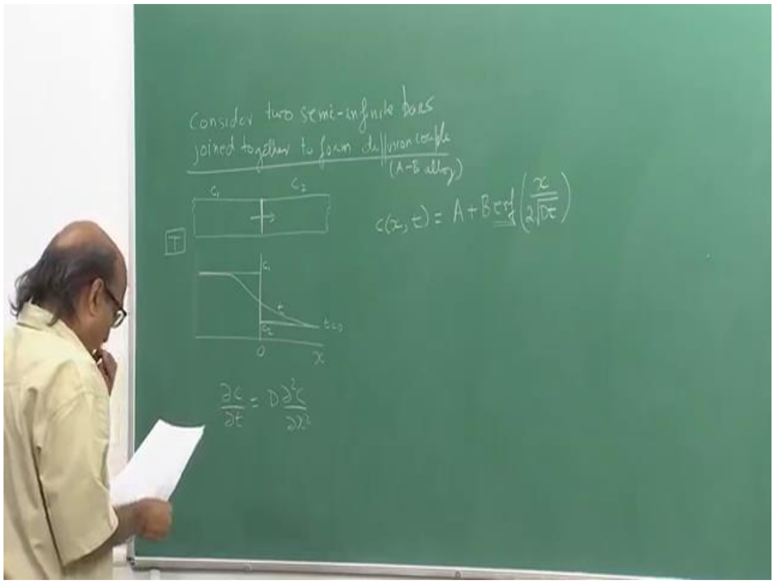
Heat Treatment and Surface Hardening (Part–1)
Professor Kallol Mondal
Professor Sandeep Sangal
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur
Lecture Number 39
Diffusion in Solids - 4

So continuing without solutions to the Fick’s second law.

(Refer Slide Time: 00:25)



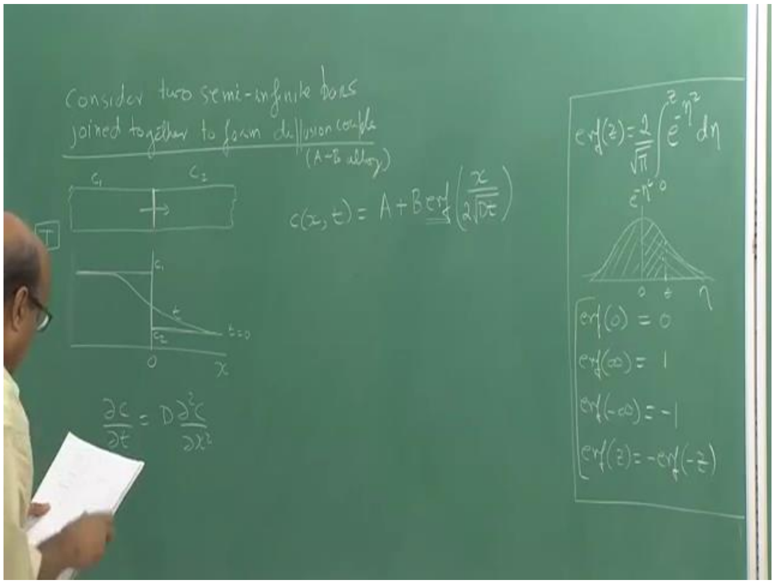
Let us consider the following case consider two semi-infinite bars joined together to form what is called a diffusion couple. So the situation is like this I have two bars which are joined together, two long bars for all practical purposes they could be considered as infinite in both directions, and of let us say some alloy A-B so B is a solute, so to begin with this bar has a concentration of B atoms given by C1 and the bar on the right hand side has a concentration of B atoms as C2.

So which means that that on the left hand side I have a concentration C1 and on the right hand side I have a concentration C2. So this is C1, this is C2 and this is the concentration profile at t equal to 0. So this entire diffusion couple is kept at an elevated temperature T, so that B atoms could diffuse from the left to right C1, the concentration of the left hand side of B atoms be higher than the concentration of B atoms on the right hand side.

