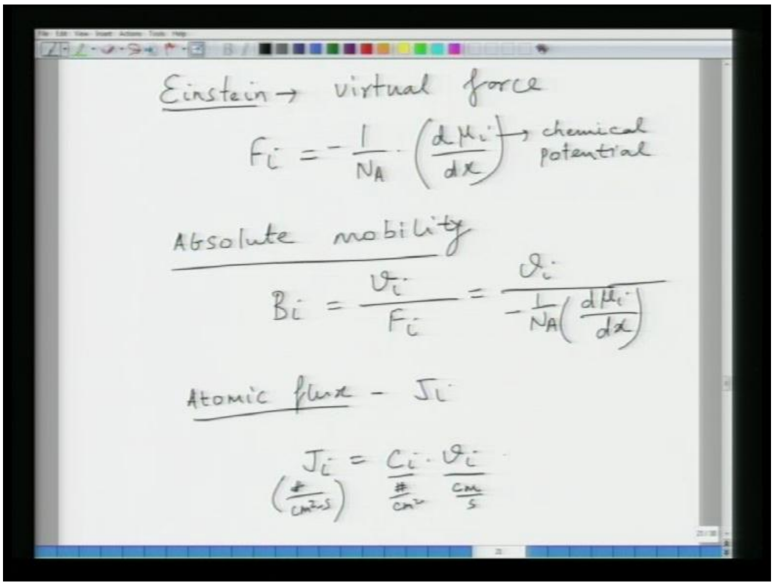

Einstein → virtual force

$$F_i = -\frac{1}{N_A} \cdot \left(\frac{d\mu_i}{dx}\right) \rightarrow \text{chemical potential}$$

Absolute mobility

$$B_i = \frac{v_i}{F_i} = \frac{v_i}{-\frac{1}{N_A}\left(\frac{d\mu_i}{dx}\right)}$$

Atomic flux - J_i

$$\underset{\left(\frac{\#}{cm^2 s}\right)}{J_i} = \underset{\frac{\#}{cm^2}}{C_i} \cdot \underset{\frac{cm}{s}}{v_i}$$

Now, this force is expressed as, so we can say this is. So, Einstein you should give credit to Einstein, who said that this virtual force is the reason is nothing but your, which is nothing but due to negative gradient of chemical potential. This force F i is equal to minus of 1 by NA, d mu i by d x. So, this is the virtual force, which acts on the particles during diffusion or transport of species in a system. So, this is the most general force. So, this mu i is nothing but your chemical potential and NA as you know is the Avogadro's number. So, in such a case I can write what is absolute mobility, the absolute mobility is B i is given as, v i I know what v i is divided by force, F i and I can write this as v i divided by minus of 1 by NA into d mu i by d x.

So, the absolute mobility, which we defined in the previous slide was basically the same thing. So, now what we have to do is that we need to find a relation between this mobility and the diffusivity, in order to write a and in order to create a formalism and to do that we need to first of all write what is the flux of atoms. What is the flux, atomic flux? So, we are considering diffusion in a system, diffusion is happening in a system.

So, diffusion of let us say any particular species, it may be defect, it may be interstitial whatever, but we are considering this as a species i. So, that diffusion is happening because of this virtual force, that virtual force arises because of negative gradient in chemical potential from higher to lower chemical potential. As a result you have a flux of atoms. So, this flux can be explained as nothing but C i multiplied by v i, that makes sense because flux is nothing but product of, what is the unit of flux? You know that mole per number of atoms or number of species passing through per unit area, per unit per square per unit time.

So, in this case this C i is the concentration and v i is the velocity and this sort of makes sense because v i is nothing but centimetre per second and this is nothing but numbers per centimetre cube. So, the units become numbers per centimetre square second.

So, flux which is also can be related to concentration gradient, we are not doing that at the movement. What we are saying is that, flux is because of negative gradient in the chemical potential. So, we are not relating it to the concentration gradient as yet. So, what we are saying is that, flux is nothing but number of atoms or a species passing through per unit square area per unit time, which is nothing, but product of concentration multiplied by their velocity.

