Introduction to Chemical Thermodynamics and Kinetics

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Lecture – 16

Phase equilibrium – Part 1

Hello, everyone. In the previous class, we discussed the properties of entropy and from there; we calculated the other thermodynamic quantities. For example; Gibbs and Helmholtz free energies and we discussed the conditions for spontaneity and equilibrium and we found the natural choice when we study a chemical substance undergoing some transformation is to look at the Gibbs free energy or the changes in Gibbs free energy associated during that transformation. Because, the Gibbs free energy associated during the transformation taken at constant temperature and pressure will be negative if the transformation is spontaneous or irreversible and it will be 0, if the transformation is reversible or the system is in equilibrium. And, since in most of the chemical or physical processes we will study a transformation usually the pressure and the temperature are kept constant the natural choice turned out to understand or to measure the Gibbs free energy change for the system.

Now, based on our previous discussion, we will discuss today phase transformation. Now, we already discussed what is a phase? If you remember by phase we said a phase will be something that is chemically uniform throughout the system.

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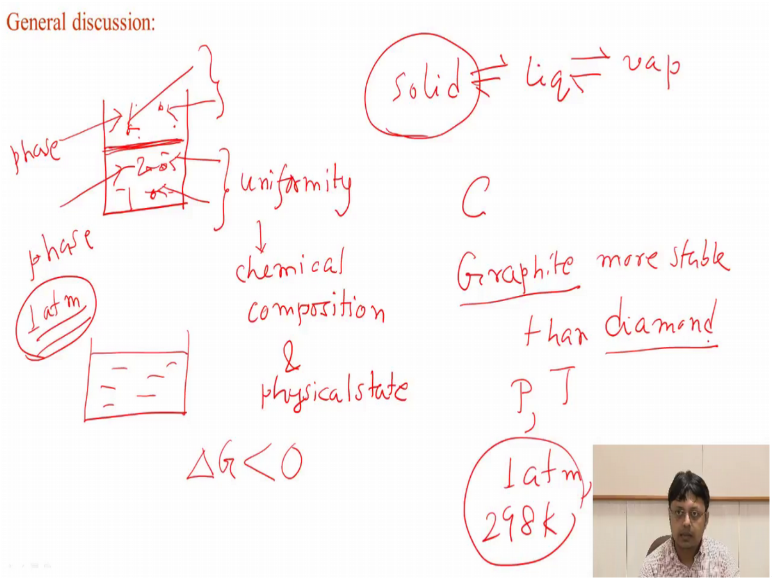

General discussion:

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The composition is a chemically uniform and also it will have a concept of physical uniformity to understand that what we mean by this uniformity we also considered a particular system where suppose I have liquid in presence of it is vapor. And, if you ask what is the chemical composition? The chemical composition here is same between two points and the chemical composition in the vapor in the same two points is also same also the densities are same inside the liquid at two different points and the densities here and here are also same. So, for these two points say I call it as 1 and 2 there is an uniformity in chemical composition as well as in physical state.

Similarly, there is uniformity also in the vapor phase; however, between the liquid phase and between the vapor phase the density is differ. So, this is a particular phase which is a liquid phase in this case and this is also a particular phase which is the vapor phase in this case and in between them there is a boundary. So, existence of a boundary when you do experiments will see you will give an example in a minute that this existence of the boundary or observation of a boundary which clearly separates the system into 2 phases is very important.

Now, suppose we take a substance say water and then if we lower the temperature you know at 1 atmosphere pressure, if we keep on decreasing the temperature and below 0 degree centigrade we will have ice as the stable form, which means since the condition of spontaneity is change in Gibbs free energy that should be negative, when the temperature is below 0 degree centigrade ice is more stable form means the free energy associated with liquid water is larger than the free energy associated with solid ice. Similarly, when we increase the temperature of this system which is liquid water at keeping the pressure same say 1 atmosphere above hundred degree centigrade water vapor is the more stable phase than liquid water.

So, in that case liquid water will have more Gibbs free energy than the water vapor. So, the system will try to minimize its Gibbs free energy and in the range 0 degree to hundred degree centigrade that range at one atmosphere water has the minimum liquid water has the minimum Gibbs free energy and that is why we see in that normal room temperature and as well as 1 atmosphere pressure we always see that water is present in it is liquid form.

