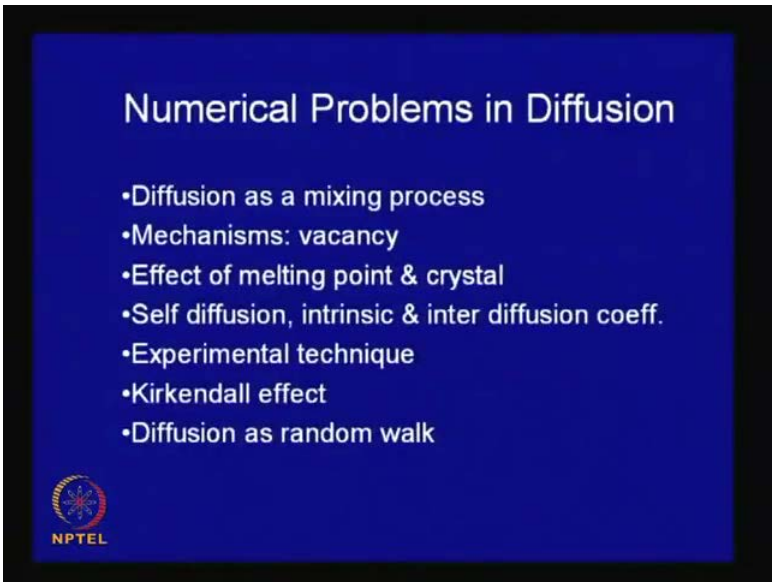
Principles of Physical Metallurgy

Prof. R. N. Ghosh
Department of Metallurgical & Materials Engineering
Indian Institute of Technology, Kharagpur

Lecture No. # 17
Numerical Examples in Diffusion

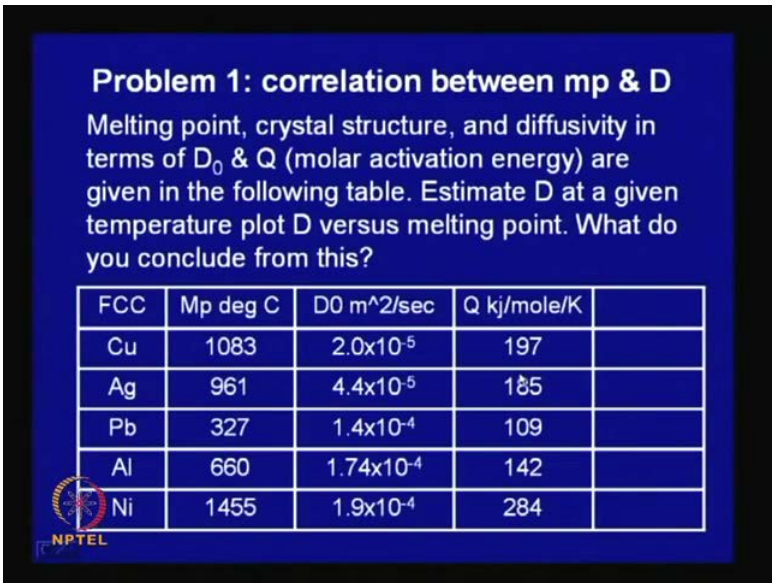
Good morning. Last two classes, we talked about diffusion in solids, we learnt about the laws that governs the process of diffusion which in reality is a process of mixing. We derive certain expressions will look at law I mean looked at expressions that describes the concentration profile in a diffusion couple. We also looked at in detail about the possible mechanisms, and what we find that vacancy place on important role and it is generally believe that most of the diffusion is either by vacancy and although we derive number of expressions based on the laws govern in diffusion. Let us look at it I mean unless we solve some numerical example often it is not possible to get a deeper inside into the subject. So I taught this class we will take up few numerical examples, and we will try and solve these.

(Refer Slide Time: 01:31)



So, this is in short what has been covered in the last couple of classes.

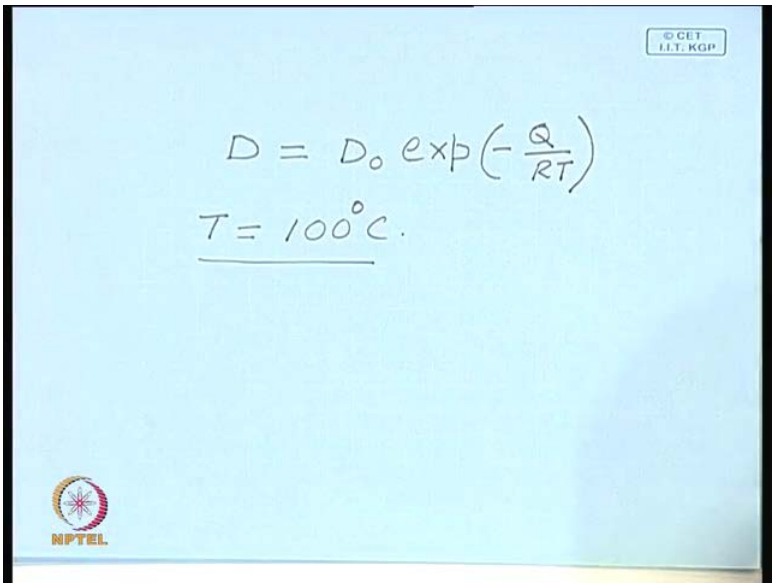
(Refer Slide Time: 01:40)



Now let us look at problem one here we try and find out a correlation between melting point and diffusivity. Now here the problem is stated like this; the melting point and crystal structure and diffusivity in term of these two constants D naught and Q, which is the molar activation energy are given in the following table and estimate D at a given temperature and plot D versus melting point and try and see what you can conclude out of this. So this first table it gives as a set of metal copper, silver, lead, aluminum, nickel; they all belong to face centered cubic structure.

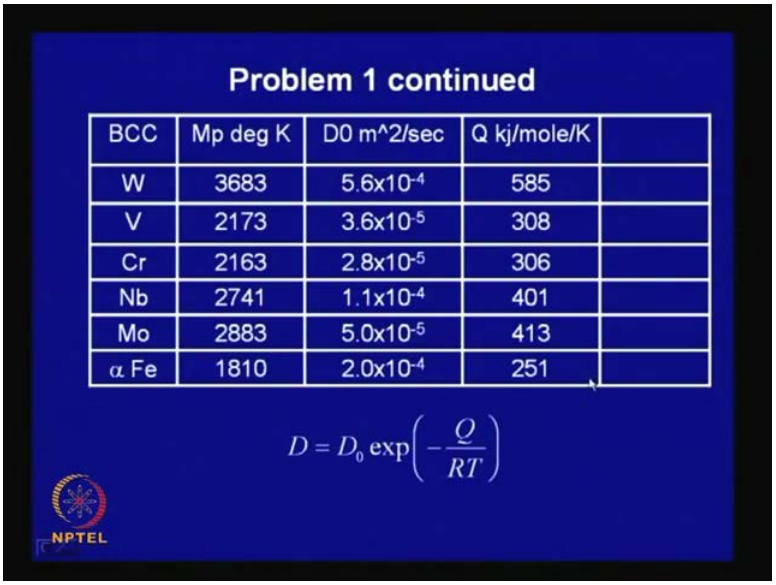
They all have face centered cubic lattice is melting points are given in degree centigrade mark the unit and here the D naught; it should be D naught D suffix zero and this dimension is meters square per second and the activation energy is given in kilo joule per mole per degree Kelvin.

