# Diffusion in Multicomponent Solids
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Lecture 30
# Mechanisms of Diffusion in Metals and Alloys

Welcome to the 30th lecture of this open course on Diffusion in Multicomponent Solids. In this lecture, I will explain some of the important mechanisms of Diffusion in metallic alloys. These include interstitial diffusion and vacancy diffusion mechanisms. I will also briefly describe direct exchange and ring mechanisms. Expressions are also derived for diffusivity of atoms by vacancy and interstitial mechanisms.

Now that we have gone through energetics of the point defects we will look into some of the mechanisms of diffusion in this lecture, specifically in crystalline metals and alloys.

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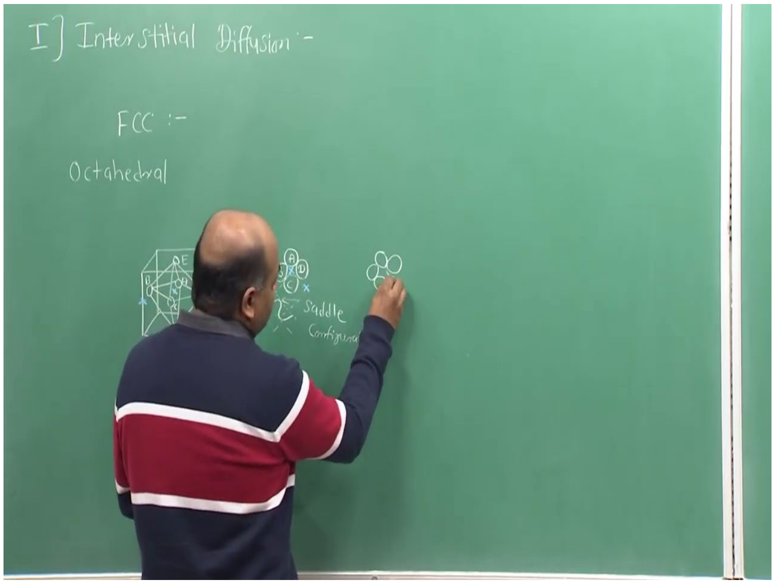

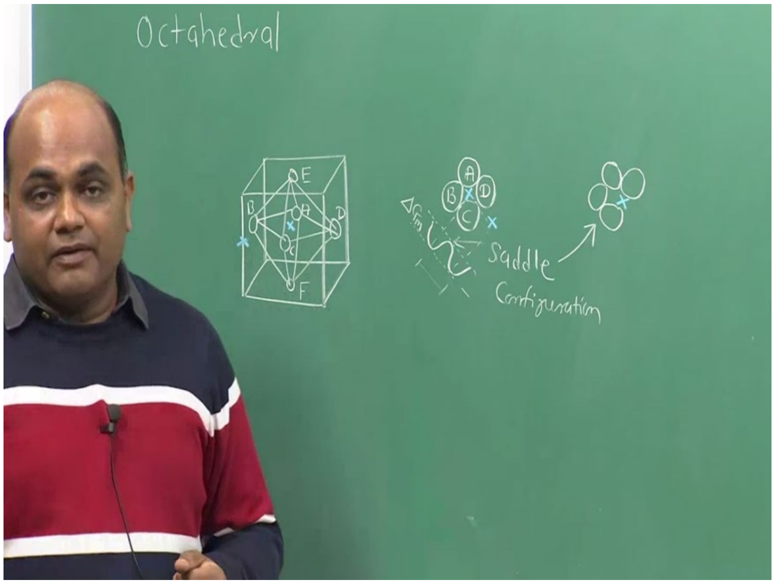

To start with, the first diffusion mechanism is interstitial diffusion. We know that if the size of the solute atom is very small, smaller than the parent atom then it can occupy the interstices between the regular atomic positions. Those are called interstitials. The interstitial atoms are also vibrating about their mean position and if a particular vibration has energy greater than that required to jump on to the next interstitial site then it can actually jump onto the next interstitial site. This diffusion from one interstitial site to the next interstitial site is referred to as interstitial diffusion or we say that the solute atom is diffusing by interstitial mechanism. An example of interstitial diffusion is the diffusion of carbon in steel. In both BCC and FCC iron, carbon occupies the interstitial site and it diffuses by interstitial mechanism. Let us visualize the interstitial sites in FCC and BCC. Let us first look into FCC. There are two types of interstitial sites, octahedral and tetrahedral. Let us first look into the octahedral interstitial site in FCC crystal. Octahedron is a figure having eight faces. Octahedral interstitial site lies at the centre of octahedron, which you can draw with the regular atoms of the lattice site at its corner. Let us draw an octahedron in FCC lattice. Consider the four face-centered atoms of the vertical faces and the two face centred atoms of the horizontal faces and if you join these atoms, they will form an octahedron. The centre of the octahedron lies at the body centre of the unit cell. So, this is one octahedral site. Similarly, you can show the other octahedral site lie at the centres of the edges of this FCC unit cell. The octahedral sites in FCC are one body centre position and others are at the edge centre. Since each edge is shared by 4 unit cells, only one fourth of the octahedral interstitial site on the edge lies inside a unit cell. So, there are total 12 by 4, which is 3, plus 1 at the body centre. There are total 4 octahedral site per unit cell in a FCC crystal.

