Material Science

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Lecture No 21

Diffusion in Solids (Contd.)

In the last class we have seen how we can measure with the help of a diffusion couple, the diffusivity as a function of temperature and also we saw if diffusivity is a function the concentration, then how can we do the same kind of experiment and grab the information. With this some more problems which we can solve with the diffusion couple is what we shall look at.

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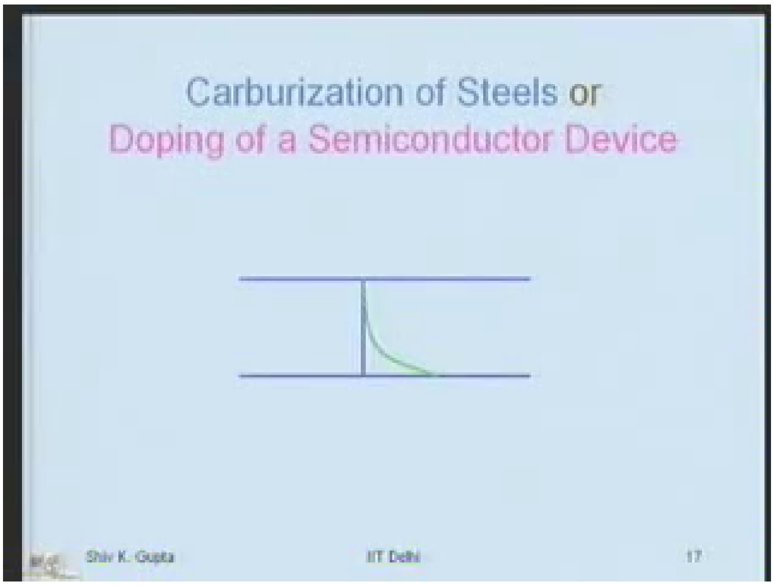

Carburization of Steels or
Doping of a Semiconductor Device

First of all the problem is carburization of steels or doping of a semiconductor device, like the chips which we are making, computer chips on silicon we have to add impurities which we call doping because it is intentionally done at a particular location to make the chip behave in a way we want it to. So this problem let us say we talk carburization of steels it is required at times, when we want the insite of the steel to be tough and very ductile, and the surface to be very hard and wear resistant, because surface is in contact.

Let us say surface of the gear teeth, it is all the time with other gears other teeth and solve going to wear out very fast if it is soft. We want that surface to be hard. We do the process of carburization, that means we add little more carbon on the surface and you know from the phase diagram if carbon is more it becomes more cemented and more hard. We will show you how we can make it more hard by the techniques with the phase transformation we will talk about after we finish with the diffusion.

So that is how we make the surfaces hard and wear resistant by introducing more carbon in surface, and the carbon as it diffuses will not go insite because the gears, the gears is my twelve inch diameter and I want only about half a millimeter, 1 millimeter surface to be hard, insite will still remain stuff, with the same 0.2% carbon steel or 0.3% carbon steel, whatever you are using there, but surface would be become, of the teeth will become hard. That is the process of carburization and the carburization usually is done gone through the process, manufacturing process, either we do it the gaseous atmosphere or we do it in the liquid bath which is the cyanide bath usually.

Or else we put it in a box of charcoal, wade by the charcoal combines with whatever close oxygen is to form carbon-monoxide, carbon-dioxide mixture, and that through the gaseous atmosphere provides the activity of carbon in the pack and the surface of the steel that gets activity of carbon, carbon can be introduced. So those are the process of things which we would like to look at here with the help of these fixed laws of diffusion and the solution to that how can we get it.

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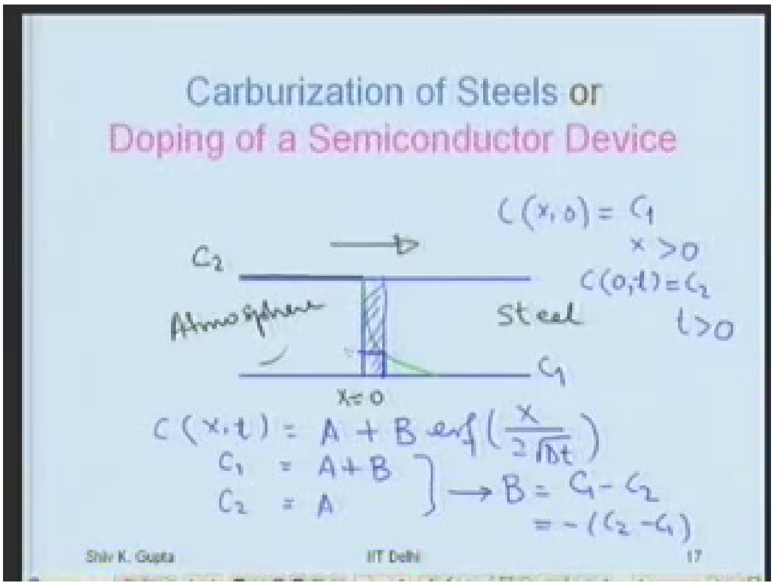

Carburization of Steels or
Doping of a Semiconductor Device

$C(x,0) = C_1$
$x > 0$
$C(0,t) = C_2$
$t > 0$

$$C(x,t) = A + B\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\left.\begin{aligned} C_1 &= A + B \\ C_2 &= A \end{aligned}\right\} \rightarrow B = C_1 - C_2 = -(C_2 - C_1)$$

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Here is my steel, here is my atmosphere, importance of this atmosphere which is gaseous and liquid is, and maintain it at a particular temperature, it is all the time in thermodynamic equilibrium and if some small carbon surface of the steel which we are carburizing goes insite the steel, that surface whatever carbon has come from the liquid of the gas, there is again recouped because the process is very fast in diffusion in the gaseous medium or the liquid is much-much faster than what is the diffusion insite the steel which is a solid.

So this is all the time in thermodynamic equilibrium, whatever is the activity of the surface that is maintained and that gives rise to let us say certain percentage of carbon, on the surface all the time it remains there. This is a gaseous or a liquid atmosphere. This is the solid steel part which start at X equal to 0 and direction of diffusion of carbon is this. So there carbon diffusing in steel starts at X equal to 0, goes up to X equal to infinity, it is a semi-infinite problem. No diffusion of carbon in a steel exists for X less than 0. So my problem is semi-infinite.

It starts at X equal to 0, goes up to X equal to infinity, right? So therefore I cannot talk of the concentrations in this because that's all the time in thermodynamic equilibrium, the rapid movement of carbon here, very-very rapid movement, right? So therefore I can write this fixed solution as C of XT is equal to A plus B error function of X upon 2 under root DT. And let us say this is the concentration of carbon in steel is C1 to start with, carbon from C2 on the surface will go insite far of the distance which still be C1, but here it doesn't built up in small skin close surface. The carbon is building up, right?