(Refer Slide Time: 03:16)



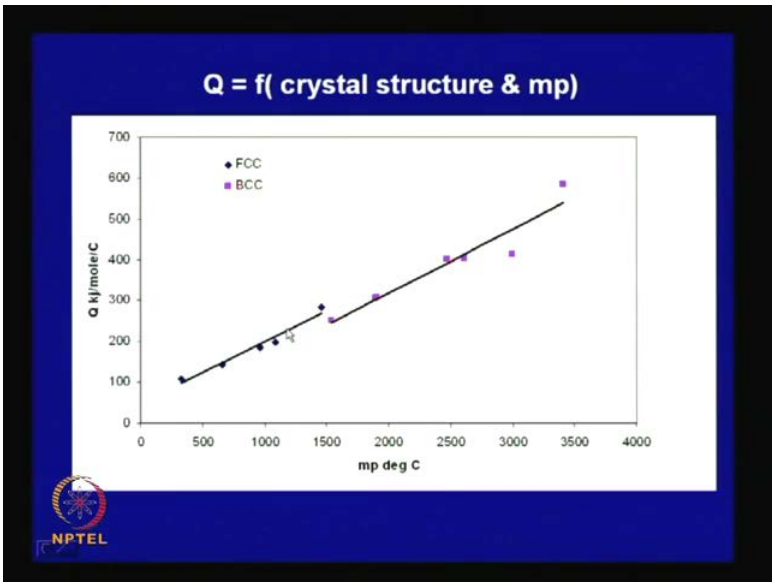
And what you need to do you know that D is given as D naught exponential Q over RT. So you can set this calculation very easily in a spread sheet and what you can do you can write the expressions over here and then estimate D as function of estimate the D for a particular temperature; so if for individual in any case at a particular temperature. Let us say we calculate D at T equal to let us say hundred degrees centigrade or room temperature and try and see does this have a correlation with the melting point of the metal.

(Refer Slide Time: 04:17)



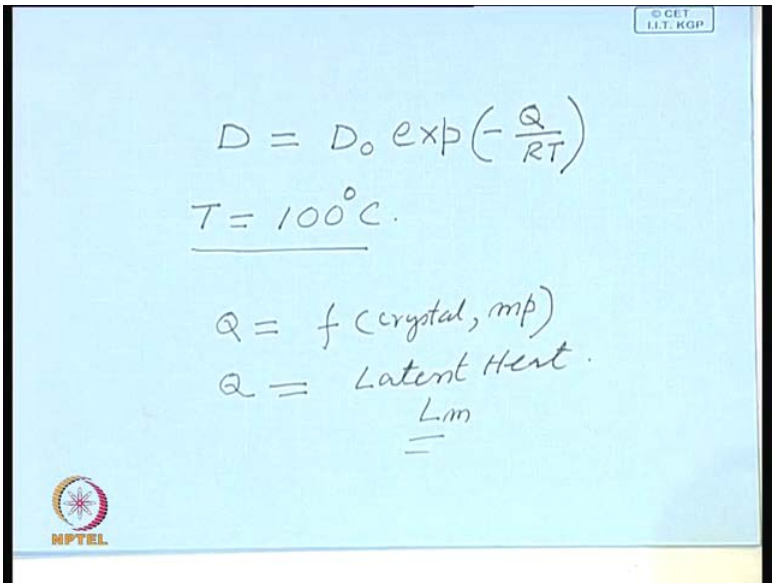
And this table gives the melting point here of course, mark this is degree Kelvin of BCC metal tungsten, vanadium, chromium, niobium, molly and alpha iron this is the melting point. This is D naught and this is the activation energy in kilo joule per mol per degree Kelvin. So here you can write fill up this with D calculated using this expression at a particular temperature.

(Refer Slide Time: 04:54)



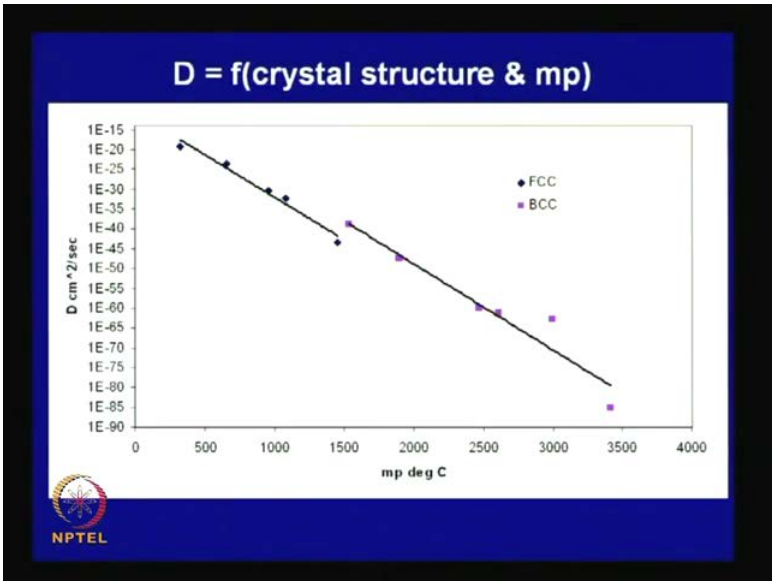
Now you try and plot this first let us look at this does not involve any calculation; just make a plot that activation energy with melting point. Now this is for FCC metal this is the line front line. So this is for the lowest possibly this must be lead and this is the highest and look at this linear trend. Similarly, this is for BCC and but if you extend say suppose here if you try and extend what you can see that if there is an any element or any metal, which exist in two crystal structure say FCC and BCC. So one example is iron and possibly a most likely this represents iron. So iron exist at high temperature as a face centered cubic structure; so if you extend it you get a diffusivity self diffusion coefficient of iron in FCC lattice, which will be somewhere here if you can extend and may be this you can try and estimate this and verify.

(Refer Slide Time: 06:21)



So in this same way what you can try we have just seen that the activation energy this is a function; this is depends on crystal structure. It is depends on crystal and it also depends on melting point. Now you can try and find out is there a relationship similar relationship between Q and latent heat of melting latent heat of melting.

(Refer Slide Time: 07:00)

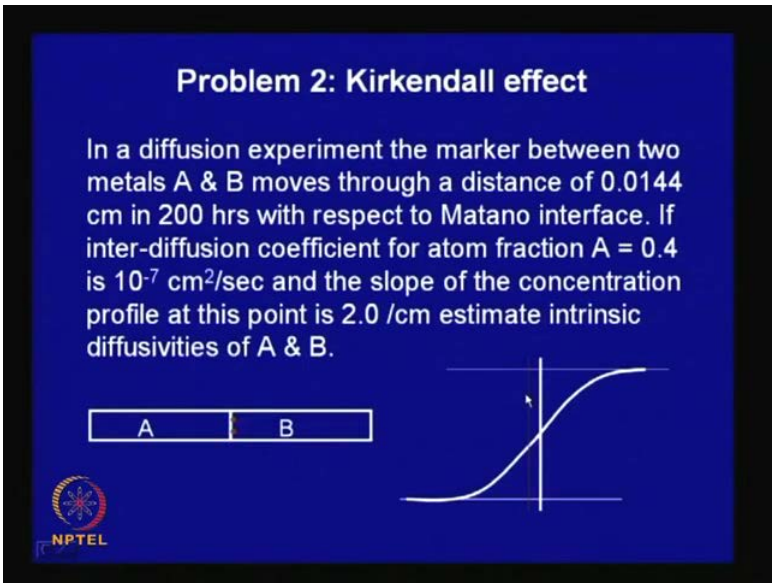


Next, if you calculate diffusivity at say fix temperature possibly I think hundred degrees centigrade and look at this plot. The diffusivity and melting point, so that means if the melting point is higher at a given temperature is diffusivity is lower. So look at this so if

for a metal melting point is low like lead here its diffusivity at a fix temperature; say room temperature or hundred degrees centigrade as so here you see this has the highest diffusivity and this also is a function of the crystal structure so look at BCC.

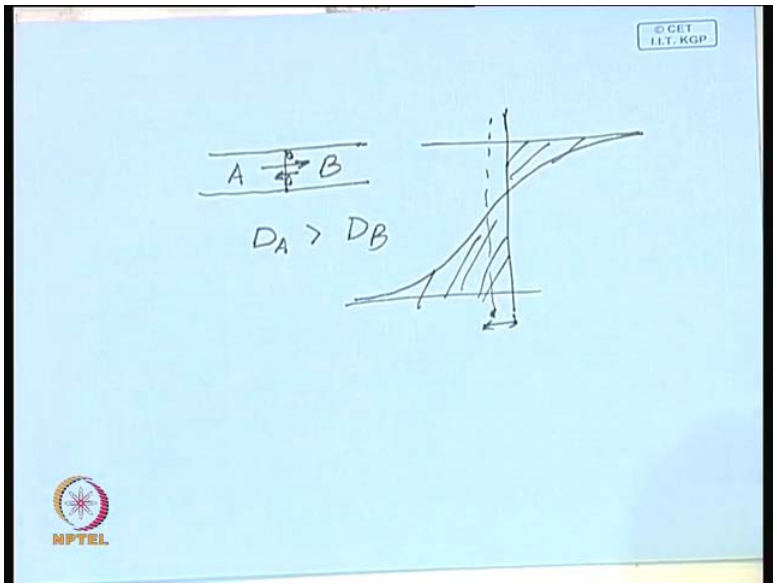
So that means diffusivity in BCC you can say if the same metal exceeds in two different crystal structures you will find that diffusivity self diffusion coefficient in BCC is higher than that in FCC. This is primarily because there is more open space in a body centered cubic lattice. So these are the two conclusions, which are quite important and this often helps you to determine the diffusivity to know about diffusivity of metals where the data are not available.

