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Lecture – 15 Fick's II Law

In this lecture we are going to discuss some more about the diffusion. And in the last 2 lectures I have introduced the concept of diffusion to you and showed that how mathematically you can deal diffusion in 2 ways. One using continuum approach that is what is normally done using Fick's law and other one is the atomic scale movement of the atoms. Let us continue with the continuum approach, we know that the Fick's has given a law which describes the flux or the matter passing through a surface at unit time, with unit area proportional to the compositional gradient. That means, we have seen J if J is the flux, which is proportional to the compositional gradient in the in the system.

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In 1 dimension we can write J is proportional to del C by del x. In the 3 D this is; obviously, capital del C. Now the proportionality constant is always known to be diffusivity or diffusion coefficient. So, delta C is a gradient obviously; that means, delta is a gradient operator, now this is a fundamental equation in the sense that it relates the all the diffusion in the material, this equation is fundamental to any kind of mechanisms we try to explain in the material.

Today using this equation I will show you how we can obtained the flux balance equation why it is known as Fick's second law in the books, that let me clarify there is no Fick's second law this we made this Fick's second law.

Ficks second law actually is derived from the Fick's first law that we will see now. So, before I do that let me just again tell you that J in a steady state J is defined as a in 1 dimension case; obviously minus D d C by d x where x is the any location in the medium.

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And I we can actually define in a very simple way, we can assume Steady-State an isotropic medium and we can simplify this equation in a very simple as way that is J is equal to minus D del C del x, and that is what you read n the books as a first law of diffusion and in this equation D is assumed to be constant.

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And J is, that would D is basically comes as a scalar quantity, normally that is not the true and del C del x is basically a d C D d x is basically writ10 as a finite form C 2 minus C 1 divide by x 2 minus x 1 where compositional variation is shown in this diagram n 1 dimensional distance are writ10 by x and compositions by the c. Thus we can actually simplify this equation very very to the level of or understanding, that we can use it any application.

So, let us assume this description of the compositional gradient, I will go back to the board and explain you how the second law can be derived.

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Let us assume that I have an one dimensional case in which this is the distance and this is the composition for any solid, now also assume that this is how the composition profile goes by. It can be a straight line and it can be curved does not matter, but for the generosity, it is let is assume that these are this is like a curve.

So, therefore, there is a composition gradient and if I go from 1 distance to other distance the composition is reducing. If I plot now the J, so J is basically proportional to the slope of this curve and so therefore slope will be just like a straight line, I can write down these things again, so this is $x \, 1 \, x \, 2$ correct. So, now, at $x \, 1$ the flux is equal to J 1 at $x \, 2$ flux equal to J 2 very clear right.

Therefore, I can actually do a simple suppose if I consider and block a material and mark these 2 position as $x \, 1 \, x \, 2$ again, where this is also x and let us suppose this surface of this is A. So, if I assume that the flux coming to this surface at x 1 is equal to J 1 and flux going out to the surface at x 2 is equal to J 2.

We can write down that the mass occupied inside the small volume is basically can be related to del C by del t; obviously, in time t and del t that is equal to or let us right down in a differential way not put the t right, now here the mass occupied is basically equal to J 1 minus J 2 divide by A and this must be obviously, equal to del t because the time the flux multiplied by time, into area will be equal to the occupied concentrations J in the small path that let us suppose this is del x .

Now, I can actually write down that del C, by del t is equal to J 1 minus J 2 by the A correct. So, that is very very logically the must remain in this path, in the time of del t can be written like that and as you know J is nothing, but now I can actually do that in terms of the distance. So, there is some mistake here let us correct this must be divide by del x, because we have to consider the distance here. Now I can write do the maths again J 1 minus J 2 divided by del x multiplied by A. So, we can actually write down when del t is or del x are actually small very small means (Refer Time: 07:10) small we can write down J 1 is equal to J 2 plus del J del x right we can do that.

So, if I take that here then we can write down del C del t is equal to 1 by del x, multiplied by del J del x because J 2 J 2 will get cancelled multiplied by area.

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So that means, what if we consider in unit area case or if you remove the area n this side, we can write down this is equal to del C del x by del J del x. And as you know J is equal to D del C del x in one dimensional case. So, therefore, we can write down these for unit area case is equal to D del C del x, this is for a equal to unit area.

Therefore, if we assume D is an independent quantity it does not depends on this space and the time, that is always you do we can say that is equal to D del 2 C del x square, that is equal actually we call as term as a Fick's second law, but this is not a second law as you clearly see, this expression has been derived basically using the concept of J, J is a flux.

