Lecture - 42
Phase Transitions

Let us understand now the simplest aspect of the Transitions of Phase of a system between the gas and the liquid phase in the liquid and the solid phase. We need to be a little more precise when I say solid phase, generally the phase that we have in mind is a phase whether liquid crystallizes into a regular array called a crystal. So, the crystalline solid phase is what we are interested in not other exotic kinds of solid phases.

So, a generic or typical in the phase diagram, so to speak which describes which help qualitatively to understand these changes of phase is provided by what is called the phase diagram or a P T diagram here and what it means is the following.

(Refer Slide Time: 01:01)
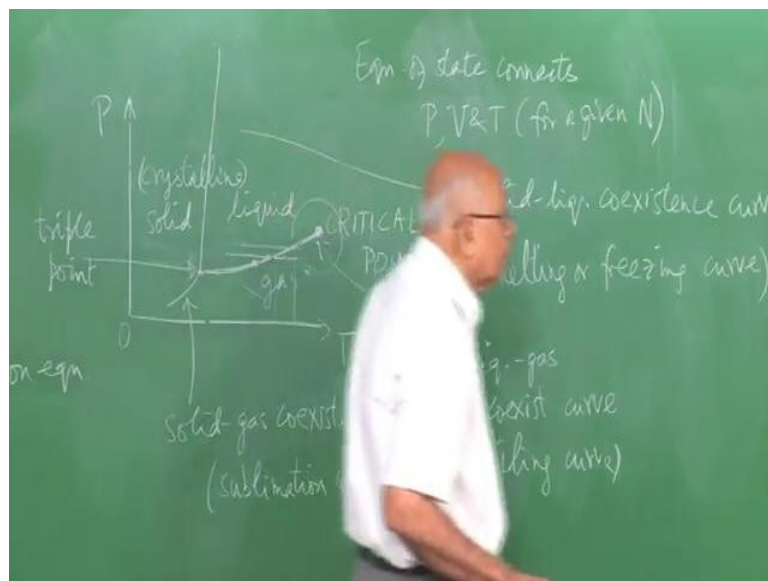
So, if you plotted the temperature on the horizontal axis and the pressure on the vertical axis, remembering that every point on this plane, on this quadrant since P and T are positive on this quadrant, any point like this is the thermodynamically stable state of the system, which we the system under study. And we are going to for simplicity look at system which have just one molecular pieces, single component, simple substances.

Such a substance every point on it would correspond to this temperature and that pressure is in a state of thermal equilibrium. The volume of the system is connected to P and T, once you tell me what P and T are by the equation of state. So, there exist a relation an equation of state connects P, V and T for a given amount of the substance for a given N the number of molecules in the system. So, we will assume that there exit such an equation of state could be a very complicated one much more. So, then the Vander Waals equation of state and every point on this plane is a thermodynamically stable system.

Now, when you plot P versus T the following is observed it is observed generically, typically that at the low pressures and sufficiently high temperatures, the system is in a gas phase and remain so in this region. At a sufficiently low temperature, that comes a point where if the pressure is increase for instance, the system liquefies and this is the liquid phase of the system with the slope which looks like this separating the liquid phase and the crystalline solid phase and there is a further curve, which goes down here is schematically actually cuts here and then it become the solid at the lowest of temperatures.

But, schematically this is all that we are interested at the moment, which separates the solid phase from the gas phase here, these curves or the curves on which two phases can coexist. So, this is called the liquid gas coexist in this curve, liquid gas and what it does it is got the following physical implication, it tells you at a given value of the pressure, what the corresponding boiling point is. In other words, if you started at this point here in the liquid, kept the pressure the same and increase the temperature as you cross that temperature, the liquid boils in to the gas.

Similarly, if you start at the same pressure here and lowered the temperature, at this temperature it condenses into a liquid. So, this curve the liquid gas coexistence curve is also called the curve which separates liquid from gas is also called the boiling curve. And right away let us remark that we know from elementary considerations that if you increase the pressure on a gas, the boiling point increases and indeed it does. You go up this here, you going up in pressure, the boiling point increases up here.

The slope of this graph tells you how the boiling point increases and if you recall, you have this thing called the Clausius Clapeyron equation which I will come back to little later, which tells you what is the change in the boiling point for a given change in

pressure, what is the increase if the pressure increases and so on. It is related to the slope of this curve which we will see, so the other name for it is a boiling curve.

