Materials Science Prof. S. K. Gupta Department of Applied Mechanics Indian Institute of Technology Delhi Lecture 20 Diffusion in Solids

Well, while talking about the microstructures of steels, when steel cools through the eutectoid temperature, we saw that 0.8 percent carbon austenite becomes a mixture of two phases, ferrite and cementite. Ferrite contains almost no carbon, roughly about 0.2 percent at 725 degree centigrade while cementite contains 6.67 percent carbon by weight which becomes 25 atomic percent. So this 0.8 percent which is getting divided into 6.67 and 0.2 is clustering of carbon atoms is taking place in the volume of the material. This movement of atoms in solid state is not translation, is referred to as diffusion in solids and we shall look at this diffusion in solids atomic mechanisms as well as the mathematical models today's class.

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Diffusion we define as the process of mass flow or the motion of atoms or molecules by which they change their neighbors or they change their position with respect to their neighbors. In gases, it is very obvious, it comes through translation only. Say for example I bring a bottle of ammonia or H2S in this room and just open the corks slightly and close it back, in no time all of you sitting here will be able to smell it. Those molecules of ammonia have got out of the bottle and gone all over the room in no time. Distances traveled are in meters and time taken is fraction of a second, a small fraction of a second. Process is pretty fast, pretty rapid. Let me give another example. I bring a bicker half filled with water, keep it here and drop from my fountain pen one drop of the ink on the surface very gently. And just do not disturb it, leave as it is and keep watching there. You can keep watching for hours, the bottom corners would not have received the color of the ink yet even after hours.

Distance to be traveled is few centimeters and time taken is more than a few hours. Now here the ink molecules have to travel from that droplet, from the surface it has to go down to the medium which is the liquid medium. Translation is not so easy, not so fast as it was in the case of gases. Similarly in solids also when there is a concentration of particular atom or a molecule in one place, it tries to go to other places, diffuse out but it takes lot of time to travel even a distance like a millimeter or a micrometer, it takes quite some time.

The process is slow and what we have seen among the three states, solid state occurs at the lowest temperature, available thermal energy is least. Gases occur at highest temperature, thermal energy available is very high. So the role played by thermal energy is very important.

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1. Thermal Energy Gradient montral IT Dehi Shiv K. Gupta

Thermal energy plays a very big role in the process of migration of atoms which I am calling the diffusion of solids. Secondly when I started, there was no ammonia in this room and when I

opened the cork where the bottle is full of ammonia, there is high concentration ammonia here, there is low concentration ammonia there, so it goes from high concentration to low concentration. Going from high concentration to low concentration is going down the gradient.

Similarly ink molecules which are there in the droplet of the ink but in water there is ink molecules are not there and it goes from high concentration to low concentration again. This is called the concentration gradient. Concentration is different and it is going from high concentration to low concentration. Now similarly electrons in the solid travel when you apply the potential, it goes from (high) well positive to, rather negative to the positive end. Electrons travel you know. So that is going again where essentially the free energy of the material is going to be become low.

So gradient could be free energy gradient. Even concentration gradient could be considered as free energy gradient. So it is going from high concentration to low concentration or high free energy to low free energy. That is the way it is going to take place. It could be a magnetic field. It could be a gravitational field. Normally anything drops from top comes to the bottom, gravitational attraction. So it goes from high potential energy to low potential energy. That is a gradient.

So the two things which are important in seeing this is one is the thermal energy which is a function of temperature. And gradient could be concentration gradient, it could be gravity, it could be electric potential. It could be magnetic field or essentially you can call it free energy gradient. This means to say that at times we have observed material goes from low concentration to high concentration because thereby doing so it is decreasing the free energy. In such situation I have to talk about the free energy gradient or the concentration gradient, observed in some alloys not always. All right. So this is, these are the two parameters which control this and we shall see the effect of these in this.

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First of all, look at the mathematical models before I come to the atomic mechanisms, is called the Fick's first law of diffusion and I shall mention this in one dimension. If you write this or add this in x direction, y direction, z direction in vectorial form, you get the 3-dimensional thing. But most of our problems we can solve by considering the problem to be 1-dimensional and we shall show you that what these kinds of problems are. So in this course, I am limiting myself to 1dimensional problems.