So we can put now here the conditions known to us at time T equal to 0, what is know is for all values of X which are greater than 0 carbon the steel is C1, this is in the steel, X is greater than 0. And for all times which are greater than 0 carbon which is built up at a surface is all the time C2 because that is all the time in thermo equilibrium. So another condition is know is C of X equal to 0 for all time which are greater than 0 it is equal to C2. So that is called the initial condition and this is called the boundary condition.

If I substitute in there you can always work out the A and B from there. So I get from the first one, C1 is equal to X is greater than 0, time T equal to 0, this becomes error function of plus infinity is 1, so it becomes A plus B. Second one is C2, here T is greater than 0 but X is equal to 0 so as error function of 0 is 0 so it becomes equal to A. So therefore I get B is equal to C1 minus C2. C2 is more than C1 otherwise carbon will not be going in, otherwise carbon will be coming out if it is other way round. So this is a negative number so you can also call it minus of C2 minus C1, right?

So got the solution A and B are got, that means you got the second (())(8:40), rest of it you can work on, you can keep it for a certain length of time, for this to happen so you know the time, you want to find out how much carbon has gone in, at a particular location you can do that, find how much carbon is there. Suppose the problem here could be that you want carbon to be not less that 0.4% wherever you want it to be hard, usually that is the case so you find out where carbon becomes point 4%.

Suppose you want it to be half a millimeter or you want it to be 1 millimeter that distance 1 millimeter should have carbon more than 0.4%, minimum should be 0.4%, and all other places are just greater than point 0.4%, so this carbon has to be more than here concentration, more than 0.4%, now I am going to try to maintain it about 1 or 1.2% so carbon can get in faster, right? And that is how this region is made to have carbon in the steel, more than 0.4% and that shall act as an hard surface, right?

Rest of it here is only the working out with the help of the tables with the error functions getting the argument and finding out the function, how long you should keep it at a particular temperature where you can find out the diffusivity so D will be known, T will be known, can work out at a distance or you know the distance you can work out the time. This is one kind of problem similarly kind of problem is there as I said for the doping of silicon with impurities like boron, phosphorous, etc. which we introduce and that is also a similar problem.

This graph, at some particular value, at T equal to infinity will be all C2. Substitute T equal to infinity here, whatever is the value of the X this will be 0, arrow function of 0 is 0, it is A, and A is already equal to C2, so it will be all C2. At infinity this is what would happen, but that infinity time is very high because this is what we are talking about a millimeter or half a millimeter, right?

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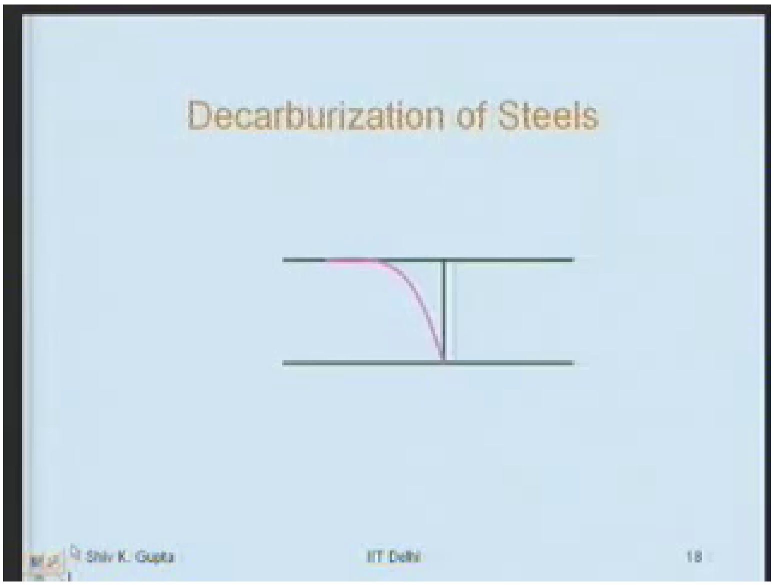

Decarburization of Steels

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Similarly a problem with decarburization. See, we are going to talk about the phase transformation, I will tell you how this steel is heated to make it austenitized, I mean to make it completely austenite, I have to go into austenitic temperature region where it is completely austenite, from there we cool it at different rates, and different rates we will cool we get different structures in it, if I cool it slowly I may get pearlite, if I don't cool it slowly I may not get pearlite I may get some other product. We will talk about those products.

So that is how we try to harden this steel and for any kind heat treatment of softening the steel we have to austenitize it first keeping at about temperature of 900 – 950 degree centigrade depending upon the carbon. If it is 0.4%, maybe 900 is good enoug, 0.6 maybe 880is good enough and this like that. So this is, when we are keeping it to make it all austenite we keep it for a certain length of time usually and that length of time as a rule of thumb one how per inch of thickness of the steel so that it becomes uniform composition of carbon all through and it is all austenite grains.

Polycrystalline austenite it becomes, that rule of thumb if it is used in one hour what happens to the carbon on the surface of the steel because we are heating the steel in the atmosphere, atmosphere contains no carbon, it has no activity of carbon and contains only oxygen, so this oxygen got combine with whatever carbon is there on the surface of the steel, and that makes it carbon-monoxide and carbon-dioxide and goes away. So carbon on the surface gets depleted, it is depleted from incite where there is more carbon that tries to diffuse the surface, when it comes to the surface it combines with the oxygen and again goes, this is the process of decarburization and there by the surface layer of the steel can become soft.

The carbon has gone down, we must know how much is the thickness where the carbon has gone down if I have kept it for one hour or I have kept it for three hours, depending about the total thickness of the specimen. So how much carbon has gone out and how much thick region has become depleted in carbon that must be machined out, if I am going to use that component I must machine out that part so that the soft layers is not used. So that is the process of decarburization and you must worry about that.

