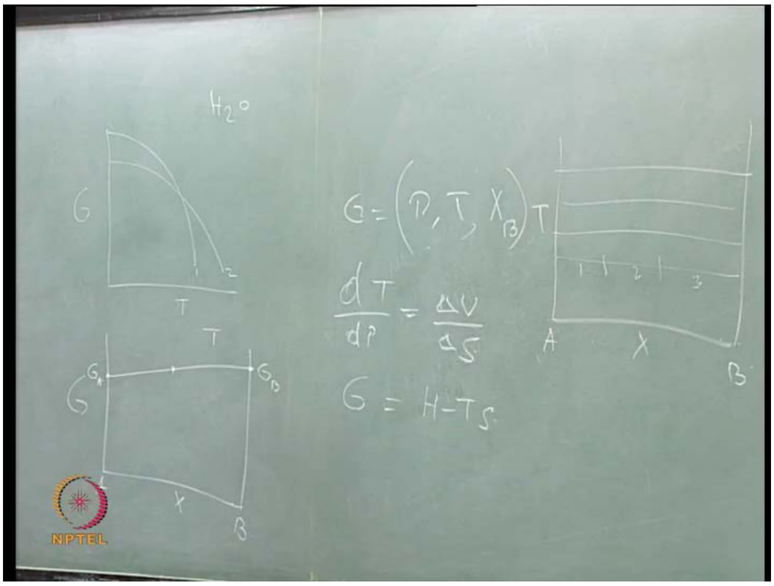
Advanced Metallurgical Thermodynamics

Prof. Dr. B. S. Murthy
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Madras

Lecture No. #04

Free energy of solutions, free energy-composition diagrams

(Refer Slide Time: 00:22)



In the last class we talked about what is called the equilibrium for single component systems, we talked even about a phase diagram for a single component system, such as H 2 O. Today we will see what happens? If I add another component to it, how does the free energy, and concepts of equilibrium start changing. For example if you remember, we have seen a diagram of G T, and then drawn the free energy curves for any two phases, I call it as phase one, phase two, and then I say based on this in principle, I can say which phase is stable under what temperatures.

And in addition actually in principle, this is not sufficient; we should have actually added one more axis there, which is for pressure. In principle, this is a three-dimensional axis, three-dimensional diagram with a pressure axis going like this, and I should have a G as a function of P and T, that is what you have seen G equal d G is v d p minus s d d, and from that you should be able to find out the free energy at a particular temperature and pressure for different, different phases and based on that c, which has a lower free energy and decide, what is more stable at a particular condition. But because most of our processes are metallurgical processes in general, and any chemical process are done usually at atmospheric pressure, what we do is in that three-dimensional diagram.

We take one section at a particular pressure, which is atmospheric pressure. And then now look at a two D diagram, which is the G verses T diagram and then we are representing the whole free energy in that. So, at the back of our mind, we should always keep, that actually it is a three D diagram, and I have taken a two D section out of that three D diagram, at a fixed pressure. In principle, if I change the pressure the whole thing changes, this particular temperature would shift this way or that way, the free energy curves may go up or down, depending on what pressure it is and that is what we have actually seen based on the Clausius Clapeyron equation in the last class, that if I change the pressure, the melting point will change, increase or decrease depends on the particular condition the particular system, whether the delta V is positive or negative based on that. We will know, whether it will increase or decrease, but we definitely know, that the melting point is never the same, when will it be the same, can you say somebody tell me, when will the melting point not change as a function of pressure.

(( ))

Yes perfect, if there is a system, where delta V is 0. If there is a hypothetical system, where a solid becomes a liquid, where there is no change in the volume. In such a case delta V is 0, if delta V is 0 dT by d P, if you remember always remember this dT by d P will be 0, if delta V is 0, then you can say that melting point never changes with pressure. You keep on increasing the pressure or decrease the pressure, the melting point would remain the same, only under that special condition. Otherwise in principle, you would always see, it would either increase or decrease depending on the sign of the right hand side, whether it is positive or negative yes.

Now, what we see is, this is ok for a pure pure metal system or a single component system. Again I should emphasize again and again to you that, when I say pure metal system, we even H 2 O, we take it as a single component system, so instead of saying pure metal system, I should say single component system. And as we go along, when we go to binary phase diagrams, you start seeing some of the intermetallic compounds also we start dealing with them as a single component, when I come to the phase rule. You will see that, how we deal intermetallics as single component system. And if you do not deal with them as single component, you get into trouble in terms of the phase rule. you will see that as we go along.

So now, looking at a single component system this whole thing is fine, I simply need to think of a three D diagram of G verses T and P, and then look at different, different sections depending on, what pressure I am working with and then get to know, how the free energy curve is and then find out. In principle in a G T P diagram, what I am seeing is not actually the curves, but surfaces is not it. G as the function of P and T surface and any surface, if you in take a section, the section of a surface, when when when a plane intersects the surface, what you see is a line. And that is what we are seeing now; all these lines that you are seeing are intersections of this plane. So, there is a G verses T and P plane for the phase one and for the phase two, and in that plane I am taking sections.

