Principles of Physical Metallurgy

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Lecture No. # 15

Diffusion in Solids

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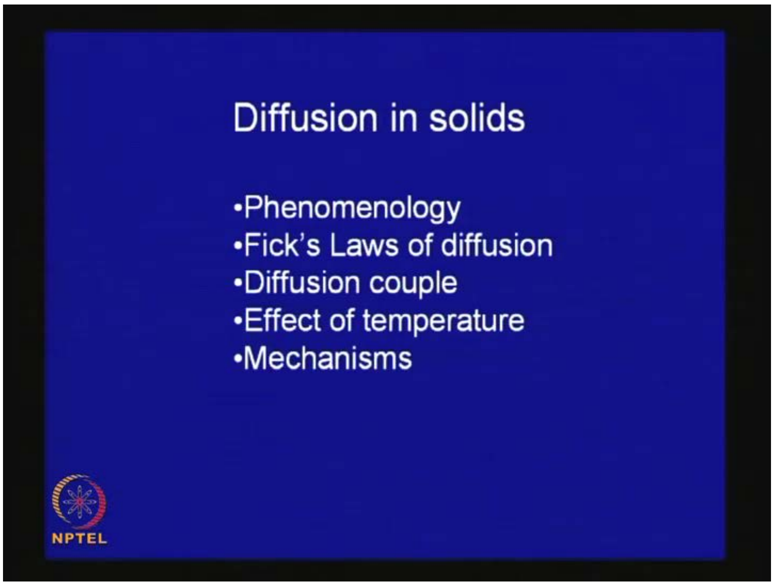

Good morning. Today we start a new topic a new chapter that is diffusion in solids. Now here, we are going to look at I mean understand, what is diffusion? Why it is important? We will also know about laws that govern the phenomenon of diffusion will take up some examples of diffusion couples. We will learn about the factors particularly the effect of temperature on the kinetics or that rate of diffusion. We will also learn about mechanisms by which diffusion takes place in solid.

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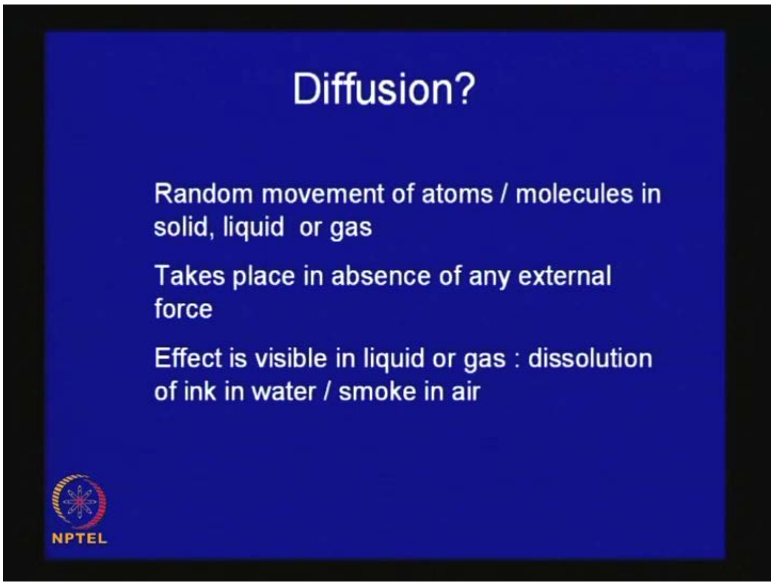

Now, the first the question comes, what is diffusion? Now, in liquid or in gas the moment of particles is very obvious. If you light a candle the corner of a room, you will see the flame and on the flame that is smoke that comes out that gradually moves, and spreads into the room. Similarly, if you put a on a (( )) some aroma essence, you can feel it in a even if it is kept at one place in the room, you it you can feel it you can smell the aroma from a distance and this takes place through a process called diffusion.

And diffusion basically what we can say is, it is a random moment of particles that is atoms or molecules in solid, liquid or gas. Now as I said in liquid or gas you know it is quite obvious and it takes place that process of diffusion does not need any external force. It can takes place even then absence of gravity or in absence of any external force. We will know about, what is it that drives that process, as we go along. Now this effect of diffusion as has been mention is quite feasible in liquid or gas such as you can say it just drops a you take a test-tube you know drop say red ink take water and drops some red ink in it; initially settles at the bottom and later on you will find that is diffuses that entire that to whole of the water becomes colored and which is shown semantically over here.

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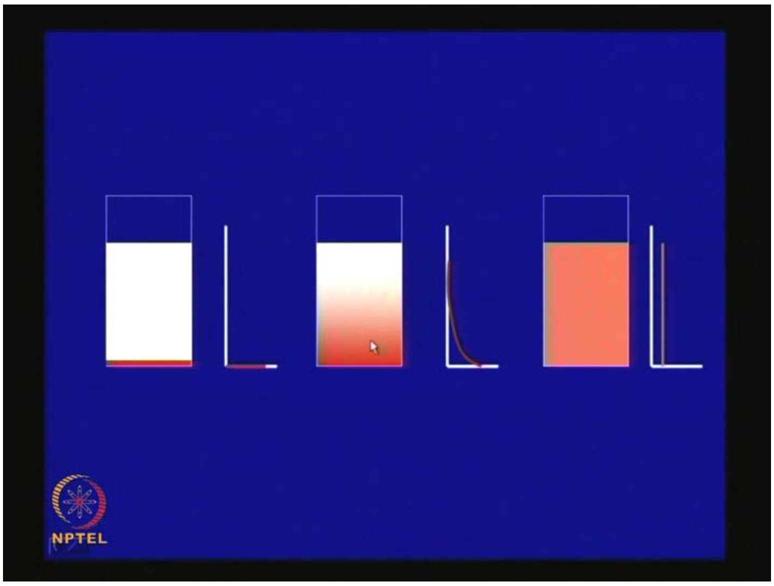

So, this is a container where you have water and on the bottom you have put some pigments, which is soluble in water and gradually you will find this dissolve and this process of dissolution basically is one called diffusion and it depends on time and that concentration that color is an indicator of the concentration. You can see that it is changing, it is deep trade over here it becomes little light. So that mentioned it proceeds here it is still the concentration of the pigment is 0 and here after some infinite length of time it will become uniform and this takes place even in absence of any external force. Now you can enhance the process by starring, which is possible in liquid but it is not possible in solid.

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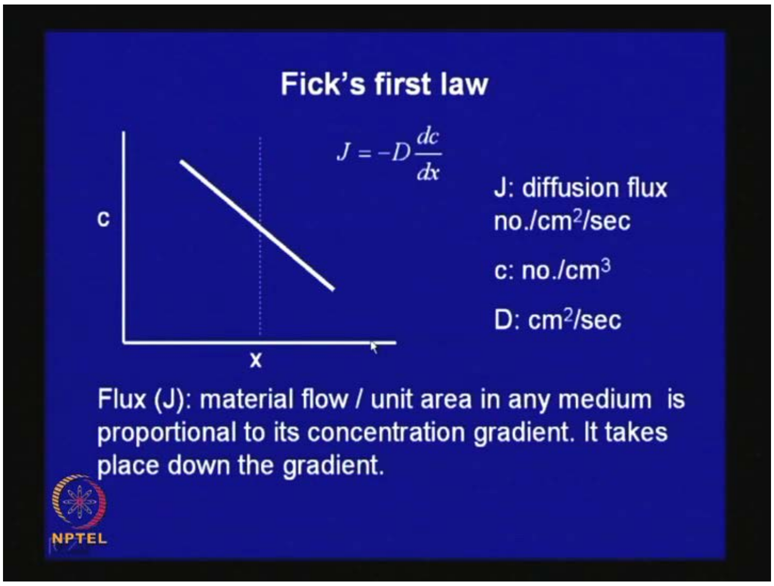

Now, let us see what is the factor that governs the process of diffusion? See basically the diffusion the driving force is the different in concentration and which is shown in the slide over here. Suppose this axis is the concentration, this axis is the distance and in any medium, if a concentration varies from point to point. There will be a diffusion flux that particular species, whose concentration is plotted, will move at a particular rate and this will be governed by the difference in concentrations; say suppose here that is one concentration here, it has another concentration.