We can draw plane formed by these atom. Let us label it as A, B, C, and D. Atoms A-B, B-C, C-D and D-A are touching each other because they are the nearest neighbour and obviously there will be one atom on top. This is the atom E and there will be one atom at the bottom. Let us call this F and these atoms will form an octahedron and interstitial or the void that is at the centre of this is the octahedral interstitial site. If an atom sits in this octahedral interstitial position, there will be another interstitial position somewhere here. As the atom jumps interstitially from this position to the next position, it has to cross an activation barrier, which means in between there will be a state which is characterised by a maximum in the energy as the atom moves from one interstitial position to the other. Since these two are the equilibrium positions, there will be a maximum somewhere in between. As I am drawing energy versus distance, this is the X coordinate, this first position is at minimum, second position is at minimum and there will be a maximum in between and this maximum position corresponds to what we call as Saddle configuration.

Now you can imagine as the atom is moving from this one site into the other, these two atoms C and D have to be pulled apart so that there is enough space for this interstitial atom to pass through and that is the saddle configuration. On its way to the next interstitial site, if we draw this configuration it will be something like this and the X atom is exactly between these two positions C and D. This is the saddle configuration or the configuration corresponding to maximum in the energy and this difference is called the Gibbs free energy of migration.

The difference between the Gibbs free energies of the two configurations, equilibrium and saddle configuration is called the Gibbs free energy of migration or that is the barrier which exists for this interstitial atom to diffuse from one site into the other, that we call as activation energy for migration of the atom.

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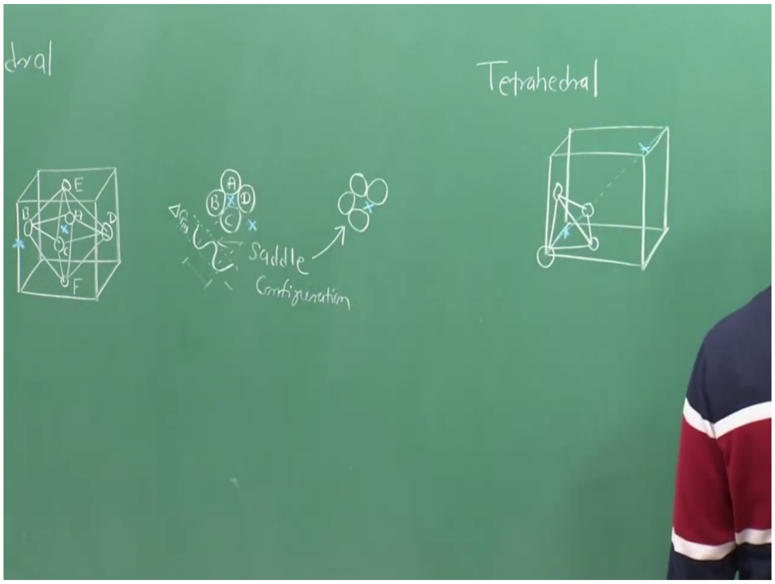

Similarly, there will be tetrahedral interstitial sites in FCC which lie along the body diagonals. Let us consider any three adjacent face centre atoms and the corner atom, of all the three face centre atom touch. Then we can draw a tetrahedron, meaning a figure having four faces and the centre of the tetrahedron we can see will lie along the body diagonal. Precisely tetrahedral interstitial site will be at a position which is at one fourth of the body diagonal length. By symmetry you can show there will be another interstitial at three fourth of the body diagonal and there are 4 such body diagonals. There will be total 8 tetrahedral sites in a FCC unit cell.