Now, what I am saying is I am introducing something else additional, I am saying there is a second component now, if I say there is a second component, whenever I say a two component system, how in this two component system, only one of the component is actually a variable. For example, if I am talking of steel iron carbon steel, I say it has one percent carbon then I need not have to say that, it has ninety nine percent of iron. As long as, it is a binary system, so only one of the variables, one of the element is a variable, the second one is a dependant variable, one is independent variable. So, that independent variable the composition also, I have to add and then what I will see is that, this particular function is also a function of X. X is the composition X or C different different books you will see them. So, I would treat it as let us say X B, B is my solute let us say, solute and solvent again change depending on which end you are in, if you are on the A side B becomes solute; if you are on the B side A becomes solute.

So, I can say that G now, has to be considered as a function of P T and X B. So, it is a four-dimensional diagram actually, and as you know it is not easy to visualize, mathematically one can represent, I do not know whether you have ever heard of what are called quasicrystals and in quasicrystals people know many of you know when you are talking about miller indices, what are the number of indices that we use for typical systems like cubic.

(( ))

Three, but the moment you go to a hexagonal you go to four, and the moment you go to a quasicrystals, you go talk about six, and then people actually believe that a quasicrystal is a crystal in a six-dimensional space and when you project that, six-dimensional solid into a three-dimensional real space, it actually does not retain it is periodicity and it becomes a quasi periodic. So, people actually do a lot of mathematics in quasicrystals, the whole crystallography in six dimensions imagining. So that, here it is a similar situation, so because one can do all the mathematics, one can calculate how G varies with P T and X B, but the thing is when you want to represent it; obviously for the sake of representation, we need to take sections. We have already taken one section, which is the section of pressure constant pressure and now now, because you have taken the section of constant pressure.

Now, you take another section, which is you add another axis here, which is X B axis now; that means, composition axis and in that composition axis, I what I do is, I now take constant pressure free energy curves, where I show G verses X curves. So, I will have a plot now, where I have G verses X, where one side is pure A; another side is pure B. And what I am looking at is a constant temperature, pressure is already kept constant, now I am looking at constant temperature, and at the constant temperature I see how the phases are stable in which composition range, which phase is stable.

At that temperature and if I do many many sections at different, different temperatures, I basically come up with a phase diagram, which is actually for us, what is called T X diagram. A phase diagram is nothing but a T X diagram for us in a binary case, where A will be on one side; B is on other side. And in this diagram what I am trying to show is, at each temperature, which phase is stable in which composition domain, and where from that I I get that information I get that information from here. So, if I draw various sections, various horizontal lines, at these horizontal lines I can say from here to here phase one is more stable; from here to here, phase two is more stable and from here to here, phase three is stable whatever it is. And if I get that information from here and I put all that in this diagram, and I can now say that what are the domains for the phase stability, which phase is stable in which temperature and composition domain, keeping again at the back of mind mind that I have already kept the pressure constant. And the moment, I bring a pressure into it, you would see that it would be a T verses X and pressure. So, again here also, I am talking of a pressure being taken constant.

So now, we try to look at, how the free energy would change with X at a different pressures, pressure is already kept constant as a function of temperature, how does it change. To know that, we have already done earlier, what is G for a pure metal for a single component system? We said G is H minus T S, so for any pure metal at any given temperature, I can calculate the G, what is the only input that I note C p, as long as I know how, what is the C p and how C p changes as a function of temperature, I can calculate the G. So, in principle because this diagram is at a fixed temperature, so if I am talking of free energy of pure A, what would it B, where would it I represent free energy of pure A in this diagram.

(( ))

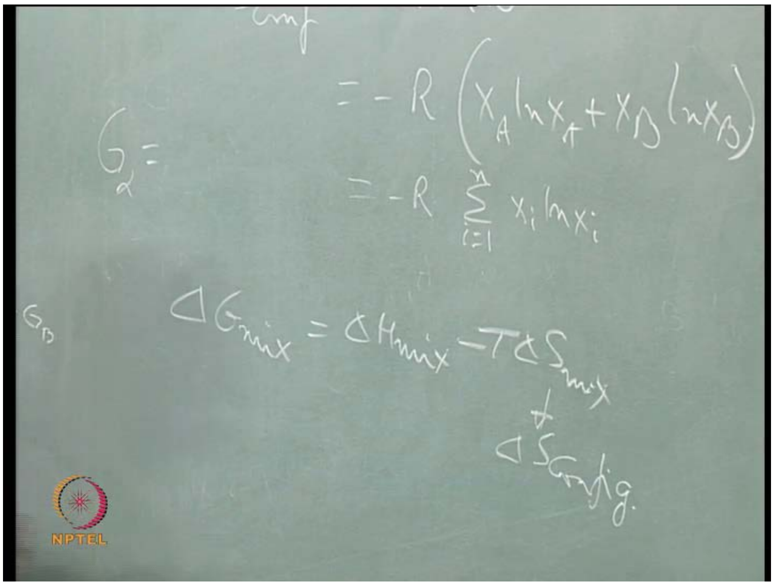
Where where should we represent free energy of pure A in this diagram, will it be a curve or what kind of… It will be a point and where on the on this line on this line it will be a simply one point somewhere. At a given temperature A has a fixed free energy, once I change the temperature, this free energy will go up or down, if I increase the temperature will this free energy go up or go come down, can you tell me. If I increase the temperature will this free energy point will go up or come down come down, because we know G is this, because G is this and d G by dT is always negative. So, the free energy should come down as I increase the temperature, this is for pure A. Similarly, if I do it for pure B, I will see another point somewhere here, this is I call it as G B; I call this as G A.

