

Physics of Functional Materials and Devices
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Lecture – 20, Week 5
Diffusion and various properties

Welcome to the third lecture of week 5. Let us continue our discussions on transformation kinetics. What have we read till now? We have read about solids. We have seen that you can make or fabricate various types of solids. Yesterday what did we learn? We learned that you can change properties of a given material and you can do that by inducing phase transformation or modulations. And we have also studied about the details of the types of phase transitions or transformations that occur in solids.

Let us today introduce a well known concept to most of us, but we will look into the same concept from a different aspect so that this process can become useful for various devices and that process is diffusion. What is diffusion? It is migration of certain entity from the region of higher concentration to lower concentration. This is what we have been studying from the school days. How can we look into this aspect from a different point of view so that this phenomenon if it occurs in functional materials can be used in devices.

This is what we will introduce to you today. We will also spend significant amount of time on understanding the theory of diffusion. What drives the diffusion? What are the factors which affect diffusion? And is diffusion similar in solid, liquid and gases or the mechanism differs when you move from solid, liquid or to you move on to gases. We will see how you treat the process of diffusion in solids, liquids and gases and finally we will introduce how the first and second Fick's law are utilized to explain the occurrence of diffusion in solids, liquids or gases. So, as I said diffusion is what? Diffusion is basically the migration from the area of higher concentration to the area of lower concentration.

So you saw that certain number of molecules or atoms or any entity move from its region of higher concentration to lower concentration so that the concentration throughout the system becomes similar. And what is the origin of diffusion? It is the random motion of atoms, ions or molecules in a medium. The density of the materials has an inverse relationship with the rate of diffusion. So, what is rate of diffusion? This needs to be explained and we will go to the concept of these things in coming slides. You know how solids, liquids and gases or gaseous systems are defined in terms of their rigidity, shape and volume.

So, what happens? In which of these states the diffusion is easily possible? Most of you have been believing and we all know that diffusion is much easier in gaseous state. But what happens in liquids and solids? Do you have diffusion or there is no diffusion? This is a question which we need to answer. And we will start answering by understanding the process of diffusion in solids because we are talking mostly about solid materials in this course. The kinetic process that results in the homogeneity of the chemical constituents in a phase is diffusion. This is another way of defining diffusion.

The kinetic process. What is kinetic process? Means you are associating some amount of energy which is inducing some motion and that is resulting in homogeneity. Homogeneity means what? The surrounding around any given atom is same from one region to the other in a given system. So, you have homogeneous mixing so that you cannot differentiate between one region of a system to the other. And chemical constituents are the next terms which have been introduced.

So, suppose you take two atoms A and B and you want to make a lattice. Then what should happen? The arrangement of A and B should be such that it is uniform throughout. You cannot have a region in a lattice where A, B are arranged as if A, A, B, B and in the other region it is A, B, B, A. This is inhomogeneous mixing. What you want is A, B, A, B, A, B throughout the lattice.

That is homogeneous mixing. Now mixing in a fluid or liquid or gas can occur at several length scales because you can observe macroscopic flow. You can have motions to longer distances in gaseous or liquid phase of materials. But in solids obviously the diffusion would be slightly different. And this diffusive mixing in solids is mostly observed at the atomic or molecular level.

And the laws of diffusion are basically the mathematical relationship that will connect what? The rate of diffusion to the concentration gradient for the net mass transfer. What is this net mass transfer? Because when you move an entity, be it be atoms, be it be molecules, be it be ions, you are transferring a mass from one region to the other. So, what is associated with diffusion? It is the movement of mass. So, you are carrying a mass transfer phenomenon when you discuss about diffusion. Fick's first law gives you that the net amount of diffusing atom passing through a cross sectional unit area in unit time which is given by:

$$J = -D \frac{dC}{dl}$$

where l is the coordinate in the diffusion direction, C is the concentration of the diffusing atoms and D is the diffusion coefficient or diffusivity.

And you will find that you have opposite sign of what? The flow and the concentration gradient. So, what if the flow is from higher region to lower region? That is correct. So, flow is from higher concentration to lower concentration. Therefore, you are indicating this negative sign comes into picture. What are the factors which will affect this diffusion? Now if you increase the temperature of the whole system, what will you achieve? You will agitate the atoms or molecules or ions further.

So, they will attain higher kinetic energy. So, now because of the energy associated is $k_B T$, when you increase T , the energy associated with atoms increase. When this increase, they have higher vibrations. So, what happens? Higher temperature may accelerate diffusion. This is what you have seen.

