Phase Transformation in Materials
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Lecture – 14
Mechanisms of Diffusion, Fick's I Law

Well, after discussing about the thermodynamic driving force for diffusion let us move into the how the diffusion happens the mechanisms. You know there are two operators to study diffusion; one which is known as continuum theory. This is what we are more used to it. It takes care of the average movement of a collection of large number of atoms. Whenever large number of atoms moving from one phase to another phase, we just take care of average movements; that means, we need to know average values of this of this atoms. And we always make observation at the macro scale very easy to apply Fick's law which we will see now, because this is continuum.

We are considering the whole system to be continuous, but you know actually speaking atoms do not move like a flock of birds moving in the sky. Atoms moves by jumps and because when the birds are flying they are moving at a continuous space with sudden fixed velocity sometime they will accelerate to decelerate, but they will move. So, we can always define a average velocity very easily, but atoms do not they actually are thermally activated and they actually move by jumps.

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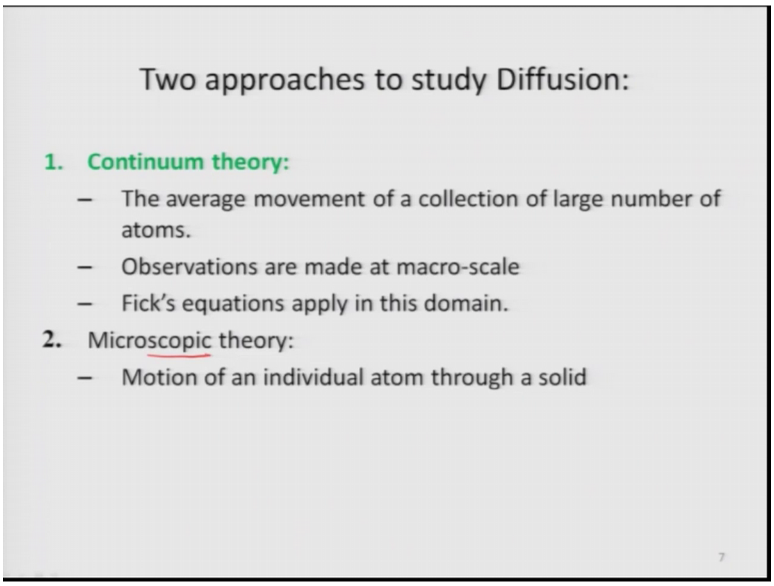

So, therefore, we need to know also, what is the microscopic theory of the sorry of the motions of the atoms if you really want to know what actually happenings to that.

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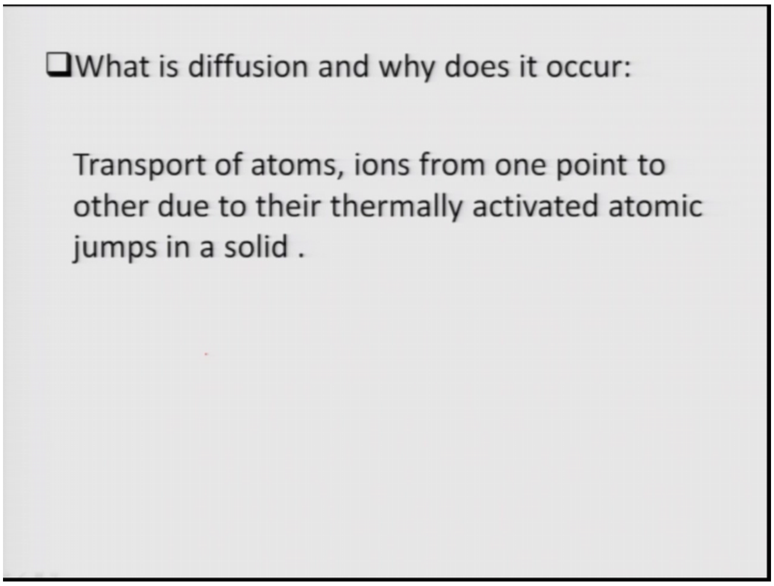

So, first we will discuss you know the continuum theory. Why is diffusion? That is already I have discussed, transport of atoms because of the thermally activated jumps and reason is basically thermodynamics you know this is will tell you what actually happens.

