Structure of Materials
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Lecture - 30
Chapter-06
Diffusion in Solids

We have been talking about certain aspects of crystals and other structures, where in there is no time element; that means, the structure is given to you with defects and that is what it remains, here we bring in certain kinetic aspects, when we talk about Diffusion of Solids.

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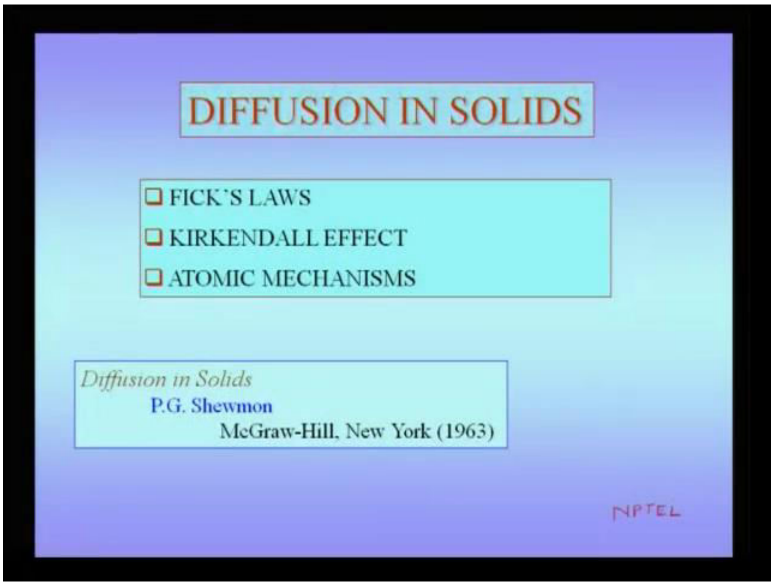

DIFFUSION IN SOLIDS

- ☐ FICK'S LAWS
- ☐ KIRKENDALL EFFECT
- ☐ ATOMIC MECHANISMS

Diffusion in Solids
P.G. Shewmon
McGraw-Hill, New York (1963)

NPTEL

This will be a brief excursion from the usual theme of the lectures, but this is important because, it is important for us to understand that how a material changes it is composition with time. And what are the important implications of these in terms of the sciences and materials and the technological applications.

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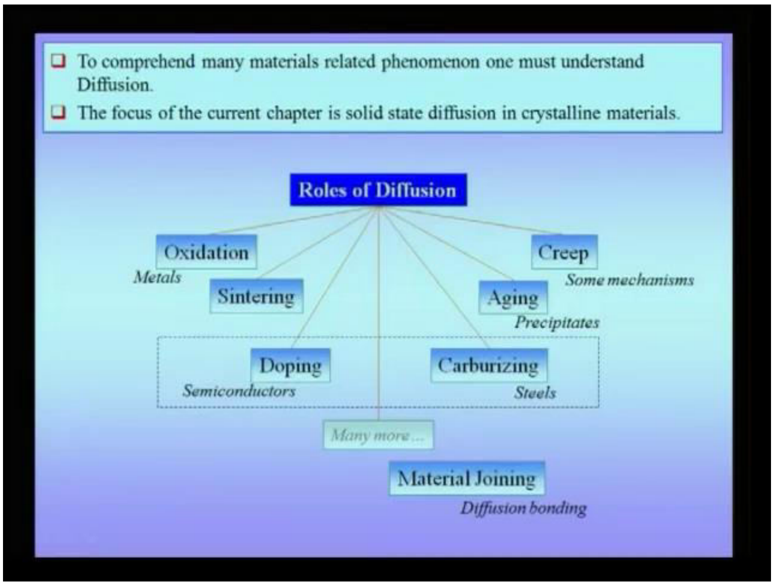

- ❑ To comprehend many materials related phenomenon one must understand Diffusion.
- ❑ The focus of the current chapter is solid state diffusion in crystalline materials.

Roles of Diffusion

Oxidation
Metals
Sintering
Creep
Some mechanisms
Aging
Precipitates
Doping
Semiconductors
Carburizing
Steels
Many more ...
Material Joining
Diffusion bonding

So, in this context we will talk about the fixed laws and certain atomic mechanisms which will, underlie in the diffusion process. The standard text in this area is the one way of mister P G Shewmon and there are other texts also which students may refer to. If you want to understand material science then we cannot ignore the roles of diffusion in material science. And the any materials related phenomenon, one must understand diffusion. And in the current chapter, we focus on solid state diffusion in crystalline materials. So, suppose you are talking about an oxidation process occurring in metals on the surface, you are talking about a pogrom metallurgical process, where in you are trying to start with the powder and you are going to sinter the powder, who make a compact.

You talking about doping of semi conductors, in which case very small quantity of say a p-type do pant is sent into silicon or you are talking about surface hardening of steels using a process known as carburizing or you are talking about how precipitates in a material which have been added to increase the strength of the material age or coarsen with time or you are talking about damage mechanisms of creep which means, that the material has been exposed to high temperatures for longer time.

And the material undergoes deformation is constant load or stress or you are talking about many other materials related phenomenon, then we have to invoke diffusion. So, diffusion is universal and when you are talking about solid state diffusion in crystalline materials, lot of important aspects come into play which students of material science need to understand.

The roles listed here like oxidation of metals, sintering, doping of semiconductors, surface carburizing of steel, aging of precipitates in precipitation hardening system or creep of metals at high temperatures are just a few examples and there are many more important areas in which we have to talk about diffusion. One other example would be, there is a process known as diffusion bonding when 2 materials are joined by using the process of diffusion.

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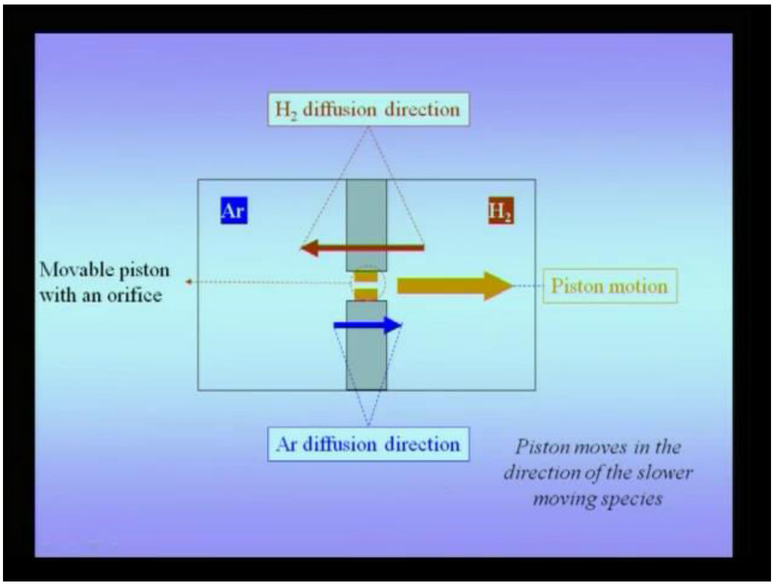

H_2 diffusion direction

Ar

H_2

Movable piston with an orifice

Piston motion

Ar diffusion direction

Piston moves in the direction of the slower moving species

Let us, start with a gaseous example, though we are going to focus only on diffusion in crystalline materials. Suppose, we consider a large chamber which has been split into 2 parts using as hard wall which is shown here in grey color. And a movable piston which is right at the center shown in the orange color, one side of this chamber has a gas like organ, the other side of the chamber has a more lighter gas like hydrogen which can diffuse faster.

Now, what happens is that, when these 2 the connections made between these 2 sides of the chamber, then organ will diffuse from the left to the right and hydrogen will tend to diffuse from the right to the left, but the rate of diffusion of hydrogen will be higher and therefore, the piston which is a movable piston the orange colored piston will move towards, the right and in other words the piston will move towards the slower diffusing, the faster diffusing species in more precise moves to the slower moving species.

And therefore, you will notice that, the volume of the left hand chamber increases on the motion of the piston.