Similarly, there exists a curve here which separates the liquid from the solid with the somewhat higher slope much higher slope you will see what that means. This thing here, this curve does not have to be a straight line, this curve is the solid liquid coexistence curve which you could also called the melting curve or freezing curve depending on how you approaching. So, if you start here at a fixed pressure and increase the temperature, you would melt at that particular temperature.

Similarly, if you started in the liquid phase and you lower the temperature, you would freeze into crystalline solid; this substance would freeze at that particular temperature here. So, the solid liquid coexist curve is also the melting or freezing curve, the liquid gas coexistence curve is also the boiling curve and both these curves tell you, how the corresponding transition point the temperature changes as a function of the pressure, this curve here separates the solid from the liquid gas phases directly.

So, it means that the solid can directly evaporate into the gas or the gas can directly get deposited as a solid, if the conditions are right and this curve here is a solid gas coexistence curve is also called the sublimation curve, because that is what is happening. If you recall sublimation is the name given to the process by which a solid evaporates into the gas directly without going through the liquid phase. The free of them typically, generically meet at a particular point and this point is called the triple point.

Since, I have said that every point on this plane is a point of thermodynamic equilibrium for the system in whatever phase it finds itself in, on these curves it finds itself in two different phases. So, the substance spontaneously separates into a liquid part and a gas part and they coexist with each other which is why it is called a coexistence curve and you have two phases in coexistence on any of these curves here. But, at this particular point the solid, liquid and gas phase all coexists and it is called a triple point here.

Now, right away I should say I am going to talk about this diagram in some detail, right away I should say that one can ask what sort of crystalline solid can one have. Well, it depends on the pressure and the temperature, it turns out that most substances would have several kinds of crystalline phases, several kinds of crystalline order such as a cubic kind of symmetry or triclinic symmetry or hexagonal symmetry these are crystal classes have been classified depending on the level of symmetry.

And you can have as you go up here, you can have as a pressure increases, you can have closer and closer fact kinds of symmetry like phase center cubic or body centered cubic goes into phase center cubic and so on. So, you can have many, many such thing happening. So, you would have things going of like that, so this is the coexistence of two different solid phases and so on, you can have various kinds of complications.

But, you could ask how do I know that the triple point, where three phases coexists is the only kind of point, where you have multiple phases more than two coexistence. Can we have four phases coexisting, can we have a picture like this for instance, with one kind of crystal here, another kind of crystal here and so on.

And there is a rule in thermodynamics called the Gibbs phase rule, which says that for simple substances, single component substances the maximum number of phases that you can have in coexistence anywhere in the P T plane is three. You cannot have more than three phases and that is why we end, stop with a triple point whether solid, liquid and gas meet and this is called the Gibbs phase rule.

For simple single component substances, one chemical specious, once molecular specious you can have know more than three phases in coexistence at any point here and this is one such example, where you have three phases in coexistence. Moreover one can ask where does the this curve end, where is it keep going well this curve as I said generally comes and heads this very, very low pressures and below that it remain as solid, so we would not get into that here.

But, this curve definitely ends at some finite point, specific finite point and this is called the critical point it is so important that I write it in capital letters, this was the critical point P C V C and D C that I mention in connection with the Vander Waals equation in the previous lecture, this is exactly the same critical point and what it means is that there comes in temperature and a pressure, beyond which you cannot distinct wise between the liquid and the gas.

This coexistence curve ends at a finite point that is an important very important statement, this critical point is a point where elementary thermodynamic fails for good reason, it fails and you need much more sophisticated techniques to understand using equilibrium statistical mechanics to understand what happens at this critical point. In fact, the problem of this critical point this is general problem of critical phenomena, this problem was solved at to satisfaction only in the 1970's are so.

So, as let us that the point here is that as you go up this curve, remember that to go from a liquid to a gas at a fixed value of the pressure, such as this you have to supply certain latent heat of a evaporation. So, when you jump from this to this phases liquid phase to the gas phase at this pressure, at this boiling point you supply a certain amount of latent heat. But, if you increase the pressure you have to boil at a higher temperature, you supply a smaller amount of latent heat.

