

Introduction to Chemical Thermodynamics and Kinetics
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Lecture – 18
Phase equilibrium – Part 3

So, based on our previous discussion, we showed that we can represent the phase transition either as the change in the chemical potential versus temperature or in a μ versus T plot. Or we could also write it in a P versus T plot which is more common way of showing the phase diagrams. Now, the RX first classification is based on the first concept where he looked at the how the chemical potential or the free energy per unit mole changes as we change the as you go from one phase to another phase.

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Thermodynamics of phase transition: Ehrenfest classification

$\alpha \rightleftharpoons \beta$

$$\left(\frac{\partial \mu_\beta}{\partial P}\right)_T - \left(\frac{\partial \mu_\alpha}{\partial P}\right)_T = V_{m,\beta} - V_{m,\alpha}$$

$$\left(\frac{\partial \mu_\beta}{\partial T}\right)_P - \left(\frac{\partial \mu_\alpha}{\partial T}\right)_P = -S_{m,\beta} + S_{m,\alpha}$$

slope is discontinuous at the transition \rightarrow 1st order phase transition

1st der is continuous but 2nd der is discontinuous at the transition \rightarrow 2nd order phase transition

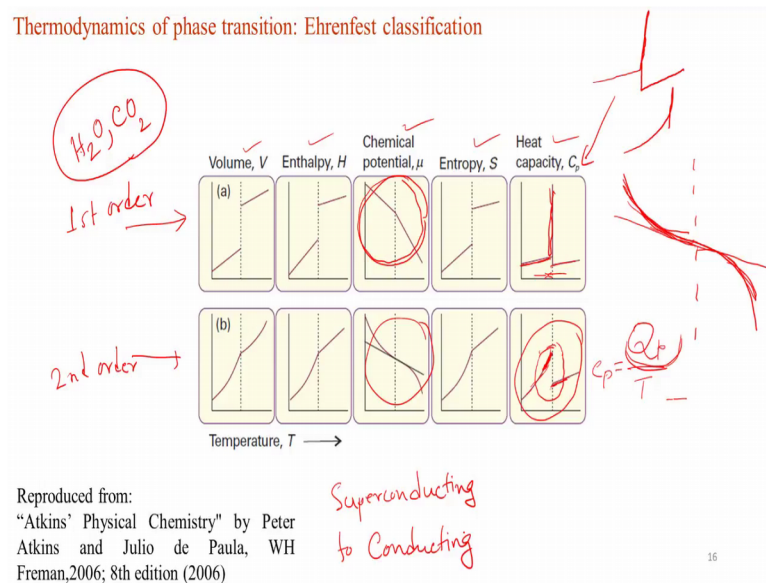
As before suppose we have 2 phases and I denote it as alpha and beta which are in equilibrium. Now, what you can write for the chemical potential in the alpha phase, which m or beta phase say, how it varies with pressure that will be nothing but equal to V beta m or we are using the sign for V m beta the molar volume for the beta phase and if you take the difference with respect to the alpha phase and take the same derivative.

So, that will be nothing but the molar volume in the alpha phase. And similarly, we can also consider the variation of the chemical potential with respect to temperature. This we

already discussed will show the plot once again. This is pressure is constant and $\Delta\mu$ ΔT . Keeping the pressure constant is nothing but minus S which is the molar entropy for the beta phase and then it will be a plus sign because I am taking negative of that and then I will have the molar entropy for the alpha phase. Now, think about it. These 2 quantities are both S_m and S_m beta, they are all nonzero and there will be a difference. So, which means the slope of the curve for the alpha phase and the beta phase should change and we already discussed it when we plot it, for say μ versus T or G versus T while going from say solid to liquid to gas, we showed that there is a change in the slope. The slope was like this or the solid and the slope is changing for the liquid.

So, Ehrenfest classification for phase transition is according to this particular definition. He considered that this how the chemical potential changes with temperature and he said that if the slope or if the basically the curve is or if the first derivative of the slope is discontinuous at the transition, will call it as first order phase transition and if the slope or the first derivative is continuous, but the second derivative is discontinuous at the transition, then we call it as a second order phase transition. Ehrenfest classified phase transition based on the slope of the μ versus D curve. So, the curves which you already had drawn for say water or for carbon dioxide, these are all examples of first order transition. Because, you can see that slope is discontinuous at these position.

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Let us give you some more examples. So, that it will be more clear. Here what is drawn in the top panel, we have drawn. These are all pressure versus mu versus T curve and this panel all these figures here describe the first order phase transition and this panel describes the second order phase transition. You already discussed about the chemical potential mu versus T curve. So, that is shown here, but during the transformation they not only that you can refer your mu versus T curve. You can actually look at many other quantities. For example, the heat capacity versus T will also change and Ehrenfest said that all these quantities like Volume, Enthalpy, Chemical potential, Entropy, Heat capacity they will all be discontinuous or the slope of the curves will be discontinuous at the transition.