(Refer Slide Time: 08:33)



Now let us look at another problem, this is a problem on Kirkendall effect and we have seen that if you make a take a diffusion couple and then you know you put a marker you put a marker.

(Refer Slide Time: 08:56)



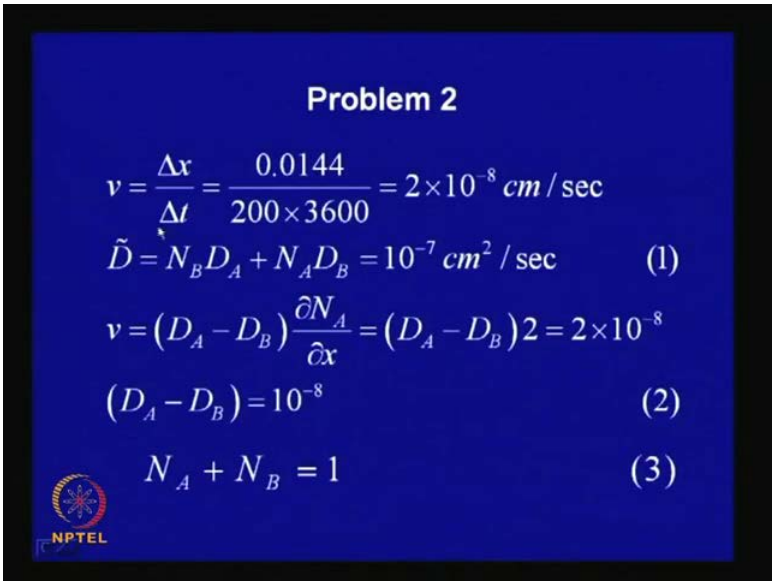
Now often the diffusivity of the two metals may not be same may be diffusivity of A is greater than diffusivity of B. In that case more number of A atom will move in this direction then the number of B atom moving in this. So obviously what will happen this interface will move like this; the marker remains constant. So basic or so, what you see here and this case you if you draw the concentration profile, you will possibly get a profile like this and you say A let us say that this is the matano interface. Matano interface is the one where this area this area and this area they are equal and the marker position is this.

So there will be a gap between this matano interface and the marker. Here is an experiment which was say suppose a hypothetical experiment has been conducted with the two metal A and B and here is the marker placed over here. Now in this diffusion experiment it has been found that the marker between the two metal moves through a distance of 0.0144 centimeters in 200 hours with respect to matano interface. So here this is the matano interface this is the concentration profile this area and this area the two are equal and this is the position of the marker.

Now this is this distance in 200 hours is of this magnitude. Now if inter-diffusion coefficient for atom fraction inter diffusion coefficient for atom fraction A is 0.4 at A equal to 0.4 that is atom fraction A equal to at a particular point say this is the concentration line say atom fraction 0.4 somewhere here let us say. So at this point that

inter diffusion coefficient is given as 10 to the power minus 7 centimeters square per second and slope at this point is 2 per centimeter then estimate the intrinsic diffusivity of A and B.

(Refer Slide Time: 12:07)

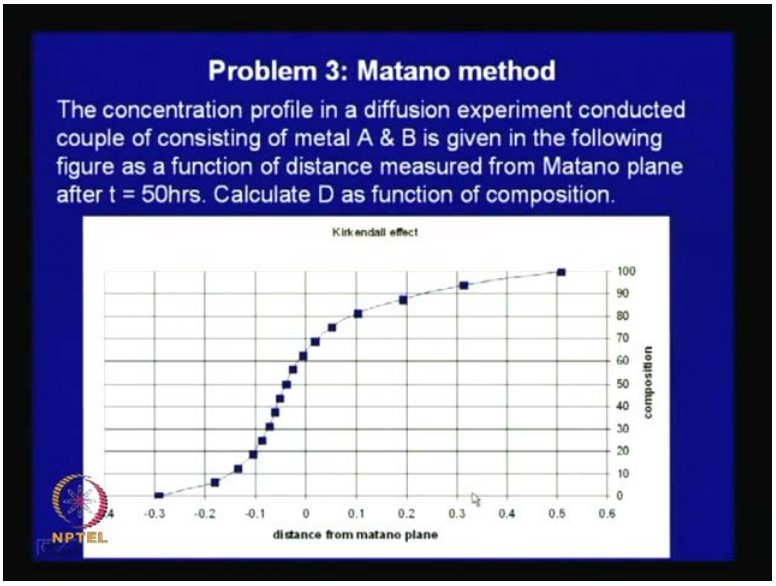


Let us see how you solve this problem. Look at this what is given so this is let us try and calculate what is the velocity with which that marker moves with respect to the matano interface. In fact the marker are stationary it is actually the matano interface, which is moving. So if you calculate this velocity delta x over delta t so delta x is this is the time in hour if you want to most like most of the cases we calculate velocity try to calculate in centimeter per second. So you convert this hour to second then it comes out to be 2 into 10 the power minus 8 centimeter per second.

Now we know that inter-diffusion coefficient is equal to the mole fraction so marks this difference the mole fraction B times the intrinsic diffusion diffusivity of A D A plus N A times intrinsic diffusivity B. So this is one expression and this is given and now the velocity of the marker is actually we have derive this expression is given as the different between the density D A minus D B times this concentration gradient so del N A del x. Now this magnitude is given estimate of this slope of this slope of slope of this plot this is the concentration this is the distance slope of this concentration profile at mole atom fraction 0.4 is given.

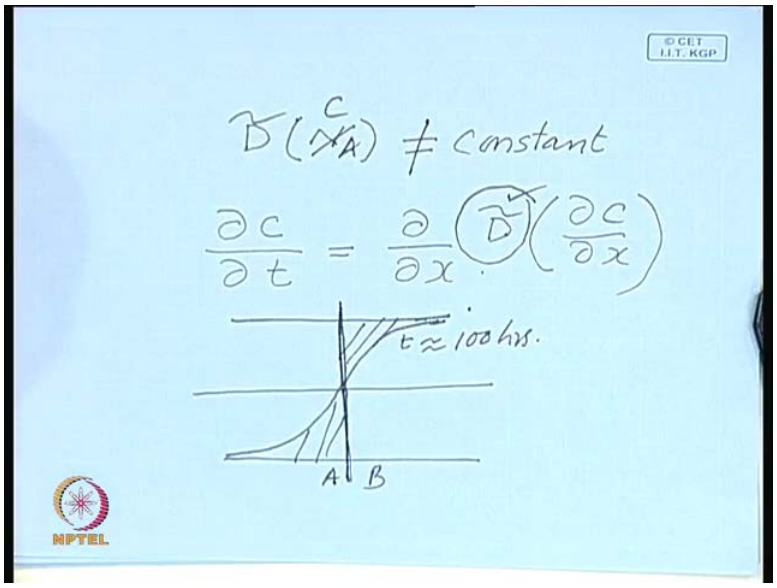
Therefore, the substitute it here so what do you get you get this D A this is 2 it is given and this is equal to this. Therefore, what you have d a minus d b equal to 10 to the power minus 8; now look at it over here you have one equation here one equation here and also n a and n b; if you add them together this are atom fraction and it is a binary system this is equal to one. Therefore, you have three equation three unknown so you can solve it easily and I leave it up to you to do this to derive or actually estimate the numerical values for D A and D B.

