Structure of Materials
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Lecture - 31
Diffusion in Solids

After talking about temperature dependence of diffusivity. Let us move to the important aspect of this set of lectures on diffusion which is the atomic models of diffusion. These models have to be understood because these will play an important role in understanding, how species diffuses? What are the critical issues? What is the activation energy for diffusion? And certain what we may call the shortcut or short paths for diffusion, which have a high diffusedly.

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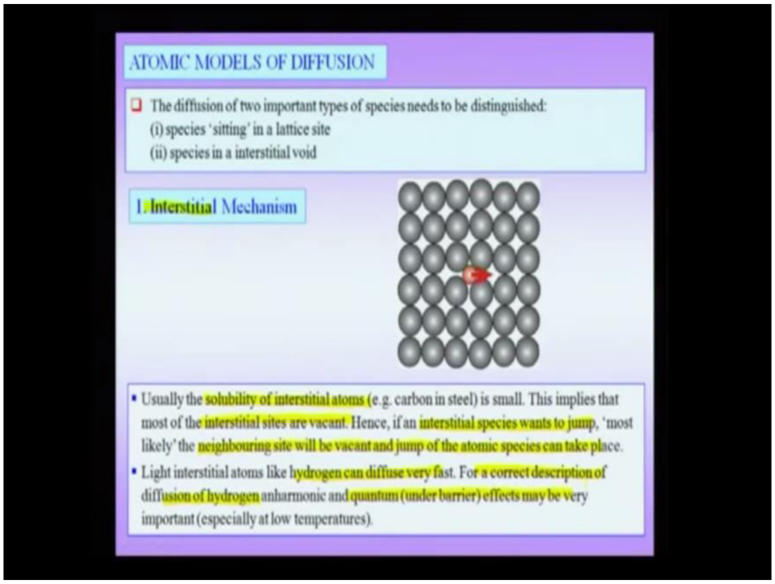

ATOMIC MODELS OF DIFFUSION

- ☐ The diffusion of two important types of species needs to be distinguished:
  (i) species 'sitting' in a lattice site
  (ii) species in a interstitial void

1. Interstitial Mechanism

- Usually the solubility of interstitial atoms (e.g. carbon in steel) is small. This implies that most of the interstitial sites are vacant. Hence, if an interstitial species wants to jump, 'most likely' the neighbouring site will be vacant and jump of the atomic species can take place.
- Light interstitial atoms like hydrogen can diffuse very fast. For a correct description of diffusion of hydrogen anharmonic and quantum (under barrier) effects may be very important (especially at low temperatures).

So, if you look at atomic models of diffusion 2 kinds of species which are diffusing are of important one are interstitial atoms and one are atom sitting in the substitutional site. Now, of course this diffusion, we are talking about focusing in the set of lectures is diffusion in metals and diffusion in ionic solids and other kind of solids may have other aspects which are not covered in this basic set of lectures.

Now, when I talking about interstitial diffusion. Usually, we have to note that the solubility of the interstitial atoms and these interstitial atoms for instance could be carbon and steel. It could be hydrogen in palladium or such kind of elements which would sit in interstitial sites. That is they do not occupy the lattice position and because the solubility is small. It implies that most of the interstitial sites are vacant only a fraction of the interstitial sites are occupied actually by atoms for instance carbon in b c c ion. If you look at, we known that the carbon actually occupies as we have discussed before the smaller octahedral void, but the frication of these voids occupied is small and therefore most of the interstitial sites are vacant.

Now, if therefore if an interstitial species wants to jump then most likely the neighboring site would be vacant and jump of the atomic species can take places. So, this jump will require something known as an activation barrier and we will try to find out what this activation barrier depends on in the coming slides, but also there are cases wherein the jump or the motion of the interstitial atom takes place by tunneling mechanisms.

This happens special for hydrogen which can diffuse very fast and for a correct description of the diffusivity of hydrogen certain quantum under barrier effects may become very important though especially, this is true at low temperatures for diffusion of hydrogen wherein over the barrier activated jump is restricted, but this kind of under barrier tunneling jumps. We will not consider or tunneling diffusion we will not consider in these set of lectures and we will only talk about jumps which involve about the barrier transport.

So, we note that there is an atom sitting in the interstitial site and this of course a schematic. This interstitial atom has many options to jump, when it wants to jump and why does it want to jump because at any finite temperatures this atom is vibrating in all directions. So, let me show this schematically in the board that there is an atom sitting in an interstitial site and this atom because of, it is temperature is actually vibrating in all 3 directions and when this atom is vibrating about these positions.

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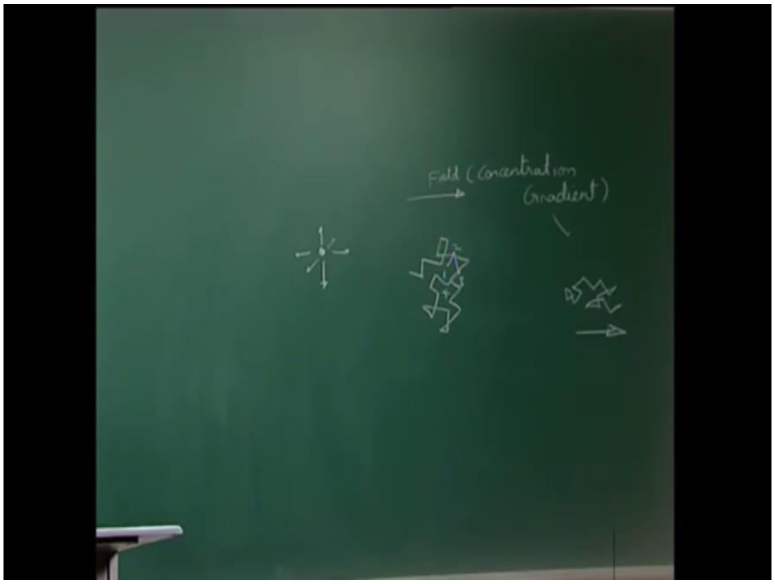

There is a chance that it will actually jump. Now, if you talk about a jump of an atom then once support this it jumps to its neighboring interstitial position from the first position. Say, 1 to 2, then further it may jump from 2 to an interstitial site 3 to it may go to some other site 4 and therefore this may undergo what is called a random walk process.

This species keeps on jumping. Now, in the absence of a concentration gradient, there is no net flow of this atom. This atom essentially remains in its vicinity and keeps on jumping, but if you track the average position over a period of time it is as good as the atom remaining in same place, but suppose there is a concentration gradient which has been applied. Of course, this gradient, we have noted can be a concentration gradient can be an electric filed or can be a driven by stress, but all these random jumps in the presence of a field and from now we are considering concentration gradient.

Then, these random jumps in the presence of a concentration gradient leads to net flow of matter that means though there are jumps against a concentration gradient the overall motion of the atom is down the concentration gradient or as the relevant quantity may be the chemical potential gradient.

So, we see that an atom sitting in its lattice position makes it is vibrating because of temperature and um because of the these vibration once in a while. It will actually, when we have these vibrations, it does not actually jump, but sometimes it jumps over the barrier and gets into its neighboring position for instance. It could be this site from site a. It could go to site b, but then further it could again jump to site c and then to a in the absence of a concentration gradient, it will not move anywhere.

There will be no net flow of this matter, but if there is a concentration gradient. Then, the atoms will tend to move in spite because of these random jumps in a particular direction, which we called diffusion the long range diffusion. So, this is true for an interstitial atom which is sitting in the interstitial void and we the most important thing. We noted from this slide is that most of the interstitial voids are vacant, because the solubility of most of these interstitial atoms in the a given system is actually small for instance carbon has very solubility as we have noted before in b c c ion. On the other hand when we are talking about diffusion of a substitutional atom and the concentration of substitutional atoms could be pretty large for instance.

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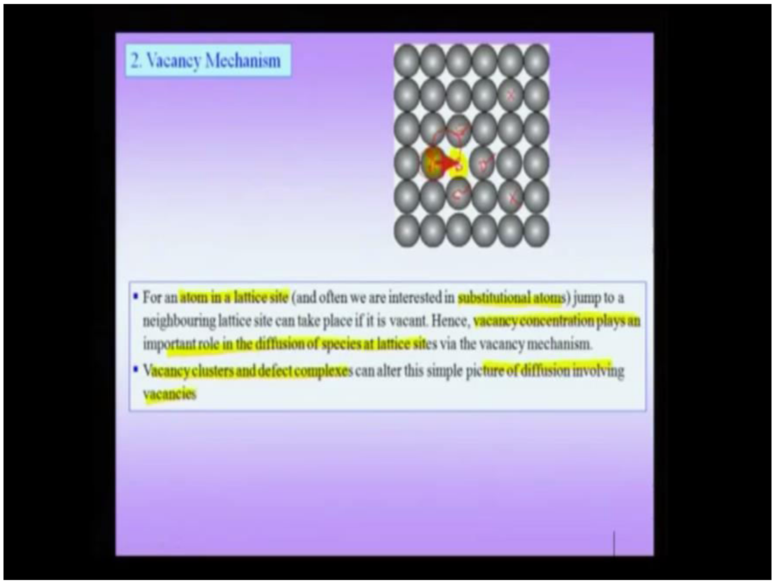

2. Vacancy Mechanism

- For an atom in a lattice site (and often we are interested in substitutional atoms) jump to a neighbouring lattice site can take place if it is vacant. Hence, vacancy concentration plays an important role in the diffusion of species at lattice sites via the vacancy mechanism.
- Vacancy clusters and defect complexes can alter this simple picture of diffusion involving vacancies

Suppose, I am talking about an a b system it could, so happen that there is 50 percent of a and 50 percent of b and suppose I am taking about a b c system there could be one third of each one of these atoms forming a solid solution and therefore, there could be I am not saying in every case this is possible, but there could be and that implies that the species which is diffusing um is in present in a very high concentration. Now, and lattice atom that is atom present in a lattice site, can only jump to the neighboring site if the neighboring position is vacant.

