# Phase Transformation in Materials
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## Lecture – 13
## Introduction of Diffusion

So, students we will be discussing today diffusion, and diffusion is a important aspects. But before is start that let me just clarify few things about the free energy composition diagrams which I have drawn in the last lecture for the peritectic system. See this is a peritectic phase diagram. On the right side you see here there is a peritectic reaction, and that is correspond to a horizontal line or curve on the phase diagram.

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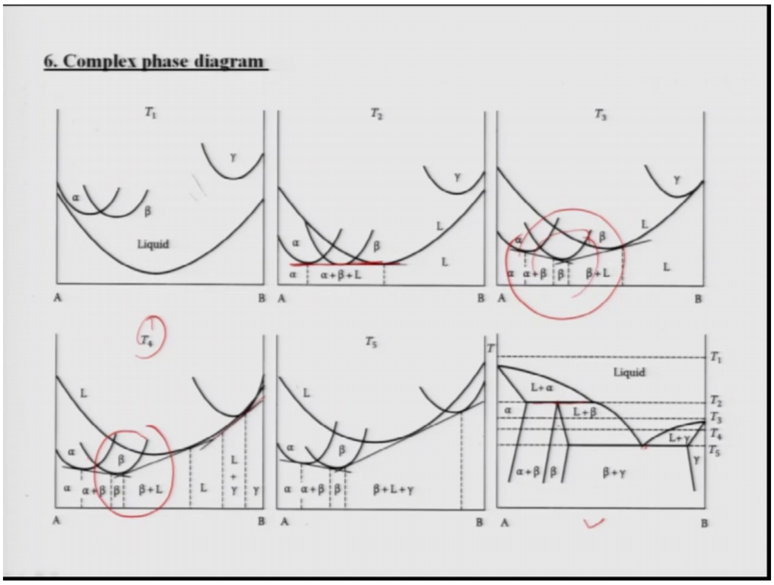

6. Complex phase diagram

And that peritectic reaction is followed by an eutectic reaction here. So, we have alpha beta gamma 3 solid phases and a liquid.

So, as you clearly see here at any temperature the free energy composition diagrams will have free energy composition free energies of 4 phases. Liquid, alpha, beta and gamma. Say at T 1 which is at high temperatures above the mainly temperature of the both the models you can see the liquid is this more stable phase. On the other hand alpha beta and gamma free energy curves are shown at on the plot. At T 2 that is on the peritectic isotherm that we referred as a T p in our in the drawings that I have drawn in the last lecture. As we see here the gamma phase is not at all stable. So, that is why gamma is much above on the other hand at the peritectic isothermal liquid alpha and beta both all 3 are actually in you know, any equilibrium or coexisting in equilibrium. So therefore, there is a common tangent to all of them that is what is you clearly see here. There is a common tangent here common tangent means common tangent to 3 curves; that means, at the temperature T 2 the gamma and the chemical potential of the alpha liquid and liquid and beta are actually same.

Similarly, at T 3 T 3 is this temperature little below the peritectic isotherm. At T 3 you have a alpha, alpha plus beta and liquid plus beta and liquid are present. So therefore, you can see here actually there are 2 tangents, clearly 2 tangents one tangent between liquid and the alpha and beta that is giving the alpha and alpha plus beta region, then a tangent between beta and liquid that is gives you beta plus liquid and liquid. And in between the free energy of beta is the lowest. This is where actually the there is some I mean drawings are not clear that is what I wanted to show you. So, at T 4 basically again at T 4 is what is a temperature above the eutectic temperature, which is additional temperature showing shown in this diagram. You can clearly see again it is alpha plus alpha plus beta and beta, beta plus liquid. But on the other hand because at T 4 you have a liquid plus gamma region. So there must be a common tangent between gamma and the liquid. That is what is shown here this is the common tangent between gamma and liquid. So, that is why liquid plus gamma and gamma both are actually phase feel happier. So, this is the most complex one to draw.

At T 5, which is eutectic isotherm or is actually little below the eutectic isotherm rather sorry, iso eutectic isotherm not little below. So there is a tangent between T common tangent between beta gamma and liquid because at this temperature eutectic temperature 3 phases must be at equilibrium. So, that is the difference you see here and on the other hand left side is looks similar. So, left side curve actually similar T 5 T 4 and T 3 there is no much change.

