Phase Diagrams in Material Science Engineering

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Lecture - 06
Single Component Phase Diagram

So, I have already told you that we are basically going to discuss about the single phase - single component phase - diagrams here. And, in a single component phase diagrams, the composition variables is fixed. Like I consider pure water, pure iron, pure carbon dioxide; there is no change of compositions. But, the variables which do get changed at temperature and pressure, so we must now look at what are the effect of pressure on these systems.

Until now, I have told you, I have shown you that the free energies of different systems and different phases as a function of temperature, keeping pressure constant. Now, we are going to see if I change the pressure what will actually happen and how we can get the phase diagrams. Please be attentive while looking at these diagrams.

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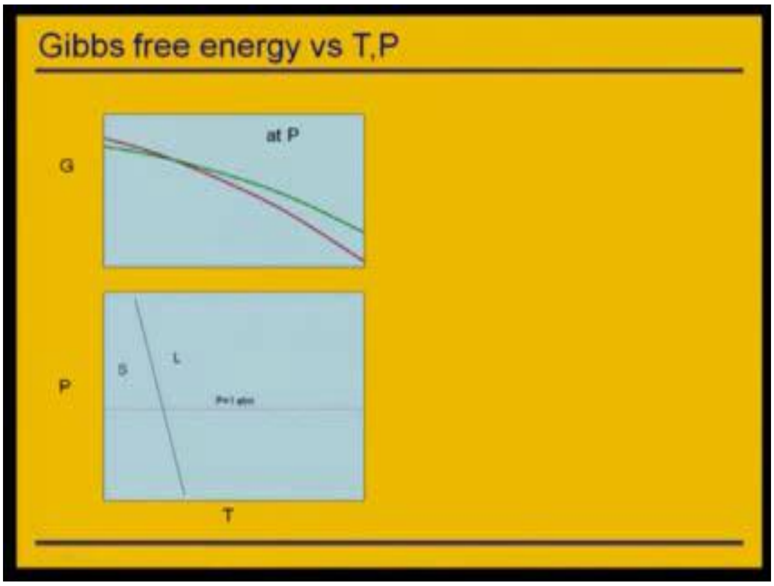

Gibbs free energy vs T,P

Let us suppose I have free energy versus temperature curve at the top and a fixed pressure - one atmospheric pressure - and I know that these 2 curves will cut or crossover at a multi temperature given by this point here, which will have been marked by red dot. So, now, can I just translate this point onto the pressure-temperature diagram? How I do it? Very simple, I just draw a vertical line across that. So, I could see that this temperature Tm - vertical line - cuts the pressure line at a point, and this point is given by a blue dot.

So, now, if I change the pressure this is one of (Refer Time: 01:46) atmospheric pressure. If I change the pressure, what will happen? Suppose, I have a pressure P, P maybe higher than that atmospheric pressure; that is what is shown here. So, if I have higher than the atmospheric pressure, the free energy curves will be changed little bit. They change means the nature of the curves will not change, but the point at which they will cross or intersect will change. That is what is shown here. It is getting intersected at a different point than the PBS point and this is given by the new point.

Now, if I can transfer the temperature at which they cut to the pressure temperature exceeds I get a new point - new blue point. So, this is the way actually I can generate many, many such blue points; you can see here; one by one I can generate many such blue points a pressure- temperature equilibrium, and also at a pressure less than the atmospheric pressure I can have a point. And this is the way I can get a boundary. What is this boundary? This boundary is between solid and liquid. Like suppose water and ice, they could quaternize this boundary.

So, I can have a boundary between solid and liquid. So, immediately we can see this is a phase diagram between solid water, like ice, and liquid, with the boundary line as where there exceeds the temperature and pressure. So, we all know that this curve or this line will have a negative slope. Why? That is very simple. If you know that that melting temperature of ice will get reduced if I apply pressure, because ice has a lower density than water, therefore ice expands when it forms water, and that if we will apply pressure it will then reduce the volume, and then, it melts at lower temperature.

So, that means, the slope of this curve dP by dT will be negative. That is why this curve is shown as a negative. But if it is not so for many other metals that this change of temperature versus pressure is not negative; in that case, it will have a positive slope. So, now, let us do it for at that temperature at which this one atmospheric pressure line cuts these axis is given as a 273K; that means, your degree Celsius.

So, let us now do some calculations. I will do it on the board that is easy for you to follow. Let us suppose, let us note that along this line we know the solid and liquid are equal, along this line.

