Fundamentals and Applications of Supramolecular Chemistry

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Week 07
Lecture 33

W7L33_Types of Phase Transition

So, hello, everybody. So, today we are going to discuss the thermodynamic classification of phase transitions. So, in the last lecture, we looked at Buerger's classification of phase transitions. That is, phase transitions can be of the reconstructive type or of the displacive type.

We looked at this in the previous lecture, and we examined Buerger's classification. As for the reconstructive phase transition, we have the major reorganization of the crystal structure in terms of making and breaking bonds, whereas in the displacive type, we only have minor structural changes that involve distortion of the bonds, and there exists a definite structural relationship between the two phases.

So, today we are going to look into the thermodynamic classifications of phase transitions. And in this regard, to start with, we are considering a compound—any compound that exists in the solid state—as two polymorphs, 1 and 2.

And we also need to consider the different thermodynamic quantities that are involved. We are interested in looking at entropy, we are interested in looking at enthalpy, we are interested in looking at volume, and we are interested in looking at the Gibbs free energy.

When a phase transition takes place, we know that it is associated with a change in the enthalpy content. Particularly, if there is a phase change from polymorph 1 to polymorph 2, then we know that this process is associated with the enthalpy change and the temperature at which this transition takes place is referred to as Tc, and the ratio of these two quantities tells us the entropy change associated now with the polymorphic transformation.

And we also know that every polymorph is associated with Gibbs free energy, which is represented as G1 and G2. And at equilibrium, that is at the point of phase transition, G1 is equal to G2, that is, the free energy isobars, assuming that we are doing it at a particular temperature and pressure; in this case, the pressure is kept at 1 atmospheric pressure. So, this is the free energy isobar; the delta G is equal to 0 at the point of phase transition from one form to the other.

So, because delta G is equal to 0 and from the expression, delta G is equal to delta H minus T delta S, this is equal to 0. So, delta H minus T delta S equals 0, and this gives the relationship

that delta H is equal to T delta S, from which we get the entropy change, which is equal to delta H divided by T.

And we can now look at the classification of the phase transitions. Phase transitions, to start with, are primarily classified as first-order or second-order phase transitions, which are the more popular ones. I would say even higher orders of phase transitions greater than 2 are also possible, but we will not be looking at those.

We will be focusing on the first-order and second-order phase transitions, and we need to characterize these phase transitions from experiments and see how we can gain an understanding of the variation in the thermodynamic parameters associated with first-order or second-order phase transitions.

So, we start with the fundamental relationship that expresses the relationship between dG as minus SdT + V dP, telling you that Gibbs free energy change is a function of temperature and pressure. So, G is a function of temperature and pressure, and dG by dT at constant pressure gives us the entropy change.

So, this is expression number 1, and dG by dP at constant temperature gives us V, which is the volume, represented by the change in G with respect to the change in P at constant temperature. And we also have the other relationship that is H is equal to U + PV, where U is the internal energy of the system, H is the enthalpy, P is the pressure, and V is the volume.

The first order phase transitions are essentially characterized by changes in entropy at the temperature of transition, that is Tc. They are also characterized by changes in unit cell volume at Tc, and this tells us that there are changes in the crystal structure between the two polymorphs 1 and 2.

So, it is not that there is a gradual continuous change from structure 1 to structure 2; effectively, the crystal structure before the phase transition is very different from the structure after the phase transition.

And it is also characterized by changes in the density of the solid before and after the phase transition, so just to give you an example of a first-order transition. We can look at the crystal structure of cesium chloride, and it undergoes a transformation to the rock salt structure; here we see that the temperature of the phase transition is 479 degrees centigrade, the volume change in cubic centimeters is 10.3, and the enthalpy change is 2.424.

We can take another example of ammonium bromide, and we will come to what changes are happening later. We will see again, in the case of the ammonium bromide compound, that it crystallizes in the cesium chloride structure and its conversion into the rock salt type involves a transition temperature of 179 degrees centigrade, a volume change of 9.5 cubic centimeters, and a delta H of 3.678 kilojoules per mole.