So, please make changes and try to that be very clear about the things which I have drawn here, and there very clearly means to be understood. So, that is about the free energy composition diagrams. We will not go into details of the various other phase diagrams, but if time permits we can actually discuss case by case. So, as I said in the beginning of this lecture we are going to discuss diffusion. And you know what is diffusion. So, as you see for the last whatever lectures may be I do not know 5 or 6 lectures which I have taken, to together it is very clear that thermodynamics plays a role in dictating the equilibrium. In the sense what are equilibrium phases will be appearing, at a particular temperature pressure condition. But you know to achieve that equilibrium system actually passes through many steps. And that is this object of phase transformation system can pass through an metastable equilibrium to a stable equilibrium distance can pass through from a you know unstable state to stable state. So, whenever these things happens; that means, whenever the phase transforms from one state to other state it is important to know how long it takes, and when the phase transformation will be half finished or quarter finished or even 10 percent of the phase transformation lower. These answers will come always from the diffusion because diffusion talks about the atomic motion.

So, I just discuss about basic concepts of diffusion, and I will just you know explain you how things happens. Let me just close this one and open a new PPT presentation where things will be shown to you. As you know diffusion is basically nothing but mass transport.

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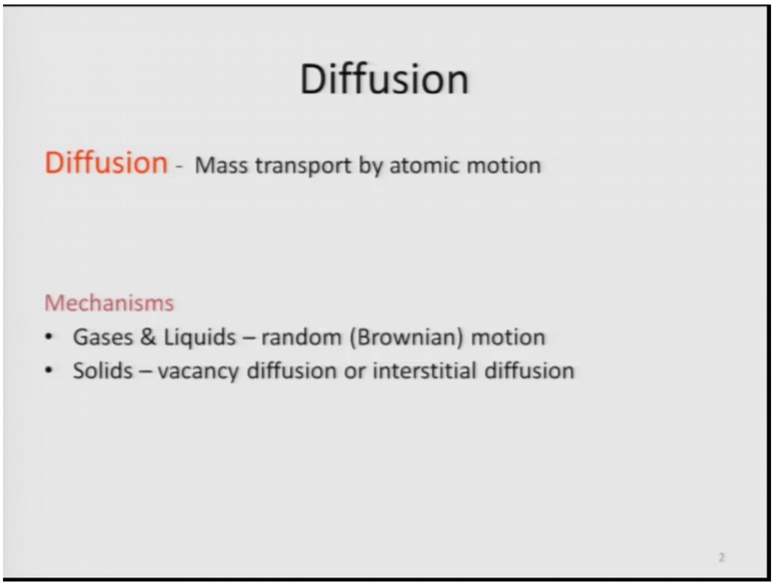

Diffusion

Diffusion - Mass transport by atomic motion

Mechanisms
- Gases & Liquids – random (Brownian) motion
- Solids – vacancy diffusion or interstitial diffusion

Obviously any phase transformations if it is a diffusion all actually, then it must be happening by transport of atoms from one phase to another phase. Like if liquid water is getting transformed to ice, so that means, the atoms or the molecules of water is getting transported from the liquid phase to the solid phase via an interface. Similarly for metals whenever you have a transformations some solid or solvent it may be you do not know which one is the physics involved will be moving from one phase to other phase and that is what is known as transport.

Now, in gases and liquids; obviously, motions of liquid atoms; obviously, random and we do always tell it is basically Brownian motion because atoms can hump and collide and move, but in solids diffusion happens and transport happens not by brownian motions, but will see it in few minutes now vacancies and interstitial. So, that is the most important things which you be will be taught because we are dealing with specifically more solid, solid transformations and a beta liquid solid transformations. So, the transport of atoms from one side phase to another solid phase which basically happens by vacancy or interstitial diffusion. So, that is very important.

Now, you know diffusion is very important. Many, many, many, many things which happens in the surrounding as well as in our engineering field. Like you know as you know if you have for if you are hungry and you buy pizza from some store, and then once you keep the pizza the corner at a corner of a room.