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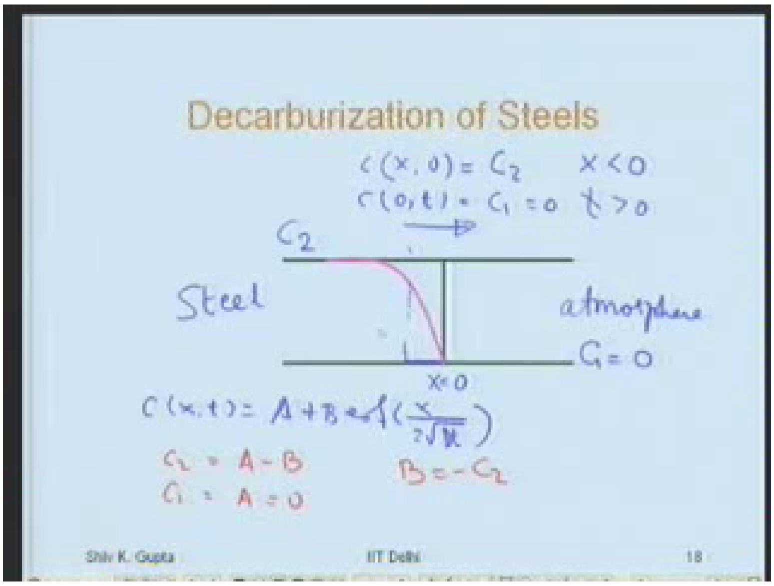

Decarburization of Steels

$c(x,0) = C_2 \quad x < 0$

$c(0,t) = C_1 = 0 \quad t > 0$

$C(x,t) = A + B\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$

$C_2 = A - B \qquad B = -C_2$

$C_1 = A = 0$

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This is the steel. Here is the atmosphere, steel to start with has a concentration of carbon C2, atmosphere concentration of carbon is 0 it is call it C1, and in here this is how the profile after sometime, this is how the profile of carbon changes, it becomes 0 at the surface and insite it is increasing and far of distance it remains C2 all the time, it doesn't change, if I am don't want it to be less than 0.6%, let us say 0.6 is somewhere here, then this is the thickness I have to machine off. Now how to work out the fix law of this? I must know what are my conditions known to me.

First of all I know X which is negative way, the steel is in the negative site, I will kept this as time, that is my direction of diffusion steel, this is X is equal to 0, C at X for at time T equal to 0 is equal to C2 for all X less than 0. I am not putting any condition for X greater than 0. I just told you there is (())(15:06) to the other problem, previous problem, why I am not putting any condition for X greater than 0. We are considering of carbon is from its steel, steel doesn’t exist from X equal to 0. So at X equal to I put the condition so that is for all times it is 0, C1 which is equal to 0 for X T greater than 0. It is all the time going to be 0 there.

So we put this condition in this solution which is C, XT is equal to A plus B times error function of X upon 2 under root DT, it is possible to get A and B, and the first condition is C2 is equal to, now X T is equal to 0 and X is negative, it becomes minus infinity. Error function of minus infinity is minus 1 so it becomes A minus B and second condition C1, here X is equal to 0 and T is positive so it is becoming error function of 0. Error function of 0 is 0 it becomes equal to A. And that is equal to 0 in this case.

So I have A is equal to 0, B is equal to minus C2. Or if C1 is not 0 then you have to put A equal to C1 then B is equal to C1 minus C2. Okay? So that is what we are getting, these conditions you put then, then you can again work on the problems, that X or that T or that D whatever you want to work out, it is possible for you to do that. So important thing is to be seen what is my problem, carbon diffusing in silicon or boron diffusing in silicon or carbon diffusing in steel.

Here also we are talking about carbon diffusing out of steel, so first of all it has to work in the steel and then come to surface, and once it come to the surface the reaction is very fast, combines with the oxygen, becomes gaseous state and the molecules are removed very fast, carbon monoxide, carbon-dioxide molecules, it goes into the atmosphere and that process is so rapid I need not worry about it. It is all the time in thermodynamic equilibrium the atmosphere is.

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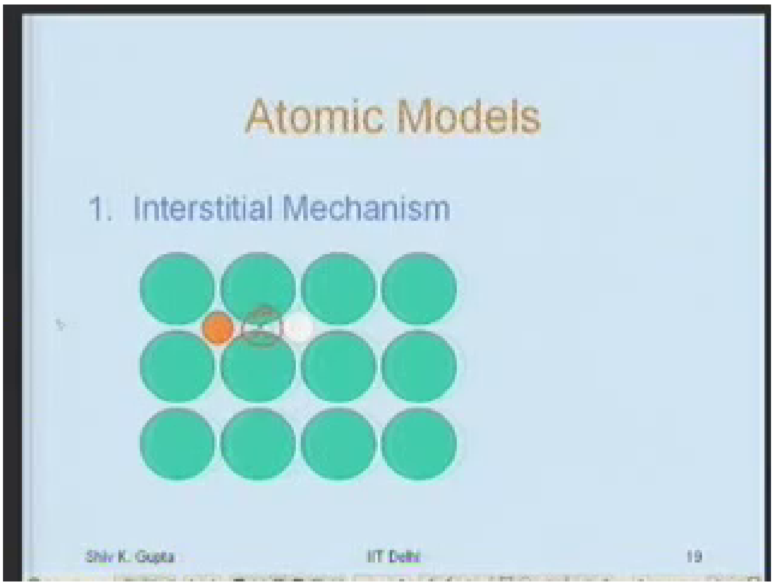

Atomic Models

1. Interstitial Mechanism

All right, now let us look at the atomic models of diffusion. First of all I show the interstitial mechanism of diffusion. Here they are talking about the solute which is diffusing in the medium is an interstitial atom, this interstitial atom will go for one interstitial site to another interstitial site, that I have shown here. This is the atom, it is going to this site which is vacant at the moment, this site is vacant, it can go to this, how will it go. It is only oscillating its position like this.

So oscillating like this, if the amplitude of oscillation becomes high that means it requires high energy, it can go into this location where it gets attracted by these neighbors here and fall into that site and then will start oscillating here. That is what interstitial mechanism is. But in the middle when it comes here there is a super imposition of this, with the super imposition of A this electron clouds here and here where the nucleus may be there, this going to high energy, very high energy and that extra energy it must acquire during this oscillations which is possible with this definite probability which is not 0.

And it can jump into that site, it is not translated, it is merely or during oscillation has got into that attraction of these neighbors and get rather jump into that site, it is a process of jumping. Okay? It can, I am not denying that, it is a thermally activated process the oscillations are but we have talked about it from the day one, this is the thermally activated process and thermally activated is going to, its oscillations would be in all possible direction, three independent directions are there always X, Y and Z. So it could be oscillating in any direction.

I am considering the fast that it is oscillating in this direction and it is able to acquire this extra energy which is required and jumps into this site. Then I say it has got change its neighbors, this neighbors, earlier it had, now once it reaches there the neighbors are these, and I will say my atom is diffused, right? So it could be jumping in any direction, direction is provided not by the thermal energy, thermal energy provides this oscillations for it to jump, but its gradient which I talked about in last class 2 things, thermal energy and the gradient.

Gradient provides you direction, in which direction most of the mass will transport, though thermal activation tells it that they will be jumping in all possible directions, I am interested in the net result ultimately. It will go in which direction, it is gradient which shall tell me in which direction they will all jump. Is it clear? Right!