So, this concentration difference is the driving force and this is suppose you imagine this is an imaginary plane and through it that is solid moves from this side to that side. And this is stated in this flow that diffusion flux, which is given as number of particles, which passes through a particular area that means a number of particles passing per unit area per second is the diffusion flux and this is proportional to concentration gradient. This is the change in concentration this is thus infinite decimal distance along x axis. So this is the concentration gradient.

Now in this case what we find that concentration gradient it is constant. So that this gradient here and here it is constant. Nowhere at every point irrespective of time has the concentration remained same. It does not build up or it does not deeply and what is known the dimension of D and it is very easy to find out.

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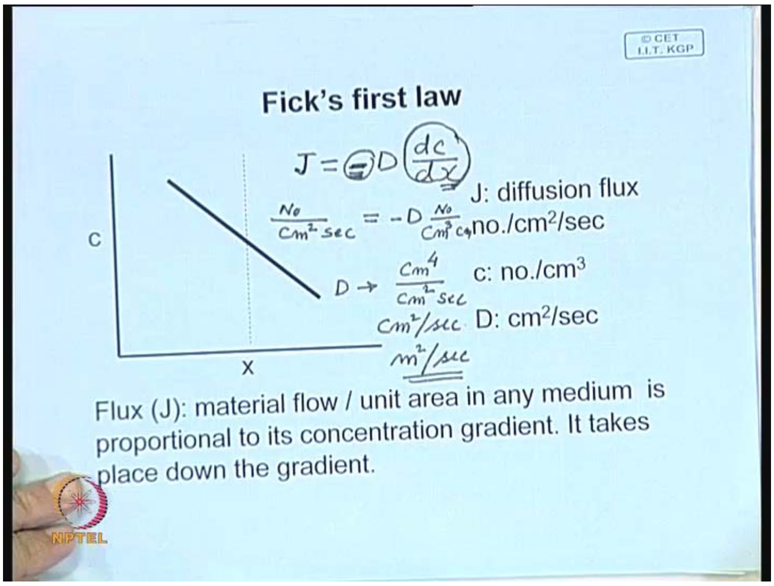

If you look at this expression, you substitute so that means the diffusion flux is minus D dc dx. So, here you see this J is dimension is number per centimeter square per second. Now, this is D. Now what is concentration? Concentration also we can say that is number of particles that is number which is dimension less per centimeter cube and you also have a centimeter dx, this is a centimeter. Therefore, what you have that means D will therefore, that is dimension of D will therefore, the centimeter to the power 4 over centimeter square second, so that means this is centimeter square per second in a side, it will be meters square per second.

Now, in this case there is a look at a negative sign, why this is negative? Because this flux takes place and that particle moment is in the direction in which the concentration decreases. Therefore, the flux is positive and this gradient dc dx, this gradient is negative. So, basically it takes place in the direction in which the concentration decreases with distance. So that is why there is a negative sign the J as the negative sign.

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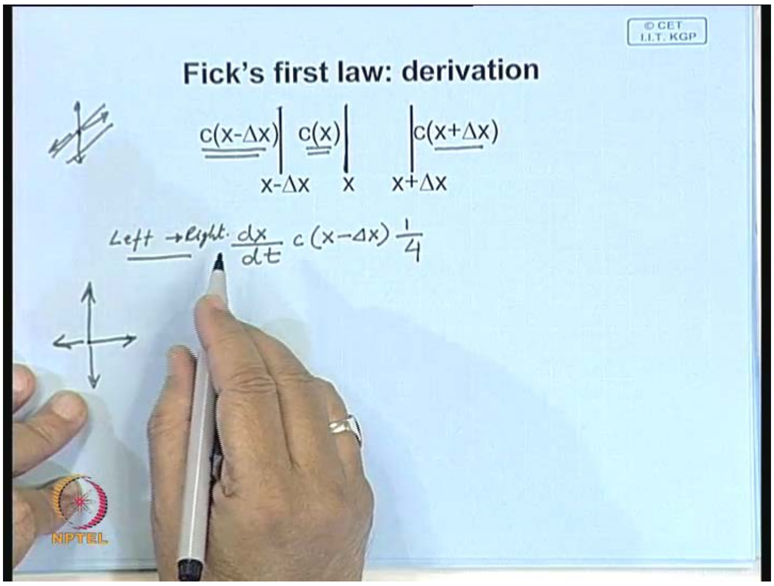

Now is there a way we can derive it, which is shown here see the atoms keep are particles are keep on moving. So, what we can visualize suppose we visualize one plane over here, where the concentration is c; c which is the function of x here and now imagine another plane delta x distance on the left and here let us say that concentration is given as c x minus delta x. Similarly, imagine another plane where the concentration is c x plus delta x. Now this function taken is expanded in a Fourier series, now which is shown over here.

You can make on approximation say the atoms number of atoms, which are moving from left to right. How do you find that out? So in a unit time that atom moment this atoms they have a velocity say dx dt is the velocity. Now and with this velocity how much of material is moving this will depend on the concentration that is c x minus delta x. So, this is the moving from left, left to right. Now this is equal to and in another case, what you can look at that atom in a particular plane. You know imagine this particular plane it can move up down it can move in this direction.

This direction so the and it can also move say suppose we consider this is a 2D case say basically you have one direction here. It can move up and it can move in this direction also it can move in this direction it can move in this direction. So in this case there will be a chance that it moves forward this will be one over 4. In fact it can also be generalized in a 3D case also that probability that will move in a given direction this comes out to be one-fourth. So this is the one moving from left to right. Similarly, number of atom from moving from right also you can write in the same fashion, which is shown here.

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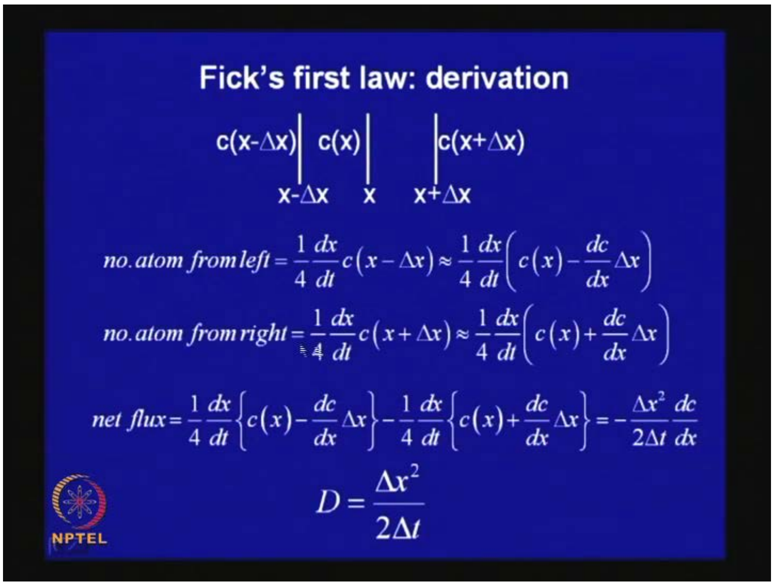

Now, this you can expand in the form of a Tailor series, and you can neglect that higher order term. So this is equal to the c x minus delta x equal to c x minus dc dx delta x. Similarly, number of atom from right is this, so therefore net flux you can say subtract this minus this, if you subtract the net flux is equal to… And this little algebraic simplification. It is possible to show that this is equal to delta x square over twice delta t dc dx.