Suppose, I am talking about an atom which is marked in blue here and I am talking about the jump of this atom to a neighboring site. Here, this jump can only take place if the neighboring site is vacant and this implies that the basic mechanism giving rise to diffusion of an atom in a lattice site which we called a substitutional atom is the vacancy mechanism in which case if the atom jumps from site a to site b for instance, of course this is site a and it jumps to site b. This can equivalently be thought of as if the vacancy is jumping from site b to site a that means after the jump has taken place the site a will become vacant here.

This implies that the vacancy concentration plays a very important role in the diffusion of species at lattice sites via the vacancy mechanism though we are focusing here on the vacancy mechanism and the interstitial mechanisms. There are other mechanisms which have also been proposed for diffusion, but typically these other mechanisms involve higher activation energies.

We will not discuss them in this basic elementary code and therefore 2 things come into picture when you are talking about a vacancy mechanism for diffusion number, one is a fact that the substitutional atom has to find a vacancy neighboring. It only then can it jump that means in this schematic picture the atoms which satisfy that criteria would be the atoms which is here or here for instance an atom sitting here cannot diffuse. This atom cannot diffuse because there is no vacant site next to it.

So, these atoms which I have marked by a tick can jump into this vacant site which is labeled b and for instance these labels could be like for instance c d e. So, this a c d e site atoms can jump into site b and diffusion can because d and that automatically implies that what is we have to, I have to estimate? What is the probability of finding a site? Which is vacant in a crystal. So, that means I have to find the concentration of vacancies in a crystal at any given temperature of course there could be a non equilibrium concentration of vacancies in a crystal.

This could happen for instance, if we are talking about as you have seen before there are 2 kinds of vacancies one is structural vacancies which comes from off stoichiometry, one is thermal vacancies which come from um the entropic stabilization of vacancy in a crystal and suppose I am talking about this thermal vacancy. Then, normally there will be an equilibrium concentration of vacancies in a crystal, but additionally it is also possible that I take a crystal to higher temperature and then quench it to a lower temperature in which case I can obtain an excess concentration of vacancies at room temperature as compared to what would be present in terms of the equilibrium concentration.

The point to be noted here, is that vacancy clusters and vacancy defect complexes can alter the simple picture of diffusion involving vacancy. So, we have to note that there are complications which can arise, but for this point of time we just progress upon the simple basics which we shall elucidate further.

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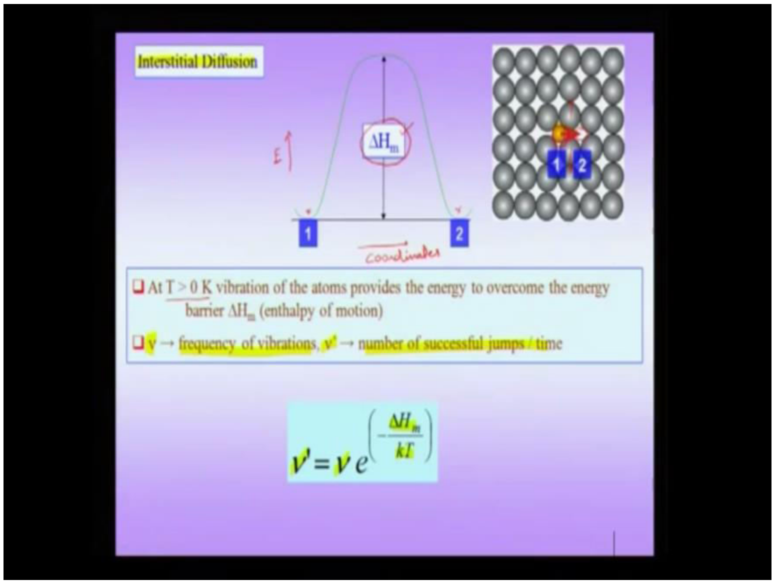

Interstitial Diffusion

- ☐ At T > 0 K vibration of the atoms provides the energy to overcome the energy barrier ΔH_m (enthalpy of motion)
- ☐ ν → frequency of vibrations, ν' → number of successful jumps / time

$$\nu' = \nu\, e^{\left(-\frac{\Delta H_m}{kT}\right)}$$

So, therefore when I am taking about the 2 mechanisms of diffusion, one involves no vacancies which is for the interstitial diffusion and one which involves vacancies which is the subtitutional diffusion. So, let us well a little further into this concept of interstitial diffusion in which case an atom sitting in site one which is shown here red atom in the interstitial side jumps to a neighboring side. Say, from 1 to a neighboring side which is label 2 the energy of the system in these 2 positions in identical. If, you talking about an energy coordinate diagram and this is now coordinates or what you may call the reaction coordinates?

Then, you would notice that the energy in these 2 positions is 1 and 2 is exactly identical, but between the 2 positions when actually this 2 atoms. If, you want to talk it in the more physical picture have to pride apart. So, that this jump can take place that is an activated state that is the state in which the system goes to an higher energy. In this higher energy state which has to be the barrier which has to crossed is called the enthalpy of migration or enthalpy of motion. For this interstitial atom and we said that at any temperature which is a positive Kelvin temperature atoms are vibrating. This atomic vibration provides the energy which can overcome the barrier, which is the delta H m enthalpy of motion.

Now, suppose an atom is vibrating with a frequency nu sitting in its interstitial position and this is the frequency of vibrations. It is not necessary that every one of those attempts or the oscillation will lead to an actually successful jump only a small fraction of that is labeled as nu prime can actually jump. This nu prime is related to nu by the activation energy by arenas kind of an equation that means nu prime is nu exponential minus delta H m by k T. That means at higher temperature more of these jumps will be successful and if you have a lower barrier delta H m then more of these jumps will be successful, so these 2 are obvious.

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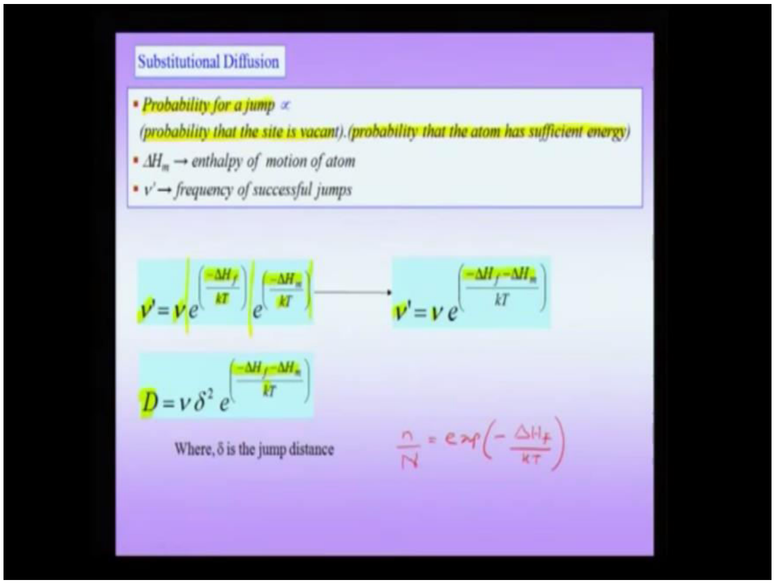

Substitutional Diffusion

- *Probability for a jump* $\propto$ *(probability that the site is vacant).(probability that the atom has sufficient energy)*
- $\Delta H_m \rightarrow$ *enthalpy of motion of atom*
- $\nu' \rightarrow$ *frequency of successful jumps*

$$\nu' = \nu e^{\left(\frac{-\Delta H_f}{kT}\right)} e^{\left(\frac{-\Delta H_m}{kT}\right)} \longrightarrow \nu' = \nu e^{\left(\frac{-\Delta H_f - \Delta H_m}{kT}\right)}$$

$$D = \nu \delta^2 e^{\left(\frac{-\Delta H_f - \Delta H_m}{kT}\right)}$$

Where, δ is the jump distance

$$\frac{n}{N} = \exp\left(-\frac{\Delta H_f}{kT}\right)$$

Now on the other hand, suppose I am talking about an substitutional atom not only I have to worry about the number of these successful jumps cost by this thermal vibration, but additionally

I have to worry about the fact that is there an neighboring site which is vacant. So, therefore the probability of the jump is not only proportional to the probability that atom has sufficient energy to jump to the neighboring site. The vibrations, but additionally if the there is a chance that the neighboring site is actually vacant.

Therefore, when I am talking about the number of successful frequency jumps as compared to the total frequency. Then, I would note that there is a term which is based on delta H m by k T and this delta H m by k T term is very similar to that what we encountered for the case of the interstitial diffusion, but in this case additional to this term which is coming from fact that the atoms are vibrating and they want to jump.

We have to note that the neighboring side is only vacant is the probability is given by exponential minus delta H m by k T, which we have encountered before in other words. If there are total number of a atomic sides is n capital N the number of sites, which are vacant is small n. Then, this is given by exponential minus delta H f by k T, where delta H f is the enthalpy of formation of an vacancy.

So, higher the enthalpy of formation of a vacancy the lower with the vacancy concentration lower will be the chance of a successful jump. That implies that lower will be the diffusion rate therefore, now when I am talking about interstitial diffusion I have 2 terms which are going to play an important role. The one which is based on the vacancy concentration and the one which is based on the usual enthalpy of migration therefore nu prime can be written as nu exponential minus delta H f minus delta H m. That is minus of delta H f p delta H m by k T, and this is quantity using a small derivation which I am not showing here can be related to the diffusivity in other words the diffusivity of a species is a substitutional species is directly proportional to the exponential of the delta H f plus delta H m by k T.