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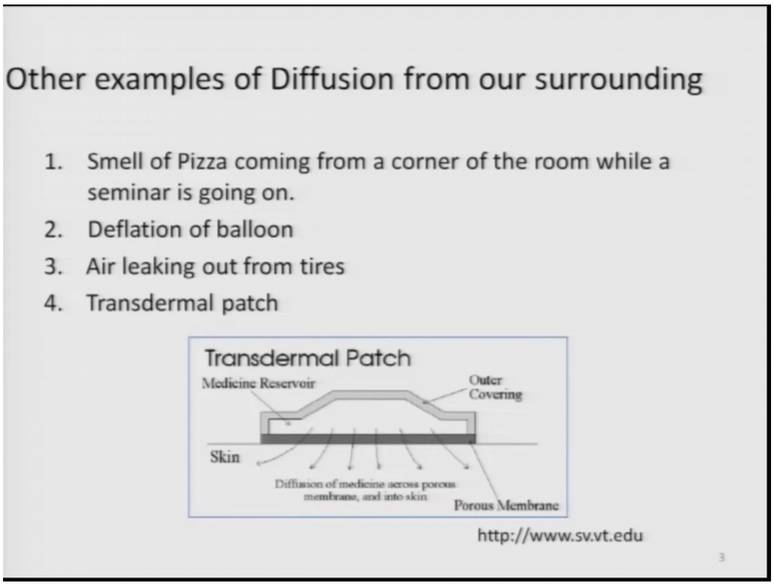

Other examples of Diffusion from our surrounding

1. Smell of Pizza coming from a corner of the room while a seminar is going on.
2. Deflation of balloon
3. Air leaking out from tires
4. Transdermal patch

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You know the whole room will be filled up with the smell. Thus basically gas molecules transports very fast, because they are getting transported by a brownian motion by collision with each other. Similarly deflation of balloon the balloon actually gets deflected because that molecule or the gaseous molecule gets transported by a from one inside the balloon to outside.

Similarly, I if you are if you are using bicycle or what that motor cycle, you know if you the moment you open the tire the knob. The air leaks out from the tires; that means, there is a transport of molecules. Not only that there is another important example which is in the in the in the you know used in the medicinal industry is basically known as transdermal patch. This is the patch which many, many of the patients use to keep the things with the body part warm, that is very important. What is that? You see here there is a there is a skin sorry, there is a skin here and skin actually is covered with an with a with a patch. And this patch has a medicine inside it. So, if you keep it the medicine and the slowly medicine will diffuse the screen, correct? Because this membrane which is put above the skin is basically porous. This is the way we can actually locally transfuse some medicine into the body. So, this is nothing but a diffusion of a where it is a liquid because medicines will be liquid form and it will transport it will be transported via this membrane into the body.

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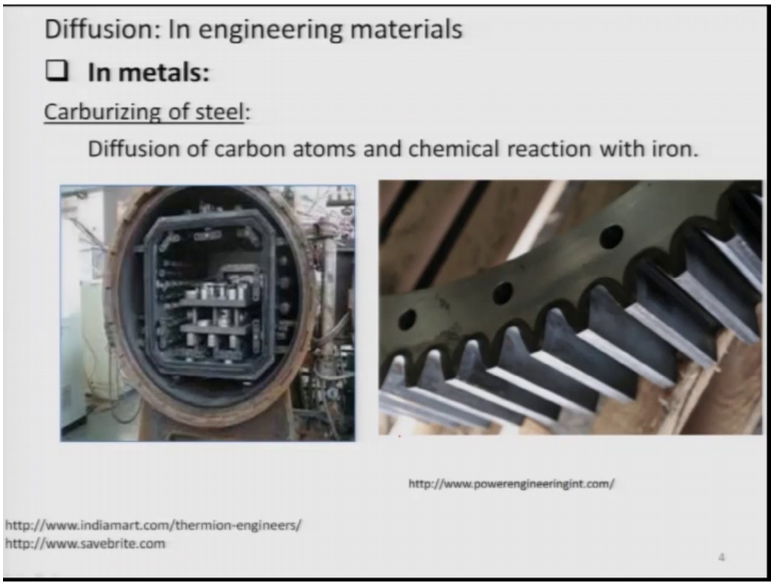