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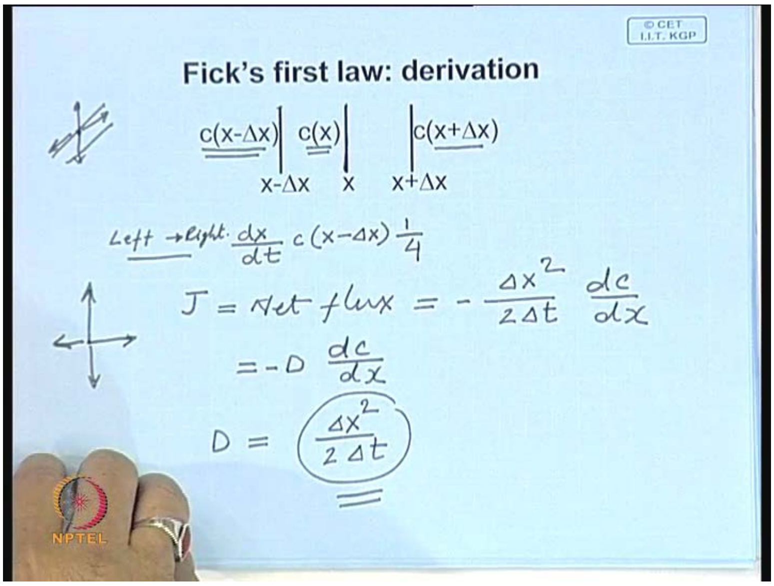

Now look at this net flux, so basically net flux here comes out to be delta x square 2 delta t dc dx. So what does it show, so this is net flux is J and Ficks law states that this is equal to minus D dc dx. So, that means that diffusivity if you derive it like this, it comes out that diffusivity if you derive it like this it comes out that the diffusivity is actually someway connect it with this delta square over to delta t. And this is something which will later see. It has a relevant in when we look at some of the diffusion equation solutions.

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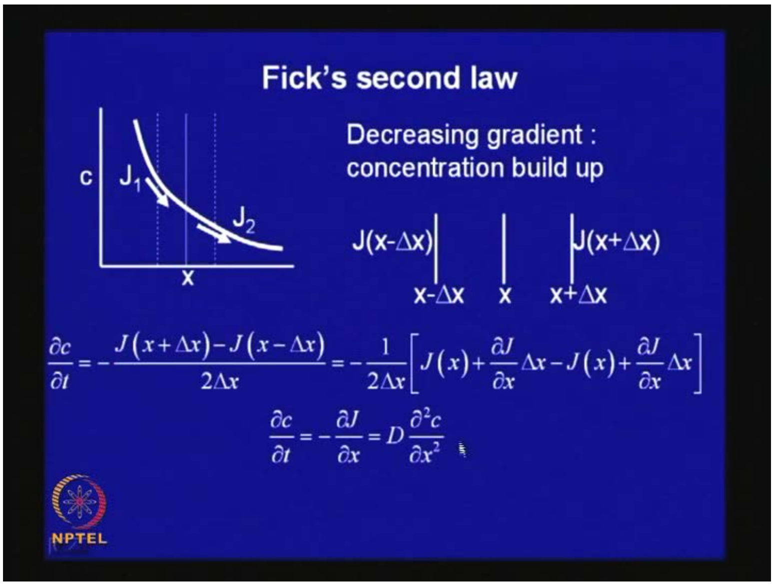

Now, let us look at Ficks second law. In this case, imagine that previous case what when we looked at we found that concentration, you know this slope is constant. So here look at that number of atom which is a moving from this side to this is actually constant everywhere that means flux whether you consider it here or you calculate flux here. That flux is constant that means if you consider a thin solid here. Another plane over here and you try and find out that number of atoms, which is going into this thin slap is same as the number of atom, which is going moving out of this slap and concentration within this slap that thins slap remains constant.

Now this situation is if we look at a situation something like this where the concentration gradient keeps on changing what will happen. You consider say this is a plane and you say that this is a position set minus delta x towards left. This is a plane plus delta x towards right. Now look at here this slope, this slope is larger this slope is smaller. What does it indicate that means number of atoms moving out is less the number of atom moving in. So, what it means that concentration with time here is going to build up and it is possible to derive this expression exactly in the same way as before and then we get the Ficks second law of diffusion.

So that means here that gradient is decreasing and this decreasing gradient leads to concentration build up. Now here you imagine that this is a plane where you flux is J x whereas, here delta x towards left a flux is x J x minus delta x and here it is given in a functional form j x plus delta x. Therefore, the concentration build up here will be the amount which is coming in and amount, which is going out minus amount which is coming in and you substitute this here and you can expand this Tailor series neglect that higher order term and expand this as well. Now what you find this J x J x cancels out. So what it turns out to be that change in concentration with time dc dt is equal to minus dJ del J del x and then what you get is you substitute J over here. You will get the second derivative.

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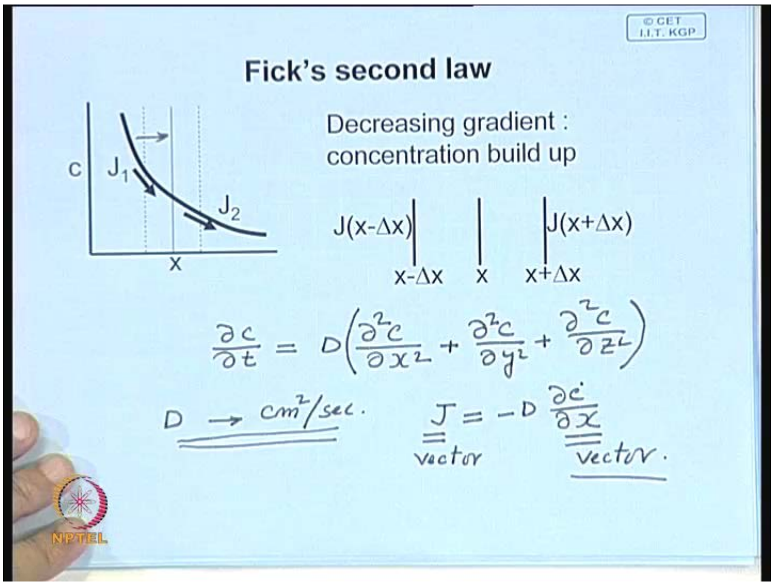

Now where we have return here as a partial derivative in fact it is possible to extend it to a much see in this case, we have considered a one dimensional situation diffusion moving along direction x only and therefore, we have return it is dc del c del t del two c del x square. So, basically what it means is that diffusion is taking place along the direction x only. But in a 3D case this can easily be extended this can also be return as d two c del y square d two c del z square. Now obviously you may wonder what is the nature of D? We have looked at its dimension its dimension is centimeters square per second but what is it nature.