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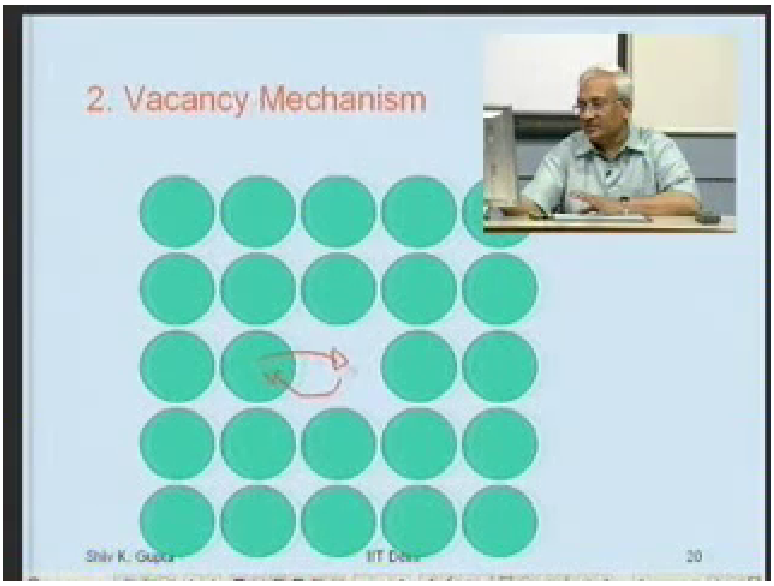

2. Vacancy Mechanism

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Then another mechanism of diffusion which is also quite possible is the Vacancy mechanism of diffusion. I have a vacancy here, and the atom which is jumping, oscillating in this position here, say this atom can jump into this site provide to cause enough oscillation to come into attraction of these neighbors and it will come here, and leave behind the vacancy there. During the process it will increase the bond length with three neighbors here but will be forming the bonds with these.

Somewhere in the middle it will have very high energy where the bond lengths are strained a lot. Because of those strains the energy would be higher, the extra energy it has to acquire through thermal activation only. Well oscillating and colliding with neighbors and neighbors are transferring their energy, it is possible and let us say it gets pushed into this. The moment it does it changes its neighbors, the moment the neighbors are changed I say the atoms are diffused.

And the process is atoms jumping into the vacancy and you can also see that vacancy is in turn jumping into that location of the atom, vacancy, wherever the atom comes from that becomes the vacant site. This becomes the vacancy and this becomes the atom. This is vacancy and that is the atom goes there. That is vacancy mechanism. Now there is another mechanism, we have talked about 2 point effect, interstitial, impurity and the vacancy, I also talked about the self-interstitial atoms, we will talk about the point effects. Those are called interstitialcy defects.

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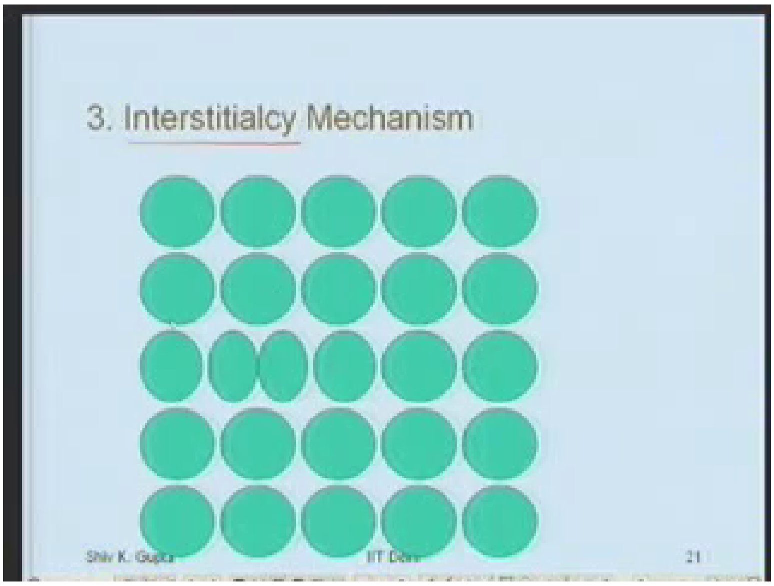

3. Interstitialcy Mechanism

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That is somehow one is pushed into the let us say interstitial site the same atom and the squeezed basically. During this oscillation this squeeze is pushed, so this atom acquires the location here and this gets pushed into this site and these two get reached here, as a matter of fact this atom would have changed its neighbor, it comes closed to these, these and these along with this. And I say the atom has diffused from here to there. This takes a site here while this gets into the interstitial location, these are all squeezed.

And the pressure is already too high, it can go in any direction like this, you know. Therefore it get just released pressure from here, but pressure will build up there, that is less probable mechanism of diffusion does occur, but it is a less probable mechanism of diffusion. There are some more mechanism of diffusion which are still less probable are direct interchanges or ring mechanism.

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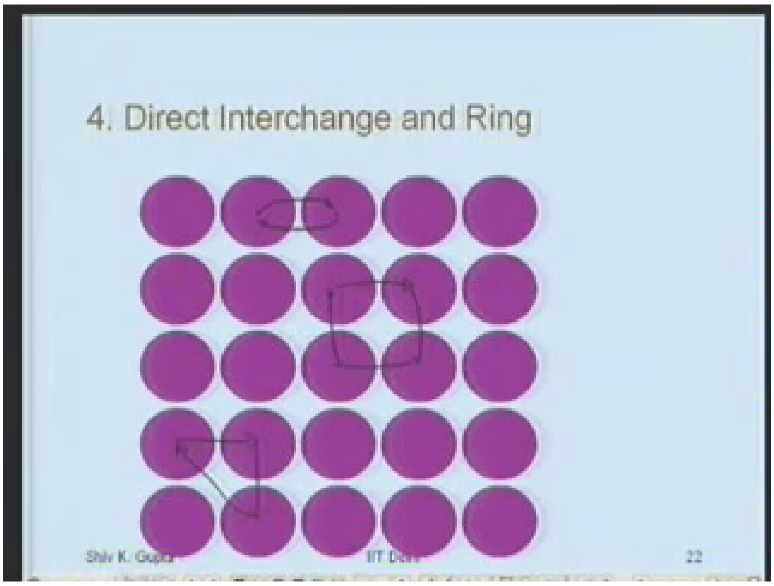

4. Direct Interchange and Ring

Direct interchange it what this atom is this nucleus basically which is here goes into this site and this nucleus goes into this site, and they are doing it simultaneously, that becomes the interchange, right? So this goes in there, this goes in there, a lot of energy change would be there when they are (())(25:48). Lot of overlap of the two electron clouds, nuclei are small species so one can go like this but the overlap of electron clouds causes lot of increase in energy, less probable, this is a direct interchange.