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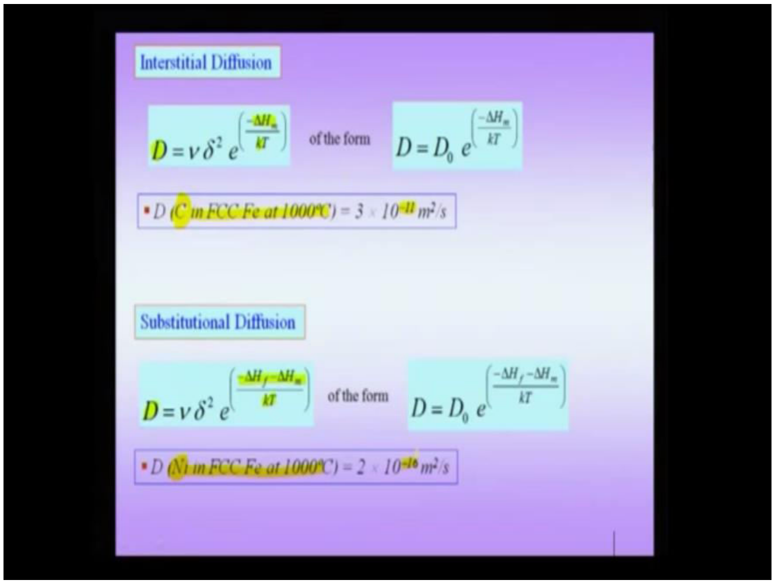

Interstitial Diffusion

$D = \nu \delta^2 e^{\left(\frac{-\Delta H_m}{kT}\right)}$ of the form $D = D_0\, e^{\left(\frac{-\Delta H_m}{kT}\right)}$

- D (C in FCC Fe at 1000°C) = 3 × 10^{-11} m²/s

Substitutional Diffusion

$D = \nu \delta^2 e^{\left(\frac{-\Delta H_f - \Delta H_m}{kT}\right)}$ of the form $D = D_0\, e^{\left(\frac{-\Delta H_f - \Delta H_m}{kT}\right)}$

- D (Ni in FCC Fe at 1000°C) = 2 × 10^{-16} m²/s

Therefore, now since if you look at the case of the interstitial diffusion. The term opposing the diffusion is delta H m, but in this case, there is a additional term opposing your diffusion which is delta H f. In this case the delta is the jump distance. Now, this additional term in the exponential plays an important role in determining the diffusivity and finally, of course the diffusion rate at a given temperature.

Now, suppose I am comparing for instance the diffusivity of carbon in F C C ion at say 1000 degree Celsius visa v nickel in F C C ion at 1000 degree Celsius carbon sit. In the interstitial nickel is a substitutional alloying element and sits in the lattice site. Now, I am comparing the diffusivity the first case the diffusivity d is proportional to exponential minus delta H m by k T. The second case, the diffusivity is proportional to minus delta H f minus delta h m by k T and now, therefore if I compute using known values from literature.

I find that the diffusivity for carbon in ion at 1000 degree Celsius comes out to be of the order of above 10 power minus 11 meter square per second. On the other hand, if I compare it with the nickel diffusivity using data from literature then I notice that the diffusivity comes to order of 10 power minus 16 meter square per second in other word carbon would diffuse a few orders of magnitude faster since a diffusivity is higher. It will diffuse much faster compare to nickel at a given same temperature given the medium is same that means it is ion at 1000 degree Celsius and both ions are at F C C form.

Therefore, the medium is same only the diffusing species either in the first case happens to be carbon sitting in the interstitial side. In the second case its nickel sitting in the substitutional side. I can see that the diffusivity changes orders of magnitude this implies that the diffusion rate also for ion nickel in ion will be much smaller. This is why you are trying to homogenized an alloy for instance.

Suppose, you made a casting and alloy turns out to be in homogenous. You want to homogenize, it the homogenizing hold has to be much longer time as compare to for instance. Suppose you are doing an carbonization experimenting which case carbon is diffusing from the surface. So, we will actually do a computation to find out how much typically takes time it takes for instance to carbon to be carbonized on the surface known of the coming slides.

So, to summarize this slide the diffusivity of an interstitial species is typically much higher and therefore, if you want to diffuse an interstitial species then you have to carry out the diffusion nahle for a smaller time so far what we talked about was what is called lattice diffusion. That means the species is diffusing through the lattice it is known diffusing through any of the defects in the crystal and typically, if you know that if there are defects present in the crystal that means we are not talking about the perfect single crystal, but we are and even in the perfect single crystal we do tolerate vacancies.

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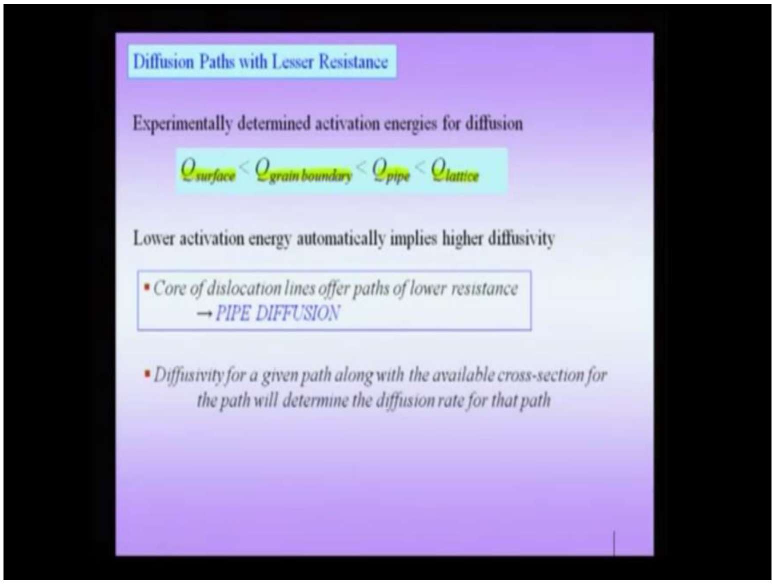

Diffusion Paths with Lesser Resistance

Experimentally determined activation energies for diffusion

$$Q_{surface} < Q_{grain\ boundary} < Q_{pipe} < Q_{lattice}$$

Lower activation energy automatically implies higher diffusivity

- *Core of dislocation lines offer paths of lower resistance*
  → PIPE DIFFUSION

- *Diffusivity for a given path along with the available cross-section for the path will determine the diffusion rate for that path*

We are talking about other presence of other defects and these defects of course one of them is inevitable which is the surface, second could be a green boundary like an a polycrystalline material or there could be dislocations which leads to something known as the pipe diffusion. So, if you experimentally observed the activation energy then you notice that the surface has the lowest activation energy for diffusion the green boundary has slightly higher energy.

The pipe has given slightly higher energy, but the lattice diffusion cost the maximum activation energy that means suppose I have some short circuit path for diffusion like the green boundary the dislocation core and typically dislocation core of edge dislocations or the surface. There is a free surface available.

Then, these short circuit paths will play a very important role in diffusion for instance. Suppose, I had a precipitate 2 precipitate. Let me consider, this scenario and this actually has been experiment has been done. I had a larger precipitate and the smaller precipitate. Now, we know that this if cold a system at a higher temperature then because of the Gibbs Thompson effect followed by diffusion this smaller precipitate has to be shrike and this larger precipitate has to grow, which is called the precipitate coarsening effect for this.

The mass transport has to take place across from here to here in the absence of any defects. This mass transport would take place for instance via the lattice, but suppose I am able to consider that for some reason this is a plastically evolved specimen and there is actually a dislocation which connects the 2 precipitates. Then, and this is an actual experiment has been carried out then what you would find that this is short circuit path connecting the 2 precipitates and mass transport can actually take place from this precipitate to the other leading to shrinking of this precipitates and may be growing of this precipitate.

So, if you talking about a coarsening experiment then you can notice that this kind of a short circuit path. Actually, gives you an enhanced diffusivity, but a point to be noted that it is not nearly the diffusivity or the activation energy giving rise to a lower diffusivity which matters, but diffusivity for given path along with the available cross section will determine the diffusion rate of that path. That means even though I may have a higher diffusivity for instance dislocation core or a green boundary as compared to the lattice diffusion, but the problem is that the amount of the dislocation density.

The cross section area available through the dislocation is much smaller compared to the lattice. Therefore, the overall diffusivity may be dominated by the lattice at high temperatures, but suppose I go down to low temperatures wherein the activation energy for diffusion through a lattice becomes prohibitive. Then, in these cases the other what might call the short circuit path for diffusion become more prominent and we will take up an example. In this slide suppose, I am comparing the diffusivity of self diffusion of silver in a single crystal versus poly crystal, so now this is silver diffusing into silver and I have 2 specimens one is a single crystal another is a poly crystal.