Now D represents connects to vector. This is concentration gradient. So that means J is also a vector because this is your flux. So, this has the direction in this case is a flux moving in direction x. Therefore, this x this is a vector concentration gradient concentration this is scalar. But the gradient this is a vector gradient is a vector.

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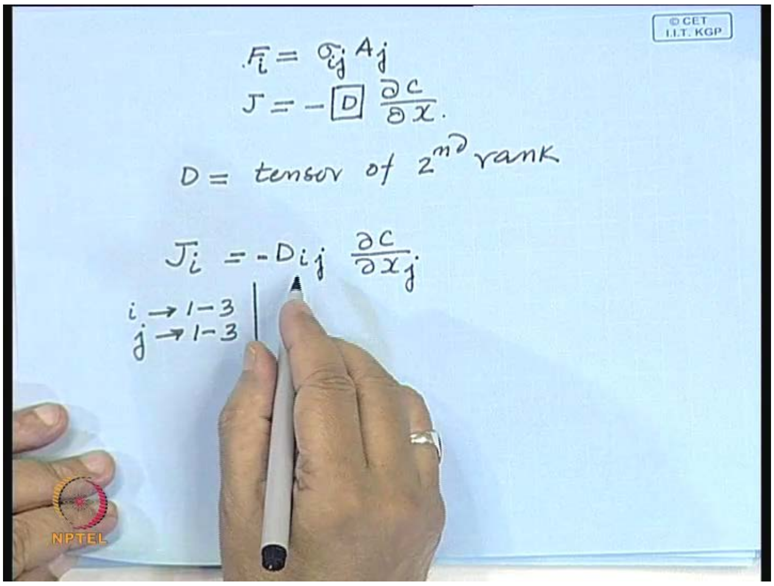

Therefore, what it means J connects as D connects two vector D connects two vectors. So in that case D is cannot be scalar this has a dimension basically it has basically what we can say D is a tensor of second rank, tensor of rank two which is exactly same as we define stress, when we define stress? How do you define stress? Stress is that is force it relates force is stress over per unit area so force equal to stress times area, area is a vector force is a vector. So, usually what we write is a suffix like this and here this is i j.

So, same logic so stress is a like stress D is also a second rank tensor. Therefore, D will have two value i j. Therefore, J i you can say that this you can write as minus del c del x j, here j means summation over j and it can be one two three. Therefore, obviously second rank tensor and i and j can take values 1 to 3. So we will come back to it little later.

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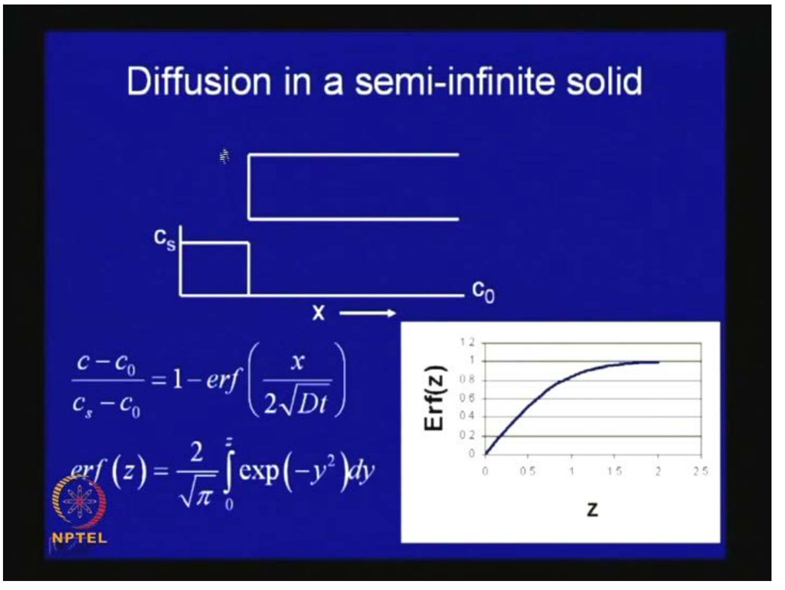

Now, let us look at few solutions. Now imagine that we want to increase suppose this is a solid we have heated at a particular temperature. Say suppose we take a piece of iron, it put it in a furnace and this side is insulated here and this surface we maintain a concentration of carbon here at a level c s. This is the concentration of carbon over here and this is heated at a particular temperature and we leave it and this is pure iron to start with. So what will happen this carbon will diffuse and this rate of diffusion will be determined by this concentration gradient?

Because inside to start with there is no carbon, which is shown over here this is the distance x. So x externs from here to here, so this side is negative, this is x 0 and here what you have is the concentration plotted and this side we are maintaining the concentration on carbon. So basically we can maintain gases in atmosphere with definite carbon potential, which is equivalent to a certain carbon concentration at this surface and here in that case what will be the solution like.

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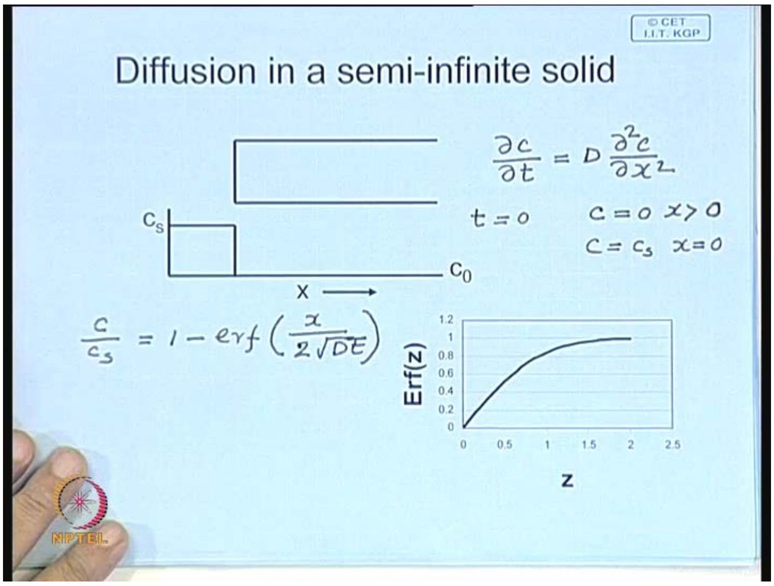

So, basically what we can say our equation that we have to solve is del c del t. This is a 1D case. This is d two c del x square. Now what we have at t equal to 0 that concentration c equal to 0 at all x, x is greater than 0. So at all x this is the boundary condition. Next is at t equal to 0 c equal to c s at x equal to 0. Now this solution in fact we will not go into the details of the solutions. But the solution is given over here. The solution is c equal to the concentration equal to concentration at any point over here at any time t is given as by this expression, which is c minus that is c 0.

In this particular case, we will say that this is equal to 0. So what we have this concentration c over c s and this is equal to one minus error function. It is a special function we will know about it little later. This is x over 2 root Dt and error function basically it is a what we say that this error function is given over here, erf error function is this integral that is 2 over root phi integral 0 to z exponential minus y square dy.

