Phase Transformation in Materials
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Lecture - 16
Fick's II law (cont.), Diffusion and Temperature

So, let us carry on diffusion. And before actually I talk about temperature dependence of diffusivity, just to let you know that there are another way of solving this diffusion equation second law of Fick’s that is known as the semi infinite medium.

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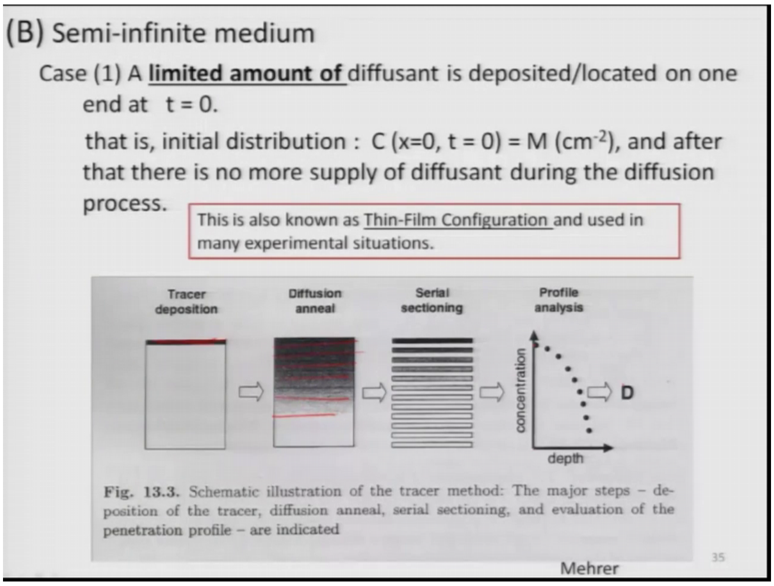

(B) Semi-infinite medium

Case (1) A **limited amount of** diffusant is deposited/located on one end at t = 0.

that is, initial distribution : C (x=0, t = 0) = M (cm^{-2}), and after that there is no more supply of diffusant during the diffusion process.

This is also known as Thin-Film Configuration and used in many experimental situations.

Fig. 13.3. Schematic illustration of the tracer method: The major steps – deposition of the tracer, diffusion anneal, serial sectioning, and evaluation of the penetration profile – are indicated

Mehrer

Suppose, let us suppose a case a limited amount of some diffusant is deposited at one end of a specimen that is what is shown here, the limited amount at time t equal to 0. So, therefore, initial distribution is that at x is equal to 0 or t equal to 0, there is a certain value of diffusant and after that there is no more supply of the diffusant, it is only supplied once, this is also known as thin film configuration.

So, what will happen if I, then heat this specimen for long time at there are something what is known as if we do a diffusion annealing slowly, this diffusing; sorry this diffusant will be diffusing to the sample, then we can actually do a serial sectioning of that you can cut small-small pieces like this that is what shown in the next picture and then measure composition of that in each of these pieces if I measure the composition and plot it as the function of depth, I should see a change like this. That means, it will be very high at x is equal to 0 and at a distance x is equal to x it will be low. Therefore, this allows us to a fully calculate or measure the diffusivity D.

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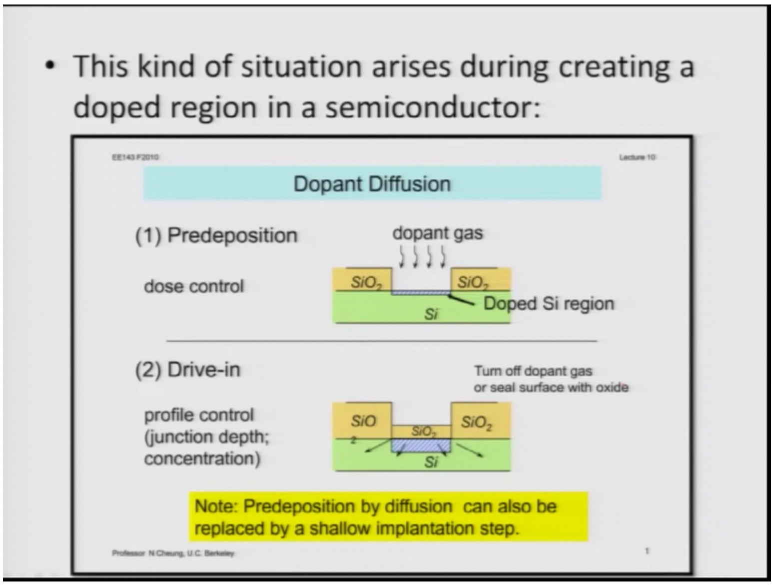