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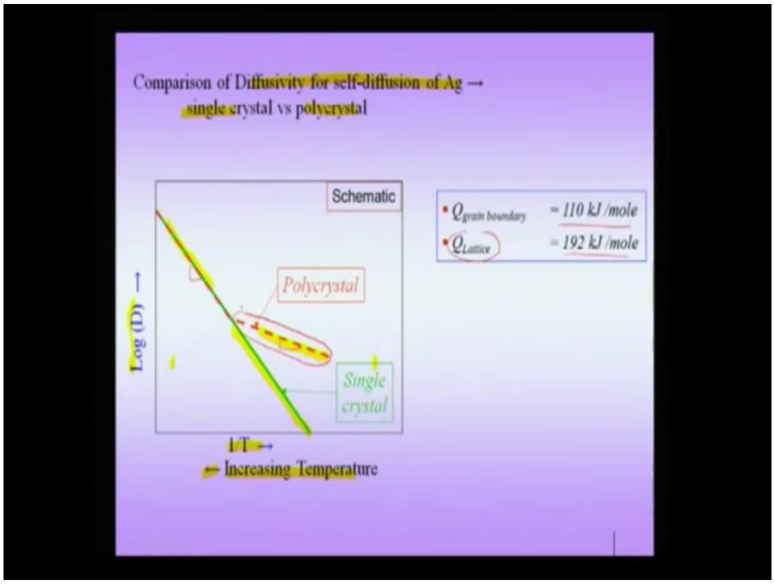

Comparison of Diffusivity for self-diffusion of Ag →
single crystal vs polycrystal

- $Q_{grain\ boundary}$ = 110 kJ /mole
- $Q_{Lattice}$ = 192 kJ /mole

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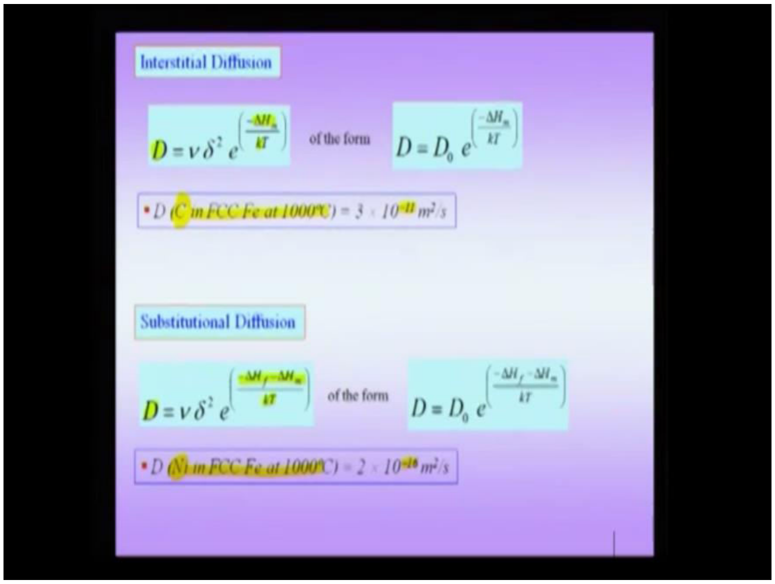

Interstitial Diffusion

$D = \nu \delta^2 e^{\left(\frac{-\Delta H_m}{kT}\right)}$ of the form $D = D_0\, e^{\left(\frac{-\Delta H_m}{kT}\right)}$

- D (C in FCC Fe at 1000°C) = 3×10^{-11} m²/s

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$D = \nu \delta^2 e^{\left(\frac{-\Delta H_f - \Delta H_m}{kT}\right)}$ of the form $D = D_0\, e^{\left(\frac{-\Delta H_f - \Delta H_m}{kT}\right)}$

- D (Ni in FCC Fe at 1000°C) = 2×10^{-16} m²/s

Now, I plot log of diffusivity versus 1 by temperature and the reason for doing so is because we know that the diffusivity depends exponentially on 1 by T. So, a log of one by T versus diffusivity log d plot should give a straight line. Now, suppose I see do the experiment on a straight line I find that this green curve is the curve corresponding to the single crystal diffusivity log of the single crystal diffusivity.

The access is such that since that one by t is increasing at right hand side the access of increasing temperature is towards the left. So, these are high temperatures here and these are low temperature on the right hand side. So, you notice that there is a straight line especially at high temperatures, but if you come to low temperatures, you notice that you will actually see that there is a branch of diffusivity comes out like this. That means the slope of the curve changes and this slope here in the high temperature regime corresponds to diffusion through the lattice.

While this slope on the right hand side corresponds to green boundary diffusion, the reason that green boundary diffusion plays a prominent role at low temperature is because the lattice diffusivity q for lattice. Say, for about say 200 Kilo Joule per mole and that of the green boundary is approximately half of that, it means at low temperatures there is not sufficient activation energy available for a silver atoms to jump from one side to the other.

Therefore, it will try to look out for a short circuit path a low activation energy path which is now the green boundary path and that path should dominate at low temperatures. Therefore, the slope of the log diffusivity versus 1 by temperature changes. So, this is an important experiment which shows that at high temperatures even though the for instance.

The green boundary assuming that the green boundary area available cross sectional area available is the same for diffusivity, but that does not dominate the diffusion because the lattice diffusion is dominates in spite of the higher activation energy, but when at low temperatures. The system does not have sufficient activation energy to drive diffusion to the lattice.

Then, these other mechanisms takes over and they can play an important role in for instance as the example we consider coarsening of a precipitate or as we can see in a poly crystal. The green boundary diffusion driving the motion of atoms sow have seen that not only that we have to consider normal diffusion in a crystal, but we also have to worry about additional path for diffusion which can play a very important role in the diffusion of a species.

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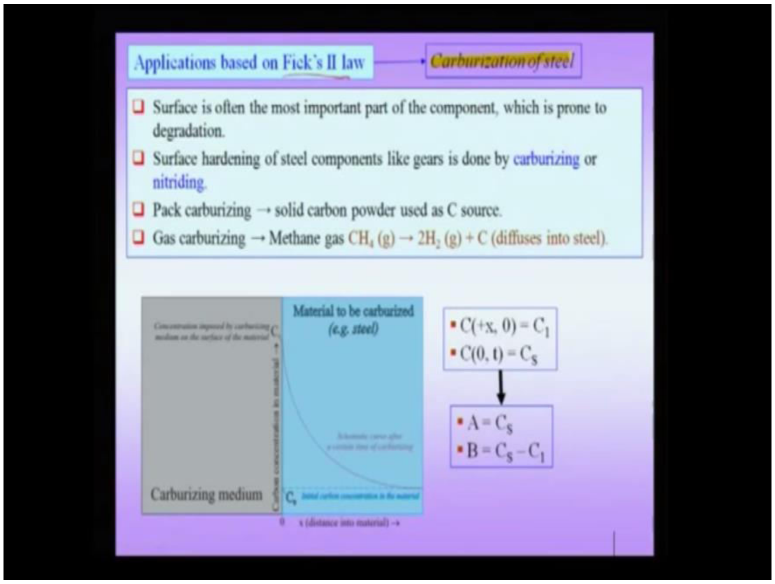

Applications based on Fick's II law → *Carburization of steel*

- ❑ Surface is often the most important part of the component, which is prone to degradation.
- ❑ Surface hardening of steel components like gears is done by carburizing or nitriding.
- ❑ Pack carburizing → solid carbon powder used as C source.
- ❑ Gas carburizing → Methane gas $CH_4\ (g) \rightarrow 2H_2\ (g) + C$ (diffuses into steel).

- $C(+x, 0) = C_1$
- $C(0, t) = C_S$

↓

- $A = C_S$
- $B = C_S - C_1$

Next, we consider an important application of the fixed second law which is the carburizing of steel. Now, in carburizing of steel, we start with the specimen which has an initial carbon concentrations for instance C 0 typically that means we talk about a small carbon concentration and as we shall solve in the next example.

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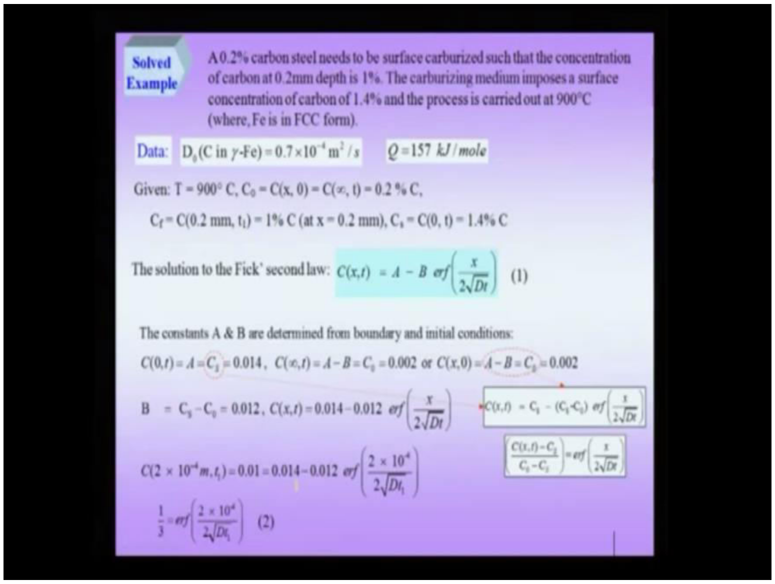

Solved Example A 0.2% carbon steel needs to be surface carburized such that the concentration of carbon at 0.2mm depth is 1%. The carburizing medium imposes a surface concentration of carbon of 1.4% and the process is carried out at 900°C (where, Fe is in FCC form).