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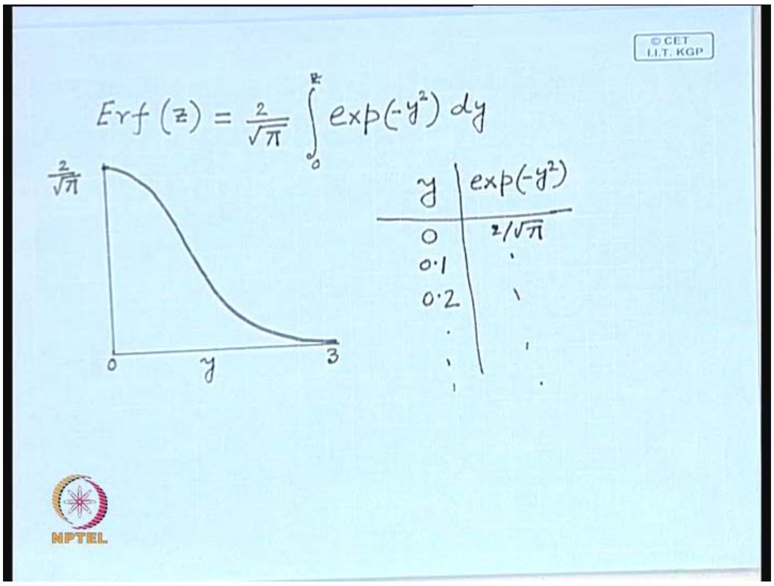

Now if we want to look at, what is the nature of this function it is very easy to do that in a spreadsheet, which you can do here as an exercise in an excel sheet. You define two columns, one you try and generate a function y, say start with 0 and with every increment say 0.1, 0.2 and in this column you just put this function. You calculate this so here in this particular case if y is zero, in that case this is 1. Therefore, this will be 2 over root pi and as this increases the power is negative this course on decreasing.

So what you will have a function you calculate this and if you plot you will get a plot say something like this and in fact this plot is quite familiar that means with a normal distribution plot where we extend it a mirror image of this on the other side. Therefore, this is basically it is nothing but a normal distribution plot that this is the probability density function and this is why many cases the process of diffusion can be simulated by generating random number.

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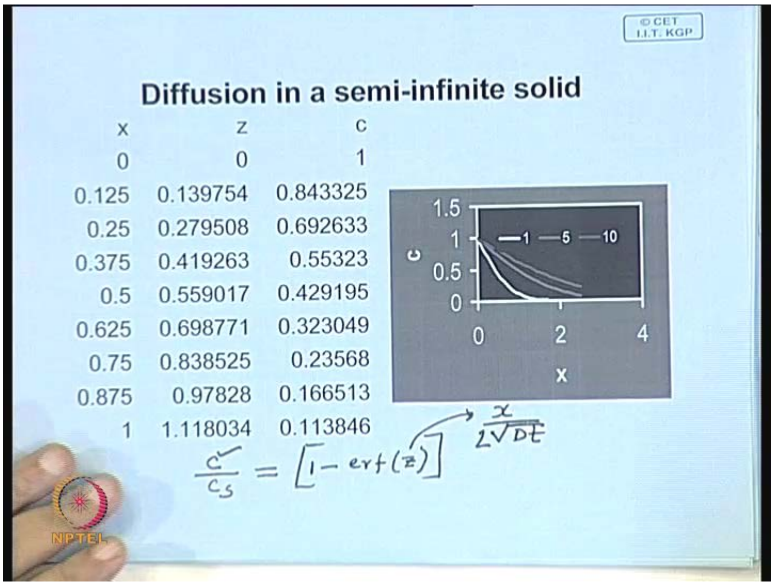

Now, this is one example of diffusion in a semi-infinite solid. We talked about just now and here you can see that if you go back on go back to this. So basically what you have is c over c is basically in this particular case you see that c over c is equal to one minus error function of z. So at various places of x this z is equal to x over root Dt twice root Dt. Therefore, at various places it is possible to calculate this concentration c; you can calculate this and which is shown over here and if you plot at a smaller time at a lowest time.

It is more clear over here at time units say one it is like this. The gradient is very steep. You keep it for a longer duration the gradient become smaller and its goes on like this and if it goes to infinity possibly you may find it becomes uniform and only then the process of diffusion will stop.

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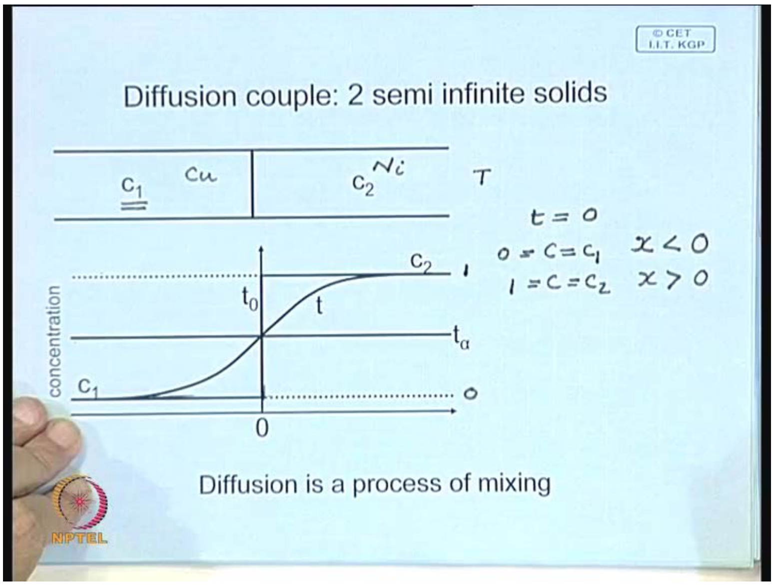

Now let us take up a case of a semi infinite basically, two semi-infinite solid which are shown over here. Say suppose we take two piece of metal, one say copper, another let us say nickel and they are soluble in each other significantly. So this side is pure copper to start with, this is pure nickel to start with. They are joint here and then we keep it the heat it to a temperature T. Then what happens then with time we will try and say that this is a concentration say suppose what we have plotted here is let us say the concentration that c 1 is a concentration of nickel on this side, which is c 1 which is c 2 is a concentration of nickel on this side.

So at T equal to 0 so basically what you have is a c 1 at T equal to 0 here virtually we can say that this is equal to 0 whereas, this is concentration is 1. So that is its pure nickel this side here there is no nickel to start with an in that case your concentration plot is like this. It is goes like this goes up like this. So that means at t equal to 0 that concentration is c equal to c 1 for x is less than 0 and c equal to c 1 for x greater than 0. If one side is pure copper and other side is pure nickel. We can say here that is c is 0 here, here c is 1.

