

Thermodynamics And Kinetics Of Materials

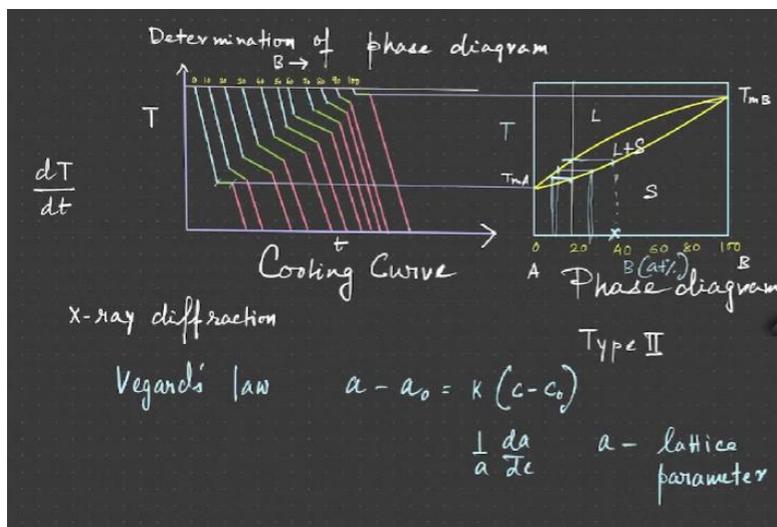
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Lecture 33

Binary alloy phase diagrams and invariant points

Talking about the type 1 and type 2 phase diagrams in the previous lectures so we will come to type 3 and type 4 phase diagrams so again let us consider the type 2 phase diagrams I have already introduced cooling curves but as you can see here for a type two phase diagram if I have to determine a type two phase diagram okay if I have to determine a type two phase diagram there are various experimental methods one of the experimental methods is using cooling curves now in cooling curves what we do we prepare a sample of different composition right say for example in the binary alloy it will be from pure a to pure b you can take any composition And then, for each composition, we will basically use, for each composition, we will basically use a furnace. We will heat it up, unless it melts, and then we will start cooling it. It is called furnace cooling. So, as we cool it, so we will basically see, with a certain imposing or certain cooling rate, we get this temperature time curve. So, if you look at these, for example, say for example for zero atomic percent of B so this is all in atomic percent then zero atomic percent B that means P over A you get a cooling curve get a cooling curve which is given like this so your liquid phase is cooling down cooling down until it comes to the freezing temperature the melting temperature now at the freezing or melting temperature as you can see the furnace when it is cooling down so furnace is giving off heat right the furnace is giving off heat and it is cooling down because the furnace so it is basically a furnace cooling that i am talking about so the furnace was heated up until the sample has melted and it has been taken up to certain temperature. So, at a given temperature, right, say for example, this is a temperature at which it was taken up, okay, T_f , okay, let us, not T_f , let us call it T_x .



So, this is like $T \times p$. So, $T \times p$ is the temperature at which temperature. If you look at T_{xp} , so if you look at T_{xp} , for example, this experiment at temperature at which the furnace was heated up, what different compositions, like these are all compositions expressing terms of atomic percent. Now, if it is zero atomic percent, it is zero atomic percent of B, that means 100 atomic percent of A. Now, 100 atomic percent of A, what you are seeing is called a cooling curve.

So, basically it is cooling down. till the freezing or melting temperature of A. Once you are at the freezing or melting temperature of A, you basically see a horizontal line. Why? Because at the freezing temperature of A, from the liquid to solid transition, during liquid to solid transition, as we have already observed before, what you get is evolution of latent heat, right? That heat is given out or heat of transition is given out. Now this is given out as the furnace is cooled, right? So basically, so giving out the heat also raises the temperature.

So if you think of it, as temperature is dropping within the furnace and then because of this latent heat evolution, there is a temperature that goes up. So at that, so basically at the melting or freezing point, when the liquid is released, at the, freezing or melting point where the liquid is released, you can see that there is a temperature, there is a heat given up which increases the temperature of furnace and there is a, and also as you can see that the temperature of the furnace is going down. So, these two opposing events interact, right? So, basically they are, they are nearly, they are same. Now, in such a case, what will you see? You will see that the temperature has now, basically, the temperature has basically now you see it here. So, the latent heat means the latent heat is giving.

So, as the latent heat is released, the temperature of the furnace is increased and the temperature of the furnace is slowly dropping. So, as a result, what you see is such a curve here, right. And since it is pure, there is no composition dependence. So, you will not see a slope, but you will see exactly horizontal line here, right? This line segment, right? Indicating this horizontal line segment indicates the onset of freezing, right? The onset of, means indicates the arrival of the freezing temperature or the transformation temperature. So, this temperature is the transformation temperature for pure A, right? For pure A, this is the transformation temperature.

This line gives me that this is where the transformation temperature or melting temperature or freezing temperature, whatever you call it is, And then beyond that, so this cooling, now you tell why is this slope? The slope is coming because of the conductivity, right? The conductivity, how conducting the liquid is. So, this is blue curve, the blue curves, the blue segments are for the liquid and the red segment is for the solid. Now, if you see, when we look at the red, the blue curve or the red curve, the heat release is basically driven by The heat release, the rate of

release of slope is basically dependent. The slope is basically dT/dt . The slope is basically dependent on the conductivity of the liquid and the conductivity of the solid.

and the conductivity of the solid, because as you know actually it depends on half and which is basically k , k is the conductivity ρC_p , C_p is the heat capacity and k is the conductivity and ρ is density. And so, it is proportional to k by R , it is equal to, sometimes this itself can be a function but if you do not assume this to be a functional position, you can write dt/dt equals to k/r is k by ρc_p , and this can be negative e to the x square. If I look at this as a 1-D problem, but it may not be a 1-D problem, it can be a full blown 3-D dimensional problem, this is a heat transfer equation. So, what I am trying to say that ultimately, it depends on the thermal conductivity of the liquid. So, the slope of these blue curves or the red lines or the blue lines for different compositions depend on the thermal conductivity of the liquid, the thermal conductivity of the solid, the heat capacity of the liquid, heat capacity of the solid, and also the density of liquid and density of the solid, which can differ, right? The slopes will not be same, right? So, so, so, so, because it can be different for the liquid and the solid.

Also, it will vary as a function of composition. So, all are possible. So, as a result, you will get representative cooling curves and this is for different compositions. So, this is for, in our case, this is like the composition, zero atomic percent and then at zero atomic percent, we get a horizontal line and this horizontal line represents the freezing or melting temperature, right? This is where the latent is given up, right? Latent is evolving. The latent is evolving which raises the temperature.

The raising of the temperature is compensated by the cooling down of the temperature, right, the falling of the temperature, raising and falling are competing. And so, there is this horizontal line, which represents this evolution, and beyond that again, just below that, you, you start continuing the cooling process, right, you start continuing the cooling process to some, some specific temperature, say for example, when the, when the furnace temperature is similar to the ambient temperature, right. So, that is where we stop the experiment, okay. So, similarly, I can start with, so, this basically, if you now draw a horizontal line and extend this horizontal line, you will basically, here, what you hit is the melting point of purée.

Okay. you go to the 10 atomic percent. In 10 atomic percent, the idea of the liquid, the liquid cooling remains the same, right, the liquid cooling remains nearly the same. In fact, here it looks almost parallel, however, it will not be parallel, right, the conductivity of this 10 atomic percent means of this liquid containing 10 atomic percent of B can be different from that with 0 atomic percent of B, right, for POA. So, with 10 atomic percent of B, what you see is, although it looks, seems parallel, but it will not be parallel. So, this is something that I am just trying to say.

Now, you have this. Now, you see, and then you have this, right. This is the, this is the cooling segment. This depends on the conductivity of liquid. This segment depends on the conductivity of solid, right.

However, if you look at the green segment, that intermediate segment, what you basically see, this intermediate segment, this sloping intermediate segment, is nothing but the segment where you have liquid-to-solid coexistence. You have two-phase coexistence in the segment because of the changing slope. So, this is one slope. Now, there is a change in slope, and then it comes back. Now, this change in slope, why is this not horizontal? This is not horizontal because I would like to say that it is not horizontal because if you take one composition given by this yellow line, if you take one composition given by the yellow line, you see, you start your freezing here, right? You are going down the yellow line.

So, you are going down, down, down. Once you are, say for example, this is 10 percent A, 18 atomic percent A or 20 atomic percent A. Now, in 20 atomic percent is again, if you look at 20 atomic percent, you have this curve and then you have this slope region, right, the slope changes and then again the slope changes when it is solid, right. So, you have this region which represents liquid plus solid. Now, how is that happening? Why is it sloping? Why is there a slope here? Why is it not horizontal like POA? Why is this line, why is this line not as horizontal as here.

This is because in B's cooling, there is a continuous composition change. So, when you are looking at 20 percent, 20 atomic percent of B, 20 atom, solution containing 20 atomic percent B, you never get a horizontal line here, but this liquid plus solid coexistence, right, here also this represents liquid-solid coexistence. This is also liquid-solid coexistence or this is also liquid-solid coexistence. However, this liquid solid persistence is continuously sloping, right? It is sloping.