Now if I am talking of an alloy, a phase which consist of A and B, then how do I talk about the free energy of this particular phase, which has both A and B inside it. One way to think about it is that this phase is nothing but just a mixture of A and B, if I think, it is mixture of A and B, the free energy of such a mixture can always be represented by simply drawing a line joining the two. All of you must have done, what are called rule of mixtures, many of us do in composites, whenever you want to know the strength of a composite or young’s modulus of a composite, where two phases are there, we use rule of mixtures, volume fraction of one phase multiplied by the modulus of the other phase. Of course, you may say whether it is plane strain condition or plane stress condition. So, think the the formula will slightly change, but otherwise we know, what is called a rule of mixture.

So, if I think, it say a mixture and having certain composition X B, let us say, when I say X B then X A is one minus X B, it is automatic and so, for that composition I can say, if I have mixture, that mixture should have a free energy of that, but in principle this is not always the case, because A and B atoms cannot be simply considered as a mixture. There is always an interaction between A and B, even if there is no interaction, the moment I take A and B, it is like a red balls and white balls, I put them into a box. There is an additional entropy that comes into the system, because of the way I arrange A and B atoms, this is what we call it as a configurational entropy. So, far we talked of one entropy here, this is actually a thermal entropy, which is coming only because of atomic vibrations.

Now, the moment I go to a second element or a second component, I need to bring in configurational entropy. So, even if A and B atoms are not interacting with each other, they do not neither attract each other nor repel each other, they are neutral to each other. Even in spite of that, there will be an additional free energy term that comes into picture because of simple configurational entropy, that configurational entropy term has to be added to this mixture to be able to know, what is the actual free energy of such an alloy and this configuration entropy, people you all must have gone through statistical thermodynamics at some stage.

(Refer Slide Time: 16:03)



We define it as delta S config as K l n w sorry. This K is not a capital; it is a small k, what is the difference between the two?

(( ))

Capital capital K is the Kelvin in temperature. So, whenever you use capital K in thermodynamics it is always fixed, it is a temperature Kelvin. So, you should never use that, so this is the bolds man's constant. So, where w is what?

(( ))

Number of configurations, number of ways of arranging a B atoms in a mixture of A and B atoms let us say, and this if you derive it, it turns out to be minus R (X A l n X A plus X B l n X B) for a binary. And in principle, this can be extact to any extended to any number of components, where we write it as X i l n X i, where i goes from one to n, in fact that is where possibly, if the time permits I will talk as we go along some time, what are called a multi component systems that people are trying now, where they use this configuration entropy as a very important tool, to generate new type of materials which we call them as high entropy alloys.

If you look at this particular equation, this equation has a very very systematic way of change of configuration entropy as a function of com position. You see that it is a very symmetric function and because it is symmetric function and by the way, look at that and tell me, what would be the sign of it, what would be the sign of configuration entropy?

(( ))

It is negative.

(( ))

X A and X B are fractions, l n of a fraction is negative is not it, l n of a fraction is negative, so and there is a minus there. So, configurational in fact, this is a very simple thing that you should know that, when I put A and B atoms I am creating randomness, and randomness is always positive; there can be never be a negative randomness, I can only say randomness is not there, when randomness is not there, we say it is 0, but you can never say there is a negative randomness there is either perfection or randomness. So, perfection is where we say randomness is 0 that is where we say the entropy configurational entropy goes to 0. So, where does the configuration entropy does goes to 0 either either on this side or on that side, for both the pure metal sides configurational entropy should go to 0, and that is why you see configurational entropy term does not come into picture, when I am talking of a pure metal. Only when I am talking of an alloy, I talk about configurational entropy; otherwise I would not talk about configurational entropy.