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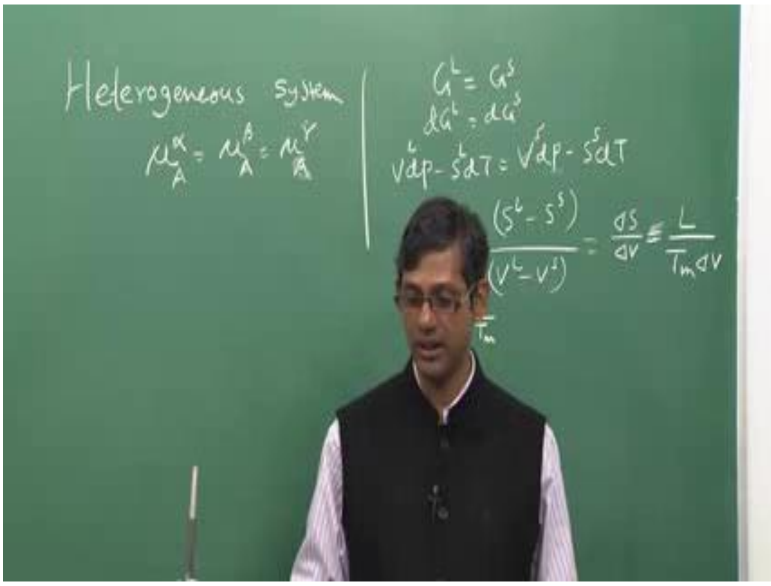

So, if they are equal, solid and liquid are equal, free energy of liquid will be equal to free energy solid along that line between solid and liquid. So, therefore, if I take a differential on both sides, this will also be equal; till the GL dGL will be equal to dGS and I know that dG is given by vdp minus sdt. So, let us write down these 2 on the both side; then, we will put the symbols vdp, sdt.

So, this is L; this is L; this is S; this is S. So, now, if I just you know do the mathematics properly what do I get? I get dP by dT is equal to dT. So, therefore, this will be SL minus SS divide by VL minus VS. That is what we will get. This is nothing but change of entropy divided by change of volume, when the transformation from solid to liquid happens, when liquid to solid happens. So, as you know in; what is called in a system like water this volume change is negative because solid SL has higher volume than the liquid; ice has lower density than the liquid water. So, that is why this is negative; that is why the slope is negative because delta S cannot be negative.

Now, delta S can also be written like this way; delta S is nothing, but entropy diffusion that is will be equal to latent heat divided by melting temperature. So, that means, this is equal to L - latent heat divided by Tm into delta v. So, as you can see latent heat cannot be negative; Tm cannot be negative because these are absolute values. So, therefore, delta v is negative in ice water system and that is why this is negative sign, correct? So, this is known as Clapeyron equation in the literature, this is what is derived in the slides; this is known as Clapeyron equation.

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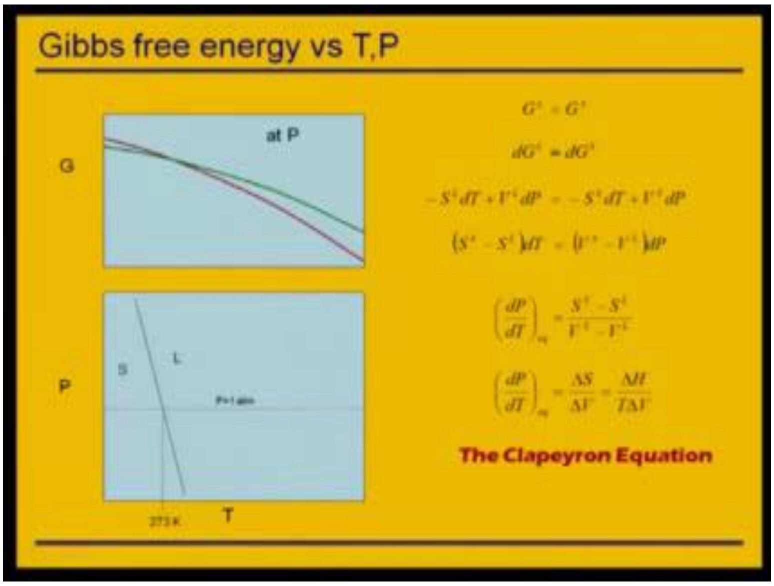

Gibbs free energy vs T,P

$$G^L = G^S$$

$$dG^L = dG^S$$

$$-S^L dT + V^L dP = -S^S dT + V^S dP$$

$$(S^L - S^S)dT = (V^L - V^S)dP$$

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{S^L - S^S}{V^L - V^S}$$

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V}$$

The Clapeyron Equation

This one. So, I write down again. I remove this part.