In 1-dimension we define the first law as dn by dt is equal to minus D of, D into A and dc by dx. Now here n is the number of species which are moving or it is the mass of the species which is moving or it could be volume, anything it could be, some quantity of the material which is moving, transported. t is the time, well c here is n per unit volume of the medium in which the motion is taking place, per unit volume of the medium in which the motion is taking place.

x is the direction of diffusion. I should say it should be the distance along the direction of diffusion, distance along the direction of diffusion. A is the area of cross-section perpendicular to x. That is the direction of diffusion. D is the proportionality constant, and we call D as the diffusivity or coefficient of diffusion. This is basically the proportionality constant. Minus sign comes from the fact that material travels from high concentration to low concentration, not from low concentration to high concentration.

So dc by dx is supposed to be negative in the direction of diffusion. And since the matter transported per unit time is not negative, we have to put a minus sign there. So this is the amount of the material transported per unit time. Well, we shall look at this diffusivity or the coefficient of diffusion as we go in the course. And A is the (proportiona) area of cross-section perpendicular to direction x and this is the gradient dc by dx. Well, c is the number whatever n is, number or mass or volume, whatever quantity you define it as per unit volume of the medium in which the (materi) the species are diffusing.

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When I define flux, flux is defined as J, written as J the variable, flow per unit time per unit cross-sectional area. That is dn by dt per unit area of cross-section, that is 1 upon A, dn by dt. From the first law, it becomes minus D dc by dx. Simply rewritten the thing, this is another way of rewriting the first law. When we write the first law like this, it takes care of the steady-state diffusion. What is a steady-state diffusion?

Steady-state diffusion is the one in which let us say I have this as the medium of diffusion. In this medium something enters from the left and something leaves to right. In a given time t, what enters the medium from the left, same thing should leave onto the right, I call it a steady-state diffusion. Understand. If in a given time let us say 10 microseconds, five atoms of copper enter this medium of brass from the left, the same five atoms, is not the same atom, five atoms same number leaves onto the right.

So in the medium number of copper atoms is not changed. That is not changed, it is the same, that is the steady-state diffusion. So say J, the flux is neither a function of distance nor the function of, distance means position, in the medium position x, nor it is a function of time. Because that means the flux remains same in the medium at all times at all places, it is a constant. That means this product is a constant.

If D is a constant, not a function of concentration, if then dc by dx can be constant, the product will be constant. It will be steady-state. But at times we find that diffusivity is a function of concentration in the medium. And if so, then this product will be constant, dc by dx need not be constant. That is what is shown here.

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In this picture here, this is the medium distance, I have shown is the direction x. This is the perpendicular plane, perpendicular to the direction of diffusion. I plot concentration here. Let us call this concentration here, okay, let us call it C2. Let me call it C2, let me call it C1 and if D is a constant, this could be a straight line here for flux to be constant. So dc by dx is a constant, the slope is constant every place.

But if D is not a constant, then it could deviate positively or it could deviate negatively so that the product is a constant. That is how the gradient could change if it is a steady-state. It means whatever is entering here must leave it out here at this point. That is important. So as a result, anywhere in the medium, infinitesimally small portion you take, the diffusing species, its amount is not changing with time. Its amount is not changing with time.

Or you take it here, its amount is not changing with time. Whatever is the concentration there, whatever is the amount of the diffusion species here, that remains same with time. It is not a function of time, not a function of distance. J, flux is a constant.

"Professor-student conversation starts."

Student: Within non-linear profile it can be a function of distance there.

Professor: No, because D is a function of distance, that the product remains constant. That is why it is deviating. This is whenever, this or this is possible when D is not a constant or D is a function of, concentration is changing with x, so let us call it distance x. If D is a function of x, that dc by dx need not be constant. So the product has to be constant, that is a flux. In other words, what we are trying to say is in the medium at any location neither the concentration of the diffusing species is accumulating or increasing nor it is getting depleted. If there is 5 atomic percent copper at a particular place with all time which shall remain 5 atomic percent.

Student: At all places?