So after some time T at this temperature the concentration profile of B atoms start to look something like this. So this is a sometime at t, so this can if I want to know how this profile is going to change as a function of time as well as of course as a function of distance. I would need a solution to the Fick's second law del C by del t is equal to D del square C by del x square.

So without going into any derivation to the solution the solution to this is given by how the concentration changes as a function of x the distance and time t cxt is given by some constant A plus a constant B times. A function called erf for the error function, x upon 2 square root of dt. Now what is this function erf or the error function.

(Refer Slide Time: 04:40)



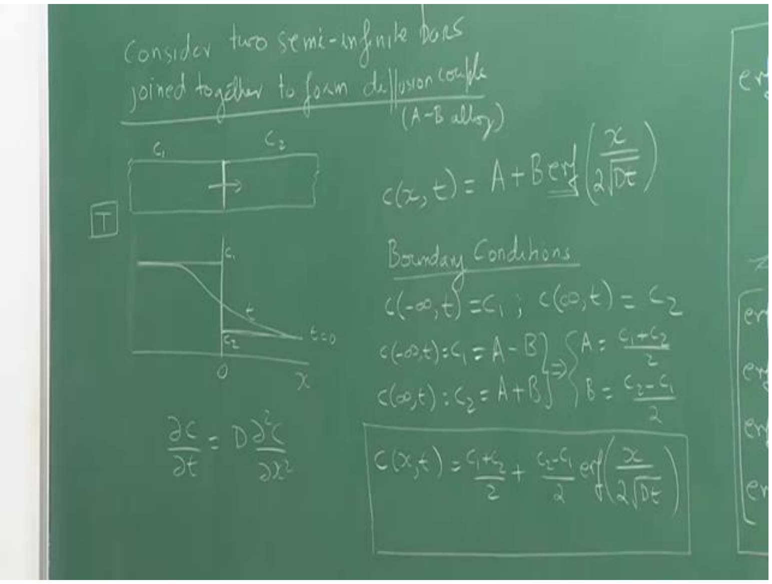
Just a quick look at this function, error function of z is equal to 2 upon square root of pi integral 0 to z, e to power minus at a square delta.

Now this integral does not have any analytical solution that is why the solution is written in the form of a error function. If I plot this function e to power minus at a square versus (())(05:08) that this is the way this is the shape of the function. So if I look at what is the error function z, so I locate z on this axis then the error function of z is nothing but the area under this curved in this region.

So if I look at it what is error value of error function at some specific values of z. For example what is the value of the error function at z is equal to 0. So error function of 0 well this integral is going to be integrated from 0 to 0. Hence this integral will become 0. The area under the curve is 0 and hence the error function at z is equal to 0 is simply 0. Another special value of the error function at plus infinity.

So we are looking at area over the entire curve from 0 to infinity then this value be simply 1. Error function at minus infinity you are looking on this site now it is simply minus 1 and very clearly error function of plus z would be equal to minus error function of minus z. So these are some specific values that you can take a note of for the error function. Values of error function at other z values for that we will make use of table of error function little later.

(Refer Slide Time: 07:35)



Consider two semi-infinite bars joined together to form diffusion couple (A-B alloy)

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

Boundary Conditions

$c(-\infty,t) = C_1$; $c(\infty,t) = C_2$

$c(-\infty,t): C_1 = A - B$

$c(\infty,t): C_2 = A + B$

$\Rightarrow A = \frac{C_1+C_2}{2}$, $B = \frac{C_2-C_1}{2}$

$$\boxed{c(x,t) = \frac{C_1+C_2}{2} + \frac{C_2-C_1}{2}\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)}$$