(Refer Slide Time: 15:13)



Now the third problem, we will look at the matano method say matano method is very commonly used to find out diffusivity in alloys and we have seen during the lecture that diffusivity is actually a function of concentration.

(Refer Slide Time: 15:39)



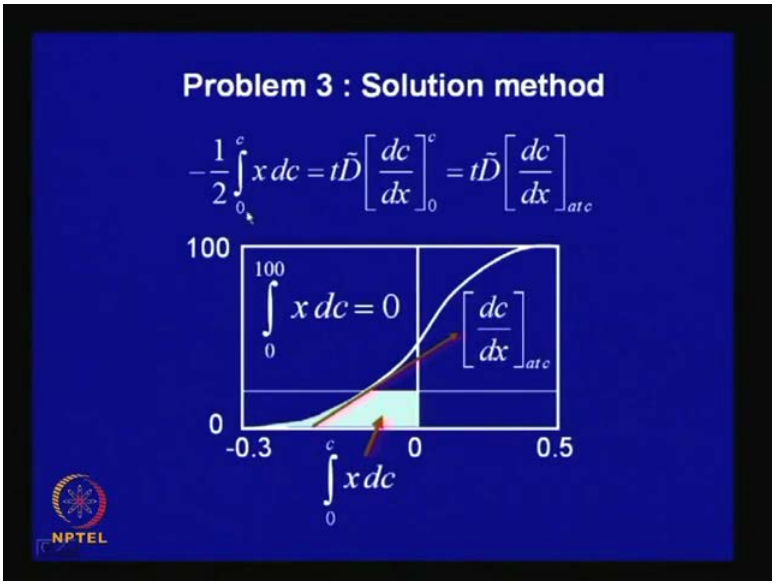
Say diffusivity it is a function of the concentration say in a binary alloy so this is not this is this is not a constant this is not constant it is a function of the composition. So that is why this diffusion equation when you try and solve even in a say one dimension we treats it like this. So this is now matano method it is a proceed which will help you to estimate D from concentration profile. So if you look at the concentration profile so if you assume D to be constant this to be constant if you assume then you will find that this profiles they are this profile they are symmetric.

So this is your initial interface between A and B and after a time t after a time t say let us say t after say 100 hours you get a profile like this if you assume D to be constant then this profile it will be symmetric an either it is symmetric about this interface between A and B and this area and this area will be equal. But in most cases we will find that this is not symmetric and which indicates that this diffusivity or which is call is a inter diffusion coefficient is actually a function of composition. Now here is an expression here is an example and if you try and solve you will get a feel about the procedural.

Now this concentration profile in a diffusion experiment conducted on a couple consisting of metal A and B is given in the following figure. Look at the figure here you know this is not symmetric even if you consider that this is the matano face, where this area and this area they are equal area may be equal but the curve is not symmetric. So this indicates that in this case looking at this concentration profile it is possible to

conclude that diffusivity in this case this inter diffusion coefficient in this case is going to be a function of composition. Now suppose this is the concentration profile at time 50 hours and calculate D as function of composition.

(Refer Slide Time: 19:18)

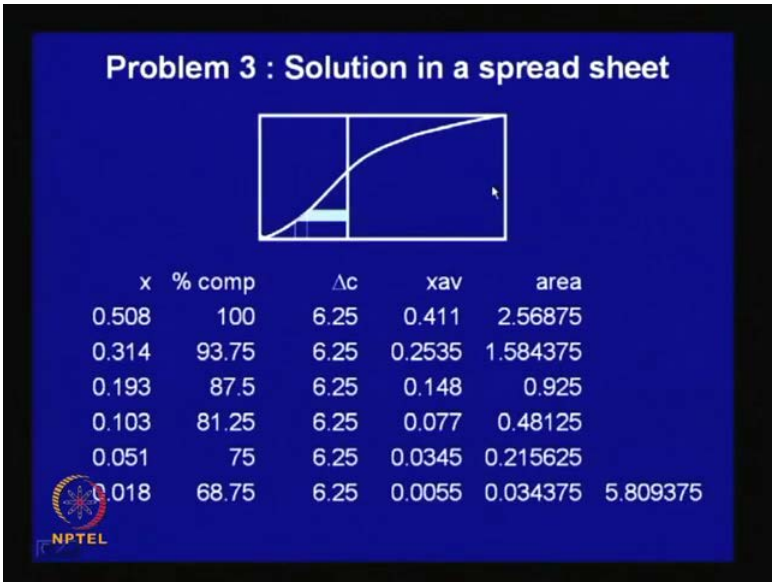


Now if you recollect this procedural we have seen that with just substitution of variables say basically that eta you substituted the I mean the variable that we transformed is eta which is x over route two, if you do this conversion then this partial differential equation gets converted into a ordinary differential equation and it can be an its solution it is possible to arrive at it solution and which is listed here. Look at this is the integral x dc, x is the distance and c is the dc, c is the concentration. Now here in this concentration profile curve is easier this axis y axis is the concentration; this is this axis is the distance.

Now to find out to locate that matano interface what you need to look at look at this concentration profile and select a place where you find that this area and this area is constant that means you try and find out this area. Now here look at this x has positive this side x is negative this side x is positive, when you calculate this area this portion will come out to be negative and this area will come out to be positive add the two you will get it will be zero that means this integral equal to zero describes this nine. Now to find out the diffusivity what you have to do you have to again find out this area zero to c say suppose this concentration is at this point that means 0.4 or 40 percent.

Say suppose this is that 0.4 lines of 40 percent line here. So you have to find out this area now area can be found out easily using Simpsons rule or graphical technique and it can very easily we done in a spreadsheet if you enter this concentration as a function of distance and once you find out this area and look at the and this slope then you have to find out slope at this point. So draw a line over here draw a line over here and this also if you have the tabulated data it is very easy to find out slope at any point. Now once you find out the slope at this concentration c; you find out this slope this is known slope at concentration c the t is known so this part is known therefore, the diffusion coefficient can be estimated.

(Refer Slide Time: 22:36)



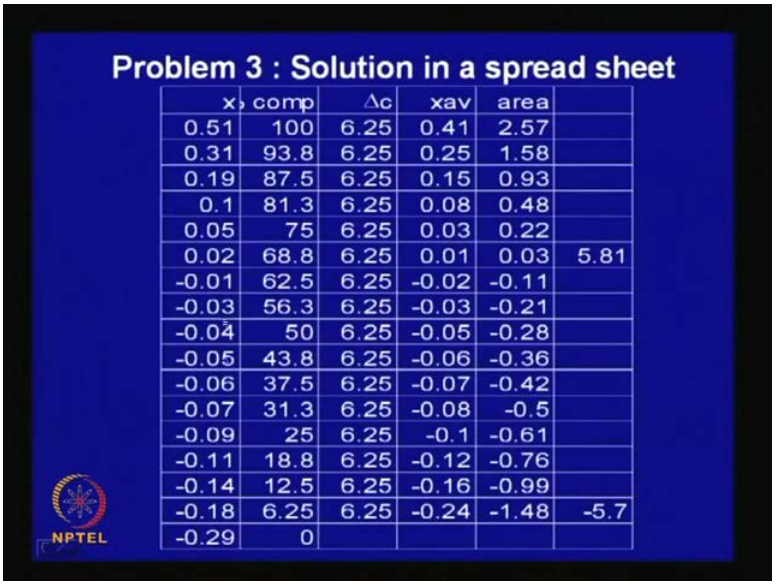
This solution can be very easily done in a spreadsheet and which is shown here in a spreadsheet; if you enter say suppose, this is the concentration profile, and this is the matano interface. Now take a small element here. So let us say that this is a concentration say c 1 here c 2 here and this difference is very small. So in that case you can approximate the area of this by multiplying this distance delta c with average value of that distance so distance also you say this is x 1 this is x 2. Say suppose average of this two is x 1 plus x 2 by two. So this is the midpoint so if you look at like this you are actually doing you making on approximation all right.

But, if you if you are element that size is small the mistake is very little; so what you are doing is here you are drawing a line midpoint an assuming this to be the area. So here

you are ignoring this but this is the additional so in a way you can say this will give the approximate area and which also can be done very easily; if you enter the data on the spreadsheet. Now look at this spreadsheet you enter the data composition percentage composition this is the delta c change in composition. So I mean the composition has been estimated at equal interval it seems say it says every element you this composition changes by the same percent 6 percent.