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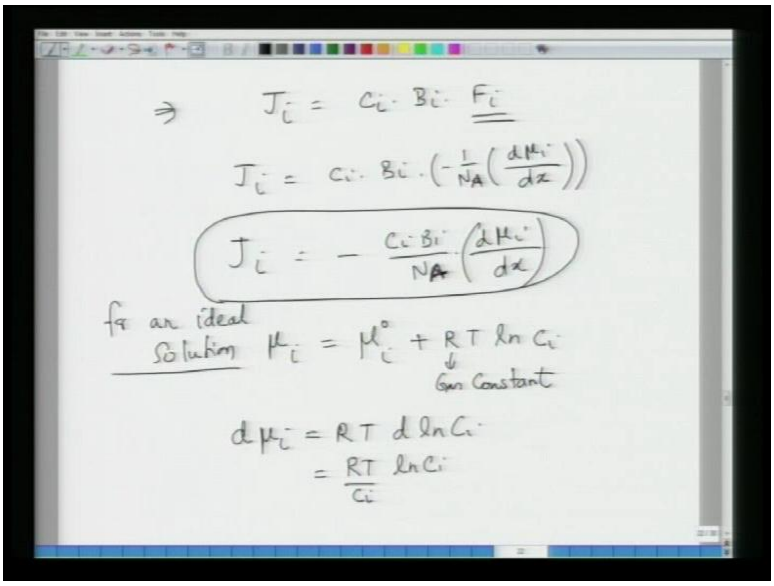

$$\Rightarrow \quad J_i = C_i \cdot B_i \cdot \underline{\underline{F_i}}$$

$$J_i = C_i \cdot B_i \cdot \left(-\frac{1}{NA}\left(\frac{d\mu_i}{dx}\right)\right)$$

$$\boxed{J_i = -\frac{C_i B_i}{NA}\left(\frac{d\mu_i}{dx}\right)}$$

for an ideal
$\underline{\text{Solution}}$ $\mu_i = \mu_i^0 + \underset{\substack{\downarrow \\ \text{Gas Constant}}}{R}T \ln C_i$

$$d\mu_i = RT \, d \ln C_i$$

$$= \frac{RT}{C_i} \ln C_i$$

So, this makes sense. Now, if J i is equal to C i, B i then I can also write J i is equal to C i multiplied by B i multiplied by F i because I know that small v i, velocity is equal to absolute mobility and multiplied by force.

Now, now what you need to do is that, I need to substitute for F i. So, J i is equal to C i multiplied by B i and what is F i, F i is minus 1 by NA multiplied by d mu i by d x. This is your J i expression and you can write it as, minus of C i, B i divided by NA into d mu i by d x. So, let us this, let us remember this expression we will come back to this in a while. Now, for an ideal solution with the unit activity of each of the species i, I can write this chemical potential as for an ideal solution. I can write mu i as mu i naught, which is the standard in the standard state plus RT l n C i.

Now, what I am saying is that. So, this R is nothing, but your gas constant, we have defined this R for the first time; so far we have been dealing with k. So, the change in the chemical potential can be written as, I can write d mu i as say this is for a standard state, d mu i naught will become equal to 0 and this will become equal to RT d l n C i. This can be further be written as RT l n C i divided by C i. So, from this what we will find out is we will found out what is d mu i by d x.