Data: $D_0(\text{C in } \gamma\text{-Fe}) = 0.7 \times 10^{-4}\ m^2/s$ $Q = 157\ kJ/mole$

Given: $T = 900°\ C$, $C_0 = C(x, 0) = C(\infty, t) = 0.2\ \%\ C$,

$C_f = C(0.2\ mm, t_1) = 1\%\ C$ (at $x = 0.2$ mm), $C_s = C(0, t) = 1.4\%\ C$

The solution to the Fick' second law: $C(x,t) = A - B\ erf\left(\dfrac{x}{2\sqrt{Dt}}\right)$ (1)

The constants A & B are determined from boundary and initial conditions:

$$C(0,t) = A = C_s = 0.014,\ C(\infty,t) = A - B = C_s = 0.002 \text{ or } C(x,0) = A - B = C_s = 0.002$$

$$B = C_s - C_0 = 0.012,\ C(x,t) = 0.014 - 0.012\ erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

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

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

$$C(2 \times 10^{-4} m, t_1) = 0.01 = 0.014 - 0.012\ erf\left(\frac{2 \times 10^{-4}}{2\sqrt{Dt_1}}\right)$$

$$\frac{1}{3} = erf\left(\frac{2 \times 10^{-4}}{2\sqrt{Dt_1}}\right) \quad (2)$$

This carbon concentration above .2 percent but then we want to introduce more carbon in the surface and the reason for doing, so is that you would like an internal toughness in the material along with the surface hardness. The whole process takes place like this. I take a material, which say .2 percent carbon, I expose it to a carburizing atmosphere which could be gaseous or solid and after carburizing for a certain time. I would note that the surface carbon concentration would be increased and the next example considered for instance.

The surface carbon concentration could go up to for instance 1 percent, ok? So, we increase the surface carbon concentration. Then, we take the material out of that bath and slowly cool it and later on we take this whole material heat to high temperature and quench it. In the process of quenching the surface the material becomes since the hardness of the depends on the amount of carbon present.

Now, there is a surface carbon concentration which is higher compared to the bulk. Therefore, I would notice that the surface hardness would increase now. There is a subtle point involved in this understanding for instance I would do this kind of a process with a component like a gear wheel. So, I want a gear wheel which is tough on the interior and on the surface.

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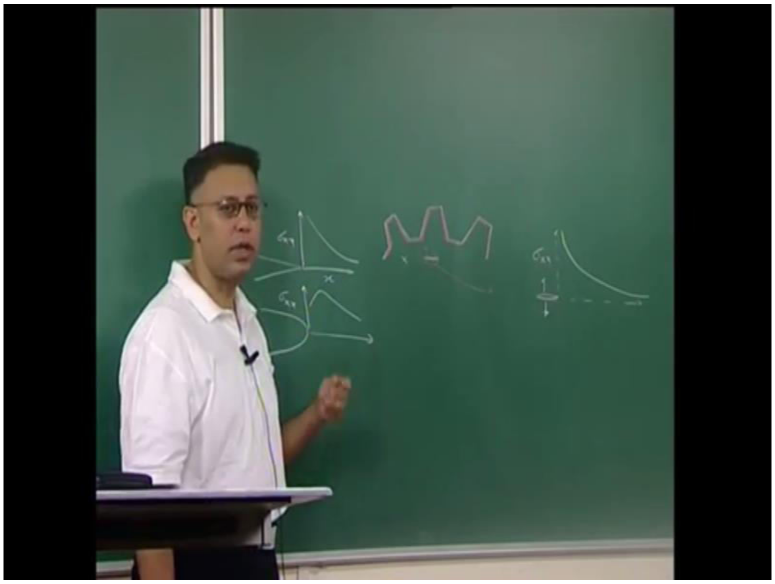

It is hard, now suppose I had taken a high carbon steel for instance like I already took a 1.1 percent carbon steel and did this entire process of hardening. Then, though I would get a very hard material, uniformly hard such a material would tend to be brittle, but a subtle point which is often not emphasized. In this context, is the fact that suppose I have a gear component gear wheel here and it has got the gear tooth.

So, I am drawing a small section of that and, so forth, so what I do is that I build up a high surface concentration of carbon here and this material after quenching becomes hard on the surface the internal hardness is also increase, but not as much as that on the surface because the hardness of the side depends on the carbon concentration. Now, as I pointed out I want a tough interior, I want a material inside to be tough. Now. if you take even usually, so called a brittle material and we know, the toughness is the measure of the energy absorb either in a tensile test or in a impact test before fracture.

So, it is an energy absorb which means, it is an area below the stress strain diagram. Now, even if when you are talking about a brittle material, a brittle material typically will at least give you a small elongation for instance intension of say 1 percent. If you notice that the kind of dimensional tolerances a gear will need to have is extremely precise because this would be mixing with another gear component somewhere else. Therefore, even this one percent ductility is way beyond what you would normally tolerate in service.

Therefore, why is that? I am talking about toughness in the interior well this component is never going to face that kind of a deformation. The reason is that this toughness helps in what you may call damage tolerance of fracture toughness. Suppose, in the interior somewhere here because of manufacturing processes. There is a crack, there is a crack and as you know, a crack is nothing but a stress amplifier.

So, suppose I am having a far field stress which is like this. So, this is my crack here in the material and I am having a far field stress which being employed somewhere of this value close to the crack tip the stress, say for instance I am talking about a crack opening mode stress sigma x. This crack opening mode stress will have a higher value and therefore even though the far field stresses are small. The stress present say, for instance far away from the flaw close to the flaw which is I am located here this is my crack here these stresses gets amplified here at the crack tip this implies that, if the material is brittle and the crack tip is sharp then the material tends to fail, but suppose this material is ductile then I will blow up my crack tip here.

So, originally the crack tip was for instance sharp, then in the presence of this ductile material the crack tip will get blunted and if you plot the stress for a sharp crack it goes like this that means it tends to blow up close to the crack tip, but suppose I am talking about a ductile material whose crack tip has been blunted in that case. You would notice that the stress field goes through a maxima and then comes down that means that you do not have that kind of a singularity at the crack tip and for this kind of a blunting. You may require large percentage ductility in the material though I am talking about a very low gross plastic deformation at the large scale. That means large lot of ductility is not required at the overall specimen level because the tolerance with which gear component with the other gear component would be very high.

Therefore, that kind of a plastic deformation is not tolerable and it is not required, but at the crack tip I need this kind of a, what you might call a plasticity. So, that the crack tip can be blunted and the material can be tough and for this high toughness and high plastic deformation and high ductility.

I need a material in the interior, which is a low carbon concentration and which can have this kind of a ductility. On the other hand, on the surface which is messing with another component where there is a chance of high aberration and there is a chance of you know, touching with other components. We need certain hardness and that is why I would like to maintain my surface at a higher hardness and this is achieved by introducing high carbon on the concentration of the surface.

Finally, quenching it to produce as to micro structure which has now this component, which is having a high surface hardness in his a decreasing hardness into the interior can be thought of as in what you might call a functionally graded material and what you may call a primitive or a original example of a functionally graded material, ok? So, to summarize the things we have talked so far.

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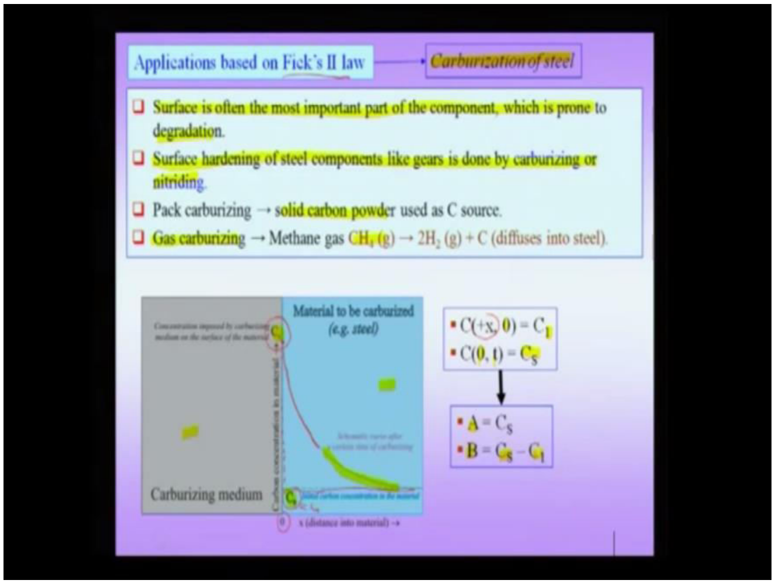

Applications based on Fick's II law → *Carburization of steel*

- ☐ Surface is often the most important part of the component, which is prone to degradation.
- ☐ Surface hardening of steel components like gears is done by carburizing or nitriding.
- ☐ Pack carburizing → solid carbon powder used as C source.
- ☐ Gas carburizing → Methane gas $CH_4 (g) \rightarrow 2H_2 (g) + C$ (diffuses into steel).

- $C(+x, 0) = C_1$
- $C(0, t) = C_s$

↓

- $A = C_s$
- $B = C_s - C_1$

The surface hardness is surface the most important part of the component, which is prone to degradation surface hardening of steel components like gears is done by carburizing or nit riding. In the current example, we take up carburizing and this carburizing can be achieved using solid sources carbon sources or even can be achieved in the gas medium, where in for instance you can take the methane gas and produce carbon which diffuses in to the steel.

So, essentially you have during the carburization process during which you are actually introducing carbon into the material. So, the blue part on the right hand side in the diagram is the material the gray part is the carburizing medium which is imposing a surface concentration on this material as C s. It is important to note that this C Sis not the carbon concentration in the carburizing medium. It is the carbon concentration, which is an equilibrium with the surface of the steel.

So, therefore this line for instance cannot be extrapolated to the left for instance. I cannot draw this line to the left this is only at the surface. This C Sis the concentration of carbon in equilibrium metal which is imposed on the surface and for now we will assume that carbon concentration C S remains a constant. So, that is a constant as imposed by the carburizing medium. Now, since we start with the material the which is shown in blue with initial carbon concentration C 0 like for instance in the example to be considered in the next slide. This carbon concentration could be about .2 percent carbon, ok?

Now, as we initially the carbon concentration profile would be that the surface would have a concentration C S the interior would have a concentration C 0. It will be a some kind of a profile which is like this which falls of the C Son throughout the service. Then, suddenly it falls to C 0, but as you hold this material for longer and longer time in this carburizing atmosphere. The steel then you would notice that the carbon would diffuse into the material and a carbon concentration profile would develop as shown in this curve.