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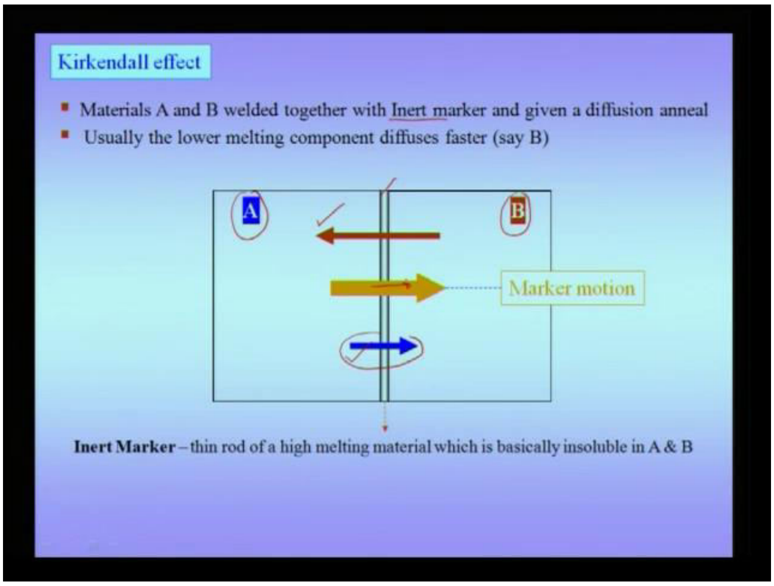

Kirkendall effect

- Materials A and B welded together with Inert marker and given a diffusion anneal
- Usually the lower melting component diffuses faster (say B)

Inert Marker – thin rod of a high melting material which is basically insoluble in A & B

This is an example, which can have a solid state analog and this solid state analog leads to an effect called the kirkendall effect. And analog goes to a chamber with 2 gases, here there are 2 materials A and another material B in contact between the 2 materials like a separator we had in the previous case of a chamber a wall. Here, we have a marker the marker is usually a material, which is considered inert and which will not diffuse either into A or into B in other words the marker remains even after the diffusion experiment has started.

Now what will happen if you heat the system and allow mass transfer. Similar, to the case of the gas flowing from the right to left and left to right we will assume that the gas B has a faster diffusion rate or a motion rate into gas the material B has a faster diffusion rate into material A and the material A has a slower diffusion rate as compared to B into A the A into B is a slower process. Then we would observe that the marker actually, moves towards the right, in other words it moves towards in the direction of the slower moving species.

So, we will notice that after this diffusion experiment has been started, you leave a sufficient amount of time, the marker would have moved to the right. So, to repeat the gist of the experiment this effect in which bi material contact is made with a marker which is essentially inert in both the materials. And we start the diffusion experiment, and typically for this you will heat up the materials. So, that the kinetics becomes faster, and then what you see at the end of the experiment is that the inert marker move towards, moves towards or moves in the direction of the slower moving species.

So, this effect is called the kirkendall effect.

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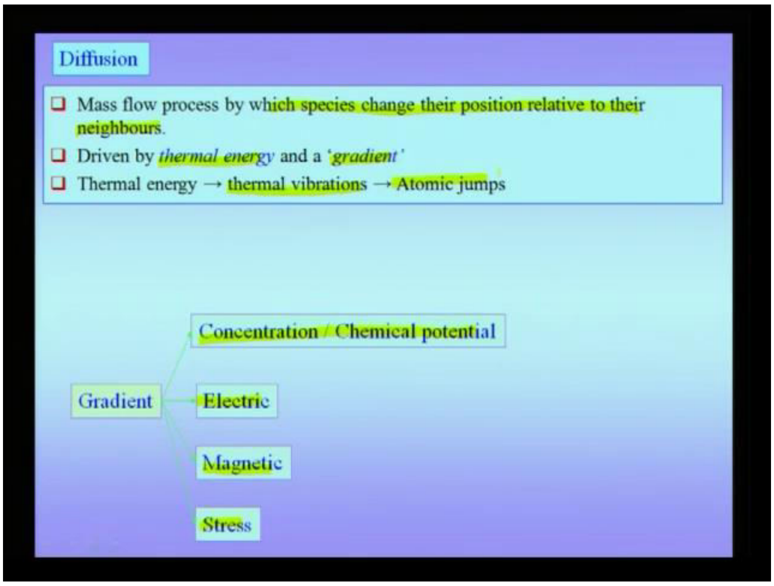

Diffusion

- ☐ Mass flow process by which species change their position relative to their neighbours.
- ☐ Driven by *thermal energy* and a '*gradient*'
- ☐ Thermal energy → thermal vibrations → Atomic jumps

Gradient

- Concentration / Chemical potential
- Electric
- Magnetic
- Stress

Now, we are in a position to in some sense to define what is diffusion and also when would diffuse we ask questions like when would diffusion occur. What are the relevant parameters which control diffusion and what are the underlying mechanisms which will give rise to diffusion. So, a basic definition a simple definition of diffusion would be it is a mass flow process by, which species change their position relative to their neighbors. Suppose, you are talking about flow of water downstream in a river then this is just not called diffusion, this is just for instance simple flow. But, suppose the atomic species in the current context move relative to the neighbors, such a process is called diffusion. And usually, this kind of a diffusion is driven by 2 things very necessary when you are talking about diffusion. One is thermal energy and second thing is a gradient. What kind of gradients can cause the diffusion.

Typically, these gradients could be concentration gradient or a more precisely a chemical potential gradient, it could be a gradient in an electric field, it could be a gradient in a magnetic field or even stress can cause diffusion. But, in the current chapter we will restrict ourselves to diffusion down the concentration gradient noting fully well that actually, at the heart of the driving of downhill a concentration gradient is actually, a chemical potential gradient.

And there are cases where in a species may diffuse up a concentration gradient, but still it is actually, going downhill in chemical potential. So, suppose I am talking about a crystalline material I need a some thermal energy and I need a gradient and this thermal energy, causes, vibrations of atoms in a material. These vibrations ultimately may lead to atomic gems of the atomic level and when all these atomic gems, which are random in the absence of what you might call concentration gradient or any gradient for the matter.

When there is a presence of a concentration gradient, then this species will have a net flowing in one direction and therefore, this leads to diffusion. So, the hearts of all this diffusion are atomic gems which are cost by, thermal energy which needs to thermal vibrations. To summarize this slide, diffusion is a mass flow process by which species change their position with respect to their neighbors. A diffusion process is driven by, a gradient and this gradient could be a chemical potential gradient, an electric magnetic or stress based gradient.

And you need thermal energy and the role of thermal energy is causing atomic vibrations which finally lead to atomic gems. And these random atomic gems in the presence of a gradient actually leads to net flow in one direction.

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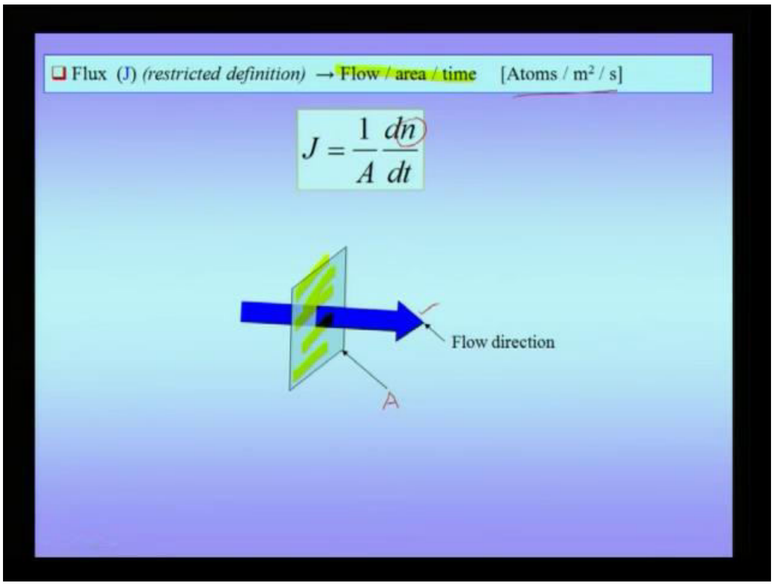

❑ Flux (J) *(restricted definition)* → Flow / area / time [Atoms / m² / s]

$$J = \frac{1}{A}\frac{dn}{dt}$$

So, we start one of the important quantities in diffusion is the flux of the material and flux can be defined as, flow of matter per unit area, per unit time. So, suppose I consider unit area a as in this figure here, and I am talking about flow of matter and this is net flow of matter in a direction shown by this arrow. Then the flux would be this one by area into number of atoms crossing this unit area per unit time. And therefore, the units of flux could be atoms per meter square, per second. And we will use as a basic definition in understanding the various laws and we will also describe laws known as the fixed laws of the diffusion.