So, fundamentally I have used this expression J is equal to D multiplied by the consonance and gradient. As I am using this expression to derive this final equation therefore, I cannot say that this is an independent equation and that is the reason we always say Fick's has given only one law that is a first law whatever it is the law of Fick's law.

So, this equation this expression especially the last one where we assume D to be independent of the x and also t; that means, t is a steady state value and it does not depends on the special variables is what we use in the metallurgical community, but for a sake of understanding it is very clear D is need not be a constant as a function of special variables, D can be assumed to be constant or D can be assumed to be independent of time because we can always assume that D has you know specific value in the whole system at time is equal to 0 at time any time, but D can never be assumed to be independent of special variables and therefore, we cannot take out D from this parenthesis and obtain such a kind of expression.

So, basically if you really want to solve this problem this which is the fundamental equation which is required to solve all kinds of diffusion problems in the literature, in the different industrial problems, academic problems, we need to not actually take this D out rather we should do little more maths and try to find out how to solve these problems in a different way.

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 $J = D \frac{\partial C}{\partial A}$ 90

If do that if I assume D is not completely independent of special variables, we can write down we can expand this equation, this will be this plus del C del x multiplied by del D del x, that is actually more logically correct expression of the Fick's second law. In this case you can clearly see we not only need to have compositional the C as a function of x, also you need to have D as a function of x, the moment we have both these things clear from the experiments we can solve this C.

So, therefore, C if I have to solve C or I can write down here C, C is a function of 3 things x , t and D clear, that in the actual books where you will see C is a function of x and t . So, the moment we assume C is a function of x and t this equation is very easy to solve why, because if C is a function of x and t we can always do separation of variables and solve these equations, I am not going to solve this equation for in the lecture it is there in the books very clearly solutions are given or you can actually do yourself you can assume the C is a function of x and t therefore, we can do the separation of variables we can always write down this is equal to F of x, F of t and do the differentiation and separate out and solve the equations same like wave equation.

Now, that is one part which you can do yourselves because that is very important that you need know you must know how to solve this expression.

Second part of this is that, let me write down this expression again the one which was written here assuming that D is a not a constant is the way it is solved is given like this now suppose at a steady state. So, this is point number 2 that is a point number 1 please remember these. Point number 2 at steady states; obviously, del C del t equal to 0.

Steady States means nothing is varying as a function of time, even the composition also, if that is the case then equation become very easy it is correct. So, you can integrate it very easily and you will find out C will be let us do that, if I integrate that what will become, C will be a straight line function C 1 plus D into some x am I right C 1. So, this becomes C 1 1 (Refer Time: 13:50) then D it will be like this somehow, there will be 2 constant because it is a second order functional equation.

So, that is also much very easy to solve, one you will need to find out these functions C 1 and C 2, when that is C 1 and C 2 will be mostly exponential functions because in the mathematics you must have read that if such a kind of things has to be solved; actually we can assume this much easily because it is only dependent on x. So, therefore, there is the this will be the del will become D, it will no longer be del that is much easy to solve. So, there are many such different situations are given in the books and I suggest that you look into it and solve that expressions. So, let us me let me go back into the slides and show you how things are done.

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I will just go to directly to these Fick's second law of diffusion, that is what I said this law is nothing Fick's first law is not much used and it is own unless we know the concentration function of distance Steady state is basically a special case remember that, and if you know the concentration of 2 points in a medium along the direction of diffusion we can calculate easily the flux. To give you an example let us see the example then we will get back that is better.

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Let us suppose you know in case of Chemical Protective Clothings, Methylene Chloride is commonly used as a ingredient of paints remover, sometimes what happens the cloths are attacked by the by the some paints or some kind of a dots. So, we can use Methylene chloride to remove that, besides being a it is a irritant basically it creates problem on the on the skin it may also be absorbed through the skin. So, when using this paint remover we need we must use protective gloves that is mandatorily, but if butyl rubber gloves which is normally used in the in the labs is very small thickness 0.04 centimetre are used. So, if it is used that much thick butyl rubber gloves then what are the diffusive flux of this hazardous chemical through these gloves.

We need to know only the diffusivity D because D is a constant is a 110 and 10 minus 8 centimetre square per second, and you know very simple the surface concentration C 2 is given as 0.02 gram per centimetre cube and C 1 is basically a 0.44 that is come basically from the concentration of the Methylene chloride used. Now we can actually divide as a problem in simple way.