So, this curve it how the carbon concentration profile would develop after a certain time. Therefore, if I want to write down my initial and boundary conditions and I want to compute what you might call the constant. The fix second law solution to the error function solution to the fixed second law which we encountered before here. So, we encountered this fix equation to the fixed second law here. Right here, which says that C x t is a minus b error function of x y 2 root d t. So, in this if I want to determine the a and b. I need to know, my initial and boundary conditions which I am going to substitute for now and get the constants.

Now, C at any positive x at time 0 is C 0, of course this is wrongly written as C 1, but you can also call I will just define the C 0 also equal to C 1 for simplicity. So, therefore that is the concentration which is present in the material before I started my carburization experiment and that is true for any positive x in the material because this is my original 0. Now, on the surface at time t equal to 0, ok. We notice that C x equal to 0 at any time because at any however long you wait the surface carbon concentration remains constant which is C s.

Therefore, using these conditions and substituting in the error function solution. I notice that a is equal to C Sand b equal to C S minus C 0 or C S minus C 1, I can get these constants now. Let us consider an actual example, solved example to understand this carburization process in other words I ask myself this question how long do I have to wait? or how long do I have to do a carburization experiment to build up a certain carburization? Carbon concentration to a certain depth in the material.

So, for instance in this example, suppose I am starting with the .2 percent carbon steel and I want to surface carburize this such that the concentration at a depth of about .2 mm which is a small depth is about 1 percent. So, I build up a high concentration about one percent to depth of .2 mm. If you look at a depth below .2 mm closer to the surface then the concentration will be higher at whatever the time may be and beyond that the concentration will be lower and as we already seen. When we talked about in the nature of the error function solution there will be a certain depth at every time beyond which the carbon has not penetrated and you will find that the carbon concentration is the original carbon concentration of .2 percent.

So, the carburizing medium imposes a surface concentration of carbon about 1.4 percent which is the C S as you saw in the previous slide this is my C Sand this is .2 percent is my C 0 or c one as I called it and the desired final product I want is at a depth of .2 mm I want a carbon concentration of one percent. So, the process we carry out at high temperature and the temperature we carry out is at 900 degree Celsius and the reason for carrying out this process at 900 degree Celsius is primarily because of the fact that the solubility of carbon in gamma end is much larger compared to the solubility of carbon in alpha end and at 900 degree Celsius.

I understand the gamma form the F C C form that implies. I can actually put in this larger amount of carbon. I am talking, if I try put this high percentage of carbon say, 1 percent of carbon or 1.4 percent of carbon in the surface diffuse inside in b c c ion. It will tend to precipitate out as a phi c 3 and therefore, it will not be present in the form of a solid solution and I need to retain it in the solid solution form because only then can, when I quench it from high temperatures, I would get a what you might call a structure.

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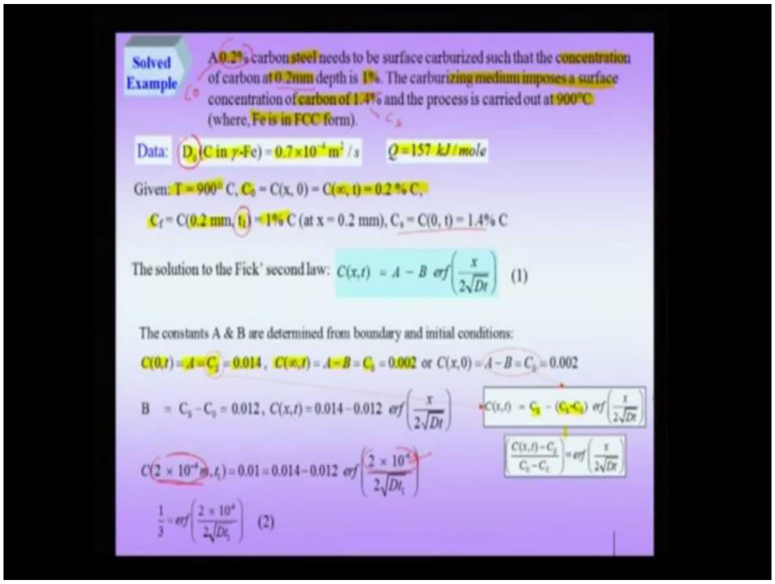

Solved Example

A 0.2% carbon steel needs to be surface carburized such that the concentration of carbon at 0.2mm depth is 1%. The carburizing medium imposes a surface concentration of carbon of 1.4% and the process is carried out at 900°C (where, Fe is in FCC form).

C_0 C_s

Data: D_0 (C in γ-Fe) $= 0.7\times10^{-4}\ m^2/s$ $Q = 157\ kJ/mole$

Given: $T = 900^0$ C, $C_0 = C(x, 0) = C(\infty, t) = 0.2\%$ C,

$C_f = C(0.2\ mm, t_1) = 1\%$ C (at x = 0.2 mm), $C_s = C(0, t) = 1.4\%$ C

The solution to the Fick' second law: $C(x,t) = A - B\ erf\left(\frac{x}{2\sqrt{Dt}}\right)$ (1)

The constants A & B are determined from boundary and initial conditions:

$C(0,t) = A = C_s = 0.014$, $C(\infty,t) = A - B = C_0 = 0.002$ or $C(x,0) = A - B = C_0 = 0.002$

$B = C_s - C_0 = 0.012$, $C(x,t) = 0.014 - 0.012\ erf\left(\frac{x}{2\sqrt{Dt}}\right)$

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

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

$C(2\times10^{-4} m, t_1) = 0.01 = 0.014 - 0.012\ erf\left(\frac{2\times10^{-4}}{2\sqrt{Dt_1}}\right)$

$\frac{1}{3} = erf\left(\frac{2\times10^{-4}}{2\sqrt{Dt_1}}\right)$ (2)

Therefore, I need to carry out this primary this process at above 900 degree Celsius, so that I can diffuse that carbon into gamma n, which is the high solubility for carbon, of course doing it in high temperature gives you a faster kinetics because now we know that the diffusivity is exponentially depended on the temperature. So, the data we have to need is that what is the diffusivity D 0. That diffusion constant D 0 in the equation D equal to D 0 exponential minus q by r t and D 0 for carbon in gamma end is about .7 into10power minus 4 meter square per second the activation energy for diffusion in carbon in F C C ion is 156 Kilo Joule per mole.

We are working at 900 degree Celsius the C 0 is C x at time 0 or equivalently. It is at any time at infinite distance because infinite really does not mean, infinite means that the distance beyond which there is no penetration is .2 percent. So, this is a concentration of material carbon in the original material. Now, what we want is the c final which is about at .2 mm. We want a carbon concentration of 1 percent and we want to know, how long do I have to wait for this? How long do I need to carry out my carbon carburizing experiment? So that I can get a 1 percent carbon concentration of the surface.

We already also given that C S which is C 0 t is also one point 4 percent so the solution to fix second law we know c x t is a minus b error functional x by 2 root d t the constants I determine from initial conditions and boundary conditions are C 0 t that means that is C S and that is equal to a and that happens to be .014 because this 1.4 percent has to be written in fraction in terms and C infinity, t is C 0 as we saw here before and which happens to be .2 percent, which is equal to a minus b because now suppose in the error function. I substitute x equal to infinity then I get the error functional value of 1.

So, a minus b C 0 is .02, so giving the boundary conditions and the initial conditions. I determine that C 0 is a minus b and C S is a and I can substitute back into the fix equation that C x t is equal to C, which is a now minus C S minus C 0 which is b error function of x by 2 root D t, which I can further write down as the equation below which is C x t which is the concentration profile. I want to know, minus C S divided by C 0 minus C S is the error function of x by 2 root D t.

So, since we have the values of C S and C 0. I can write down the equation as C x t equal to .014 minus .012 error function of x by 2 root D t and I want to now determine. I know, the x at which I want to know, the carbon concentration and that x happens to be .2 mm which is 2 into10 power 4 minus meters is equal to the right hand side as before .01 which is equal to .014 minus .012 error function of this x, which is now the same as this x substituted here. ok? by 2 root D t 1. I am now labeling this t s t 1 because that is the time I want to know.

I have to wait. I have to do this heat treatment at 900 degree Celsius so that I build a carbon concentration of one percent at a distance of .2 milli meter. So, simplifying this I can find this one third is error function of 2 into10 power minus 4 divided by this error function of 2 into10 power minus 4 divided by 2 root D t 1. So, now I need to know, the diffusivity at 900 degree Celsius for carbon in gamma n given the fact that my D 0 value has been given here to be .7 into10 power minus 4 meter square per second.