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

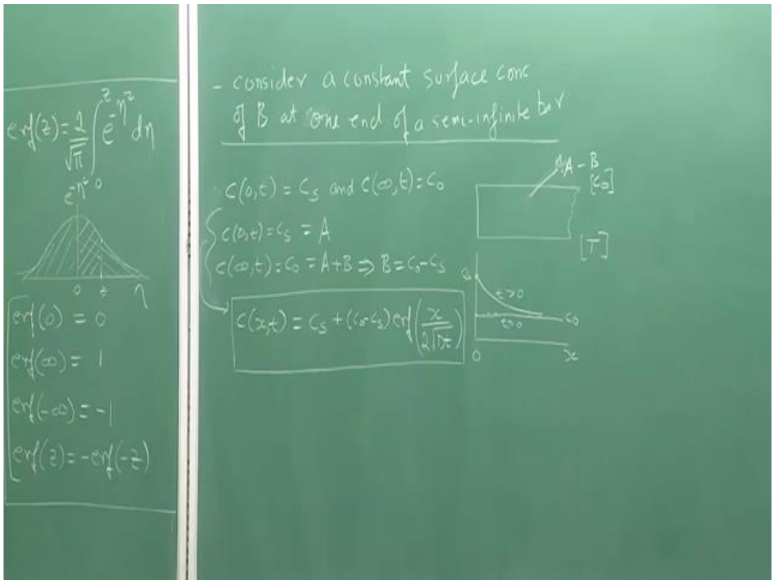
So now coming back to the solution cxt is equal to A plus B error function of x upon 2 square root dt. We need to find the constants A and B, so let us apply the boundary conditions. So let us look at this problem. What is the concentration far away from the interface on either side of the interface but far away. Far away on the left the concentration will be C1 far away on the right of the interface the concentration will remain as C2.

So therefore the boundary conditions I can write is at C on the left hand side at x going to minus infinity at any time t, the concentration is fixed at C1.Similarly on the right hand side C plus infinity at any time t so far away on the right hand side the concentration is fixed at C2. We substitute these boundary conditions in the solution here. Which means on the left hand side putting x is equal to minus infinity.

C1 is equal to A and if look at I substitute I put x for minus infinity, this will become error function of minus infinity and error function of minus infinity is minus 1. Hence this is equal to A minus B. Similarly the second boundary condition C infinity comma t is C2 which is again A but this time we will put it x is equal to plus infinity so this will be error function of plus infinity and error function of plus infinity is plus 1. Hence C2 is equal to A plus B

From here I will get A equals C1 plus C2 divided by 2 and B equals C2 minus C1 divided by 2. Hence now we have it that the profile concentration profile of the B atoms in this diffusion couple is given by C1 plus C2 divided 2 plus C2 minus C1 divided by 2 error function of x upon 2 square root of dt. So this gives me the solution of how the concentration is going to change in a diffusion couple. So if I know what is a diffusion co-efficient at the temperature at which we are studying this then from here I can predict how the concentration of the solute B atoms is going to change at different location x and at different times.

(Refer Slide Time: 11:30)



$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-\eta^2}\, d\eta$$

$\mathrm{erf}(0) = 0$

$\mathrm{erf}(\infty) = 1$

$\mathrm{erf}(-\infty) = -1$

$\mathrm{erf}(z) = -\mathrm{erf}(-z)$

- consider a constant surface conc of B at one end of a semi-infinite bar

$C(0,t) = C_s$ and $C(\infty,t) = C_0$

$C(0,t) = C_s = A$

$C(\infty,t) = C_0 = A + B \Rightarrow B = C_0 - C_s$

$$\boxed{C(x,t) = C_s + (C_0 - C_s)\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)}$$

When a similar solution or the same solution applies is the following. Consider a constant surface concentration of solute atoms, so surface concentration of B atoms at one end of a semi-infinite bar. So the situation is I have a semi-infinite bar where I am keeping the concentration so this is let us say a bar of let say AA atoms and I am keeping or for that matter not just A, it is an alloy of AB with some concentration C0 to begin with of C0 concentration of B atoms.

And if I look at this, so this is how so this is C0 that inside the bar there is a C0 concentration of B. The surface is kept at a concentration of B atoms as C sub S, the surface concentration. This can be done for example in the case of carbon one can have a carborizing gas that the this surface is exposed to in such a way that the concentration of the surface of carbon atoms is fixed at cs.

So initially the concentration profile of B atom is simply this, after some time t the profile would become something like this. So this is at t equal to 0 and this is at some time t greater than 0 again we are talking about some temperature t at which we are doing this experiment, and the concentration of the surfaces is kept fixed at cs all throughout.