Professor: At that place. It is not changing there. Concentration, of course is a function of distance. But at a place if it is 5 atomic percent, it remains 5 atomic percent. Here if it is 3 atomic percent, it remains 3 atomic percent, it is unchanged. With time, it is unchanged. Is that clear? So that is what steady-state diffusion. There is neither accumulation nor depletion of the diffusing species anywhere in the medium at any time.

"Professor-student conversation ends."

Well, that was for the steady-state condition but most problems which we face are not steadystate. When 0.8 percent austenite containing 0.8 percent carbon is splitting into ferrite and cementite, it is not a steady-state diffusion. There is accumulation of carbon in one region, there is depletion in another region. So the problem is not usually steady-state. Problems are usually non-steady-state. We shall try to look at this with the help of infinitesimally small part of the medium, infinitesimally small, that means delta x tending to 0. And then add it up to get the whole medium, integrated rather from there.

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So I now first of all look at this medium at x here and x plus delta x here. That is the direction of diffusion. That is the whole medium. I am taking infinitesimally small volume, delta x is tending to 0, x plus delta x, this is the one. And area of cross-section is A, so volume of this region is A into delta x. Delta c by delta t, let us say is the concentration which is changing in this volume per unit time, multiplied by the volume, that is amount of the diffusing species which has increased here.

c is number per unit volume, multiplied by volume it becomes a number. And in time delta t it has happened, so this is the total material which is accumulated in this volume which is coming from the left and the difference between this and what is going to the right. That means what comes from the left is more, what goes to the right is less, therefore there is an accumulation. Accumulation is positive, therefore I am talking about accumulation. If this number becomes negative, it is depletion.

In that case what is coming from the left is less, what is going to the right is more, then there is a depletion. So I define this as matter entered at x in time delta t and minus the matter exited at x plus delta x in time delta t, it is this number. Is it clear? Any doubt on that?

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Matter entered = $J_{\nu} A \Delta t$ $= J_{x+\Lambda x} A \Delta t$ Matter exited Matter accumulated = $[J_{y} - J_{y+Ay}] A \Delta t$ Re-writing = [Jx - (Jx + 2J Ax) DJ (A DX St (A SX) St

Now matter entered can also be said that what is flux I define, matter transported per unit area per unit time. So flux at x multiplied by the area of cross-section multiplied by time in which it enters, there is a matter entered. It is another way of writing the same thing. Matter which is exited is the flux at x plus delta x because non-steady-state this will be different, almost same. Multiplied by area of cross-section, multiplied by delta t. So I can say the matter which is accumulated is matter which is entered minus matter which is left out.

On the right, that is Jx minus Jx plus delta x into A delta t. I can rewrite this by expanding this about J, about x rather and leaving out the other terms. You can use the teller-series or you can do the expansion of Jx plus delta x at J at x plus delta J delta x into dx, plus you can do the higher order on d square, Jx square plus d square x and so on and so forth you can go on. But we can deduct the high ordnance to make it simpler. So when we do that, what I am getting is this J cancel with G, I am getting minus of delta J, delta x, dx times A times delta t.

I think I should write delta x like this because it is x plus delta x. We will take the limit delta x tending to 0 if whenever is required. All right. So this is what I got the matter accumulating in the region, delta x with cross-section area A. Volume is A delta x and that is what I wrote was equal to the previous slide, delta c, delta t into A times delta x into delta t. And this is equal to minus of delta J, delta x, A times delta x into delta t. Well, this term can get cancelled here. Well,

that so then we get delta c by delta t is equal to minus of delta J, delta x. So the another form I can write as....

"Professor-student conversation starts."

Student: Sir, (())(27:53) first law still hold, J is equal to minus dc in (())(27:59).

Professor: I am using that, that is, that I said it becomes steady-state diffusion in the big volume. But infinitesimally small volume benefit is J flux is not constant, that is definition of the flux will remain. Matter transported per unit time, per unit area of cross-section, that is definition of the flux, that remains. But that definition itself tells me how much material is getting transported if it is steady-state. That is only definition of the flux. Is not it? How much the material transported at a cross-section per unit area per unit time across the given cross-section of the area at a crosssection.

Student: What will be the, what is J into minus d into dc by da less than whole?

