Advanced Metallurgical Thermodynamics

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Lecture No. #03

Effect of Pressure on equilibrium transformation: Clausius Clapeyron equation, phase diagram for unary system

But the only thing when we are talking about stability, we are always talking about stability with respect to some other thing, as a as per as that particular phase is concerned, it is becoming more and more stable with increasing temperature.

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Yes. Why should you think that more randomness means it should not be stable, do you think you are perfect. So, we are all stable. So, it does not mean that imperfection means lack of stability, that is the reason why we are saying that either enthalpy or entropy alone cannot talk about stability. A combination of these two, which is the free energy alone, can tell you. So, if I simply use only entropy concept, if you say that the more the lower the entropy, the more stable it is, that is a that is not the right way of looking at the more the lower the entropy, the more perfect it is, it does not mean that perfect means stable, may be spiritually. So, in materialism at least we cannot say that. So, so that is why, we are saying that when we say stability it is only in terms of the free energy that we try to look at it enthalpy; for example, if that is a case even the enthalpy wise the the lower the enthalpy the phase is more stable.

In principle, for example, look at case like the electrons around a nucleus in various orbitals, the closer the electron to the nucleus the more stable it is, there it is only enthalpy that we are looking at. And that is why you know, we are talking about x ray generation that when you knock of one of the electron from a higher shell the electrons falls into a lower shell. So, there we are basically looking at the the the energy aspect of it, the bonding energies, is it not? So, basically when you look at convert all these things into free energy term, it is the free energy that dominates, and that is what we have seen in the last class, and let us try to continue from there.

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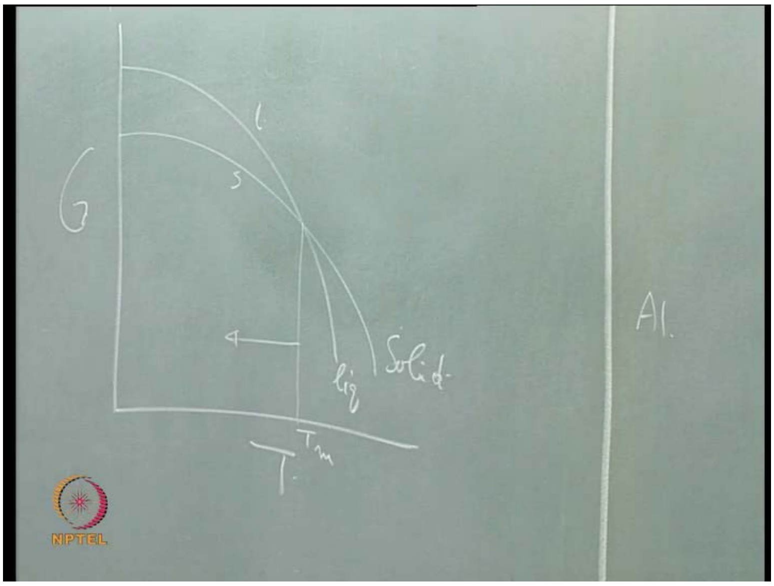

So, we looked at this (No audio from 02:31 to 02:35) and we said, if this is let us say liquid and if this is solid, we say that there is a temperature called T m, you can call it as T m or T f freezing point or melting point depending on how you look at it. And below which you say the solid has a lower free energy than the liquid and above which you have the liquid having a lower free energy and that is why, we say we always can say that any phase with a lower free energy is more stable, when you are comparing two phases, this is comparing two phases. And in principle, if particular system has a large number of phases possible, I should be able to put all of them. For example, if I am taking a metal like aluminum, what are the possible phases, that I can think of in aluminum?

Alpha

Alpha

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What is beta aluminum?

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If I take aluminum and keep on changing the temperature, increasing the temperature, what are all the possible phases that I can expect in aluminum. Anybody knows.

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Aluminum as a solid has only one structure, up to it is melting point. So, it is only one single phase up to it is melting point and from the melting point up to it is boiling point, it is one single phase, which is a liquid and then from the boiling point onwards, you can call a gaseous aluminum. So, if I want to bring the third phase, you can call it a third state of matter and thermodynamically any state of matter can be even called as a phase, how do you define a phase by the way?

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One of you talk.

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(( )) correct. So, as long as it is chemically homogenous and physically it has a boundary, to distinguish it from something else, we can call it as a phase. So, whether you call gas as a phase or a state, it does not matter. You can separate a gas from a liquid; there is a boundary between them. So now, if I want to put gas on to this free energy diagram, how it looks like, how should it look like.

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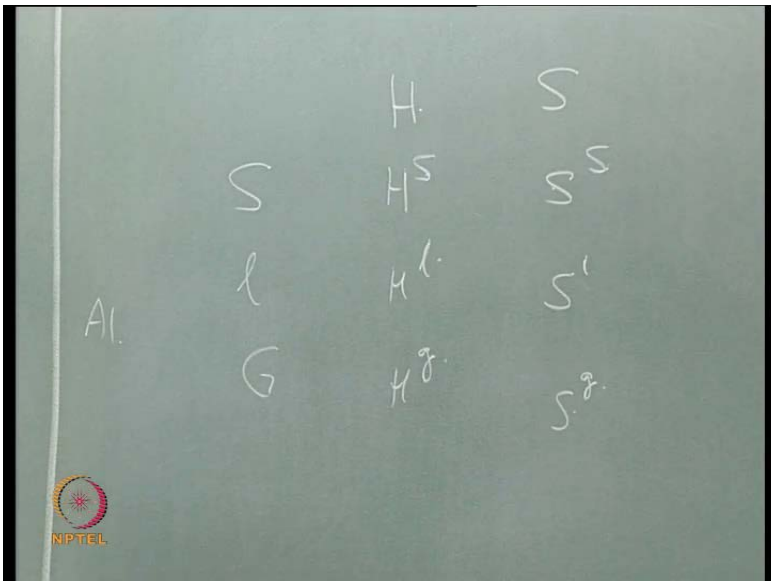