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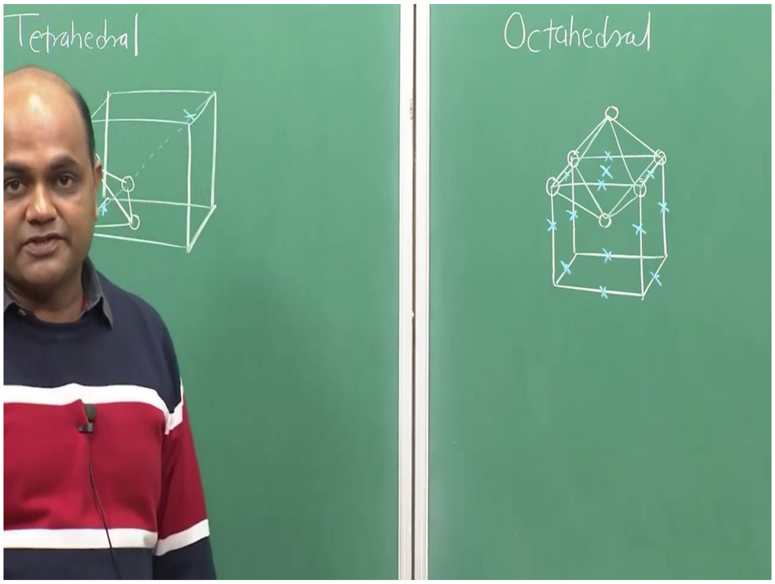

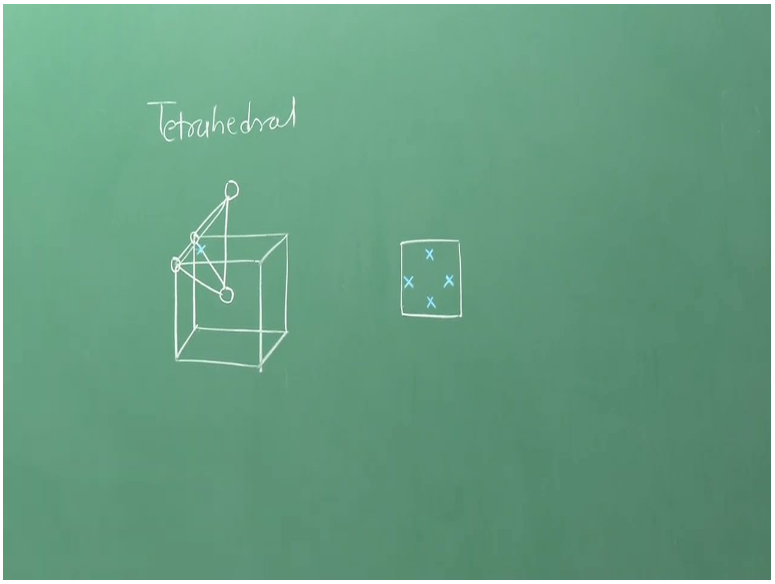

You can also show octahedral in BCC. To show octahedral in BCC you can consider body centre of this unit cell and the body centre atom of a unit cell which lies on top of this unit cell and join those to the four corner atoms. If you join this you can form an octahedron and the centre of this octahedron lies exactly at the centre of the top face. Similarly, there will be other octahedral positions at the centre of the edges. The octahedral sites in BCC are on the centres of the faces and centres of the edges.

For tetrahedral sites in BCC, let us consider the two body centre atoms. One at the body centre of this unit cell, which is drawn and one at the body centre of the unit cell which is on top of this one. Consider any two side corner atoms and you can join them to form a tetrahedron. The centre of this tetrahedron lies somewhere on the face and its position is at one fourth of the lattice parameter from the centre of the edge. So, the tetrahedral interstitial sites are located at one fourth from the centre of each of the edge.

These are the octahedral and tetrahedral interstitial sites in FCC and BCC and the interstitial atom diffuse by jumping from one interstitial site into the next interstitial site and this is the interstitial mechanism of diffusion.

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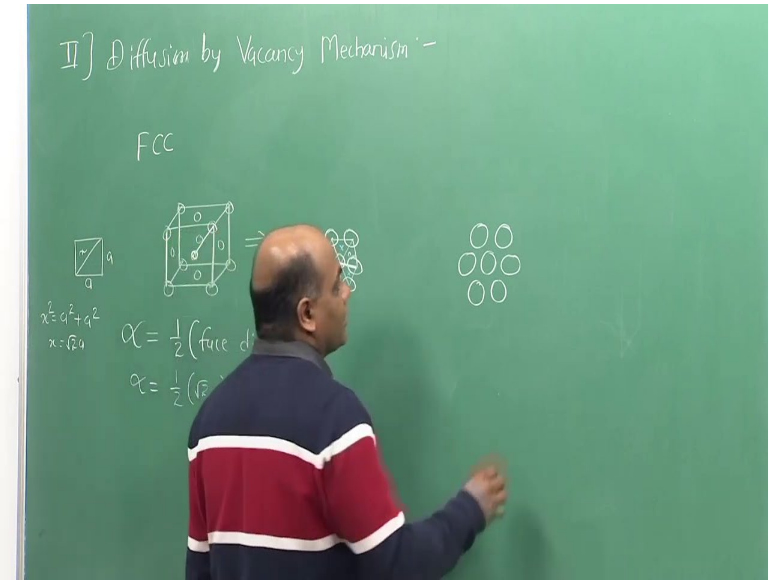