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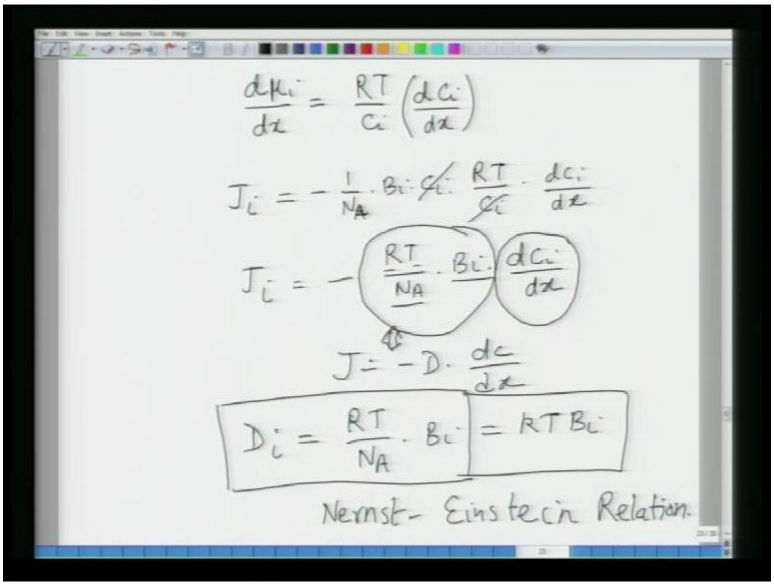

$$\frac{d\mu_i}{dx} = \frac{RT}{C_i}\left(\frac{dC_i}{dx}\right)$$

$$J_i = -\frac{1}{N_A}\cdot B_i\cdot \cancel{C_i}\cdot\frac{RT}{\cancel{C_i}}\cdot\frac{dC_i}{dx}$$

$$J_i = -\left(\frac{RT}{N_A}\cdot B_i\right)\left(\frac{dC_i}{dx}\right)$$

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

$$\boxed{D_i = \frac{RT}{N_A}\cdot B_i} \boxed{= kT B_i}$$

Nernst- Einstein Relation

So, d mu i by d x would be equal to RT by C i into d C i by, excuse me I made a mistake somewhere. This would be not correct. So, basically if you remove that what basically it is. So, d mu i is equal to RT d l n C i. Now, if I take this d mu i by d x, which will become RT by C i into d C i by d x. Now, you substitute this expression in this expression. So, what we get now is J i, expression for J i is minus of 1 by NA into B i C i into RT by C i into d C i by d x. C i, C i will cancel each other and what you will get is minus of RT by NA into B i into d C i by d x.

Now, in this expression if you look at this expression. Now, you have this has some similarity to the Fick's first law because you have a concentration gradient here and you have another factor, which is a constant or you can assume it as a constant at the movement. Because you have what you have is absolute mobility, Avogadro number temperature and gas constant, and what does this look like? This has a form of J is equal to minus d d c by d x. If you now compare these two what you can find is D i is equal to RT by NA multiplied by B i and this is a relation, which is between diffusivity and mobility. So, these two properties can be related to each other or alternatively you can write it as k T B i and this is called as Nernst Einstein relation.

So, this is the first formalism that we have established after knowing what diffusivity is and this diffusivity of a species can be related to another parameter, which is called as mobility. This mobility at the moment we are not defining it as any electrical mobility or anything, we are just saying this is a mobility which is because of because of virtual force, which is due to a negative chemical potential gradient, which causes diffusion in a system.

So, now what we will do is that, we will, now that we have found a relation between the mobility and the diffusivity we will take it further and we will establish an analogue to the electrical properties. In the end what we are going to use it in the context of electrical these only.