In this situation also this particular solution applies and all we need to do is find the constants A and B for the given boundary conditions of this particular problem. Now what are the boundary conditions here, well this is x is equal to 0, so at x is equal to 0 for any time t the concentration is kept fixed to cs as I have already mentioned, so this is one condition this is a semi-infinite bar so far away from the surface the concentration of B inside this bar is simply C0.

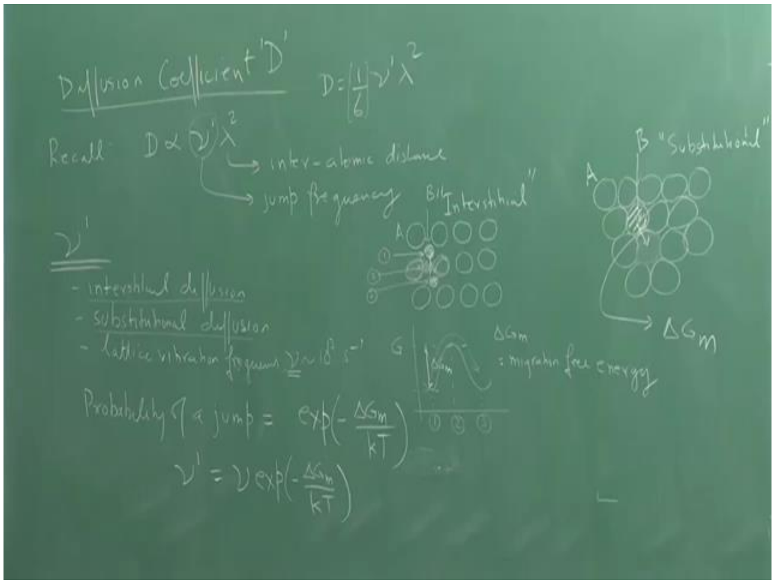
So the second boundary condition is C at plus infinity at any time t is equal to C0. Apply this boundary condition to the solution so I will get C0t equals cs is equal to at x is equal to 0. So if I look at this at x is equal to 0 I will get an A plus error function and x is 0, so error function of 0 we already know is 0. Hence I get cs is equal to A.

Apply the second boundary condition C infinity t is equal to C0 is equal to coming back to the solution I will get A plus B error function of infinity. Error function of infinity we know is 1 and hence C0 is equal to A plus B from here I already have now A is equal to cs and B is equal to C0 minus A or C0 minus cs and hence from these boundary conditions I get the solution cxt of the concentration profile is a function of distance and time as cs plus C0 minus cs error function x upon 2 square root dt.

So this is the solution in this case now this we will take up in the next lecture not in this lecture we will take up problem where we can actually apply this solution this this particular relationship has a great practical application as we will see in the next lecture. Now we have looked at the solutions we have solved this solutions of the fixes second law, the co-efficient D has kept coming up in all the solutions and in fact you will notice in all the solutions the term square root dt keeps coming up.

Right from the first lecture on diffusion but we have not really talked much about the co-efficient D and therefore in this subsequent part of this lecture I will now talk about the diffusion co-efficient D. What is it made up of, we have some idea of the diffusion co-efficient D right in the first couple of lectures and we will expand from that, so I am now going to examine this diffusion co-efficient and what does it depend on.

(Refer Slide Time: 18:00)



You would recall from the first couple of lectures on diffusion that the diffusion cop-efficient D we found out was proportional to the jump frequency of atoms times Lambda square where Lambda is a jump distance. So Lambda would typically would be an inter atomic distance and this jump frequency and in fact one specific case when we have taken diffusion in a simple cubic crystal we had found D to be equal to 1 upon 6 mu prime Lambda square.

So there was this factor of 1 upon 6 and some other situation this factor of 1 upon 6 could change, so in general the diffusion co-efficient is going to be proportional to mu prime upon Lambda square. Now mu prime times Lambda square. So Lambda just put as enter atomic distance for the jump and mu prime is the jump frequency per second. So this is clear now let us explore mu prime the jump frequency what is it going to depend on.