Now, the question is around 0 degree centigrade we can make a transformation where ice can melt into water or water can freeze into ice. So, the system water and ice are in equilibrium which means the Gibbs free energy at that temperature which is 0 degree centigrade at that pressure which is 1 atmosphere must be equal and then when you talk about the phase transformations we will utilize this condition. Now, the example I gave you is something like an example between a solid to liquid phase transition and vice versa and a liquid to vapor phase transition and vice versa. Now, there can be many other phases also we will which we will discuss there can be some metastable phases also which we will discuss when we discuss the phase diagram of carbon dioxide and water also.

However, also keep in mind that even when you talk about solid, the solid also can exist in different forms which are called allotropes and there can be phase transformation between them. These are not called allotropes, these are called isomorphs and for example, they for a say carbon and you know that carbon in the solid phase can exist in diamond as well as in as a form of graphite. Now, graphite has graphite is actually more stable, which means it has less Gibbs free energy than diamond at normal pressure and temperature see if we keep the room temperature which is around say 25 degree centigrade or 298 Kelvin and if we keep the 1 atmosphere pressure. So, then we know under these two condition, graphite is more stable. But, we also see the diamond exists which means there is a kinetic barrier from going from diamond to graphite.

So, this kinetic barrier we are not going to discuss about. What we are going to discuss about is, only the thermodynamics of the problem meaning which form is more stable or which form is less stable. We are not going to discuss how one form is going to get transformed or the timescales associated with that transformation that is a realm of kinetics, but in chemical kinetics when you discuss we will not discuss any topic or we talk about phase transition or the kinetics of phase transition, but that is a very important subject, but we will keep ourselves limited to only discussion on the thermodynamics of phase transition.

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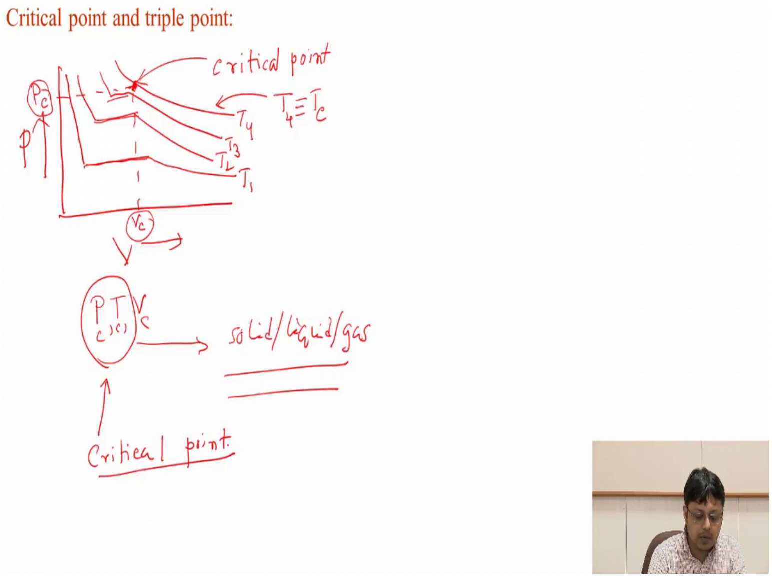

Critical point and triple point:

Now, we discussed when we were talking about the real gas and remember that we talked about Andrews curves there and it look like something like if we draw the pressure volume diagram and we discussed that there is a liquid phase and then there is a long range on of vapor, but the system actually stays in liquid vapor equilibrium and then eventually the there is a gas phase which actually is exist for a low pressure regime and if you keep on increasing the temperature we will get to a point where basically the liquid and the vapor coexist and all this range of liquid vapor equilibrium gets reduced to a particular point and that point we talked about critical point.

And, the critical point happens for a particular temperature these are all isotherms. So, this isotherm we are the temperature corresponding to that isotherm we called as critical temperature. So, if these are the temperatures of respective isotherms in this case critical temperature is nothing, but the point and the corresponding pressure and the volume we talk we called as critical pressure and critical volume and we also changed our equation we the model we used that time was the Van der Waals gas equation and we inserted the values of critical constant P c, V c and T c and we got we kind of modified the equation.

Now, remember that we could also draw and pressure volume temperature simultaneously and get a particular point which is the critical point. So, the critical point in this case do not think that it only is described by only the pressure and volume because it is a p v diagram the temperature is also important. So, there is a particular combination of pressure, temperature and volume where the phases actually coexist and then we will discuss that it is not only the liquid and the vapor phase that we have drawn here there will be a particular combination of pressure and temperature where all the, of course, the volume will be also fixed and there or the molar volume will also be fixed that time for each phase and if you take that combination we will see that all these 3 phases which are mainly the solid and the liquid and the gas they will coexist. So, that point we call as critical point.