And as you go up here it turns out that there comes a stage, namely the critical point, where the latent heat require to go from the liquid to the gas phase tense to 0. So, no liquid no differencing occurs between the two phases, you do not see anything at all. On the other hand, you can also distinguish the liquid from the gas by the fact that the liquid as a surface tension. So, there is a surface to the liquid, but as you go up this curve the surface tension decreases in the ((Refer Time: 12:35)) slowly disappears and at this point it is gone all to gather.

So, you do not have any distinction between the liquids and the gas it is some homogeneous flow it phase beyond that, that is a very crucial observation. Because, it also means that you could start here at some point in the gas phase and you could by a sequence of steps, all of them in thermal equilibrium sequence of states move in this fashion and get to the liquid phase by going up of the critical point and coming back by decreasing in the pressure and temperature.

Such that, without crossing any sudden transition point or boiling point or anything like that you can go from the gas phases continuously to the liquid phase. So, this is the very, very important observation, it says that beyond this critical point with distinction between liquid and gas vanishes and you can go continuously from the gas phase to the liquid phase by going around the critical point in the P T plane, can we do the same thing here, can we do same thing for the P T the go existence curve between the melting curve between the solid and the liquid.

Well, we cannot we cannot do so, because if you could do so there exist a critical point here, it means you could go from the liquid phase which has complete symmetry it looks isotropic in our directions it is completely the same properties in all directions such of liquid cannot get into a crystalline phase which has a lower symmetry then the liquid gas a liquid look exactly the same in all directions, this properties are exactly statistically the

same in order directions, where is a crystal definitely in different directions the atomic arrangements are different directions.

Therefore, a crystal is an isotropic a liquid is isotropic and there is a breaking of symmetry as you go from here to there. And this means that you cannot continuously go from where to here, because you cannot continuously deform isotropic completely symmetric rotation invariant phase into a crystalline phase which has got a lower degree of symmetry. So, the crystal has undauntedly greater degree of order, atomic order arrangement, but it has a lower degree of symmetry, because it is not isotropic on the other handle liquid is isotropic.

So, this is another lesson which goes contrary to what on my ((Refer Time: 15:08)) think the greater the symmetry the lower the order. In fact, the gas phase is very, very symmetry in the fashion, because gas is completely isotropic statically in all directions. So, again the dictionary meaning of symmetry and order actually quite different all though in daily usage one tends to use the two synonyms it is not true, they are antonyms in some sense and that is important to remember.

So, no critical point here these goes on forever or else it hits other phases, there are other branching and so on, other curves etcetera and this could therefore, have no end at all no critical point exist here, but a critical point exist in the liquid gas coexistence curve. The sublimation curve pretty much behaves like the liquid gas curve this no critical point here, because this comes and hits this origin here and then it becomes a solid. So, it hits a physical boundary and therefore, this does not display critical point. But, the liquid gas phase this place a critical point here. Now, what we will be saying about the Vander Waals gas is applicable this point here is the coexistence region in the Vander Waals isotherms.

(Refer Slide Time: 16:20)
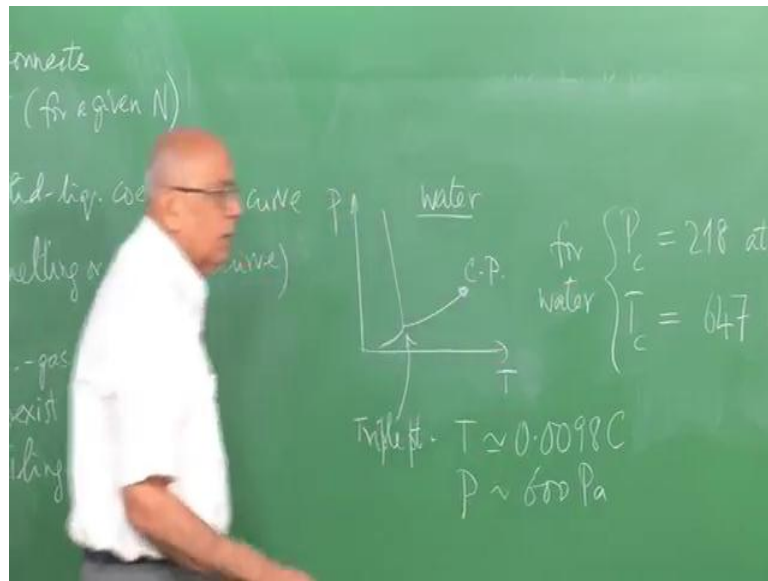
So, if I plotted V here and P here and looked at this line out here such a point as this for instance, this would correspond to the coexistence of a liquid and a gas and that remember is given by an isotherm like this. So, it means that if you brought the system to this pressure and temperature and therefore, could compute the volume you would have it some point like this which would then phase separate into proposition that is a gas and a position and that is a liquid by a well defined rule and this single line here ((Refer Time: 16:56)) corresponds to that region there.