Now, as before the transition is shown here as a vertical dotted line and this already we just discussed how the mu versus T looks like for a first order phase transition. For a second order phase transition look at the curve that the curve mu versus T curve suppose looks like this and suppose this is the transition temperature. Now if you see the slope is actually continually changing. So, the first derivative is continuous; however, look at the second derivative. The second derivative is nothing but the curvature. It was a negative curvature here and it is a positive curvature here. So, the second derivative is changing which is this curve and due to the, as it is shown here. That this is basically the slope. The slope is same for around the transition temperature; however, the curvature is changing or the second derivative is changing. That is why it is a second order phase transition.

Similarly, if you ask this question how the heat capacity will look like? You can see here that we are increasing the temperature. The heat capacity increases. It is not a constant of temperature which we assumed in we usually assume in many cases. So, the slope does not change that much and then all of a sudden the slope changes at the transition temperature and during the transition, an interesting thing happens. You can see that the heat capacity actually blows up.

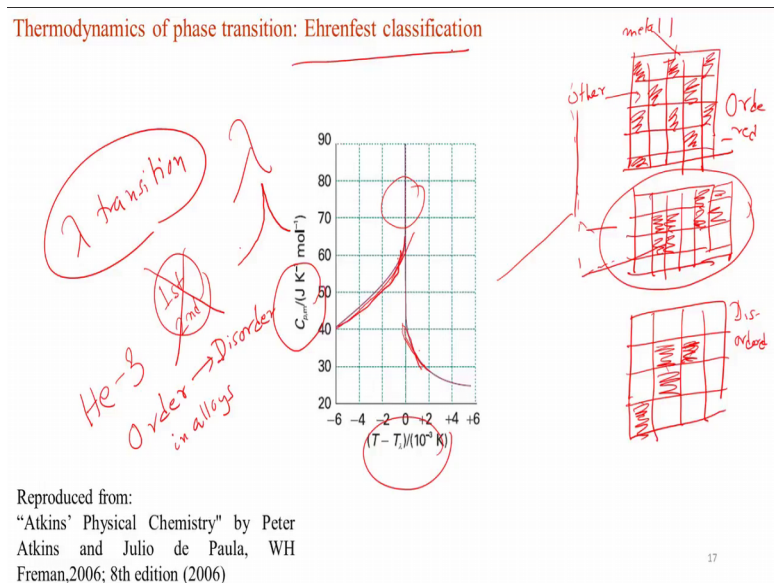
The reason is you are supplying heat to the system; however, the temperature change is very little. So, what will happen? By definition heat capacity is this is C_p . This is nothing, but Q_t at that temperature. That is the meaning of C_p and then you are supplying finite amount of heat or energy for over an infinitesimally small range of temperature. So, c_p which is a nothing, but the change in c_p which is the change in heat divided by

change in temperature that will blow up because the dt is very small here all the dq_p is finite here. However, for the second order phase transition, you can see here that the slope gradually changes and the slope also does not change here. It is near the phase transition or near the transition temperature. The slopes are not so different; however, they are second derivative.

All of a sudden changes because the curvature of the curve changes but, here notice that the heat capacity is not going to infinity in this case. Now in the sense that it is not blowing up or it is a continuous in the first derivative, but the second derivative it is not continuous in the first derivative. It is the second order phase transition and the second derivative is discontinuous, but interesting thing is that change is not happening like the heat capacity is not blowing up. The reason is, the curve is actually changing much before the transition temperature is attained. In this plot what do you see here? There is a slow change and then all of a sudden there is a huge change because only at that transition temperature you are exchanging temperature and then in this case what is happening? The curve look like this. It is changing as it is approaching the transition temperature.

So, it is becoming finite. There could be a third possibility.

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Which is neither first order or nor second order. It is not first order in the sense that these slopes are discontinuous here. I have a slope here and here I have a very different slope;

however, if you look at it carefully that this is unlike the first order. In the first order case we had something like this, the temperature is heat capacity is going all of a sudden infinite and then again we have a change in the slope; however, in this case the slope is different, but the heat capacity is changing all of a sudden. Meaning that it is neither the first order or nor the second order. It is a very specific example. This is known as the lambda transition, where just like the second order it is changing smoothly. I mean it is not blowing up. So, much as the first order, but it is also like first order in the sense that the slopes have been discontinuous we have basically 3 types of phase transition. The examples which I gave you earlier like the carbon dioxide phase diagram or the water phase diagram and at few regions they are mostly follow the first order phase transition.

Examples of second order phase transitions are rare, but you can think of like. So, this example is for water carbon dioxide you will see these kind of phase transition for second order phase transition. The examples are say for example, when a metal goes from a superconducting phase to a conducting phase what do you mean by superconductor is that for a conductor or for a metal at room temperature what happens if we increase the temperature? The conductivity actually decreases because actually there will be lot of thermal scattering of the electrons because, the electrons are the charge carriers in metal; the free electrons which are in the conduction band of the metal and the valence band and the conduction band in the metal overlaps. So, there is no band gap. At room temperature you have enough number of free electrons in the conduction band that conduct the electricity and if you increase the temperature, there will be a thermal scattering and that is why the conductivity decreases; however, for a superconductor it should be independent of the temperature.