It has a slope. This liquid solid persistence has a slope. This liquid solid persistence has a slope. So, why is that slope there? So, you go there. For example, this liquid is cooling down, cooling down. Now, at this point, at this point, you basically start getting.

.. So, this is your solidus line, right? This is your solidus line. And now, at this point, as soon as you just go at the heat the liquidus, you start seeing there is a solid of composition given by this point, given by this point, which you start nucleating, right, which will nucleate in the

microstructure. The microstructure initially conserves entirely liquid. Now, at this point, at this point, you start getting liquid. nuclei of the solid phase, nuclei of the solid phase.

Now, you go further just below. Now, if you go below, you start to see that the liquid phase and the solid phase composition has changed, right? The liquid has now, the liquid now has more of A, right? Here, the liquid initially had only 20% A, but now the liquid has more of A, right? So, basically, the liquid will have slightly more A, now it goes further down, go further down, if you go further down, you will suddenly see that the liquid composition and the solid composition are changing further. The solid has more A, the liquid has more A, the amount of B overall is getting distributed, and you have a different composition of the solid and the liquid, right? The solid and liquid composition continuously changes until it goes to the solidus, where you have solidus and the remaining liquid. So, if you now go to the solidus, point when you are touching solid. So basically remember this is what I am trying to say that this segment the way you are thinking is may not be the case because if you see you have some solid here you have some liquid here now this is your liquid composition now this is what is melting and then basically this is what is freezing so now if you look at that that this is your liquid composition that now this liquid when it is coming down Then again, there is a shift in composition.

So, there is a continuous shift in the liquid composition that is getting solidified. When you have a solution, then basically there is a continuous shift in the composition of the liquid and that of the solid as solidification is progressing. As solidification is progressing, you will basically see a change in the composition of the liquid that is getting frozen and change in the position of the solid that is coming out. So, as a result, as a result, your cooling curve will always show a sloping two-phase region, right? It will show us inclined two-phase region. So, this inclination will be there.

See here, all of these cases have inclination. Again, it becomes horizontal when you have POB, 100% B. So, on 100% B, you have horizontal line. Otherwise, you have these sloping lines, right? You have these different sloping lines. If you look at the sloping lines, and see, just follow my pointer.

If you look at my pointer, if you look at my pointer, and if you just see the change in slope here, and you can follow my pointer, you can change slope here. So, basically, you have got your phase diagram. So, basically, what I am trying to say is this. So, you have of phase diagram here. So, if you look at that drawing right here.

Basically, what you have is the phase diagram. This represents the liquid-liquid coexistence. So, this represents the liquid-liquid coexistence. We have class S and then there is S and this is L. And see, this is what exactly I have drawn here.

temperature versus composition curve, this is the temperature axis, this is the composition axis now. This is not time axis. Here it is time axis. In the cooling curve, this is the time and this is temperature and these are the compositions. For discrete compositions, we have, for different compositions, we have different cooling curves.

Now, I have looked at this two-phase coexistence region to draw this So, and we have looked at this changing slope here. So, basically joined here, where we see this changing slope from liquid to liquid plus solid. And again, you have this liquid plus solid to solid. So, these points. So, all these basically mark the phase boundary, the liquidus boundary.

So, this is the liquidus boundary and that guide gives you the solidus boundary, right. So, basically, you basically see that how you obtain the, so this is your fuel A and your B. So, how you obtain the phase diagram, right? So, basically your phase diagram is like this way. So, this one is like that and this, yeah. So, if you, if you exactly do this, you will basically see a phase diagram like this, right? So, this is your phase diagram that you have drawn and this is again I have redrawn the phase diagram, the same phase diagram of type 2, right? So, this is one of the ways of determination of phase diagram by doing this experiment of cooling curves.

So, basically, if you look at late TNU techniques, there also you use these cooling curves for different types of phase diagrams. You use different types of, the idea of constructing the phase diagram remains the same. You take samples of different compositions of A and B. Then put it in the furnace, take it to a temperature where all of these will melt to liquid, right? Where all of these will melt to liquid. That means you go above the melting point of B, right? You have to go above the melting point of B, right? So this is what is your starting temperature.

Your starting temperature should be above the melting point of B, right? Slightly above the melting point of B. where everything is homogeneously liquid, all compositions are homogeneously liquid. Now, for each of these liquid samples, you start doing this experiment of cooling, right, the furnace cooling. As cooling is happening, the liquid is cooling down. As liquid is cooling down, at one point, it reaches the At one point, when it starts freezing, there you have this melting point or freezing point where there is a liquid-solid coexistence.

However, as you know, liquid-solid coexistence for pure A will be at a different temperature than that of a mixture of A and B. And, depending on the amount of A and amount of B, as you can see, there will be a variation in the liquid and solid composition in the two-phase region as it pulls down. As a result, as you know that for any solution of A and B, there will be this, there will be a changing slope, but this, this changing slope that you see here, this is basically marking the two-phase coexistence in a solution, two-phase coexistence in a solution where there is a slope here, right. You can assume liquid and solid to be ideal solutions and you can basically also construct this phase diagram analytically and you can see that, you can see that The idea remains almost there. You basically are looking at a composition and then you are trying to construct a tie line.

You are basically trying to construct a tie line and then you do it analytically. You are constructing a tie line and then joining the ends. But here, just because of this change in slope that is happening between the liquid phase and the solid phase, this intermediate changing slope is basically marking the two-phase coexistence. Now, remember for POA or POB, the two-phase coexistence is marked by a horizontal line, while for a solution of A and B, it is always marked by an inclined line. So, this is how a cooling curve can be used to construct a phase diagram of type II.

Now, you see there is another method, it is called X-ray diffraction. X-ray diffraction depends on the measurement of, now it becomes easier to use X-ray diffraction, not in the case of liquid to solid transformation, but in the case of solid to solid transformations. Say, for example, you have an alpha phase and you have a beta phase and you have a separating alpha plus beta. Now, in X-ray diffraction, basically, we look at these different solutions and measure the lattice parameters.

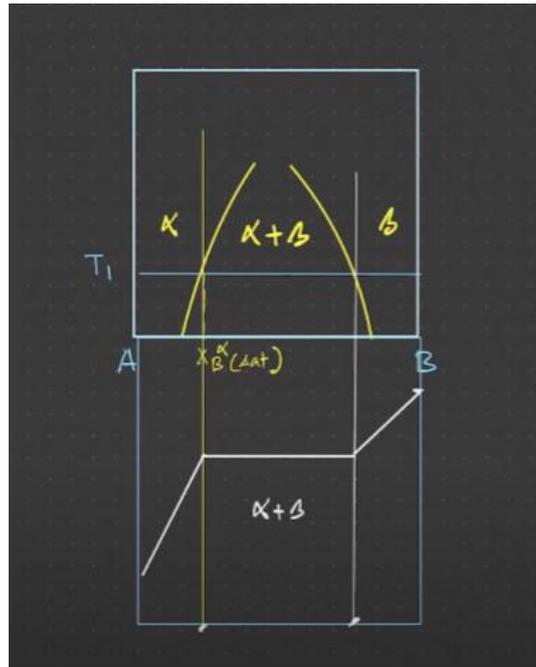
Now, there is something called Weger's law. Weger's law is basically, Weger's law basically states that the change in lattice parameter with composition, right, A of C, basically, A of C is basically, you can write, so as the composition changes, as the composition changes, there is a change, there is a composition of the solution changes, that is, say, for example, look at this condition when you have alpha phase as you go from pure A As say for example, at temperature T1, we go from pure A to the saturation value. The saturation value is the maximum solubility of B in A. Alpha is a solution of B in A. Amount of B in A. This is the maximum amount of B that can dissolve in A at temperature T1.

The maximum amount of B that can dissolve in A at temperature T1. Now, as you can see, continuously there is a change in the content of B. As B atoms have been introduced into A, in the alpha solution, what you basically see, the outcome is basically a composition dependence of the lattice parameter, right, a composition dependence of the lattice parameter. So, this

composition dependence is given by something called Vegard's law, which states $a - a_0$ is proportional to $(C - C_0)$, and Vegard's law basically tells that the composition dependence $a(C)$, the a as a function of C , is a linear function. That means, you can write $a - a_0 = k(C - C_0)$, where k is basically called a Vegard's law constant, which is $1/a_0$.

So, basically, what you are telling is, a_0 was your initial, initial, that is, parameter, say, basically, it is based on p or a , and now, it is changing from a_0 , and the change is basically proportional to how the change happens from C_0 . Now, C_0 or a_0 can be any arbitrary composition, means arbitrary composition and the reference lattice parameter corresponding to that arbitrary composition. Now, as you can see here, that it is a linear relation and that this Vegard's law of emissions is $1/a_0$, right, $1/a_0$, which is basically k , right. Now, the idea is that if you know this k for different solutions, say for example, for α , then you basically can plot the lattice parameter and again the variation lattice parameter will be linear, right, the variation lattice parameter. So, say for example, A had small lattice parameter, now adding B , you increase the lattice parameter, it goes on increasing.

till it hits the saturation limit, till it hits this limit. So, this limit is where you get one lattice parameter, but now as soon as your composition enters the two-phase region, the lattice parameter does not change, it becomes horizontal, that there is no lattice parameter variation because you have now two phases. If you look at the other way, say from β , so again β , let us assume that pure B had more. Obviously, you can see from here that adding B increased lattice parameter. So, pure B has the maximum lattice parameter. Now, if you go below pure B , that is you have some A here, you have some very little amount of A here, slightly more amount, slightly more amount, up to this temperature, at this temperature again, I am doing a temperature T_1 , right? This curve corresponds to temperature T_1 , you have this saturation point. This saturation point is the maximum amount of A that can dissolve in β , or β is basically primarily B , right? So, the maximum amount of A , so if you draw this vertical line, this is the composition, this is the maximum amount of A that can dissolve in β .