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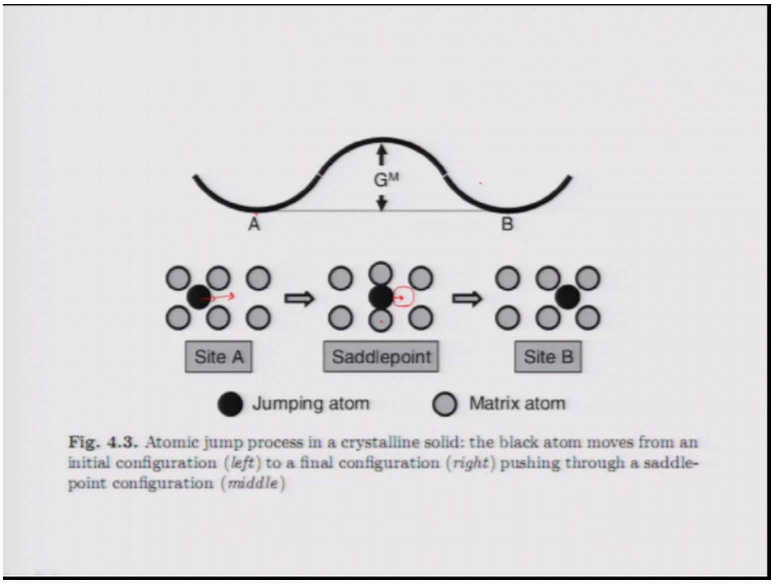

Suppose, this is taken from the book of diffusion in solids by Paul Shewmon and you know this is suppose I have (Refer Time: 02:10) of atoms you see here 1, 2, 3, 4 atoms and there is a central black atoms and there is another flow atoms, but central atom is missing; that means, there is a wide gap. So, now, this atom black atom wants to jump wants to move actually from here to there that is what is discrete jump. Discrete means one step, but it is not like a play that we can simply jump over a barrier and reach like high jump or along jump here it will happen in a steps.

So, when this species will try to jump from here to there it will go through a saddle point. As you see here this is saddle point. Saddle point means the atom will be in between these two grey colour atoms. And if the sizes are different; obviously, sizes will be different and the space available here in between these two grey colour atoms is not sufficiently large enough to accommodate this atom black atoms. So, the black atom will push these grey colour atoms now; that means, it requires certain amount of a barrier to cross, because pushing requires energy. And that is what is shown here. So, once this pushes these two atoms it causes this barrier and then reaches this position here very easily.

So; that means, diffusion happening at discrete steps. First step is that atom moves from here to this position, then it pushes these atoms second step and finally, it reaches from here to there. In the whole process atoms moves from A point to B point, A and B both are is a low energy configurations as you see here on the curve, but it also goes through a barrier just like a you know in Olympics people have hurdle race. So, if somebody is coming there is a hurdle he jumps over the hurdle and reaches the point B. So, atom A actually doing that, atom actually passing through a passing through a barrier or base basically jumping over the hurdles and reaching the point B. So, this is how actually atomic jump that happens in the regular in a species. This is microscopic picture of the system.

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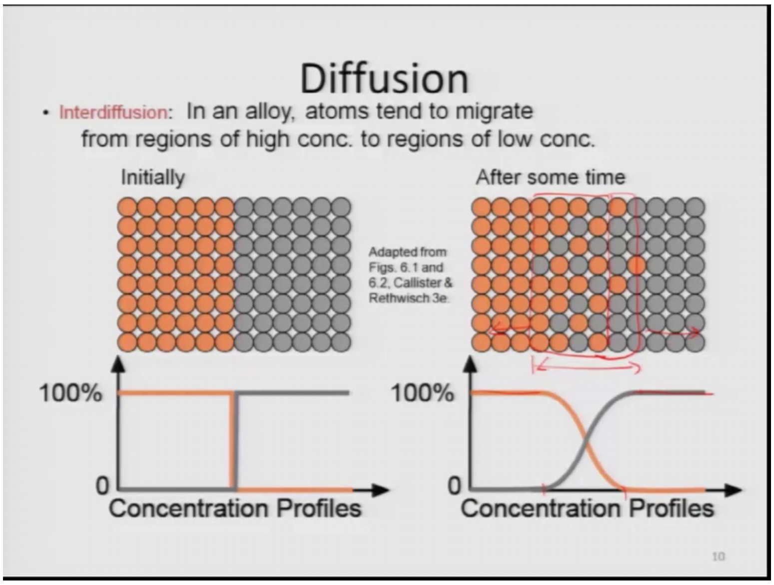

Now, let us do it for a couple of you know collection of atoms that is one atom. And the what is known as the inter diffusion? Inter diffusion means one part to other part. Suppose, initially I have two you know again taken from Callister because this represents a nicely written there you can see here this is one colour of atoms. Let us suppose this is A type and there is a another colour atom here in the right side is called B type. And if I plot the concentration profile in this region is 100 percent A in the region 100 percent B.