One is now; I am trying to compare solid, liquid and gas. If I look at H and call it as H of s and H, I mean H of l and H of g. And similarly, I talk in terms of entropy entropy of the solid, entropy of the liquid, entropy of the gas. Compare all of them, among all these, which one should have the highest enthalpy.

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Gas; obviously, because integral C p d T, if I look at it C p of the gas should be higher than the C p of the liquid and in turn higher than the C p of the solid. And similarly, entropy also, entropy of the gas should be higher than the entropy of the liquid and that of that. So, as a result, if I am now, I am plotting the the free energy of liquid and solid, I have already plotted. Now, if I want to super impose free energy of the gas on this, what should it be the nature of that curve is with respective to these two curves.

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Top. Yes and then what about it is slope.

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It will have, it will be steeper it will be steeper curve. So, and as a result and also now, if I look at, it should intersect the liquid somewhere and that is what will be the temperature were the gas intersects the liquid, what you would call that, as the boiling point.

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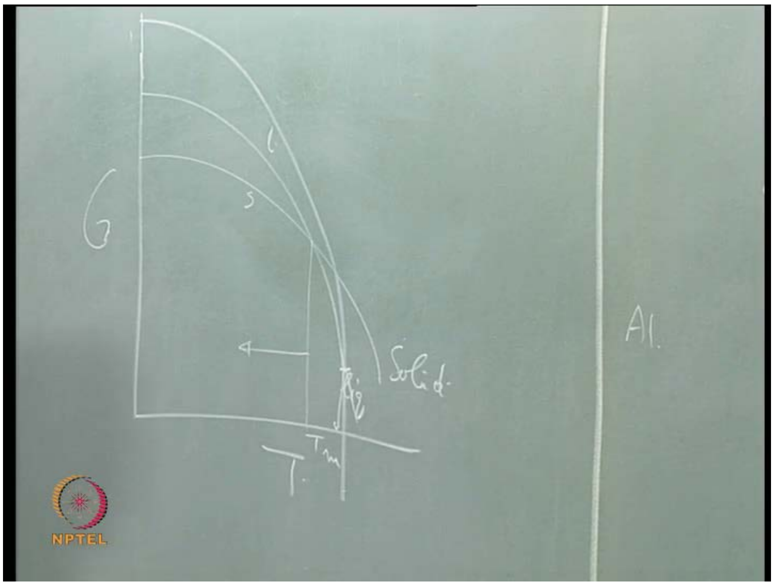

So, if you look at it, so you should have, if I extrapolate extend that, it would be something like this, where it intersects the liquid curve at some point. It will be steeper, in principle, I am all I am just simply, I know doing schematic diagrams one can actually calculate all of them, what you need to calculate the free energy?

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Yes what is the fundamental quantity that you need C p, as long as you know C p as the function of temperature. One can simply integrate, if I know the C p function a plus b t plus c t minus two, what are the a b c values for a given material over a certain temperature ranges interestingly, if you carefully observe it. If I take C p of a solid and that particular function with the a b c values, these a b c values will not remain the same for the same metal when you when I go from solid to liquid. It will have different a b c values, because the rate at which C p changes with temperature in a liquid will not be same as the rate at which it changes with temperature in a solid, because atomic vibrations in a solid will be different from atomic vibrations in a liquid so similarly, in a gas.

So, the same that is why, whenever you go to a hand book and look for a C p values. There are large numbers of handbooks, which we will talk about C p values. For example, hultgran is one of the very popular handbook, which will give you and c r c handbook is another handbook, which will give you. The thermodynamics parameters C p parameters even if you go to simple book like smittel metals handbook, smittel metals handbook also gives you for all metals the a b c values for the C p and of course, if necessary d value also and these values they always tell you this is the range over, which these values are valid temperature range and once you cross that particular temperature range these are not valid, you have to use another values of a b c.

So, as long as, I know these values of a b c and I know the C P function, I can happily integrate it get the H, get the s and once the I get these two, I can calculate the g and plot it as the function of temperature. So, whatever schematically I am drawing these are all calculatable and people have been doing in fact, there is a journal which is a dedicated for this have you heard of journal were people do a lot of thermodynamics. The journal called cal fade calculation of phase diagram. So, were all the phase diagrams that we know in standard handbooks have been calculated using thermodynamics principles, what is the connection between the thermodynamic principles and phase diagram, we will see as we go along in this particular course itself.

One can in principle any phase diagram that you see in a handbook by the way how do people get phase diagrams. Have you seen phase diagram like iron carbon phase diagram, how did people get that phase diagram?

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How do you do you mean you will do a high temperature x r d.

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d s c, how can it tell you what phases are there?

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But x r d are doing it by cooling it back to room temperature only is not it. Are are you doing x r d at different different temperatures change in resistivity anything else.