Well first of all it will all depend on whether we have what is the mechanism of this diffusion, so whether we have the interstitial diffusion or we have substitutional diffusion, and it would also be dependent on the lattice vibration frequency, mu which has can be generally taken as 10 to power 30 per second. So let us examine the two cases of interstitial and substitutional diffusion and how is a jump frequency going to depend on the on these two mechanisms.

So let us consider interstitial diffusion say, imagine that this is a interstitial atom. So this is atom A and out here is atom B. Now if it has to jump from one interstitial site to another interstitial site out here, it has to squeeze between these two atoms so one can imagine a situation that in order for this to jump there would be a position where these two atoms would be displaced and this atom would have come to this position and the next position would be that it jumps from here to an intermediate position and finally to the position to the neighboring interstitial site.

So I have let's say position one, position two and position three and if I were to look at the energies associated with each of these positions, so the situation would be something like this, so this is at position one, this is at position two and this is at position three. So position one and position three are equilibrium positions low energy positions while at position two the crystal is taken to a high energy state.

Therefore for this jump to be successful the interstitial atom has to have sufficient energy for it to jump over this energy hill and what is this energy hill, we will call this as delta Gm, the migration free energy. So we will call delta Gm to be equal to a migration free energy. Something similar like this so this is for the case of interstitial, let me write it here.

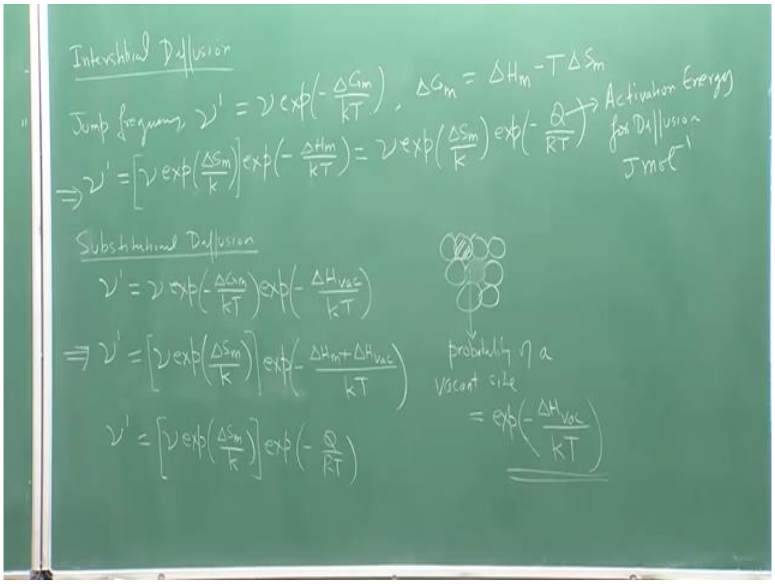
What about substitutional a similar situation also exists for substitutional diffusion. Let us say this is my salute atom so is A atom this is B atom now if it has to jump to a neighboring site, this neighboring site has to be vacant. So let us say this is vacant site so in order for this to jump again it has to squeeze between the other neighboring atoms and as a result this jump would also be associated with a migration free energy or an energy hill of this kind.

So therefore it both interstitial as well as substitutional diffusion. There is a migration energy involved for an atom to jump from one location to a neighboring location. So, hence there is a probability of successful jump, so what is that probability. So probability of a jump would be equal to exponential minus delta Gm divided by KT. Just like we had seen in the case of nucleation also or jump of atoms across interface etc.

It is a similar kind of expression that this is going to be related to a probability of a jump and hence what is the frequency of (())(26:05) then well atoms are vibrating with a frequency of mu and hence mu prime, the jump frequency is equal to mu times exponential minus delta Gm upon KT.

Now this is the situation for the case of interstitial diffusion.