So, therefore, here to here there is 0 percentage A, here to there is a 0 percent B that is what you see here. So, what happens if I if I just allow at some time temperature from some time what will happen; obviously, some B atoms will move from the right side to the left side some atoms will move from the right left side to right side that is what is done in the concentration gradient. And if we if it moves there will be a range in which inter mixing will happen. You see here this is where all at A atoms this is where almost all are B atom this is where almost all are B atoms and this is the range where you have to inter mixed between A and B together; that is why we call inter diffusion, because they are inter mixed.

So, this layer is what is a diffusion zone actually called that is why the inter mixing is happening. Now if you plot the concentration gradient what will happen. It is completely A here till this point it is completely B here in this point and in between these two inter mixer of A and B. Now this diffusion zone will slowly expand they will move from this position to this A side this position to the B sides.

This is what is microscopically will happen and it is understandable, but each time this collection of atom moving from A side to B side or vice versa the process which I have discussed with you here will happen so; that means, each atom will pass through a barrier diffusion barrier. And things will happen like that way. So, in an alloy I would say very nicely that atoms tends to migrate from regions of high concentration region to low concentration region, but does not matter the high or low it is basically at the concentration which I have drawn in the last class is basically tells you it is happening down the chemical potential gradient.

Now, let us look at few interesting stuffs does not mean that if I have only A atoms in the in the system there will be no diffusion well that is not the correct answer you can always have self diffusion like if I have pure copper still copper had now from one point it diffused to other point that is mainly because there will be always a vacancy you know there is always some finite number of vacancies present at any temperature of absolute zero. So, because of these vacancies atoms can diffuse.

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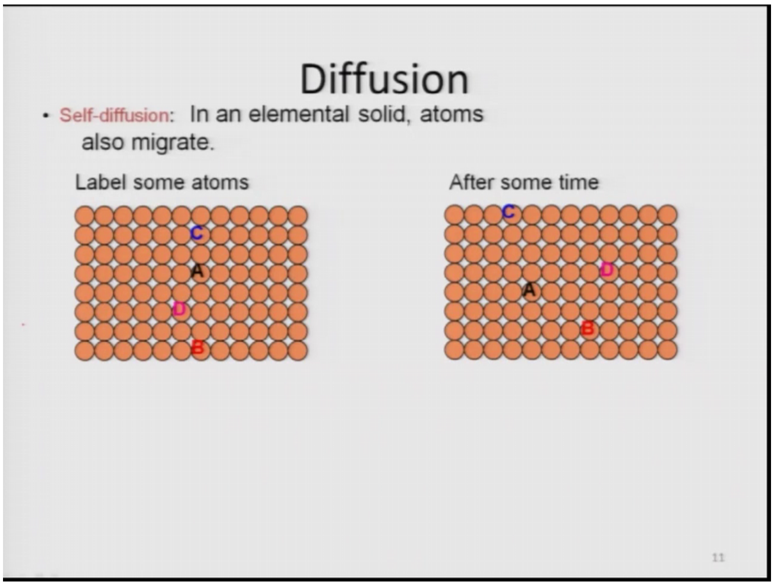

So, here actually let us level some atoms like A, B, C, D. Now what happen you see here after some time A atom has moved from here to some where there the you know left side of myself D atoms move at right sides, C atoms will move at left side, B atom will move in the right side there is; obviously, have I written random because that depends on availability of the vacancies atoms will move.

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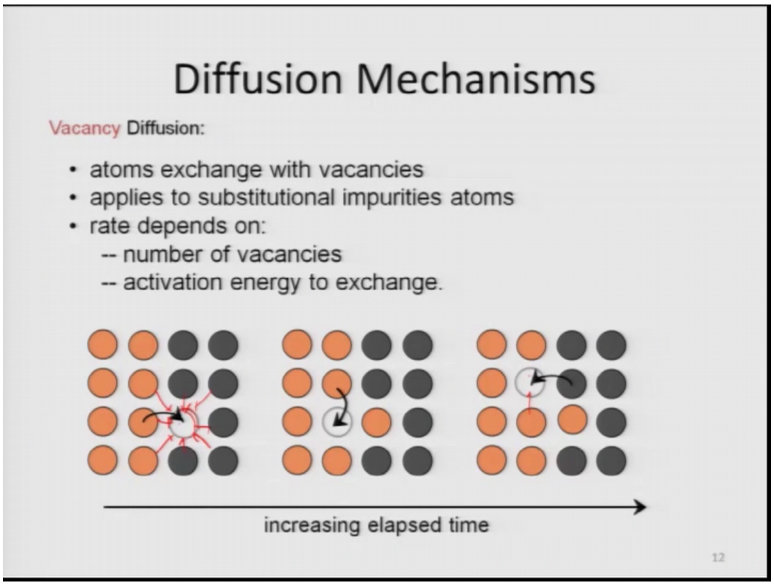

Now, so basically what I am telling you for the last you know few minutes that atoms do move from one part to other parts, but; obviously, movement requires presence of the vacancies that is exactly I have shown you at the beginning, when I showed you the diffusion barrier.