- This kind of situation arises during creating a doped region in a semiconductor:

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Lecture 10

Dopant Diffusion

(1) Predeposition

dose control

(2) Drive-in

profile control (junction depth; concentration)

Turn off dopant gas or seal surface with oxide

Note: Predeposition by diffusion can also be replaced by a shallow implantation step.

Professor N Cheung, U.C. Berkeley

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So, this is known test are diffusion this kind of situation arises in many-many cases, the one example is the semiconductor doping. Suppose, we have silicon here and this is silicon dioxide in the surface and you want to dope this region of silicon with some boron or some let us say phosphorous whatever; you must put a gas and this gas will simply allow this dopant to be diffuse in to this. So, once a certain depth to which it diffuses the dopant gas is stopped actually a specifically speaking initially the; it is expressed the gas; in the gas is stopped and then it will be slowly diffusing inside the surface and finally, an Si2 layer is built up.

So, the first process is known as pre deposition that is where you control the dose and the second one is known as diffusion or drive in. So, predeposition by diffusion can also be replaced by shallow implantation; that means, you can implant boron or phosphorous normally boron is can be implanted very nice easily. So, you can implant to certain depth and then stop it then you can actually allow the things to diffuse or you can do the diffusion annealing. So, that is kind of situation arises in the real life and this is nothing but a semi, nothing but infinite semi infinite medium. So, semi infinite medium do exist in the actual in actual practice and that is why you need to this is experimental that we can actually solve the equation and get the values.

So, in all this remember one thing, we are assumed D is independent of time temperature sorry, but D is never independent of temperature whenever doing the diffusion annealing we are assuming D is independent of temperature, but that is not the case and that actually changes the diffusivity. So, how we can deal with that?

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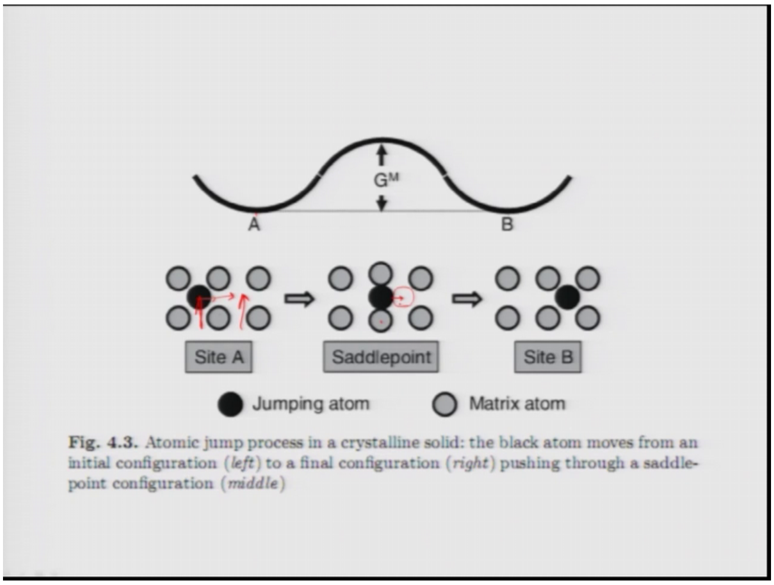

Fig. 4.3. Atomic jump process in a crystalline solid: the black atom moves from an initial configuration (*left*) to a final configuration (*right*) pushing through a saddle-point configuration (*middle*)

Let us as go back to the; our earlier lectures, then how the diffusion happens in a substantial solution.

Let us suppose that there is a vacant site and an substantial atom is diffusing from one position to other position, if it diffuses one position to other position, what will happen? This will push the atoms which is present at this positions and this pushing will lead to certain kind of a work done by the system. That means, what from A position to B positions, this atom need to if that atom needs to go it will has to cross over a barrier and that barrier is nothing but a migration barrier that is what it is written Gm and this migration barrier needs to be bypassed or needs to be like that crossed by the atom to reach from equilibrium position here in this position to this position that is what is shown here.