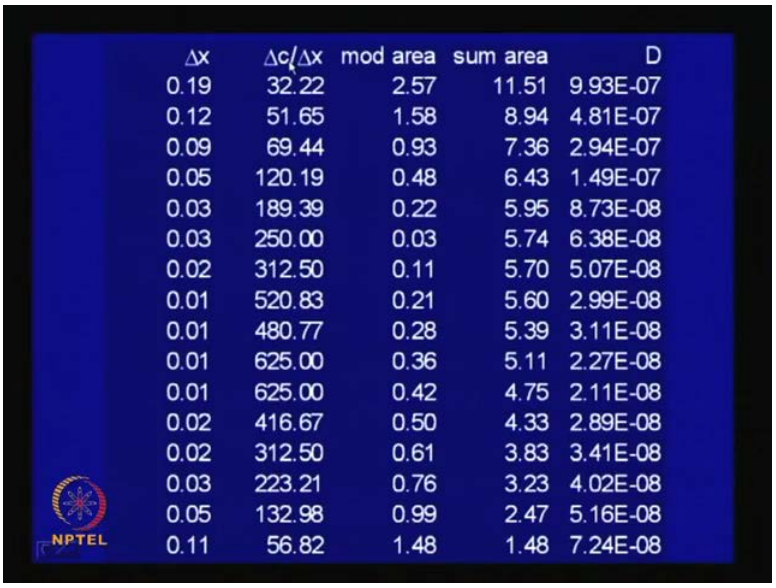
Then you can find out average of this distance, which is listed here and then you can find out the area and look at here it you have found out area almost up to this point and you can add up add that area this is the area of the small element; say somewhere here. Next one will be the next element so this is how you can set up your spreadsheet and you can some all these when you get this area.

(Refer Slide Time: 25:12)



Now same thing you do for that entire concentration profile and here you see if you add up to this that is five point areas is 5.81 and you add this part here it is this. So, more or less you can see that the location of the matano interface is correct the area this is a plus almost of same magnitude it is negative. So net area is zero therefore, that means the matano interface location is alright.

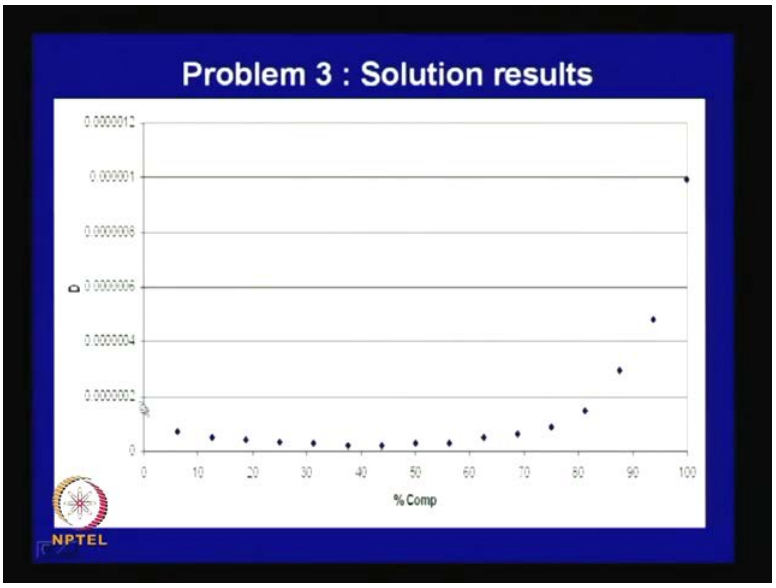
(Refer Slide Time: 25:50)



And now you can try and find out this slope of the plot. So you just divide delta c we have found out delta c, similarly you can find out delta x as well and the ratio of the two it gives you the slope of the plot. And then you can get, and when you calculate this area, you have to calculate ignore that negative sign. Because the total area gives you that amount of mass transport; so you so mod area modules of that area which is listed here, then you can sum the area and summation has to be from the concentration 0. So, if you go back summation has to be from this negative end, area from here up to this then this area plus this area plus this. So, that way you have to estimate all along the distance.

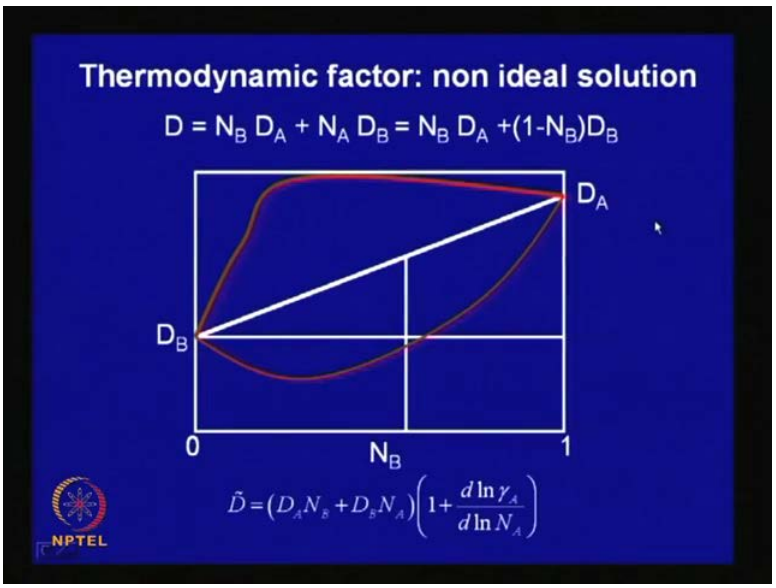
And which has been done and you can and after having done this, then you can calculate diffusivity and diffusivity is calculated using that expression. Look at this you have calculated area at up to a different compositions, this area is known. This also the slope of the plot also has been determined and the time t is given 50 hours, so substitute that time t as 50 hour and then therefore, it is possible to calculate that inter-diffusion coefficient as a function of distance or composition.

(Refer Slide Time: 27:58)



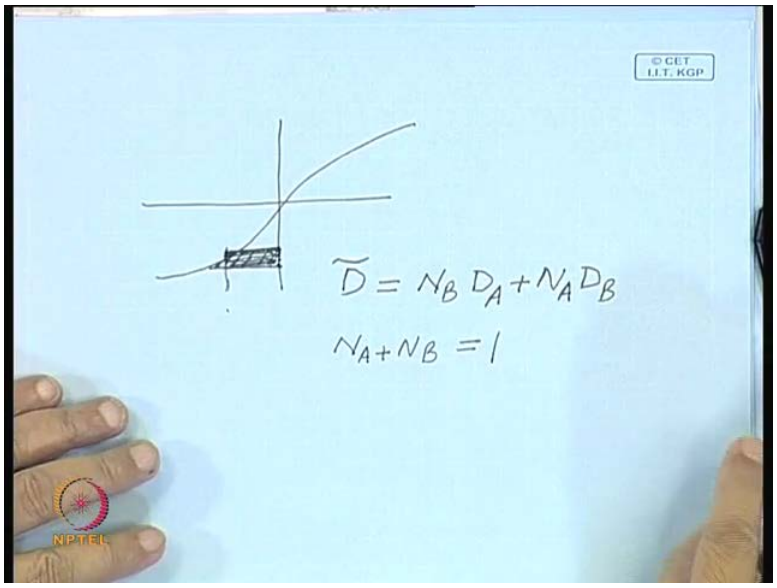
Having done this you try and plot and what you find here is that inter-diffusion coefficient is function of composition. So these are the intrinsic that diffusivity similarly, here also there be intrinsic diffusivity point somewhere here. But in between this inter-diffusion coefficient initially its goes down then again it goes up, so this is interesting look at it.

(Refer Slide Time: 28:36)



And try and let us look at it little more carefully; now when we derive that inter-diffusion coefficient that darkens expression equation.