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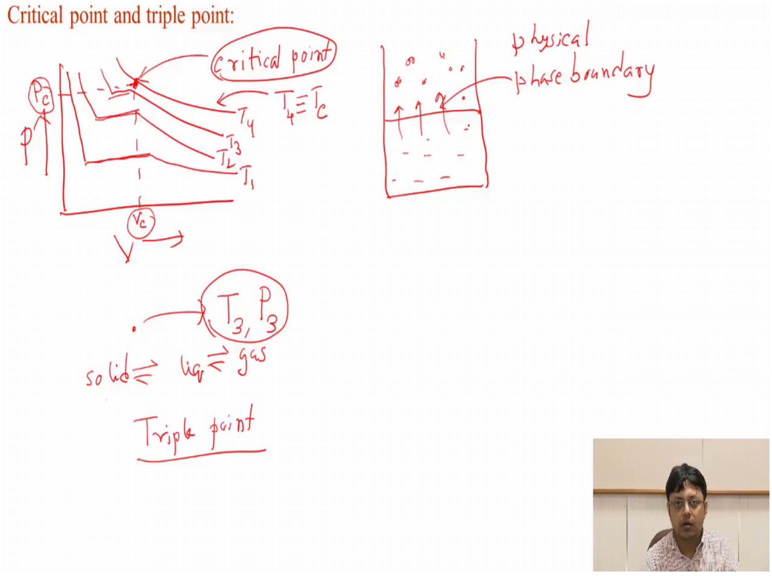
Critical point and triple point:

So, critical point not only means that now, just like there exists a critical point there also exists a point corresponds to a particular temperature and a particular pressure, where all three phases mainly the solid phase, liquid phase and the gas phase they coexist. And, then this point we call as triple point because it is a three phases coexisting for some temperature and pressure combination and, obviously, the Gibbs free energy for any phase beat liquid or gas or the solid must be equal at the triple point and usually we denote the triple point as T with a suffix 3 to denote that it is a triple point, that there is a 3 number associated with it.

Now, there are also important things which we discussed when we have a discussion on phase transition one of the things as I said is the boundary or which is known as phase boundary. Now, this phase boundary is a physical boundary. We will also talk about boundaries in the phase diagram which is a pressure temperature diagram and right now we are talking about only the physical boundary. Now, suppose we have water and we are heating the water then what will happen is that water will evaporate at 100 degrees. At any time temperature there will be a equilibrium between water and the water vapor there will be a evaporation, but at 100 degree centigrade water will start boiling and then eventually the water will be transformed into vapor. Now, what happens at that point, the vapor pressure of this water vapor equals to the vapor pressure of the liquid and then this is a condition for boiling we will discuss about it.

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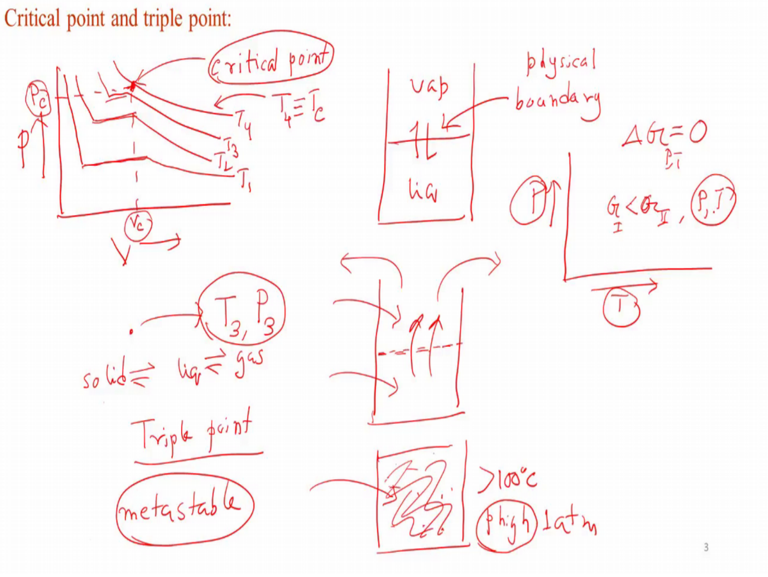
Critical point and triple point:

Now, consider a physical phase boundary a liquid is in equilibrium with it is vapor. Now, there will be a pressure of the vapor which we call as vapor pressure and under equilibrium condition if we keep a container as sealed the vapor pressure will be the pressure exerted on the liquid. Now, if we keep on hitting the liquid there will be a condition say for water it is 100 degrees centigrade at one atmosphere where boiling will happen and this meniscus or this physical boundary will slowly and slowly disappear. So, this physical boundary which sometimes call as is called as a phase boundary, but by phase boundary we will describe the line which actually separates the two phases in the pressure temperature diagram, now this is a kind of physical boundary right now we are saying which actually you experience in your day to day experience day to day life and then this boundary gets vanished as we increase the temperature and eventually this container will be filled with water vapor only it is above say 100 degree centigrade and of course, at a every the pressure in this case will be very high.

If we keep it at an open vessel like there is no say for example, there is no the container is not a sealed container, then the situation will be slightly different, and then when the vapor forms the pressure will be 1 atmosphere. However, if we make it a sealed container then the pressure will also build up and we will have a very interesting situation where the entire vapor like phase will cover the entire container, but that vapor we usually call it as a supercritical phase, the reason being that the pressure is not one atmosphere there because as you are transforming the liquid in this case water into vapor the pressure of the vapor is increasing and at a very high temperature and pressure you will see that meniscus is completely vanished and then a uniform phase appears; remember, there are two distinct phases here liquid and vapor and that disappears and some kind of new phase appears.

So, those kind of phases are actually are metastable phases in the sense that if you had done it in an open container you will never see that because the it will always see that during boiling the vapor comes and then eventually everything will be just a water vapor which will of course, escape this container, but if you had done it in a sealed tube or sealed container you will realize the existence of metastable phases. Now, all this discussion metastable phases or the triple point existence of a triple point and also critical point which we realized when we discussed Andrews curve, all these things can be actually plotted in a phase diagram.

Now, by phase diagram definitely we mean a diagram which is the variation how the pressure and the temperature varies for the system as the system undergoes a transformation from one phase to another phase and we are going to discuss that and the choice of pressure and temperature is obvious because then we can make this condition that during the phase transformation the change in Gibbs free energy should be 0 and for a particular pressure and temperature that phase will be the most stable for which the Gibbs free energy is negative or Gibbs free energy is less compared to the other phase.

So, if we have 2 phases G 1 and G if G 1 is less than G 2 then at some fixed pressure and temperature then in that pressure and temperature G 1 is more stable form and this can be observed, but this may not be observed as I said that in normal pressure and temperature graphite is more stable, but we also see that diamond exists which means that there is a kinetic barrier and to make the graphitic like arrangement of carbon atoms from diamond we need to supply a lot of energy and under normal temperature and pressure this is not possible, so, both forms exist although diamond has much less much higher Gibbs free energy than graphite.

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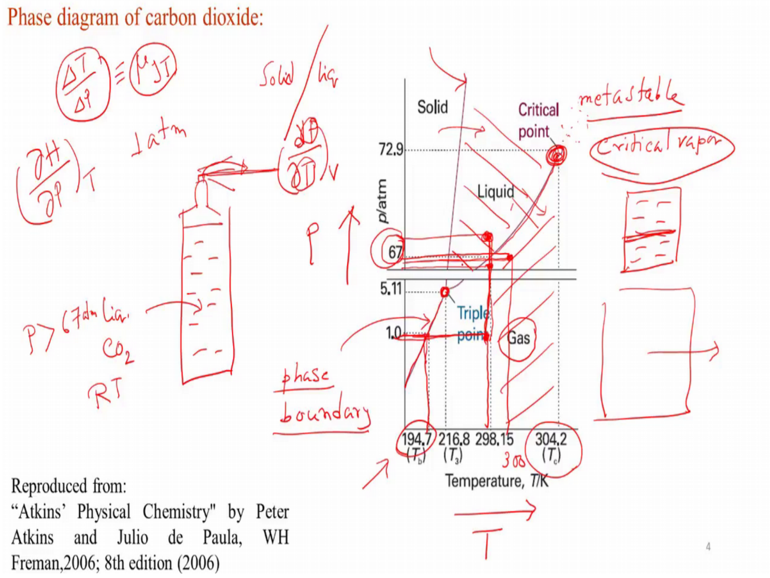

Phase diagram of carbon dioxide:

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Now, we will discuss first few typical phase diagrams of three substances carbon dioxide water and liquid helium or helium 3. So, let us first consider the phase diagram of carbon dioxide. Now, on y axis we have pressure and on x axis we have plotted temperature. Now, as you can see there is a distinct line here which we will call as phase boundary. So, this is different from the boundary we just discussed that was a physical boundary which you can see just like a for example, if I have a piece of solid in equilibrium which is a vapor, then you can see clearly surface of the solid or that there is a physical boundary, but we are now talking about a phase boundary which appears in the pressure temperature diagram and now, let us consider where is the normal pressure and temperature.