(Refer Slide Time: 26:50)



Interstitial Diffusion

Jump frequency $\nu' = \nu \exp\left(-\frac{\Delta G_m}{kT}\right)$, $\Delta G_m = \Delta H_m - T\Delta S_m$

$$\Rightarrow \nu' = \left[\nu \exp\left(\frac{\Delta S_m}{k}\right)\right] \exp\left(-\frac{\Delta H_m}{kT}\right) = \nu \exp\left(\frac{\Delta S_m}{k}\right) \exp\left(-\frac{Q}{RT}\right)$$

→ Activation Energy for Diffusion $J\,mol^{-1}$

Substitutional Diffusion

$$\nu' = \nu \exp\left(-\frac{\Delta G_m}{kT}\right) \exp\left(-\frac{\Delta H_{vac}}{kT}\right)$$

$$\Rightarrow \nu' = \left[\nu \exp\left(\frac{\Delta S_m}{k}\right)\right] \exp\left(-\frac{\Delta H_m + \Delta H_{vac}}{kT}\right)$$

$$\nu' = \left[\nu \exp\left(\frac{\Delta S_m}{k}\right)\right] \exp\left(-\frac{Q}{RT}\right)$$

probability of a vacant site

$$= \exp\left(-\frac{\Delta H_{vac}}{kT}\right)$$

So we have seen that in the case of interstitial diffusion jump frequency mu prime is given by mu the lattice vibration frequency multiplied by the exponential minus delta Gm upon KT. Well delta Gm is the migration free energy for the jump.

Now we can write delta Gm in terms of enthalpy and entropy as delta Hm the enthalpy for migration minus the temperature at which the jump is taking place times the migration entropy delta Sm. So substituting this the jump frequency for interstitial diffusion is given by mu exponential substituting for delta Gm. I will get exponential delta Sm upon K times exponential minus delta Hm divided by KT.

If we can assume delta Sm to be independent of temperature then I have the pre exponential term mu exponential term delta Sm upon K to be independent of temperature while the exponential term is dependent on temperature. Now consider the substitutional diffusional case where the vacancy mechanism is active. So in the case of substitutional diffusion also one can write mu prime to be equal to mu exponential minus delta Gm upon Kt these terms would be still be there.

However there would be one more term that would have to be added to this expression because for a jump to be successful the neighboring site to which the jump is taking place has to be vacant. So if I, have I have an solute atom jumping here which means this site must be vacant. What is the chance that this site would be vacant, so therefore we have to multiply this expression by the probability that this site is vacant and what is the probability for a site to be vacant.

So probability of a vacant site has to be given by what is the enthalpy of formation of vacancy and this is given by exponential minus the enthalpy for formation of vacancy which I am calling as delta H vacancy divided by KT. This probability will have be multiplied here. Now this particular probability comes from a simple exercise in a very basic material science course, so I will not go into the details how this expression is coming.

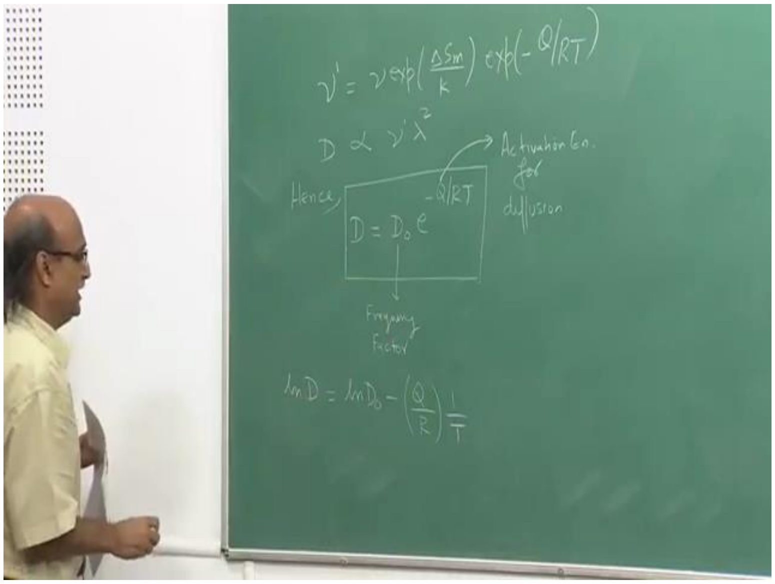
So very clearly the substitution diffusion is going to be more difficult or the jump frequency is going to be less than in the case of interstitial diffusion because you have an added term which is a probability of a site being vacant.