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Yes what you can heat the sample to a different temperatures no problem, but at that temperature what phases present, if you want to know the only way to know is doing a high temperature x r d. If you cool back and then do a room temperature x r d you do not know whether that phase has transformed to something else during this cooling, in most of the phase diagram we see this is happening, most of the time the phase diagrams that we see regularly in our phase diagram handbooks. Particularly the liquid us and solidus is obtained by a particular method forgetting about solid state transformations.

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Cooling curve cooling curve that is what is called thermal analysis. So, if you draw a cooling curve temperature, what is time heat the sample to a higher temperature above the melting point, cool it and then you see what is called a changes in the slopes at the liquid us and at the solidus and from that we can, we get if I can do this for various compositions. I will be able to get what is the liquid us, what is the solidus then coming to what about room solid state transformations.

Let us say in iron carbon diagram, we have a eutectoid transformation, we also have gamma go becoming alpha, how do I get these things that is where you can use x ray diffraction, if you have red x ray diffraction there is a chapter in (( )) which talks about how to get phase diagrams. Particularly the solve us lines, how to get solve us lines using the phase using the x r d. So, one can do it, but what I am saying is whatever you have generated from the cooling curve analysis, which is what we see in all the phase diagram handbook that you see, most of them accepting in cases were experiments are difficult.

For example, if you are talking about radioactive element is not so easy to do an experiment; you have to do it under very controlled atmosphere. If an a element has a tendency to oxidize, you can still do a phase diagram measurements by you know melting and casting and doing cooling curve analysis in vacuum or in (( )) atmosphere, but some of the elements, which are which are not stable elements, which have a very half life being very small some other radioactive elements, how do I do that phase diagrams are in some cases, where the melting point of one of the metal is so high.

For example, think of tungsten I want to generate aluminum tungsten phase diagram, how do I do it, I cannot melt tungsten I do not have crucibles available, where I can melt tungsten because tungsten melting point is three thousand four hundred degrees are so, the only way to do in such cases is this kind of calculations. So, what we do is I can generate the phase diagram on the aluminum side of the phase diagram because aluminum can be easily melted no problem. So, aluminum titan tungsten phase diagram on the aluminum side, you can generate experimentally do thermodynamic calculations and see if the thermodynamic calculations the phase diagram that you get from the thermodynamic calculations fix well with the experimental phase diagram. And if the fit is good then you get a confidence on the thermodynamics and then x assume that it i can extrapolate it towards the tungsten side lot of people do this the whole cal fade journal is dedicated for this kind of thing.

And people do various and we are talking of simple binaries life is not just binaries even steel for that matter very very rarely use binary steel, which is simply iron carbon. We have so many elements in steels; you go to a stainless steel. You have additional elements, you talk about a super alloy you have so many elements there, they can be super alloy. So, then how do I do experiments is not easy to find out the phase diagram for a four component system doing experimentally. If you want to take every one percent of the element and do a thermal analysis, you can imagine your whole life will go for that that is when multi component systems particularly they try to do experimentally and thermodynamic, we will see it as we go along.

So, this is what we talk about, what is called the boiling point. So, because the free free energy curve for the gas will be different. This is I can call it as a gas and I can talk about wherever this gas intersects that of the liquid, I can call this as T b. Now, if you carefully observe there is one more interesting intersection here, what is other intersection were the gas is intersecting the solid that is this. In principle this tells me that if I can take a solid keep on heating it and this solid does not become a liquid for some reason that solid. In principle the moment you reach their beyond that temperature the solid will have a higher melting, higher free energy than that of the gas. So, that solid should catastrophically start becoming a gas sublimate.

Some for some materials this sublimation temperature can be below the boiling below the melting point. So, that solid directly sublimate without even becoming a liquid there are many case like that. So, where these intersections are there that is going to give you idea of this. So, this is what is called a meta stable state, meta stable transformation there are cases were things like that can happen. Particularly, when you come to nana materials many cases you can see things like that happening we will see as we go along.

So, you can see that kind of so, if at all I will I have to call at, I would call it as a sublimation temperature T s were if solid is remaining. You may say, why should a solid remain without melting for some reasons if I am let us say heating the solid very very rapidly there is no time for the liquid to nucleate. All these are hypothetical cases of course, there is a possibility and of course, this whole phase the free energy diagram can be affected by pressure, which is what we will see right now and then all these temperatures can even change with pressure and that is what is what is called the Clausius Clapeyron equation, we will try to see, how does it come to…

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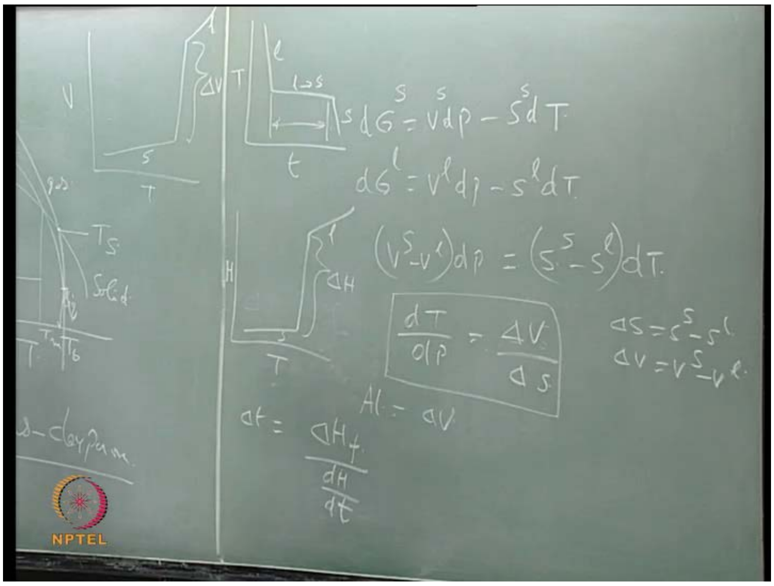

All of us have seen in the last class that G d G is V d P minus S d T am I right. And what is the definition of equilibrium in a single component system that we have defined in the last class.