When salt is added to warm water, it dissolves quickly and much faster. This is observed quite routinely. You can do the same exercise with sugar. You want to dissolve sugar in water. When you have a slightly warmer water, you can observe the same phenomena what you observe when you dissolve salt in warm water.

The other factor which will affect diffusion is the size of the molecules. For example, you want to diffuse a much bigger size ball through the membrane or across a unit cross section area or you want to diffuse a very small shape particle. What will happen? Clearly a much larger size system will be difficult to transport than a smaller size particles or molecules or ions. Hence the small size molecules diffuse quicker than larger size molecules. You can check the example of hydrogen gas diffusion which is nearly 4, 5 times faster than that of carbon dioxide gas. Now if I take the area where the gas is diffusing from region A to region B. So, right side of my hand, palm and to the left side. Now if I have a very small cross-sectional area, this is the cross section here I am not talking about. The molecules will come but this is not able to cross because there is no boundary here across which I have to diffuse through.

But then I increase the cross-section area then I get a much larger sized interaction and hence you will be able to pass or push a greater number of atoms across this wall to the other side. So, the rate of diffusion rises or increases as the area of interaction also increases. The magnitude of concentration gradient also is a factor which will affect diffusion. Now what is this? The concentration gradient can be small or it can be large. But diluting the solution increases the concentration gradient and thus the diffusion rate.

So, if you dilute the solution, you increase the concentration gradient from one side to the other and hence the diffusion rate increases. You can carry out this exercise when we add salt to water which is already bits are because you had some salt in it previously added. The rate of salt dissolution in the solution is much slower. However, if you add water to a salty solution this will accelerate the rate of dissolution. So, you have actually modified the concentration itself and then you can change the rate of diffusion.

Finally, you have the factor phase which comes into picture and it also contributes in the diffusion mechanism. The diffusion of a gas into different gaseous mediums occur very quickly because it has much lower molecular weight. However, if you consider the examples of solids or even dense liquids this would be slightly different and much slower than what you observe in gaseous medium and that is why it is more gradual in solids or you have dense liquids. You have seen these examples. The odor of ammonia is immediately detectable in air.

Why because ammonia mixes up easily since it is lighter than air. So, the molecular weight also plays a critical role in diffusion mechanism. Let us take the case of solids. So, you have crystal lattice. So, atoms are periodically arranged.

Let us say we have taken a 2D lattice. Each of these atoms are undergoing vibration around a mean position. So, the atom is undergoing vibration along the mean position. So, what you always plot is the mean position of the atom, not that that atom is fixed at this lattice point. It can be found here or it can be found here or it can be found here or it can be found here, but what you plot is the mean position.

Now because of these vibrations there are some frequencies associated with the vibrations. So, vibrational frequencies. In the majority of the situations the atoms return to their original location. Majority of the situations. Why because in the previous lecture we have seen.

That if you increase the energy and you force the atoms to have large variation in the vibrational frequency, they are forced to then go to a new atomic position so that they can again minimize the Gibbs free energy and the two neighboring atoms are not impinging each other's territory. Because if the atoms are still very near and you go on increasing the temperature they would end up getting lot of energy that means they will be forced to break the concept of distance of closest approach. That is not possible because like charges would repel and So, if you have lot of energies and the atoms are being forced to come near to each other because of this increase in energy which is being given by increasing temperature they are then forced to move slightly away that is called off-centering or atomic displacement in terms of crystals and what happens now they have again some more space to vibrate and dissipate this extra energy and they have gone to a lower Gibbs free energy. This is the concept why phase transitions take place and that is why it is written in majority of situations the atoms will return to their original location that is the mean position and if you induce a phase transition by continuously increasing temperature, they will go to a new location but they will continue to have vibrations. Now if the atom is moving from one location to the other this must occur at the same moment throughout why because you are forcing the lattice to go a new phase.

What will happen if the change has to occur nearly simultaneously you will have to have input of energy such that all the atoms are able to cross the energy barrier and at the same time the nearby atoms must be in such vibrational states that the jumping atom can pass through. What will then the general case look like in a different crystallographic direction the diffusion coefficients may fluctuate due to variation in the value of the frequency which is associated with the jumping atom and the effective jump distance given as $f_{u,v,w}$ and $d_{u,v,w}$ respectively. The diffusion coefficient would then become equal to D is equal to half summation $f_{u,v,w} d_{u,v,w}^2$ and you will sum over all u v w's. Jumping of atoms movement of atoms transport of atoms these are the terms which we are talking and they can be interchangeably used and if that is happening what is the mechanism by which they will take place. You will find that in crystalline solids diffusion if you talk in terms of volume diffusion mechanisms then they can occur in eight different ways.