So, this has to be a thermal driven process, if temperature is not temperature means thermal submission energy is not provided, the atom at the central position here cannot move to the next position; rather diffusion cannot happen, this is why actually the diffusivity must be dependent on temperature. So, simple analogy tells you that now how can you actually make it very clear this is why actually I had taken some slides from the from the internet and I am explaining you more detail manner 3 different configuration are shown nicely here.

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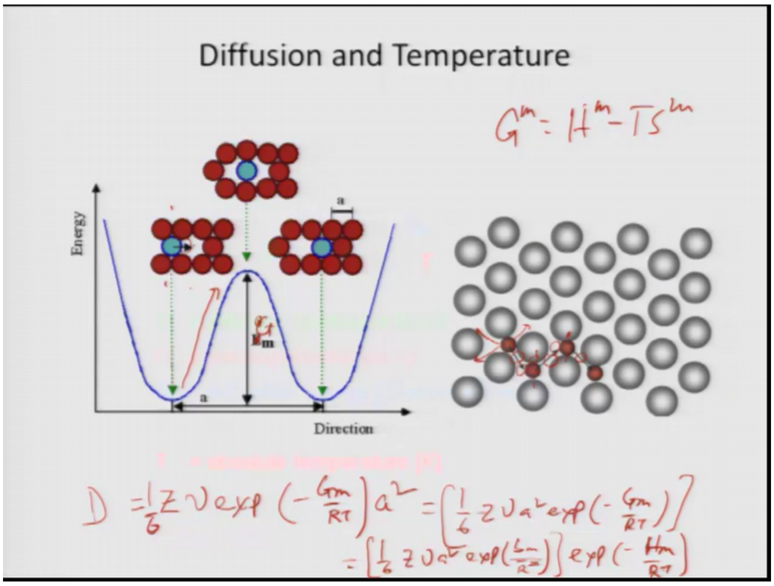

Diffusion and Temperature

$$G^m = H^m - TS^m$$

$$D = \frac{1}{6} Z \nu \exp\left(-\frac{G_m}{RT}\right) a^2 = \left[\frac{1}{6} Z \nu a^2 \exp\left(-\frac{G_m}{RT}\right)\right]$$
$$= \left[\frac{1}{6} Z \nu a^2 \exp\left(\frac{S_m}{R}\right)\right] \exp\left(-\frac{H_m}{RT}\right)$$

Let us; suppose this is the configuration where one atom is sitting there solid atom is little bigger size and this atom is has to move from here to there. So, if has to move it will it will first land up there that is what is shown in the second step then finally, from there it will go. So, there is a barrier that is very clear, we need to explain more further now in a interstitial case same thing will happen interstitial atoms suppose going from here to there. So, from here to here if it goes it will again push this 2 atoms then it reach here again reach here again from here to there it will push this 2 atoms again that similarly here.

So, every time it has to pass from one interstitial position to other interstitial position the atom will pass through barrier so; that means, system is to do some work and this remember atoms in a finite medium at a certain temperature t, they are vibrating or they are actually colliding each other and they are vibrating with certain frequency let us suppose this vibration frequency is equal to nu right. That means, what every time atom is making an atom to cross this barrier very simple it will just make an atom jump to cross this barrier.

So, as this barrier height here its e let us write G; G is better this barrier height is Gm. So, the probability of the number of atoms which has sufficient energy to cross for this barrier will be this because that is; obviously, an exponential term and it will be G by RT because your RT or R is for one mole and it K is for a single atom. So, Gm by RT or Gm by KT is nothing but energy available to the atom to cross the barrier. So, RT is the thermal energy and Gm is the barrier height. Therefore, the fraction of that energy is the what is the probability that atom will cross over this barrier, right.

So, now; obviously, it has a frequency; that means, it is doing the atom is doing the atoms certain number of atoms per second and this is given by nu. So, nu into exponential of minus Gm by RT what is giving us a total number of jumps successful jumps which it can take to cross over this barrier. So, that is possibly for one position, but it might be there are many positions available many vacant position available. So, it will try for not only for one sides, it can try even in this side this side this side like here when the when the interstitial atoms is moving, it can move this way, it can move this way, it can move this way, it can move that way. So, depending on whichever directions its availability of these free sites free positions it can do that.