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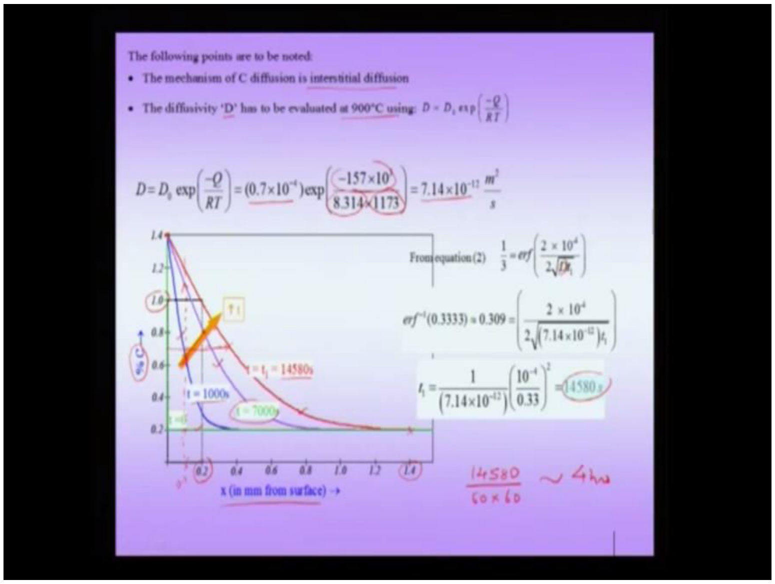

The following points are to be noted:

- The mechanism of C diffusion is interstitial diffusion
- The diffusivity 'D' has to be evaluated at 900°C using: $D = D_0 \exp\left(\frac{-Q}{RT}\right)$

$$D = D_0 \exp\left(\frac{-Q}{RT}\right) = (0.7\times10^{-4})\exp\left(\frac{-157\times10^3}{8.314\times1173}\right) = 7.14\times10^{-12}\ \frac{m^2}{s}$$

From equation (2) $\frac{1}{3} = erf\left(\frac{2\times10^{-4}}{2\sqrt{Dt_1}}\right)$

$$erf^{-1}(0.3333) = 0.309 = \left(\frac{2\times10^{-4}}{2\sqrt{(7.14\times10^{-12})t_1}}\right)$$

$$t_1 = \frac{1}{(7.14\times10^{-12})}\left(\frac{10^{-4}}{0.33}\right)^2 = 14580\ s$$

$\frac{14580}{60\times60} \sim 4\ hrs$

So, to summarize some important points which we have used so far, the mechanism is interstitial mechanism which is diffusion of carbon in gamma end and the diffusivity D has to be evaluated at 900 degrees using the expression D equal to D 0 exponential minus Q by R T. So, of course we are using R T because we are talking about a mole of material instead of a single R T D equal to D 0 exponential minus Q by R T that is equal to D 0 value is given to us and the activation energy as we saw in the data before is 157 kilo joule per mole. I substitute that minus 157 here and this10 power 3 because it is kilo joule per mole. I substitute the value of the gas constant and the temperature now in Kelvin the diffusivity to be 7.14 into10 power minus 12 meter per square per second.

Now, I have to substitute this value of diffusivity at 900 degree Celsius into equation which I call the equation 2 here, which is the simplified form of the solution written here. I take this and substitute this into for D into this equation which now reads that one third is equal to error function of this diffusivity 7.14 into10 power minus 12. Now, if I take the error function on the other side the error, the error in function inverse of .3333 is about 0.309.

So, I get 0.309 is equal to 2 into10 power minus 4 divided by 2 root D t and therefore I can solve for T 1 to be about 1458 0 seconds that means I have to wait approximately for 4 hours. Suppose, I divide this by, so this 14580. I have to divide by 60 minutes into 60 seconds to get it in hours and this is approximately about 4 hours.

So, I have to do this experiment for 4 hours such that I build up a carbon concentration of about 1 percent at a depth of about .2 mile meter. So, this depth which we have carburized is called the case depth in the case of carburizing experiment that means this is the now the case which has higher carbon concentration and if you do a cross sectional optical metallographic. You will see, this region to have a distinct color as compared to the interior of the material.

So, suppose I plot by the way the diffusion profile C x tor the carbon concentration profile C x t varies with time. I would notice initially, of course the surface concentration is 1.4 percent the y axis being carbon concentration and the x axis is the distance from the surface and I would obtain a square function which is at t equal to 0 which is known by this green color. Now, as time progresses, now suppose at I am working at 1000 seconds then I can substitute for 1000 in this error function solution given this diffusivity at 900 degree Celsius. I would get a blue curve as shown here that means that carbon has penetrated into the material, but after a certain depth I would know that say this depth is approximately about .4 mm.

There is practically no carbon and the material has not been affected by this influx in carbon from the surface. Now, suppose I wait for even longer and I wait about 700 seconds then I would notice that the carbon concentration profile is increasing along this orange arrow. Now, I am working on this purple curve means that actually the carbon is penetrating more into the material and not only and if you take a given x for instance.

Suppose, I am working at a given x which is say .1 mm then I would notice that the initially the carbon concentration of .2 percent at time t equal to 0. Then, a certain time later time, so I can draw the distance of point I would notice that the carbon concentration increased to about more than .6 percent at 7000 at about 1000 seconds. Then, at 7000 seconds a carbon concentration would have increased about more than about 1.1 percent, and if I wait still longer then I would get a curve which is shown in the red curve and what I have specifically chosen this red curve. We drawn exactly at the time equal to t 1 wherein my solution lies this solution 1400 and 14580 seconds.

So, the solution lies such that, now I get a red curve for waiting for this amount of time about 4 hours then I would notice that, if I take a depth of about .2 mm from the surface then I plot the carbon concentration profile. It would be exactly about 1 percent of carbon further into the material beyond this .2 mm the carbon concentration dies of and about and but still carbon has penetrated up to about 1.4 mm into the material, but suppose I use a definition of a case depth as being 1 percent carbon.

Then, I would call this that .2 mm is the case depth, suppose I want to use a different dimension of the case depth for instance. Suppose, I use the fact that I want half the surface concentration which is now .7 and then I would use the case depth which comes to be about say .4 mm. So, I can use the definition of case depth based on the kind of criteria for concentration which I want, but you see that the below about .2 mm into the surface the carbon concentration is even higher than 1 percent and reaches about 1.5 percent when you reach the surface, but beyond about 1.4 mm.

The material is the original material start off with about .2 percent carbon which means that it is going to be tough beyond the material will have a tough property or higher toughness beyond about this 1.4 mm. So, these are this is a nice illustrative example wherein we are taking interstitial species which is diffusing into the substrate.

This is, we are doing using in an engineering application to harden the surface and this is involves the concept of phase transformation, which will come to in one of the coming lectures. Wherein we make the surface instead of keeping it in the gamma end form we make it by quenching it and this and we will study more about, how this is obtained? Why is that the is tough etcetera in the coming lectures, but essentially we note that this is an hard phase or a hard produces the microstructure which is very hard and that is what you want as a surface property.

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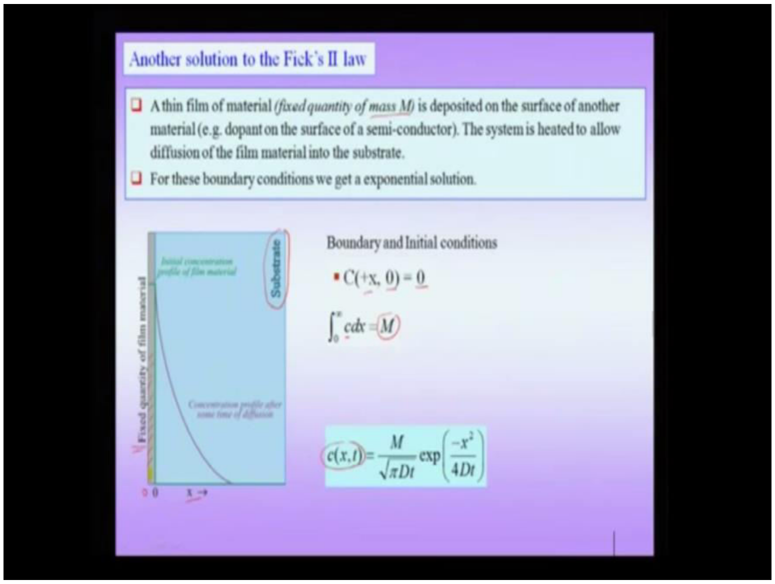

Another solution to the Fick's II law

- ❑ A thin film of material *(fixed quantity of mass M)* is deposited on the surface of another material (e.g. dopant on the surface of a semi-conductor). The system is heated to allow diffusion of the film material into the substrate.
- ❑ For these boundary conditions we get a exponential solution.

Boundary and Initial conditions

- $C(+x, 0) = 0$

$$\int_0^\infty c\,dx = M$$

$$c(x,t) = \frac{M}{\sqrt{\pi D t}} \exp\left(\frac{-x^2}{4Dt}\right)$$

So, this is an nice example of diffusion used in an engineering example. Equivalently you could also talk about an another nice example, which is actually taking for instance diffusion of for instance that do pant into a material. In this case, of course the boundary condition would be slightly different for instance. Suppose, I am talking about a diffusion experiment wherein I am putting in certain a quantity of do pant on the semiconductor for instance. The substrate could be a semi conductor in this example and I am putting a fix quantity of material on the surface which is for instance a p type do pant which is going to diffuse into this substrate for instance, which could be silicon and after putting this fixed quantity of material.

I do a diffusion Nahle; that means I hold this material at higher temperature and this material slowly diffuse into the material, but for this the boundary conditions are different and we can actually obtain a different solution say for instance. Suppose, I am talking about this kind of a system wherein the fix quantity of material which does not change in the system throughout the diffusion process for instance. In the previous example, when carburizing of steel, we note that as carburizing media is held at longer time in contact with the metal or the steel more and more of carbon is getting into the material.

Therefore, we are actually push pumping in more and more of carbon into the material, but here if you notice suppose the p tab material which is put on the surface which is shown gray color.

Here, this p type of material is the fix quantity of material and the overall quantity does not change with time. Therefore, I can actually write down one of the conditions as integral 0 to infinity which means a 0, here to infinity.

So, I can actually place my 0 here, because initially I start with the material which is a thin film of c d x. That is integration with respect to x which is the coordinate is the fix quantity of material m, which had fix quantity of mass M material which has imposed on the surface, but usually of course I notice that at time t equal to 0 at any positive x the concentration of this do pant is 0.