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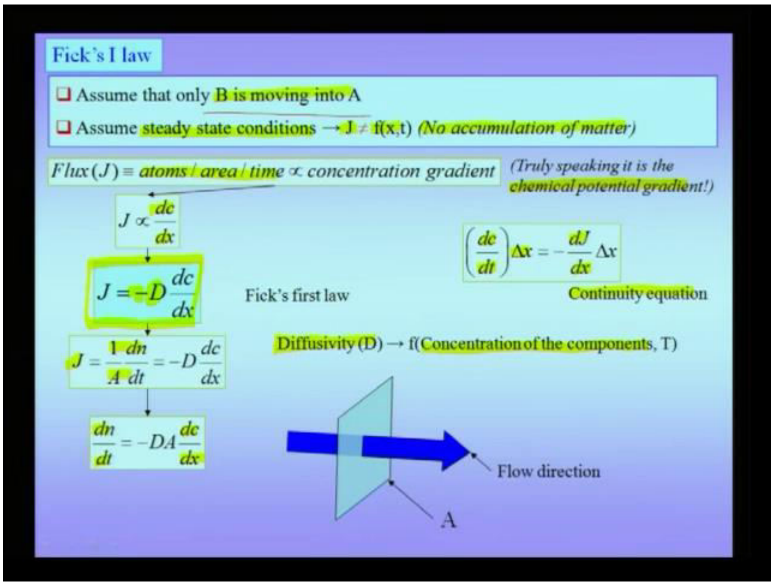

Fick's I law

❑ Assume that only B is moving into A

❑ Assume steady state conditions → $J \neq f(x,t)$ *(No accumulation of matter)*

$Flux(J) \equiv atoms\,/\,area\,/\,time \propto concentration\ gradient$ *(Truly speaking it is the chemical potential gradient!)*

$$J \propto \frac{dc}{dx}$$

$$\boxed{J = -D\frac{dc}{dx}}$$

Fick's first law

$$J = \frac{1}{A}\frac{dn}{dt} = -D\frac{dc}{dx}$$

$$\frac{dn}{dt} = -DA\frac{dc}{dx}$$

$$\left(\frac{dc}{dt}\right)\Delta x = -\frac{dJ}{dx}\Delta x$$

Continuity equation

Diffusivity (D) → f(Concentration of the components, T)

So, suppose I am talking about diffusion of a species B which is moving into A, this is a simplistic description. So, we are not actually talking about inter diffusion, but the species B moving into A and we also additionally assume something known as steady state conditions we will have a few more things to say about the steady state conditions in one of the coming slides. But, essentially steady state conditions mean that flux, that the flux is not a function of x of time; that means, not a function of position or of time and essentially, physically speaking there is no accumulation of matter in the material.

So, it is reasonable to assume that this flux which is the number of atoms, which cross a particular unit area, in a unit time, is directly proportional to the concentration gradient. And as we have pointed before, truly speaking we have to consider the chemical potential gradient. So, change the flux is directly proportional to dc by dx and the proportionality constant is D which is called the diffusivity or the diffusion coefficient. And this D as we shall see later is a function of the temperature at which the diffusion experiment is being carried out.

Now, suppose we write down the larger expression for flux and this expression which is in the blue box is called the fick's first law, which says that j equals to minus d dou c by dou x and the negative sign in the front implies, that the flux is down the concentration gradient. Now, we can write down the expression for j which we can consider in the previous slide as 1 by A d n by d t therefore, J becomes 1 by A d n by d t is equal to minus D dc by dx and therefore, if you want to write down the expression for number of atoms crossing this area in a interval of time d t.

Then it becomes d n by d t is equal to minus D A d c by d x, in other words the concentration gradient is related to the number of atoms crossing this area per unit time. And the heart of this expression is it is material parameter known as diffusivity, as we shall see later this diffusivity not only depends on the temperature, but also depends on the kind of species, diffusing and in other words the mechanism of diffusion. And additionally diffusivity could also be a function of the concentration of the components.

And we shall see that if there is a simplification possible then we may consider it independent of the concentration of the components. What is their equation which might be of interest to those is a familiar equation known as the, continuity equation in which we talk about the concentration changing with time into in a delta x length of material which is related to the flux gradient as dou j by dou x into delta x.

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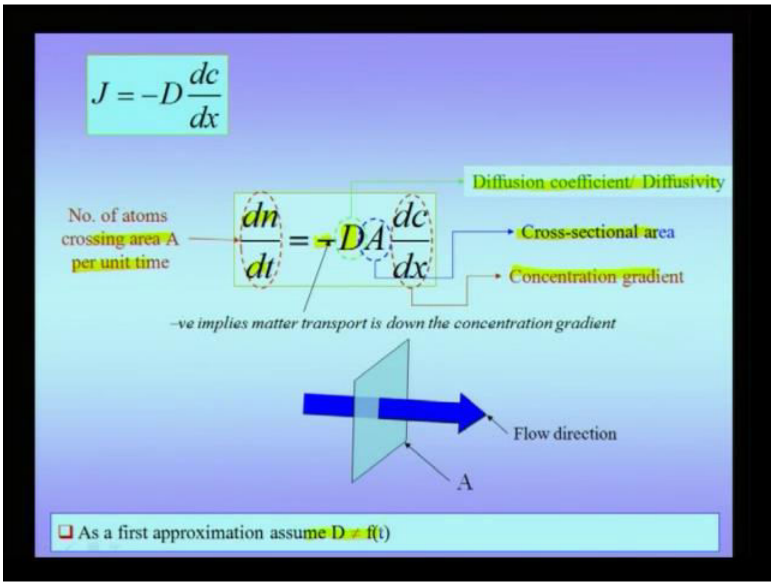

$$J = -D\frac{dc}{dx}$$

$$\frac{dn}{dt} = -DA\frac{dc}{dx}$$

No. of atoms crossing area A per unit time

Diffusion coefficient/ Diffusivity

Cross-sectional area

Concentration gradient

–ve implies matter transport is down the concentration gradient

☐ As a first approximation assume D ≠ f(t)

So, let us analyze this equation we just now, derived a little more the left hand side d n by d t is number of atoms of A crossing into the material B per unit time. And the right hand side is the material parameter D and the negative as a pointed out is to accommodate the fact that this flow is down the concentration gradient. D is known as the diffusion coefficient that diffusivity A is the cross sectional area across which the diffusion is taking place, and d c by d x is the concentration gradient.

And often as a first approximation we will assume that D is not a function of time or of concentration.

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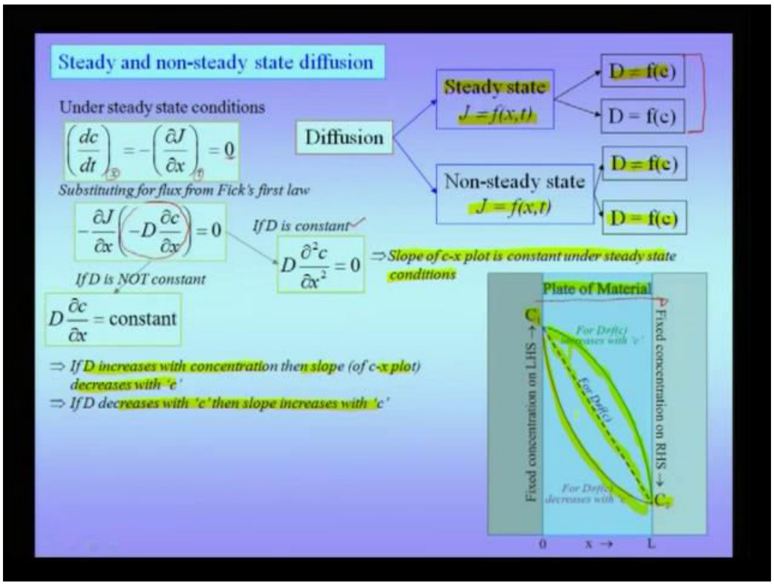

Steady and non-steady state diffusion

Under steady state conditions

$$\left(\frac{dc}{dt}\right)_x = -\left(\frac{\partial J}{\partial x}\right)_t = 0$$

Substituting for flux from Fick's first law

$$-\frac{\partial J}{\partial x}\left(-D\frac{\partial c}{\partial x}\right) = 0$$

If D is constant

$$D\frac{\partial^2 c}{\partial x^2} = 0$$

⇒ *Slope of c-x plot is constant under steady state conditions*

If D is NOT constant

$$D\frac{\partial c}{\partial x} = \text{constant}$$

⇒ *If D increases with concentration then slope (of c-x plot) decreases with 'c'*

⇒ *If D decreases with 'c' then slope increases with 'c'*

Diffusion

Steady state $J = f(x,t)$

$D = f(c)$

$D = f(c)$

Non-steady state $J = f(x,t)$

$D = f(c)$

$D = f(c)$

So, we have used a term that we will often consider something known as, steady state diffusion. So, what is steady state diffusion and what is the opposite of that which is non-steady state diffusion. In steady state diffusion the flux is not a function of either the position in the material or of time. And even when you are talking about steady state either we can have diffusivity which is a function of the concentration or diffusivity which is not a function of the concentration.

So, and in non-steady state diffusion the flux would be a function both of the position and time. And in non-steady state diffusion again we can talk about the diffusivity being a function of the concentration or as simplification the diffusivity being not a function of the concentration of the species, for most purposes during these elementary lectures we shall talk about, what we might call the steady state diffusion and we shall see that there are some simplifications possible when we consider steady state conditions.

Under steady state conditions the concentration change with time at any point x in the material is 0. And equivalently, we can write the D the flux change at the gradient in flux at a certain time is also equivalent to 0. And now, suppose we take this aspect dou J by dou x and substitute for J in terms of the fick's first law, which is what is substituted here. Then we can write minus dou J by dou x of minus D dou c by dou x is equal to 0.