And now, this configuration entropy also you would see, it would it is positive first and foremost, and it is 0 on both the sides, and it is maximum at at the center of the phase diagram. It is very easy also to understand, when I have ten atoms of A, I mean B and ninety atoms of A, the number of possible configurations. If I compare this with thirty atoms of B and seventy atoms of A, you will have more possible combinations of how to arrange B atoms, if you have more and more number of B atoms and this would; obviously, go to maximum at 50 50, when I am coming to other side then automatically B becomes I mean A becomes a solute and B becomes a solvent.

And this is such that, it is always symmetric, whether I am taking seventy thirty case or thirty seventy case configuration entropy is the same, and also one more interesting important param point that you should note is that configuration entropy does not bother about, which elements that I am considering, whether it is a steel, iron carbon steel or whether it is a aluminum copper alloy, configuration entropy is always the same, provided the amount of the elements the percentage of elements are the same. If I am taking iron with one percent carbon alloy and aluminum with one percent copper alloy both of them will have the same configuration entropy.

(( ))

Yes very interesting question, thermodynamically no, when we do this, after doing configuration entropy, after doing the free energy function, we will prove this for you, just may be at the end of this class; you all remind me or may be in the tomorrow's class. So, once I put the free energy function then we will be able to prove it, we will prove that is not possible, thermodynamic is not possible, only thing is you can you can keep increasing the purity. We can we can talk about four n purity, five n purity have you heard of these things, when I say four n purity, what does it mean?

(( ))

No never heard, what is this n?

(( ))

Four nines, if when I say four n purity 99.99 percent, have recently attended a conference where they were talking about a copper which they made seven n purity copper. So, 99.59, so and for certain applications for example, if you want to have a exceptionally high conductivity, you know conductivity is one thing, where the any impurities, I do not know whether we have heard of the all the conducting copper wires, that we use have a special name anybody knows?

(( ))

What what copper is this, it is a special name.

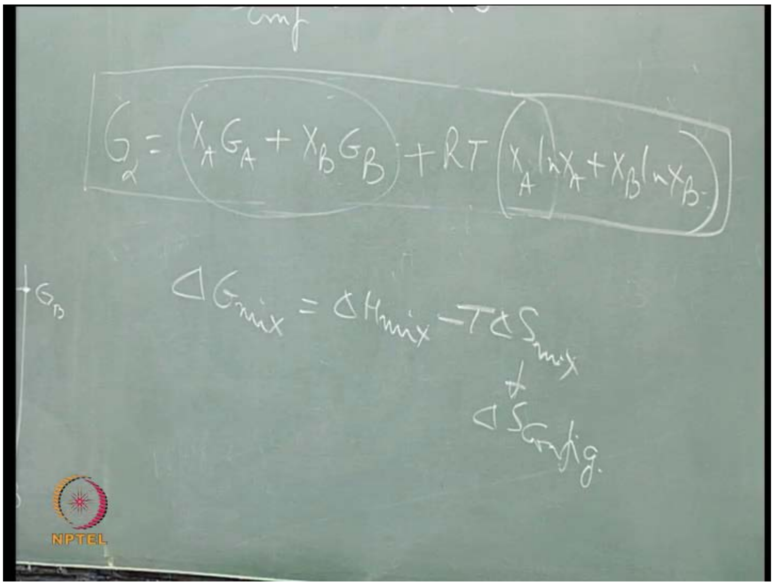
(( ))

Electrical one.

(( ))

Yes, they are called o f h c copper, o f h c oxygen free high conductivity copper. So, they want to eliminate oxygen as much as possible, because oxygen is not suppose to be good for the conductivity any way, we will come back to that later.

(Refer Slide Time: 23:07)



$$G_\alpha = X_A G_A + X_B G_B + RT\,(X_A \ln X_A + X_B \ln X_B)$$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