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Correct, the definition is G of liquid is equal to G of solid or delta G is 0 this is the definition of equilibrium. For any unary system, we call them as unary systems single component systems. We can use this and if this is the case, if let us assume that solid is becoming a liquid then I can write this expression for both solid and liquid. So, I can write d G of a solid can be written as V P, V of solid, S of solid into d T. I can also say d G of the liquid should be equal to V of liquid into d P minus S of liquid into d T.

And at the transformation temperature, where the solid is becoming liquid both of them should be equal and if I equate both of them then you would come up with an expression that it is like, this is equal to this, if this is equal to this I can say V s minus V l into d P should be equivalent to what S this goes that side V s minus V l. So, this should come this side so, S should be equivalent to S s minus S l into d T. So, if this goes that side that comes this side. So, I can no write it as d T by d P is equal to delta S by delta V were delta S delta S is S s minus S l and delta V is V s minus V l and what is this d T by d P means, d T by d P is the rate of change of transformation temperature as a function of pressure is equal to this. So, I can simply say that this is equal to that and in principle the delta S can also be correlated to delta H, we can write it as delta S is equal to delta H by T f delta.

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Any problem this is delta V sorry sorry you are right this is delta V by delta S correct sorry for the mistake. So, what it tells us is the rate of change of melting point in the, in our case it is the melting point it can be for any transformation. It can be alpha iron transform into gamma iron, it can be gamma iron transform into delta iron, it can be a liquid transform into the gas. For any such transformation the rate of change of transformation temperature with pressure is going to be this. And now depending on the sign of it and the magnitude of it, you would see the the sign of d T by d P can be either negative or positive or highly negative or highly positive.

For example, take up this particular case of aluminum. In case of aluminum, if I look at delta V delta V is V s minus V l V s minus V l for for aluminum is it positive or negative. At the melting point, if I look at what is the volume of the solid and what is the volume of the liquid.

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It is negative. In fact that is why, if you carefully observe, we would have, you would have seen, if I plot V verses T, you would see a step like this, have you seen things like that and that is what, in fact all those foundry people talk about shrinkage, when a liquid becomes a solid, there is a shrinkage, because this is liquid, this is solid and this difference is the delta V and in fact, we give what is called a shrinkage elements for the patterns excepting in few cases, where we know that the there is no shrinkage are there is even a possibility of an expansion, grey cast iron, why in a grey cast iron there is no shrinkage.

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Yes graphite has a lower density in a grey cast iron, when a liquid is solidifying, you get gamma plus graphite during the solidification and graphite has a much lower density than that of the iron. As a result it occupies more volume. So, there is a volume expansion in fact, depending on how much of graphite is coming, you may have a 0 a lower shrinkage or 0 shrinkage are even an expansion, depending on what is your composition of the cast iron. And how much of graphite is coming one can impress full see even an expansion that is why, we even some cases of grey cast iron, we give what is called a negative allowance, when pattern allowances, you would have heard about it. So, this is what is it as far as delta delta V is concerned.

Similarly, you can also plot H verses T and see a similar thing, this is for the liquid, this is for the solid and what we call this, what is that it, latent heat of fusion that is why, whenever liquid is transform into a solid. Solid at that temperature, at the melting point cannot take all the enthalpy that is contained in the liquid and liquid has an excess enthalpy. This excess enthalpy has to be given out then only the solid can transform to a… the liquid can transform into a solid, otherwise liquid cannot transform into the solid. Unless you remove that excess heat and that is the reason why, when you pour a liquid metal into a mold, is the mold, is the one which extracts all this heat and that is the reason why, if you carefully observe, what is called, if I draw this t verses T, you would have seen this plots, why does, why do you see this.

It is because there is certain delta H associated with a liquid to solid transformation, when liquid is becoming solid and this is where liquid transform to solid. And there is certain delta H associated with this transformation and depending on the rate at which the mold is extracting the heat. It need certain amount of time, you can imply simply see that, if I want to know, what is the delta t time required for the solidification that can be found out by, what is the delta H of fusion divided by d H by d T, what is the the heat extraction rate, if I know the heat extraction rate that the mold has and which basically depends on the conductivity of the mold. I can find out, what is the heat extraction rate and if I divide the enthalpy of fusion with this, what you get is this is this is small t not capital T.

In thermodynamics always capital T is temperature, small T is time. So, always remember so, if I divide this with this, what you get is the time. So, in principle in any solidification process, what is the time of solidification, when somebody talks about it, the time of solidification depends on two parameters, what are the two parameters? one is heat of fusion, second is the rate of heat extraction. So, if I pour the same liquid metal into a sand mold or a permanent metallic mold. You would see the solidification time comes down, when I pour it into a metallic mold basically because I am increasing the denominator; I am not changing the numerator because the same metal is being solidified because I am increasing numerator it changes. So, you can see this happening (No audio from 26:50 to 26:54) coming back to this.