Professor: That is a definition of which I make, I will have to go back now. I am sorry, all right.

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Mathematical Models Fick's I Law of Diffusion (in one-dimension) Shiv K. Gueta IT Dehi

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This is the first law we defined. Okay and then I defined the flux as matter transported per unit time per unit area of cross-section. The first law, then if we write that, it becomes D dc by dx. This is the definition of the flux and I said this itself becomes the definition of the law or that self-defines the steady-state condition. Because what is happening, I have defined the (cross) this cross-section, same is happening at this cross-section, same is happening at this, same is happening at this, that is a steady-state.

But definition of the flux is at this section how much material is transported per unit time per unit area of the section. And I have used only this definition of the flux in there. I am talking about infinitesimally small. There I can make use of this. But when I talk about the big volume, not particular cross-section, big volume, this definition itself is working because condition is steady-state. Is this clear?

Student: Yes.

Professor: I can always use this for infinitesimally small cross-section. Thickness is now tending to 0, that means you are talking about at a particular plane. What comes and crosses this over is definition of the flux, that is what I am making use of.

"Professor-student conversation ends."

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All right, so that is what we wrote here was delta c, delta t is equal to minus delta J, delta x.

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If I write it from the first law, now I am writing that. That is the definition of J and I have written D dx of J. If D is not a function of concentration, it is possible for me to take D out. And I take this D out, that is what it become, D times, and this is called Fick's second law of diffusion. You notice from this, actually law of diffusion is only the first law. This we have derived from there only. But this considers non-steady-state while that is good enough only for steady-state not beyond.

This is in one-dimension. You can write this in three dimensions by adding delta square c delta y square plus delta square c, delta z square and so on so forth. So that shall be 3-dimension but as I said we shall look only the one-dimensional situation because most of the problems can be solved by considering one-dimensional situations and we will be able to work the problems out.

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The solution of the Fick's second law which I wrote, one of the forms of the solution could be this. Concentration c at a distance or at location x at a time t is a constant A which is a constant of integration. B is another constant of integration, erf stands for error function. Call it error function of, the argument of the function is x upon 2 under root Dt. Well, what is error function is shown here.

On this axis I have the parameter let us say eta and this is exponential of minus eta square. Since it is minus of eta square, whether eta is positive or negative, my exponential of minus eta square is same, so you find this function to be, what do we call it? Even function, odd function?

"Professor-student conversation starts."

Student: Even.

Professor: It is an even function. Okay. So we define the error function of the theta as 2 upon under root pi integral 0 to theta, exponential of minus eta square d eta. In other words, integrated from 0 to a value theta here. This is 0, this area is what is given by the integral. This is the value

of theta, this is 0, this is and this is exponential minus eta square, d eta. Then we have multiplied outside by 2 upon under root pi. That is the value of the error function.

Now this integral 0 to theta, exponential of minus eta square d eta, theta is made infinity, it is possible to solve. And otherwise it is not possible to solve, then it becomes under root pi by 2. So from here we would notice that error function of infinity would be 2 upon under root pi multiplied by under root pi by 2, shall become 1. Now similarly look at the another character in this figure itself. If I take theta, instead of theta I take minus theta, what is this area?

Student: Same.

Professor: Same as 0 to theta but....?

Student: Negative.

Professor: Negative sign because x axis is negative. y is still positive but x axis is negative. So area has become negative. So error function of minus theta is minus of the error function of theta. So these are some characteristics.

"Professor-student conversation ends."

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Some properties of the error function f(0) = 0f(-0) = -exf(0)Shilv K. Gupta IIT Dehi 11

Some properties of the error function. What we find from here is error function of infinity is equal to 1 and then we find error function of 0 will always be 0. 0 to 0 is the integral is always 0

and we will find that error function of minus theta is equal to minus of error function of theta and therefore I have error function of minus infinity is equal to minus 1. And from this itself we can see error function of 0 would be 0. Okay. So these are the properties of the error function and this error function of course normally comes in statistics, property distribution function. And that is what we are getting as the solution of the Fick's second law and we exploit this and use it.