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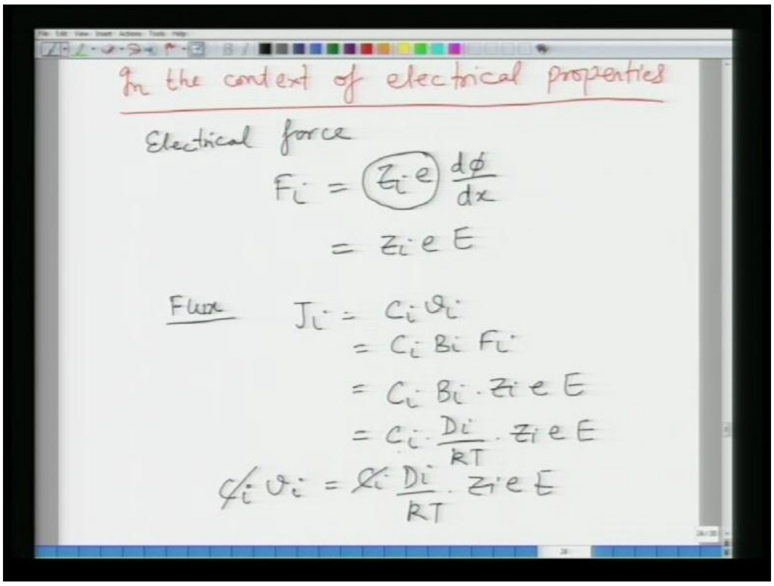

In the context of electrical properties

Electrical force

$$F_i = \boxed{z_i e} \frac{d\phi}{dx}$$

$$= z_i e E$$

Flux

$$J_i = C_i v_i$$

$$= C_i B_i F_i$$

$$= C_i B_i \cdot z_i e E$$

$$= C_i \cdot \frac{D_i}{RT} \cdot z_i e E$$

$$\cancel{C_i} v_i = \cancel{C_i} \frac{D_i}{RT} \cdot z_i e E$$

So, in the, let us say context of electrical properties. So, here in the, in the when we take about in the context of electrical properties we have to define the force, what is the electrical force. We have so far defined that diffusion is taking place and that diffusion is taking place because of a chemical potential gradient. Now, if you talk in terms of electrical context the movement happens because some electrical force.

This electrical force electrical force I can write it as, F i the force F, which acts on i’th particle. This is nothing but equal to z i e, d phi by d x, where z i e is the total charge on the particle and d phi by d x is equal to basically the potential gradient. This is equal to z i e E, which is the electrical filed v by v by d as you know it is. So, z i is the total charge or rather z i e is the total charge, z i is basically the atomic number and e is the not atomic number rather you can write, the valence of the species and E is the electronic charge.

So, using, if you use this relation you can write the flux as, flux we knew that it is nothing but C i into v i and this is nothing but C i to B i into F i. This is equal to C i B i into z i e into E, capital E. I know what is B i, B i if you look at the previous expression B i is equal to D i divided by k T. So, I can write this as D i divided by k T into z i e E. So, or alternatively you can write it and J i. So, I can write this as, so basically what you can do here now is C i into v i is equal to C i, D i by k T into z i e E.

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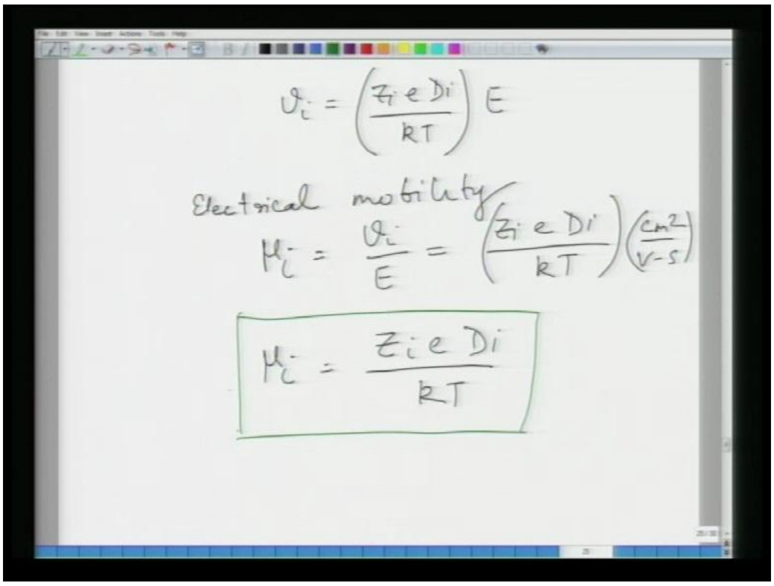