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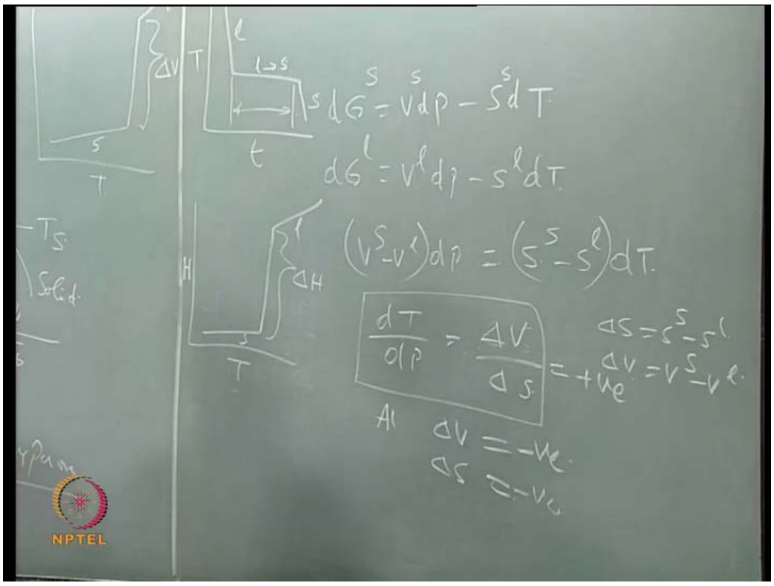

So, we know that for aluminum delta V is negative, what about delta S, what is delta S in this particular case.

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Change in entropy from where to where. So, it is S S minus S l, we have already defined it. So, S s minus S l is negative, it cannot be positive it cannot be positive so, it is negative and because both are negative, this has to be positive, the ratio has to be positive that what does it tell you. It tells you that if I increase the pressure, the melting point of aluminum will increase; if I decrease the pressure, the melting point of aluminum will decrease; that means the same aluminum instead of melting it in at atmospheric pressure. If I melt it at ten to power minus six for vacuum, it should melt at a lower temperature than six sixty unless I know this Clausius Clapeyron equation. I would not be able to know that, this is the very very crucial thing.

And all those people, who do what is called secondary steel making, they should know this; otherwise they will not know at what temperature they should heat the steel to melt all the secondary steel making is vacuum refinement. So, all those people, who do vacuum refinement of any metals and alloys. They should know, what is the rate of change of the melting point with pressure so, that at the particular vacuum level that they are maintaining, what is the melting temperature to which; otherwise either if you assume that the melting point is same as the atmospheric pressure. You are unnecessarily wasting energy because you know pretty well that it would be lower accepting in some cases, where it will not be lower that is one case can be just now, we have seen grey cast iron, where the delta V will be positive, but delta S is negative. So, the ratio is negative; that means, in case of grey cast iron so, there is a difference between a melting a white cast iron and a grey cast iron.

If I am taking a grey cast iron and melting it, the rate of change of melting point of grey cast iron with pressure is different and it is negative there, whereas in case of white cast iron, the rate of change of melting point with pressure is positive there. The melting point will increase with increasing temperature, whereas here it decreases with increasing pressure or it increases with decreasing pressure. So, if I melt a grey cast iron in vacuum, it is melting point will be higher than it is usual melting point whereas, if I melt a white cast iron in vacuum, it is melting point will be lower than the usual melting point. Similar thing, we also see in case of water and a few other metals. For example, few metals such as you know antimony, bismuth they all have delta (( )) negative solid to liquid, whenever I say delta V, we need to know, which minus word.

And in thermodynamics, we always take the product minus the reactant, whenever we are talking of any delta V, any change in any property, any thermodynamic property it is product minus the reactant. So, you need to know, which direction is the reaction taking place and the product minus the reactant. So, in our case, let us say, you are talking of liquid to solid transformation then it is V s minus V l, if it is solid to liquid transformation, it is V l minus V s, but because we are consistent in our direction, whatever you take here, if you take same thing here, there is no problem even for example, here you interchange here and also interchange here, there is no problem the sign is going be the same.

So, you will see that this is very crucial and if you want to see from another point of view, whenever I take a solid and start heating it under pressure. Let us say, we know pretty well that pressure and volume are always inversely proportional. So, under pressure always the phase that is more stable is the one, which occupies low volume. Thermodynamically, whenever I apply a pressure the phase that occupies low volume, less volume is more stable, what among the liquid and solid in case aluminum, I am if I am considering aluminum, what has low volume? It is a solid, so solid is more stable, it wants to be stable up to higher and higher temperatures as I put more and more pressure and what does it mean, it means the melting point increases and that is why, if you look at this curve once again.(No audio from 31:53 to 31:58)