So, let us suppose that is; what is the Z; if the Z is number of sites available. So, this is tells you this is what is tells you the diffusivity nothing but diffusivity, but remember this is not the actual diffusivity in a 3 dimensional this must be equal to 1 by 6 alpha square where sorry; a square the a is the distance I have written here a is the distance written there I am sorry. So, a square correct that is come basically when you assume that there are 3 x y z directions because this is done in 1 D. So, in 3 D there are 3 directions. So, there are 6 different directions it can do plus x minus x plus y minus y plus Z minus Z that is why it is divided by one by 6 and a is the distance.

Therefore, the diffusivity has to be square of distance that is why a is put it there and nu is basically frequency that is per second or per hour hertz. So, that is why exponential term has no, no, units that is why it is there. So, now, you can actually write down this as very simple equation very simply you can write down that I am sorry goes back is Z nu a square exponential minus Gm by RT, right. So, that is nothing but 1 by 6 Z nu a square exponential Sm by RT because Gm is nothing but Gm is nothing but a minus minus minus T Sm this is any free energy migration or does not matter this must be equal to h minus T S.

So, therefore, if I can take out the Sm term Sm term is Sm term is the entropy. So, there is the minus sign. So, minus minus will become plus I can write down this as like this minus H m by T. So, first term this is always consider to be constant why at a temperature T remember that sorry the I will vanish why T will be here because we have already taken R T; so Sm by R.

So, as you know Z number of vacant sites available to which the atom can diffuse is also constant nu is the frequency of vibration that is also constant a is the distance between 2 lattice side that is a constant and Sm by r is also constant Sm is the entropy of migration r is universal gas constant that is why this is whole thing is a constant only thing is here is exponential minus by R T is not a constant as a temperature.

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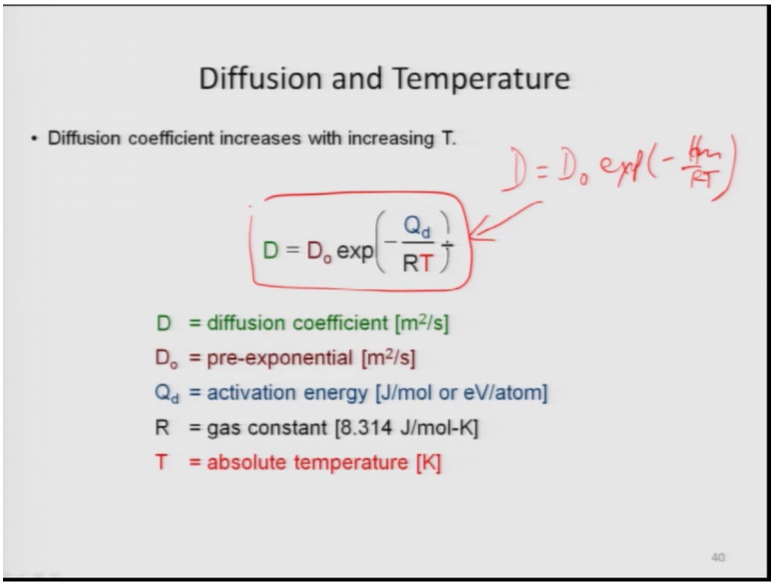

Diffusion and Temperature

- Diffusion coefficient increases with increasing T.

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

$$\boxed{D = D_o \exp\left(-\frac{Q_d}{RT}\right)}$$

D = diffusion coefficient [m²/s]

D_o = pre-exponential [m²/s]

Q_d = activation energy [J/mol or eV/atom]

R = gas constant [8.314 J/mol-K]

T = absolute temperature [K]

So, if I go back on the next slide. So, I can write down D is nothing but a constant term D 0 exponential minus h m by r t and that is what is written here is replaced by Qd it H m is nothing but enthalpy of migration that is nothing but the activation energy activation energy for migrating one atom from one side to other side. So, that is why you see this fundamental equation always D is equal to D 0 exponential minus Q by RT where Q is nothing but activation energy for the diffusion happen and R is a constant universal gas constant; T is a temperature.

So, temperature must be in absolute scale temperature, it is never considered as a normal Celsius or its has to be in Kelvin and R is constant and it is known as a 8.314 joule per mole Kelvin. So, simply we can actually calculate D at any temperature provided we know the Qd and we will discuss about Qd more may be next 5 minutes time, but please remember, this is again in diffusion is a very fundamental equation this directly derive from the from the assumption that diffusion of atom requires some activation barrier to be crossed.