So, that is another condition I can use and for such kind of circumstances instead of using the error function solution. So, this is a different boundary condition problem I use a solution which is an exponential solution. We, I can write down c x t is equal to M by root of pi D t exponential minus x square by 4 D t, that implies that based on the boundary conditions. I have multiple solutions of fix second law and there are nice examples, wherein I can go and use the solution to find out that how say for instance, how much time do I hold? What is the concentration profile into the material, etcetera, and I can design my process parameters taking in account the time of diffusion towards the end of these lectures.

Let us consider one another important thing which is called the approximate formula for depth of penetration, so we will define appropriately what is called depth of penetration and this approximate formula is useful because often we want to quickly calculate.

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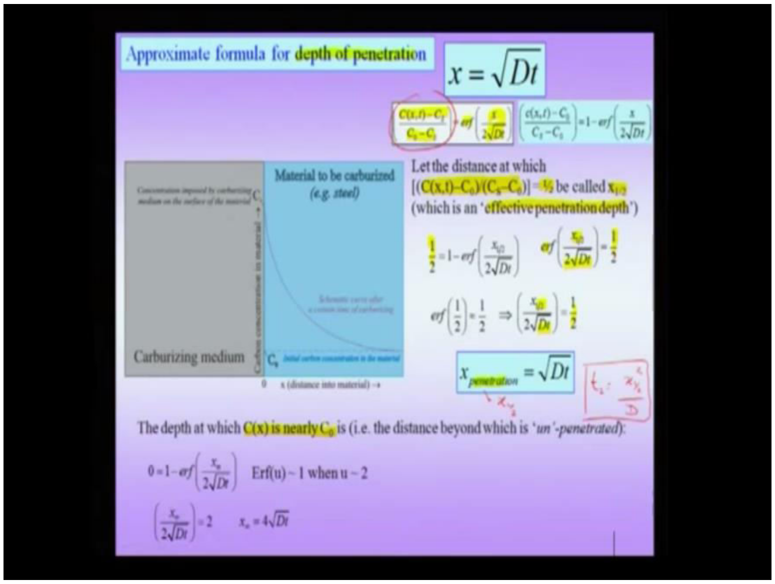

Approximate formula for **depth of penetration**

$$x = \sqrt{Dt}$$

$$\frac{C(x,t)-C_s}{C_0-C_s} = erf\left(\frac{x}{2\sqrt{Dt}}\right) \qquad \left(\frac{c(x,t)-C_0}{C_s-C_0}\right) = 1-erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

Let the distance at which $[(C(x,t)-C_0)/(C_s-C_0)] = ½$ be called $x_{1/2}$ (which is an '**effective penetration depth**')

$$\frac{1}{2} = 1-erf\left(\frac{x_{1/2}}{2\sqrt{Dt}}\right) \qquad erf\left(\frac{x_{1/2}}{2\sqrt{Dt}}\right) = \frac{1}{2}$$

$$erf\left(\frac{1}{2}\right) \approx \frac{1}{2} \Rightarrow \left(\frac{x_{1/2}}{2\sqrt{Dt}}\right) = \frac{1}{2}$$

$$\boxed{x_{penetration} = \sqrt{Dt}}$$

$\to x_{1/2}$

$$\boxed{t_{1/2} = \frac{x_{1/2}^2}{D}}$$

The depth at which C(x) is nearly C_0 is (i.e. the distance beyond which is '*un*'-*penetrated*):

$$0 = 1-erf\left(\frac{x_u}{2\sqrt{Dt}}\right) \qquad Erf(u) \sim 1 \text{ when } u \sim 2$$

$$\left(\frac{x_u}{2\sqrt{Dt}}\right) = 2 \qquad x_u = 4\sqrt{Dt}$$

How long do I have to carry on? And experiment and for instance a diffusion nahle experiment or carburization experiment. So, that I can quickly calculate, how long do I wait for a given concentration? I need to obtain a certain distance, ok. So, let us again work with the example of a carburizing medium and a steel to be carburized and you already noted this solution. There are function solutions given the boundary conditions and the initial condition is C x t minus c x by C 0 minus C S is error function of x by 2 root D t.

Now, let us call the distance at which this ratio the concentration ratio C x c minus C S by C 0 minus C S and, if of course I assume that C S c 0 is actually 0. Then, I can think of this as about half a as the ratio more physically visible but then I assume that this ratio is half and I call the distance at which this is obtained is x half, which I, which I can visualize as an effective depth of penetration.

So, I need to carry on and diffusion experiment such that this concentration ratio turns out to be half and I call that distance to be x half at which it is obtained after certain time t. So, I substitute for the left hand side as half and I write down the error function solution. So, I call since I am calling this x half and I am calling this error function of x half by 2 root D t is equal to half and we noted that for small values of x error function of x is approximately x.

Therefore, I can write down error function of x by x half by 2 root D t is half from this I can see that I can cancel these 2 halves and x half which I call now the depth of penetration. So, this x depth of penetration is x half which based on this concentration ratio is can be approximately written as root of D t that means. If I quickly want to calculate the time, say for instance I have to do an annealing such that say for instance to a depth like in the previous experiment to a depth of about .2 mm. I want to get a concentration which is given as half for this ratio then I need to do an annealing time which will be given the time will be given t to given by x depth of penetration which is x half square by D.

So, using this I can quickly calculate my time to which I need to do my diffusion experiment of course using the same kind of formula. I can also know as I pointed out the depth at which C x is nearly C 0 and this again we noted is because of the nature of the error function solution the way the error function solution works.

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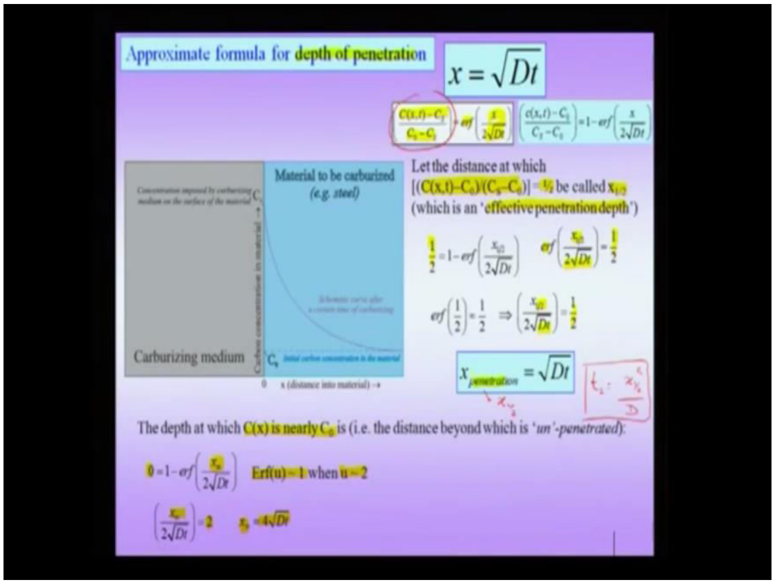

Approximate formula for depth of penetration

$$x = \sqrt{Dt}$$

$$\frac{C(x,t)-C_s}{C_0-C_s} = erf\left(\frac{x}{2\sqrt{Dt}}\right) \qquad \left(\frac{c(x,t)-C_0}{C_s-C_0}\right) = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

Let the distance at which $[(C(x,t)-C_0)/(C_s-C_0)] = ½$ be called $x_{1/2}$ (which is an 'effective penetration depth')

$$\frac{1}{2} = 1 - erf\left(\frac{x_{1/2}}{2\sqrt{Dt}}\right) \qquad erf\left(\frac{x_{1/2}}{2\sqrt{Dt}}\right) = \frac{1}{2}$$

$$erf\left(\frac{1}{2}\right) \approx \frac{1}{2} \Rightarrow \left(\frac{x_{1/2}}{2\sqrt{Dt}}\right) = \frac{1}{2}$$

$$x_{penetration} = \sqrt{Dt}$$

$x_{1/2}$

$t_{1/2} = \frac{x_{1/2}^2}{D}$

The depth at which C(x) is nearly C_0 is (i.e. the distance beyond which is '*un*'-*penetrated*):

$$0 = 1 - erf\left(\frac{x_0}{2\sqrt{Dt}}\right) \qquad Erf(u) \sim 1 \text{ when } u \sim 2$$

$$\left(\frac{x_0}{2\sqrt{Dt}}\right) = 2 \qquad x_0 = 4\sqrt{Dt}$$

We noted that previously that as x tends 2 the error function of solution almost tends to 1. So, the area under the curve beyond about this x equal to 2 is negligible in the error function solution. Therefore, there is a region beyond which practically no material would have penetrated by diffusion. So, therefore I can now write down, I want to know, where the beyond the distance beyond which there is no carbon concentration as what you might call penetrated and that distance I call x infinity.

So, therefore I put 0 is equal to 1 minus error function of x infinity by 2 root D t and error function of u is approximately u 1, when u is equal to 2 we have noted this before therefore x infinity by 2 root D t is 2 and that implies x infinity is about 4 D t. So, if you look at this x infinity versus x penetration you know that this is of the order of D t while this of the order of 4 D t, So, at D t you can think of it approximately that it is the case depth the depth which want your penetration and beyond 4 D t. It is about 4 times as length scale, you notice that there is no penetration.

So, all the scene of diffusion is between the surface and 4 D t and between that important number which is root of D t. So, with this we come to a sort of a brief introduction to diffusion, but we shall note that this diffusion plays a very important role in the coming 2 chapters which one of this happens to be on phase equilibrium that means, if I want a system to be an equilibrium. Then, diffusion plays a very important role to achieve that equilibrium and later on we will talk about phase transformations wherein again many other mechanisms of phase transformation which are called diffusion transformations involves process of diffusion. Therefore, I need to understand the basics of this definition keeping in mind especially the mechanisms involved in diffusion.