$$v_i = \left(\frac{z_i e D_i}{kT}\right) E$$

Electrical mobility

$$\mu_i = \frac{v_i}{E} = \left(\frac{z_i e D_i}{kT}\right)\left(\frac{cm^2}{V\text{-}s}\right)$$

$$\boxed{\mu_i = \frac{z_i e D_i}{kT}}$$

So, here C i, C i cancel each other and what you get is an expression for v i and v i is equal to z i e D i divided by k T multiplied by E. So, this basically trick I have done to get a equation for v i with respect to E with some proportionality constant. This if you remember, now electrical mobility is defined as, mobility is basically defined as mu i is equal to v i divided by electrical force, which is nothing but electrical electric field. This is nothing but your z i e D i divided by k T and if you look at the units of this is in centimetre square per volt second.

So, this is the relation mu i is equal to z i e D i by k T this is the relation which you obtain for electrical mobility in an ionic system, where electrical mobility is of i'th species is related to that diffusivity. So, this relates and atomic property, which is diffusivity to the electrical property, which is mu i the electrical mobility. So, this is for an ionic system, we will further take it we will we will we will do some more things with these equations a little later on, but at the moment what I have done is basically, I have showed you how the electrical mobility of species in an ionic system can be related to their the diffusivity of species, at a given temperature.

So, first before we go further into ionic conduction, we will we will briefly look at how the conduction take place in the metallic conductors. Then compare this with the conduction in the ionic solids. So, while the you can apply the Nernst Einstein relation to the motion of ions electrons in whether in ionic systems whether in electronic system or metallic system. It is possible to apply this relation to both the systems, but in reality the motion of electrons and ions in both the systems is quite different.

Now, typically in electron in metals and semiconductors the electrons and holes we consider them as quasi free particles. These quasi free particles under the influence of electric filed acquire a drift velocity v d and this the motion of the electron in these systems under the influence of electric field and is governed by various phenomenons, which are called as Scattering phenomenons. So, when you apply electric field.

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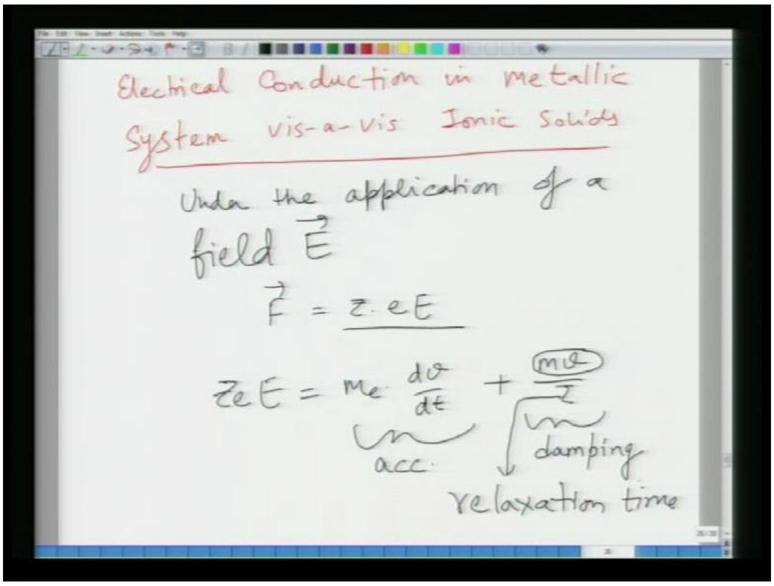

Electrical Conduction in metallic System vis-a-vis Ionic Solids

Under the application of a field $\vec{E}$

$$\vec{F} = \underline{z.eE}$$

$$zeE = \underbrace{m_e \cdot \frac{dv}{dt}}_{acc.} + \underbrace{\frac{\boxed{mv}}{\tau}}_{damping}$$

relaxation time

So, basically what we will do here is… So, when you apply an electric field. So, under the application of a field E, the force on an electron F is given as z e E. Now, when you apply a force to an electron it acquires a drift, it acquires a velocity the question is can it does it keep on accelerating or is there something else, which stops the electron from keep on getting accelerating. So, when you apply force this force has to be balanced by acceleration force z e E is equal to m e d v by d t.