Diffusion: In engineering materials

☐ **In metals:**

Carburizing of steel:

Diffusion of carbon atoms and chemical reaction with iron.

http://www.powerengineeringint.com/

http://www.indiamart.com/thermion-engineers/
http://www.savebrite.com

So but in the industry there are many see the you know the carburisation of steel which you may not be knowing, but this is a widely used technique to make the gear teeth harder. Normally gear teeth are actually after it is made after a machine out in normally will not be hard enough to resist the wear and tear during the motion.

So, to make it harder we normally inject lot of carbon inside these. So, that some hard phase is formed and this is done by putting this gears inside a furnace at a higher temperatures where the carbon is here gas is present. And the gas from the gas carbon gets deposited onto these onto this gear surface and then starts slowly diffuses inside it.

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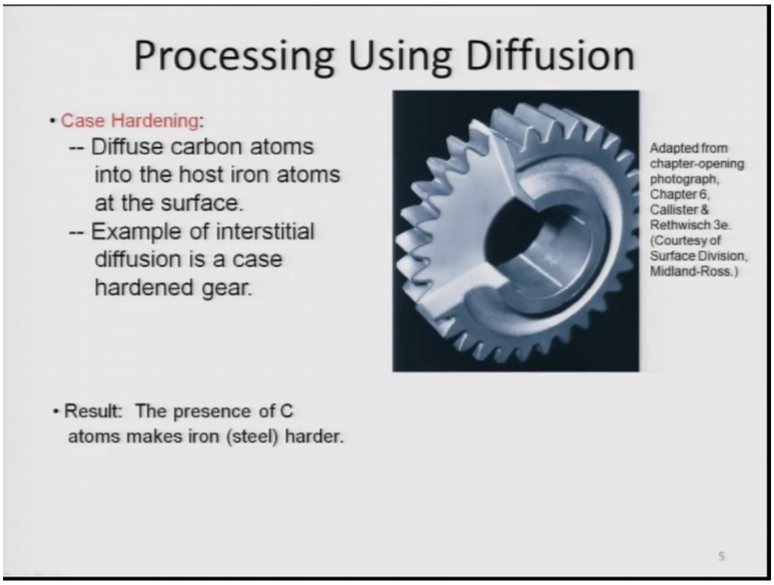

## Processing Using Diffusion

- Case Hardening:
  - -- Diffuse carbon atoms into the host iron atoms at the surface.
  - -- Example of interstitial diffusion is a case hardened gear.

Adapted from chapter-opening photograph, Chapter 6, Callister & Rethwisch 3e. (Courtesy of Surface Division, Midland-Ross.)

- Result: The presence of C atoms makes iron (steel) harder.

So, this is another example and you know this is what is shown here this is known as case hardening in the in the in the industry, because case is outside layer this is a section of the teeth it is it is taken from the callister books you see here. The eliminatory books available you know anywhere, in the even the internet. So, this is these are the teeths as you can see all you see there is a thick black layer around it. This layer has formed because of the carbon diffusion from the surface to inside. And because of this diffusion of carbon some hard phases will form you know for that you need to know the little bit of steel metallurgy which will be taught later, and this hard phases will protect these teeths to withstand the severe atmosphere of wear tear all even corrosive atmosphere. So obviously, carbon has interstitial elements it is not which is which will be diffusion inside a iron lattice because there is a steel piece.

So, diffusion in solids diffusion actually happens solids ok.