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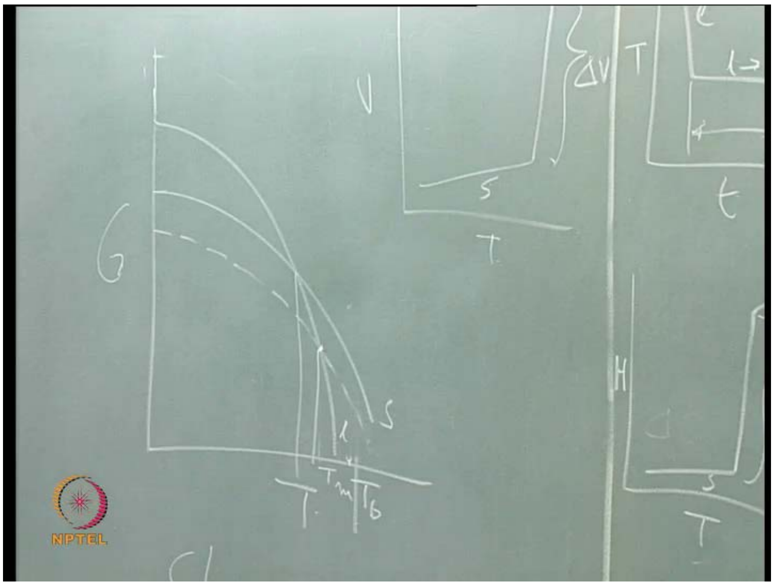

I can, if I take this as liquid; this as solid, when I apply pressure on the solid, you would see the solid becomes more stable under pressure. So, the free energy of the solid decreases and when the free energy of the solid decreases imagines it is decreasing. This is at the atmospheric pressure, this is let us say at high pressure two atmosphere, three atmosphere whatever it is and what does it influence, you will see the intersection temperature as changed, what has happened? The melting point has increased, when I apply a pressure. So, you can see, you can use free energy diagrams to explain all these things.

And as we go along, we will see in this course that, we can use free energy to explain every phenomena that, we see in in our material science and we will see and the same thing holds good, if you take a graphite and apply pressure, why does, why do you see that diamond comes is just because of that and diamond occupies less volume, when compare to graphite is more close pack structure, diamond cubic is much more close pack structure than graphite. And that is the reason why, under pressure diamond is more stable and that is why you find diamond that deep inside of course, temperature is also important, high temperature, high pressure in fact, people have done experimentally.

There are many many physicists, who have developed high pressure dies. And they have taken materials and applied very high pressures and pressures of the order of few giga Pascal and things like that. And could show that the structures of materials change and we can in principle talk in terms of a phase diagram were you having both temperature and pressure. And if I want to see such a phase diagram the simplest phase diagram that, we all know about is that of water.

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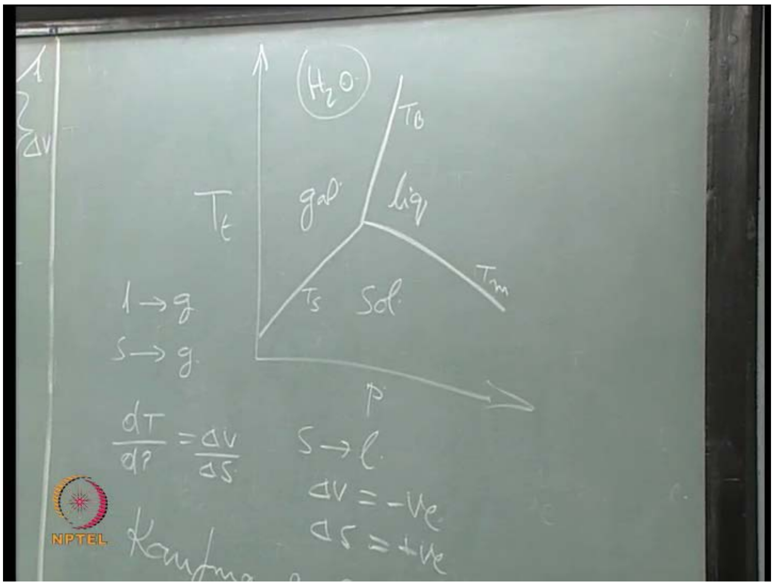

Let us look at water phase diagram, all of you might have seen it, but let us look at it from this thermodynamic angle right now. For example, if I plot temperature verses pressure, I can show this is solid, this is liquid, this is gas. And and these lines that you are seeing are the transition temperatures from one state to other at various pressures. For example, if I look at this line, what this line tells you, this line is where the solid is transformed into gas; that means, it is a sublimation temperature T s, how does T s change with pressure? You can see from here as I increase the pressure, T s is increasing why because if I again go back d T by d P is delta V by delta S. And for a solid to gas transformation, V of gas minus V of solid is positive; S of gas minus S of solid is positive, so the whole ratio is positive, so the slope has to be positive.

Similarly, if I look at this line, it is a liquid going to gas; that means, it is a boiling point and for the same, I can say liquid going to gas. Again you would see that the d T by d P has to be positive, that is why you see a positive curve, excepting this one single line, which is negative, which has a negative slope, the reason is when a solid is going to a liquid delta V is negative, whereas delta S is positive for water, this is for water, we are doing are I would not call it as water, I will simply call it as H 2 O, because water is ones state of matter of H 2 O. So, if I am talking of the face diagram of H 2 O it is, it looks like this.

And in principle, I can draw face diagrams of every metal, every single components. This is the face diagram of single components, by the way, you may ask me, sir why I should call H 2 O as single component, there is H and O there, there are two components there, but why should I call it as a single components phase diagram.