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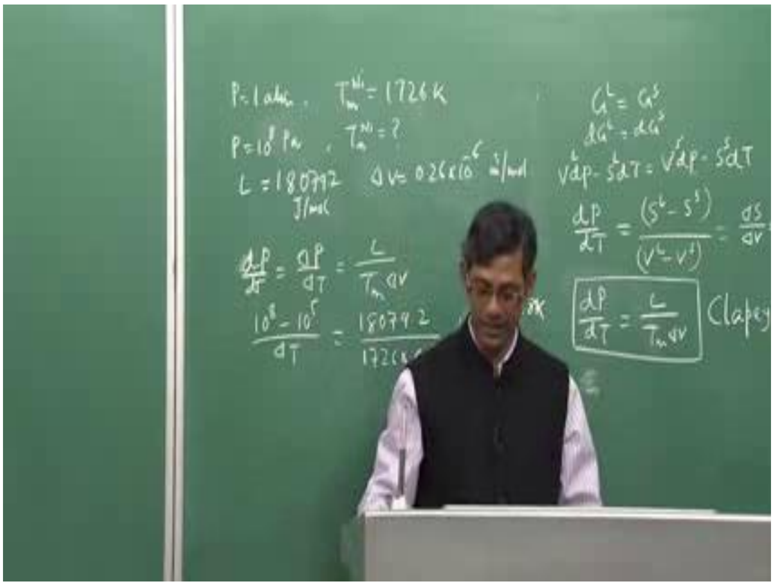

So, dP by dT L by Tm delta v is known as Clapeyron equation. What is Clapeyron equation? It is this this is - Clapeyron equation. Some people say this is Clausius-

Clapeyron equation; they were 2 scientists; they have derived. So, Clapeyron equation tells you the how the pressure will change as a function of temperature for a pure component, correct?

So, let us now move ahead. Before I move ahead, let me just also like. I to try to solve a problem, because you will be solving many problems in your assignments or something, because some of the cases it is important to know how to apply this rule. Let us say there is a problem, which I will read out to you. The pure nickel - pure nickel, I hope you understand - melts at 1726 Kelvin at the one atmospheric pressure. Determine the melting point of pure nickel when it is acted upon by pressure of 10 to the power 8 Pascal.

So, pure nickel melts at, suppose when pressure is one atmosphere pure nickel melting temperature is equal to 1726 Kelvin. Now, if I apply pressure of 10 to the power 8 Pascal, what will be it is melting temperature? You need certain values and these values are actually latent heat and delta v. So, what is the latent heat value is given in this problem? Latent heat is about 18079.2. Now, 18000, something wrong 18000, yes 18079.2, I am only writing wrong, joule per mole, and this is 0.026 into 10 per minus how much? 3, minus 6, sorry meter cube per mole. So, this is my problem. I need to find the melting temperature of pure nickel when this much pressure applied.

So, very simple I just write down dP by dt. I borrow this Clausius-Clapeyron equation. This can be written like this, is equal to latent heat by Tm delta v. Now, put all the values. So, delta p is the pressure difference. One atmospheric pressure is equal to the 10 to the power 5 Pascal; please remember these. So, therefore, this is 10 to the power 8 minus 10 to the power 5 divided by delta T. This is the pressure difference, latent heat is given 18079.2; divide joule per mole multi temperature is 1726; this is given 0.26 into ten to the power minus 6. You can put down all the units should be equal. So, the value which will get is equal to I think 2.48 Kelvin delta T. So, delta T will be 2.48 Kelvin. If you do the maths properly, that is how it can be solved. This is a very easy problem. One can do very easy to test his knowledge on there.

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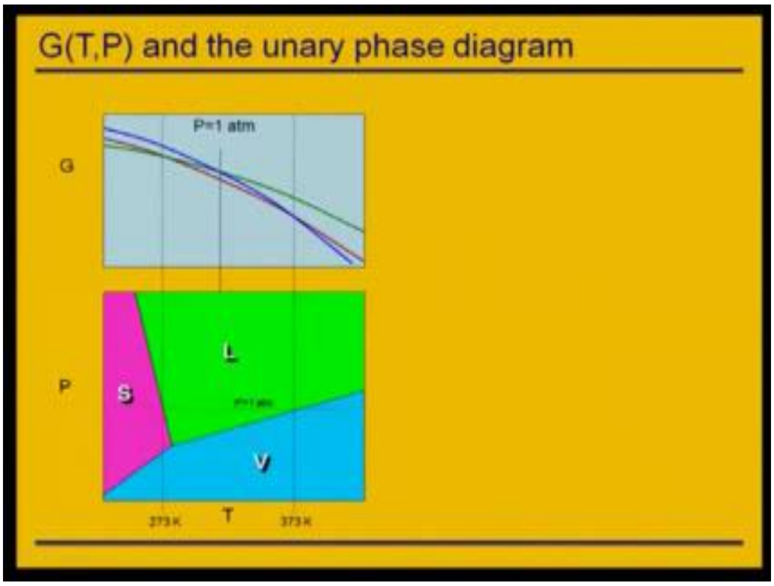

G(T,P) and the unary phase diagram

Now, let us move on and do the, see the, other parts of the diagram. So, this is what I have done. This diagram shows you exactly what I have done for the solid and liquid. Now I do for the liquid and vapor, and solid and vapor, both. So, I draw a green curve. We can see on the G versus temperature curve. I draw a green curve; green curve corresponding to vapor. So, this is corresponding to solid; this corresponds to liquid; the green curve corresponding to vapor, water vapors.