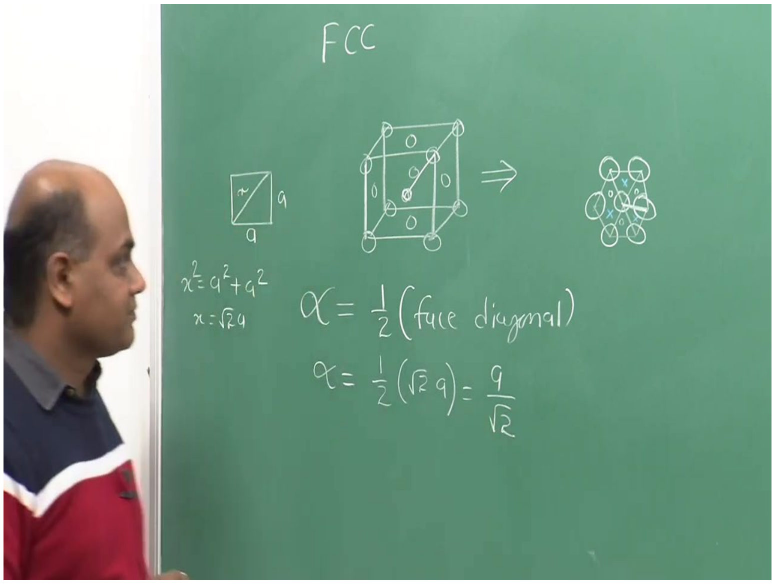

The next mechanism that we are going to look at is by vacancy. As we have seen in previous lectures, at any given temperature above 0 Kelvin, there is an equilibrium concentration of vacancies in any crystalline solid. It means at any given temperature, there exists certain number of vacant sites in a crystalline solid. If a regular atom vibrating about its mean position gains enough energy, it can jump into the next site provided it is vacant.

This is also equivalent to the vacant site making a jump in a reverse direction. This is the diffusion by vacancy mechanism. The hopping of atom from one regular lattice site onto the next lattice site is mediated by vacancy and this is the vacancy mechanism of diffusion.

Let us try to visualize these particular jumps in a FCC lattice. If we look particularly at (111) plane, each atom is surrounded by 6 nearest neighbour atoms within plane and there will be 6 out of plane. 3 of them will be on top, 3 of them will be at the bottom of this plane and we can place those atoms by joining them in the hexagonal arrangement. Then there will be 6 triangles, 3 pointing up, and 3 pointing down. We can place dots at the centre of the triangles which are pointing up and cross at the centre of the triangle which are pointing downwards. So, these are the 6 out of plane positions or the 6 nearest neighbours which out of plane.

These cross are the 3 nearest neighbour atom of this central atom which are lying below this plane and the dots are the 3 nearest neighbour atoms of this central atom which are on top of this plane. 6 + 6=12, so there are 12 nearest neighbour and the vacancy diffusion most probably takes place by nearest neighbour jumps. So, this central atom has 12 possible sites on to which it can jump if a particular site happens to be vacant site and what would be the jump length? Let us consider the central atom with 12 nearest neighbour. The jump distance that is the distance between the nearest neighbour atoms will be essentially any face centre atom moving on to the corner site. This will be one nearest neighbour jump and we can see the jump length which we write as $\alpha$ is half the face diagonal. What would be the length of the face diagonal, if we denote each edge as $a$, the lattice parameter and the face diagonal length as $x$, then we know:

$$x^2 = a^2 + a^2$$

$$x = \sqrt{2}a$$

and the jump length in FCC by vacancy mechanism would be half the face diagonal which is:

$$\alpha = \frac{1}{2}\left(\sqrt{2}a\right) = \frac{a}{\sqrt{2}}$$

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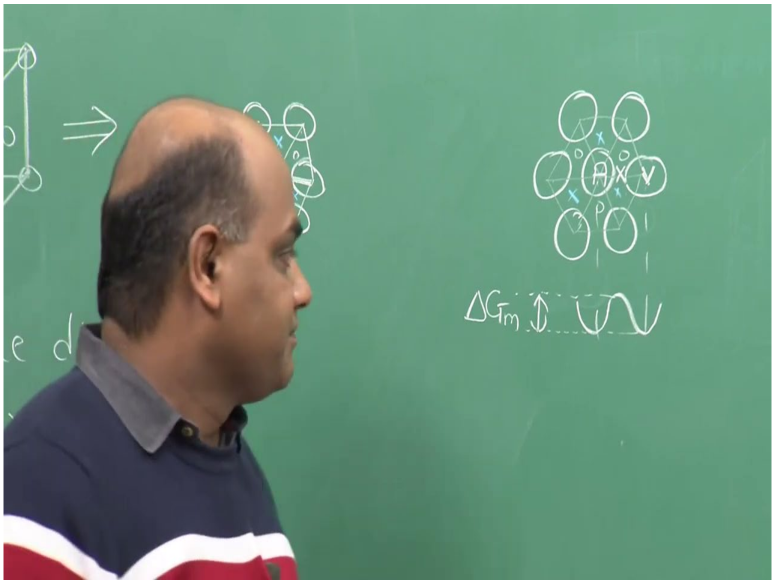