So, this is the acceleration term, but electron we know it does not keep on getting accelerated at a quasi drift velocity and this is due to something called as damping. So, this is the damping term and this damping term, which you can relate for example, to something like friction and this prevents the electron from capturing an infinite velocity. So, it captures…

So, this m v by tau basically you can write m v is nothing but momentum. So, basically this is nothing but p by tau and this tau is nothing but your relaxation time. This arises, this term arises because when electron undergoes, when electron moves in a in a lattice under the influence of electrical field, why does not keep on accelerating is because it undergoes many collision events.

This collision may be because of lattice, lattice phonons etcetera impurities, grain boundaries. So, as a result of these collisions the electrons do not acquire. So, electron since it travels a distance x, then it collides again travels some distance x then again collides. So, there is a average distance which it travels and there is a average time between two collisions and this tau represents that average time, which is called as relaxation time. Not I have written as relation time, it is not relation it is relaxation time. So, this relaxation time is basically the average time spent between two collisions, which electron undergoes while it moves in a lattice.

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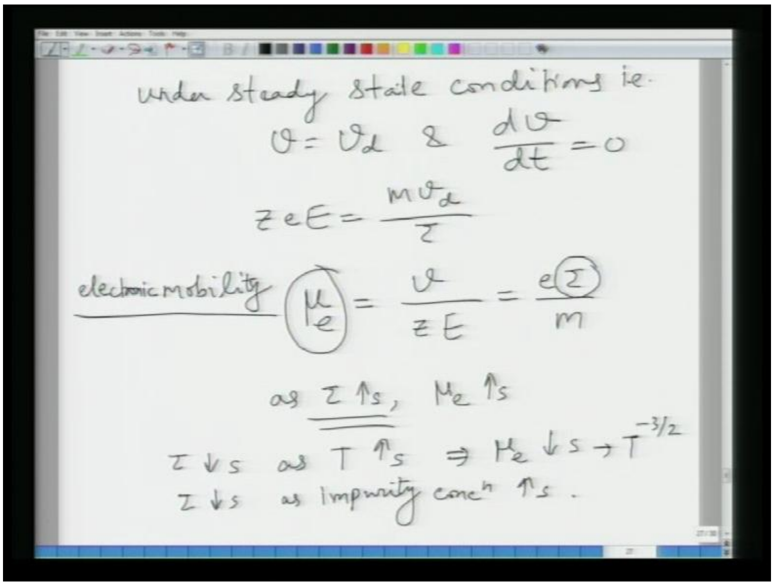

under steady state conditions ie.

$$v = v_d \quad \& \quad \frac{dv}{dt} = 0$$

$$zeE = \frac{m v_d}{\tau}$$

electronic mobility $\boxed{\mu_e} = \frac{v}{zE} = \frac{e\boxed{\tau}}{m}$

as $\underline{\underline{\tau \uparrow s}}$, $\mu_e \uparrow s$

$\tau \downarrow s$ as $T \uparrow s \Rightarrow \mu_e \downarrow s \to T^{-3/2}$

$\tau \downarrow s$ as Impurity concn $\uparrow s$.

So, under, let us say under steady state conditions when it acquires, v becomes equal to v d when it acquires, when and d v by d t is equal to 0. Under such a situation your z e E becomes equal to m v d by tau. In such a situation the mobility is defined as electronic mobility. So, this is electronic mobility, mu e and this is defined as v divided by z E. This is nothing but your say if you if you take v divided by z E this becomes equal to e tau divided by m. So, what it basically tells you is that higher tau is higher mu e is because we know that conductivity is equal to n e v d and this v is proportional to mu or I can write this expression in slightly differently. J is equal to sigma E and sigma is equal to n e mu and you know that mu is proportional to v because we know that. So, this becomes n e into v by, so this becomes n v by e. So, this or let us just drop it.