Now, this A dissolving in beta, what does it do? It reduces or contracts lattice parameter, right? Pure B has the maximum lattice parameter. Now, the more A is entering, the less is the lattice parameter, right? So, this is parameter again shows the different slope here. If you look at this, there is a different slope here. However, within the two-fifth region at temperature T_1 , there is no change in slope and you see basically a horizontal line, right? Lattice parameter is not changed. So, Basically, again looking at this curve, you can see that this is at temperature T_1 , then you can have it at temperature T_2 and so on.

Say, for example, at temperature T_2 , the curve will basically look like something like this. So, basically it will look something like this. So, basically now you have this point and this point. So, means as you can see again you are getting these two points, right, these two points.

So, this is these two points correspond to these two points. Similarly, you can have say some points here which correspond to these two points at some other temperature. So, as a result, again, you get the points of the phase boundary, join the points, and you get a phase boundary. You get a phase boundary that separates alpha from alpha plus beta, and this one separates beta from alpha plus beta. And remember, remember that this phase boundary also represents a limit of solubility of one component with another. For example, This phase boundary, this phase, this alpha phase boundary or sometimes it is also called alpha solvers, it presents the amount, the maximum amount of B that can enter A or that can dissolve in alpha at a given temperature, right? At any, as a function of temperature, as a function of temperature because this is temperature axis, right? This is the temperature axis.

So, if you know that this is the temperature axis, So, this basically gives you the maximum amount of B, right, alpha, the solvus curve, this solvus curve gives you, this solvus, it separates alpha from alpha plus beta, gives you as a function of temperature, the maximum solubility of B in alpha, the maximum solubility of the solid B in alpha. Similarly, this curve represents the maximum solubility of A in beta. Beta is a B-rich solution, right? So, basically B is the solvent and A is the solute in beta. In alpha, it is an A-rich solution.

So, in alpha, A is the solvent and B is the solute. Okay. Now, we have done this. Now, we will go back to the phase diagram, type of phase diagram. So, we have looked at phase diagrams of type I where there was infinite or infinite solubility of A and B in the liquid, right? Or basically, it was completely soluble. A and B were completely soluble or infinitely soluble or in the liquid state. However, in the solid state, in type I phase diagram, you had zero solubility of A and B, right? A and B coexist as POA and POB in the solid state.

In the solid state, POA and POB do not mix. For example, bismuth cadmium, they do not mix at all. However, in the liquid state, they completely mix, right? They completely mix. See, this one has a practical example, this lens, lens, one practical example is an isomorphous diagram between copper and nickel. Similarly, the type I phase diagram also had a practical example, and the type I phase diagram, the practical example was this, right? This also has many practical examples. So, this is a case, in type III, you have a case where, although the, so, so type I you had, infinite solubility of A and B or solubility of A and B in the liquid is infinite, but solubility of A and B in the solid was zero.

Now type II, what happens? Solubility of A and B or A and B in the liquid is infinite as well as in the solid that is infinite. So basically it is completely miscible or completely soluble. A is completely soluble in B or B is completely soluble in A over the entire composition range. right in the liquid state as well as in the solid state that gave rise to lens shaped phase diagram. However, type 3 is a very special case of type 1 and this it is a more general in fact I will tell you that it is a more general case of case 1 and this in type 3 what we were looking at is the solubility of A and B in the liquid is infinite.

The solubility of A and B in solid is limited or finite, right. It is basically limited. The solubility is limited. There is a solubility limit. So, when I tell solubility is limited of, that means, in the A solid, in the A solid, the limit of, the amount of B that can dissolve is limited, right.

That is a limitation on solubility or there is a solubility limit, right. At a given temperature, there is a solubility limit. This curve, this solver's curve, as I discussed before, represents the

amount of A that can dissolve in beta goes up as the temperature increases. Now, look at a very special point here, which I have already discussed this type of a reaction.

So, the reaction previously we considered is basically liquid goes to A plus B, where POA and POP in the solid state, right, the liquid transforms to POA and POP. One thing you have to understand, and this is again, I am repeating myself. So, the one thing you have to understand is the point E, at the point E, where there is a transformation from liquid to alpha plus beta, you have a special point. Why it is special? From this phase rule, you can understand, you have two components, three phases coexisting, and you have the degree of freedom to do the same, right? So, basically, degree of freedom equal to 0 at this point. Even at this point, we have liquid alpha beta coexistence or at this point, right, along this line at this point.

What are the phases? So, now, you will tell me what is this composition? This is the liquid composition. This is the alpha composition, terminal composition and this is the beta terminal composition. So, at this temperature, which is the eutectic temperature. So, eutectic temperature and composition, this is called eutectic composition.

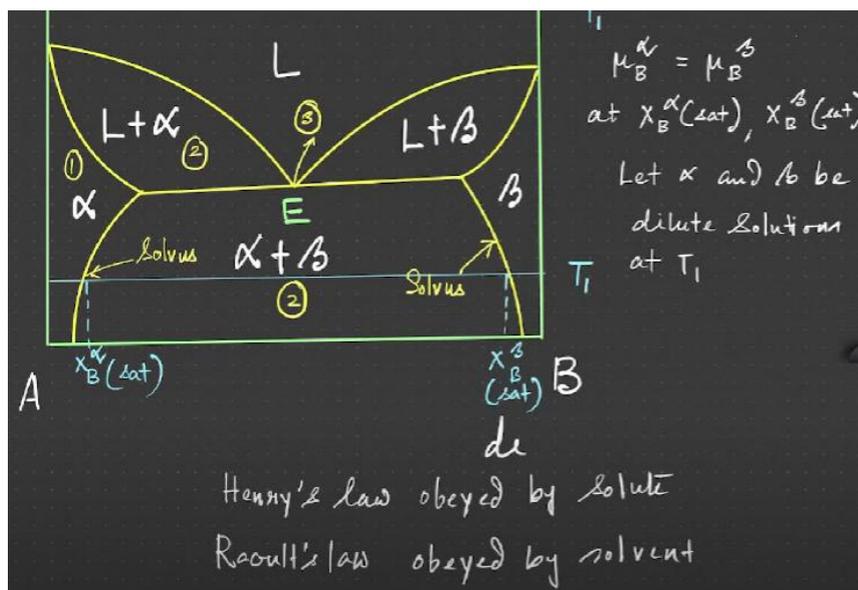
You will see something interesting. If you look at phrasing, the liquid is now coming down along this white line. The liquid is now coming down and at this point, you see exactly some the same horizontal line, right, which depends, which does not depend on the position, right, and then it transforms into two phases, alpha and beta, right? So, this is basically a eutectic transformation. And the eutectic can be in the form of lamellae, in the form of rods, right? It can appear in the form of alpha plus beta, arrange in the form of lamellae, alternating lamellae.

They can be in the form of rods. They can be in the form of, right? Plates right. So basically you have like alternating plates or lamellae. So so so so all different types of The types of eutectic microstructure can be obtained but you have to look at the eutectic reaction the reaction is very interesting because first of all this eel represents a freezing point or melting point of the mixture of A and B at the eutectic composition or mixture of two phases alpha and beta and This eutectic point represents the lowest melting point of the solid. If the solid is having this composition, then this solid below the eutectic temperature is having only alpha plus beta, right, below the eutectic temperature. So, this composition below the eutectic temperature will have alpha plus beta.

Now, at this temperature, it just transforms to, it just has a transformation to liquid. And so, you just go slightly above, you have the liquid of same composition, right. When it comes down to alpha and beta, then you definitely at a given temperature, you have alpha of this composition

and beta of this composition, right, at an immediately. So, basically, this is a eutectic, it presents a low melting, a low melting mixture of phases, right, a low melting mixture of phases, okay, our eutectic composition is a low melting composition, lower than that of pure A, right, that of pure A and pure B, right. So, eutectic temperature is a temperature that is lower than either of the melting points of A and B, this is for a binary system, And this is the invariant reaction, L transforms to α plus β or α plus β transforms to, right.

This is the invariant point E below the melting point. So, it is basically below the melting points of pure A and pure B, right. So, this basically is a very useful, is very useful concept in casting, right. So, basically if you look at casting, you do not want to go to temperatures like that is like very high, right, like if you are looking at casting of factory alloys. You don't want to go to, you do not really want to go to temperatures which are like the corresponding pure A or pure B melting point, right? But you can now go Say, for example, you can now go to temperatures like this eutectic temperature that is there, which is lower than either of the melting temperatures, and at this temperature, you can do a casting. So, if you do a casting, what will happen? The liquid will solidify into, the cast structure will contain a mixture of α and β , arrange the form of lamellae or rods or whatever.