So, normal pressure is one atmospheric pressure which is here and suppose, normal temperature is say 298 Kelvin which is here. So, if we draw a point here which corresponds to normal pressure and temperature you can see the phase which exists there is the gas phase, so, at low pressure at the gas phase exist. Now, suppose we are increasing the temperature then what happened at some point we will have a existence of all these three phases together. Now, before that let us consider this thing if we just freeze or lower the temperature of the gas carbon dioxide, what will happen at this temperature which is 194.7 Kelvin below that temperature the gas will just form the solid and you know that is called dry ice.

So, dry ice you can just get by cooling down the carbon dioxide gas which is very interesting it is unlike water, the gas is not going through liquid to solid the reason being that at one atmosphere pressure the there exist a phase boundary between gas and the solid. Now, that solid if we again heat up there will be a temperature where basically we have the gas. So, that temperature we call it as a solid to vapor transformation means actually it is a sublimation temperature. So, here for carbon dioxide the sublimation temperature is 194.7 Kelvin.

Now, suppose we are increasing the pressure. So, what will happen? If we increase the pressure you see that if we start from say here at some point, but the pressure is very high around say above it is actually not to scale it is say around 60 degree or so, and suppose you start with a temperature of say something around said 300 Kelvin then we find that of course, here also the gas is stable. But, if you now cool down the temperature what will happen? First, liquid will form and then the solid will form. Now, it behaves very naturally which we see for ice; however, this happens for a very high pressure.

So, when we use carbon dioxide cylinders for different purposes carbon dioxide is used as low temperature matrix dioxide used as a inert gas in many chemical reactions to keep that environment. So, in those cases we need to carry or transport carbon dioxide. Now, if you think that if we carry the gas itself the gas will occupy a huge volume. So, we need to have a compressed condition.

Now, one way is that if you use the cylinders usually what they do they actually keep the pressure much above 67 degree so that the at normal temperature which is 298 Kelvin you will have actually the liquid phase more stable. So, they pressurize the gas in the cylinder and then you have a liquid and you know that that liquid carbon dioxide is more dense. So, you can now carry more amount of the substance which you could not do for a gaseous carbon dioxide. So, just by applying pressure you form the liquid and you seal it in a container which is the cylinder. Now, once we open the cylinder an interesting thing happens.

So, suppose this is a cylinder at a very high pressure where inside that we have liquid carbon dioxide at room temperature, but which means the pressure has to be much higher than the 67 atmosphere and at this condition liquid is more stable. Now, moment you open it and let the carbon dioxide come out what will happen the outside temperature is 1 atmosphere. So, the pressure immediately will try to drop and you can think that inside pressure is very high and the outside pressure is very low, then the liquid is kind of expands at a very I mean against a very almost 0 pressure and you will see something like a cooling effect which is nothing, but your Joule Thomson effect because remember that this is nothing, but change of heat capacity because the at constant pressure you have hot constant sorry at constant temperature you have you are changing the pressure. And, as a matter you are cooling down the gas and usually that is connected to if you remember that we measured some quantity which is it is del T del P meaning as I change that pressure how the temperature drops down which is connected to the Joule Thomson coefficient this is equivalent to writing the Joule Thomson coefficient and that talked about some cooling which we talked called as adiabatic cooling.

The same thing will happen here and since now the pressure drops the gas phase exists and the gas tries to cool down and if the gas tries to cool down, it will directly form ice. So, if you open the cylinder you will see actually the very small a jet like ice is coming up and this is the reason for formation of the ice. It was initially a liquid phase which were at 67 or more atmospheric pressure and then all of a sudden if you open the cylinder the pressure drops down to 1 atmosphere and then since the pressure has dropped down there will be an adiabatic cooling just like joule terms on experiment and then due to the cooling the gas directly forms starts forming the solid. So, you have to take care when you use these carbon dioxide cylinders.