There is no scattering effect and then all of a sudden you see our huge enhancement in the conductivity. So, that kind of phase transition follows the; whatever we have talked about the second order phase transition meaning the first derivative is continuous; however, the second derivative or the curvature is discontinuous. The third example which is neither first order or nor second order which is mainly known as the lambda transition. That name actually comes from the particular shape which we see here. It looks like the Greek letter lambda. If you look at the curve here and lambda because it is just doing a smooth transition and then something like that. That is why it is a lambda transition we already discussed it when we talked about the liquid helium to another

liquid helium transition which is for helium 3 we discussed, but this is also shown by other substances. For example, it is also shown by order to this order transition in metals where you can think of that particularly in metallic alloys.

Now, an alloy is a mixture of 2 or multiple metals as you know and if we have a very perfect alloy suppose I have one region of the alloy which is having one metal and the other region is another metal. So, think about say something like amalgam, which you already know, that it is alloy of mercury and then you can think that suppose this is one metal, this is metal 1 and this is basically the other metal and at normal temperature it is very much ordered. So, what will happen if you keep on increasing the temperature, then at a very high temperature you will see a disorder. In the sense that one site will or regions will look like this. It is very random nests will come. As you see that all these same metals are coming closer together, but there is no perfect pattern which will be maintained. It will be very random. It is an order phase or ordered phase and this is a disordered phase, but in between something interesting happens when it goes from the order to disorder transition, you might see that it is going to order to disorder, but still it is maintaining some kind of order over some length scale.

So, it is neither the order is completely lost not the disorder also is not there. Both are present there. The change is rather smooth something like we already discussed for this lambda transition. This is the change is something small. In that case it is now it will not be a plot of C_p versus T . It will be a plot of some order parameter versus temperature, but that is also another kind of phase transition and that is also kind of lambda transition. So, according to Ehrenfest all these phase transitions can be divided onto all these 3 categories. First order where the first derivative is discontinuous or the slope is discontinuous. Second order where the first derivative is continuous, but the second derivative is discontinuous or the curvature is discontinuous and there are also lambda transitions, where you see something of the kind of partly first derivative and partly if the first order phase transition and partly the second order phase transition which you cannot categorizes, strictly first order drastically second order and we give 2 examples one is for the helium 3. One is for the order to disorder phase transition.

Now, let us summarize this part. So, in lecture 6 what we discussed is we talked about phase transition in general we started with the concept of phase boundaries and many other parameters. Most importantly the chemical potential which is a thermodynamic

quantity, which is defined as the Gibbs free energy per unit mole and we showed that how the chemical potential varies with temperature and then we talked about the effect of pressure on the changes in that slope of μ versus T plot and we talked about very interesting example like how 2 IC's can be brought together and with pressure they can be joined together and then we talked about also different systems and the phase diagram for different system and usually the phase diagram is drawn in a pressure temperature diagram. So, we talked about it and then we try to make a quantitative analysis why the phase boundaries look like straight line or nearly straight line for say liquid solid equilibrium, but it looks like a curved line for the liquid vapor or solid vapor boundary.

So, we tried to make our formulate some equations and for the liquid to solid or basically the solid to liquid, the melting curve which was approximated to be a linear we derived that equation and that is known as the Clapeyron equation and the same equation for liquid to vapor, you can also show where actually for the vapor phase consider the ideal gas equation and you get a logarithmic or exponential relationship. That we called as a Clausius Clapeyron equation. Similarly, we did not show it for the sublimation process what happens for solid to vapor equilibrium, but that will also show a similar effect and then we try to explain why the nature of the phase diagrams are like that we discovered, but those phase diagrams are only first order phase diagrams or phase diagrams for first order phase transitions we also talked about that there could be a second order phase transition according to Ehrenfest notion and there could be in between transition which we called as the lambda transition. So, in the next lecture we will talk about mixtures we are here actually we talked about only phase transition of one component.

Except the only example we gave like order to disorder transition, where I start from an alloy, but otherwise it is only one component. In the sense, when you talk about helium 3, it is only helium 3. So, the chemical composition is same. It can exist in different phases where the densities are different, but the chemical composition is the same. So, it is a phase diagram of water or phase diagram of carbon dioxide. It is not like; it is a phase diagram of water ethanol mixture we will first talk about mixtures in the next class and in the next lecture which will be lecture number 7 and in the lecture number 8 we will talk about chemical equilibrium and in the lecture number 9 we will be talking about the electrochemistry part or the equilibrium electrochemistry part and then we will start our discussion on chemical kinetics.

Thank you.