In fact, this entire curve every point on this corresponds to region, this region on this P V diagram here. One has a similar V T diagram which I am not going to talk about here, but this suffices to understand certain basic issues here. So, no critical point on this the region critical point on this, just for reference you could ask when does is happen with water this is the common substance, the most common substance we could think of well the critical point is much higher than the normal boiling pointed one atmospheric pressure and that is you know is a 100 cells here is or 373 Kelvin whatever.

But, the critical point for water P c and T c for water, this is of the order of 218 atmospheres. Remember, one atmosphere is 10 to the 5 Pascal's approximately and T c in this case is of the order of is about 647 Kelvin, so 374 something like that in Celsius. So, it is very much higher very, very much higher than the normal boiling point at a 100 Celsius and the pressure of course, is not a one atmosphere, but 218 atmospheres here. Again for reference in the case of water one can ask whether.
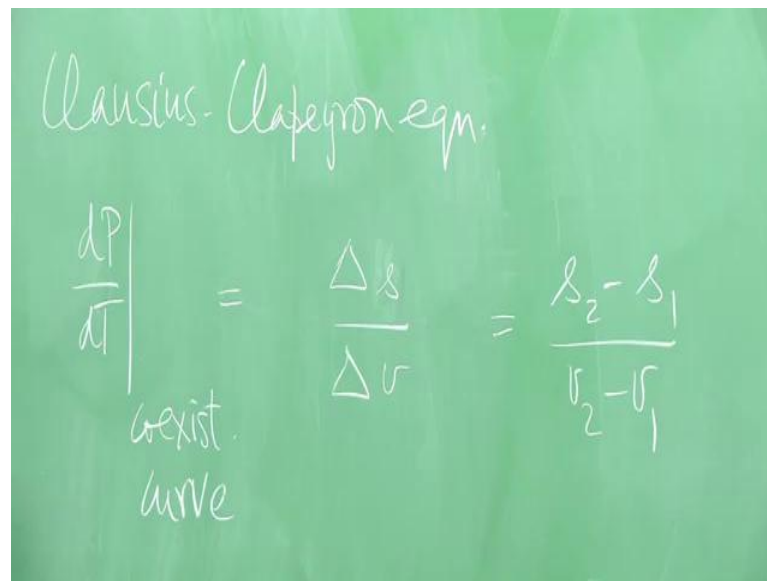
So, here is the schematic for water triple point and then a slope is goes this way that is the surprise for water. Of course, we know this is true, because what happens P T what happens in the case of water is well known, if you press on it if you press on ice it melts. So, it is clear that in this case the slope the P verses T diagram d p over d t is actually negative here. So, this means if it your positive it would say that this melting point increase with increase pressure.

But, now the melting point decreases with increasing pressure which is why you can skit, the skit applies the pressure and it remains at the temperatures at 0 Celsius it becomes liquid phase that stage in the skit slights, you need to low the temperature further in order to solid defined. So, that is what is reflected by the negative slope here, but the magnitude of the slope is still very high, but it is negative out here this triple point is approximately at set of very low pressure and the temperature T triple point T is of the order of by remember right 0098 Celsius.

So, just a little above in the freezing 0 degree is the freezing point at one atmosphere, but the pressure is much lower is of the order of a remember right it is about 600 Pascal's. So, it is almost 0 Celsius in the pressure of course, the much lower than one atmosphere it is 600 Pascal's remember one atmosphere is 10 to the 5 Pascal's little more than 10 to the 5 Pascal's. So, low temperature, low whatever it is pressure, but the T C is a crucial this thing has not here critical point and it has these and the volume of course, it depends on the amount of substance.