So, you can see the green curve cuts both the solid curve and liquid curve. Let us follow one by one. If I have a one atmospheric pressure, I know the water boils at 100 degree Celsius temperature. You all know 100 degree means 373 Kelvin. 273 plus 100 is 373 Kelvin; everybody knows. So, therefore, this line which is to which corresponding to the solid vapor equilibrium, we will be cutting this one atmospheric pressure (Refer Time: 11:08) at 373 Kelvin.

So, now I can have 3 equilibria: solid liquid, solid vapor, liquid vapor. These 2 equilibria solid vapor, liquid vapor, is exactly same measure as the solid liquid equilibria measure I have shown you. Now, I will do the maths later. Let me just do all this step. We can apply Clausius Clapeyron equation and get that. Let us forget about those things right now. Now, let us go ahead and see the phase diagram properly. So, now, actually I can see there are 3 lines: one solid vapor, solid liquid, liquid vapor. 3 lines on this diagram (Refer Time: 11:47) the temperature. This is basically phase diagram of water, exactly, and you can see the (Refer Time: 11:54) temperature is 373. 373 is the boiling temperature. At this point where the 3 curves - solid liquid, liquid vapor, solid vapor - 3 curves meet it is known as the critical point. And these are the regions of solid, this is the region of liquid, this is the region of vapor. So, this is solid; this is liquid; this is vapor.

So, what is the transformation between solid and vapor? This is known as sublimation; very simple if you see. Suppose, if you take out, you know, in a very moist day, in a winter like December, if you have a rainfall, and you open the refrigerator, you will find vapor up, water vapor is coming out from ice; that is because sublimation happens very easily at the temperature and pressure. Similarly, liquid if we boil the water it will form vapor. So, this line corresponded liquid vapor equilibrium; this one corresponds to solid vapor equilibrium, and this one is basically solid liquid equilibrium temperatures. This is what I have written. So, let me just remove my writing, so that you can see properly.

So, you could, you have got the idea that this is actually way the phase diagram of a single component system is measured or determined. Now, I just wanted to use this Clausius Clapeyron equation. Even in this lecture, Clausius Clapeyron equation again and solve the problem for you, so that you can do it. I just keep it, this part, and remove everything else, and do these things for solid vapor, a liquid vapor rather.

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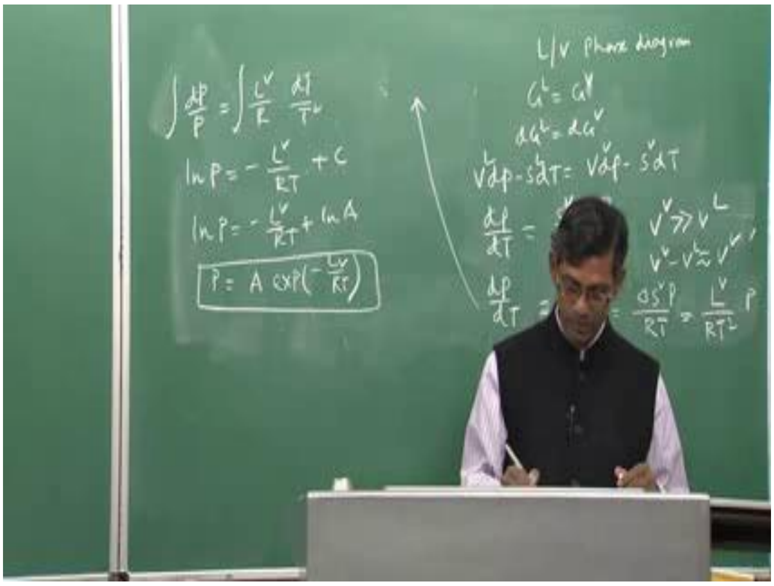

Let us go for liquid vapor; it will remain same. So, for a liquid vapor system, liquid vapor phase equilibria, I like this liquid vapor phase equilibria for phase equilibria line, liquid vapor phase equilibria line, the free energies of solid and vapor will be same; that is very easy to understand.

So, therefore, the difference will also be same, therefore, vdp minus sdT. So, I have derived this expression in the class before vdp minus sdT. This is liquid; this is liquid; this is vapor; this is vapor. So, I what is dP by dT? Very simple, we have already done that. This is nothing but I will let me write down SL minus SV, yes, is it correct? Yes. SL minus SV and this is VV minus VL. No, this will be SV minus SL. That is correct. Now, I know that for any liquid vapor system, volume of vapor will be much greater than volume of liquid; that is obvious; volume of the vapor will be the volume of the container minus the volume of the liquid, when each were boiling the water, right? You can take a big container put a small amount of liquid, when it is boils excepts the liquid is present represent whole volume will be occupied by vapor.