So, they can be, they will be arranged in this different, this microstructure typically that you obtain is called an eutectic microstructure, which is a mixture of these α and β phases. And so, basic, but what happens is, as you see, the liquid of this composition, of this composition as shown by this red dot, the liquid of this composition will basically transform at a much lower temperature or freeze at a much lower temperature or solidify. at a much lower temperature than either of PO A or PO B, and it will form a eutectic mixture of phases of α and β . So, eutectic mixture of phases α and β .

I do not want to go back or explain the Liverpool and tie line. I just want to tell these are the salient points. We are representing this invariant reaction. So, this is the invariant reaction.

Now, think of a point here. So, if you see, I have marked with various phase regions. So, within 1, if I look at 1, if I look at 1, f equals to 2, right, because this is 2 components minus 1 phase plus 1. So, this becomes 2. Now, at 2, f equals to 2 components minus 2 phases plus 1.

So, f equal to 1. So, basically, when you have point 2, f equal to 1. Now, at point 3, it is a special point, a equals to 2 minus 3 plus 1, right. Now, 3 is the eutectic point, which basically this is real. So, basically, the point E, you cannot independently specify. So, basically, at point E, degree of freedom is 0, that is the composition temperature, both have to be specified, right.

Composition temperature, both have to be specified. There is no degree of freedom, right. You cannot basically specify. specify temperature or specify composition or you can specify both, your temperature and composition. As soon as we are thinking of an eutectic point that reaches coexist, the composition and the temperature are different, right? The composition and the temperature are different. Now you can see here that this eutectic point, you have the, this is the point where you have the three-phase coexistence, right.

Three-phase coexistence means e to the power equal to 0. Now, if you look at this point or this composition, right, at the eutectic temperature, you again see a liquid alpha beta coexistence, right, liquid alpha beta coexistence. Now, the idea that you have, then why is this E so different? Because when you are solidifying here, You say, you see that this liquid of composition, this is the liquid composition, you see that this liquid upon entering the, entering the, below the liquiders, it will transform to alpha of certain composition. Now, if I, now there will be some alpha of certain composition, or it go a little, little less, little more, then you will have another liquid composition here, and this will be your solid composition. Now, with this liquid composition, this liquid is now going to solidify.

So, as this liquid is solidifying, again you see the change in composition of the liquid. So, as you can see, the liquid becomes more and more enriched in solute, that is, the solute is getting rejected to the liquid, right, and the alpha becomes more, so alpha again also becomes more and more so basically that the alpha composition is also changing right the alpha composition is also changing alpha is containing more b but the liquid is also becoming enriched in the solid right on this side in this case say for example if i take the composition like this here you will have the first beta here and now as you just go below you will have the liquid composition changing and the beta composition changing right the beta has become becoming basically the

solid that you are forming is becoming slightly poorer in B, right? It is becoming more interesting. A, right? So, again, if you look at beta from the point of view of beta, A is the solid and B is the solid, right? B is the solid. Now, we look at a phase diagram. Now, the, look at a problem here, the problem of phase equilibrium, right, at the temperature. Say, for example, at temperature T1, right, you are looking at a temperature T1, this is the, given by this horizontal line, this is your temperature T1.

Now, at temperature T1, these are the saturation compositions, these are the equilibrium saturation compositions, at this one piece. So, this point and this point are the equilibrium compositions. So, this basically represents a temperature T1. the alpha-beta equilibrium that is the alpha-beta coexistence and the compositions at which alpha-beta co-exist are Xb alpha sat and Xb beta sat, Xb beta sat or saturation or Xb alpha saturation.

B - solute, A - solvent

$$\mu_B^\alpha = \mu_B^\circ + RT \ln X_{B(\text{sat})}^\alpha + RT \ln \gamma_B^\circ$$

In saturated β ,

B - solvent

$$\mu_B^\beta = \mu_B^\circ + RT \ln a_B^\beta = \mu_B^\circ + RT \ln X_{B(\text{sat})}^\beta$$

$$\therefore \ln X_{B(\text{sat})}^\beta = \ln X_{B(\text{sat})}^\alpha + \ln \gamma_B^\circ$$

$$\gamma_B^\circ = \frac{X_{B(\text{sat})}^\beta}{X_{B(\text{sat})}^\alpha}$$

So, this is basically the saturation or the solubility limit at temperature T1. This is the solubility limit at temperature T1 and if you look at the tie line here that we have drawn, this is your, this n-composition is the alpha-composition and this, this, this guy is your alpha-composition and this is your beta-composition and this alpha-composition and this beta-composition coexist, right, alpha and beta coexist. Now, if they are coexisting that means the chemical potentials are equal, right. if we use B instead of A, we can use B or A, it does not really matter, you see μ_B^α equals to μ_B^β , right, and this μ_B^α equals to μ_B^β at X_B^α saturation and X_B^β saturation, right, because X_B^α saturation and X_B^β saturation are the equilibrium values, right, we have got that in from the tie line. So, X_B^α saturation is the equilibrium composition of the alpha phase which is in equilibrium with the beta phase with equilibrium composition X with beta saturation. Now, and at these compositions, at these compositions, the chemical potentials of alpha and beta with respect to B means basically chemical potential of B in alpha equal to chemical potential of B in beta.

Similarly, chemical potential of A in alpha should be equal to chemical potential of A in beta. Here we are only considering one component B. Why? Let us assume that at this temperature T1, alpha and beta are dilute solutions. Now, if we consider alpha and beta to be dilute solutions in saturated alpha, in saturated alpha, this is very, very important point that I am trying to say. In saturated alpha, so this point is what I am talking about, this composition is what I am talking about at temperature P1, and this is your saturation composition, and this is including this. Now, at this point, in saturated alpha, P is the solute phase, right, and A is the solvent phase, that we have already told.

So, now, we are also assuming it is a dilute solution. Now, dilute solution, which obeys, so we can tell now, we can do a little bit more and tell that this is basically ideal dilute solution where the ideal dilute solution where Henry's law is obeyed by solute and Raoult's law is obeyed by the solvent. If you look at the saturated alpha composition, you have B solute, B as solute and A as solvent. In such a case, the chemical potential of B in alpha can be written as μ_{B0} , which is the chemical potential of POB, right, chemical potential of POB or molar free energy of POB. And then you have $RT \ln a_B$, right, but $RT \ln \gamma_B$, say for example, alpha, in alpha. $RT \ln a_B$ is the activity of B or you can write this as $RT \ln x_B$ plus $RT \ln \gamma_B$, γ_B is the Henry's law coefficient, ok.

So, Henry's law coefficient and you have $RT \ln x_B$ alpha saturation, right. This is the x_B alpha saturation is the composition. So, you have μ_{B0} plus $RT \ln x_B$ alpha saturation plus $RT \ln \gamma_B$, that is Henry's law. Now, but in saturated beta, you will see that μ_B beta. Because again, we are assuming ideal solution.

So, B is solvent now. Now, if B is solvent, B obeys. So, here B obeys Henry's law, right. In the saturated alpha, B obeys Henry's law. The solute obeys Henry's law. So, because B is a solute, but in saturated beta, B is solvent. So, basically, here γ_B equal to 1 and a_B equal to x_B . So, basically in such a case, μ_B beta, right, because B is solvent, μ_B is 0 plus $RT \ln a_B$ beta, which is basically a_B beta is nothing but x_B beta, right, saturation.

So, x_B beta saturation is nothing but your a_B beta. when you consider round slump, right. So, you basically have μ_{B0} which corresponds to the chemical condition of B in the standard state of the pure state of B, okay. So, this μ_{B0} is nothing but the molar free energy of pure B, right. Now, if you look at this, if you compare this, you know that ultimately at this temperature μ_B alpha equals to μ_B gamma. Now, if you name this as equation number 1 and if you name this as equation number 2, you will have μ_B beta equal to μ_B alpha, right.

So, you have μ_B^β , μ_B^β equals to μ_B^α , right, this one and this one are equal. So, as a result, 1 and 2, the right-hand sides are also equal. So, if that is so, you have $\mu_B^0 + RT \ln a_B^\beta$ is $RT \ln a_B^\beta$. So, if you see that μ_B^0 is here, μ_B^0 is here, so that cancels out, right? But you have now RT , RT and again you have another RT here.