So, vacancy is the most important you know vacancy diffusion is the most important diffusion mechanism in the in these materials. And here there is a vacancy you see here this is a atom is missing here. So, therefore, this atom can move here this atom, this atom, this atom, this atom, this atom, any atoms can move depending on the which has who has the sufficient energy to cross that barrier. Now this vacancies are only applied to substitutional type atoms here we are talking about atoms are almost similar sizes; that means, they can only sit in the lattice positions they cannot sit in the interstitial positions.

Here, the rate will depend upon number of vacancies present and; obviously, the activation energy to cross that barrier which I have shown you few minutes back. Now we can also have see here these are the diffusions happening see this black arrow shown the atom has diffused from here to this. So, vacancy has moved also. So, the vacancy moves then the another atom can move into the vacancy. So, another configuration of atom will happen the vacancy has moved above. So, basically diffusion can be also to reduce the movement of vacancies. Vacancy is moving from here to there and in the process atoms are also interchanging their positions many situation possible.

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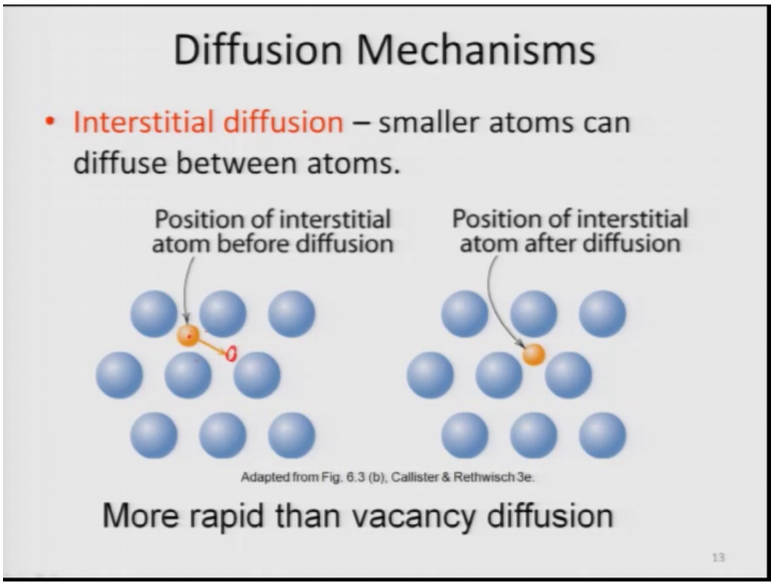

But similar situation is not true; when we have the interstitial atoms like carbon and steel, boron in a nickel aluminium alloy. Atom interstitial is very small. So, they will be sitting interstitial positions. Interstitial position means in between these lattice positions there will be interstitial position like **(**Refer Time: 09:45) I already you again taken from callister. As you see here the atoms actually the interstitial (Refer Time: 09:55) atoms at the beginning was at these positions then it has moved there. For the interstitially assumed to move you do not need vacancies. Vacancies are present all throughout the system, because these are the voids. So, there were large number of voids are automatically present. And only thing remain is that this atom needs to push these two atoms and reach here; that is what needs.

So, that; obviously, this also this atom also needs to pass through barrier, but suppose the sizes of these atoms are very big. So, that void size is big, then what will happen this size is enough the void size is much enough the for the atom to smooth movement of the atom from this position this position to this position, but that is not the always case. There will be always the size is available here will not be sufficient enough for the this small atom to move. So, there will be always some pushing is required and this pushing is leads to diffusion barrier, but whatever be the reason these diffusion by interstitial atom is much faster. In fact, all are might be faster than this substitutional atom diffusion, because of the availability of large number of vacant positions and the size of the this smaller atom ok.