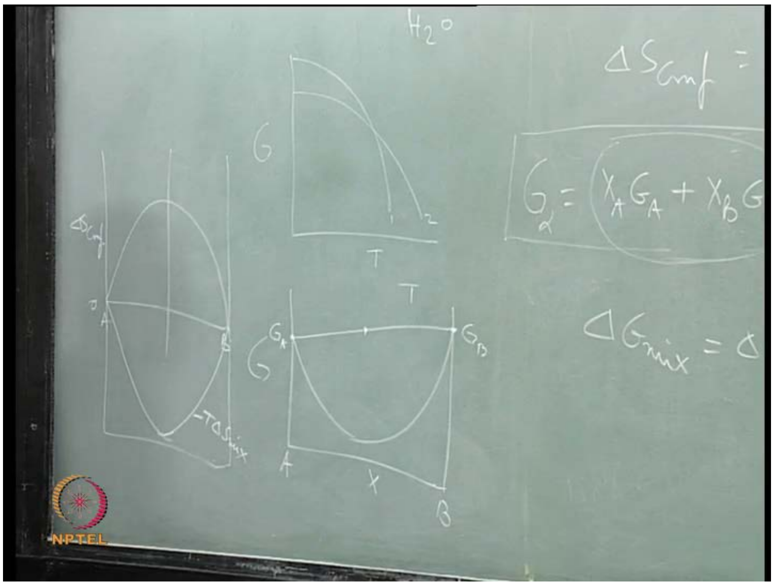
$$\Delta S_{config.}$$

So, that we are now looking at, is now the free energy of any phase alpha, which has two elements in it, can be represented as a combination of the two pure metals components plus an additional term, which comes because of two things one either A and B have an interaction between each other, that they either like each other or do not like each other, there attract or repel each other, even if that part does not arise that they are neutral to each other. You have an additional term called the configuration entropy, and that particular thing is what is called delta G mixing, which is a combination of delta H mixing minus T into delta S mixing or the same delta is mixing is also called it as called as delta S configuration.

So, I can write the free energy expression as X A G A plus X B G B plus delta G mixing this is the free energy of any n component systems I mean here I have done it for two component system; you can extend it to any n component system, excepting that this initial term. So, these are pure metal terms this is simply a mixture, pure metal mixture, and I am adding a further term, which is actually this, and this delta H mixing can be 0 negative or positive depending on whether there is an attraction between A and B or repulsion between A and B or in ideal solutions it is 0, all ideal solutions delta H mixing is 0; that means, the A neither gets attracted to B nor gets repelled from B, but in most of the cases it is not like that.

So whereas, so in case of an ideal solution, I can write this expression as how, minus T delta H mixing, so; that means, I can write this as R T (X A l n X A plus X B l n X B) and put one more bracket there. This is the expression for an ideal solution, the moment I say an ideal solution, what is the free energy of any ideal solution it is this X A G A plus X B G B plus R T X.

(Refer Slide Time: 26:10)



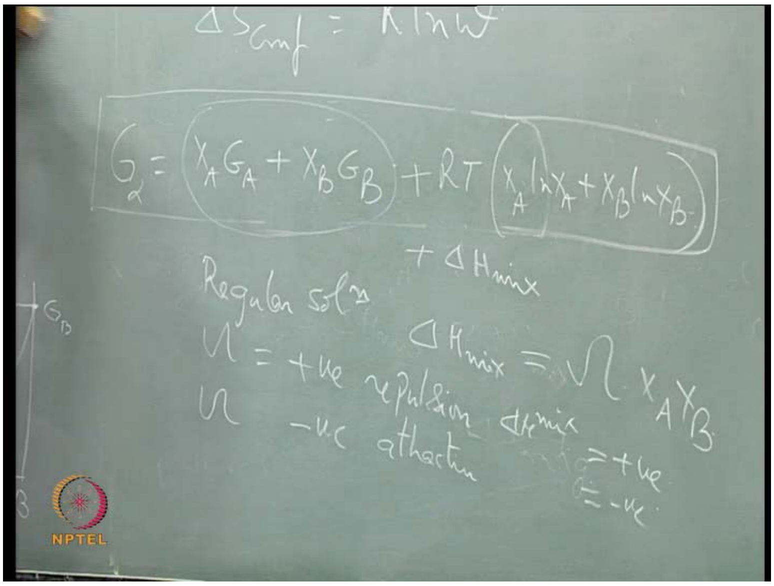
And that, if I want to represent it on the on the free energy curve, I can show it as something like this, because if I look at the entropy the entropy is always positive like this. This is delta S config, this is 0; this is pure A; this is pure B and at 50 50 it is maximum and because we are going to be talking about minus T into delta S configuration, I have to multiply this with T. So, if I draw now, what is minus T into delta S mixing, so this would be something like this (No audio from 26:51 to 27:02) of course, you have to remember that this scaling will not be same as this scaling, because here, I am multiplying with T, so; obviously, this value is much larger negative.

And the higher the temperature the more this is, but because I am simply taking this configuration entropy and multiplying with some constant number called temperature, this the nature of the curve does not change, it still remains symmetric excepting that from the press side it has come to the negative side. And now, this side if I take and add it to this, what I get is the G of any phase called alpha, as a function of composition. At a given temperature, this is for a given temperature; the moment I let us say again the same ideal solution and I keep on increasing the temperature, what should happen. This curve should become more and more negative and anything else should happen.

(( ))

Yes G of A and G of B also will decrease, where this curve intersects on the Y and X axis also, I mean the the two two Y axis on the pure A and pure B side also, it is also going to change, because these two quantities are going to change as a function of temperature clear. So, this is how, we can talk about any free energy curve and once I have that kind of a curve, I should be able to find out whether now, if I try to talk about two different phases, and talk about equilibrium, we can start talking about equilibrium provided, I can calculate this, but this is very simple for an ideal solution and life is not really ideal is not it. So, I should talk in terms of non ideal solutions and the moment I say non ideal, I have to bring in a term called delta H mixing.