So, the enthalpy changes associated with these processes are not very large. These are very small, volume changes are finite, and the temperature of the phase transition is also represented. So let us look at these quantities more closely. So, we have the Gibbs free energy as a function of temperature T, and this is representative of the first polymorph; this is representative of the second polymorph.

So, Tc is the temperature at which the G curves intersect. So, G1 is equal to G2, and before the temperature Tc, the G1 value is lower than G2. So, polymorph I is the most stable phase. However, after Tc, what happens is that G2 is less than G1. So, G1 has the greater value; if you take any particular temperature, say this particular temperature, you can see that G2 is lower than G1.

So, I is stable. After the phase transition temperature, II is more stable. And we can also probe this by looking at the changes in G as a function of T at constant pressure, which is a measure of my entropy. So, the entropy, the change in delta G versus delta T, is more for the second polymorph compared to that of the first polymorph. Therefore, there is a more rapid fall for polymorph 2 after the phase transition temperature compared to that for polymorph 1.

So, it is very clearly illustrated that after the phase transition temperature, the entropy of the higher temperature polymorph is greater compared to the first polymorph. Now that is because you are increasing the temperature of the system, and you are forming a high-temperature polymorph.

Not only does the high temperature polymorph have higher entropy, as is reflected in the more negative slope of ΔG by ΔT. We can also look at the corresponding H as a function of temperature, and here it is very clearly shown that at the temperature Tc, there is a discontinuity in enthalpy; that is, H1 is not equal to H2. And this much amount of heat has to be given to the system, and this much enthalpy change takes place at a constant temperature because the heat that is taken by the system now goes into bringing about the phase transformation.

So, there is a discontinuity in H at the phase transition temperature. So, the enthalpy content of the higher temperature polymorph is also greater in comparison to the low temperature polymorph that exists before the transition temperature.

So, the high temperature polymorph not only has a higher heat content but is also associated with higher entropy. You can also look at the corresponding Tc, and we can see that there is also a discontinuity. If you were to actually look at -TS1 with respect to -TS2, there is also a discontinuity at Tc.

So, we have a discontinuity in entropy. And we have discontinuity in enthalpy, and these are characteristics of a first-order phase transition where you have these variations. So, it is important to keep in mind now that at the phase transition temperature, delta G is equal to

0. Our delta H is equal to T delta S, which is not equal to 0, and this allows us to evaluate the entropy change associated with the process. So, the first-order phase transition, we see very clearly, is marked by a discontinuity in enthalpy and entropy; we also observed the volume change, and the structure has also changed.

Now let us look at the second-order phase transitions. The second-order phase transitions are essentially characterized by a discontinuity in the second derivative of the free energy. So, we are now looking at the second derivative. We are now going to look at these quantities. That is del squared G by del P squared.

So, we now look at the second derivative of this quantity: del square G by del P square, and this is equal to dV by dP. This is actually -V times beta, and beta is called the compressibility of the substance. We can also look at $\partial^2 G/\partial T \partial P$, which is equal to $\partial V/\partial T$, because that is the second derivative we are taking with respect to temperature.

And this is V times alpha, where alpha is the thermal expansion coefficient. Beta is the compressibility factor, and we can now take del squared G by del T squared, which is minus del S by del T, and at the phase transition temperature, this is equal to minus Cp by T, and Cp is the specific heat capacity of the substance.

So, these are the three very important relationships: the second derivative of G with respect to P, the second derivative of G with respect to T and P, and the second derivative of G with respect to T. These tell you that there are discontinuities in the compressibility factor, thermal expansion, and specific heat capacity, and these are characteristics of the second-order phase transition.

That means that the quantities reflect the first derivative; that is, for example, the entropy changes, and we have also got the enthalpy change. So, we have the quantities H and S. H and S are continuous at Tc for a second-order phase transition.

So, we are able to determine a first-order phase transition by looking at a discontinuity in H and S. However, for a second-order phase transition, these quantities H and S are continuous at the Tc for a second-order phase transition.