But, you can compute it from the equations of state are the system, by the by water has very complex phases diagram as a pressure increases in the temperatures lowered there are 14 or 15 different forms of ice is ice 1, ice 2 and so on the have very exotic properties and the full phase diagram of what is not known as for as I know even, because there we could go up and pressure arbitrarily high and you could get all kinds of exotic phases. So, we will not discuss that, but now at like to turn to what is meant by the slope of this curve here and that is the equation a Clausius-Clapeyron equation.

Now, in elementary treatments you are used to the statement that the Clausius-Clapeyron equation gives you the rate of change of the boiling point with pressure or the freezing point of substance with pressure and it basically reads the elementary way of writing it d p over d t on the coexistence curve, either solid liquid or the other coexistence curve either the solid liquid or the liquid gas coexistence curve, this is return generally as the latent heat corresponding latent heat divided by T times v 2 minus v 1 where T is a corresponding tangential temperature boiling or freezing temperature and v 2 and v 1 other specific volumes of the system in a given phases in phases 1 and phases 2 cross this.

Now, the problem I have with this equation is that you always have an confusion as to which is v 2 and which is v 1 should be completely arbitrary. What you call one what you call two? I mean whether I call this phase one ((Refer Time: 22:49)) and this two and this or this one and that two is should be relevant completely in one case you have to supply latent heat in other case you got remove latent heat. So, I guess that fix as this, but this is not the right way to write this the correct way to write this is the following.

Remember that this latent heat is the amount of heat supplied or removed at the transition point. So, it is like delta cube, where q is the heat and T is the corresponding temperature, but we know the delta cube over T is the change in the entropy. So, the right way to write this equation is to write it as delta s divided by delta v specific entropy, entropy per particle if you like is specific volume per unit mass or unit part whatever.

So, this of course, you could write it as s 2 minus s 1 over v 2 minus v 1 you could also write this as v 1 minus v 2 in the denominator and s 1 minus s 2 in the enumerator and it would not change at all.

So, in the case of a liquid gas the slope this here is the slope of the boiling curve is equal to we going from liquid to gas or gas to liquid does not matter. So, let us write this as s gas minus s liquid over v gas minus v liquid, where s is the entropy and we know that entropy is a measure of disorder and we know that the gas phases much more disorder then the liquid phase. So, this is much bigger than that and the numerator positive as I return it here.

The gas has a specific volume which is also much greater than the corresponding volume of same amount of liquid. In the case of water for instance, we know that one CC of a liquid of water gets into at the normal condition boil at one atmosphere pressure, it becomes 1600 CC of gas or water weeper. So, we gases much greater then we liquid s gas is much greater than s liquid, the numerator is large positive the denominator large positive, this is very large positive, this denominator is a very large which means with the whole thing is then the quantity itself is very small and positive.

So, this implies small positive slope which is what we see, we see a small positive here, if you apply the same thing to the liquid crystalline solid transition point, slope of the melt in curve then this would be s solid minus s let us write this as s liquid minus s solid. So, that it divided by v liquid minus v solid, now we see there are two possibilities, the

entropy of the liquid is always greater than that of the solid, no question about it the liquid is formal disorder then the crystalline solid.

So, the numerator is large and positive, but the denominator can be positive or negative this nothing with says that the liquid could not be more tensed in the corresponding solid and the most notable example is water itself, which as know at 0 Celsius ice has only 92 percent of the density of water which is write floats on it. So, in that case we liquid is actually smaller than we solid and the slope is negative. So, that is the reason why water had this very funny phase diagram, where this actually when negative in this fashion.

But, for most substances they actually contract on freezing and then we liquid is bigger than we solid and it is positive. So, this will always be large magnitude, but plus or minus could be positive or negative usually positive. But, could be negative there are substances which expand on freezing like this much for instance, we could this much will expand on freezing or water itself does not. Now, you could ask why should be large in magnitude, well this is certainly bigger than that.

So, already large number, but this quantity here is small, because a liquid does not have a compressibility which is very higher than that of the solid. Solid and rowdily most cases will have the even more incompressible than a liquid, but the change in density between a liquid and a solid is not very high. So, the specific volumes are not very different as we saw it is about 8 percent in the case of water it is small. And therefore, the denominator is small of either sign, the numerator is large positive and therefore, the ratio is large in magnitude, but could be of either sign.