And further if I assume that the diffusivity is constant in other words, we are assuming that the diffusivity is not a function of the concentration of the species, then we can take the D out of the equation and we can write down the expression as for steady state condition as, D dou square c by dou x square is equal to 0. In other words if my curvature of that c x plot is 0; that means, that the slope of the c x plot is a constant under steady state condition.

In other words under steady state conditions, if the diffusivity is not a function of the concentration then the slope of the c x plot will be a constant. And so suppose, to understand this physically suppose, I have a higher concentration of material on left hand side of a plate, which is shown in blue color here and a lower concentration on the right hand side; that means that I would expect that the material see now, we consider we may would diffuse from the higher concentration to the lower concentration.

Under steady state conditions I would assume that there is no accumulation of mass within this blue plate of material and whatever, mass enters this blue plate of material leaves from the left hand side actually, leaves from the right hand side. So, this is the steady state conditions and further as we saw, just now if the concentration or the diffusivity is not a function of the concentration then the slope of the c x plot would be constant in other words I would obtain the line which is shown by the dotted line here.

So, this would be the profile of the concentration across the blue plate, under steady state conditions given that the diffusivity is not a function of the concentration; however, if D is not constant the 2 possibilities, though we are not going to the details of this if we can write the fact that D dou c by dou x will be a constant; that means, that either D can increase with concentration or D can decrease with concentration and under these 2 conditions we would obtain not a straight line profile of concentrations from the left hand side of the plate to the right hand side of the plate, but we would obtain a curved profile as shown by, this brown line or the green line.

So, under simplified circumstances we want to consider what we might call steady state conditions and further the fact that the diffusivity, can be approximated perhaps to the that it is not a function concentration, in that case the concentration profile would be safe straight between, under steady state conditions, but if the concentration diffusivity is the function of the concentration.

Then we would obtain a curved profile and for the case when D decreases with c then the slope will increase with c and for the other case when D increases with the concentration then the slope of course, the slope we are talking of is c x plot decreases with c and thus will lead to the 2 cases which are marked in green and brown. So, to summarize this slide, there can be a steady state and non-steady state diffusion and each one of these further there could be a sub classification based on the fact, if the diffusivity is a function of the concentration or if it is not a function of the concentration.

Under the most simplified circumstances that is the steady state and the diffusivity not being a function of the concentration, we would obtain a linear profile under of the concentration with the position in the steady state condition. Now, we move on to what is known as the fick's second law and in fick's second law.

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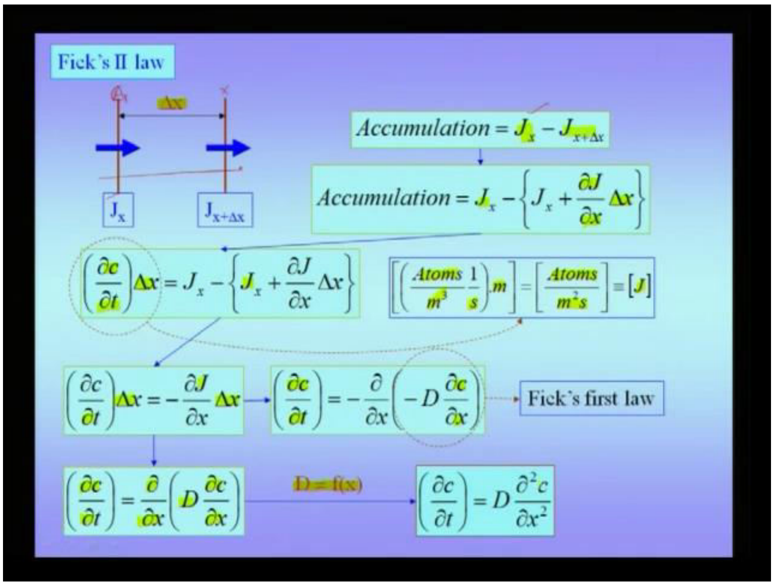

Fick's II law

$$Accumulation = J_x - J_{x+\Delta x}$$

$$Accumulation = J_x - \left\{ J_x + \frac{\partial J}{\partial x} \Delta x \right\}$$

$$\left(\frac{\partial c}{\partial t} \right) \Delta x = J_x - \left\{ J_x + \frac{\partial J}{\partial x} \Delta x \right\}$$

$$\left[\left(\frac{Atoms}{m^3} \frac{1}{s} \right) . m \right] = \left[\frac{Atoms}{m^2 s} \right] = [J]$$

$$\left(\frac{\partial c}{\partial t} \right) \Delta x = - \frac{\partial J}{\partial x} \Delta x \rightarrow \left(\frac{\partial c}{\partial t} \right) = - \frac{\partial}{\partial x} \left(- D \frac{\partial c}{\partial x} \right) \rightarrow \text{Fick's first law}$$

$$\left(\frac{\partial c}{\partial t} \right) = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) \xrightarrow{D = f(x)} \left(\frac{\partial c}{\partial t} \right) = D \frac{\partial^2 c}{\partial x^2}$$

Suppose, I have a length of material delta x across which I am considering the flow of a diffusion of a material A or a or atoms of A in this direction from to left to right. The flux entering this cross section a here or I may call this cross section c 1 and leaving at this second cross section here at this point. The net accumulation of matter between these 2 lines which are shown in brown, is the flux entering a flux entering at the left hand side which is given by J x minus the flux which is actually, leaving at the right hand side which is a distance of delta x from the left hand side.

So, the accumulation can be written as J x minus J x plus delta x and for a small delta x we can write this accumulation as J x minus J x plus dou J x by dou x into delta x and using the fact that dou c by dou t into delta x is equal to J x minus J x which is the expression which you take down from here, this in other words can be thought of as the accumulation of the material, in this length of matter or length of material which is given by delta x.

And now, if you look at the units of the left hand side which is dou c by dou x into delta x then, we note that it is number of concentration can be written as number of atoms per unit volume, the time can be written as in seconds and the delta x is m. So, this is the accumulation we are talking about then simplifying it, we find that its atoms per meter square per second which is nothing, but units of flux which is the right hand side. So, we can clearly see that the left hand side is the accumulation of matter in the length which is described by, delta x.

Now, therefore we can simplify this expression by writing dou c by dou x, dou c by dou t into delta x is equal to minus dou j by dou x into delta x which by, introduction now for flux I can substitute the fick's first law, which I know that J is equal to minus dou c by dou x therefore, dou c by dou t is equal to minus dou by dou x into minus D dou c by dou x, in other words dou c by dou t which is the change in concentration with time on the left hand side can be written as dou by dou x which is the gradient of the flux which is D dou c by dou x.

And in the case, that the diffusivity is not a function of x we can write simplify this expression as dou c by dou t equal to D dou square c by dou x square which is known as the Fick's second law.

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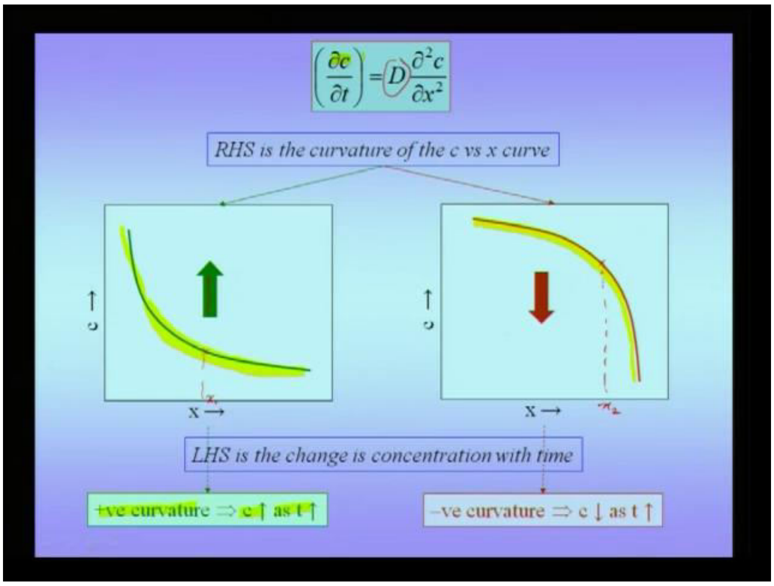

$$\left(\frac{\partial c}{\partial t}\right) = D\frac{\partial^2 c}{\partial x^2}$$

RHS is the curvature of the c vs x curve

LHS is the change is concentration with time

+ve curvature ⇒ c ↑ as t ↑

−ve curvature ⇒ c ↓ as t ↑

So, the fick’s second law states that the concentration change with time is equal to the diffusivity into the curvature of the concentration distance profile. Now, what happens if this concentration distance profile has a negative curvature or if the concentration profile has a positive curvature. Now, if dou c by dou x square which is the curvature of this concentration x profile and on the right hand side we got a negative curved kind of a profile of concentration with x and on the left hand side we got positive curvature of a c x plot.

And if the curvature happens to be positive, then the composition will increase as time increases in other words under these conditions we notice that, the curve will actually will go up because, now dou c by dou t is a positive quantity; that means, the concentration at any x. So, I can consider any x here suppose, this is x 1 at this x 1 the concentration with time will actually increase because, the right hand side is positive.