Group one is as exchange mechanism or ring mechanism. So, in exchange mechanism there is a direct exchange of two adjacent atoms they are observed in close packed crystal structures whereas in direct exchange three or more adjacent atoms take part in this movement. It is complex and a mechanism which is mostly not observed in solids but likely to occur in liquids. So, what is happening in exchange mechanism the atoms exchange their positions. What will happen in ring mechanism you saw that the three or more atoms which are nearby took part in the movement.

Then you have the two most common mechanisms which are a result of such exchange or ring mechanism are interstitial or vacancy mechanisms. What are interstitial mechanisms? So, you have a atom which moves from one interstitial site to the other. It is very common in imperfect crystal lattices specially for tiny and small interstitial atoms. Then you have indirect interstitial mechanisms. What will happen? There can be two cases an interstitial atom of nearly the size of the lattice atom moves to an interstitial site or a collinear impact or by a non-collinear impact you move the atom from its site to a interstitial site.

Then you have a crowdion mechanism. What will happen? You move a group of atoms through the lattice and you have much larger shift and variation in the arrangement of the atoms in the lattice. So, let us see the examples interstitial mechanism you are moving the atom from site 1 to site 2. Then you have interstitial one. What happened? The atom moved from the vacancy move from the interstitial site to a lattice site and the atom moved to the interstitial site. In the second the lattice then forced the atom to move to an interstitial site.

Then you have the crowdion movement you have a group of atoms moving together and forward. So, you have various kinds of motions. Then you can have single vacancy only one vacancy moves you can have two vacancies moving that is die vacancy or you can have relaxation mechanisms that you have a vacant site in between the lattice positions or where the atoms are in an imperfect crystal and then they all try to occupy a position near the vacant site. So, vacancy mechanism is quite frequent in imperfect crystals and is quite

useful. It can be single or the vacancy mechanism. So, in single vacancy one vacancy the atom moved here and left behind a vacancy.

So, you can see here there are vacancies here and here when the atoms move they occupy the site and vacancies are then absorbed the places where the atoms were initially available. Then you have the relaxation mechanisms a group of atoms they try to go to an interstitial site and then they generate the vacancies in certain places and then on the other side you have the group of other atoms moving and taking their positions. So, if you look into the theory of diffusion in solids what will you find? You will find that the concentration of point defects in crystals and in these solids at equilibrium would be what? They would find that to a lesser or greater degree every crystal has defects this is what you have seen and therefore you are going to observe diffusion even in solids. What we know there is an equilibrium number of defects per unit volume at a particular temperature in these imperfect solids that concentration of defects can be calculated. So, you can now know what are the available vacancy sites or interstitial sites and then you can go on talking in terms of concentration and how diffusion will take place in these imperfect crystals.

The equilibrium concentration of defects depends on temperature because you can modulate these defects by changing the temperature meaning what? You can change the energy associated with these atoms or entities which are going to undergo the process of diffusion. Now for example if you add a point defect that is you add a vacant site or an interstitial site it will increase the entropy and the overall energy of the crystal. And the temperature dependence of the diffusion coefficient is given as

$$D = D_0 e^{-\frac{U_a}{k_B T}}$$

Now moving from solids to alloys you will find that diffusion in alloys which have two or more components is going to be slightly more difficult. Why because you will then have to consider more than two or at least two diffusing components and these components can have different size, they can have different radii, they can have different shapes and they can have different vibrational frequencies and therefore their diffusion would be slightly more complicated than in solids which you were till now considering to be a well defined structure with lattice that is constituting of well defined molecular units.

And you also know that atoms of different kinds interact differently. So, if there is an atom which is passing through another atom there will be interaction here. So, the atom is trying to diffuse through but the other one interacts midway and then changes the path of the motion of the diffusing atom and hence you will have a much more complicated diffusion. So, if you see let us say copper nickel trying to diffuse. Initially you have 100% nickel on one side and 100% copper on the other but when you heat this system, so, when you heat the system the diffusion takes place and then you can see that the concentration profile starts to get modified.