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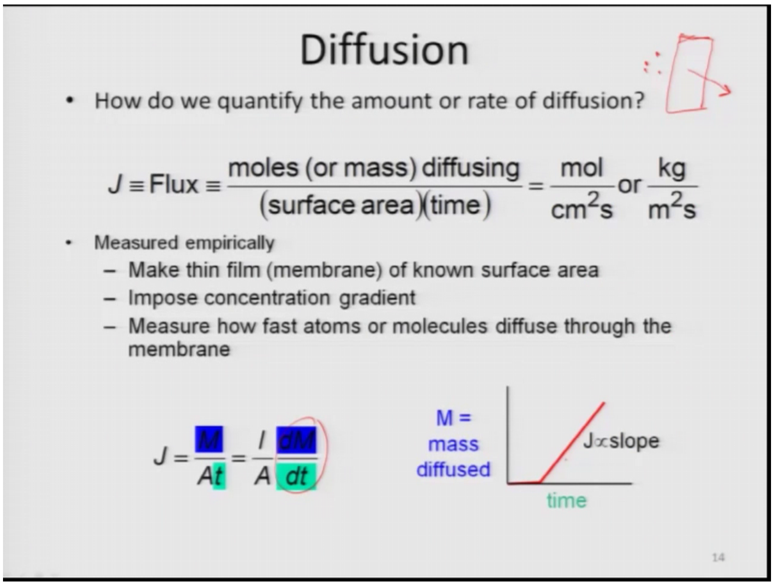

So, now you got an idea, because we cannot discuss diffusion in lectures we need to you know wind up somewhere; you got an idea that diffusion do happens by atomic movements, that is what is the microscopic feature of diffusion.

Now, let us put it into mathematical form Mathematical form in the sense mathematical form of equations. So, whenever we talk about movement of atoms, we need to talk in terms of flux. Flux means number of moles diffusing per unit time per unit surface area. And because flux is a vector so, therefore, it has must be directions. So, whenever we talk about flux, we always assume; suppose unit area like this is an unit are and we assume diffusion happens direction perpendicular to this surface area so; that means, if the atoms here they are moving through this area in the direction perpendicular to this area in certain times. So, the flux is basically given by moles per unit area per unit time.

So; that means, this is unit of k g per meter square second, because there will always be some moles per centimetre square second or moles per meter square per second it will be either mole or k g it is a mass or number of atoms whatever it is you can weight you can define. So, this can be measured if a very very nicely remember this is a measureable quantity flux can be easily measured. You can make a thin film or known surface area you can always impose a concentration gradient and you can measure the number of atom passing through that thin film. So, it is very clear that J which is the flux is nothing, but M by A t. So, we can write down I by A d M by d t. What is that? Let us look at it. So, this is the mass and time, because it is nothing, but d M by d t you see here we can always write d M by d t, I is a constant here d M by d t we can write down. So, d M by d t is nothing, but a slope of this curve; initially it has zero slope then there is a finite slope sorry; there is a finite slope so; that means, J is proportional to the flux; where this slope of this curve that is the mass transport by time.

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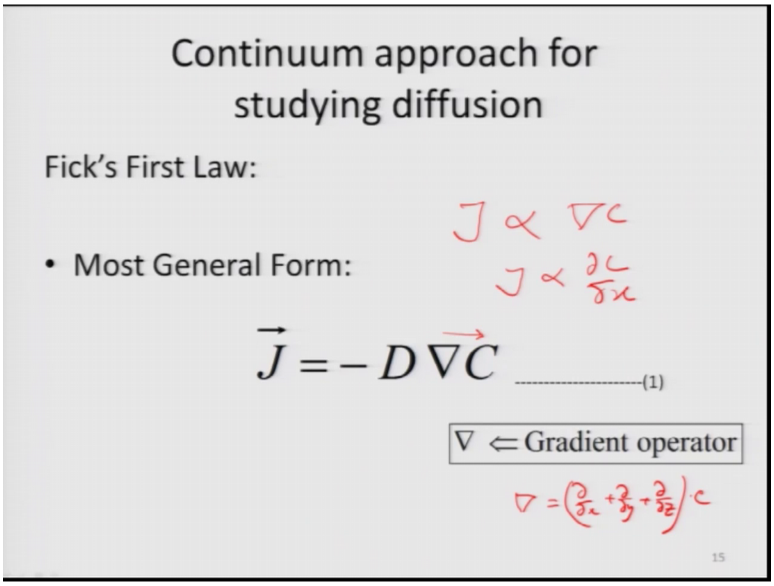

So, we can actually put it down in a very nicely; that this is nothing, but J is equal to minus A constant and concentration gradient, because this one which I have shown you in the last class this is nothing, but a gradient that is the gradient of this slope is nothing, but a gradient d M by d t.