(Refer Slide Time: 29:08)



And that term, if I add to this, I have to add to this whole term. So now 1, 2, 3 terms are there in the free energy curve. And this delta H mixing can be positive or can be negative depending on whether there is attraction or repulsion. And now, looking at this people have come up with different different models, one of the simplistic model, people have talked about is what is called regular solution model, without this term it is ideal solution. So, what is a regular solution? In a regular solution, we define delta H mixing as certain parameter called omega into X A X B.

And this omega is called interaction parameter. So, depending on how strong or how weak is the interaction, if this omega goes to 0, what does it mean, we are talking of a ideal solution again. If the interaction is zero; that means, there is no interaction between A and B; that means, it is an ideal solution. So, depending on how strong or how weak is the interaction, we can talk about delta H mixing. And now, this omega can be positive or negative, whenever omega is positive this is a repulsion and; that means, delta H mixing is positive, and whenever omega is negative, it is an attraction and this is negative.

And usually you see this kind of a second case, more and more in case of inter metallic compounds, whenever there are compounds. In all the cases of whenever you see a phase diagram with compounds; that means, in that phase diagram A and B have an attraction like cemmantide f e three C or n i three al n i al or mg two s i in a magnesium silicon phase diagram. All these are indications that varies a strong attraction, but there are also phase diagrams, which are something like about let us say copper silver, I mean copper sorry copper gold or any other let us say silicon germanium, wherever you see an isomorphous phase diagram, where there are no compounds, that kind of a situation is very close to an ideal situation, where there is neither attraction nor repulsion.

So, the moment you see a attraction between A and B, there is a tendency for the formation of inter metallic compounds. We will slowly start seeing, how phase diagrams evolve based on the free energy concepts and wherever there is a repulsion, you start seeing that there is what is called something like a eutectic or a paratactic. You start seeing that the solubility of one of the element in the other starts getting restricted, whenever there is a repulsion; that means, A does not want B to be dissolved into it, to a lar large extends like we have, we are selective in our friends, we want somebody, we like somebody, we do not like somebody else. Similarly, A does not want B to a large extent, so you start seeing the the lesser and lesser solubility of one element in the other, that you see, it gives you an idea that greater and greater repulsion between A and B.

For example, you might have seen eutectic phase diagrams, where there is some solubility of A and B on one side, on both the sides or one side. You will also see that, as we go along, we will talk about what is called sub regular solution model within a minute, where you will see that there could be possibility that on one side there is solubility, and the other side there is no solubility.

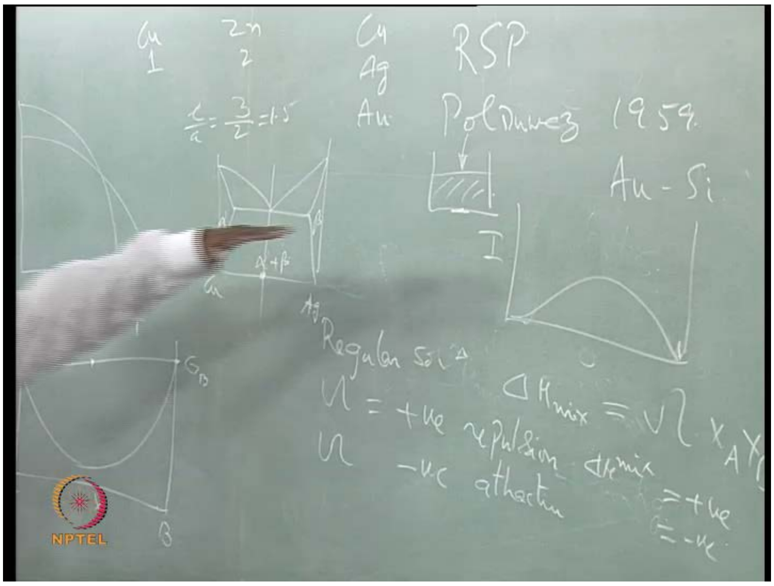
For example, I give you an idea of copper zinc phase diagram, how many of you have seen copper zinc phase diagram. Every metallurgy should have seen, because it is supposed to be brasses, do you know anything about copper zinc phase diagram, something about solubility of copper in zinc and zinc in copper. Do you any of you remember, how much of zinc is soluble in copper at room temperature approximately around forty percent, somewhere between thirty five forty, what about copper in zinc, is less than one percent less than one percent, how does this… I mean happen, one element disso wants to dissolve into another or one element accepts the other element very easily up to forty percent, but other one does not accept; that means, it is like one sided love, something like that. So, you see this, that copper accepts zinc, but zinc does not want to accept copper, see this is, we explain this from a valency point of view.