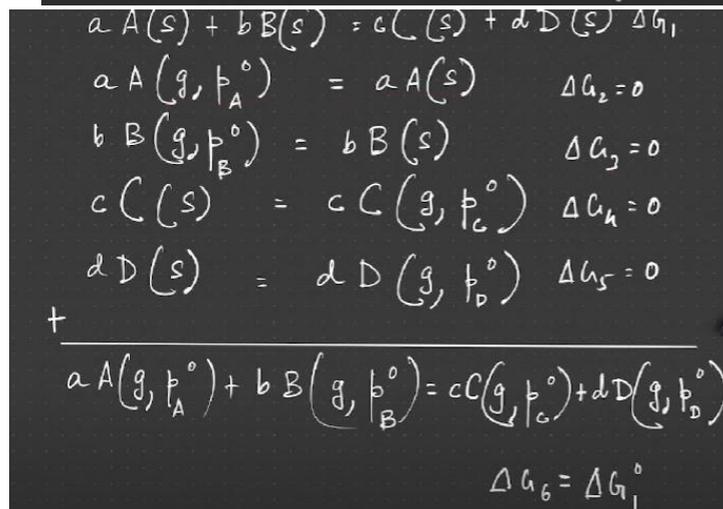
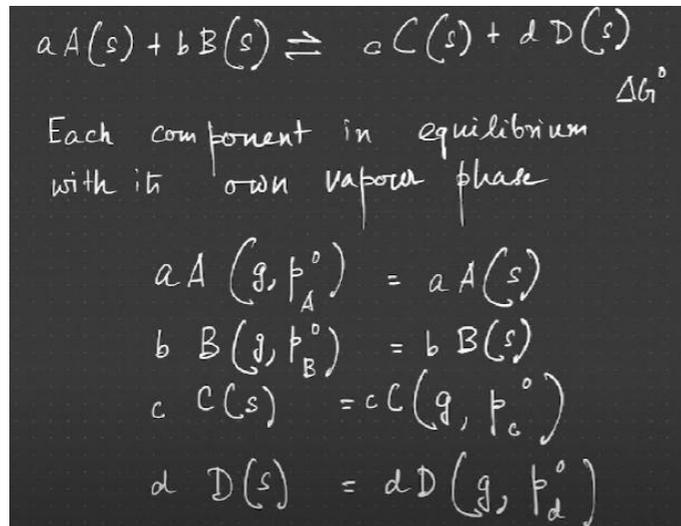
So, this RT , RT and RT basically are non-zero, so they can be removed. So, you have $\ln a_B^\alpha$ plus $\ln a_B^0$ equals to $\ln a_B^\beta$, right? Because, see, this is, this is where we solve and so there is Raoult's law. So, this is Raoult's law. So, basically, from here, you can find out what is γ_B^0 , right. You have \ln here, you have \ln here, you have \ln here.

So, basically, if you look at that $\ln \gamma_B^0$ is $\ln a_B^\beta$ minus $\ln a_B^\alpha$. So, basically, γ_B^0 is basically ratio of a_B^β by a_B^α , right. That basically gives you the Henry's law coefficient. This is something that becomes very useful, this is something that becomes very useful to understand, say, for example, If we have such a condition, we already know that angle is not sufficient. So, basically now we can use this to find out the saturation, to find out the ratio at the saturation and it becomes very very useful to understand the phase diagram.

It gives me a nice way to understand the phase diagram. So, for example, I will give you a problem. nickel and an element A, there is an element A which is mixing with nickel and they are related by a type 3 integrated phase diagram at 1000 Kelvin, A dissolves 4 atomic percent nickel and nickel dissolves 6 atomic percent A, right. A dissolves 6, 4 atomic percent nickel, that means the A rich solution, A rich solution has a solubility limit of 4 atomic percent nickel and nickel rich solution has a solute limit of 6 atomic percent A, right? So, nickel can dissolve up to 6 atomic percent A at 1000 Kelvin and A can dissolve 4 atomic percent of nickel at 1000 Kelvin. So, when I am looking at A rich solution, A dissolving 4 atomic percent nickel, then basically 4 atomic percent is the Saturated solution is a saturated composition of nickel in the A rich solution.

So, nickel is here acting as a solute, right? Nickel here is acting as a solute. This is acting as a solute in the A rich solution. And when I am talking at nickel dissolves, when I am telling nickel dissolves, then nickel is a solvent and it is dissolving how much, what is the limit? It is dissolving maximum of 6 atomic percent of A at 1000 Kelvin. Now, what we are telling is calculate the oxygen partial pressure at which nickel dissolves, nickel dissolved in A to the extent of 1 atomic percent. So, amount of dissolution is only up to 1 atomic percent and then nickel dissolved is beginning to oxidize to nickel oxide. And we are also telling that A is more

stable. A is more stable, right? Because in the other case, A is more stable and it is not oxidized, okay? So, basically, the amount of nickel that dissolves in A starts oxidizing, okay? And if it is, so basically, if it has to start oxidizing, what should be the oxygen pressure? This is what we have to find, right? So, now, we will go to certain, we will just take a little bit of aside and this aside is nothing but the reactions, right, thermodynamics of reactions.



So, we are looking at thermodynamics of, we will just visit a little bit of thermodynamics of reactions to solve the problem. We require a little knowledge of thermodynamics of reactions. Now, as we know, delta G. So, this is something that is well known, this relation, delta G equals delta H minus delta S. And we are considering this reaction, where A, A is the small a, the small a moles of A solid react with small b moles of B solid to give small c moles of C solid and small d moles of B solid.

right. So, this lowercase d, lowercase c, lowercase d and lowercase a basically represents the stoichiometry or the balance, right. There is a balance of the amount, right. So, amount of a is a moles, volume moles and or lowercase a moles and amount of b solid is lowercase b moles. They react to form c moles of C solid, right? C moles of C solid and D moles of D solid. Now,

in this case, what is the ΔG ? How do we find out? Now, see, each component is in equilibrium with its own surface.

That we already know. Each solid is in equilibrium with its own vapor phase. So, basically we can tell ΔG in the gaseous phase or the vapor phase with a partial pressure of P_A , right, a partial pressure or pressure of P_A . That is, the P_A is the vapor pressure of the gaseous phase that is in equilibrium with the solid phase, so ΔG . So, this is a reaction that we are talking about, a reversible reaction. ΔG , G is the vapor phase, G means gaseous vapor phase, with a vapor pressure of P_A , which is equal to ΔG solid, right? Because the solid and the vapor are in equilibrium.

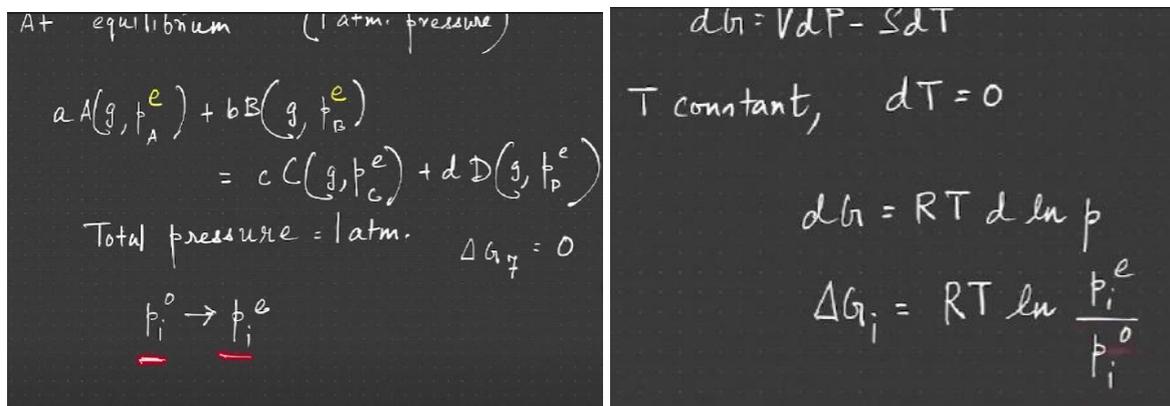
Similarly, we can write for B , B , B , G , G is basically gaseous state or vapor state and P , B , not because B , B solid. Similarly, for C as well as for D , right? P_C not and P_D not. Now, the P_C not, P_D not, P_A not and P_B not are the pressures, are the pressures when we are considering only pure A , pure B , pure C or pure D , right? That is the vapor pressure. So, P_A , for example, is the vapor pressure at equilibrium between the solid A , pure solid A and vapor of A , right? Vapor of A and pure solid A , the equilibrium, basically at that equilibrium, the vapor pressure is P_A . Similarly, P_B is the vapor pressure when B solid is in equilibrium with the B vapor phase.

Now, all these equations that I have written, all are equilibrium, right. These are all equilibrium equations. So, basically the ΔG here will be equal to, so this, there is a ΔG here to understand the feasibility of this reaction, right. ΔG is negative. Basically, if you look at ΔG which is negative, then basically this reaction is possible. If it is equal to 0, then both, all of these are equilibrium at that given temperature and pressure. And then, if it is ΔG is positive, then basically this reaction, the forward reaction $A + B \rightleftharpoons C + D$ at the temperature that we are considering may not happen.

But what I am talking about that each component in its pure state is in equilibrium with its own phase, right? Each component in its pure state, right? Pure non-reacting state, right? This is a pure non-reacting state where we are looking at solid vapor equilibrium, solid vapor equilibrium and the vaporization of P_A . Similarly, there is a pressure of P_B and then P_C and P_D . Now, if you look at that, if you add all of this together, so you have, say, a ΔG_1 or ΔG_2 in this case because it is in equilibrium. ΔG_2 is equal to 0, ΔG_3 is 0, 0 and ΔG_5 is 0. So, basically, if you look at that, If you write this, so ΔG solid and here again there is an ΔG solid, ΔG solid, again ΔG solid and then you have ΔG solid and ΔG solid and here also you have ΔG solid and ΔG solid.