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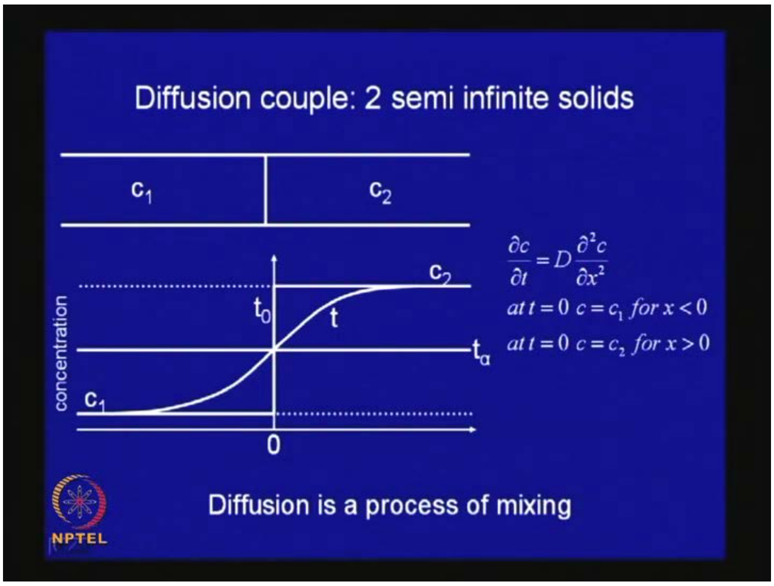

And then it is also possible to solve this. So basically what we are trying to do I mean here also if you go through the solution, you will find that this keeps on changing with time at intermediate time. So this will go like this. At infinity it will be uniform all through. So that means here when it becomes uniform it becomes homogeneous, then there is no diffusion flux on the number of nickel atom moving from left to right is equal to number of nickel atom moving from right to left. So net flux becomes 0 at T in infinity, so one way we can say diffusion is a process of mixing.

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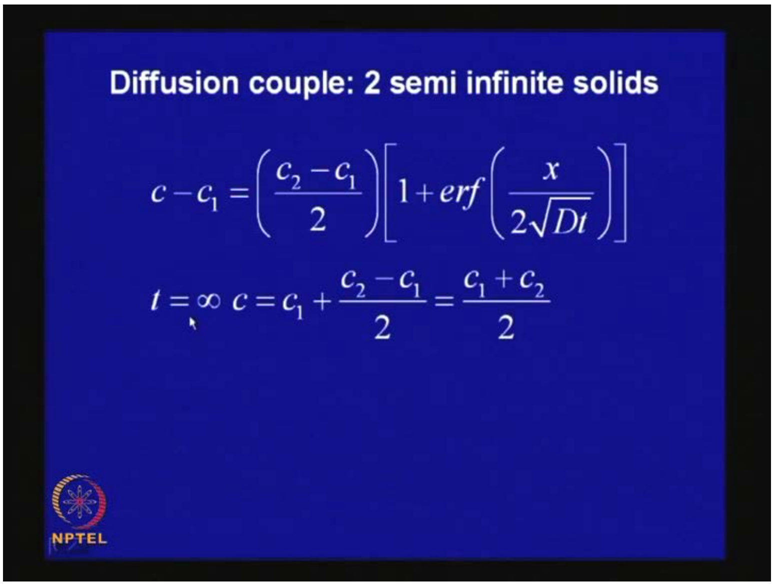

And in this case solution also is based on that error function and which is shown over here and here you can clearly see when t equal to infinity in that case this concentration it is just average of the 2. So, this is c 1 plus c 2 by 2. So this is somewhere midway so that means this will fifty percent copper, fifty percent nickel.

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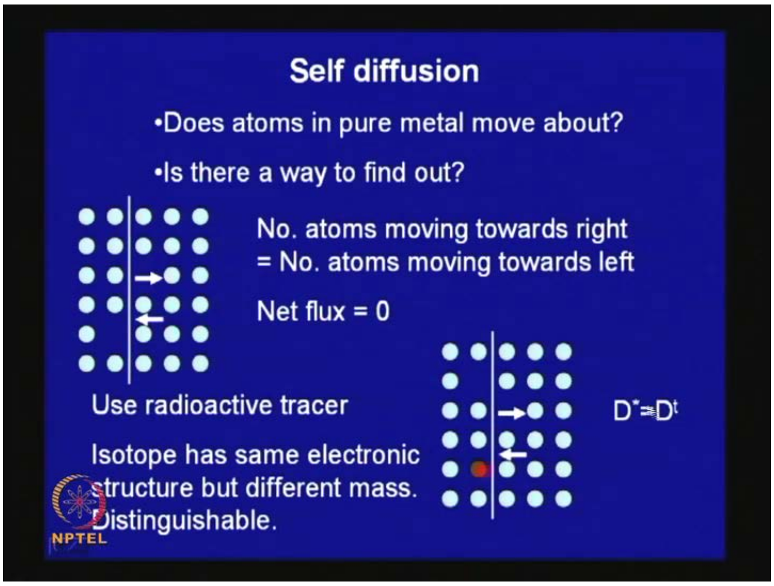

Now a question that comes up obviously what happens if the system it is a single component system say if it is pure copper of pure nickel of the atom stationary or do they move and is there a way of finding this out. So certainly we know that atoms particles keep on moving at any instant in a pure metal. The flux possibly, which is shown over here schematically. Say in most cases is a solid the atoms are arranged in a definite order which is shown here. It also has some vacancies and later on we will see that vacancy play an important role in diffusion and now here take consider a point over here.

The number of this atom say if it is copper number of atom moving towards right is will be equal to that towards left. So that net flux is equal to 0. Now is there way of finding out or estimate that what will be the diffusivity that D capital D. What will be the diffusivity? The one of the easiest thing to do is we know that most elements they have radio isotopes and which can be detected. They are if this radio isotope is added as a tracer, so which is shown over here and this also is more or less nearly identical to other atom. So if you add a small amount of this radioactive tracer then there is a possibility, you will be able to track its moment by some counter here placing the counter it is possible to tracks this moment.

This isotope they have exactly same electronics structure but it different mass through in a way. Therefore, distinguishable and from its radioactivity can be detected. In fact this tracer diffusion that D t we can take that this is nearly equal to there is a slight assumption because they are true there is they are nearly identical but not exactly same. But still we can say make an assumption that this diffusivity of this tracer element. We can say that diffuse the self diffusion coefficient of this species that metal atom.

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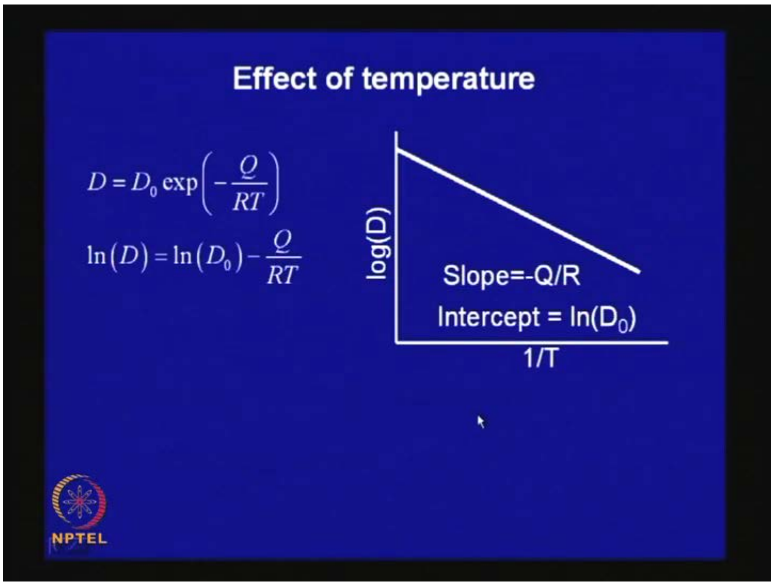

Now, what is the effect of temperature? Temperature plays a very important role temperature plays a very important role an moment of atoms are that which is shown over here. That diffusivity is a strong function of temperature it is represented D is equal to D naught exponential minus Q over R T. Now this R is a universal gas constant and Q is the activation energy. Later on we will look at its exact significant of this activation energy.