All of you (( )) rules you have gone through, we say that because copper and zinc have different valency. We say whenever an element goes into another, because of the metallic bond present, you metallic bond accepts an increase in the e by a ratio and not a decrease in the e by a ratio. For example, if you take this particular case a copper has a valency of one; zinc has a valency of two, when I add copper to zinc. You see the total valancy electrons are three and total number of atoms are two, because one copper atom; one zinc atom, two atoms are there, and the numbers of valance electrons are two are already there, I am adding one more, so the total number becomes three and the e by a ratio is 3 by 2, which is 1.5.

So, if there was a pure zinc, it had two e by a ratio, two valance electrons for each atom two by two by one is two, whereas the moment I have added one atom of copper to zinc, I have seen that from two it has fallen to 1.5, so there is a decrease in the e by a ratio; that means there is the decrease in the valance electrons for unit atom. And this is something a metallic bond does not like, whereas on the other side, you see when you add zinc to copper, two electrons are added. So, the total number of electrons become again three one plus two becomes three and there are two atoms, it is again three by two 1.5, but here this time from one it has gone to 1.5, but then you may say sir, why cannot then hundred percent of zinc atom go into copper, that is where we talk about the other things. If you want 100 percent solubility of one in the other, there are number of other (( )) rules should be satisfied.

And the most important one among them is what, same crystal structure. If you want hundred percent solubility, the first and foremost is same crystal structure, it does not mean that if the structure is the same, that it will have hundred percent solubility then the rest of the things come into picture.

(Refer Slide Time: 37:08)



Yes very easy example is copper silver and in fact, copper silver has led to a entirely a new field of metallurgy called RSP, who knows what is RSP rapid solidification processing. A person by name Pol Dewey in 1959, he started worrying about, why does copper and silver do not get mixed with each other. If you look at the three elements copper, silver, gold. Three elements and look at the phase diagrams of three of them, copper and gold is an isomorphous diagram; silver and gold is an isomorphous diagram whereas, copper silver is not an isomorphous, it is a eutectic diagram. Silver dissolves into copper up to approximately let us about nine percent also. And similarly on the other side, it is the eutectic why this is so, when we look at the valency, they all have the same valency; they all have similar electro electro negativity. Atomic sizes are slightly different, but based on atomic size itself.

People are not able to understand this for for many many years. This is not clear then he thought let me do an experiment, where I take melt this alloy, and try to cool this alloy very rapidly, and see what would happen. So, what he did was, he developed a technique called gun quench technique, what he did was, he took this alloy in a crucible with a small hole in it, and then melted everything, and then put before the experiment itself, put some kind of a diaphragm of a higher melting metal. So, that it does not melt, when this alloy is melting and then after everything is molten. He applied a high pressure of organ such that this diaphragm gets sphereséd and the liquid comes out of this in the like a bullet from a gun, that is why it is called gun quench technique. And allowed this to fall on a slanted copper plate, copper having a high conductivity. He excepted that this liquid the moment it falls on it, it gets quenched very fast.

And in fact, when people calculated the cooling rates that he could achieve or the order of ten to the power of six Kelvin per second, a million Kelvin per second a very, very high. And just for a comparison, if you use a permanent mold casting, you take a liquid metal and pour it into a cast iron mold, you usually get around hundred degrees or two hundred degrees or maximum, if you have water cooled copper mold may be you can get about three hundred, four hundred degrees. So, in comparison he achieved very high cooling rates and what happened was each droplet of water that is falling has become like a small flake and when he took these flakes and put it into an X ray machine to do the X ray diffraction, what would be the difference between… you tell me, if a copper and silver are existing as a eutectic mixture.

Let us say, I take a phase diagram all of you are aware of eutectic phase diagram. Let us say, I take this alloy at room temperature, what should it contain?

(( ))

Of

(( ))

Eutectic mixture of what alpha plus beta, you call this as alpha, and you call this as beta only is problem that comes is usually in crystallography, we use this alpha and beta for different crystal structures, whenever I use the term alpha, it basically means one crystal structure, beta means some other crystal structure, but incidentally here both of them have the same crystal structure, but whatever it is, we will assume it as alpha plus beta. And if that particular sample containing alpha plus beta and if you send X rays through it, what would be the x r d pattern, how many of you have gone through X ray course or one chapter in X ray on X ray at some stage, X ray diffraction you are all aware of, you all raised your hands very like this. So tell me, what should be the x r d pattern look like, what should it contain x r d pattern, x r d pattern what are, what do you see whenever, I show you a x r d pattern something here, what will you see in the x r d pattern.

(( ))

Peaks, one thing at least, some of you have seen, you see peaks provided it is a powder diffraction pattern. Again different different types of diffractions are there, powder diffraction gives you peaks. Now, if I take a alpha plus beta mixture and then send an X ray, I get peaks and what should these peaks correspond to correspond to…

(( ))

Correspond to the alpha and beta phases separately, alpha should give each characteristics whatever, h k l peaks depending on it is crystal structure and beta should give it is… and incidentally because both of them have the same crystal structure f c c. And again, if I prove you a little more for f c c, what should be the type of peaks that I should see, many of you have a B tech metallurgy background. So, you should know, what peaks I should see in a x r d pattern of a f c c metal.