Rings can be formed as this goes under this location, this goes under this location, simultaneously this goes there, and this goes there, then they form a ring, they all rotate, but the moment they are done, this atom has reached here, this has reached here, all of them have changed their neighbors, surrounding neighbors have been changed, I say atom has diffused. These rings can be smaller or these rings can be bigger, it could be this goes here, this goes there and this goes here.

But probability of these things happening is small, but these are definitely the mechanism by which things can happen, probability is never 0, but less probable. More probable ones are the interstitial mechanism wherever I have the solute in the form of interstitials like carbon in steel and carbon in iron in interstitial location and that is the interstitial mechanism. When I do boron or phosphorous into silicon it is the vacancy mechanism of diffusion because it is the subtitutional impurity. It goes in substitute, these are the ones which are going to diffuse vacancy mechanism.

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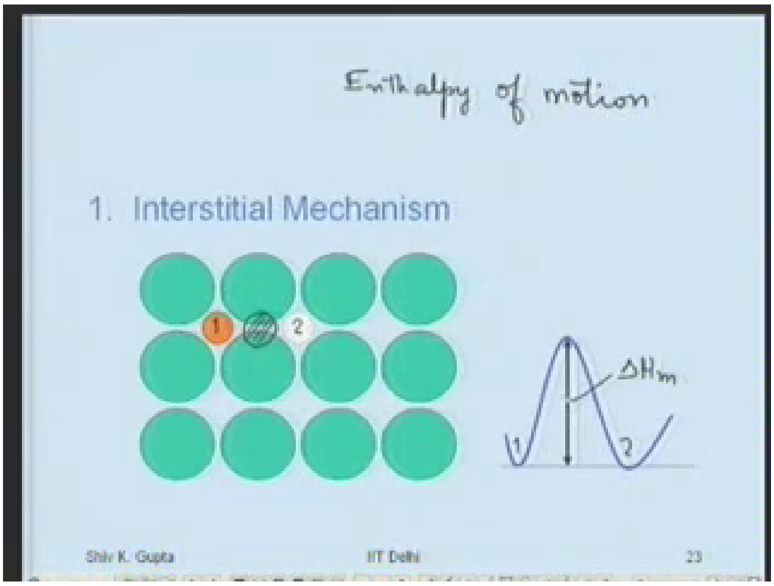

Enthalpy of motion

1. Interstitial Mechanism

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All right, now let us try to look at these models, try to get some numbers and see what we have understood about the experiments from the fix law at the model which we developed the mathematical model, first law, second law solution and how do you measure the diffusivity and etc, let us try to rationalize all that what we have done.

In the interstitial mechanism of diffusion when this, as I just showed you the picture that this overlaps here, this I call position one, this I call position two and which I show here on the energy diagram, energy distance diagram, position 1 here, position 2 there and this is the intermediate potion where the energy is high, and this extra energy is delta H sub M I call it, but in one position and two position the energy of the system would be same.

Once the atom has jumped and come in here the location two the energy would be the same, only when the intermediate location where there is an overlap on electron clouds energy is the maximum or enthalpy is the maximum which I call delta HM is called also the enthalpy of motion, M stands for motion. For it to move from 1 to 2 it has to go through this stage in the intermediate stage where the energy is the maximum, this thermal activation is required.

Now if I want to find out the what is the rate at which one goes to two in a successful manner, it is trying, (())(29:24) is saying as my friend said it would go in the opposite direction also. It is oscillating about, it can go in any direction, but I am looking for that it is towards 2 and jumping there and acquiring the energy, so what I have to be worried about is… all three things.

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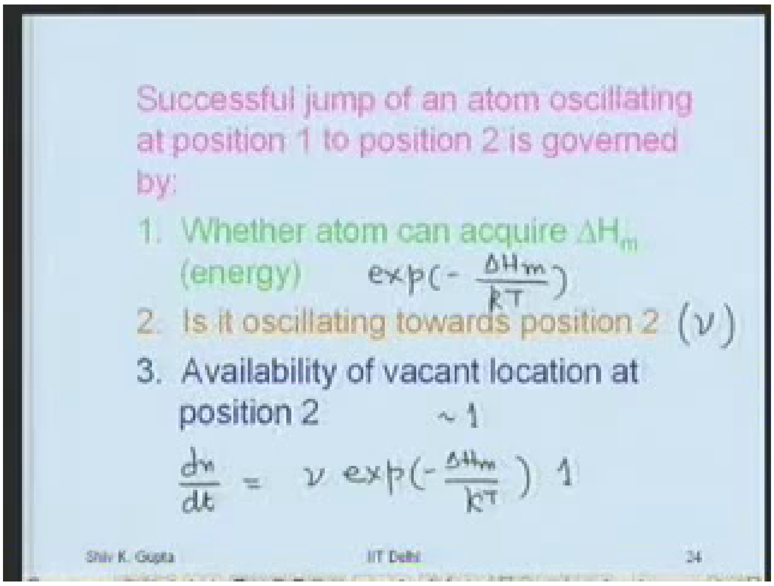

Successful jump of an atom oscillating at position 1 to position 2 is governed by:

1. Whether atom can acquire ΔH_m (energy) $\exp(-\frac{\Delta H_m}{kT})$
2. Is it oscillating towards position 2 (ν)
3. Availability of vacant location at position 2 ~ 1

$$\frac{dn}{dt} = \nu \exp(-\frac{\Delta H_m}{kT})\ 1$$

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Firstly, whether atom can acquire that intermediate state where the activation energy is been there at delta HM. That much enthalpy it can acquire. Then is it oscillating towards position 2 or is it oscillating somewhere else. And at what rate it is oscillating towards 2. Usually it is lattice vibration frequency with which it oscillates. And available of vacant location and position 2. Suppose already some atom is sitting at position 2, can one go and even if it acquires can energy go and sit there, it cannot. It will be pushed back by the one which is sitting there. So it will not be a successful job.

These are three things I must know, and the three things you already know, we have done it earlier, atom can acquire delta Hm energy can push the Maxwell Boltzmann statistics, the probability is exponential of minus delta Hm by KT. Is it oscillating towards position 2, that is why the basic frequency that 8 at which it is oscillating. Availability of vacant location at position 2, if it is an interstitial mechanism, in interstitial mechanism the content, the interstitial impurity content is small usually, it is not larger.

For carbon in iron I said it is, it is BCC form of iron 0.2% can be in solution at 725, at room temperature it is point 0.0028%. This 0.0028% is roughly 0.01% atomic percent, 1 in 100. 1 in 100 location, 1 in 100 of wholes are occupied by the carbon remaining will be empty because in the, if it is FCC form let us say even they will have (())(31:50) wholes which is as many as in number of atoms, right? So I have a large probability that neighboring site is waiting.