Now let us substitute for delta Gm in terms of delta GM and delta Hm as we have done here, for substitutional diffusion the jump frequency would become mu exponential delta Sm upon K, the temperature independent terms as in the case of interstitial diffusion times exponential minus delta Hm and there will be additional term an additional enthalpy term vacancy enthalpy for creation of a vacancy. So delta Hm plus delta H vac divided by KT, so you can compare the relationship for jump frequency for interstitial diffusion and in the case of substitutional diffusion the additional difference is simply the enthalpy for creation of vacancy.

Now in general I can express for interstitial diffusion mu exponential delta Sm upon K times exponential minus Q instead of writing delta Hm I am writing Q and I am writing this Q in terms of energy per Boltz and hence instead of writing the Boltzmann constant K I will replace it by R and write it in this fashion where Q is the called as the activation energy for diffusion in terms of typical units can be Jones per mole inverse and R is the Gauss constant instead of writing the Boltzmann constant.

Similar thing I can do for the substitutional diffusion and I can get an identical relationship, vibrational frequency mu times exponential delta Sm upon K, the temperature independent part time exponential minus Q divided by RT, where here Q consists of delta Hm plus delta vacancy. Here Q simply consists of delta HM but we can write both of the equations in a very similar way except the activation energy would be different for the substitutional diffusion and interstitial diffusion.

(Refer Slide Time: 34:20)



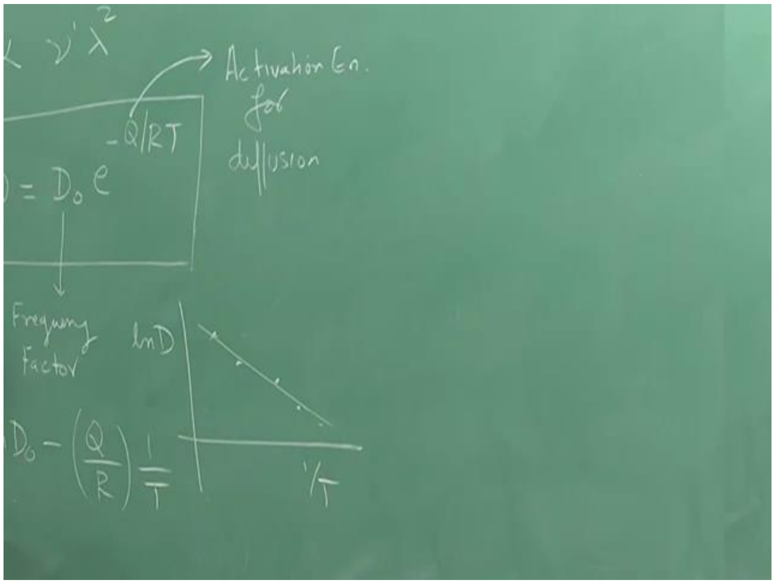
So going from here jump frequency whether it is interstitial or substitutional diffusion is I am simply rewrite that as mu exponential delta Sm by K exponential minus Q by RT and write in the earlier part of the lecture I have written diffusion co-efficient is proportional to mu prime Lambda square hence we can write the following relationship for the diffusion co-efficient.

I can lump there will be some constant of proportionality here which is going to be a function of geometric factors like what kind of a crystals structure in what direction you are considering diffusion etc and in addition to that jump distance and mu prime which is coming from here so D could be written as all the temperature independent terms can be lumped into parameter D0 e to power minus Q by RT.

So this represents the final expression for diffusion co-efficient as a function of temperature. Here D0 is also termed as the frequency factor and Q is called the activation energy for diffusion and one final thing before I terminate this discussion in this lecture. If I collect different values of diffusion co-efficient from diffusion experiment as a function of temperature then I can find out from that data Q and D0 and then I will be in a position to determine D for different values of temperature and how can I find Q and D0.