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Suppose this is your paint remover that is where C 1 is there and this is your glove which is definite thickness 0.04 centimetre and this is C 2 C 2 is concentration in the skin because C 2 is the level in the skin which will not create any irritation or any kind of a infection. So, that is 0.04 02 actually gram per centimetre cube. So, we can write down flux J is equal to minus D del C del x that is equal to D C 2 minus C $1 \times 1 \times 2$ we have seen that and let us calculate that. So, D is given, C $1 C 2$ are given and $x 2$ minus $x 1$ is 0.04 centimetre. So, what do you get? You get 1.16 into minus 5 gram per centimetre square second is the flux.

So, that is this number of or moles actually of Methylene chloride which is basically at coming to the surface of the skin and it is not very dangerous, if that is the case if that is sorry that is the case it is not very dangerous, because this is very small a number. So, that is why actually the gloves thickness are actually decided I am just giving a example.

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So, as you let me give another example which is more interesting, that you know if you want to calculate diffusive flux in a during an carburizing experiment carburising I have already explained you in the last lecture.

Suppose a plate of iron is exposed to a carburising atmosphere and in one side and decarbonising atmosphere there is carbon deficient, atmosphere on the other side and temperature is at 700 degree Celsius temperature. If a condition of steady state is achieved; that means, there is no variation of the compositional function of time, calculate the diffusive flux of carbons through the plate if the concentration of carbon at position, 5 and 10 say millimetre, beneath the carburising surface of 1.2 and a 0.8 gram per k g per meter cube, respectively and you can always assume diffusivity of carbon is pretty high because it is a the (Refer Time: 18:56) 3 2 3 into 2 minus 11 meter square per second at this temperature, that is very easy just to apply Fick's first law. J is basically as we have seen D d del C del x and that would D is 3 into minus 11 and this C 1 is 1.2 C 1 is here and C 2 is 0.8 and distance differences are given.

Therefore, we get about 2.4 into minus 9 k g per meter square per second is a flux. So, Fick's first law is really used in a actual expression, because this only gives you the value of flux it does not tells you anything else. So, if you really want to know different aspects of that we need to use Fick's second law, because steady state is basically a special case, we most of our problems are non steady state; that means, it depends on the time. So,

therefore, we cannot actually use Fick's first law so much, that is why Fick's Ficks second law has been derived from the first law.

So, Fick's second law is nothing, but a continuity equation mass balance, we have basically whatever I have done in this board is basically I have done in the mass balance. I have considered 2 plains and calculate the flux differences that is nothing, but mass plans. The form in which equation is used is in this case is based on the assumption the mass conservation, that is the mass of diffusing entity is neither, being created, or nor being destroyed. So, that s nothing, but continuity equation and we know the continuity equation is like this, this is nothing, but different way of writing Fick's second law del C del t is equal to divergence of J and you know gradient is written del J divergence written del dot J please understand that this is divergence and we will now make you show what is divergence.

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Let us see what is divergence, now suppose this is a flow pattern, suppose something is flowing water or gas or something and these arrows indicate direction of flow and the length of the arrow indicates the magnitude of the flow velocity let us suppose. So, suppose if I make a kind of a suppose circle, same diameter ellipse actually how you can see.

Now if I look at it you know if I look at these plots gradient factor fields showing 3 regions 1 2 3 upper one; upper one is basically negative gradient negative divergence midle one you see there is one more divergence what is why it is **so**? Because all the arrows are directed in one directions, there is no change of direction of the arrow. So, therefore, there is no divergence of the path; path is not diverging at all that is it the meaning of divergence. On the top and the bottom you see there is a divergence, on the top you have a change of slope in the negative direction that is why it is called negative divergence here it is positive direction that is why it is called positive divergence.

So, when you basically you do not need to know what is positive negative divergence you must know divergence is nothing, but deviation of the slope lines that is where the divergence comes into picture; that means, divergence is not a slope, slope can be simply a gradient of the any functions as a function of distance, the divergence is a change of direction of the slope now. So, that way we can write down the continuity equation which I have shown you del C del t that is del dot J and J is nothing, but D gradient C and we can put it together and get exactly the same thing what I have done in the in the board.

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So, that is a del C del C equal to D and you know that is the square of del C and this del square time is known as a Laplacian operator in the mathematics and which always denoted by opposite of delta is always denoted in the mathematics, the reason I am talking the mathematic is small because, these are the things is never discussed in the books they simply write the equations, but you must know what is the meaning of each of these terms very clearly.