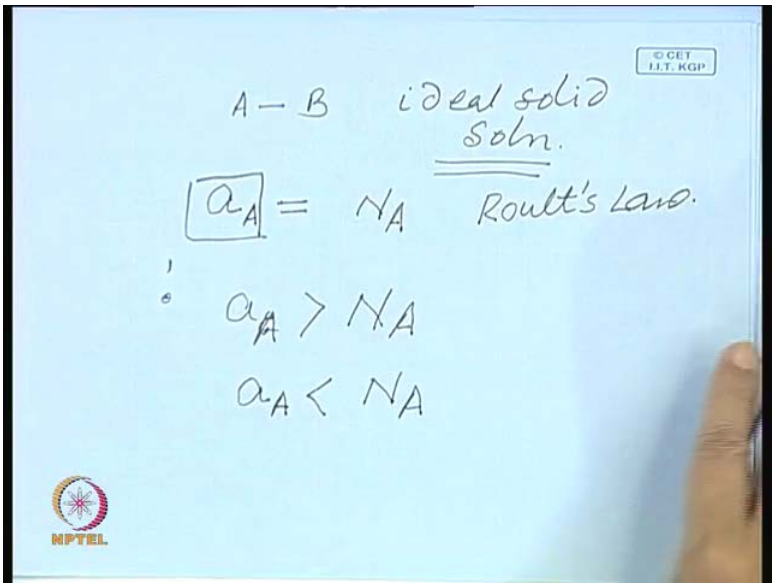
(Refer Slide Time: 28:55)



You will recall that inter-diffusion coefficient was derived at N B times diffusivity of A plus N A times diffusivity of B. Now here if we know that N A plus N B equal to 1. So if you substitute this what is the type of variation to you expect? So in this case say suppose diffusivity intrinsic diffusivity D A is over here this is the other one; if you follow this then the inter-diffusion coefficient should be given by this line and which is very evident from look at this expression.

So this is the inter-diffusion coefficient for this N B. So this is D minus D B, so which clearly comes out here D B times one see and this is this D B you take it out it goes that side so it comes out to be D minus D B D minus D B is this and this portion is D A minus D B. Therefore, what it shows that this point this line should be linear? But what we actually get over here is something like this and why do we get it this is because when we derive this expression; we make some implicit assumption and that assumption was that system that that two A and b metal A and B form ideal solid solution.

(Refer Slide Time: 31:02)



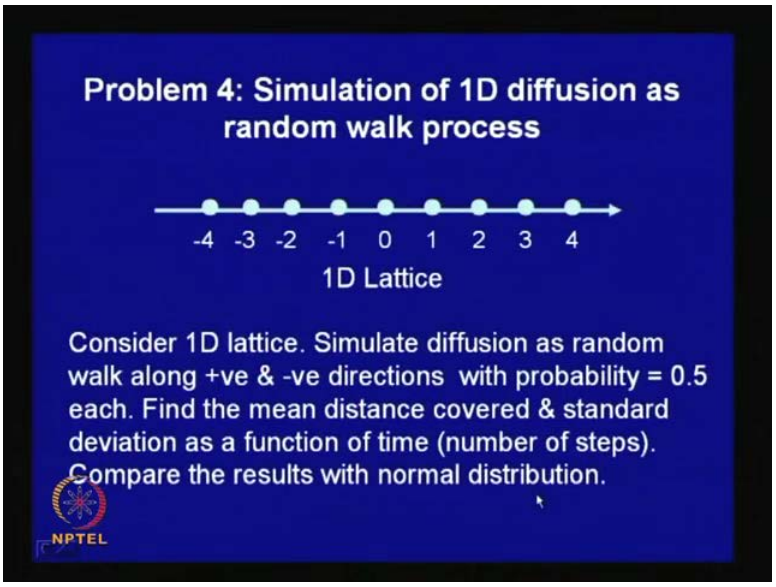
That means A and B that is system binary system is an ideal solid solution. Now in a ideal solid solution we say that actual local concentration or activity what we say that in thermodynamic; we define a term called activity, which actually means activity A which means effective concentration of A at a particular point and this we assume that this is equal to atom fraction A. So that means it follows law called Roult's law. So at any time so if you have A and B atoms at any time number of B atom surrounding A will be exactly equal to that given by the composition that derive from the composition.

But very often this kind of ideal system is non-existence many times we will see formation of cluster or formation of or some kind of ordering. So in case if it is a cluster formation takes place then what happens is activity of A is greater than N A atom fraction that means a cluster some locally that concentration of a will be higher than actual atom fraction of that particular alloy. Similarly, if there is an ordering in that case A will like to have B as its neighbor I mean that will be more preferred in that case this will be less than N A and similar thing it is happening over here.

Therefore, we get a concentration profile like so that means the system we just described there is tendency of ordering and that activity that is local concentration is lower than, what it should have been local concentration of A is lower than what should have been. Therefore, what we need is another correction factor which we called a thermodynamic correction factor and this is defined over here as an activity coefficient and this in

thermodynamics this has been worked out in detail and may be you can refer to course book on thermodynamic for this derivation.

(Refer Slide Time: 34:01)

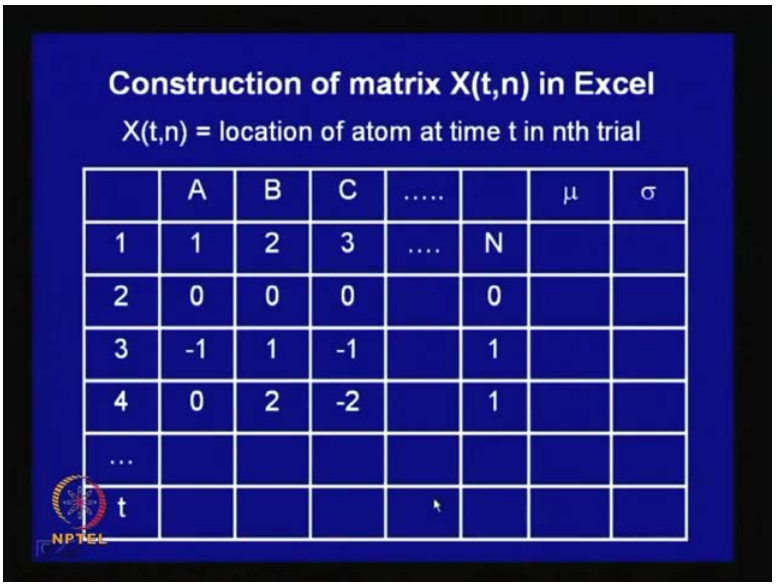


Now we have during the lecture, we have talked about the actual process of diffusion as one of random walk. Now let us see is it possible to simulate the moment of atoms say I will solve a case for 1D and is if it is possible to solve at 1D the method is given and you can take it an extend it to 2D and 3D. Because 2D and 3D it will be little more computer intensive. So I am giving say one particular case which is solved over here and here we are trying to simulate 1D diffusion as random walk process. Say suppose initially an atom is here and 1D suppose what happens on a next times step it can either move say one step forward or one step backward and this is define the decided randomly and this goes on with time say after some time.

Say suppose after one time step if it comes to occupy here. Next again it has to be a random choice say it can move here or here; if it comes back then it remains in its original position and this process continuous and this can be easily simulated in a computer and most of these and even in a spreadsheet. Normal spreadsheet provides random number generated and here is an example, which has been solved using electronic spreadsheet and this instruction which are given here; they consider 1D lattice simulate diffusion as random walk along positive and negative direction with probability

equal to 0.5 each. Now find the mean distance covered and standard deviation as function of number of steps and compare the results with normal distribution.