So, that means, volume of vapor will always have the volume of liquid. So, I can write down VV minus VL is almost equal to VV. So that means, this is equal to SV minus SL by VV, and if I apply the gas law, that what is the gas law? That PV is equal to rT per one mole, then I can write down this one delta s divided by, delta s divided by, delta SV actually divided by RT. RT into P, correct? That is obvious. So, what is delta s? Delta s is nothing but this can be written like this, there is a latent heat of vaporization divide by RT square because LT by TR into P, right? This can be written like this; this can be written like, say, like this.

So, I get this expression dP by dT equal to this. So, now, I take out this expression here and solve this. So, I can write down dP by P is equal to LV by R dT by T square, right? So, if we integrate that you will get log of P is equal to minus LV by RT plus a constant; that is integration constant; if I integrate on both side. So, this means log of P is equal to LV divided by RT plus suppose integration constant is log of A. We can always have to change that. So, P is equal to it is multiplied by A exponential minus LV by RT. So, you can clearly see, the curve between solid and vapor, liquid vapor will be exponential in nature and that is easily obtained from these diagrams; that is easily obtained from this diagram. Very carefully it can be proved by their free energy, equilibrium free energy equations, that the equations of these 2 curves of equilibrium of solid and vapor, and liquid vapor.

Let me just take it down again to show you this line - this is basically a curve, and this is also curve. These are equilibrium between solid vapor and liquid vapor. They will be exponentially increasing line. That is what is basically shown in these diagrams, very very nicely. Now, one can actually solve problem to know a better idea about this equation. So, let me just do that, then I can get back to you in a detailed manner. How I can do that? I just keep this part and remove this particular portion for you benefit, but I urge you to do these problems, to do these derivations yourself; otherwise, you will not be able to understand or solve the problems in the in the exam.

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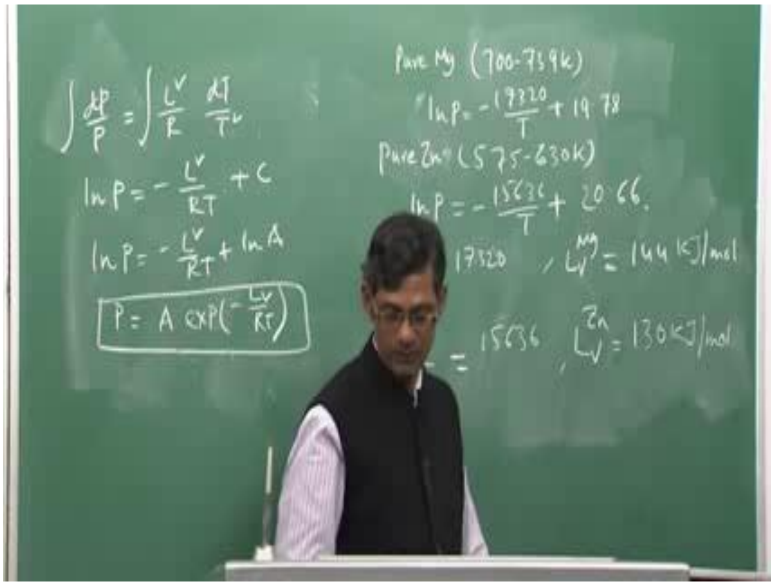

Let us suppose vapor pressure, the problem is like this; vapor pressure of pure magnesium in the temperature range. So, pure magnesium, vapor pressure in the temperature range of 700 to 739; 700 to 739 I think we should 700 to 739 Kelvin is satisfied by this expression. What is that? Log of P is equal to minus 17320 divided by temperature plus 19.78; this is for pure magnesium.

So, again for pure zinc, same kind of expression is valid for the temperature range of 575 to 630. Why this temperature is given? Because at that temperature, the vaporization happens, this is given by log of pressure p of G, forgot to write zinc; log of p is equal to minus of 15636 divided by temperature plus 20.66. The popular question is that determine the heats of sublimation. That mean determines the heat of sublimation for magnesium and heat of sublimation for zinc. How you do that? It is very simple; anybody can do that; there is no problem.

I have to compare this expression with this. How do I compare? This one log of pressure is equal to minus LV by RT plus log of A. So, that means, this one is equal to this term; 17320 by temperature is equal to LV by r, correct? So, for magnesium I can write down LV by r. So, let us do for magnesium first. LV by r equal to minus LV by r equal to minus will get cancelled, so 17320. So, LV is basically this multiply r and r is the value of 8.314 basically joule per mole per Kelvin. So, that is it will give you 100 and something like 144, 144 kilo joule per mole. This is sublimation of a later attentive sublimation for the magnesium.

Similarly, I can compare zinc 1 with this equation log of p is equal to minus LV by RT plus log of A with this you can see here therefore, zinc LV zinc by R is equal to LV zinc by R is equal to minus of this one or my plus of this one because minus once it get cancelled. So, therefore, LV zinc is equal to something like 130 kilo joule per mole. You have to know the value of r. Value of r is 18.314 joule per mole Kelvin.