So, what basically this mobility is? Mobility is nothing but velocity divided by force and this becomes from the previous relation e tau divided by m. So, as tau increases mu e increases and what does tau depend upon? Tau depends upon your scattering events. So, what are the things which is scattered?

So, basically tau decreases as temperature increases, temperature increases means the lattice vibration increases, as the lattice vibrations increase the electrons tend to scatter more and more. So, as a result the tau decreases. So, as a temperature increases tau decreases and hence mu e will decrease. This relation goes as T to the power minus 3 by 2. Similarly, tau decreases as impurity concentration increases. So, in a system in a metallic system as the temperature increases and as the impurity concentration increases both the relaxation time decreases as a result the electronic mobility decreases. That is why in metallic systems what you see is that, as you heat the solid the conductivity goes down because conductivity is proportional to the mobility.

On the other hand, ionic motion the ionic conduction is rather different. In case of ionic conduction it is not similar to metals and it is not similar to metals or semiconductors, even because in the case of metals or semiconductor the electrons and holes. If you talk about semiconductor also holes metals and semiconductor they undergo a band transport, which means they tend to move in the band. Where as in and the conduction in these solids is affected by things like temperature, impurities, the defects, the dopants, etcetera.

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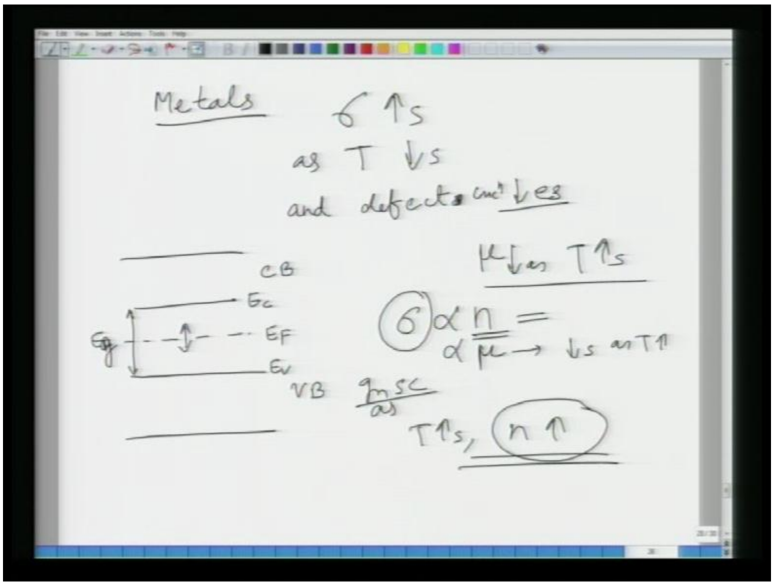

So, in metals conductivity increases as temperature decreases and defects decrease, defect concentration let us say decreases. In case of, on the other hand in semiconductors the situation is slightly different. In case of semiconductors you have a conduction valent. So, this is your conduction band, this is your valence band and this is your E V this is your E C. The electrons have to overcome gap which is E F, sorry E g and this is the position of your firm energy, which shifts up and down depending upon what type of semiconductor it is, whether n type or p type.

Now in case of semiconductor, now in both metal semiconductor a transport is of band transport, it happens in the band itself, but there are some differences. The mobility goes down, mu decreases as T increases that this two for both the systems. The only difference is that since conductivity is proportional to n as well as mu, so temperature decreases mu decreases in both the cases, but change in n is different. So, in case of semiconductors since the carrier concentration is dependent upon the band gap, as the temperature increases in semiconductors as temperature increases, n increases. So, as a result the conductivity tends to increase in semiconductor as the temperatures are increased.