So, J is proportional to delta C which is or J is proportional to one dimensional del C by del x, that is the gradient here you see here slope anyway. So, this is what is known as first Fick's first law and J has a directions. So, del C also has a directions, diffusivity D is a basically tensor quantity. And this delta is basically gradient operator and it tells you if I write delta is nothing, but del del x del del y plus del del z in 3D and you operate on a concentration. So, therefore, it tells you constant gradient in three directions x, y and z. So, this is my first law of Fick's first law, where this is basically the law of Fick's. And this is we derived from the continuum mechanics or continuum approach we are not using atomic jumps; obviously, this can also be derived to using atomic jumps this is there in the books.

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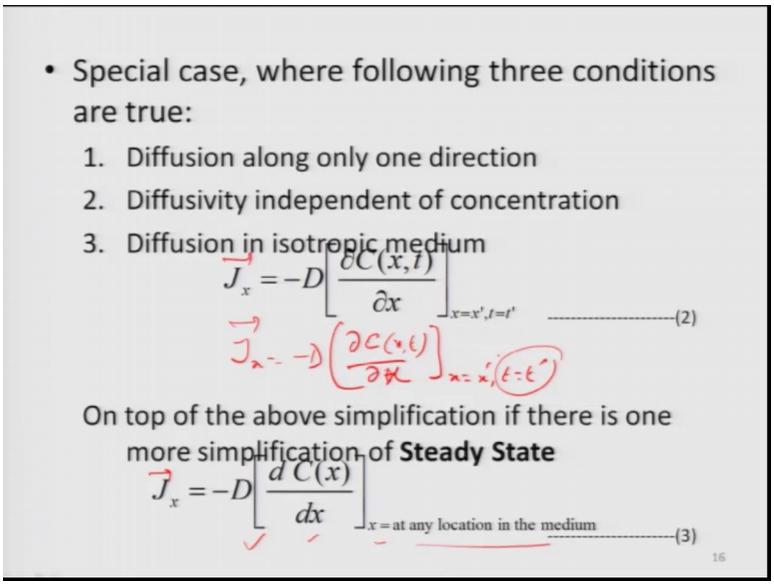

Now, something has moved up; I will explain it special case for the following conditions are true; suppose diffusion happens you know only one directions. We can always think of a 2D thin film and diffusion already called as a supplying from one directions and D is let me explain what is D? D is a constant it is known as diffusivity. Diffusivity is stability of a material or atom to diffuse. That is what a diffusivity a more will come when you discuss about the other laws. And the when the D is constant in an isotropic medium we can always write down J x is minus D del C by del t at some time and some space. That is simplifies our life because we can actually use a one dimensional format of the equations.

On the top of the above simplification, you can always write down. So, this is x always write down steady state. Steady state means suppose I have down a experiment at after long time and things are reached its steady state or steady state means. So, there is no change of time or there is no effect of time on the concentration gradient. Then we can write down J x is nothing, but J x is nothing, but minus D del C del x del has vanishes become D because x C is only function of x no long as a function of x and t, because t is it we have passed we have actually done the experiment for large time influencing large time you k. Now, therefore, things has become stabilised.

So, temperature time has no effect only the space variable has effect. So i we can write down this; this is a very simple equation we can integrate it very nicely, because we have del C by del x sorry; D C by d x and at any location x equal to t x equal to x not t. So, this t equal to t prime vanishes the moment you assume steady state. These are all assumption we are going to make, when you develop our phase transformation rate theories. So, yeah here it is showing how the what the steady state. Steady state mean concentration of diffusing entity of the given location does not change with time.

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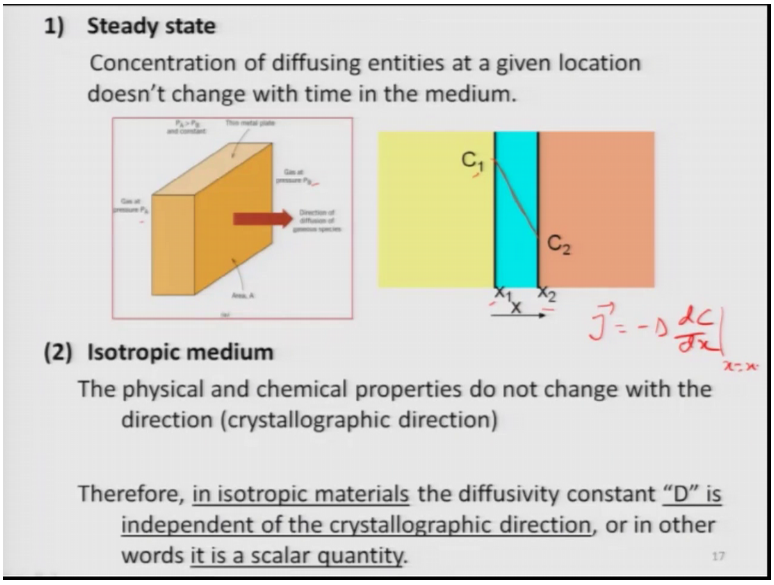

Suppose, see have if you have a you know this is thin metal plate, you have gas pressure as P 1, gas pressure as P 2. So, this is the way diffusion will happen gas atoms will diffuse to these its just like a porous membrane and you have a gas in one side has a high pressure other side is a low pressure.