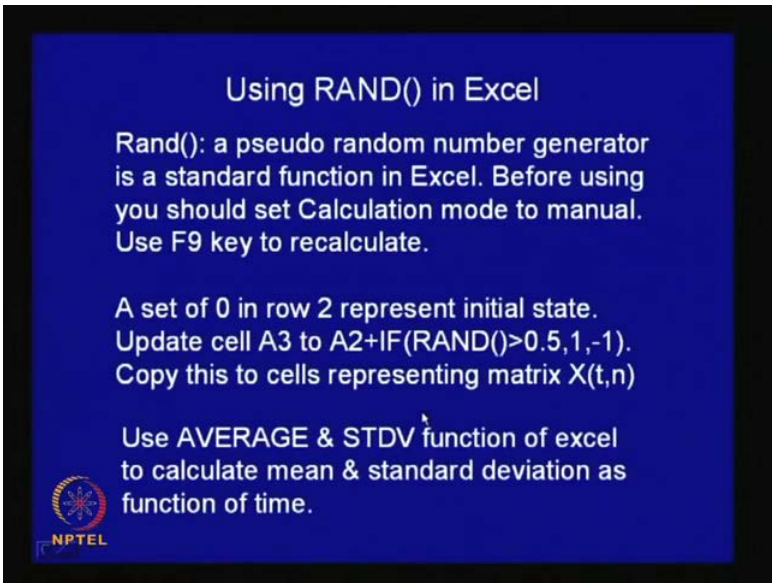
(Refer Slide Time: 36:12)



Now you can setup a spreadsheet and like this say constructs a metrics X these are two suffix a t and n, t represents time, n represents let us say number of trials n is the number of trials and this is the step. Now here we say that number of trial as we put in columns A, B, C it continuous up to N let us say and here each time step; so we can number each of these column as 1, 2 up to n and this is your initial position every trial. So this is the first trial, this is second trial, third trial, n trial every trial initial position is the zero that is zero and then its goes one changing say here its goes to minus one here its plus one here it is minus one.

So that way it goes on continuing up to time t and then what you can do you can find mean of say after what is the most likely a location after the first time step you can find out its average and its standard deviation and you can do the same for each time step and this can be easily setup in a spreadsheet.

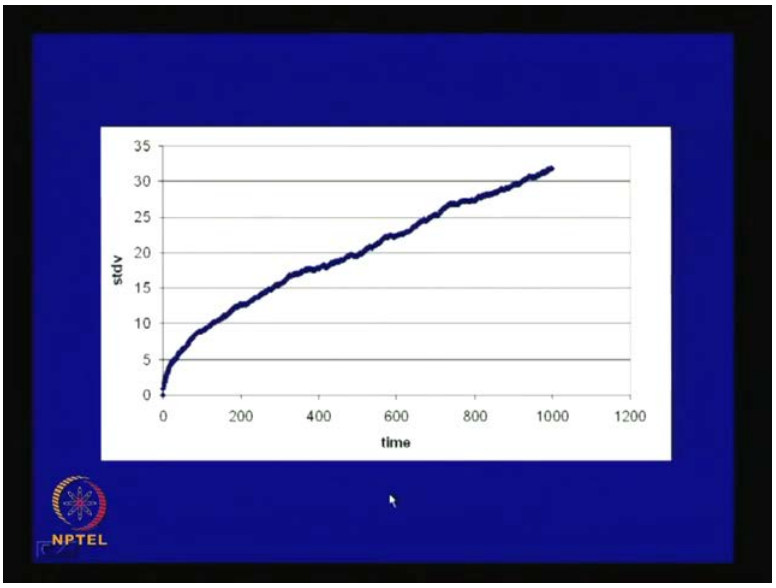
(Refer Slide Time: 37:43)



Say suppose excel, excel has a function as a random number generated which is RAND is a random number is a pseudo random number it is may not be exactly perfect. But still in many cases it is simulates quite well is and now before using you set this calculation mode to manual. Every time you enter a data in excel it re-calculates every cells and then use the F9 key to recalculate after you have enter the data use this. So this is the first initial setup you have to do then put set row as zero in row two and this represents that initial set.

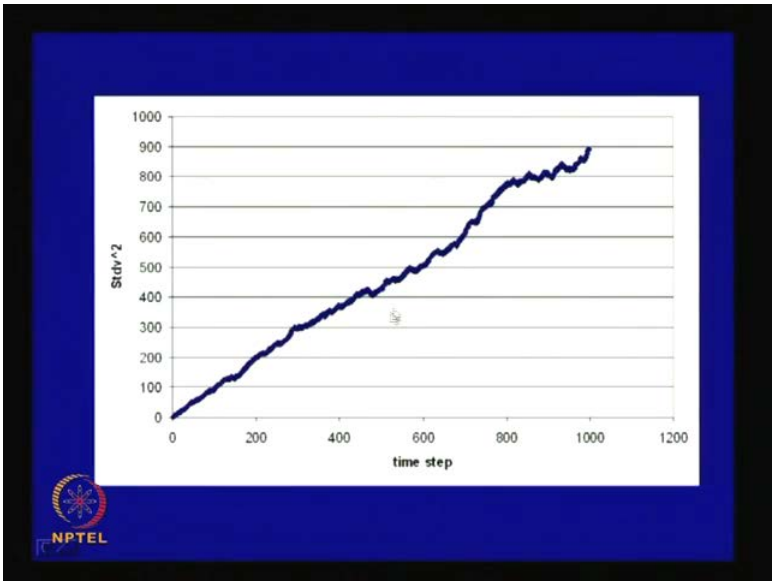
Then update all cells down below this two using this expression this expression can be enter and copied it. So this is will be A 2 plus you give a conditional state meant if random number is greater than 0.5. The random number generated generates random number between zero and one. So if you say that if it is greater than 0.5 that means the probability is half basically; so in that case if it is greater than 0.5 than it is goes to plus one direction that means you will add one to this if it is less than 0.5; you will subtract one from eight two A 2 and this is how each of these cells you can copy formula you can copy in cell of this l say down below so formula which is enter all this cell is exactly the same. Now use at excel also provides average and standard deviation as a standard function; so you can fill up the column for mean and standard deviation.

(Refer Slide Time: 40:00)



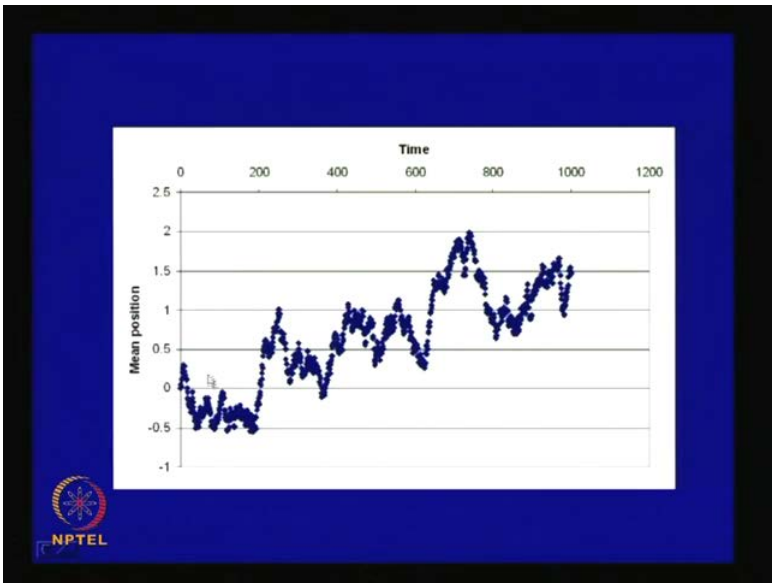
Now you can generate do that solve and generate look at the sum of this plots that standard deviation. You will find that standard deviation its rather sensitive number of trials whatever you do it always follows a definite curve whereas, the distance cover may not you go on and say like previous one here and this is the parabola.

(Refer Slide Time: 40:34)



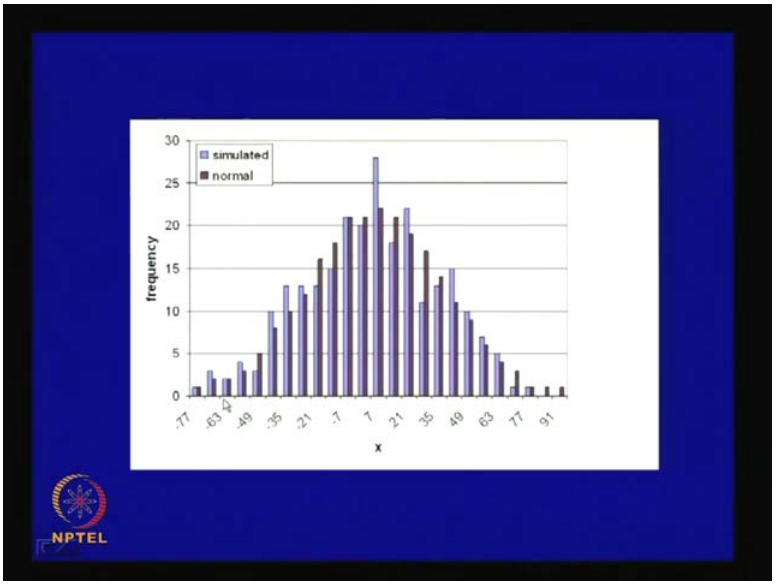
And if you plot standard deviation square you get a straight line and look at this slope is constant. This slope is constant next its mean position their keep on fluctuating here so and in fact this is not same.