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Yes, when it is melting or solidifying or evaporating, it does all these as a single entity H 2 O does not split into H and O, when a ice is melting, it does not split into H and O and then melt, it melts as a single entity. This is, what you would see even, when we come to normal phase diagrams also many inter metallic compounds, when they are melt, they melt as one single compound. For example, if I take as f e three c f e three c actually melts as a single compound, that is the reason why phase rule, when we are doing p plus f equal to c plus 1 or c plus 2, we will try to see it in a minute. And this phase rule has to be looked at it carefully, because there is a term called c comes, number of components comes, this number of components you have to understand it carefully, otherwise you get in to troubles in terms of the phase rule. So, we will try to see that in a minute now.

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Liquid to gas transition

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d P why you are talking of d P, we are not talking of d P negative, what we are talking is, if I change pressure, if I keep on increasing pressure, the pressure is increasing in the in this direction, whether the melting point would decrease or increase, whether the transformation temperature would decrease or increase is what we are looking at and that, depends on this two is not it. So, what I am saying is, if I increase the pressure, whether the liquid to gas transformation temperature, which is the T B boiling point, this is the T s, this is the T m, whether the T m would decrease or increase here, you can see T m is decreasing with increasing pressure.

This is the temperature, which is increasing in this direction. This is the transformation temperature, I would call it as T t, this is not simply temperature, it is the transformation temperature, we are talking about, the temperature at which one phase is changing to another phase, that is what we are plotting here, if you look at it then you would see that the…

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Which which phase will be there yes, it is a question of you know, I do not know whether you got worried about this any time, whenever you take a metal like aluminum. I think day before yesterday, somebody was asking I was talking about it, if you are ever bothered about, why should a liquid when it becomes a solid aluminum know that it should become a f c c aluminum. And, if I take a iron iron, when it becomes a solid, it becomes a b c c iron. And, if I take a zinc, the moment I melt zinc and solidified zinc, it becomes a f c p zinc, how does this liquid know, liquid is random atoms atoms are randomly arranged such a random arrangements of atoms suddenly at the melting point changes into a ordered structure, ordered arrangements of atoms.

And then that ordered arrangement of atoms has a has a fixed crystal structure and this structure changes from material to material. And how does this liquid come to know about it and that boils down to a problem in thermodynamics, what we call it as, what is the ground state for a particular material at any given temperature. The ground state for a particular material ground structure are; that means, the stable structure is the one, which is what you will apply obtain, when a liquid transform to a solid, but this structure, what is the structure, again is going to depend on the electronic configuration.

So, in principle people have done, if you go to a book by name Kaufman and Berstrim (No audio from 41:16 to 41:28) not very sure about the spelling here, but Kaufman is very famous look for Kaufman, the title of the book is calculation of phase diagrams and if you look for in that book, the first chapter is dedicated to this, what we call first principle calculation of, what should the structure of a particular metal at a given temperature. For example, if I try to calculate, what should be the free energy of f c c aluminum, h c p aluminum, b c c aluminum as a function of temperature, if I do this calculation knowing, how the electronic configuration in aluminum is though, it is easy to say, but it is more difficult to calculate because all first principle calculations for more and more number of electrons if you have, the the calculations become more complicate because we have to take multi electron interactions.

People are able to do with for hydrogen, helium, but beyond that, the calculations are more and more difficult aluminum if is know, the atomic number we know, so the number of electrons we know, so each electron interacts with other electron. So, you have to consider that, but if I can calculate this, I would be in a position to find out, what should be the structure, what should be the free energy of different structure. And look at those free energies, you find out that for aluminum f c c structure would have the lowest free energy, it is ultimately the free energy, the only way is how do I calculate the free energy for a particular metal.

As long as, I can calculate it, you would see that it is, what happens then the question is, how does this liquid know f c c has the lowest free energy for aluminum, why should this liquid become f c c aluminum then it has a low free energy, but inside liquid there is no f c c structure, how does suddenly at melting point f c c structure comes in, that is where you need to understand that liquid always has what is called as short range order. This is different from, how do I differentiate a solid from a liquid and a gas, this is what differentiates, the solid has a long range order, a liquid has a short range order and a gas does not have.

In a gas, we do not see a short range order clusters, in a liquid you always have clusters, within clusters you have a periodicity, you have a unit cell and these clusters are of different different sizes, you have different sizes clusters, this is what we call them as embryos, inside the liquid. And then one of the clusters attains that size of a nucleus at the melting point, that nucleus starts growing. And all other clusters are still there inside the liquid, but they do not grow only that, which has a size of the nucleus, is the one which starts growing. So, in every liquid, in fact one can even calculate thermo dynamically, what is the size of that cluster as the function of temperature, all this you must have done in a nucleation kinetics.

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When I say no orderliness molecules are there, I am talking of in case of metals let us say there is single atom. So, there are only single atom molecules inside the gas of aluminum and there is no clusters at all that, I can talk about as a as a particular unit cell.