So, depending on the type of diffusion it is a substantial atom diffusing or interstitial atom diffusing or a vacancy diffusing as I mentioned in the first lecture the vacancy can also diffuse the atomic motion can called considered to be a the vacancy moving depending on whichever the pieces or which is the type of diffusion; difussing pieces this Qd is going to be different; obviously, for interstitial atom Z is very large. Therefore, dj is very large and activation energy for a Q is also low because there the interstitial atoms are. So, small the amount of pushing requires by the atoms to move from one position to other position is also very low that is why the interstitial atoms diffuses faster that is why carbon nitrogen oxygen they diffuse faster in steel not iron not manganese not the other substantial elements this is the main reason.

Remember D 0 does not change much D 0 is the peak exponential term, it is always assumed to be constant; it is the Q which actually dictates the value of D at any temperature and Q depends on type of type of diffusion mechanisms we are seeing in the literature. So, that is the very important aspects please remember, now I can actually get.

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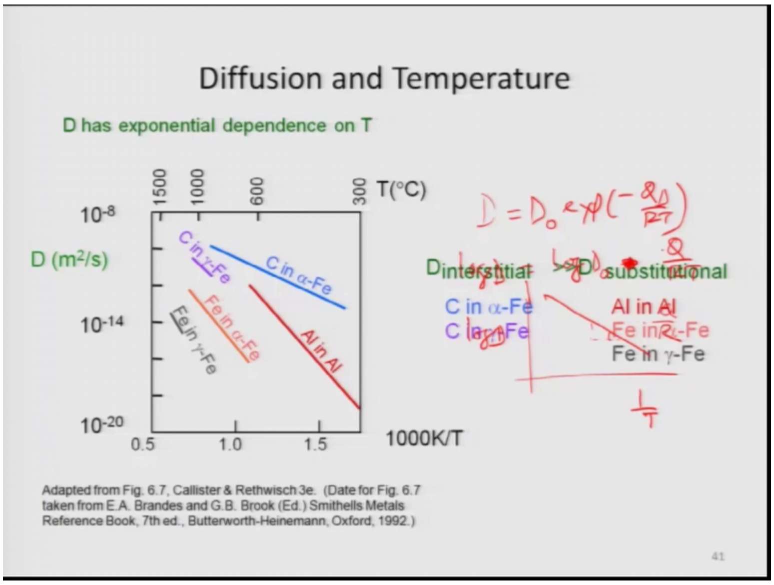

Diffusion and Temperature

D has exponential dependence on T

$D_{interstitial} >> D_{substitutional}$

C in α-Fe
C in γ-Fe

Al in Al
Fe in α-Fe
Fe in γ-Fe

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

Adapted from Fig. 6.7, Callister & Rethwisch 3e. (Date for Fig. 6.7 taken from E.A. Brandes and G.B. Brook (Ed.) Smithells Metals Reference Book, 7th ed., Butterworth-Heinemann, Oxford, 1992.)

Let me just write down the expression again and explain to you. So, we have write down D equal to D 0 exponential minus Qd by RT, it is always important to measure Qd because Qd tells you; what is the kind of diffusion mechanism taking place in material. So, to do that you can actually simply take a log on both side then write down log of D is log of D 0 plus sorry; minus minus 2.303; oops sorry, not 2.203; it is Q by RT, right this log here is lan ln.

So, now actually I can plot I can always make a plot of log of D versus 1 by T, what I should get? I should get a straight line with a negative slope and the slope of this curve is basically is basically Q by R, this slope and intercept is log of D 0, this is straight line equation y is equal to mx mx is this plus C. So, therefore, if I measure D at different temperatures D means capital, it is D 1; D at different temperature and plot log of D as a function of 1 by T, I should be able to measure the Q and this Q is very important the Q tells you what kind of diffusion mechanism is relevant in a particular material and that is why Q needs to be measured always.