So, that is the reason why in certain substances this slope force the other way, but in usual substances goes in this fashion here and that is the origin of the classier clipper on equation here. Now, one could ask finally, one could ask what is it that is common between two phases, what is the quantity that does not change when you go from one phase to another. For this we need to go back a little bit and look at the conditions under which we boil the substance.

For instance, when I boil water or I boil substance in liquid ((Refer Time: 28:57)) I go across like that by keeping the pressure phase and changing it and then at a certain temperature it boils. When you boil beaker of water on a slope in one atmosphere pressure, the pressure is a same in both phases, the temperature is the same at the boiling point and both phases. So, we have a system, where the temperature and pressure do not

change the across the phase and we need to know now what is it that is the same, what kind of energy is the same in both cases.

(Refer Slide Time: 29:24)
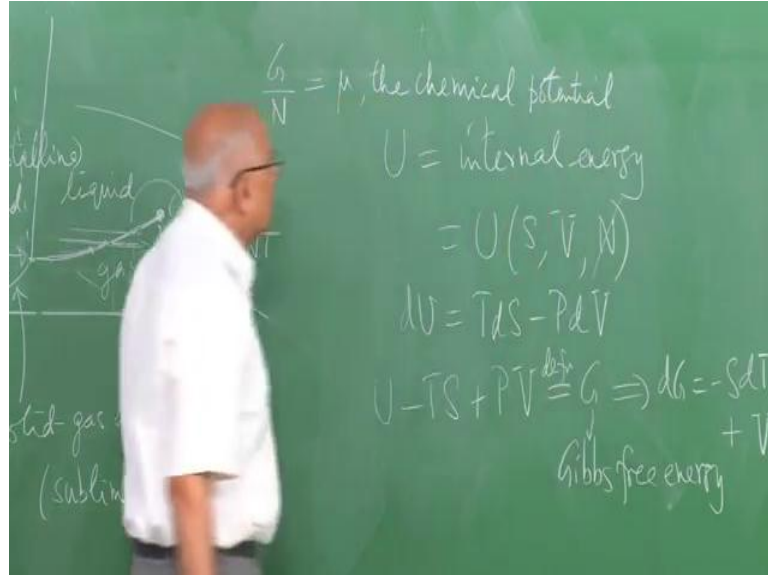
Well, remember that the internal energy was a function of the entropy of the system, the volume of the system and the number of particles. So, for a fixed amount of substance which is what we are looking at all the time, this thing is not there is fixed is the function of the entropy and the volume. And we indeed saw that d u was equal to T d s minus P d V. But, now I would like to be able to control the temperature and the pressure those are my control parameters, if you like and I would like to maintain those at fixed for both the phases across a phase transition.

So, I need to go from this thermodynamic potential if you like to another energy whose differential will have at d t here and d p here. So, that I can put those two quantities to 0 well how would I go do that if I took u and subtract a T s from it then it is clear that if I take the derivative here d u minus T d S minus s d you end up with minus S d T this gets canceled out. And similarly to kill this I need to add up P V here then this P d V gets canceled out and is replaced plus by a plus V d p.

So, if I call this G it is the definition of an energy called G, the Gibbs free energy implies that d g is minus S d T plus V d P for a fixed amount of substance and then you are saying that at constant T and constant P when it is boiling this and this as 0, because d p is 0 across a transition d p 0. Therefore, d g is 0 it is another way of saying that the gives

free energy per particle is the same in two phases, when you are on a coexistence curve that gives you the definition of this coexistence curve.

So, on every coexistence curve the gives free energy per particle of this phase and the other phase are the same ditto here and this side here, the gives free energy per particle G over N is equal to the chemical potential. So, the physical significant of the chemical potential is that it represents the Gibbs free energy per particle and in a coexistence of two phases in the P T plane ((Refer Time: 32:16)) across a coexistence curve the Gibbs free energy of the two phases are equal to each other that is what determines the phase equilibrium and that translated to the case of three phases gives you the triple point as well.

So, this is an extremely elementary introduction to the idea of a change of state more precisely of a phase transition and specifically we looked at the face transition of a liquid to a gas and vise versa and introduce the idea of a critical point. So, statistical mechanics starts at this point and goes on to understand the intricacies of this phenomenal call phase transition.