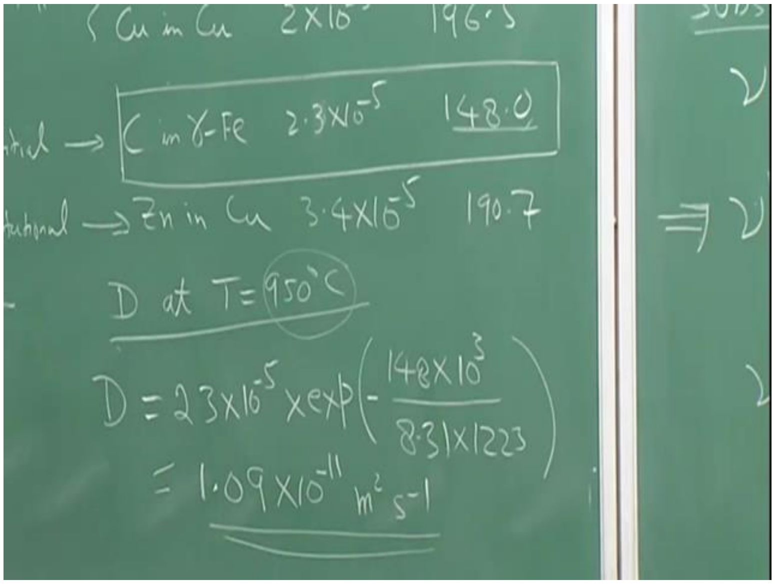
So I will get diffusion co-efficient values D for different temperatures and suppose I take logs of this equation then log D is equal to log D0 minus Q by R times 1 upon T and if I plot log D versus 1 upon T and I put I in the data points that I get for different temperatures, what is the diffusion co-efficient.

(Refer Slide Time: 37:00)



They should fall on a straight line so I put a best (())(37:01) line through this and from the slop and the intercept I can get the value for activation energy and D0 and after that I can get D values for other temperatures.

(Refer Slide Time: 37:45)



So just to give you an idea of the order of magnitude estimates for the diffusion co-efficient let us consider some data that is available. So order of magnitude estimates consider the system what is the value for D0 for it, what is the value for Q for it. D0 is in units of meters square per second inverse. Q one is going to put it as Kilo Joules per mole. So consider diffusion of aluminum in aluminum that means we are considering self-diffusion.

D0 is 2 into 10 to power minus four and Q is 143.4, copper and copper D0 is 2 into 10 to power minus 5 Q is 196.5, so this is these are couple of examples of self-diffusions. Consider R1 in Gamma iron that is we are saying carbon and austenite if it entered cubic form what is the diffusion. Diffusion of carbon in the body centric cubic form of iron would be different from the diffusion of carbon and austenite form of iron.

In this case I get two point D0 as 2 point 3 into 10 to power minus 5 and Q to be 148 kilo Joules per mole. Zinc and copper, now this is the case of interstitial diffusion and here it is the case of substitutional diffusion. So zinc and copper D0 as 3.4 into 10 to power minus five and Q is 190.7

kilo Joules per mole, if we take just one case let us consider this case and let’s find out what is D the diffusion co-efficient at t equal to 950 degrees centigrade.

Well D is equal to D0 e to power minus Q by RT, so D0 is 2.3 into 10 to power minus five times exponential minus 140 (())(40:41) value of Q but it is in the kilo Joules so I have to multiply it by thousand to convert to joules divided by the gas constant. We are going to take it as 8.31 Joules per Kelvin times the temperature in Kelvin so I have a temperature of 950 degrees centigrade add to this 273 to give me 1223 Kelvin as the temperature I calculate this and I get a diffusion co-efficient value at 950 degrees centigrade for carbon and gamma iron as 1.09 into 10 to power minus 11 meter square second inverse.

What would happen if I increase the temperature, well it is very clear from the equation that the diffusion co-efficient value will go up so you will have faster diffusion as the temperature is reduced the diffusion co-efficient value goes down and you will have slower diffusion. So this brings us to the close of this lecture and in the next lecture would be the concluding lecture of this course where we will conclude what we have done and what kind of applications we can apply the fundamentals that we have done here. Thank you.