Now, the next system which we would like to study is water, but before we go there let us also discuss some other interesting phenomena if we keep on increasing the pressure and temperature we see that there exists a critical point. Now, this critical point is something which we discussed and CO 2 carbon dioxide critical point was very important, because if you remember that Andrews curve the curves we showed that time where all critical point or critical experiments that were done with a carbon dioxide and that time we said that corresponding temperature is a 304.2 degree centigrade 2 Kelvin and at that temperature you see that the liquid and the vapor are in equilibrium they are in equilibrium along this line. So, you have to also change the pressure or change the temperature and above this critical point you have all the gas that was the meaning of the critical point.

Now, here usually above the critical point the state which you see is actually not exactly the gas state which you see here. So, this state is the gas state. So, what does it mean is that you had some kind of metastable phase which we call as a critical vapor and that critical vapor exist above critical temperature. So, exactly it is something like the same example which we just give that if we take water in a sealed container and keep on heating it then, we will see that the boundary disappears and then there will be a uniform phase that will appear at a very high pressure and very high temperature. The pressure is getting high because the container is sealed.

So, as we are heating the there are we are getting more and more water vapor and which is increasing the French pressure more and more and that is how we reach the critical state now there is also a solid liquid equilibrium which we discussed, but that occur is a very high temperature now point here to note that the slope of this curve of this solid and liquid interface or the phase boundary is positive which means the slope is given by nothing, but it is the pressure temperature curve. So, it is del P del T keeping the volume constant. So, that del P del T v is positive which means, if we increase the temperature we will see the pressure is actually increasing and we will quantify it in the sense that we will show that this quantity del P del T at constant volume will be nothing, but changes in the molar volume from going from one phase to the other phase and it is usually the liquid has more molar volume than the solid when the solid goes into the liquid at the volume we can get increased. So, that is why the slope is positive we will see exactly an opposite effect when we discussed the phase diagram of water which we are just going to discuss.

So, this is the carbon dioxide phase diagram. Once again to summarize at a normal temperature and pressure the gas form is the most stable which you can easily see here and then at keeping the pressure constant which is 1 atmosphere, if we cool down the gas it will immediately freeze which means there will be dry ice forming. Now, to get to the liquid we have to increase the pressure, if we do not change if we keep on increasing the temperature it will be always gas as you can see at 1 atmosphere. But, if we increase the pressure as well you can reach to this region which is the liquid region and then you can compress the liquid inside a cylinder and if you very slowly change the temperature of the liquid you can go from liquid to solid and what happens when you open, all of a sudden cylinder then the cooling happens and the pressure of the gas actually drops down and because there is an external pressure which is equal to 1 atmosphere and then due to severe cooling the gas actually forms directly the ice and then you see it as a formation of nice ice like filaments in air which is nothing, but the dry ice and there exist a triple point which corresponds to a 5.1 atmospheric pressure and 216.8 Kelvin temperature and there also exists a critical point and the critical point is the same critical point which we discussed during the pressure volume curves of idea and real gases and there we showed that at critical point the we denoted it as the terra parameters as T c, P c and V c.

Now, remember that, in that case we are showing the curve as a pressure versus volume. In this case we are showing pressure versus temperature and in the pressure temperature curve you realize that there is a triple point and again than the choice of pressure temperature naturally follows from the equilibrium or spontaneity condition of the associated change in Gibbs free energy.

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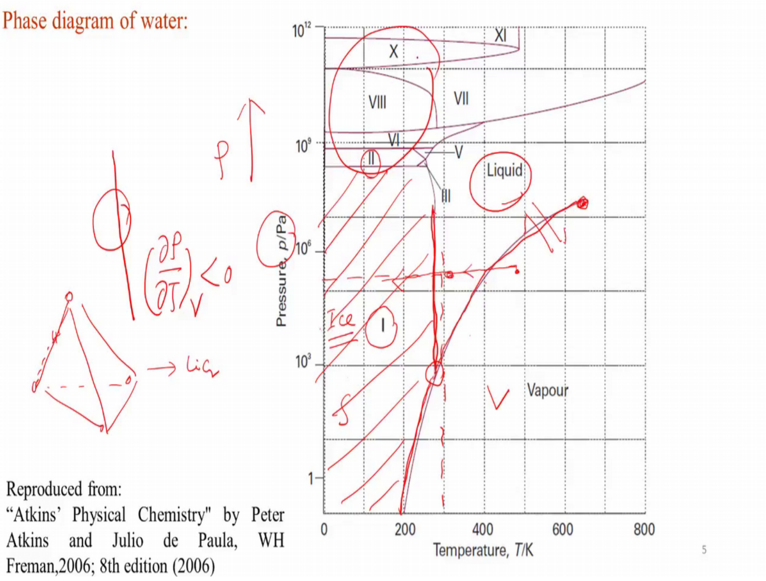
Phase diagram of water:

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Now, let us look how the water phase diagram looks like. Now, for water it is a very interesting phase diagram. Now, if you look at the phase diagram of water you see that if we draw a line at one atmosphere and at room temperature room temperature let us say it is a 300 Kelvin, this line and 1 atmosphere will correspond to this unity is Pascal. So, one atmosphere will correspond to 10 to the power 5 Pascal or so. So, the line will be somewhere here. So, you can see that the most stable form is the liquid form here and here we have the vapor form and here we have the solid form and this is the boundary which basically separates the liquid from the solid and this is the boundary which separates from the solid from the vapor and this is the boundary which separates from the vapor to the solid.

So, as before we have a triple point here which exists around 10 to the power 3 Pascal and it is close to some 300 it is around 275 or so Kelvin. Now, the point here is that at normal pressure, if we cool down the vapor which is existing here say at high temperature above say the boiling point of water and if you cool it down then it will first experience the liquid form and then eventually at the solid form. In this case the solid form is called as ice. Now, ice will come to that can exist in various isomorphs and as you can see here, there are many isomorphs of ice which are called ice 1, ice 2 something like that which exists at a very high pressure, but usual at a low pressure ice 1 is the most stable form of the solid phase and ice 1 is just the ice which we know about.

Now, interesting thing is that there is also critical point and which we discussed that the critical point has a meaning only when we consider the liquid and vapor equilibrium and there as before there is triple point. Now, if you consider the slope of this curve which is the solid liquid equilibrium curve the slope of the curve is slightly negative it is slightly like this. So, the del P del T v is negative and as we will see that we can connect it to the change in molar volumes. Now, for ice a different thing happens. So, when ice melts, you know that ice has a very typical structure where it has a open structure all the water molecules are oriented in more or less in a tetrahedral fashion where the oxygen atoms are located on the four corners of a regular tetrahedral and then also the hydrogen atoms are bonded to hydrogen atoms for 1 oxygen mole atom 1 water molecule is a making a hydrogen bond or with the oxygen of the other water molecule and that is how ice structure is stabilized, but the structure is very much open.

So, when it forms liquid water the structure partly collapses and you know that up to 4 degrees centigrade the structure keeps on collapsing. So, which means the molar volume of liquid water at 0 degree centigrade is more than the molar volume of ice at 0 degree centigrade. So, there will be a decrease in molar volume which makes this slope negative and after 4 degree centigrade again you see the regular behavior that if you keep on increasing then molecules are having more and more kinetic energy. So, they go far apart and then the volume increases or the density drops down, which is a normal behavior. But, from ice to water near at 0 degree centigrade you should see a decrease in the molar volume that causes the slope of the curve the phase boundary between the liquid and the solid phase to be negative.

Now, what do we mean by the different isomers of ice is as follows. We see that at very high pressure we can get different forms of ice. Now, when I say different forms is just like graphite and carbon. So, you see a different structure of ice altogether now these structures also exist in nature for example, if you think about a glacier; a glacier is a big chunk of ice and at the bottom of the gate glacier what will happen that due to it is huge pressure and suppose that glacier is forming on a rock and then we in between the rock and that surface I mean they are exerted huge at that interface a huge pressure is exerted and the water molecules act that interface they form a ice which is something like this isomorphs like. At a very high pressure and low temperature you have different forms of ice and those forms are very important because those forms actually now control the mobility of that glacier whether the glacier will move or not how it is sticking or interacting with the rock surface that it is formed on. So, everything depends on those isomers of ice which is not a normal ice. Normal ice we call as ice 1.

So, these isomorphs or these phases of these isomers are usually called as metastable phases, some people call it as exotic phases. You can also create them in laboratory by increasing the pressure to a very high extent, but usually the point here is that they also exist in nature.