So, that is actually a way you can actually solve these problems. We can solve many problems and I will give you with some problems also to solve in the interest of yours which you can do it yourself. These are very simple, even like class twelve standard problems which anybody can do it; that is not a big issue. So, you understood the basic phase diagram. This is called unary phase diagram in T, P space. Therefore unary phase diagrams will be in special numbers of fields or space.

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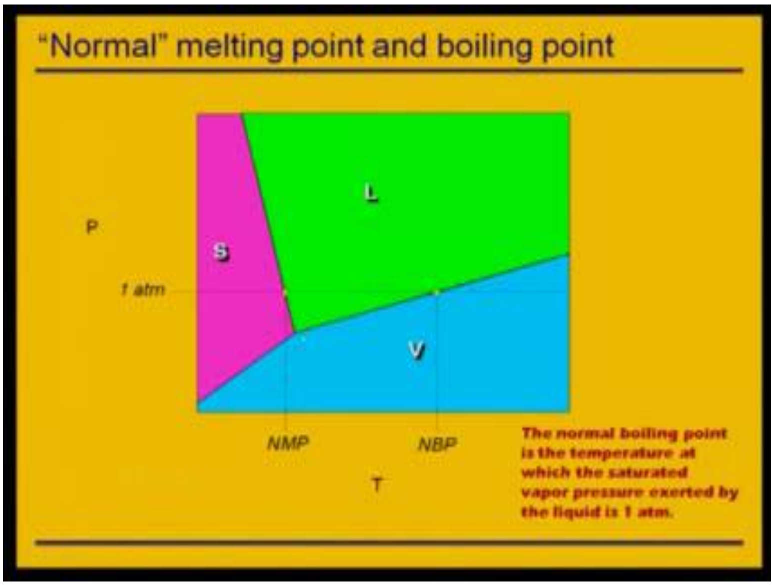

"Normal" melting point and boiling point

The normal boiling point is the temperature at which the saturated vapor pressure exerted by the liquid is 1 atm.

Now, let us go into detail of this diagram. This is another such diagram, again, for water system or water like system. This is the line for one atmospheric pressure, and this is the normal boiling point, because it crosssect, it makes a cross section with liquid vapor. This is the normal melting point because it makes a cross section with a solid liquid. Normal boiling point - the temperature at which they were saturated vapor pressure exerted for the liquid is one atmospheric pressure. That is why I have drawn a one atmospheric pressure horizontal line.

Now, this point, I told you, this is known as triple point. Why? Because at this point both liquid side vapor has going (Refer Time: 22:57) and very rarely you find this happens for water system, because this is the point at which only this can happen. Now, I just drawn several lines for that - saturated vapor pressure of solid, saturated pressure of liquid. So, what I will do for the next 8 minutes or so, in this lecture, is that I will show you how to apply phase rule.

So, let us apply here. As you know, phase rule, sorry, phase rule is basically given by what? Forgotten, right? Phase rule is given by this equation. What is that? f equal to the degrees of freedom f is equal to c minus p plus 2. Why 2? Because when pressure and temperature both are changing, that is why. So, f is the degree of freedom, c is number of components, p is the number of phases, and 2 is this.

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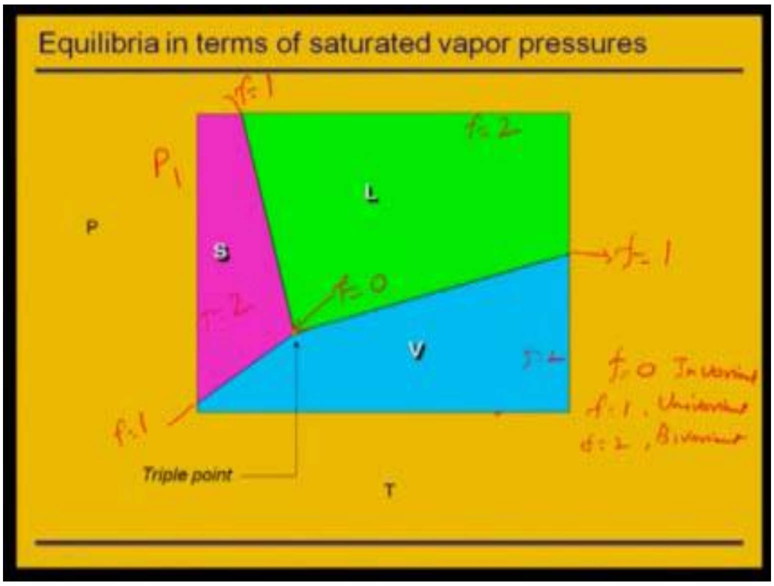

Equilibria in terms of saturated vapor pressures

Now, in this system this is a single component system, c is equal to 1, because component is 1. So, f is equal to 1 minus p plus 2 that is equal to 3 minus p. So, p is the number of phases.