Any site being occupied is just 1%, any site being occupied is just about a percent, any site not being occupied is 99%, but if your 1 site is occupied neighboring site being vacant probably will be still higher than the 99%, so almost 1 you can say that this probability is almost 1. For dilute interstitial solid solutions, right?

So if you want to work out the successful jumps rate at which it is jumping times the probability that acquires energy to move towards at position, times the probability that neighboring site is vacant. This is the rate at which it can jump successfully to the position tool. Alright, let us go back to look at the atomic model of the unit step in diffusion. What the unit step in diffusion is?

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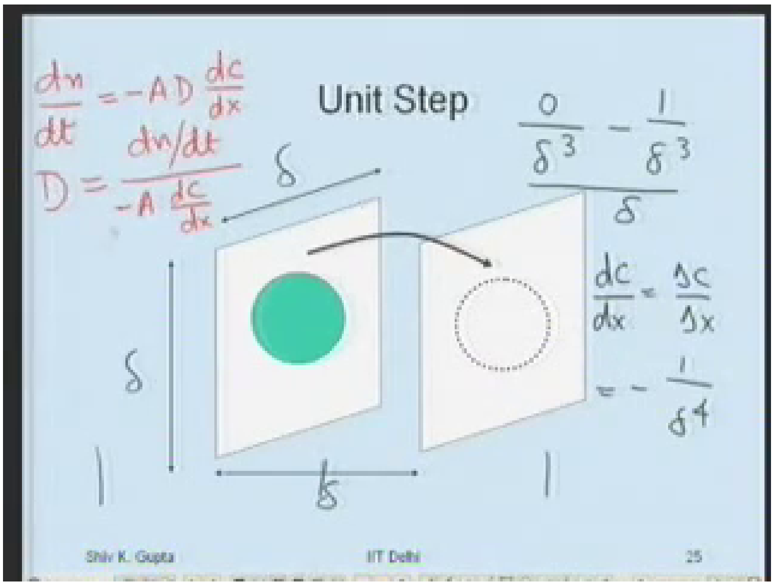

Unit Step

$$\frac{dn}{dt} = -AD\frac{dc}{dx}$$

$$D = \frac{dn/dt}{-A\frac{dc}{dx}}$$

$$\frac{\frac{0}{\delta^3} - \frac{1}{\delta^3}}{\delta}$$

$$\frac{dc}{dx} = \frac{\Delta c}{\Delta x} = -\frac{1}{\delta^4}$$

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This atom is there in this white space of the interstitial site and one should jump to the neighboring vacant site which is interstitial site and vacant. How much is the volume around this is proximately in terms of this distance is atomic diameter, this distance is also atomic diameter, this distance is also atomic diameter of the order or (())(33:56) calculations we make.

Now so the volume around in which this atom lies is delta cube, and volume in which this lies in this matrix is also delta cube. You can take the volume for 1 from the middle of the gap between them to the middle of the other one, this one from middle to this to this, it will be same, delta here, delta there, delta cross section (())(34:27). Area of cross section perpendicular direction of diffusion is delta times delta is delta square, right? So I can see what is the concentration in this position 0 divided by the volume. Concentration is defined by the number per unit volume.

Final stage I have the concentration 0 divided by delta cube. Initially I have it 1 upon delta cube that is delta C, and divided by the distance over which distance of diffusion it becomes delta C by delta X, and DC by DX therefore is equal to delta C by delta X equal to minus 1 upon delta 4, right? What is the first law? Alright, I have written A first doesn't matter.

I want to get D from here, diffusivity suppose then it becomes minus A, alright let us put the minus A here. Alright? Now you know the dn by dt, you know dc by dx, you know A, put them, let us see what you get.

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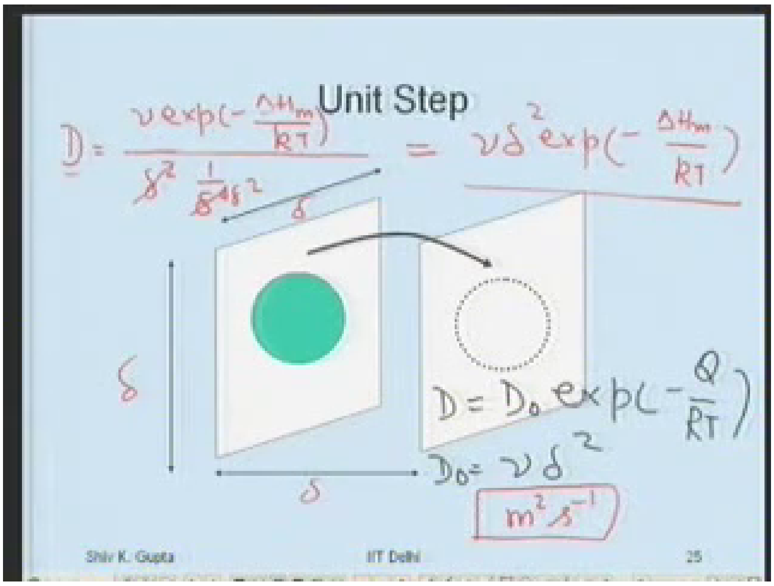

Unit Step

$$D = \frac{\nu \exp(-\frac{\Delta H_m}{RT})}{\cancel{\delta^2}\,\frac{1}{\delta^4}\delta^2} = \nu\delta^2 \exp(-\frac{\Delta H_m}{RT})$$

$$D = D_0 \exp(-\frac{Q}{RT})$$

$$D_0 = \nu\delta^2$$

$$\boxed{m^2 s^{-1}}$$

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Let us put it again, so if I write that D becomes, dn by dt we have worked out is new times exponential of minus delta hm by kt. A is delta square and minus dc by dx is 1 upon delta to the power 4. And if I simplify this, this becomes delta square here, that goes in the numerator it become new times delta square exponential of the order of magnitude, that is the distance, that is what we took, this distance we took delta, this we took delta, this we took delta, not our magnitude calculations.

Now let us compare this formula which we have obtained for D with whatever we have got experimentally, experimentally we got D is equal to D0 exponential of minus Q by RT. From this comparison I get D0 is nothing but new time delta square. If we workout for different crystal structure this new delta square may have some constant close to 1 varying from 1, in different crystal structures but order of magnitude will be the same.