So, there is a concentration gradient, and because of that diffusion will happen this is going through passing through area a. And if I plot in one dimension, because we can always assume this is happening in only in X directions; this is what will happen to concentration difference at X 1 that is on this side at X 2 that is on this side and there is a concentration gradient you can see here del C del X is present, but it does not depend on time; this is completely steady state thing. So, that is why its depends on does not depend on time; and we can use that flux is equal to minus d c d x. This is what we actually used to see all metallurgists or metal scientist we used to see such a kind of things such a kind of you know derivations of the flux, but this derivation comes after making some assumptions. And we assume it is isotropic medium; that means, physical and chemical properties of the of these you know system the thin metal plate is does not depend on the crystallographic directions it is all same it is a isotropic system.

Therefore, in isotropic material diffusivity constant D is also independent of the crystallographic directions, in a other words it is an scalar quantity. D becomes a scalar quantity, because t is independent of time D independent of directions or x, y, z anything. So, therefore, it is a scalar quantity we can treat actually it is a like a scalar quantity it is not a scalar quantity. And we can also integrate because this is a differential form of equation integration is required very easily; we can get the total flux and all this stuff ok.

Now, you know just to explain you what is gradient? You know what is gradient.

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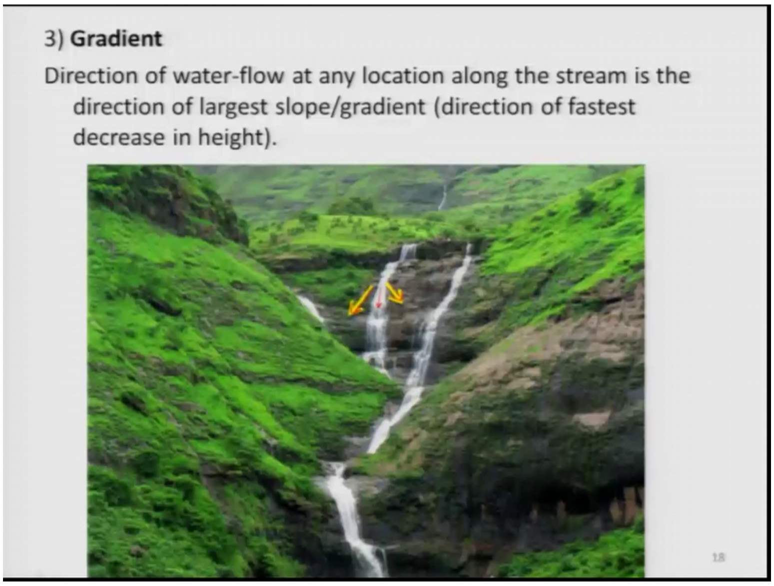

If you are looking at a waterfalls, and you know that the water is falling passing falling down the you know slope. So, at any locations this is suppose this is a location this is one gradient here; this is another gradient there this we are taking slopes, but water is passing through this so; obviously, water will always pass through this. So, steepest gradient directions that is normally the case, because energy can be reduced largest if it is flowing in the steepest possible direction; that is why you have waterfalls that is a main reason.

So, direction of the decrease direction of fastest decrease in the height is what dictates the diffusion directions same as like here. So, that is why the saddle point concepts is very important, because that is why the saddle points barrier can be reduced extensively. So, this is the first law of diffusions you know diffusivity or diffusion coefficient D i have already told you it is a constant, but it is not a scalar quantity all the beginning which is basically tensors.