Now we shall try to see, look at the problem, real problem what we face. I call it a problem of diffusion couple. I have two semi-infinite rods. One is of brass containing 30 percent zinc and 70 percent copper. Another one is that of pure copper, no zinc in it, 0 percent zinc. And I weld them at the interface at x equal to 0. Once I weld it, it becomes an infinite rod, extends from minus infinity to plus infinity. You will be able to notice after you have solved few problems, the distances involved in diffusion which are fractions of millimeter sometimes or even less, that even 20 millimeter is going to be a long distance for you.

So even if I, I made a rod 10 centimeters and 10 centimeters welded, it is infinite for us because the distances over which any movement is taking place is much much smaller fraction. Nothing is happening at the ends of it which is about 10 centimeters away from the interface. That is the meaning of infinity here. One has to very carefully understand because we must know how much are the distances involved in the motion of atoms which are taking place, small distances.



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So I have two semi-infinite rods. These semi-infinite rods are welded at this point at x equal to 0 which is the interface. That is the interface. Here I have brass and here I have copper. This contains 30 percent zinc, this contains 0 percent zinc. To start with, in here you can see the composition difference or concentration difference is not only for zinc, it is also for copper. While zinc can move from left to right, copper can move from right to left.

Generally what we find because of the diffusivity, one travels faster, other travels slower. So one which is traveling slower we can neglect it or ignore it. The one which is traveling faster is the one to be considered. Let me consider the zinc in this case hoping that is the one which is traveling faster. So zinc travels from left to right, so my direction of diffusion is this. To start with, the concentration gradient at time t equal to 0 is something like this. It is 30 percent here and is 0 percent here.

It is a step function here. It is a step function. 30 percent of this, 0 percent on that side. As the time progresses, some zinc atoms from here go to the lower concentration and concentration gradient changes with time. That is at time t equal to 0, at some other time where time is greater than 0, some finite or the concentration is changing with time. What I can do is write down the solution for whatever we know. To get A and B which are the constants of integration, I have to substitute two conditions.

Since it is infinite problem with two semi-infinite rods, I can put my conditions at time t equal to 0. At time t equal to 0 what I know is 0 percent zinc for x greater than 0. And another thing I know is it can go up to infinity x greater than 0, is equal to 30 percent zinc but for x less than 0. I know these two conditions, both are there at t equal to 0. These are called the initial conditions. If I know a condition at a boundary, then I will call the boundary condition but these are all, both of them are initial conditions. If I substitute these on that, I have space this only.

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When I substitute this in there, what I get is 0 is equal to A plus B error function of x upon 2 under root Dt. t is 0, x is positive, it becomes plus infinity. Error function of infinity is 1, so therefore it is A plus B. Second one I get is 30, is equal to A plus B error function of x upon 2 under root Dt. t is 0, but x is less than 0. It is minus infinity, minus infinity error function is minus 1, it becomes A minus B.

"Professor-student conversation starts."

Professor: I can solve for this and when I solve this, I get A is equal to, and what do I get B equal to?

Student: Minus 50.

Professor: Minus 50. So that the, in the diagram we said this is 30 and this is 0. In the middle is the 15. So solution for this is now c of xt is equal to 15 minus 15 error function of x upon 2 under root Dt. So this solution is now available to you. Constants are known to you. If you know x, you know t, you can find out D. If you know D and x, you can find out t. So like that. So let us say....uhh?

Student: Sir, we cannot calculate the error function.

Professor: We cannot calculate the error function.

Student: This is best way to talk of.....

Professor: Numerically it is possible to integrate. Numerical solutions are there and these tables are available to us in the form like this. That is what, and I am coming to the next. The tables are available in the form of theta, an error function of theta. Starting from 0, maybe 0.05 and so on so forth it will go on up to a large number, 10, 20, by the time it is reaching almost infinity for us. And these values are known to us. So we can look up these tables whenever we want to, whenever there is a need for doing that.

"Professor-student conversation ends."

Usually it will be that you find out error function, you want to find out then theta. Maybe you find out the error function between 0.05 and 0.10 somewhere here. So we will have to interpolate between these two. That interpolation is possible, it is not difficult, we can do that. All right, this is the solution. Now I am using this diffusion couple to measure the diffusivity of zinc in copper. I make one rod like this, infinite rod like this, keep it at an elevated temperature like let us say 800 degree centigrade where it is still not melting or 700 degree centigrade.