Where will be the saddle point? If this atom A at the centre has to diffuse onto the next site V which is vacant we can see that these two atoms have to be pushed apart. Similarly, there is one atom on top and one atom at the bottom of the blackboard plane, which also have to be pulled apart. So, the saddle point would be somewhere in between represented by this peak.

If we draw the energy versus distance you can see there will be a maximum at the saddle configuration and the difference between the Gibbs free energy of the two states, the equilibrium state and the saddle configuration is the $\Delta G_m$ or Gibbs free energy of migration of this atom A. This jump of A into vacancy is equivalent to the reverse jump of vacancy into the site A and both the diffusion of A by vacancy mechanism or the diffusion of vacancy would have the same energy of migration, $\Delta G_m$.

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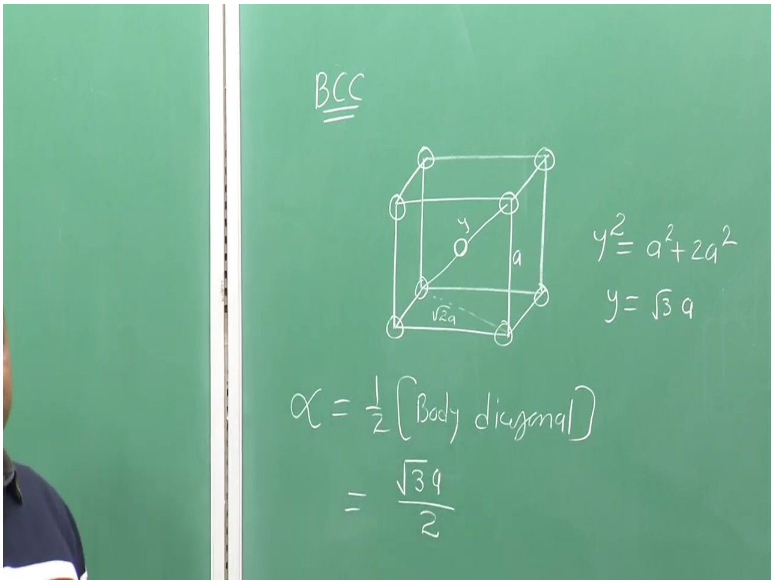

In BCC, what would be the jump length ? In BCC, there are 8 nearest neighbour to any particular regular atom position. To show the nearest neighbour, consider the body centre atom and all the eight corner atoms are its nearest neighbours. So, the jump length is typically half the body diagonal. We can evaluate the length of body diagonal. Length of the face diagonal is $\sqrt{2}a$ and edge length is $a$. If $y$ is body diagonal length, then it would be:

$$y^2 = a^2 + 2a^2$$

$$y = \sqrt{3}a$$

The jump length for BCC would be $\frac{\sqrt{3}a}{2}$. Now the saddle point configuration for BCC would be a little more complicated. To visualize that saddle point configuration, let us draw two interpenetrating BCC unit cells.

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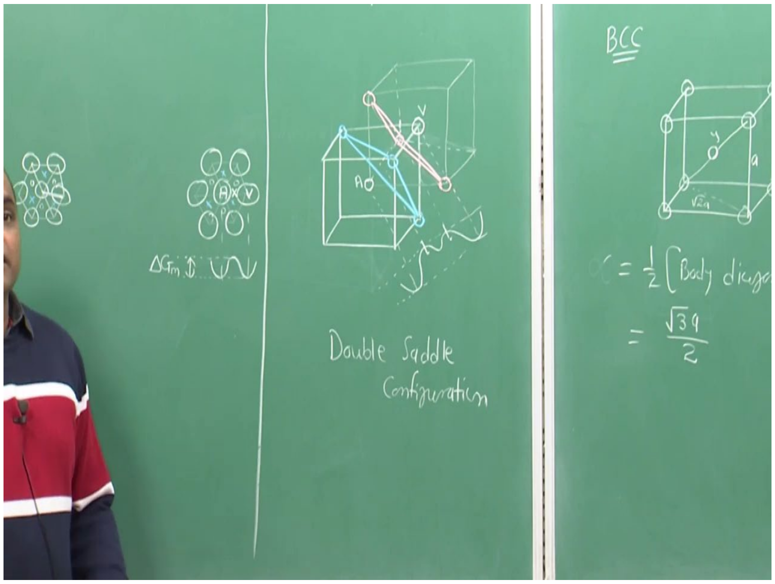

This is the first unit cell, and the second one is drawn such that body centre of this unit cell is one of the corners of previous cell. The body centre atom of first cell denoted by A has to jump on to one of its nearest neighbour, let us say on V denoting vacant site. Then it has to pass through two saddle points that is on its way from A to V. So, the atom will encounter two states in which there is a maximum in the Gibbs free energy.