This therefore, the curvature of the c x plot will determine if the concentration is going to increase with time at a given x or it is going to decrease with time at a given x and suppose the curvature happens to be negative as if of the red curve on the right hand side. So, therefore, at any distance x 2 if I evaluate the curvature and I find that the curvature is negative; that means, dou c by dou t is negative and that implies as diffusivity is a positive quantity. Always therefore, dou c by dou t is negative; that means, the concentration at this point x of species say B will decrease with time and the curve this point will go down in time.

So, as we see that the fick's second law is a differential equation which connects the change in concentration with time with the second differential of change in concentration with the distance.

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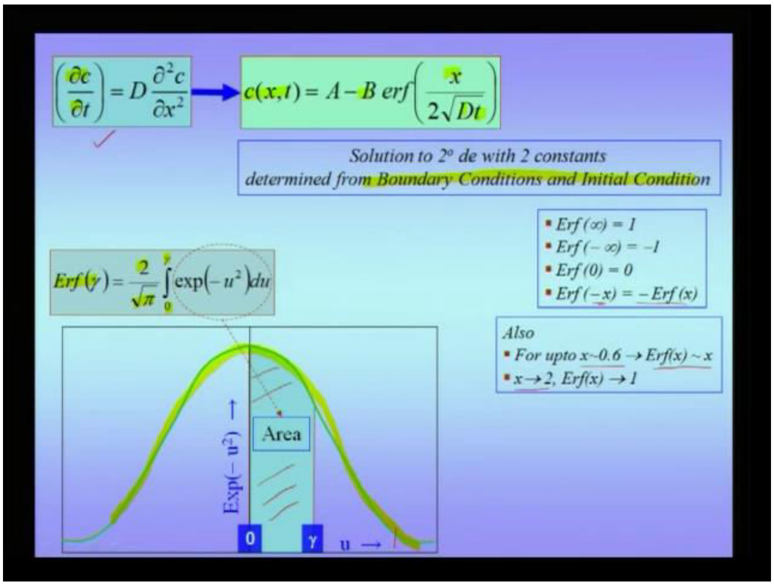

$$\left(\frac{\partial c}{\partial t}\right) = D\frac{\partial^2 c}{\partial x^2} \rightarrow c(x,t) = A - B\,erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

Solution to 2° de with 2 constants
determined from Boundary Conditions and Initial Condition

- $Erf(\infty) = 1$
- $Erf(-\infty) = -1$
- $Erf(0) = 0$
- $Erf(-x) = -Erf(x)$

Also
- For upto $x \sim 0.6 \rightarrow Erf(x) \sim x$
- $x \rightarrow 2$, $Erf(x) \rightarrow 1$

$$Erf(\gamma) = \frac{2}{\sqrt{\pi}}\int_0^{\gamma} \exp(-u^2)\,du$$

And if we solve the fick's second law then we should be able to get the concentration profile at any given time. So, that means; we should be able to get the concentration as a function of both position and time. And therefore, I can find how the concentration profile changes into a material at different times. Now, this is a second order differential equation on the left hand side here, and the solution to a second order differential equation can be determined based on the boundary conditions and the initial condition which we are imposing in a given problem.

A standard solution which works for many cases and we will consider some of these examples in the coming slides, is what is called the error function solution. And the error function solution for this fick's second law, which is dou c by dou t is equal to D dou square c by dou x square is c x t; that means, the concentration at any x at any given time is A minus B error function of x by 2 root D t D being the diffusivity. So, the right hand side inside the error function are the 2 variable which is x and time and the diffusivity is under square root in the denominator.

A and B are arbitrary constants and D is arbitrary constants, will be determined based on the given physical problems which is in other words boundary conditions and the initial conditions. Now, physically to understand this error function the definition of error function is suppose, I want to consider the error function of gamma it is defined as 2 by root pie, which is the constant outside the integral is equal to integral log 0 integral from 0 to gamma of exponential minus u square d u.

So, suppose I plot exponential minus u square, you see the plot of this in the green curve here, and this integral the definite integral from 0 to gamma represents the area under the curve in an exponential minus u square versus u plot. So, the exponential u square plot as the green curve, the area under this curve is this area which is shown in blue color and this area from 0 to gamma represents the error function of gamma.

So, there are standard tabulations of error function; that means, not only a error function, but also the inverse error function and from these tabulations I can solve for a give diffusion problem. In other words determine c x t uniquely given the boundary conditions and the initial conditions. There are some special properties of these error function, like error function of infinity is 1 error function of minus infinity is minus 1 error function of 0 is 0 because, the you can clearly see the area enclosed if you interfere from 0 to 0 will be 0.

And error function of minus x is equal to minus of error function of x; that means, it is if you substitute minus x instead of x then you will get the negative of the error function. Also, as pointing out certain additional properties of error function help us, understand certain physical situations which will take up in some of the coming slides. Like for instance if you consider a value of up to approximately about 0.6 the error function of x can be approximated to x.

Suppose, I am talking about error function of 0.5 the value of the at x equal to 0.5 then the error function is also approximately 0.5. And additionally, suppose you are talking about x tending to a reasonably small value like 2 then the error function of x tends to 1, in other words quickly the error function saturates the area under the curve is mostly found in the small region in the axes which is close to 2 and the area found beyond that is actually very, very small.

So, suppose I am considering a physical diffusion situation then these properties of the error function will come in handy and understanding that which part of the material will not be affected say for instance diffusion of a species from a surface to the inside. So, these are good thumb rules which will help us understand certain physical situations based on the properties of the error function. So, to summarize in this slide the fick's second law as a solution which is a second order differential equation.

As a solution which is the based on the boundary conditions and initial conditions one of the important solutions is the error function solutions. Which is A minus B error function of x by 2 root D t A and B are arbitrary constants and can be determined from the boundary and initial conditions, the error function is defined as the area under the exponential minus you square versus u plot from 0 to gamma.

So, that will be the error function of gamma. The error function has certain properties like error function of e infinity is equal to 1, error function of minus infinity equal to minus 1 error function of 0 is equal to 0 and error function of minus x is equal to minus error function of x. And additionally as a point down that when x goes to about 2 most of the area of the entire row is enclosed almost there; that means, error function of x tends to quickly to 1 beyond that then for about x equal to 0.6 the error function of x can be approximated to x itself.

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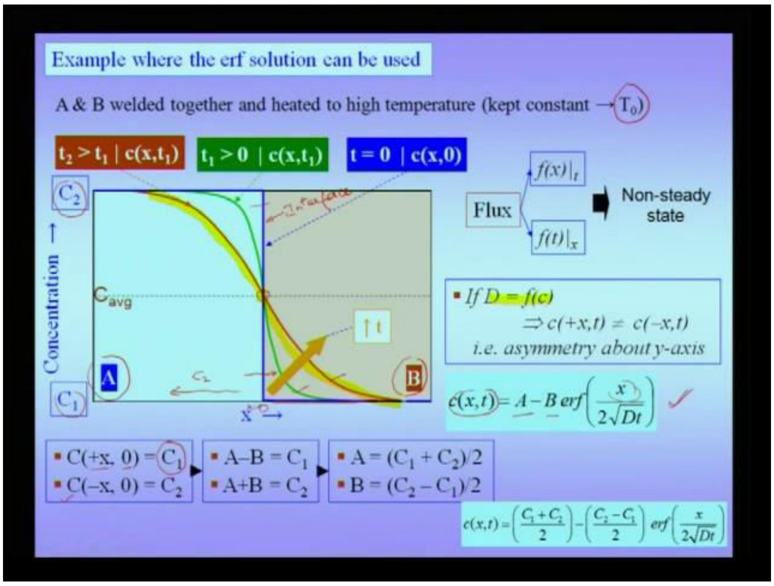

Example where the erf solution can be used

A & B welded together and heated to high temperature (kept constant → T_0)

- If $D = f(c)$
  $\Rightarrow c(+x,t) \neq c(-x,t)$
  i.e. asymmetry about y-axis

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

- $C(+x, 0) = C_1$
- $C(-x, 0) = C_2$

- $A - B = C_1$
- $A + B = C_2$

- $A = (C_1 + C_2)/2$
- $B = (C_2 - C_1)/2$

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

So, let us consider an example, where this error function solution can be used. So, let us construct a bi material contact by, taking a material A in contact with the material B. So, and suppose I am tracking the concentration at time t equal to 0 at time t equal to 0 the composition on the left hand side is C 2 of say of certain species and the concentration on the right hand side is C 1. So, the concentration provide is given by, this blue curve C 2 on the left hand side entirely and this is the joint part this is the interface.

And on the right hand side of the interface you would notice that, the concentration is C 1. So, this is the starting concentration profile and we are heating typically heat the system and hold it at a constant temperature t 0. So, that the diffusion process can start, and the concentration can change with time. Now, what happens suppose I try the concentration profile at a certain different time interval I would have noticed that, that material would have diffused from the left hand side on to the right side.