And I know I keep it for a few hours. After that few hours when I have kept it, this is the let us say the profile of the concentration, the distance. Here it would be always at 15. If you do not trust me, put the x equal to 0. Error function of 0 at any time greater than 0 it will be 0. So cxt will be 15. So this is always 15 at all times. The moment the time is greater than 0, it is always. That means interface has come to the equilibrium the fastest. The moment the diffusion begins, it comes to the equilibrium and it reaches the steady value of 15. It remains there.

So what I can do is after keeping it for a certain length of time, I know how long I have kept it, 4 hours, 6 hours, that I know. I take a slice at a distance x, take it to the lathe machine and slice out a small quantity at a position x and take it to the chemistry lab and analyze how much zinc is there. So I would know this value of concentration. That means I know the left hand side. I can find out the error function from the right hand side.

Once I have found out the error function, from looking into table I can find out the value of x upon 2 under root Dt because theta in my case is x upon 2 under root Dt. That value I got from this column. I know the value of x, this distance, I can substitute it there. I know how long I kept

it at that temperature, I know the time, I can find out D. Like this I can do this experiment at different temperatures and then find out how the diffusivity varies with temperature.



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Well, that is what I have just shown here, the same thing what I have shown there. So we can take this slice, analyze this and find out the value of, yeah, D.

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When we do that and plot this D on the logarithmic scale, reciprocal of temperature we find out to be a straight line with a negative slope. That means D is following an equation of this kind.

Like what we saw in the Arrhenius relationship, D is following, D0 exponential of minus Q by RT. Slope of this graph is minus Q by R. R is the gas constant and Q we call the activation energy for diffusion. And D0 is a constant. Okay, that would be D will be equal to D0 when temperature is, what is the temperature when D equal to D0?

"Professor-student conversation starts."

Student: Infinite.

Professor: Infinite. When temperature is infinite, exponential term would be, exponential of 0 would be 1 and that will be D0. All right. So that means here it is D0. This is your logarithm of D0. And this is what we have found because this is experimentally found, these values are there, experimental values like this. So that is how the diffusivities have been worked out, activation energies have been worked out and these are all listed. D0 value have been worked out, they are all listed.

"Professor-student conversation ends."

In this model I have considered D is not a function of concentration. In case D is a function of concentration, I can also do these kind of experiments and find out how does it vary with concentration at a given temperature. How do I do that? I take, I had taken a diffusion couple made of brass with 30 percent zinc and copper with 0 percent zinc. Now since I am worried about the variation of D with concentration, make the variation of the concentration difference between the two rods different, means less.

That is one I take brass with 30 percent, another I take brass with 28 percent zinc and I can find out the diffusivity at a given temperature like the one I have done it now. And you can say that this is the diffusivity at the average of 29 and 28, and 30, 29. Diffusivity at 29 percent zinc. Then make another one with 28 and 26. Say this is the diffusivity at 27, so on so forth. It is possible for us to find out at a given temperature how the diffusivity is varying with concentration. Those experiments have always been done. It is not that and it is known. Okay.

So these parameters D0 and Q are available, this is given in the table, form of table in your textbook. Whenever the problems, we are using a particular value of D0 and Q is to be used, we can take it from that table.

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That is what I say, it is a function of concentration, make diffusion couples with smaller differences. This is 30, this is 28 percent zinc and this is 29. So the D value you say work out, you say it is D at 29. Then make another one like this with let us say this is 28 and this is 26. This is 27, so call it the diffusivity at 27. So on so forth you can find out number of diffusion couples and you can work out the diffusivity. Only thing is every time you have to make a couple, keep it in given temperature. Temperature must be fixed where you are keeping it so that you are getting at particular temperature.

If you want to see its variation with temperature also, then you have to do the similar set of experiments at a different temperature, another temperature. Like that you can get for 29 at different temperatures, 27 at different temperatures.

"Professor-student conversation starts."

Student: Now in this case both are at same temperature.

Professor: Now these are both temperatures, same temperature. All right, we shall start from here in the next class.

"Professor-student conversation ends."