The first state is at the centre of the triangle formed by these three blue atoms and the second saddle point is at the centre of the triangle formed by these three pink atoms. If we draw the energy versus distance as the atom moves from position A to position V, there will be two positions where the energy will be maximum. Of course A and V are the equilibrium positions. So energy there will be minimum there. There will be two states in between, where the energy will be maximum. This is the double saddle configuration in BCC.  Now let us try to find an expression for diffusivity by the vacancy mechanism.

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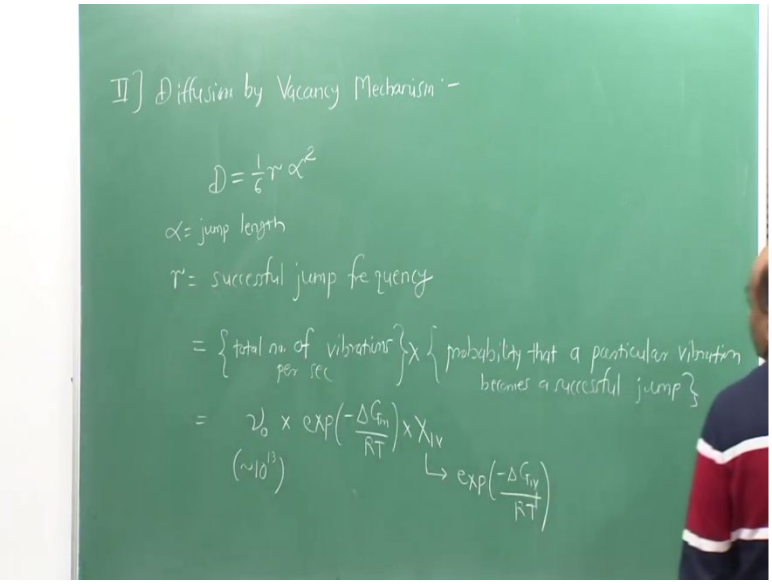

II] Diffusion by Vacancy Mechanism :-

$$D = \frac{1}{6}\Gamma \alpha^2$$

$\alpha$ = jump length

$\Gamma$ = successful jump frequency

$= \{\text{total no. of vibrations per sec}\} \times \{\text{probability that a particular vibration becomes a successful jump}\}$

$= \nu_0 \times \exp\left(-\frac{\Delta G_m}{RT}\right) \times X_{1v}$

$(\sim 10^{13})$

$\hookrightarrow \exp\left(-\frac{\Delta G_{1v}}{RT}\right)$

In a previous class, we derived the expression for diffusivity for any cubic lattice which was:

$$D = \frac{1}{6}\gamma\alpha^2$$

$$\alpha = Jump\ length$$

$$\gamma = Successful\ jump\ frequency$$

By knowing the lattice parameter, we can know the jump length for a particular type of lattice FCC, BCC, etc. Successful jump frequency is the number of jumps which are successful per second. A successful jump is the one in which atom jumps from one regular site on to the nearest neighbour vacant site. In order to evaluate the successful jump frequency in terms of the vibrational frequency of an atom we can write:

$$\gamma = \{total\ no.\ of\ vibrations\ per\ sec\} \times \{probability\ that\ a\ particular\ vibration\ becomes\ a\ successful\ jump\}$$

Each vibration of an atom we can consider it as an attempt to jump on to the next site. So, the total number of vibrations is the total number of attempts that the atom makes per second to jump on to the next site and it will be equal to $\nu_o$, the Debye frequency which is roughly constant at:

$$\nu_o \sim 10^{13}$$

What is the probability that a particular vibration will be successful? For the jump to be successful, there are two conditions. First the atom has to acquire energy equal to or greater than the migration energy, $\Delta G_m$ and second, at the same time the next site has to be vacant. That is there has to be a vacancy in the next site. The probability that the atom has energy equal to or greater than $\Delta G_m$ is $\exp\left(\frac{-\Delta G_m}{RT}\right)$ and what is the probability that a particular site is a vacant site? It will be total number of vacancies divided by the total number of lattice sites, that is, the site fraction of vacancies or what we denote as $X_{1V}$ and $X_{1V}$ we know is:

$$X_{1V} = exp\left(\frac{-\Delta G_{1V}}{RT}\right)$$

If we substitute back into this we get:

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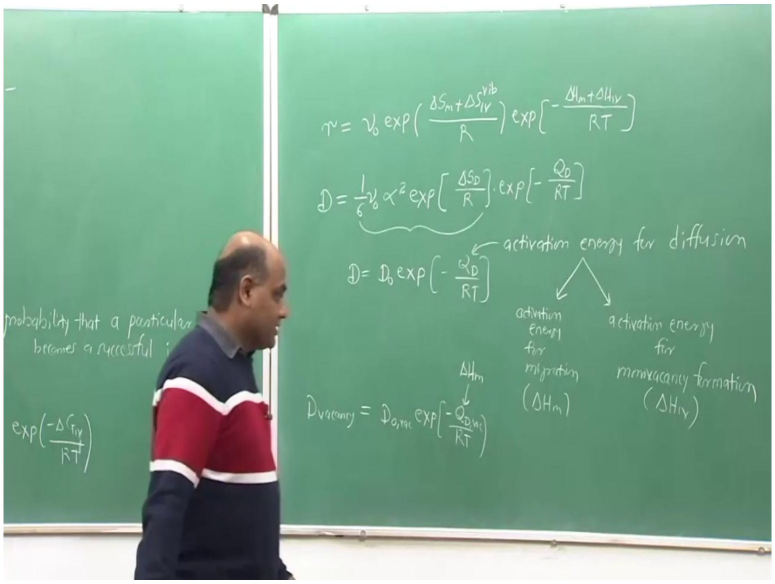

$$\gamma = \nu_o \exp\left(\frac{-\Delta G_m}{RT}\right) X_{1V} = \nu_o \exp\left(\frac{-\Delta G_m}{RT}\right) \exp\left(\frac{-\Delta G_{1V}}{RT}\right)$$

Now if we write:

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

and then if we take the entropy and enthalpy terms together we can write:

$$\gamma = \nu_o \exp\left(\frac{\Delta S_m + \Delta S_{1V}^{vib}}{R}\right) \exp\left(-\frac{\Delta H_m + \Delta H_{1V}}{RT}\right)$$

Here $\Delta H_m$ is the enthalpy of migration and $\Delta H_{1V}$ is the enthalpy of mono-vacancy formation. $\Delta S_m$ is the entropy of migration or it is the difference between the entropy of the equilibrium state and the saddle point and $\Delta S_{1V}$ is the vibrational entropy change due to formation of a mono-vacancy. We substitute into the expression for $D$ which becomes:

$$D = \frac{1}{6}\nu_o\alpha^2 \exp\left(\frac{\Delta S_D}{R}\right) exp\left(-\frac{\Delta Q_D}{RT}\right)\ where,$$

$$\Delta S_D = \Delta S_m + \Delta S_{1V}^{vib} = entrop\ of\ diffusion$$

$$\Delta Q_D = \Delta H_m + \Delta H_{1V} = enthalpy\ or\ energy\ barrier\ of\ diffusion$$

Now $\frac{\Delta S_D}{R}$ is typically relatively independent of temperature, compared to $\frac{\Delta Q_D}{RT}$ term. Second has an exponential dependence on temperature. So, on combining temperature independent term into one parameter denoted by $D_o$ we get an expression for $D$ as:

$$D = D_o \exp\left(-\frac{\Delta Q_D}{RT}\right)$$

$Q_D$ is called the activation energy for diffusion and from here we know that it has two contributions. One because of the activation energy for migration of the atom and the second from energy for mono-vacancy formation which are denoted as $\Delta H_m$ and $\Delta H_{1V}$ respectively. This is for the diffusion of the atom by vacancy mechanism.

The two types of diffusion that take place by this mechanism are self diffusion and substitutional diffusion. Self diffusion means diffusion of an atom in its own crystal and the substitutional diffusion refers to diffusion of a solute atom by the vacancy mechanism. Typically if the solute atom is large in size, it cannot occupy any interstitial position. So, it will occupy the regular atomic sites in the parent lattice or solute atom substitutes the parent atom. So, it is called the substitutional atom and such a substitutional atom jumps from one regular atomic site to the other by vacancy mechanism, it is called as substitutional diffusion.