New is 10 to the power 13 per second, yeah this has been done. For all temperatures which are above 200 calories is about 10 to the power 13 per second and delta of course we know, so delta square is meter square, new is per second, so units of this D or D0 for that matter, meter square per second by the unit of D0 or for that matter D because exponential term has no units. It is a probability term. Now comparing this from this Q by RT must be equal to delta hm by RT, near about KT, so delta hm by k is equal to Q by R, this is what I have told you earlier also, and it is shown here.

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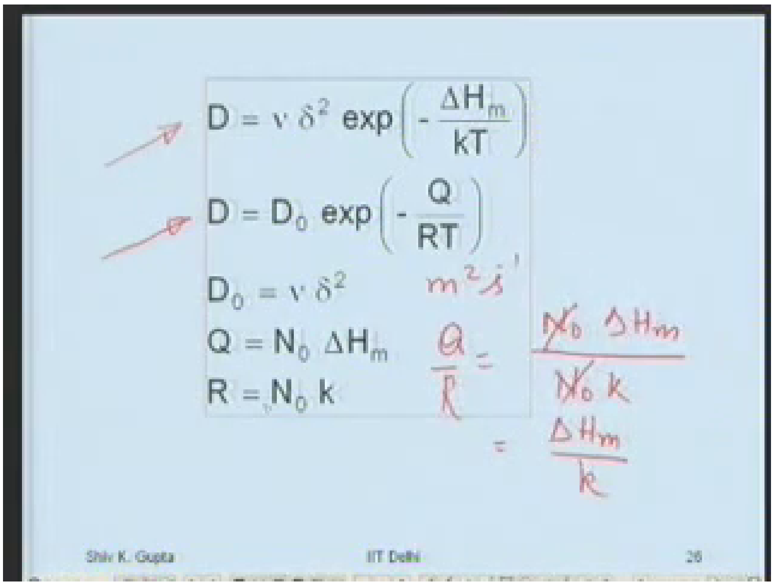

$$D = \nu \delta^2 \exp\left(-\frac{\Delta H_m}{kT}\right)$$

$$D = D_0 \exp\left(-\frac{Q}{RT}\right)$$

$$D_0 = \nu \delta^2 \qquad m^2 s^{-1}$$

$$Q = N_0 \Delta H_m \qquad \frac{Q}{R} = \frac{\cancel{N_0} \Delta H_m}{\cancel{N_0} k}$$

$$R = N_0 k \qquad = \frac{\Delta H_m}{k}$$

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Q if I write as, I have got the number 10 delta hm than Q is energy per mole and R is written as N0 times K it is equal to, so when I substitute that so delta hm by Kt, K would become equal to Q by R. Q by R will be delta hm by k. So that is how we rationalize this experimental observation with the model we worked out, that is what you worked out for interstitial mechanism and these two have been rationalized, this one is new delta square and the units are meter square per second, while this is Q is N0 delta hm and therefore Q by R will be equal to N0 delta hm divided by N0 K. N0 cancels with this and this is equal to delta hm by K.

This is the same thing for that. Right? This is for the interstitial mechanism of diffusion, come back to the vacancy mechanism of diffusion that is also an important one because though the interstitial mechanism is much-much faster than the vacancy mechanism we can see that why.

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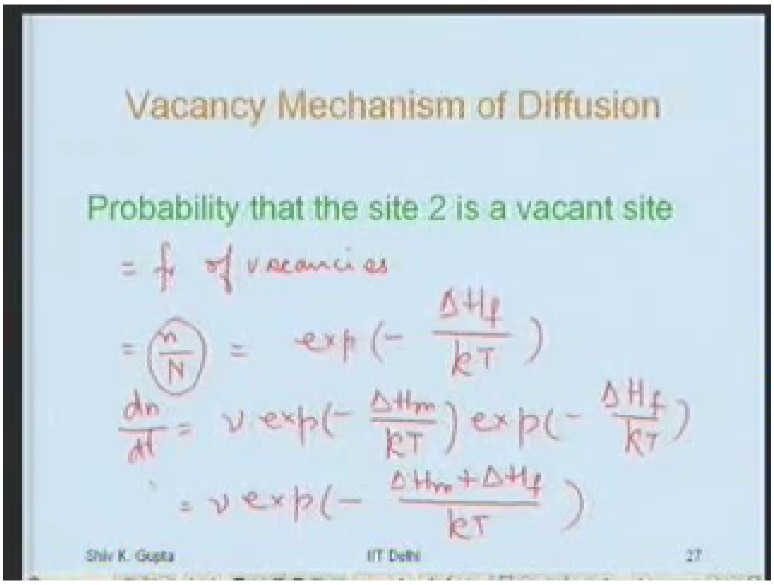

Vacancy Mechanism of Diffusion

Probability that the site 2 is a vacant site

= fr of vacancies

$$= \frac{n}{N} = \exp\left(-\frac{\Delta H_f}{kT}\right)$$

$$\frac{dn}{dt} = \nu \exp\left(-\frac{\Delta H_m}{kT}\right) \exp\left(-\frac{\Delta H_f}{kT}\right)$$

$$= \nu \exp\left(-\frac{\Delta H_m + \Delta H_f}{kT}\right)$$

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Now the probability that the neighboring site is a vacant site, probability is that the site 2 where the atom is jumping is a vacant site, it is not one, I can’t take it close to 1. It is equal to the fraction of vacancies which I have in the system. So this will be equal to the fraction of vacancies or probability that the site is a vacant site, it is the same thing and that is equal to exponential of minus enthalpy of formation of vacancy divided by KT. So when you substitute that you get, this is the fraction of vacancies, right?

This n and this N do not mean the same thing. Dn by Dt we have got this new times, exponential of minus, let us see enthalpy of motion required for in goes from state 1 to state 2 intermediate step energy is to be increased, then multiply the neighboring site being vacant, and these two exponential terms can be put together. Now if you substitute in there you can get again the D and you will find the D0 is again the new delta square and Q is not delta hm plus delta hf.

Delta hm and delta hf all these activation energies for different processes are in the range of, the order of 1 electron volt, this becomes 1 plus 1, two electrons volts, probability of this happening becomes smaller, process becomes slower much much slower, so diffusion of a subtitutional impurity by vacancy mechanism is a much slower process than diffusion of an interstitial impurity by the interstitial mechanism, which is a much faster process, okay?

Alright! So that is how we find, suppose I have a steel, steel usually contain more elements than iron and carbon, carbon is a must, if I want to call it a steel iron must have carbon. Carbon is interstitial but other elements like manganese, chromium, vanadium, nickel, these are there smaller quantity to larger quantity depending on what steel I want to make, what properties I want it to have, or if it is a tool steel I may have vanadium, tungsten, chromium, etc. and large quantities there.