So, basically what we are now looking at is the reaction of vapour phase. Now, if you look at that, this is like AA vapour at partial pressure of P_A , at an oxygen pressure or vapour pressure of P_B naught is reacting with B, B, B moles of B. which is again in the vapor phase with the oxygen pressure of P_C naught, and here also you have C moles, the react, and it produces C moles of component C, C moles of component C in the vapor phase, right, in the vapor phase with the vapor pressure of P_C naught. and this is P_D naught. Now, remember, naught basically is a superscript that we use for pure components. Remember, it is like pure A, pure B, pure C, and pure D, the vapor pressures, right, at equilibrium are the P_A naught, P_B naught, P_C naught, and P_D naught respectively.

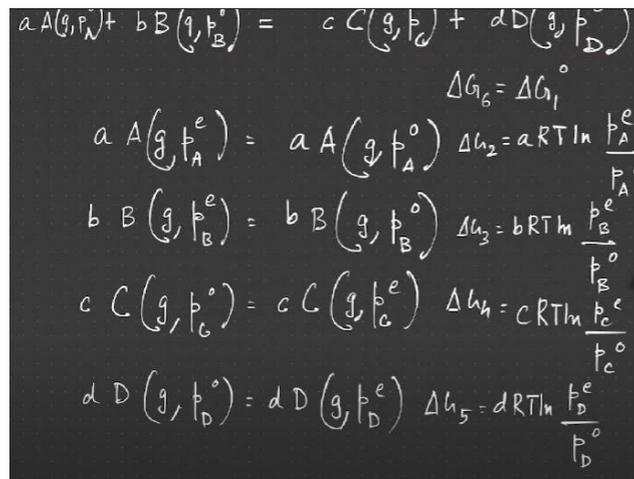
Now, ΔG , then, basically, if I had sum, then it is equal to ΔG , right. Now, at equilibrium, that is at equilibrium and we are assuming say the ambient pressure is 1 atmosphere, at equilibrium you basically change the subscript. So, basically the superscript is now E, right, the superscript is now E, right. So, basically what we are telling is at equilibrium where the overall pressure is 1 atmosphere, you have this reaction where A moles of A in the vapor phase at an equilibrium partial pressure of A. So, here we are looking at an equilibrium partial pressure of component A, right, equilibrium partial pressure of component A, this is equilibrium partial pressure of component B and that of C and D and this G indicates vapor phase and they are combining, if they are combining with total pressure of one atmosphere, that this reaction, ΔG , the change in free energy for this reaction is equal to zero.



right, because it is an equilibrium. Now, if it is an equilibrium, for example, here, so this is $\Delta G = 0$ because this is an equilibrium, this is again an equilibrium, this is again an equilibrium. Now, we are having a slightly different equilibrium because of this E. E basically tells the equilibrium partial pressure when A, B, A and B are reacted together. So, you have an AB mixture where it becomes of the P_A^E is the partial pressure of A in the vapor phase at equilibrium.

at equilibrium with the entire, with the entire mixture of A and B. Now, see, basically total pressure is 1 atmosphere. Now, as you can see, for each component I, each component I, there is a change in pressure from P_i naught to P_i^E , right, from P_i naught, P_i naught to P_i^E .

Now, if that is so, you know dG equals to $V dP$ minus $S dT$, and you are telling T is constant, so dT equal to 0, right, dT equal to 0. So, then dG equals to $RT dN$ and P and ΔG . So, basically if I integrate for each component ΔG equals to RT and then P equilibrium by P naught. P naught is the pressure, the vapor pressure of component I in the pure state when the component I is in the pure state and this is vapor pressure of component I when that is in the equilibrium state with other components, right? Other reacting components, right? So, P is the partial pressure of component I in the state where I is reacting, means there is a reaction between these I 's and they are all at equilibrium, right? So, basically P is basically when A , B , C and D coexist, right? They can coexist.



Now, if you look at that, if you look at that, you have this reaction, right, A moles of A in the vapor phase with P_A naught as the pressure, the vapor pressure, and B moles of B at a vapor pressure of P_B naught, okay, in the vapor phase, they react to form these C , C moles of C and B moles of D , where again these are also vapors with the pure, the standard pressure being the standard vapor pressure of P_C naught and P_B naught, this P_D naught and P_C naught or P_B naught and P_B naught, they correspond to the vapor pressures at equilibrium of pure solid with the, with its own vapor, right, pure solid with its own vapor, right. However, what we have to look at is that there is a, so when A , B , C and D coexist, then there is this, that A and B are reacting to form C and D . So, if you look at that, A and B when they react, the, the pressure has no longer remained P_A naught or P_B naught, because you are now reacting them together, you are mixing them together. So, as a result, you will see the partial pressure becomes P_A equilibrium and P_B equilibrium, so that the total pressure remains one atmosphere, and you have A moles of A equals to A moles of A , but you have now P_A equilibrium, and you initially had P_A naught, right, the equilibrium pressure is P_A equilibrium, equilibrium partial vapor pressure is P_A equilibrium.

Similarly, P-B equilibrium is the equilibrium pressure of material P. Now, again the B moles are getting transferred. So, they are getting transferred from here to here. So, which is equal to B-D. So, this is a pure state and this is where there are reactions.

So, basically you have P-D-E and here you have P-D-O. Similarly, for C, now in C you had this pure state that was known. Now, this is now converted to G, this is the vapor phase, but P c that is in equilibrium, right, is the equilibrium vapor pressure, right, the equilibrium vapor pressure when both of them coexist. Now, in that case, the delta G 2 in this reaction, right, from A naught equals to A equilibrium, right, there is this reaction. So, basically, your delta G2 becomes A R T, right, because see here, this is for basically, if you look at BG equal to BGT minus BGT, this is basically what I am trying to say is that this is for one mole of component I, right, for one mole of component I, you have RTL and PIE by PI naught, but here you have A, because there is this A, now A is the number of moles of A, so A is the number of, A is the number of moles of A, right? So, basically delta G2 is A R T 1 and P A equilibrium by P A naught. Similarly, delta G 3 is B times, B is the number of modes of B, R T 1 and P B equilibrium by P B naught and similarly, delta G 4 is C, C is the number of components.

So, remember, these were the reacting, these were the reacting components, right. These reacting components, you are already in P A equilibrium and P B equilibrium vapor pressure. Now, P A equilibrium vapor pressure or P B equilibrium vapor pressure is that vapor pressure where A and B both coexist, right? A and B coexist and they combine to form a coexistence of C and T, right? So, basically, if you look at that, C and D originally exist in the PO state. C and D originally exist in the PO state. From the PO state, we have to go to the equilibrium state. Now, if you look at that, in this case, what will be delta G4? This will be PCO by Pc and this is also going to be PdO, O is the zero, Pd0 that is a vapor pressure where D, pure D solid is in equilibrium with its own vapor at a vapor pressure of Pd naught, Pd naught by this will be PdO.

$$\begin{aligned}
 & aA(g, p_A^e) + bB(g, p_B^e) = cC(g, p_C^e) + dD(g, p_D^e) \\
 & \Delta G_T = 0 \\
 & \Delta G_T = 0 = \Delta G_0 + \sum_i \Delta G_i \\
 & \quad = \Delta G_0 + RT \ln \left[\frac{(p_C^e/p_C^0)(p_D^e/p_D^0)}{(p_A^e/p_A^0)(p_B^e/p_B^0)} \right] \\
 \therefore \Delta G_0 &= -RT \ln(k) \\
 a_C &= \frac{p_C^e}{p_C^0}, \dots \quad a_i = \frac{p_i}{p_i^0}
 \end{aligned}$$

Now, if that is so, you have all these reactions, you can just add them up. If you add them up, what you basically get is AA. Now, if you see here, you have equilibrium here, you have

equilibrium here, and you have the opposite here. So, you have equilibrium, equilibrium, and see, you have also here PA naught, PV naught, and here also you have PA naught, PV naught.

So, this you cancel. So, you have this one, this one. where the superscripts are equilibrium. Similarly, on the right-hand side, you will have these numbers because these guys and these guys will cancel out, right. So, as a result, what you basically see is that AA reacting with BB, again in the vapor phase, but you have now partial pressure of A at equilibrium with the partial pressure of B at equilibrium and you have partial pressure of C at equilibrium and partial pressure of B at equilibrium. So, the total pressure is more atmospheric. Now, in this case, delta G7, this is the equilibrium reaction. Now, in this equilibrium reaction, you have, right, when you have equilibrium between the reactants and products, basically the free energy is 0, right, delta G7 equal to 0 for the reaction.

Now, if delta G7 equal to 0, Now, if you see, delta G7 is the sum of all these reactions, this one plus this one plus this one plus this one. So, basically if that is so, delta G7 is equal to 0, because all are at equilibrium. Delta G7 is nothing but delta G6, delta G6, we use delta G10. So, delta G6 plus summation of summation over i delta g i and delta g i is given by this like delta g 2, g 3, g 4 and g 5. So, basically you have delta g 1, delta c c is nothing but delta g 1 plus R T n, P c equilibrium by P c o, P d equilibrium by P d o.