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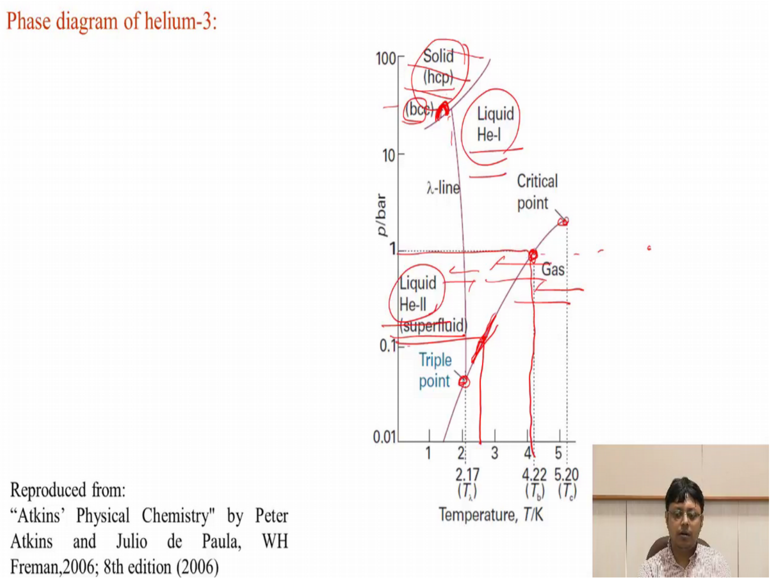

Phase diagram of helium-3:

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Now, the third thing which we will discuss is the phase diagram of helium – 3. Now, helium – 3 exist in a it is a very interesting phase diagram as you can see and usually we call it as a lambda curve why lambda it will be clear when you talk about the Ehrenfest diagram Ehrenfest classification of phases. Now, you see here that at normal temperature and pressure which is here at 4 Kelvin we have actually normal temperature of course, it will be very high and there the gaseous helium will exist, but at around 4 Kelvin, what happens that there is a transition between the gas to the liquid and this liquid is known as liquid helium one and then with subsequent cooling it forms liquid helium – 2 which is a super fluid meaning the viscosity is almost 0 at a and it flows in the inside a tube or inside a container without any friction, since the viscosity is 0.

Now, you can also see here that there is a triple point exists. Now, this triple point is not between gas liquid and solid it is between gas liquid helium one and liquid helium – 2 and also there exists a critical point which is between the gas and the liquid helium – 2 there are also other forms of helium. You can see the solid helium also exists which has a hcp structure and you can also have a very small region of the solid which is a bcc structure by hcp we call as a hexagonal closed pack a learn it in when you talk about the solid state chemistry which is not which will of force now will not be covered in this course and the basis is body centered cubic.

Now, you see that within the solid also you have a very small phase that exists over this region and the other bigger region is basically the hcp phase and there can be also a phase transition and then there is a liquid to solid equilibrium also at this very high pressure and around this temperature. So, liquid helium we will see that when you classify the transitions or the phase transitions according to a rule or according to a methodology which Ehrenfest developed we will see that liquid helium is slightly or helium actually slightly behaves very differently. It cannot be categorized something like first order or second order phase transition it has its own unique features.

So, based on this discussion what we had so far, we will now discuss the thermodynamics of phase transition. So, to summarize what we have discussed so far we discussed about the definitions, what is a phase, what is the phase boundary and we also argued that will draw phase transition in a pressure temperature plot rather than a pressure volume plot because the natural choices when a transformation happens are the pressure and the temperature are kept constant and the Gibbs free energy during the transformation for the 2 phases must be equal and then we will see it is not exactly the Gibbs free energy the more useful quantity will be the Gibbs free energy per mole which is known as chemical potential.

And, then we will also discuss that at when that transformation happens or at a particular temperature and pressure one phase one particular phase is more stable than the other phase, but when it reaches near a boundary that separates the two phases then both phases are equally stable which means the Gibbs free energy is neither less or neither more nor more for one particular phase they are just equal. So, these two the substance will exist at the two phases on this surface.

So, all these lines which we draw which are basically phase boundaries if you ask that what happens on the phase boundary. So, for example, at this pressure say for and say at this temperature what happens at that particular pressure temperature combination the we see that the substance actually lies on the phase boundary on the line which is separating the phase phases. So, both things are possible or both phases are possible it can exist either in liquid, it can exist either in solid. So, in general, it basically exists as a equilibrium between the two phases that separates that as those are separated by that line.

So, we will now in the next lecture, we will continue on this and we will talk about first the thermodynamics of phase transition, where we will discuss how the chemical potential or the Gibbs free energy per unit mole changes as we vary the pressure or the temperature.

Thank you.