So these the all subtitutional impurity atoms, a solute, subtitutional solutes, they can diffuse only by vacancy mechanism, if let us say during casting or something my steel got, heavier elements got concentrated in the bottom and lighter ones come on top, now if I want to make it uniform composition it will take my lot of time, normally what we do is, we heat it, soak it, deform it, whatever shape we want to give it.

During deformation process it is possible that diffusion becomes faster, I will tell you that, it can happen. We deform it during deformation I get more imperfections, and more imperfections can help it to diffuse faster, otherwise if I simply soak it I may have to soak it for 15 – 20 days, if you want to homogenize it. But as carbon is concerned I told you that one hour per inch of thickness.

That is enough, not only it homogenized the carbon it also make it complete uniform austenite. Right? So therefore interstitial mechanism is a much faster process of diffusion than the vacancy mechanism, all other mechanism usually don't work and I am not going to talk about them.

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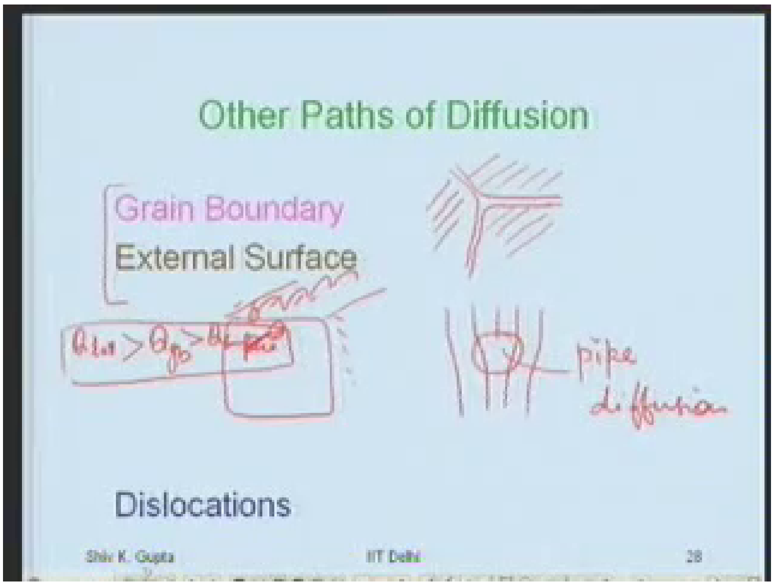

Other Paths of Diffusion

Grain Boundary

External Surface

Dislocations

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Now, other than this there are other parts of diffusion, in the solid Grain boundary, external surface, dislocations. Let us look at the Grain boundary. You recall the Grain boundary, this is the region in Grain boundary where atoms are lying in a not in a crystalline form, they are very openly placed; the packing efficiency is not very high. Not like inside the crystals. Where it has to diffuse through the vacancy mechanism where electron clouds have to overlap when it diffuses or an interstitial mechanism, electron clouds are overlapped.

Here it doesn't have to do all that, it is an open space, it can move faster. But if I come to the external surface atoms in the surface have no constant on this side, if this atom in the surface has to jump, let us say this is the direction in which it is jumping, you can keep jumping like this, but if it has to jump here it has to go oscillate and go through the next vacancy if it is a vacant site, here it doesn't have to bother, it can keep jumping on the surface, that is a much faster process.

And similarly in dislocations here in the core of the dislocation space is there, a lot of space is there, because if you look in the interstitial has a much bigger wide space, you look at the carbon, can simply go like this inside as if it is moving in a pipe. This kind of diffusion is also called the pipe diffusion and it is a faster process. Faster meaning the activation energy required is going to be less for such processes.

Between gain boundary and external surface which one has a lower activation energy, grain boundary or the external surface? External surface because there is no constant work ever in one side, activation energy must smaller, so activation energy if I look at this, we compare this with the, with the one which is diffusing across into the volume of the solid rather, that is also called the volume diffusion or the lattice diffusion.

The activation energy for lattice diffusion is higher than that for the grain boundary, and is higher than that for the external surface. And this can be, has been seen and observed in experiments, one experiment I will demonstrate here.

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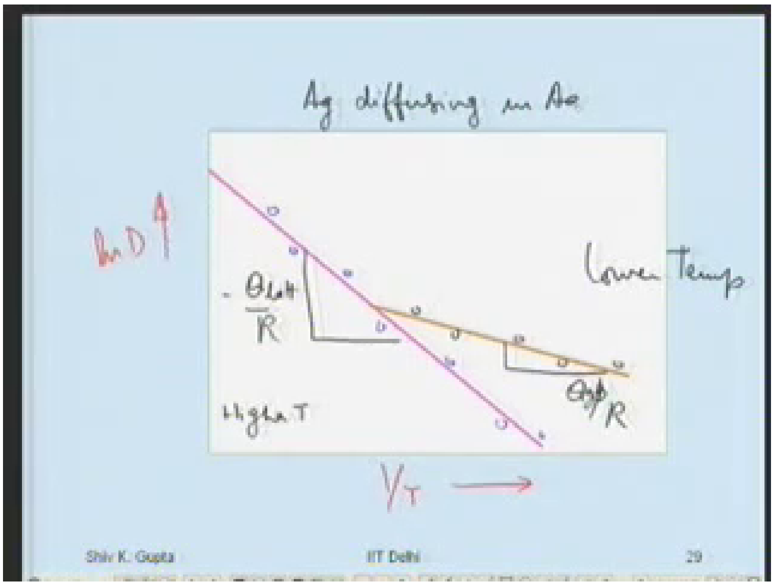

On this scale, this is the logarithm of the and this is the (())(49:54) of temperature, diffusion in silver. Silver diffusing in silver, poly-crystalline silver. Well in a single crystal it diffuses like this, that is where the single crystal, the points falls let us say these are the… But when I have a poly-crystalline substance at lower temperature it starts diffusing like this. And this gives me the Q by R. And Q by R here is this.

In a single crystal it goes like this so it is a lattice diffusion, this is a Q for lattice diffusion, and this is a poly-crystalline a grain boundaries are playing role, this is grain boundary. Grain boundary diffusion is not a taking place at this range we is the higher temperature, temperature is higher on this side, this is a higher temperature. And this is the lower temperature. This is 1 upon T.

At low temperatures this becomes so low the rate of because Q is high so its slope is very fast, the diffusion through the lattice becomes so much slower as compared to that for the grain boundary. So grain boundary takes over because slope there is a small. And these rows could be different for these two. So that is what shows the lattice diffusion is a difficult and more slower process than the grain boundary diffusion. This is for silver diffusing in silver.

How do we measure this, how do we observe this, silver is not identifiable from another silver, if you take radio-active silver and let it diffuse so you can measure the activity to find out how much radio-active atoms have come in that particular cross section. Thank you. I will start on the phase transformation in the next class.