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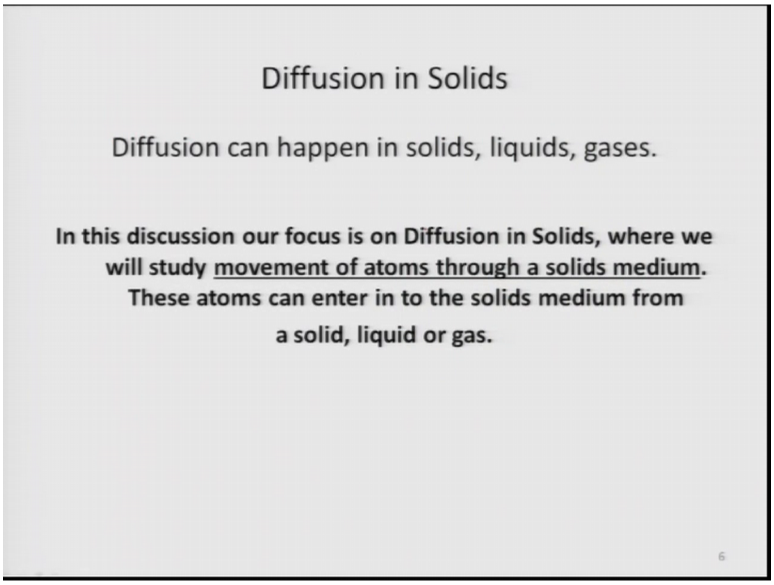

## Diffusion in Solids

Diffusion can happen in solids, liquids, gases.

**In this discussion our focus is on Diffusion in Solids, where we will study movement of atoms through a solids medium. These atoms can enter in to the solids medium from a solid, liquid or gas.**

You know, but most of our discussion which we will be doing here it will be basically based on the diffusion solid. And diffusion solids is basically deals with moment of atoms. Moment of atoms just solid medium, these atoms can enter can either into a solid medium or from a gas or liquid or solid. That is what I have given you example of a atom diffusing from. So, gas because in carburising we are keeping carbon dioxide or a carbon monoxide gas at a high temperature in which the gears actually kept. So therefore, from the gas carbon actually slowly diffuses into the solid steel.

So, it also can happen liquid, because liquid phase carburising or liquid phase nitrating is also ether existing. Or I have given a example of a transdermal patch in which liquid medicine is slowly diffusing into air and the body so, it is possible. Now we before we go into the various approaches of the diffusion, let me just tell you that why the diffusion actually happens. The reason for diffusion happening is basically thermodynamics. So, in the next few minutes we are going to spend time to explain you how diffusion actually happens and what is the basic reason for diffusion to happen.

So, I will go to the board and draw few pictures. Let us suppose I just take 2 pieces of metal or 2 pieces of alloy actually, let us let me check for few colour chalks, otherwise it will be difficult for you to see it. So, if I suppose if I take 2 pieces of alloy. One piece is like this and other piece is like that ok.

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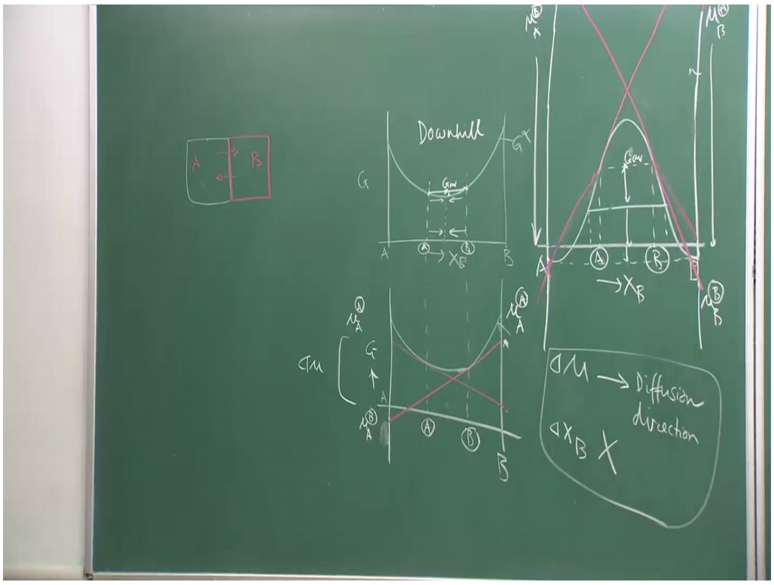

So, let us suppose this is A this is B and this is welded here that is why there is a white and pink colour lines. So, this is welded. Now I take these you know these 2 joint pieces at a high temperature. So, the moment I keep it high temperatures atoms here will diffuse this, similar atoms here will diffuse to this because there is a compositional difference. So obviously, diffusion will happen through this interface because the composition of A in the A is different then composition in B. So, because of that there is a gradient automatically. Now, but this gradient is obviously, in a very microscopic sense they responsible for the diffusion to happen, but that is not the main reason. Main reason for diffusion happening is the thermodynamics.