Now, for a, suppose for a field like liquid, only one phase is present; p is 1. What will be the value of this? p is 1, it is 2. What is the meaning of that? So, I mean to say is that in the area liquid, whole liquid or vapor or solid is present, in this area marked as you know, blue, green and pink, within that f value is 3 minus 1; that is 2; clearly the gives (Refer Time: 24:41) with. What is the meaning of this? Let us make it simple. So, if I draw a line here, like this, let me change this color of chalk, it is not visible. I do a line here and erase the other line. So, this line is basically at a constant temperature p 1 supposed.

Now, the meaning of f equal to 2 is that, in this case f is equal to 2, is that what is the degrees of freedom is 2 is that, I can change both the pressure and temperatures simultaneously. Suppose, I have this pressure, now I can choose as many as temperature possible; you can see here, but still I will remain on the vapor phase, liquid phase. Similarly, if I change the pressure, I can again see there are many temperatures, thus vapor like (Refer Time: 25:34) pressure. So, this is the meaning of Ap is equal to 2. Same thing will valid for vapor field and liquid field.

Now, this is not the case when you do it all on the line, on this lines, this line or this line or this line, there are 2 phases are present liquid and solid, solid and vapor, or vapor and liquid. If 2 phases are present, so here, suppose on this line, 2 phases are present p is going to 2. So, f will be equal to one because 3 minus 2 is equal to one; 3 minus 2 is equal to one. So, what is the meaning of that? That means, very simple. If I choose the pressure suppose here, like this, if I choose, if I have that permission to choose the pressure I can choose this pressure. My temperature is fixed at which both side and liquid and vapor can co-exist. I have no choice of temperature. I cannot choose; that means, I want degree of freedom; I can only choose the pressure or the temperature.

Similarly, if I choose the temperature, then I have no choice of pressure; pressure is fixed because it is on the line; that is the meaning of degrees of freedom equal to one. These perpendiculars to one means I have only one freedom that is either pressure or temperature to choose. If I choose one of these 2, then other variable is automatically fixed by the equilibrium condition; that is what is the meaning of this. So, that is what is the meaning of the f equal to 1.

Now, there is a pressure point - in this diagram in which both, the 3, all the 3 pages co-exist; that means, at this triple point - number of phases equal to 3; p equal to 3; if p equal to 3, f becomes 0. So, that means, at this point f is equal to 0. So, that means, I cannot change pressure, temperature, anything at this point; these all are fixed because this is a point. The moment I change pressure little bit all the 3 phases will not even co-exist, they will change, equilibrium condition will be change or if I change little bit of temperatures, equilibrium condition will be changed. The meaning of this f equal to 0 is that I do not have any freedom to choose any of these processing variables - pressure or temperatures - in my disposal.

So, this point f equal to 0 is known as invariant point. Invariant means I cannot vary; this is f equal to 0, and f is equal to one means univariant point; unvariant means I can vary one of the variables pressure or temperature not both. f is equal to 2 means bi-variant. So, I can vary both simultaneously pressure and temperature. I would not change the phases. So, that means, within this color areas - between solid and liquid solid or liquid or vapor - I have a bi-variant system. On these lines I have univariant system and on this triple point I have non-invariant system to exist in a water liquid phase diagram.

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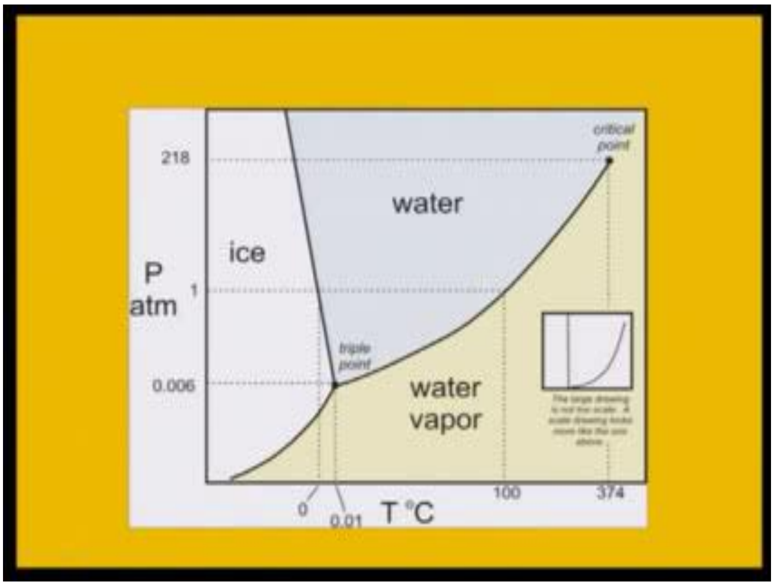

So, let me just quickly show you the actual phase diagram. Actual phase diagram looks like this - this is ice, this is water, this is water vapor. You can clearly see these curve is a negative slope because of the next thing I explained, and these are all both look like exponential curve, actually. The values are given; values are given for triple point pressure is 0.006; atmospheric temperature is point 0.01 degree Celsius.