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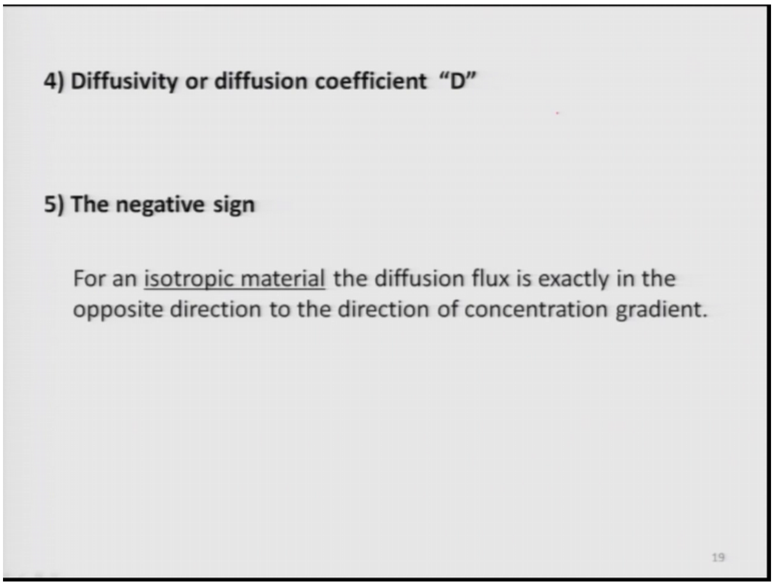

But, we can always assume in one dimensional case assumed medium to be a scalar quantity.

Negative sign: for an isotropic material diffusion flux is exactly opposite direction in the opposite direction of the concentration gradient. That is why it is a negative sign, because diffusion happens always in the opposite direction opposite to the down concentration gradient. So, that is what is happening concentration gradient is concentration is reducing from here to there that is why we have to have negative sign to obtain the flux ok.

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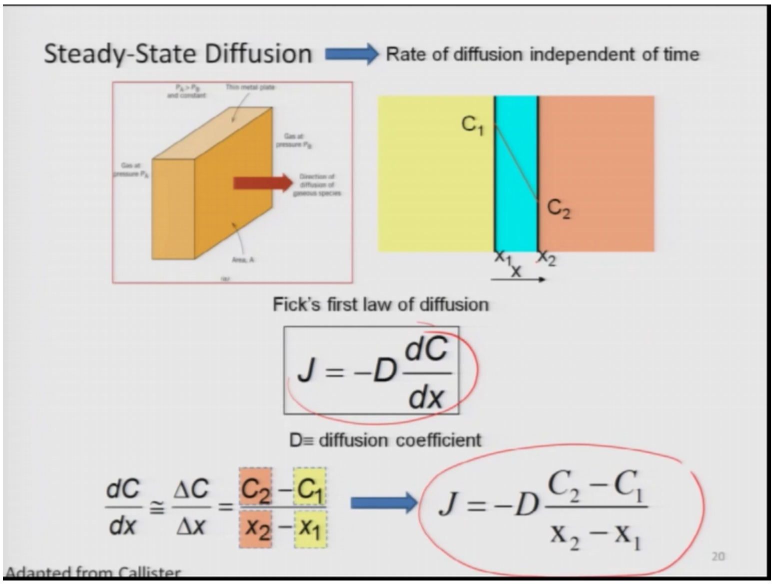

So, I have already explained you this; just to tell you that this is the Fick's law. We can always do a simple maths and del C by del x can be written as C 2 minus C 1, X 2 X minus X 2 therefore, in a microscopic scale we can write down the flux Fick's first law as J equal to minus D the concentration difference divide by the distance difference of the distances x and y ok.

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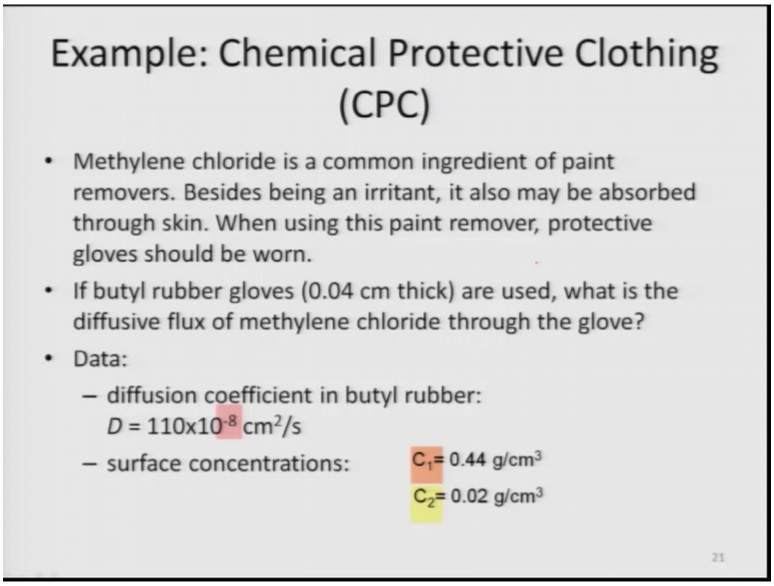

So, let us not spend more time on that; we will get to in the next lecture Fick's second law, and how to solve this different aspects and how we can actually explain different phenomena which, we observe in the real experiments.