So, basically you have, so this is P c o by, so you have delta g 1 equals to minus RT ln k. So, Pc equilibrium by PcO. So, yeah. So, Pc equilibrium by PcO. So, this is also PbO by Pb equilibrium, right? Yeah. Now, if I have this, so you have to be very careful here this is your equilibrium the way we are using the convention so here this will be PD equilibrium by PDO and PC equilibrium by PCO however this will be yeah, this is O by E, O, E. If you add them, what you get, So, if you add, then you have PAO by PAE, PBO by PBE.

Now, if that is so, this is nothing but PAE, inverse of the PAO and PBE by PBO. So, basically, you have LNPAO by PAE and you have LNPBO by PAE, which is PBE. So, basically, LNPAO. this is something that I tell PBO by PBE is nothing but ln minus ln This will be minus ln PBE by PBO.

It is just an inverse. This is basically 1 by PBE by PBO. So, ln 1 is 0. So, ln 1 minus ln PBE by PBO. Similarly, you have ln PAO by PAE is minus ln PAE by PAO. So, basically, if you now rearrange, you basically get now rearrange, you basically get this relation, you have in the numerator PCE by PCO and PDE by PDO and numerator this PAE by PAO and this is PDE

by PDO and there is an RTM and you have this is delta G6 is nothing but delta G1. So, basically as you can see here, Now, delta G1 or delta whatever you call it, you can call it delta G1.

So, delta G7 is equal to 0. So, delta G1 is basically, call this as delta G1. So, yeah. So, this is delta G1. which is equal to minus RTln k, where this guy, we call it, this entire thing, we call it an equilibrium, an equilibrium constant, okay, for these reacting gases or reacting gases. So, this is, this entire term is called k, right, equilibrium constant. So, you have delta of G1 naught equals to minus RTln. Now, if you define AC or the activity of C as PC equilibrium by PCO, where PCO is the vapor pressure in the pure state, for pure component C, PC equilibrium is the vapor pressure when you have a mixture of component A, component B, component C, and component D.

So, AI can be written as AI equals PI. I am just, instead of putting an E here, So, it is nothing but P i, P i e is that in the mixture, right, is the partial pressure of component i in the mixture or the equilibrium partial pressure of component i in the mixture. So, basically you can just write this P i, P i by P i naught, right, is the pure form, naught basically tells the pure form. DG is RT DLN AI, right. So, basically, you know the change in free energy is basically proportional to the change in activity, DLN AI, right, RT DLN AI and DG.

Now, if I equate, so you have this S as the standard state and if we just basically you are integrating this equation, you are integrating this equation. So, basically, get GI minus GI standard or GI reference because RT LN AI by AL naught. Now, if you look at this, nickel oxide is dissociating into half oxygen and nickel solid. Now, delta G naught for this reaction is 14600 Joules, which is basically nothing but equal to minus RT by 1 K.

So, K comes out to be 2.34 into minus 8, which is basically activity of nickel. So, you have the products, right, and this is the reactor. So, this is the reactant, this is the product. So, you have AnI, right, because it is a solid and PO2 to the power half, right, there is a half here, right. So, half PO2 or basically you can write PO2 to the power half, right.

So, this becomes PO2 to the power half. And you have AnI, the activity of, divided by activity of nickel oxide, right. So, basically you have the activity of nickel oxide. So, basically, if you look at that, see, again, you have A here, right? So, the A goes here. So, basically, this is nothing but P A naught by P A equilibrium by to the power A. So, right? That is the stoichiometric coefficient. So, in this case, C, the small c is half, right? Half moles of O2, right? So, basically, if it is half moles of O2, then you have P O2 to the power half.

So, you have P_{O_2} to the power half And to ANI, right, these are your products in the numerator divided by NIO and that basically gives me the equilibrium constant. Now, ANIO is basically pure NIO is equal to 1. Again, ANIPO is equal to 1. So, basically, if that is so, what will be the activity of nickel in one atomic percent solution? So, basically, you know, nickel rich solution where nickel follows Raoult's law because nickel is a solvent. A-rich solution, nickel follows Henry's law.

$$dG = RT d \ln a_i$$

$$G_i - G_i^S = RT \ln \frac{a_i}{a_i^S}$$

$$NiO(s) \rightleftharpoons \frac{1}{2} O_2(g, 1 \text{ atm}) + Ni(s)$$

$$\Delta G^\circ = 146000 \text{ J} = -RT \ln K$$

$$K = 2.34 \times 10^{-8} = \frac{a_{Ni} p_{O_2}^{1/2}}{a_{NiO}}$$

$$a(NiO) = 1 \quad a(Ni_{\text{pure}}) = 1$$

Activity of Ni in a 1at% solution?

Ni-rich soln, Ni follows Raoult's Law

$$X_{Ni} = 0.94 \rightarrow a_{Ni} = 0.94$$

This phase is in equilibrium with A-rich phase with $X_{Ni} = 0.01$

A-rich soln, Ni follows Henry's law

$$a_{Ni} = \gamma_{Ni}^0 X_{Ni} \quad \gamma_{Ni}^0 = \frac{0.94}{0.04} = 23.5$$

$$a_{Ni} (1 \text{ at\% solid solution}) = 0.01 \times 23.5 = 0.235$$

$$\therefore p_{O_2} = 9.6 \times 10^{-10} \text{ Pa}$$

Now, X and I basically, if you look at the nickel-rich solution, if you look at the nickel-rich solution, the maximum solubility limit was 6 atomic percent. Look at the nickel-rich solution. You had nickel that dissolves, so nickel-rich solution, The amount of A that dissolves is only 4 atomic percent. So, amount of A that is dissolving is 4 atomic percent.

And the amount of nickel that dissolves is only 6 atomic percent. Now, if you look at that, when you have X_{Ni} , so basically when you have X_{Ni} equals 0.94, corresponds to a in i equals to 0.94. So, basically if you look at this, so the relation, so if you look at the relation, what is

the relation that we obtained there? We obtained γ_{B0} , where I am looking at is $\gamma_{B, XB}$ beta, $X_{B, XB}$ beta by $X_{B, XB}$ alpha.

You have $X_{B, XB}$ beta and you have $X_{B, XB}$ alpha. So, $X_{B, XB}$ beta saturation is 0.94 nickel. So, $X_{B, XB}$ beta where nickel is basically a solid where basically nickel is a solution, nickel is a solvent. So, nickel, the amount of solvent is basically X_{Ni} comes out to be 0.94, what is the X_{Ni} .

See, at A dissolves, so basically A dissolves 4 atomic percent nickel. But nickel dissolves 6 atomic percent in A, right, nickel dissolves 6 atomic percent in A.

So, x_{Ni} in this case is 0.94, right, and here, so x_{Ni} is 0.94 and here x_{Ni} is 0.04, x_{Ni} is 0.04 in the A-rich. So, basically, let us look at this. So, if you look at this, A-rich solution nickel is solid and there X_{mi} equal to 0.04 and nickel rich solution X_a equals to 0.

06, right? A is the solid but nickel is the solvent, right? Nickel is the solvent. That follows our Routh's law. So, in this solvent, you have X_{Ni} equals to 0.

94, right? So, X_{Ni} equal to 0.94 in the nickel resolution. So, X_{Ni} equal to 0.94 basically gives A_{Ni} is also 0.94 because it is a Routh's law. Routh's law tells activity equal to mole fraction. Now, this phase, this nickel-rich solution is in equilibrium with the a-rich phase with x_n equal to 0.

04, right. This phase is in equilibrium, this phase is in equilibrium with the a-rich phase with x_n equal to 0.04, right. So, basically, this phase is in equilibrium with x and i equal to 0.04. So, this is the a-rich solution and nickel follows Henry's law, nickel follows Henry's law. So, if, when you have a-rich solution nickel is a solute and that follows Henry's law and here the equilibrium is x and i equal to 0.