Now, if I simply draw free energy composition diagram, similar to the once which I have drawn in the lectures previously. Now let us suppose this is the free energy composition diagram free energy of the phase which is taken in the both the alloys. Both the pieces and this is suppose G of alpha, am I clear? So, that is the free energy composition diagram of the free, because it is it is of same alloy little bit composition differences are there.

Suppose this is steel only carbon concentrations is different here to there. So therefore, the free energy curves will be only 1. Now if I if I mark the compositions here let me just mark by white line composition here composition there for A and B. Suppose this is A metal composition or B this composition. Now obviously, free energies of the solid solutions are marked by these 2 points. Now very clear the average free energy system will be somewhere like there right. Because we have joined them together this is the average free energy of the system, am I clear? That is why this looks like. So, because of the average free energy is you know much higher actually quite higher than the free energy of the system at this composition. You see here this is the average free energy of A and B. So, because of that the system can reduce the free energy by again going like this way; that means what? System can actually atoms can diffuse from A to B, and B to A that is what it is. So therefore, there is a thermodynamic driving force for the diffusion to happen. And this is very evident this thermodynamic driving force tells you diffusion which happen at down the compositional gradient. Composition if some suppose element is higher here lower there composition tell that element to diffuse from A to B. So, when it goes from A to B. So therefore, the compositions of the A will change composition of B will also change and because of that free energy system will reduce.

So, that is the main reasons why thermodynamically things happen this way. Now one can actually explain also using you know many others, let me draw it here. You can explain even using chemical potentials that is not a big deal chemical potential I have already taught you. So, if I draw this curve again I can actually explain easily this is G alpha. So, if I draw the tangents here. Let us draw with a different colour. This is my this was corresponding to alloy A corresponding to alloy B. So therefore, it says you this is the chemical potential of component A at corresponding to alloy A. Chemical potential of B corresponding to alloy A, am I clear? Similarly if I draw another tangent here, it will go down does not matter. So, this will be chemical potential of A in alloy B, chemical potential of B in alloy B. So, as you clearly see there is a chemical potential gradient. Even I look at the pure a end that is the component suppose A in the alloy A and alloy B there is a change of chemical potential.

So that means, because of these difference of chemical potential there is a delta mu here there is a delta mu there. And this delta mu which is the chemical potential different will drive the systems to equilibrate or drive the systems to produce to have a atomic mass transports, correct? But is it is true that here the diffusion happening down the concentration gradient, but it may not be the case always. It is this case is very clear the diffusion happening down the concentration can a will try to reduce it is chemical potential from here to there, B will try to reduce chemical potential from here to there.

So, that is what it is you know how to do that they are actually diffusing in the down the concentration gradient. So, elements here will defuse in this elements there will diffuse in this. So, that is what actually happens in the normal situation. But you can also have abnormal situation, which is looks like abnormal, but need not abnormal situation. What will happen?

Suppose this is my free energy curve. So, looks little bit awkward little bit different. If it is like this or let us draw it the way it is there in suppose if free energy curve looks like this. So now, how it will happen? And let us first show it there only erase it up. And suppose I am here A and B similar to these this is composition of the alloy A composition of alloy B of the any component B suppose. So, average is somewhere there G average. So, as you can clearly see this, this system can draw the free energy by dragging that, still drop the free energy by doing that, still drop the free energy by doing that. So, from here I can draw the free energy extensively very large content, why because I can actually reduce the free energy systems free energy system was somewhere there at the beginning now free energy system has climbed go down from here to there, there to there, to there to the inflection point here where this inflection point; obviously, because it is slope change.