Here actually I am plotting D as the function of 1 by T, but it is not 1 by T 1000 multiplied by 1 by T because that is makes the numbers easily understandable and the top axes you see temperature as a as shown exact temperatures what you see here carbon in gamma iron carbon in alpha iron. Let at first look at this 2, you see this slopes of carbon in gamma iron is very high steep slope the higher the slopes higher is the value of D that is why you see here D is something 10 to power minus 8 10 to minus 9 carbon in alpha iron is also very high, but slope is slanted. That means what the barrier for diffusion of carbon in gamma iron is much lower than carbon in alpha iron that is. Obviously, gamma iron is FCC structure number of you know octahedral or tetrahedral voids and their sizes are different than in alpha iron and that is makes the carbon diffusion in gamma iron much easy.

That is why in steel metallurgy we always hit the sample to the gamma phase because you want carbon to diffuse uniformly this is the reason main reason for that now if you look at iron diffusion in compared to that iron is a solid sorry iron is substitutional element. So, iron in gamma iron and iron in alpha iron they are having same slopes, but they are much much lower 10 to the power minus 9 and 10 to the power minus 14. This almost ordered 3 orders of magnitudes or 4 order magnitude lower value as compared to carbon iron temperature that is the reason why substitutional things diffuses very slowly and that is basically Qd is very very high and as the Qd increases it is a negative. So, therefore, exponential term decreases and that is why the diffusivity decreases.

Aluminum; in aluminum is even much much difficult more difficult why because its slope is still lower that because aluminum is a self diffusion and self diffusion is more difficult iron in alpha iron is not a self diffusion in already carbon manganese. So, many things are there. Therefore, you cannot call as a self diffusion. So, that is the taken from callister. So, that is very simple way to explain how the values actually is there in the actual literature and how D depends on time.

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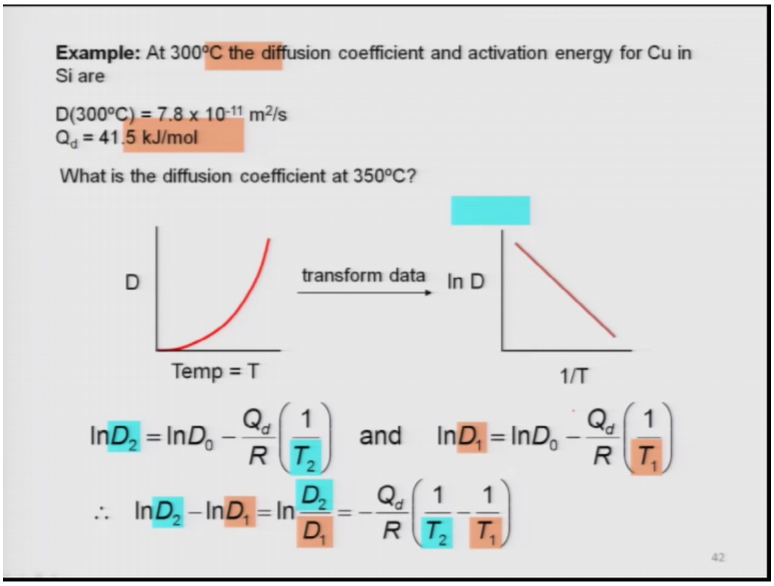

Example: At 300°C the diffusion coefficient and activation energy for Cu in Si are

$D(300°C) = 7.8 \times 10^{-11}$ m²/s
$Q_d = 41.5$ kJ/mol

What is the diffusion coefficient at 350°C?

$$\ln D_2 = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T_2}\right) \quad \text{and} \quad \ln D_1 = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T_1}\right)$$

$$\therefore \quad \ln D_2 - \ln D_1 = \ln\frac{D_2}{D_1} = -\frac{Q_d}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Let us give one example mathematical example at 300 degree Celsius temperature, the diffusion coefficient and activation energy of copper in silicon are actually given by these 7; these basically 7.8 into 10 to power minus 11 meter square per second and the activation energy is Qd is basically 41.5 kilo joule per mole. So, what is the diffusion coefficient at 350 degree Celsius temperature; you need to know the many things. So, what we have; we have a D versus temperature, we need to transform into D versus 1 by T.

So, log of a lan of D 2 is basically lan of D 0 minus Qd by Q by r t that is why equation, I have already shown and you can always write down D 1 is like that. So, at T 1 we know the D 1.