So, on the other side also you start seeing certain amount of atoms from nickel atom going to copper side and copper going to nickel side. Ideally you want that the profile of nickel and copper should be overlapping. So, that is you cannot predict that there would be regions of higher concentration of nickel or there would be regions where nickel would be much lower in concentration. You want that it should be uniform mixing that is called homogeneity considerations. Now in addition to these kind of alloys what will happen to liquids? You will find in liquids if you want to treat the whole phenomena theoretically it becomes slightly more difficult because the relative motion of atoms is easy in liquid So, it is difficult to fix the position and find the concentration.

There is no unique activation energy associated with the atom but still a simple model for liquid is given as:

$$D = D_0 e^{-\frac{U_a^{diff\ act}}{K_B T}}$$

D_0 is a temperature independent constant, U_a differential value at across the activation barrier is the average activation energy of diffusion per atom and K_B is the Boltzmann constant and T is the temperature in Kelvin. To understand these diffusion processes there are four models which are used. First is the fluctuation theory. What happens? This diffusion model is for pure metal and it says that the metal melts based on fluctuation theory.

But diffusion in liquids is thought to be the cost by atoms moving through small and variable distances. So, there are no fixed distances up to which the atoms can move. They would be variable distances and these movements are produced by random local density fluctuations and the corresponding value for diffusion coefficient is given by this formula. So, you can clearly see it is much more complicated because then you have molar heat of vaporization of melt coming into picture, you have the coordination number coming into picture and you also have a material constant which comes into picture itself depends on various factors. Then you have the second model that is significant structure theory, the Eyring's theory and the base of the Eyring theory is the difference in specific volume.

Fluid has higher specific volume than a corresponding solid and this excess volume is due to the fluidized vacancies and the diffusion coefficient then has another material constant coming into picture and then you can get some estimate of the diffusion coefficient. And finally you have the random barrier theory. This impact of disorder in liquids is considered in this random barrier theory and here you have the concept of effective medium being considered. Horner assumed a statistical distribution of effective activation and enthalpy from 0 to maximum value and based on that the diffusion coefficient can be calculated for the occurrence of diffusion in liquids. And finally you have the Enskog dense gas theory which gives you that the diffusion coefficient is dependent on the pair distribution function

and also it depends on the hard sphere and as the temperature changes what happens to this motion which is going to give the diffusion

$$D = \frac{3}{8} \frac{V}{\sigma^2} \sqrt{\frac{K_B T}{\pi m}} \frac{1}{g(\sigma)}$$

So, you have various models, you have various equations which gives you the value of diffusion coefficients in these materials. If you go back to the concept of current theory of diffusion in gases we have seen what happens. We knew that you will find that because of the motion of gases when the molecule collides no energy is gained or loss. Gas molecules in a container occupy relatively small space and the motion of these molecules is always linear and based on these concepts you have the calculations for diffusion rates which would depend on the temperature, pressure and molar weight along with the radius of the molecules. This is what we saw why pressure, temperature, molecular weight and the radius of molecules will impact the diffusion mechanism.

So, based on this you can actually find that if you have diffusing atoms within a volume which is given by:

$$A \times 2\pi \overline{v_{kin}} dt$$

then if you have the diffusion taking place across a cross section then the diffusion coefficient is

$$\frac{dN_{total}^*}{dt} = -\frac{\overline{v_{kin}} A l}{3} \frac{dN^*}{dy}$$

where $\overline{v_{kin}}$ is the average velocity of molecules and l is the mean free path. So, the concept of mean free path being taken from the current theory of gases and then you can find out the diffusion coefficient in these materials. Then came the second Fick's law. The law builds a relationship between concentration and diffusion flux under unsteady state.

Earlier we had seen the first law was under steady state. The second Fick's law tells me that

$$\frac{dJ}{dt} = -D \frac{\partial^2 c}{\partial y^2}$$

So, you have the unsteady state and you can again find out the value of diffusion coefficients. We have seen once again surface area, thickness of the membrane and concentration would be the three factors which would affect the diffusion in such systems. So, I hope you have understood the diffusion mechanism in solids, liquids and gases. What are the theories which are used to explain diffusion in such solids and the factors which

affect diffusion in solids and question which I would ask is if you move from one type of solid to another what will happen to diffusion? This is one thing which I will ask and if you have understood what we discussed today you should be able to answer this question.

If not then we will discuss this during the live sessions. You can follow these books for understanding more about the diffusion mechanism and I thank you for attending the third lecture of week 5.