But, if this D can be estimated at different temperature by just that example which I just sited before and then you can plot in a logarithmic scale if you plot log D again reciprocal of temperature, you will get a line and this slope will be minus Q over R and then intercept you can find D naught. That diffusivity at a particular case this is the intercept, so basically when a 1 over T is 0 at infinitely large temperature.

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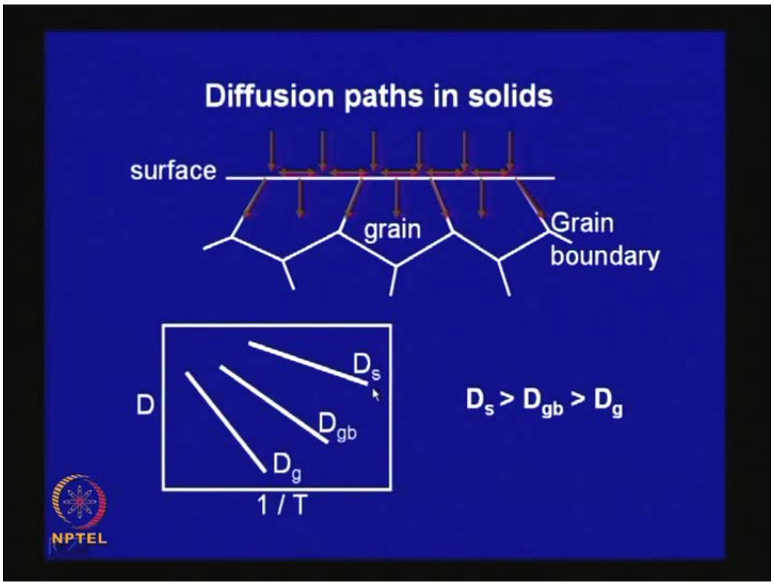

Now, diffusion also depends on the path through which it moves. Now we know that mass metals that solid they are not made of different crystals. They are oriented differently there is a grain boundary there is a surface, so which is pictorially shown over here; say this is the free surface we are maintaining some pieces here say some gas a hydro genetics exposes to a metal and you have hydrogen and then hydrogen is soluble in most metals to some extends and here that how will this hydrogen will diffuse into the metal. Now one way it can move through the crystal lattice this is the one grain of a particular orientation it can move through this, it can move along the surface. So this is the surface diffusion, it can move through the grain boundary.

So, whenever your performing an experiment therefore, it is quite difficult I mean each of these will have some role to play and what we can understand is that grain boundary we have looked at the structure, grain boundary has a little more open space then the crystal lattice itself. So what we except the diffusivity along this the moment of this species that hydrogen or any atom along the grain boundary will be faster than the lattice. Similarly, on the surface which is an expose surface here the freedom of moment will be even greater.

Therefore, the diffusivity along the surface will be even higher and which is shown semantically here this is the D again basically in the logarithmic scale log D plotted against one over temperature. Now the moment of atom through the lattice will be slowest. So if you draw a line from over here what you see the diffusivity here is lowest. Next the diffusivity along the grain boundary is higher and this is the highest.

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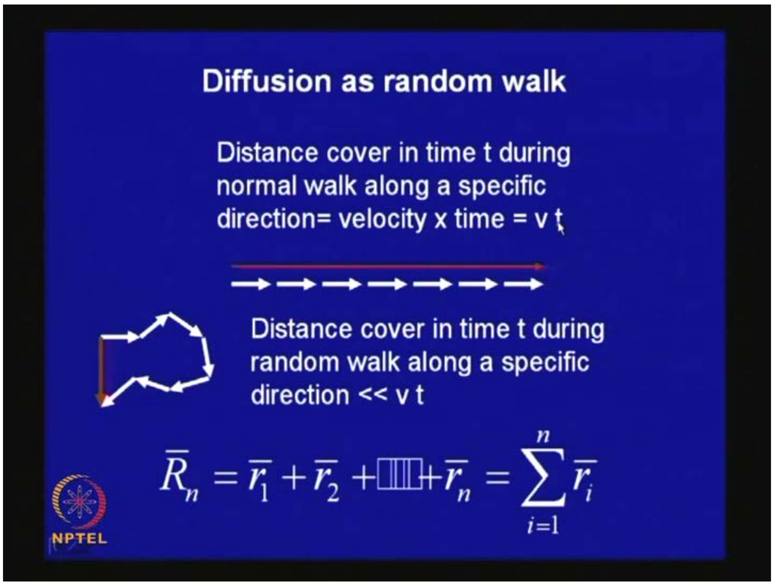

Now we when we looked at the case of that distribution that error function what it came out is that it has a probability distribution, which actually replicates the one of normal distribution. Therefore, we can say that diffusion we can model as a random walk phenomenon what happens if someone if an atom is moving with a velocity v. Let us say and if it moves for a time t it will cover if it moves along the same direction without encountering any obstacle. Then the distance covered will be v times t. So this is a moment along a particular direction. So this is a particular directional moment. So if a person is walking so imagine is walking with a speed with a velocity v along a direction specific direction.

So in time t you will cover a distance v t and suppose is moving randomly say which is a one can say when you moves you will be may be moving like this at one instantly moves this distance; then suddenly he changes the direction and it keeps on every step keeps changing the direction and then finally, after a certain number of step is here and then you can find out, what is the total distance and this distance definitely is say if you count 1 2 3 4 5 6 7. So seven steps seven steps here take in around seven steps takes in this long distance. So whereas, same number of steps takes in only the shorter distance. So basically what we can say that the distance covered in time t during random walk along during random walk is much less than v t and this is a way it is possible to simulate the process of diffusion and which is quite easy.

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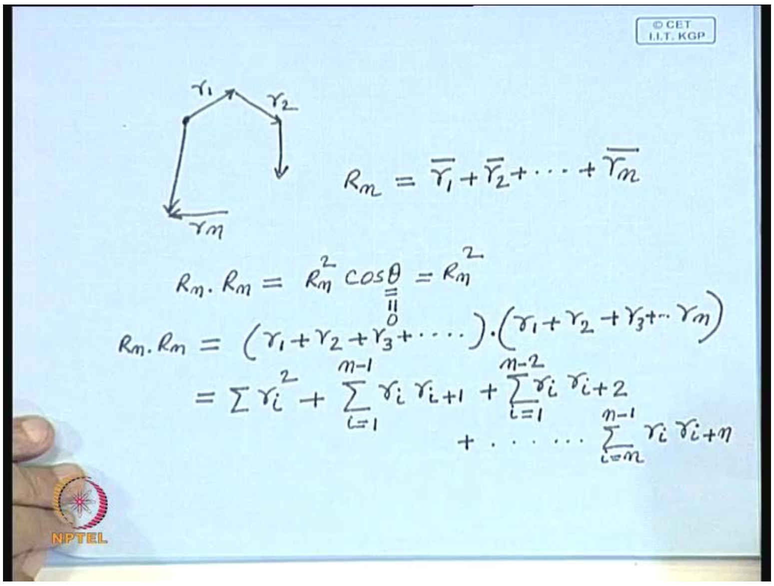

Say, suppose you try that you are moving say you are here, you move a particular distance r 1 here, you move another distance r 2, another distance r 3. So in this same way and finally, you come here after the n th step you come here, then you are effective displacement is from here to here. Now how will you calculate this, so total distance covered in n step will be the vector some of each of these are vector plus, so now how do you find out that magnitude of this distance? Now, we know that vector dot product if you say take a dot product R n dot R n, this will be equal to R n square cos theta.