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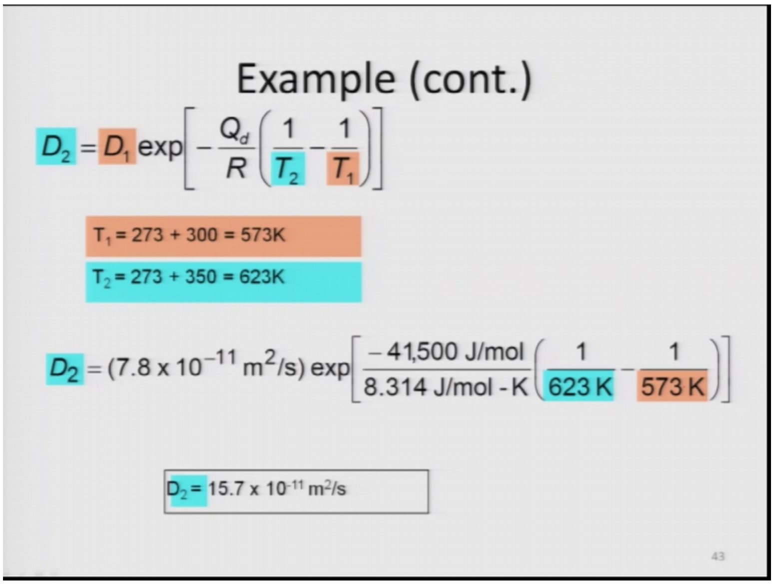

Example (cont.)

$$D_2 = D_1 \exp\left[-\frac{Q_d}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\right]$$

$T_1 = 273 + 300 = 573K$

$T_2 = 273 + 350 = 623K$

$$D_2 = (7.8 \times 10^{-11}\ \mathrm{m^2/s}) \exp\left[\frac{-41{,}500\ \mathrm{J/mol}}{8.314\ \mathrm{J/mol\text{-}K}}\left(\frac{1}{623\ \mathrm{K}}-\frac{1}{573\ \mathrm{K}}\right)\right]$$

$$\boxed{D_2 = 15.7 \times 10^{-11}\ \mathrm{m^2/s}}$$

So, we can measure easily D 0 and also we measure we can measure D 0 because Q is given already to us. So, as you clearly see that you can do the maths very easily temperatures must be converted and D 2 is basically 7.8 into 10 to the power minus eleven multiply divide this terms this is Q Qd. This is R and these are temperature differences. So, what you get it is basically 15.7 into 10 to the power minus 11 meter square per second. So, that is what you get.

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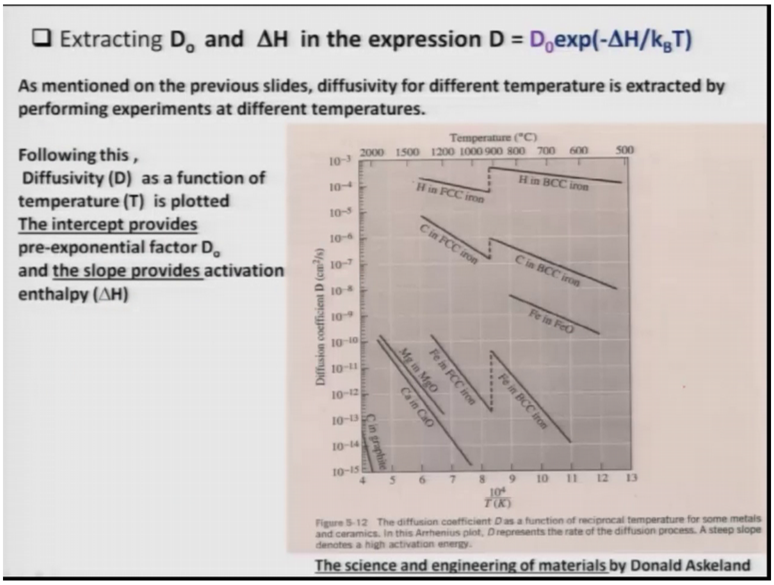

☐ Extracting D_o and ΔH in the expression $D = D_0\exp(-\Delta H/k_BT)$

As mentioned on the previous slides, diffusivity for different temperature is extracted by performing experiments at different temperatures.

Following this ,
Diffusivity (D) as a function of temperature (T) is plotted
The intercept provides pre-exponential factor D_o and the slope provides activation enthalpy (ΔH)

Figure 5-12 The diffusion coefficient D as a function of reciprocal temperature for some metals and ceramics. In this Arrhenius plot, D represents the rate of the diffusion process. A steep slope denotes a high activation energy.