Similarly, from the left hand side to the right hand side the material would have been lost and therefore, the concentration profile would look something like the green curve. And even later time you would notice that, you will observe a profile which is like a red curve in other words the concentration C 1 concentration on the right hand side originally matures only material B is increasing with time.

Now for such a system, we can apply the error function solution as written here, on the right hand side. And we can notice that, we can use a initial conditions and the boundary conditions to evaluate the constants A and B in the error function solutions. So, briefly again to tell you that what we are considering here, we are considering a bi metal contact for instance which could be another material, but simplify could be a bi metal contact which is been welded together and therefore, there is an internal interface now, and this whole system is been heated and kept at a constant temperature t 0 and we allow diffusion to take place.

The diffusion would lead to change in concentration profiles with time and; that means, that originally on the right hand side the concentration of a species was C 1 which is constant, but with time the concentration increases, and you will obtain profiles like the green curve and the red curve. So, I would like to know what exactly is this curve the profile the red curve and green curve, in other words I would like to know C x t and then

I can for instance know how much time do I have to wait for to stop my diffusion experiment.

Now, we know that at time t equal to 0 for any positive x the concentration is C 1. So, this is one of the initial conditions. So, the right hand side the concentration is C 1 for any x, but time equal to 0; that means, initial condition. Similarly, at any minus x this being the origin of the experiment. So, the x equal to 0 lies here, so on the left hand side for any x the concentration is C 2 at time t equal to 0 and putting in these initial conditions I can notice ,that if I put x equal to 0 and from the previous slide we know that error function of 0 is 0 sorry we put t equal to 0.

And so, this becomes error function of infinity and therefore, error function of infinity is 1 therefore, I obtain C 1 is equal to A minus B. Now, suppose I introduce a second initial condition which is C minus x 0 is equal to C 2 therefore, I can write C 2 is equal to on the left hand side this C x t becomes C 2 s equal to A minus B and now, for we are working in minus x domain and therefore, at t equal to 0 this goes to minus infinity and we know that, error function of minus infinity is minus 1 therefore, C 2 is equal to A minus 1 into B which means it is A plus B.

So, A minus B is equal to C 1 A plus B is C 2 therefore, from these 2 equations we can evaluate the 2 arbitrary constants involved in this equation therefore, A becomes C 1 plus C 2 by 2 and B becomes C 2 minus C 1 by 2. Now, therefore, suppose I substitute this C into the equation the error function solution. You can see that C x t becomes C 1 plus C 2 by 2 minus C 2 minus C 1 by 2 into error function of x by 2 root D t. Therefore, if I am talking about a certain time t suppose I have been done this diffusion experiment for say 15 minutes or I can convert that into seconds of course.

And I want to know the concentration profile C as a function of x at after 15 minutes then since, I know all these are all constants therefore, I can plot C x as a function of error function of 2 root D into t knowing the of course, for this of course, I need to the material I need to know, the material property which is diffusivity of say this species B.

Therefore, we can see that if I have certain initial conditions, then I can determine the arbitrary constants involved in the error function solutions of the fick’s second law and therefore, I can solve for the profile of the concentration at various times t and I can stop the diffusion experiment based on the requirement of how much material I need to diffuse. In this simplistic solution let us assume that the diffusivity is not a function of concentration and if diffusivity happens to be a function of concentration then you would notice that, this concentration profile which is simplistically shown here has a center of inversion here.

So, this point at the center here, around the C average is a point of inversion and this inversion symmetry would be lost if situation happens to be such that, the diffusivity happens to be a function of a concentration. So, as a first approximation if I assume that the diffusivity is not a function of concentration then this C average point along the at the interface will be a point of center of inversion of all these concentration profile curves which have been obtained for various lines.

So, this is a nice example, where we are talking about what you might call the error function solution for a given set of initial conditions. So, when we talked about the fick's first law and when we introduced a constant called the diffusivity.

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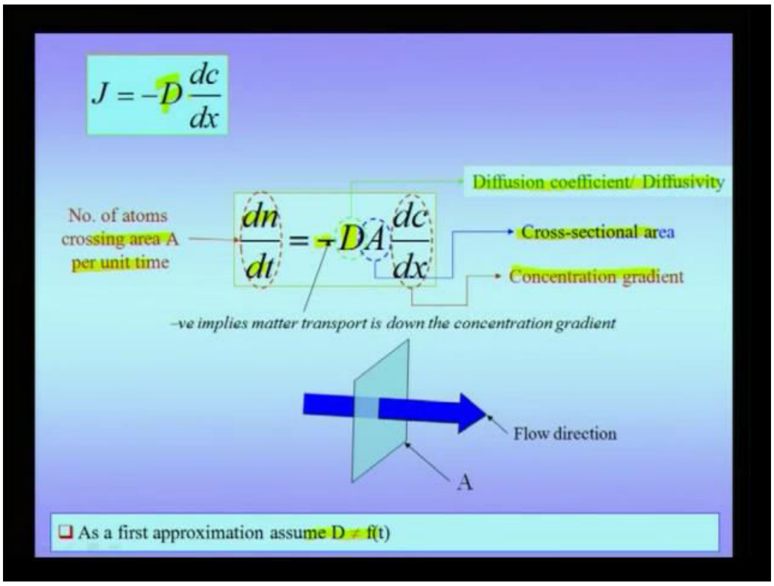

$$J = -D\frac{dc}{dx}$$

No. of atoms crossing area A per unit time

$$\frac{dn}{dt} = -DA\frac{dc}{dx}$$

Diffusion coefficient/ Diffusivity

Cross-sectional area

Concentration gradient

–ve implies matter transport is down the concentration gradient

❑ As a first approximation assume D ≠ f(t)

And we had pointed out that this diffusivity is a material property.

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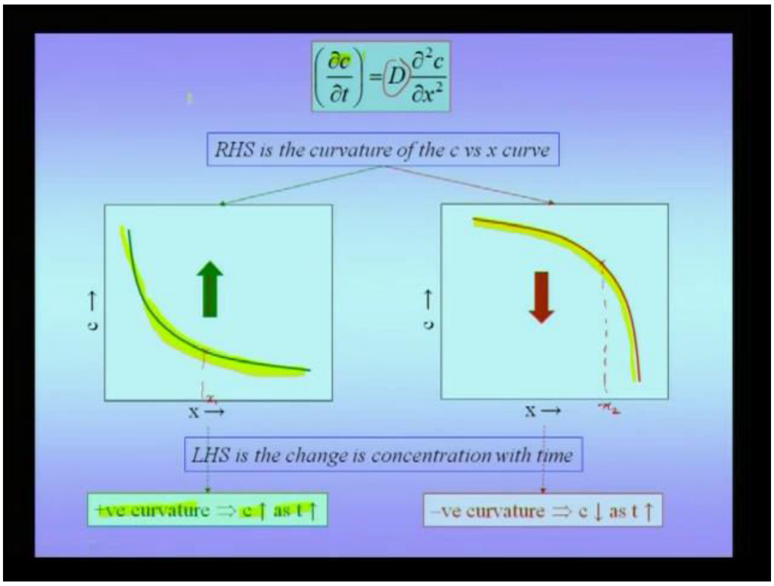

$$\left(\frac{\partial c}{\partial t}\right) = D\frac{\partial^2 c}{\partial x^2}$$

RHS is the curvature of the c vs x curve

LHS is the change is concentration with time

+ve curvature ⇒ c ↑ as t ↑

−ve curvature ⇒ c ↓ as t ↑

And could actually, depend on the concentration of the material into for instance suppose, species say for instance copper is diffusing into an alloy of say aluminum copper then it could, so happen that depending on the percentage of aluminum and copper, the diffusivity of copper would change.

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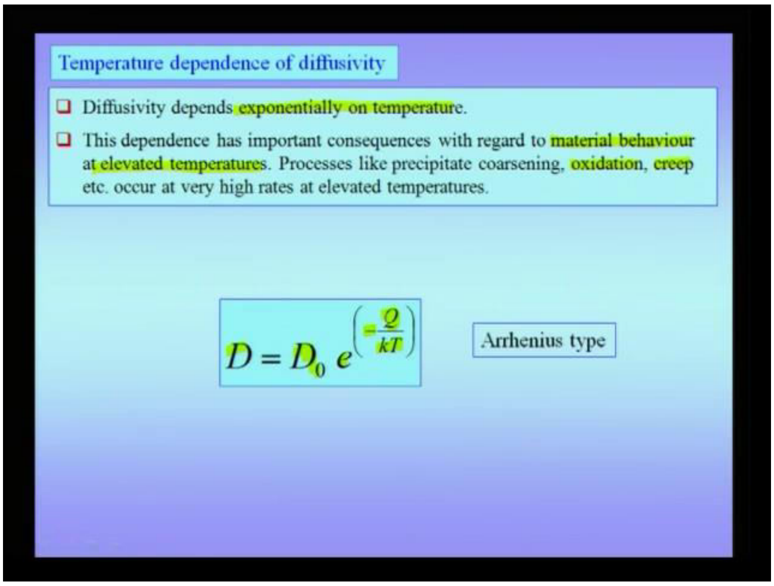

Temperature dependence of diffusivity

- ☐ Diffusivity depends exponentially on temperature.
- ☐ This dependence has important consequences with regard to material behaviour at elevated temperatures. Processes like precipitate coarsening, oxidation, creep etc. occur at very high rates at elevated temperatures.

$$D = D_0\, e^{\left(-\frac{Q}{kT}\right)}$$

Arrhenius type

But, we said often we would like to assume that as a first approximation that diffusivity is independent of the concentration. But, one thing is very clear as we pointed out that this diffusivity which is a material property is going to depend on the temperature, the way this depends on the temperature happens to be exponential in nature and therefore, I can write diffusivity as d 0 a temperature independent component. And exponential of minus Q by k T where k is the Boltzmann constant.