So, how do we represent these continuous changes that happen in the structure until you reach Tc, and what happens after Tc? In order to understand the representation of the second-order phase transitions and the variation of the thermodynamic quantities with respect to temperature, we can now plot, to start with, G versus T. So, this is polymorph II, and this is polymorph I. This is a supercooled phase II.

So, this is the temperature Tc, where you can see that there is no discontinuity in the process; however, there is a gradual increase in temperature. So, this is the temperature axis T; there is a continuous change happening from I, and after Tc, it has completely converted into phase II. So, now the interesting thing is that, when you can actually go low in

temperature and can still supercool phase II, you cannot superheat. You cannot go here; this is not allowed. Why? Because the process of conversion from I to II has already started at 0 Kelvin.

So, in principle, say, even if you are at room temperature, and then you start heating the substance, by the time you reach Tc, the phase transition has already started from 0 Kelvin and continues at an increasing rate.

Because you also need to keep in mind that thermodynamics is an important factor here, but the rate is already integrated into the system. So, there is also a rate associated with the transformation process.

So, we are assuming that this transformation is happening slowly as a function of temperature, and by the time you reach Tc, the phase transition, which had already started from 0 Kelvin, is now at room temperature and continues at an increasing rate with increasing temperature, such that when Tc is reached, the phase transition is complete. And now, when you go across the phase transition temperature, there is no reason for a discontinuity in the value of the entropy change.

There is no reason for a discontinuity in the entropy change or the enthalpy change because the process has been happening in a continuous manner, and essentially, this tells you that when you reach Tc, the conversion from I to II is already complete.

So, there is no reason why you should be able to superheat I, because I had already completed its conversion into II. So, it is not possible to superheat I, but it is definitely possible to supercool II and progress along the dashed line, if given an opportunity to do so.

So, you can actually supercool II gradually, and you can prevent its conversion to I, but you cannot superheat I, because one has already been converted into II. Now, in order to understand this picture more carefully regarding what is happening at the structural level, these kinds of transitions are also referred to as order-disorder phase transitions, and this can be easily understood.

If you consider, for example, an AB solid in which, at 0 Kelvin, the positions of A and B are well defined, but if you now start increasing the temperature, then A and B start randomly getting redistributed at different sites.

So, at 0 Kelvin, the crystal structure was characterized by long-range ordering, which we call LRO, and by the time we have almost reached the transition temperature, that is Tc, there has been an extensive redistribution of A and B at different sites. And this increase in randomness essentially contributes to the disorder of the crystal structure.

By the time you have reached Tc, and if you go even beyond Tc to higher temperatures, there is now a random arrangement of A and B such that statistically A would like to be surrounded by B and vice versa. Therefore, this is referred to as short-range ordering.

So, at Tc, the long-range ordering has been completely removed, and it is only the short-range ordering that exists at Tc. That means the structural changes had already started with the increase in temperature, and this is referred to as the order-disorder phase transition. This allows us to understand the gradual changes that are taking place in G as a function of temperature, particularly when we go across the phase transition.

So, this process can also be quantified. As the long-range ordering as a function of temperature where we see that the phase I is converting gradually into phase II and when you reach the temperature, Tc here, it is completely converted into the phase II.

So, the long-range ordering goes to 0; it is the short-range ordering that exists at Tc. And these are, this essentially is a signature of a second-order phase transition, which is of the order-disorder type.

And it is also now important to look at the corresponding enthalpy changes, which take place, because we know that there cannot be a discontinuity, because a discontinuity where H1 is not equal to H2 is a characteristic of a first-order phase transition.

So, we now look at H as a function of temperature, and this is the Tc. At Tc, H1 is equal to H2, and this is not exactly a first-order phase transition because, in a first-order phase transition, we saw that H1 is not equal to H2.

And it indicates that they are very close to the transition temperature Tc; there is a substantial anomalous increase in enthalpy. The enthalpy value, or the H component, increases. Close to the Tc, there is an anomalous increase in H.

Therefore, it is not discontinuous; it increases from H1 to H2, and it increases gradually, but it is anomalous in the sense that we are not able to account for its origin. But then we need to re-categorize our concept of phase transition, because we need to understand that on one side we have a discontinuity, and on the other side we have a continuity of the thermodynamic parameters.