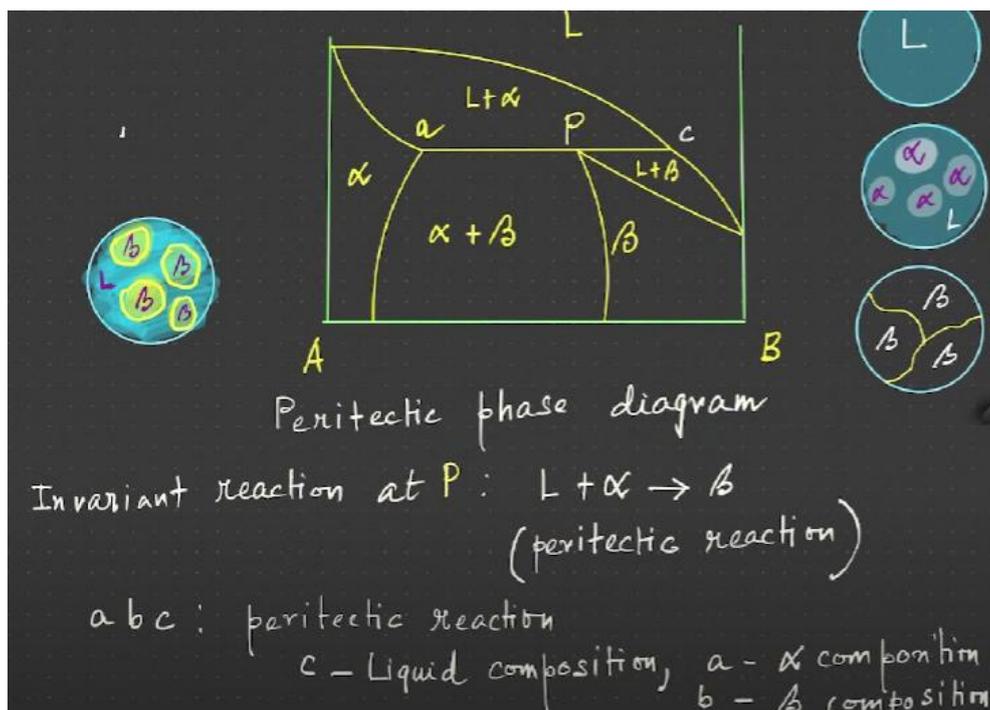
04. So, a n_i which is $\gamma_{n_i 0}$ into x_{n_i} , now If it is so, A and I basically is 0.94 in one case, A and I is 0.04 in the other case.

So, you have $\gamma_{n_i 0}$ which is the Henry's law coefficient for the nickel solute. The Henry's law coefficient is 0.94 by 0.04, which comes out to be 23.5, right, which comes out to

be 23.5. So, A_{Ni} for 1 atomic percent solution, so basically if it is so, A_{Ni} is basically γ_{Ni} A_{Ni}^0 into x_{Ni} .

Now, A_{Ni} at 1 atomic percent solution is 0.01, right, 23.5 into 0.01, right, it is 1 atomic percent of nickel. So, basically 0.01 into 23.5 gives you 0.235, A_{Ni} comes out to be 0.235, A_{Ni} is basically So, basically now if you plug in, then if you plug in A_{Ni} is 0.235, P_{O_2} to the power half and then A_{Ni} is, P_{O_2} is 1. So, then basically and k is this value, right, this value comes from this ΔG equals to $-r \tan \theta$. So, basically this is 1, this is 0.

235 and this is P_{O_2} to the power half, then basically what you see, the partial pressure of oxygen at which nickel oxide will basically, at which nickel, nickel will form nickel oxide is 9.6×10^{-10} Pascals, right, or Newton per meter square. Partial pressure of oxygen is 9.6×10^{-10} Pascals at which nickel will oxidize to nickel oxide. Now, we have another type 4 phase diagram, type 3 phase diagram where we have another type of an invariant reaction and that is called a peritectic, right, it is called a peritectic reaction.



So, basically this is called a peritectic reaction. Again you have, so here what happens is you have liquid plus alpha, you look at this point looked at this line, along this line, A, so you have alpha solute solution here, you have beta solute solution here, but you see here, you have liquid and then the liquid freezes. So, basically if I look at the concentration corresponding to point P say for example. So, what you are seeing is you have liquid which is changed to liquid plus alpha, right, at this point P, where at the point P, this C is the liquid composition, C represents the liquid composition, A represents the alpha composition and you see there is some point P which is basically the beta composition.

So, basically L plus alpha at point P, you can see there is an invariant reaction where L plus alpha changes to beta, L plus alpha changes to beta, right. So, this is called a peritectic reaction. So, basically if you look at this, A capital P C basically gives you this line where A is representing the, so at the peritectic pressure, A represents the concentration of alpha phase, C represents the concentration of liquid and P basically tells you the onset of this peritectic reaction where L and alpha with these compositions basically transform to beta with the composition given by P.

We put the beta at the composition given by P, right. So, this is what is called a penetrative reaction. So, basically you have pure liquid. So, you have pure liquid. Now, you have as you go down at the penetrative composition, you have this liquid plus alpha, right. This alpha are there and liquid is there. As soon as you go to the, just below the peritectic reaction temperature, you start seeing this L plus alpha spontaneously transforms, completely transforms to beta, right? L plus alpha completely transforms to beta. Now, if you, but if you say go from any other point other than P, so you go to like something like this, like where you have liquid plus beta.

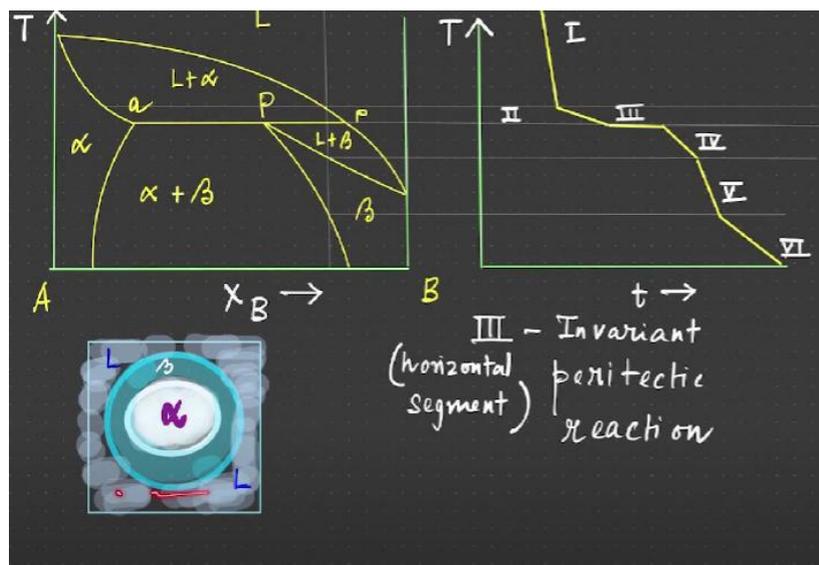
Now, in such case, what you will see, instead of this, instead of this that I have formed where L plus alpha has transformed to beta, we get, some amount of liquid as well as beta. So, we get a mixture. So, basically if you look at this composition, we have a mixture of liquid and beta, right, liquid and beta. So, this is the liquid phase and these yellow particles that you can see are the beta phase, right. So, this is the idea, okay, in a peritectic reaction. So, how does this peritectic reaction happen? The peritectic reaction, when it happens, basically you have L plus alpha.

As you can see, this is L This guy is, this is L, L liquid, so this is the liquid that you have and then you have this solid alpha and what is happening is L plus alpha goes to beta, right, so alpha forms a core. you have this beta shell which is spreading right beta liquid shell that is spreading right beta salt itself sorry not liquid so you have alpha core and then beta salt cell that is spreading so L plus alpha goes to beta right and the beta is basically the beta shell starts and continues to spread right now if you look at the cooling curve corresponding to this composition You can see that in these up to this composition, you have pure liquid, you have pure liquid. But as soon as you enter this one, this is like liquid plus alpha, right? As soon as you enter this segment, you have liquid plus alpha. Now liquid plus alpha, again the composition is varying, right? The composition is varying, right? Or liquid plus beta.

If you are going here, so first is liquid plus alpha. So, as soon as you enter here, you have liquid plus beta and that is the, sorry, liquid plus alpha. As soon as you enter here, you are going from this line, you are entering this region, which is L plus alpha. In this L plus alpha region, again, if you see that there is this tie line. So, this tie line basically represents that the compositions will continuously change, right? So, L plus alpha.

The stage 2 basically is a sloping line, another slope, right? From pure liquid, the slope has changed to L plus alpha. Now, there is this stage 3, that is this point where you have L plus alpha going to beta. This stage 3 is the most important one because it represents this L plus alpha going to beta, right? Stage 3.

Then comes stage 4. Now, just below stage 3, if I go, then you start now having this stage. So, now having this liquid beta mixture. So, beta particles are there embedded in the liquid phase. Beta particles are forming embedded in the liquid phase. So, that represents stage 4. L plus beta represents stage 4.



Now, from stage 4, you go further down, you have this segment where you have pure beta. Again, your slope has changed again because your beta is different from L plus beta, right? The conductivity will be completely different. Now, from, if you go further down, if you go further down, then if you go further down, you basically see that again this beta, again this beta composition has changed to alpha plus beta. So, alpha plus beta has a different slope. So, you have all these places where 3 is the most interesting one where you have the predictor reaction or invariant reaction happening.

So, I will next, in the next lecture, I will discuss how this, how these types of phase diagrams can come up. We will look at the free energy composition diagrams also as a basis of phase

diagrams in the next lecture. Thanks for your attention. So, we have type 3, so we will also discuss type 4 and type 5 type and type 6 phase diagrams quickly and then I will go to this idea of this free energy composition diagrams because we are looking at this different equilibrium. We have also looked at how Raoult's law and Henry's law can be used to basically find the activity of the activity coefficient or the Henry's law coefficient if we are considering equilibrium between alpha phase and beta phase and in alpha phase one component behaves as the solvent and the solvent follows Raoult's law in the other component and the other and the same component behaves as a solute in a dilute solution and follows Henry's law right where again you can use Henry's law and Raoult's law to look at various properties of the phase diagram right of the equilibrium of the phase equilibrium okay so thank you for attention for your attention and we will See you next time.