So, this is also true about ionic solids. In case of ionic solids as you increase the temperature the conduction the concentration of mobile species goes up, such as vacancies. So, coming back to the conduction type; the conduction in metallic and semiconductor solids whatever with the relation of concentration and mobility with the temperature is, the relation is, what we are interested here is in the mobility. So, mobility in case of semiconducting solids and metallic solids, semi conductors and metals decreases, as a function of temperature. As a temperature increases the mobility goes down and the transport is of type band conduction.

So, electrons and holes tend to move in bands. On the other hand the conduction in ionic solids tend to be rather different, it tends to be hopping or let us say polaronic type of conduction. So, what basically a happens in these systems is that, the carriers the carriers, which are present in lattice they tend to polarise the lattice and this polarisation of the lattice results in association of the carrier with the lattice. This association of proximity of the association or proximity of the carrier with the lattice results in what in what is called as a polaron. So, this polaron can be longer than the size of the unit cell, it can be quite big and.

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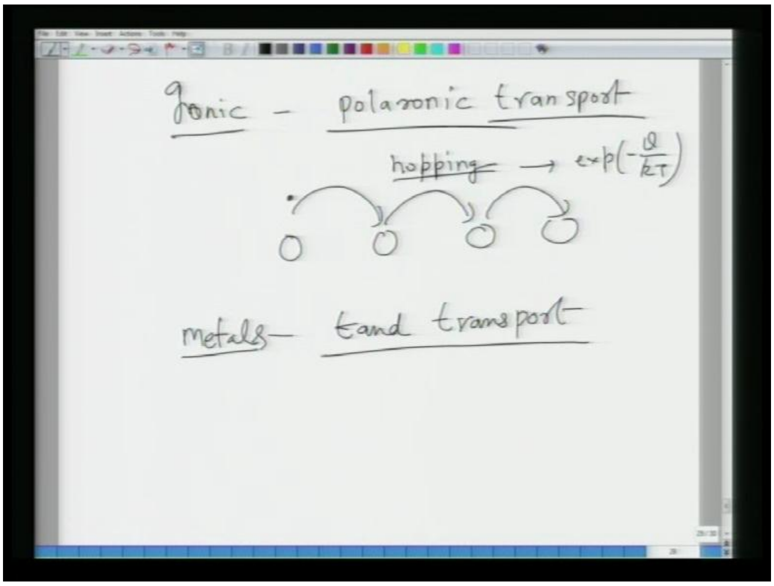

Ionic – polaronic transport

hopping → $\exp(-\frac{Q}{kT})$

metals – band transport

So, in this in this system the, in case of ionic systems the transport is polaronic. This polaronic transport happens because of hopping. So, you have since the charge is associated somewhere here. So, when it has to move to other site, it does by hopping, like this. So, this is the crucial difference between metals, semiconductors and ionic solids. In case of metals it is band transport, which means electrons travel within the energy bands. If you go into the band theory of metals you will find the reasons for of band transport, but at the moment let us just stick to this fact that, electrons tend to move within the bands; so within the bands means, under different energy levels. So, there we are not looking at the conduction as a function of let us say, the transport distance.

Here in case of ceramics or ionic solids what happens is, if it has to if the charge has to transport, it transports by hopping from one site to another site and then another to another. This hopping as we know is an activated phenomena and this goes as exponential minus Q by k T. So, typically what you see is that, in these systems the mobility is a is a function of exponential minus Q by k T. So, in contrast to metals and semiconductor in ionic solids the mobility tends to increase with temperature.

So, this is the crucial difference, which arises because of difference in transport mechanism. The transport mechanism in case of metals tends to be, I repeat again tends to be band transport type, which is which is a the, which is the movement of electrons between the energy levels. Here it tends to be hopping type between the atomic sites and this requires energy barriers to be overcome, as a result the mu is a function of exponential minus Q by k T. So, I will finish the lecture here today. In the next class we will learn more about the ionic conduction and then we will look at what the ionic conductivity and ionic solids is like.

Thank you.