The science and engineering of materials by Donald Askeland

So, very simple we are actually applying this exact equation D 2 is known D 1 is known Qd is known D 2 sorry, D 1 is known not D 2 is known Qd is known T 1 and T 2 are known therefore, D 2 is nothing but calculation of the exponential term well we can actually shown even much many data you see is hydrogen in FCC iron is very high, because it is interstitial 10 to the power minus 4. Remember these; this is very high value carbon is 10 to this is centimeter per second.

Therefore, in meter square, it will be 10 to power minus 4 has to be multiplied as 10 to power minus 7, 10 to power minus 6 will be 10 to the power minus 10 and you see iron in iron oxide is also very high because all these are substitutional, but still because there is open spaces available, but iron in FCC iron and iron in BCC iron is pretty low magnesium in magnesia and calcium in calcia is very very low.

Look at here one important aspects the carbon in graphite self diffusion carbon in graphite is extremely slow because graphite has very less number of sites available vacancies are very low and graphite normally has high melting temperature materials. So, vacancy concentration is very low carbon melts at 3600 degree Celsius. Therefore, at a temperature of something like how much something like 1000, 2000 degree Celsius temperature, number of vacancy is relatively low. So, therefore, carbon will where the carbon will diffuse self diffusion is that is why very low that is why actually graphite is used in all kinds of high temperature applications because diffusion is slow graphite will not getting will not get affected that is another reason I just wanted to show you.

So, just to give an idea before I wind up self diffusion is always very slow and self diffusion is always happens. Let me let us consider copper wires copper wire is basically actually very pure copper with a very little amount of oxygen that is why it is called oxygen free copper which is used to in the all the wirings.

Now once electricity flow inside the copper wires because of joule effect temperature will rise the pressure rise may not be very high, but it will rise depends on the value of the current. So, because of that diffusion of copper will happen copper atoms will diffuse it is in through, it is copper lattice itself and that is what is known as self diffusion remember this very slow, but this is not you know negligibly small.

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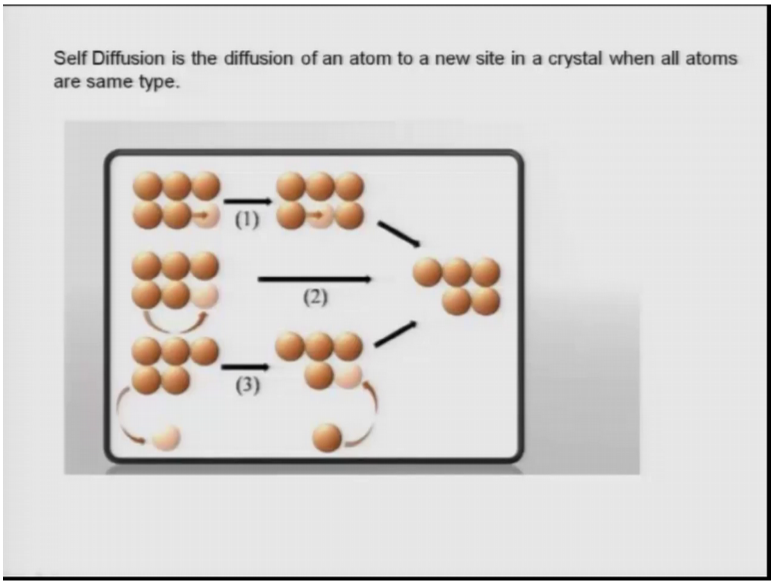

Self Diffusion is the diffusion of an atom to a new site in a crystal when all atoms are same type.

So, self diffusion is the diffusion of an atom to a new site in its crystal all atoms are same type that is what iron in iron aluminum; in aluminum here am saying copper suppose there is a some kind of a atom here and some vacant side here. Therefore, vacancy is moved atom will move this side and we can have many many different mechanisms. So, therefore, the Qd value for self diffusion is always it is very high that is why the self diffusivities are pretty low. So, with that let me wind up with the diffusion.

And the next lecture we are going to talk about interfaces. Interfaces means, what are different type of interfaces, how do interfaces play role in dictating different-different aspects of phase transformations. And subsequently that will start actually phase transformations different types of phase transformations.