And it is at this time that the scientist who came into the picture was Ubbelohde, who defined phase transitions as being continuous or discontinuous in nature. And one thing I must also mention here is that when you have this kind of response in the H versus T plot, what you can now plot is Cp versus T.

And there, as we showed you, if you plot Cp versus T, there is a discontinuity in Cp at Tc. So, you can now plot the specific heat capacity as a function of temperature, and you can see the discontinuity in Cp at Tc. This is a finite discontinuity in Cp at Tc, and that characterizes the second-order phase transition.

So Ubbelohde had said that when you have a first-order phase transition, it is definitely discontinuous, but for a second-order phase transition, there is a gradual smooth change and a continuous change in the structure of one polymorph to the other.

This process is already taking place before you have reached Tc. These kinds of changes that happen before Tc is reached are called premonitory changes. The premonitory changes, which take place because of the gradual and continuous change in the crystal structure, cannot be ignored. So, the premonitory changes are very important, and they occur for the thermodynamic parameters, that is, for S and H, and they are more of a continuous kind; these premonitory changes are already happening below Tc.

And after Tc, there is again a continuous change in S and H, indicating that the second-order phase transition has already been completed. Ok. That means technically, for a second-order phase transition, we know that H1 is equal to H2. That means delta H is equal to 0.

But in reality, when you will actually map the second order phase transition, using for example, DSC, you will see that there is a minor drift from the baseline, indicating that no matter whatever be the order of the phase transition, as long as there is a structural change, even of a very subtle kind, it will always have the character of first order in it.

So, you cannot have a pure second-order phase transition or a pure first-order phase transition; these are ideal things. First order is still very well understood and characterized, but second order is something where you need to look at the changes in the thermodynamic quantities in a more careful way because these can also involve subtle changes, and you cannot ignore a first order phase transition, the character of first order phase transition and also second order phase transition as well. So, on the same line, if you were to actually look at Cp versus T for a first-order phase transition, it is discontinuous.

So, you see it becomes infinite at T equal to Tc; it is characterized by an infinite discontinuity at T equal to Tc. And the driving force for the order-disorder phase transition that I would like to mention is the entropy change that takes place at the phase transition, characterized as R ln(omega 2) by omega 1, where omega 2 is the number of independent orientations at high temperature, and omega 1 is this number at low temperature.

So, it is kind of a contribution to the statistical entropy, and in this regard, the entropy changes are primarily the configurational entropy, vibrational entropy, and rotational entropy; but here it is the configurational entropy that contributes to and drives the phase transition processes.

We can look at this order-disorder phase transition with respect to one particular example: ammonium bromide. And we have the ammonium ion sitting here, and these are hydrogen bonded here with the two bromines, and then here with these two bromines.

So, there is one set of ammonium here that involves hydrogen bonding with these two bromines, but in the other one, we have the other four bromines involved in hydrogen bonding.

That is these ones. So, you have two different orientations of the ammonium ion. Now, in the ordered phase, you have the ammonium ions in only one particular orientation in all the unit cells.

But in the disordered phase, you will have the ammonium ions in either this orientation or that orientation, and this is statistically distributed randomly in different unit cells. So, the number of configurations is only one for the ordered phase, but the number of configurations is two.

And that tells you that delta S is equal to ln R plus ln 2, and this is the magnitude that drives the process of phase transition favorably, because there is an increase in entropy associated with this process, thereby validating the order-disorder phase.

So, these subtle changes in the entropy can actually guide these phase transition processes as well. So, I hope that with this discussion we have been able to appreciate the nature of phase transitions, first order and second order.

And now, keeping these things in mind, we will look in the next lecture at how these phase transitions take place under different conditions. These conditions can be chemical in origin, electrical in origin, and we can look at the temperature, pressure, different factors, and different kinds of stimuli, such as light; for example, we can change the pH, apply mechanical stimuli, introduce different kinds of stresses, and put in different chemicals, to which the structure can respond and change from one structure to another.

So, all these stimuli can lead to phase transition processes and we will discuss more about this in the coming lectures.

Thank you.