For self-diffusion or substitutional diffusion, this expression is valid. Any atom making a jump from its regular site into the next vacancy is equivalent to vacancy making a reverse jump. So, you can also consider it as diffusion of vacancy. Now how the expression for $D$ will be modified if we consider the diffusion of a vacancy? At any given temperature, the vacancy concentration is very low. We have seen that close to melting point the equilibrium vacancy concentration is around $10^{-4}$. It means any vacancy will have only atoms as its nearest neighbours. The probability that a vacancy is on a nearest neighbour site to a vacancy is very low. At any given instance, a vacancy has 12 nearest neighbour sites onto which it can jump. An atom can jump only if one of the nearest neighbour site is vacant. For vacancy diffusion, the second contribution is not required or the second condition that the next site should be vacant is not required. The only barrier to the diffusion of vacancy comes, because of the activation barrier for migration of the atom. For D vacancy, we will have:

$$D_{Vacancy} = D_{o,m} \exp\left(-\frac{\Delta Q_{D,m}}{RT}\right)$$

$\Delta Q_{D,m}$ has only contribution from $\Delta H_m$ and in $D_{o,m}$, $\Delta S_{1V}^{vib}$ will be absent. So, the only contribution to $D_o$ in terms of entropy would be from entropy for migration.

Similar equation will be valid for an interstitial diffusion. Because an interstitial is occupying a void, it generates a lot of strain within the crystal lattice. Typically the equilibrium concentration of interstitial atoms is very low. For example in FCC steel, maximum solubility of carbon is only 2 % whereas in BCC the maximum solubility is about 0.025 %. That means that at any given instant, an interstitial atom will have all its nearest neighbour site vacant. The probability that two nearest neighbour site will be occupied by interstitial atoms is very low and even for interstitial diffusion the second condition is not required, the condition that next site should be vacant. Because most of the time any nearest neighbour site will be vacant and the contribution to activation energy for diffusion of an interstitial atom is also only from the activation energy for migration of the interstitial atom. Of course, the activation energy for migration for the substitution atom will not be same as that for the interstitial atom.

So, these are the two important mechanisms of diffusion, interstitial diffusion and substitutional diffusion in a metallic crystal. There are a few more mechanisms which were proposed, I will briefly mention those.

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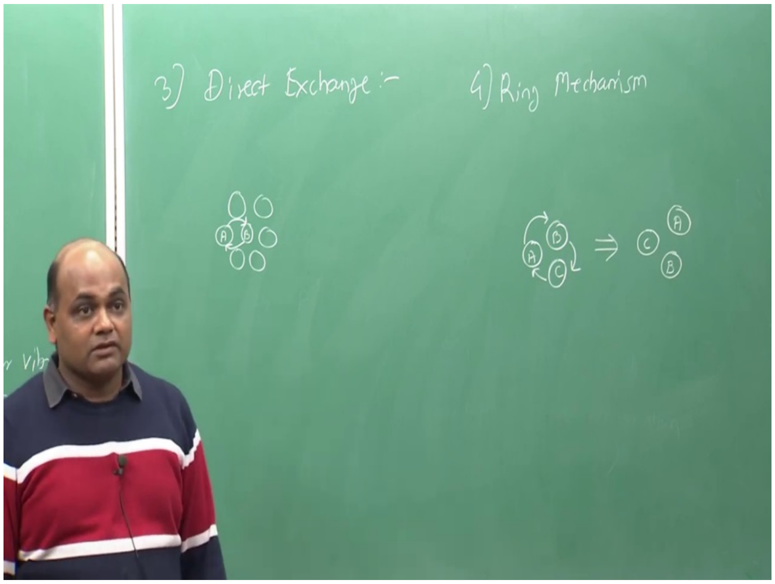

One of them is called direct exchange. As the name suggests it is a direct exchange between two atoms. If you consider atoms on their regular lattice sites, let us say atom A and B here, in direct exchange mechanism A will move to B, at the same time B will move to A. At the end of this exchange, the positions of A and B will be swapped. After the successful direct exchange this will become A, this will become B. Now you can imagine, the activation barrier for this particular mechanism will be very high. Because for this to happen, many conditions have to be satisfied. A has to gain enough energy so that it can push apart all the neighbouring atoms and move into B. At the same time B has to gain enough energy so that it can move into A, it is a very high energy process. So, this rarely occurs. Even if the jumps of atoms are taking place by direct exchange mechanism their net contribution to the diffusivity will be very, very low because the activation energy would be very large.

Another mechanism is which is referred to as ring mechanism. In this case, there will be minimum three atoms involved. Let us call them A, B, C and in this they exchange their position among themselves in a ring fashion. In this case A will move to B, B will move C, and C will move to A. After diffusion, the configuration will be, A has moved to B, B has moved to C and C has moved to A. Again you can see, the activation barrier for the ring mechanism would be very high if you compare it with the vacancy mechanism. So, the substitutional diffusion will most possibly and most easily will take place by vacancy mechanism.

These type of mechanism, which have very high activation barriers, will contribute insignificantly. Because of the high activation barrier, the probability of such jumps would be very low and the net contributions from these mechanisms will be very low. So, the most important mechanisms are vacancy mechanism for substitutional diffusion or self diffusion and the interstitial mechanism for interstitial diffusion. We will stop here for today, thank you.