So, what is happening here? Very clearly atomic species in the alloy A should have gone to B and B in the atomic species in the B which is the region B should have gone to A, but it is not happening. It is happening other way. This composition is in a composition in the alloy A you see this is region in a this is or the composition at the beginning this is region in B. This is again more region in a because you are close A end this is again more region in A this is more in region in B. So that means what? We are slowly diffusion atomic species of diffusion in the regions which is a region and which is B region; that means, it is not happening down the concentration gradient. It is rather happening above up the concentration gradient. Instead of making it more equilibrium like here or more at the at the center, better this composition excess for the things diffuse from here and things diffuse from there and they make it uniform. That is why I can reduce the free energy, it is happening other way compositions are actually going far away from each other.

So, that is what is known as diffusion above the concentration gradient or uphill diffusion that is what you always deflect call. This is downhill diffusion, downhill it means down the hill. And this is uphill diffusion. If you draw the free energy composition diagrams which I should have did because if I do everything in the class then you will not get. It you can do similar construction here on this points here, do it you can draw this free energy composition diagram here. And there you will clearly see diffusion happens down the chemical potential gradient. So that means what? The chemical potential gradient is what dictates you the diffusion it is not the compositional difference. Composition difference we all perceive suppose if I draw a simple you know drop of a ink into water, you will clearly see after few minutes ink will sink disperse in the liquid water nicely. That is what is downhill diffusion, which we are all used to know. We all used to know this fact that if there is a high concentration region atomic species will diffuse from the high concentration to the low concentration region.

We are not used to things like this where a system is waving in the opposite directions. That is atomic specieses are actually diffusing above the composition gradient. The species in the alloy A is becoming region a this is in the alloy B is becoming region B, which is something which is difficult to understand or difficult to believe. That this happens, because of thermodynamics, because of free energy curve it happens. We will simple it how it happens because the same invincibility we know that this kind of nature of free energy curves lead to invincibility in the systems; that means, delta h is positive and very high because delta h is positive or rather enthalpy of mixing is positive by the system and high. Then atoms actually will not likely to stay together. A and B will like to go away from each other, because they are bond energies are higher. A any point energy is much higher than A and B bond energies.

So, system will not like to form A B bond at bonds. System will like to be staying with A bond and B bonds. That is why this kind of free energy curves appear in the in the system we have already discussed about quasi chemical theory and told you the reasons for having such kind of a free energy free energy curves. So, the movement you have such a kind of free energy curves your behaviour will be different, but remember it is this chemical potential gradient there also here also which dictates you the diffusion directions. The free energy the basically this is the main aspect the change of the chemical potential always dictates you diffusion direction. This is not I want to you to understand very clearly because most of us has a concept you know concept that is the compositional difference which dictates the free the diffusion directions, no. It is this chemical potential difference that is what tells you why these things will happen.

So, by now you could have understood you could have learnt how to draw these diagrams. So, let me just draw it here. So, as you can clearly see it has to be drawn in a very big way otherwise things will not be clear. So, if I draw it will be going there it will be going there, similarly if you draw here. So, you can clearly see this is your a chemical potential of A in the alloy A, correct? This is the chemical potential of B in the alloy B. And this once where it will meet I think it will be chemical potential of A in alloy B, because this is where it is meeting this is chemical potential of B in alloy A.

So, you can clearly see there is a gradient. So, a will go to A, B will go to B. There is a huge change of chemical potential this is B in A. So, all the atoms which are there B atoms which are there in the A will slowly go to into B. All the atoms which are present in B A atom present in the B alloy will also go to a alloy. That is what actually happens. So therefore, these large change of a chemical potential is what is dictating your diffusion direction. So, diffusion happening down the chemical gradient, but it is happening up the concentration gradient. So therefore, thermodynamics is not failing here. Thermodynamics is giving us the real answer why diffusion happens inside a systems above the concentration gradient or after diffusion happens. So that means, the basic driving force for the diffusion to takes place is basically a chemical potential gradient it is the chemical potential gradient which tells which gives you the direction of diffusion. And In fact, it does not tell you how fast the diffusion will happen how the slow happens. That will dictate decided by the other aspects, let me be very clear about it.

So, please keep this in mind because in the course we are going to discuss various aspects of the rate of transformations. And diffusion is going to come into picture. So, thermodynamically this is what actually explanation for diffusions. Now we will see how kinetically we can explain the next lecture.