Since, T is in the denominator and this exponential has a negative they both contract can counter cancel each other and that implies that the diffusivity depends increases exponentially with temperature. Therefore, suppose I am doing a diffusion experiment at say 100 degrees Celsius and do another experiment at 200 degrees Celsius I cannot merely visualize this as a stunt 100 degree increase in temperature, but I had to understand that since, diffusivity lies in the temperature this is the diffusion rate is going to be extremely fast as compared to 100 degrees when I do the experiment at 200 degrees Celsius.

This exponential dependence of diffusivity on temperature has extremely important consequences with regard to material behavior at elevated temperatures. And therefore, It becomes very challenging to design materials at high temperatures because, the fact this very dependence of diffusivity with temperature of course, there are other issues which come in when one is trying to design a material for high temperature applications.

Now, suppose, I was talking about precipitate coasting in the context of diffusivity; that means, I am putting a second phase particle, second phase precipitate which is used as a prostration hardening system. Then if I hold the system at high temperatures then what happens is that because, of the enhanced diffusion rate at high temperatures the coarsening at the precipitate will be very, very fast and this material may lose it is strength at elevated temperature.

Similarly, oxidation involves mass transport. So, suppose I have a layer of metal on which there is an oxide forming; obviously, the oxygen from the atmosphere has to diffuse to the metal oxide interface to oxidize further material and this or of course, inversely of course, a metal also could diffuse outward and get oxidized, but both in any case you involve diffusion as the primary phenomenon which is going to control this kind of a oxidation process.

And since at high temperatures this diffusion is going to be much faster the oxidation rate could be very fast and therefore, you could have catastrophic oxidation of a surface at high temperatures, which would be extremely deleterious. When we are talking about creep mechanisms, many of the creep mechanisms actually involve diffusion they may involve as we shall see later lattice diffusion or grain boundary diffusion, but they could involve diffusion and many of the some of the other creep mechanisms involve dislocation claim and dislocation claim further as we have had seen before that actually, involves diffusion.

Therefore, if you the diffusion rate is very, very fast this implies that there is going to be an enhanced creep rate and with increasing temperature also the creep mechanism may also change and leading to what we might call a faster creep rate and earlier failure of the material. Therefore, the problem of diffusion becomes very, very important to address in the context of service of materials and with use of materials at high temperatures given the equation D equal to D 0 exponential minus Q by k T where Q is the activation energy for diffusion.

And later on we will try to correlate this activation energy Q with certain atomistic mechanisms which will tell us what kind of an underlying mechanism is actually giving rise to this activation barrier for diffusion.

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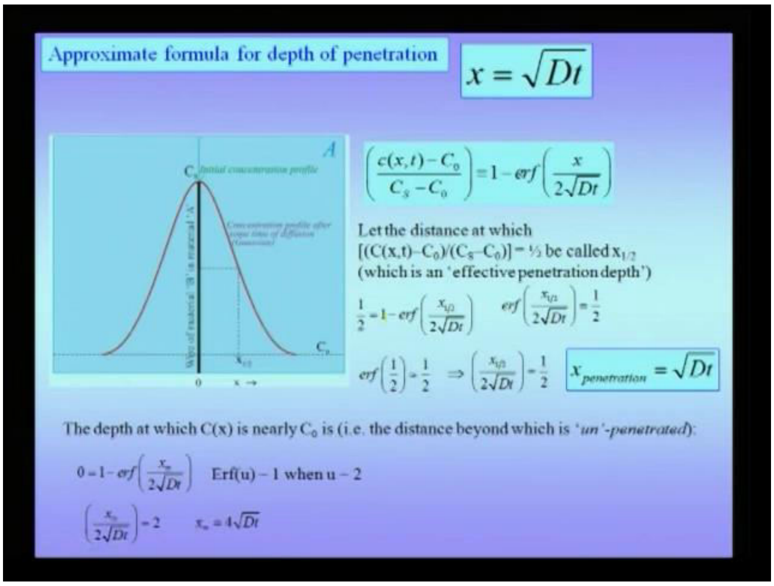

Approximate formula for depth of penetration

$$x = \sqrt{Dt}$$

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

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')

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

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

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

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

$$\left(\frac{x_\infty}{2\sqrt{Dt}}\right) \approx 2 \qquad x_\infty = 4\sqrt{Dt}$$

Now, before we go into the mechanisms of diffusion which is coming up in the next slide we had pointed out.

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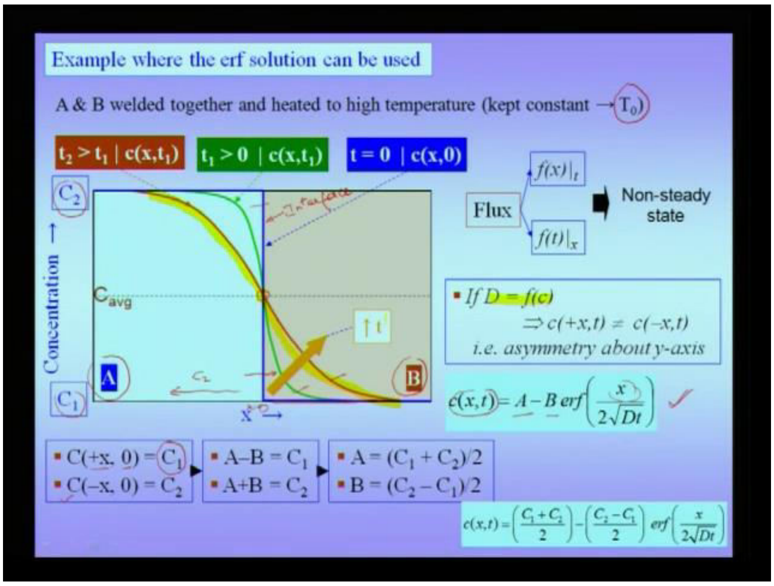

Example where the erf solution can be used

A & B welded together and heated to high temperature (kept constant → T_0)

Flux → $f(x)|_t$, $f(t)|_x$ → Non-steady state

- *If D = f(c)*
  $\Rightarrow c(+x,t) \neq c(-x,t)$
  i.e. asymmetry about y-axis

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

- $C(+x, 0) = C_1$
- $C(-x, 0) = C_2$

- $A - B = C_1$
- $A + B = C_2$

- $A = (C_1 + C_2)/2$
- $B = (C_2 - C_1)/2$

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

That that suppose I am holding a bi metal strip here, and I wait for diffusion to take place I notice that, with progressing time for instance you find that the say for instance material is slowly penetrating into the right hand side into material B. And I would like to have an effective measure of what is known as the penetration depth, suppose I want to carry on this experiment such that, my concentration profile reaches some value which I can call as C x.

So, I want to know at some x what if I reach my concentration profile I can stop my diffusion experiment and suppose, I am talking about a different kind of an experiment in which I am taking a material. And I am imposing say for instance t 2 a carburizing atmosphere. And this will be actually, one of the experiments we will take up and solve a problem, then I would like to know how long do I have to carry on this carburizing experiment.

So, that I am I achieve an effective penetration of carbon to a certain depth which I would call pre penetration depth. So, to understand this there are some effective formula which I can use and one of these effective formula is the approximate formula for the depth of penetration.