First of all these equation which is the final which rather more correct equation del C del x equal to del dot D del C divergence of this parameter D del C is nothing, but a second order partial differential equations; obviously, because there is a divergence terms here. We will use the simplified form which is based on the assumption that D is independent of concentration, which is not the true I told you that. So, therefore, you get this expression when you do that remember although, we assume D is independent not independent of composition, but we never bothered in the actual calculations we always considered D is independent composition and solved this differential equation which is much easy.

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Now, next comes is that we can write down expression in many ways the best way is writing this way, which is the double derivatives of the C as a function of x or we can write down this way is a in a single dimension, when you have a simple cases of diffusion in x we can do that.

There are some special cases first special case I have already discussed with you that is this steady state, as steady states the composition has a function of time 0 and therefore, we get this and I told you this C is a function of a x plus b that is what is written in the class in the board, C 2 D multiplied D is the also a constant. So, therefore, concentration profile will be just like a straight line as a function of x you (Refer Time: 24:20) do that. Remember this is a Poisson equation in the literature waves, waves equation this is nothing, but a Poisson equation.

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So, Poisson's equation solution exactly done the same way, otherwise if it not the case if it is no longer steady state then this will be like this and whenever you have such equations you have to solve the equations in a after looking at several assumptions, you can always use infinite medium or semi infinite medium and we are going to show whatever time we have in this lecture how we can actually simplify the solution of the equation that is what I told you I am not going to solve in that case

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Infinite medium means what? Diffusion located at a on a plane of 0 thickness; diffusion means the diffusing species here you see this is medium actually on a plane which has 0 thickness x is equal to 0, that is initial distribution s nothing, but a delta function. What is delta function? Simple like this, this is a delta function; that means, there is a spike at one position x is equal to 0. So, as you go on time what is happening it is diffusing both the sides see here this fellow is diffusing on the both the sides as you go more time and the infinite time it will be fully homogenised.

So, that is what is known as infinite medium; that means, you assuming the medium is very very large in dimensions. So, that everything can be diffused very nicely, that is the first thing we can do, analytically how will you solve this problem very simple.

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You can assume initial condition $x \, C$, $C \, x$ t is equal to 0 is 0 because that is what you assume by, and also at infinity boundary condition as infinity it is also 0 for all t. Just remember the initial condition means only at x is equal to 0 C has a finite composition, at any positions other than that C is 0 that is the initial condition that is what is known as delta function.

So, and you will get this is the solution finally, if you do that that is nothing, but error function solution what you get doing is basically M divided by 2 root pi D t exponential x square by 4 D t; x square of 4 D t is basically a exponential term here and that has that value has to be calculated you now separately.

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If you plot that solution that is what x equal to 0 that is a spike here at you see here then slowly the spike is getting reduced as you see this is D t equal to 0; that means, t equal to 0, t equal to 0.25 that is D t is 0.25 D t will be 0.5 0 2.75 0 to 0.25 and 3. So, when D t is very large or time is infinite, it will be homogenous all throughout that is the idea. So, this plots actually Gaussian type because is this equation is Gaussian you see here this is a Gaussian equation this are all taught in details in diffusion, now this is the best way otherwise you can always assume semi infinite medium and solve the same equation, you will get again this solution that is what is known as error function solution.

So, we will you know you must read it carefully, because as a part of assignments there will be problems based on these equations, and you must know how to solve this equation very easily. Please practice yourself otherwise you will not be able to do yourself just practicing this mathematical equations require some time. In case you do not understand it very clearly or you do not you have problems in even mathematically dealing the equations, please get back to us we will we will put up some ore notes so that you can understand that.

In the next lecture I am going to talk about how diffusivity varies with time sorry temperature, because temperature has a strong role to play in deciding the variation of diffusivity. Because diffusivity D is very important parameter it comes in all solutions. So, diffusivity must be known. As I told you in the lecture that we always diffusivity

independent of x the special variables that is also not correct. If you really want to know how we can solve the equations in which diffusivity is assumed not assumed to be independent of special variables then it is a separate discussion that requires we to you know look deal that problems in the separate manner it is there in the books, actually mortano first time solved the problem in a assuming plane 0 flux plane, but we are not going to do it here because that is a separate issue which may not be required in a first transformations. So, in the next class we will discuss about the time temperature dependent diffusivity.