(Refer Slide Time: 40:53)



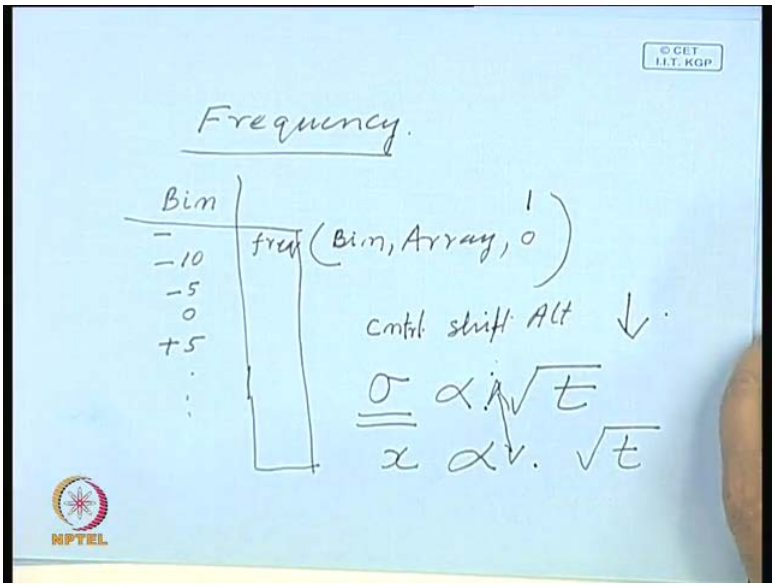
You repeat the trial number of times may be this plot after say thousand steps. So here it is located over here next time; you do you will the plot will not be exactly same but does not matter what is more important is thus this particular plot and why and the reason lies in the nature of the distribution that you get.

(Refer Slide Time: 41:30)



Now excel also provides some standard functions called which you can array functions and which you can use to calculate the frequency distribution.

(Refer Slide Time: 41:48)



So this frequency distribution what is you can setup a bin; so bin means a say let us say that position is the bin where it is, so this is a mean position say suppose this is mean somewhere here is 0, minus 5, minus 10 something like this the location this is plus 5 you can setup a bin and then you here you enter this frequency function over here. Frequency function it will ask for the bin you define the bin you define array you define bin define array and there is a logical variable; if you want to determine the frequency whether it is cumulative or the probability that distribution function, you can put either as zero or one.

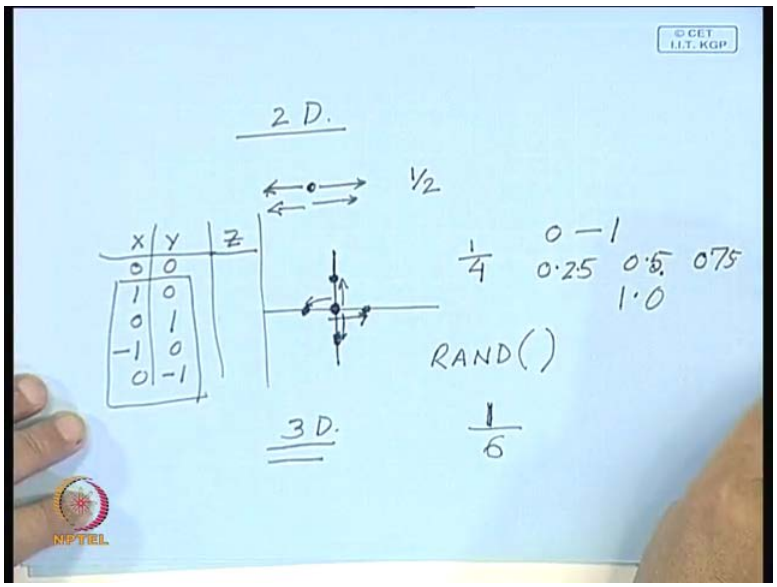
So I do not remember the exactly the which one but when you enter this you have to mark that whole area paste this function and what you have to enter when you enter just do not press just the enter key then you entire array will not be entered you put Control Shift Alt you press three and then enter. Then entire array is entered and this is what has been done here and the entire data has been divided into different class intervals and this is the frequency this to be the blue one what you see is the simulated and now you can easily calculated the mean and plot that normal distribution.

So it is shows that this trial this distribution function is very close to the normal distribution function and in a normal distribution function that one important factor is this standard deviation sigma and this standard deviation; we have found that this standard deviation is actually is proportional to in this particular case root over t and we

also have seen that diffusion distance, diffusion distance also is also diffusion distance is also proportional to root t and this so that means here is also a concentration here is also a proportionality constant here also there is a proportionality constant.

So these two proportionality constants they have a relationship. So basically both will be identical; so what it means go back this slope is actually give you a measure of diffusivity. So with this I hope you had a now if good idea about diffusion solving some problems in diffusion and what you have try to show you today is try to solves a few problems and one problem, which we have take can while during the lecture that is the determination of concentration profile and we have looked at one day solutions only and many of the cases of our interest. We will be looking at one day solution itself gives you a good inside into the material behavior and transformation processes.

(Refer Slide Time: 46:15)



But you can extend it easily to 2D and 3D and may in this try and simulate this random walk process to a 2D case now in a 2D what you need to do a in 1D we have seen that a point is here it can go this one step this side or one step this side only. So the probability is half moving probability of moving this direction is half of probability of going to this position is half. Now if we extend it in 2D so 2D what you have you had a grid? So you have a point here now this point is moving here it can go here it can go here it can go here.

So this means the probability of going in a particular direction is one-fourth. So here also you can consider an array and then you can setup you have that spreadsheet the calculation in a such a way that use random number generator and random number generator generates number between zero and one you go group into four groups say 0.25, 0.5, 0.75 and one and you can setup this I leave it to you to set it up. So if it is say suppose 0.5 it goes from here to here if it is point if it is between this and this then its goes here if it is between 0.5 to 0.75 it goes there and if it is one it goes here.

So what is change is say every point in this particular case one cell could define every point and in this case you have to setup x and y both coordinates x and y. So you will have different combination of x and y zero zero is your start. So next is could be one zero it could be zero one minus one zero zero minus one; so you these four option and this can be repeated and this is how you have to update keep updating these two fills together and I will leave it up to you to tune this spreadsheet and simulate 2D and if you are satisfied with this you can extend this to 3D as well.

Now in 3D this probability of transition there will be six positions if you assume is simple cubic lattice visualize simple cubic lattice. In that case there are three axis and an each side one point this probability will be one six and in that case you will have another coordinate x y and z. So with this I think we cover our lecture or finish our lectures on diffusion under this we looked at the process of diffusion and it is a method of mixing. We have also seen that if you assume that diffusivity to be independent of composition; you get symmetric concentration profile and but in most cases in reality you do not get a symmetric concentration profile and this inter-diffusion coefficient they are function of composition.

We derived an expression for inter-diffusion coefficient for an ideal system and we also have solved some cases where in ideal cases you get linear dependents. But in most cases you do not get linear dependents of concentration dependents of diffusivity. So in that case you have to adopt if you one to module this you have to bring in thermodynamic factor and we also looked at mechanism of diffusion we learned about several experimental techniques by which can be done to find out diffusivity, simplest is the diffusion couple and simplest way of finding out concentration profile is take a section take a section and then take the (( )) do the chemical analysis.

And this is how most of the data diffusivity data have been collected and in case if you do not have diffusivity data for certain material; it can also be calculated from the data available for similar material you have to look at there is a correlation between diffusivity and melting point and it is possible to calculate from the available database and thermodynamic database can be used to calculate diffusivity. Thank you.