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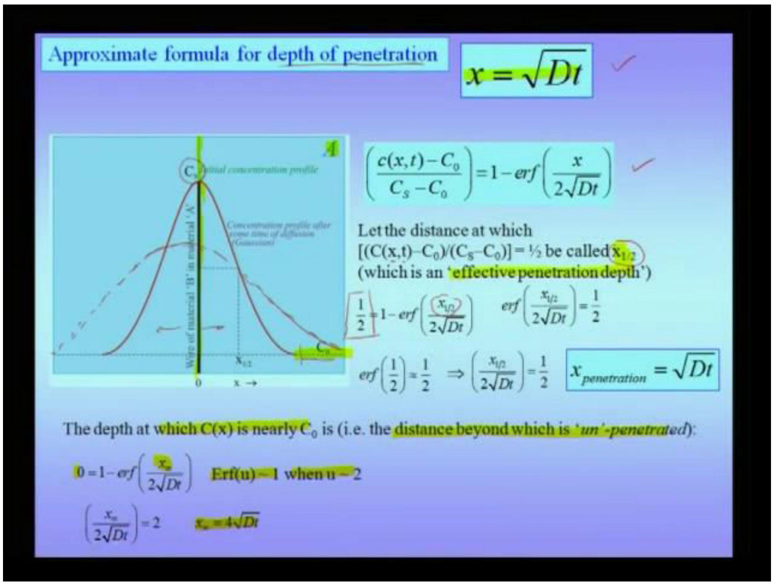

Approximate formula for depth of penetration

$$x = \sqrt{Dt}$$

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

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')

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

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

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

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

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

So, from this formula which is now, you can see that I can see is given x equal to square root of D t I can use this formula, knowing the diffusivity to know that how much time do I have to conduct an experiment before, which I have say for instance a penetration of the material to a desired level. Now, for this we will consider one example briefly, and this example happens to be for instance suppose, I introduce a wire of material which is shown in black here.

Say call this material A in a matrix of material A and start my diffusion experiment slowly of course, I could the initial concentration of the material will be little higher than the rod shown here, later on you will see that this material which is shown in black actually, will spread outward is wire which has been embedded the material will diffuse outward. And slowly, you will notice that the concentration profile keeps changing with time, I might delay the time you might find a profile which is like this.

So, initially there was a concentration C 0 and later on and you impose a central concentration C s and this concentration changes with time. And I would like to know for instance say for instance I define a penetration depth to be a depth, at which I obtain half the initial concentration and the half the initial concentration in other words I obtain C at that distance x at a certain time t minus C 0 and C s minus C 0 C s being the central concentration of C 0 to be half.

So, I call that the penetration depth for a given time. In this penetration depth suppose, I denote by a x subscript half, similar words I do my diffusion experiment for a certain time D such that, at that distance the concentration is half that which is originally imposed at the center. Because, this concentration is not a assuming if suppose C 0 happens to be 0 then x value the concentration will be half of C s, but suppose, at initial concentration of the same material in the matrix say then I will have to talk about C s minus C 0. As the with respect to I need to obtain the half the fraction.

And an error function solution for this can be written down as shown here, let C x t minus C 0 is C s minus C 0 equal to 1 minus error function of x by 2 root D t. So, on the left hand side I know that the concentration ratio I am interested is in half; that means, the concentration there is half what was originally imposed. And the right hand side will be 1 minus error function of x of half that is a distance I am interest I where the half the concentration is achieved by 2 root D t.

And suppose I am talking about error function of some number being half.

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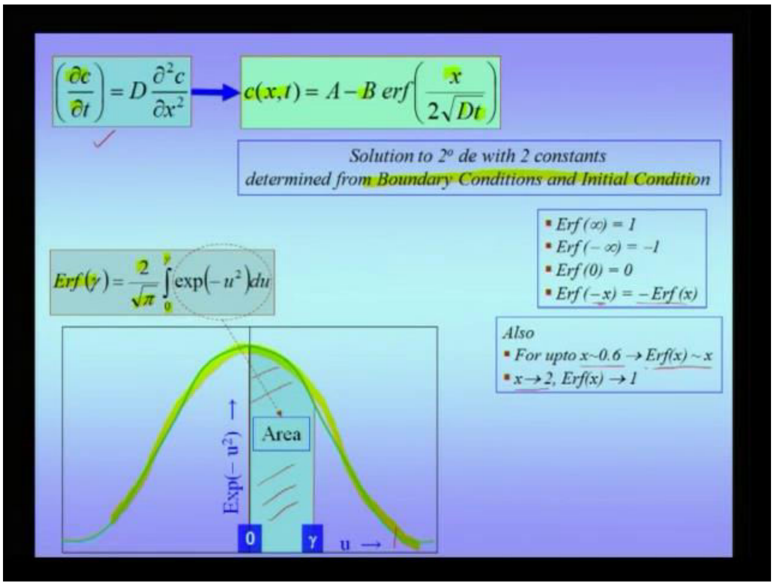

$$\left(\frac{\partial c}{\partial t}\right) = D\frac{\partial^2 c}{\partial x^2} \rightarrow c(x,t) = A - B\,erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

Solution to 2° de with 2 constants determined from Boundary Conditions and Initial Condition

- $Erf(\infty) = 1$
- $Erf(-\infty) = -1$
- $Erf(0) = 0$
- $Erf(-x) = -Erf(x)$

$$Erf(y) = \frac{2}{\sqrt{\pi}}\int_0^y \exp(-u^2)\,du$$

Also

- For upto $x \sim 0.6 \rightarrow Erf(x) \sim x$
- $x \rightarrow 2$, $Erf(x) \rightarrow 1$

That means, that effectively I told you that we are going back to previous slide about the properties of error function of x being approximately, equal to x for x values less than 0.6.

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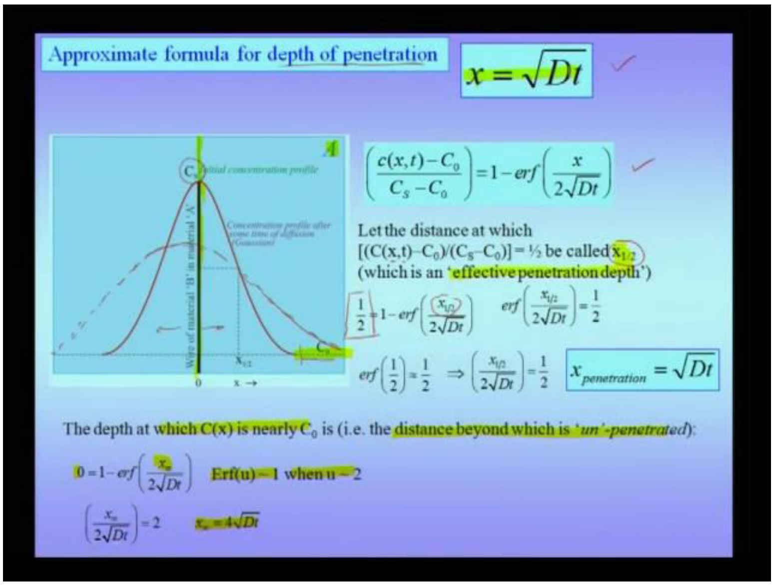

Approximate formula for depth of penetration

$x = \sqrt{Dt}$

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

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')

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

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

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

$0 = 1 - erf\left(\frac{x_\infty}{2\sqrt{Dt}}\right)$ Erf(u) ~ 1 when u ~ 2

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

And here I am talking about x value half; that means, that error of error function of half is equal to half; that means, x square root of x I am sorry x half divided by 2 root D t is equal to half and which can lead to this expression that x is equal to root of D t. So, we can see that we can have an approximate formula, for what we might call the depth of penetration.

And this approximate formula I can use as a quick thumb rule calculation to find out that how long do I have to carry on this experiment, to obtain a certain concentration functions in this case it was half the concentration imposed at a certain at what depth I mean at how long do I carry on that the concentration at the certain x becomes half that of what I imposed on the surface. If we look at the concentration profiles at various times you would notice that, again based on the fact that this solution is a narrow function solution.

That beyond the certain depth practically there is no material; that means, all the material that distance for a given time behaves like as if that distance is infinity. So, I call this distance is x infinity I that is the depth at which the concentration remains as the original concentration; that means, I carry on my experiment for a certain time t and in spite of we can diffusion taking place after a certain distance, along the x axes there has been no penetration of material and therefore, the original concentration which is C 0 remains.

Similar words I would like to know what is the distance beyond which the material remains un-penetrated in spite of me carrying out diffusion experiment for a certain time t. So, therefore, the left hand side becomes 0 and the right hand side becomes 1 minus error function of x infinity which is the un penetrated distance by 2 root D t and error function of u is approximately 1 when u equal to 2 we saw this property, that by that time this error function tends to 2 the error function of x tends to 1.

And therefore, I can write x infinity where 2 D t is equal to 2 and this implies x infinity, is about 4 root of D t. So, at distance which is 4 root of D t beyond that the concentration profile has not been affected the concentration remains C 0 and therefore, now I have to formulate 1 is for a penetration depth where, which we call the effective penetration depth where x can be called as x half. And another number a number which is called x infinity a distance which I call x infinity beyond which there has been no penetration.

So, suppose I actually, have a sample and I am talking about carrying on a heat treatment for instance to introduce carbon into the material I can define an effective penetration depth and based on that I can do my experiment for a certain time and I can calculate the time quickly based on a distance to which I want to penetrate the a species from the surface. So, this is a quick effective thumb rule formula which I can use in various experiments.