(( ))

1 1 1

(( ))

2 0 0, what is the condition? Now, let us go to the condition.

(( ))

Is

(( ))

Unmixed, h k l are unmixed not h plus k plus l, h k l should be unmixed, what does it mean, and that all three of them should be either odd or even. So, 1 1 0 is not possible, 1 0 0 is not possible, because one is odd and 0 is even. So, the first peak that is possible is 1 1 1 and then you have 2 0 0 and the next one is what?

(( ))

2 2 0 then the next one will be 3 1 1, and 2 2 2, and so on. So, but interestingly here, because it is a mixture of coppers based solid solution and a silver based solid solution, what you see is two sets of f c c peaks, 2 1 1 peaks, 2 2 0 peaks, 2 2 2 0 peaks and so on. One corresponding to copper based solid solution, another corresponding to silver based solid solutions, what he has seen interestingly when he did this gun quenching technique is that instead of two sets of peaks, he simply saw one set of peaks, giving an indication that it has become one single solid solution rather than a two phase mixture, that was the beginning of what is called rapid solidification processing. And he started doing this with different different eutectic systems, thinking that every eutectic should become from a two phase mixture to a single phase mixture.

And what he proved from that is inherently there is a tendency for A and B to mix with each other to dissolve into each other, but because of some reasons in the solid state there is some kind of repulsion and in the liquid state there all soluble completely. And, if I somehow pull it rapidly, I am able to somehow prevent this separation, and this it is like a it is like a you know quenching from a higher state. Unfortunately in a steels, we see when you quench from austenite, you get a marten side different structure, but there are also cases where, when you quench from the higher thing the same structure remains.

Now, when he started doing it with various eutectics, in one case which is called a gold silicon eutectic, he found that suddenly the pattern rather than showing you a pattern like this, where intensity verses theta, you see peaks like this, usually if this is the solid solution, this is the 1 1 1 and let us say and I have to be careful, if it is a f c c, you would see a typical f c c will become like this, that is how we actually differentiate an f c c from a b c c, whenever you have you are looking at an f c c, you will have two plus one plus two, kind of peaks two peaks will be closer that is because one is 1 1 1, another is 2 0 0. The h square plus k square plus l square is three and four, and the next one will be eight then eleven and twelve that is three 1 1 1 and 2 2 0 0 will be closer and so on and so forth. So, whereas, in a b c c, there will be equally spaced, that is the difference, so here instead of two peaks see simply got one single peak, I mean 2 1 1 1 peaks, he got one single, in a case of copper silver.

In case of gold silicon, what he saw was a peak like this that was the first, so called metallic glass in 1959 Pol Dewey has discovered. The first metallic glass till then people knew about glasses in silicate systems, we know that, what you see in front of you is a glass there, and people always believed that only silicate glasses, silicates can become glasses easily, why silicates become glasses easily, anybody knows? When I take a liquid of silicate and I simply cool it very slowly, it becomes a glass why?

(( ))

Crystal structure is very complex in a in a in a silicate solid, the crystal structure is network three- dimensional network structures. They are so complex for the liquid to really crystallize into that crystal structure, instead the liquid it would easily become a glass. In fact, long back turn bull, there is a person, who said every liquid wants to become a glass, unless crystallization intervenes, because for a liquid to become glass is easier, because the structure of glass is same as that of the liquid, whereas crystals once take start coming from the liquid, they have a different crystal structure, when compared to the liquid. So, they will be different, whereas here, you would see they would, it is more difficult for the crystal to come out, whereas in simple metals like aluminum or silver or copper, f c c kind of structures are simple structures can easily come out of liquid, that is why, if you really want a metals like this to become glasses.

You need to cool the liquid at such a high speed, that the nucleation of this f c c crystal is made very difficult, what is the nucleation means somehow atoms have to come together and form a unit cells of a cluster, which is of the size of r star and then only growth starts, if that is difficult then it does not… So, by using such high cooling rates of ten to the power six Kelvin per second, he was able to suppress crystallization and get a glass. And now, there are so many people, who have been working on this and got many many glasses. Now we are talking even about, what are called bulk metallic glasses? People are able to take liquid and pour it into a three inch mold, and get the whole rod three inch rod, which is a glass.

Again basically what they have done is they have added a large number of elements into the alloy, and made the crystallization very difficult, when they have too many elements, when a liquid becomes a crystal. It does not know, where these atoms should sit. So, there is a some kind of a confusion, we call this is as confusion principle. As a result, liquid instead of becoming a crystal, it would remain as liquid are similar to a silicate glasses. People are able to get glasses, which are very, very thick glasses by this kind of a process what is called bulk metallic glasses. So, like that there are number of glasses available, we will talk more about it as we go along, thank you.