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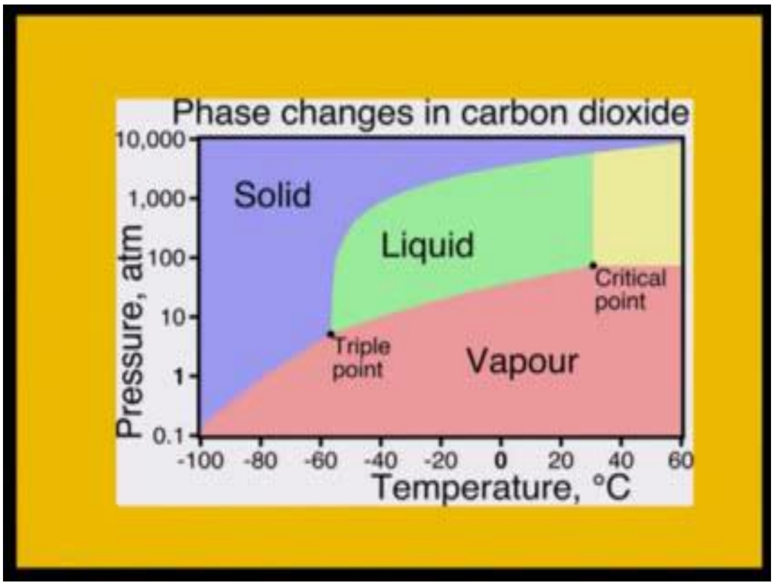

Similarly, for carbon dioxide you have a solid liquid vapor. There is a triple point here plus the critical point there for the liquid vapor also. We will not discuss the critical point right now, because that is comes a difference separate things. Pressure and temperatures as shown here, everything happens (Refer Time: 29:34) temperatures for carbon dioxide. There is something known as dry ice - pure carbon dioxide - solid carbon dioxide is known as dry ice, which can be (Refer Time: 29:42) at a very high pressure; that is what you can see here at low temperatures. You have to go to below about say 20 degree Celsius, and apply pressure about 1000 atmospheric pressure to get dry ice.

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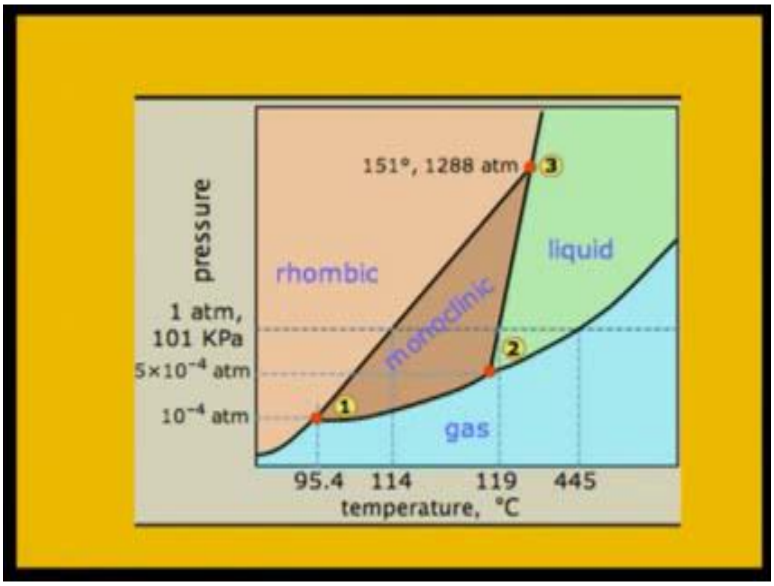

This is for Sulphur; Sulphur has rhombic Sulphur, monoclinic Sulphur, and they are actually having a triple point with the gas, and there is a liquid at high temperatures. So, liquid, before Sulphur become liquid transfer it to monoclinic Sulphur. You all know that. So, this is what the Sulphur phase diagrams has done You can search on Google you will find all these phase diagram very nicely; even the values are given.

So, by this I just wanted to show you the end the phase diagram r at which I have already shown to you. (Refer Time: 30:28) r n phase, alpha phase, gamma phase, and delta phase. Alpha and delta are bcc; gamma is fcc. And also, this is actually beta which is known as acb page at a higher pressure about 18 map at Giga Pascal.

This pressure, this is acp iron is present, and at a very high temperature it becomes liquid, and these are the slopes of the different curves. You can see this is negative, this is positive, depends on the change, delta v will change, delta v is basically dictates this slope of this curves. Slopes are given here. This is negative; this is positive; and this is also positive. So, that is how actually we can actually explain the different unary phase diagrams.

So, next time I come, I take the next lecture, I will be spending a little bit time on these diagrams again, and I move ahead for the binary phase diagrams.