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Correct

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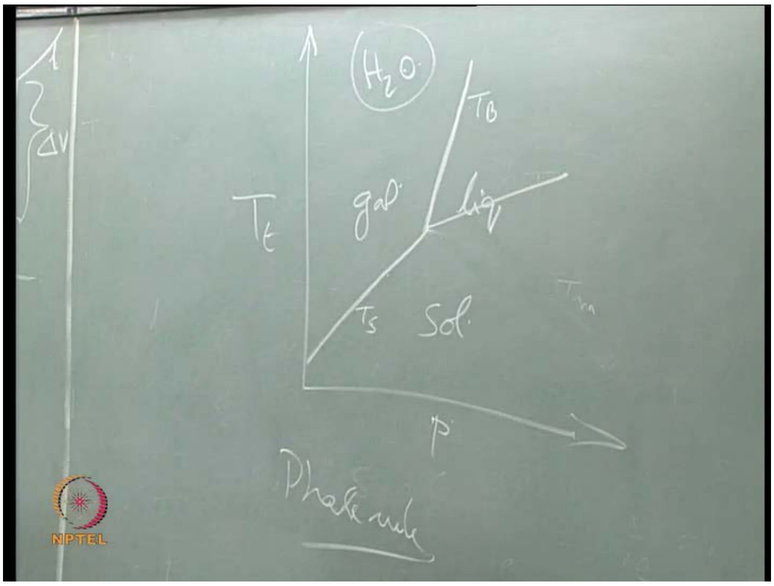
In principle, there are cases where people have done, when people have done meta stable transition, when the when you quench a gas, there is a possibility that you you over take one of the stable state, possibly whenever some of the structure stable structures, if they are very complicated structures. For example, there are cases, which as we go along we will see, what are called meta stable phase diagrams. For example, a simple thing like f e three c, which we have seen last last time, why does f e three c form, why not graphite form because this splitting takes a long time. So, the system prefers to that and there are cases, where some of the intermetallic compounds have a complicated crystal structure. And as a result, if I take a liquid and quench this liquid, this liquid instead of forming that inter metallic compound can form some other (( )) a simple structure or can even form a glass, that is what we see glass formation, we will see as we go along. So, this kind of meta stable states are possible and we I will show you a few meta stable phase diagrams, where instead of a stable state, which is available in the phase diagrams something else comes out.

And that is what, I have shown you early also in case you can stabilize solid beyond the melting point, it would become a gas and this gas is now forming at a temperature below the boiling point. In principle below the boiling point, it should not have gas. So, that is what you would start seeing. So, this is possible and if you go to that, one can find out that, so in principle one can talk about, what are the states that are possible and if i continue here and look at here, now now seen a slope.

(Refer Slide Time: 46:52)



You have only talked about the the the positive or negative of the slope only, we are not talked about what is the absolute magnitude of the slope. Absolute magnitude depends on delta V by delta S, as long as, I know what is the delta V; what is the delta S at different pressures then; that means, I should have a knowledge of how V of solid changes with pressure, how V of liquid changes with pressure. And, if I know that, in principles at different pressure, if I know what is delta V and what is delta S. In principle, I can calculate that, so this though I am plotting it as a straight line, it may not be a straight line. And similarly, when we draw these two as straight lines, they may not be straight lines. In principle, V as a function of temperature might increase not as a straight line.

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Yes that is what, we are going to come to possibly today, we will not discuss, if you know the phase rule. So next class, we will talk about the phase rule, where we will be able understand this particular triple point because at this triple point, you would see the three phases are coexisting and when the three phases are coexisting, you will see that, what is called the degrees of freedom becomes 0. So, this is fine for a single component system.

Now, what happens, if I take a binary system, let us say this is for aluminum phase diagram accepting that for aluminum, this is not the correct phase diagram, what should be the correction that, I should incorporate for aluminum.

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Yes, these lines should be like this that is the only change, of course when I say that is the only change the actual slopes in water in H 2 O will be different from the actual slopes in the aluminum, but the aluminum, all the three slopes will be positive, all the three slopes will be… So, aluminum, iron most of the metals, where you do not have that anomaly of the delta V, the volume of the solid being higher than the volume of the liquid. As long as, that anomaly does not exist, this is true, we can do that.

And now the moment, I say a binary; I have to add something more there. If, I am talking of two component systems, let say aluminum, copper. I have additional element there, so this phase diagram, I have to add one more axis there, which is nothing but, the percentage of copper. So, it becomes a turnery kind of diagram. A three dimensional diagram and in that three dimensional diagram, we will start working on it, we will talk about it in the next class, how to do such a thing. (No audio from 49:35 to 49:40)

I am stopping because it has to come to 0 there, can we continue even after it goes to 0, no problem, we will stop. So, that is why. I will follow that (No audio from 49:50 to 50:04) this is the problem for a teacher, no teacher wants to stop. yeah tell me.

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Correct correct, so because the C p as you knows below the de by temperature, at very very low temperatures, it is the electronic configuration contribution come into picture.

At a higher temperature, it is more of atomic vibrations, very low temperature you know closer to 0 degree 0 Kelvin actually, we do not actually have much of atomic vibrations, but this is the electrons inside the atoms, they turn to vibrate and that is the reason why, you get but that value is too small. And as a result, C p is very small, but the rate of change of C p with temperature will be different, because those vibrations are going to be different from that of the atom.

So, there are you know different different expressions that are available for the C p at low temperature, at higher temperatures, one can calculate it, they are available. You have to go to the standard handbooks, and for definite materials that are, but most of the cases because we deal with metals, above room temperature. We do not actually talk about that contribution at all, that contribution is insignificantly small, when compare to atomic vibrations, at temperatures above the atmosphere room temperature. And accepting physicist, typical metallurgist, mechanical engineer or a chemical engineer is not really concerned about such low temperatures, we will stop.