So this is the same, so same vector so here theta is equal to 0 so this is equal to R n square. Therefore, what you have to do is just multiply R n with the R n so basically it will have r 1 plus r 2 plus r 3 times r 1. Now it is quite easy to do it and in fact what you can do is try this method. So r 1 every time so basically you can this can be written as summation r i square plus summation r 1 with each one of these. So basically I can write it r 1 with r 2 so r 2 is 1 plus 1. So i plus one we can write it like this and i extends from 1 to n minus 1. Similarly, there will be another term r 1 you will be multiplying with r 3 here. r 1 with r 3 r 2 with r 4 that way so which becomes therefore, r i r i plus 2. In that case this will be i will be 1 to n minus 2 and in the same way it will continue up to i n to n minus 1. So here it will be r i r n.

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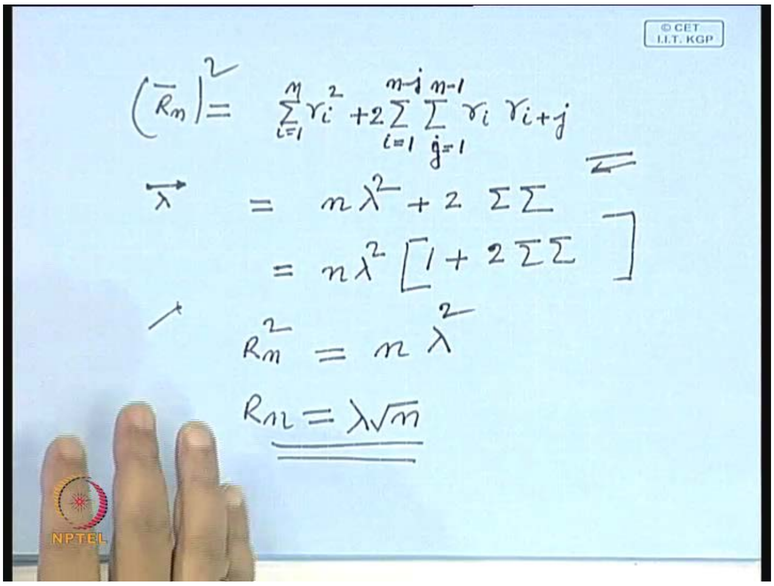

So, this is a series and this you can still simplify and if you do I can leave this is an exercise and if you go on and solve this, what you will get is that this random distance. This will be equal to summation r i square plus r i plus j and here there will be a term 2 here. So here this will be i equal to 1 to n minus j and the next is j equal to 1 to n minus 1. So, basically this comes out to be suppose we say that these atoms they are moving through crystals and each step may have a specific dimension. Say suppose lambda in that case i here it is one to n. So it actually turns out to be n times lambda square plus twice this summation.

So this if you take this common this is equal to twice plus this summation. Now in case of a random process if this moment of atom they are not correlated, they can move in any direction there is no restriction. Then what you can say that there is every likely when you some up so one may be in this direction another may be in this direction. So this may come out to be 0. In such case in that case R n square basically this is square is equal to in that case this will be 0 this is equal to n lambda square. So that means after n walk the distance move is equal to root n lambda.

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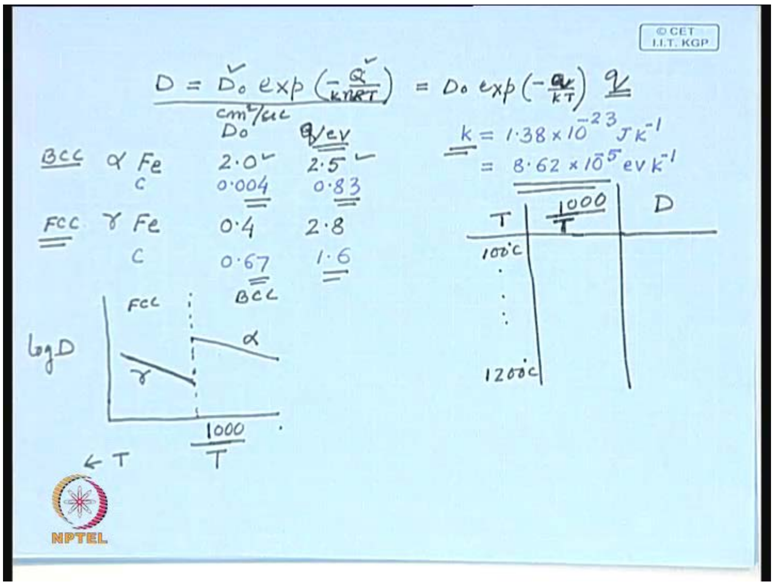

Now it is also important to look at having done this let us look at the nature of diffusion in certain crystals. Let us look at the moment of iron atoms, iron lattice self diffusion iron in iron. Say iron existing two crystalline form one is a alpha iron, which is a low temperature this is BCC an at higher temperature iron has a face centered cubic structure. Now just now it has been mention the diffusivity can be express by a function like this whereas, this magnitude of D naught and this activation energy, which is given over here and this dimension of D naught is centimeter square per second and that activation energy is in an electron volt.

So, if it is electron volt basically you we can say that this is R is Boltzmann constant Avogadro times number and q over n is this small q which is electron volt will say that this is small q which is in electron volt and these are the magnitude and same is for diffusivity of iron atom in austenite lattice, which is given over here, 0.4 at 2.8 electron volt is the activation energy. Now we know that k is equal to 8.62 into 10 to the power minus 5 electron volt per degree Kelvin. So, here also you can set up a basically you can set up this easily in an excel spreadsheet put the temperature one axis and you say the temperature is may be from you try and find out from 100 degree c on wards and calculate it up to let us say 1200 degree centigrade.

But, in this expression T has to be substituted in degree absolute make that conversion and calculate 1 over T and usually this will be less than 1 actually. Therefore, multiplied by 1000 over T if we do this and then you calculate diffusivity and make a plot make a plot of log of diffusivity against 1 over temperature. Then how will this plot look like. Now here the temperature this side is a low temperature this is 1 over so 1000 over T. So basically the T is increasing in this direction. So at a higher temperature it is iron will existing face centered cubic lattice. So this side it is face centered cubic this side its crystal structure is BCC.

Now you look at this values now you look at this D naught is quite large whereas, this is this is little lower whereas, this is higher. So higher activation energy means it is more difficult to for the atom to move. So another way we can say that in FCC that diffusivity will be lower and so basically you will get a plot like this. So diffusivity plot this is in gamma this is in alpha. Same way you can calculate diffusivity for carbon the values which are given here of this constant D naught and q they are given here this also will show similar trend.

So therefore, to D what we looked at is a we looked at the phenomenon of diffusion would learned about what is diffusion, we learned about Ficks laws of diffusion loss that governs the process of diffusion and we also looked at the solution of certain diffusion couple solutions and how the concentration changes when in a particular you join the two metal heat it then how the concentration of both changes with time and we also looked at the nature of D and D is that is the coefficient of diffusivity, it is actually a second rank tensor and next class.

We will looked at the mechanism of diffusion, because most cases what we have is metals a crystalline and atoms are arranged in an orderly fashion, and we will see how diffusion takes place. And today just now we have calculated diffusivity self diffusion in two crystal structure BCC and FCC, and we saw that at the same temperature the diffusivity in FCC is lower. And why it is, so we will answer this question once we go through the mechanist approach of diffusion. Thank you.