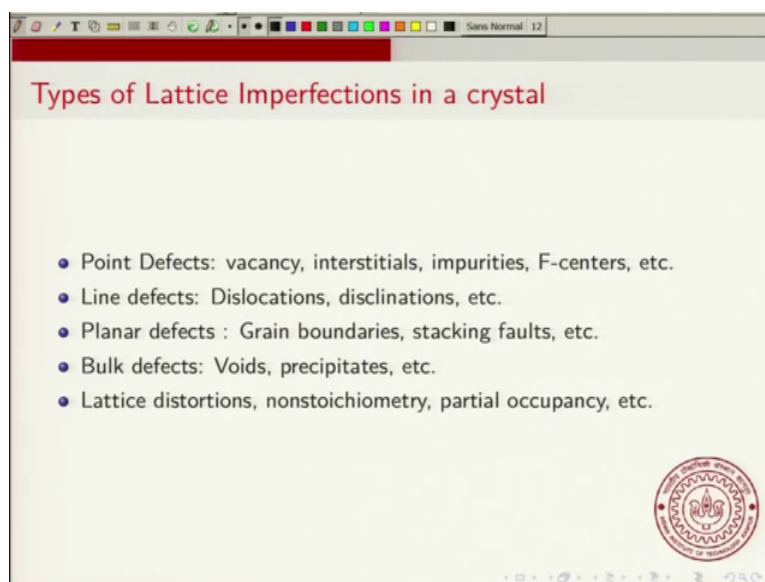


Solid State Chemistry
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Lecture – 34
Thermodynamics of defects in crystals

In the 4th lecture of this 7th week of this course, we will talk about the Thermodynamics of defect formation. We look at very basic thermodynamics and a little bit of statistical mechanics ok. So, this will be slightly mathematical, but it is not very difficult ok. So, week 7, lecture 4 will be Thermodynamics of defects in crystals.

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Let us again remind ourselves of the types of lattice imperfections in crystals. We saw point defects, line defects, planar defects, bulked effects and lattice distortions. Now most of the thermodynamics that we will be talking about will be in the context of simple point defects, but you can also extend them to line defects. Only thing we will realize that things are more difficult to calculate for line defects and other defects.

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Entropy and Temperature

Defects increase energy of crystal → ENERGETICALLY UNFAVOURABLE

Presence of defects increases entropy → ENTROPICALLY FAVOURABLE

$$\Delta G = \Delta H - T \Delta S$$

$$\Delta G = G_{\text{defect}} - G_{\text{perfect}}$$

$$\Delta H = H_{\text{defect}} - H_{\text{perfect}} > 0$$

$$\Delta S = S_{\text{defect}} - S_{\text{perfect}} > 0$$

⇒ More defects at higher temperature

CONFIGURATIONAL ENTROPY

Illustrative Example

N sites

Consider 1 vacancy → can be at any of N sites ⇒ N configurations

2 vacancies ⇒ ${}^N C_2$ configurations
 $= \frac{N!}{2!(N-2)!}$

So, what is the basic thermodynamics of defects? So, the basic thermodynamics of defects has to deal with the idea of entropy and temperature. Now the idea is that defects increase energy of crystal; energy of crystal that means, they are energetically unfavorable ok. Now however, presence of defects increases entropy; presence of defects increases entropy; entropy of crystal that means entropically favorable.

So, you want to have higher entropy and you want to have lower energy ok. So, the defects increase the energy. So, they are energetically unfavorable, but they are entropically favorable ok. And now, if you look at let us say you say delta you imagine some relation like delta G is delta H minus T delta S and let us say delta equal to the difference or I will just say delta G equal to G of perfect crystal minus G of defect crystal or yes or let me write it the other way.

Delta G is G of defect minus G of perfect and so if the G of defect is lower than the G of the perfect, then the defect will be far favored ok. And what we realize is that if you write in this way, then you have delta H is equal to an enthalpy of the defect; the defected crystal of the crystal with a defect minus the enthalpy of a perfect crystal and we know that the enthalpy or the energy of defected crystal will be higher than that of a perfect crystal, so, this is greater than 0. And similarly delta S which is entropy of a defected crystal minus entropy of a perfect crystal, this will be less than 0; no sorry, this will also be greater than 0.

So, the defective crystal also has higher entropy and so, what that means is that if your temperature is very low, if your temperature is very low ok, then the effect of enthalpy will be negligible and so, ΔG will be greater than 0 so, defects will not be favored ok. So, at low temperature, there you will have very few defects at high temperature you will have more defects.

So, this implies more defects on the period in a different color; more defects at higher temperatures. So, physically you can understand this, you can imagine that you know you have this crystal where all the atoms are at their perfect lattice positions and there for me you know as you heat the crystal ok. Then, the atoms start vibrating a little bit from their lattice position. As you heat it more and more, then they start vibrating more and more and at some point, they start leaving their lattice position and they start forming defects ok.

And so, as you increase the temperature more and more you will have more and more defects and so, all this intuitively agrees with our idea of defects and you know how of having more defects at higher temperature. Now, let us look at this idea of entropy ok, we I said that the presence of defects increases the entropy.

Now, how do we understand this? How do we understand this statement at the presence of defects increases the entropy ok? To understand this we need the idea of what is called configurational entropy and I will just take one example ok. I am taking one particular example ok, I am illustrating let me emphasize that this is an illustrative example. It is not a; it is not a general formula for configuration entropy or anything it is an illustrative example of how configurational entropy works ok.

So, imagine you have a crystal and let us say you have this crystal with various sites which contain atoms and for simplicity let us just take a on a monatomic crystal and let us say you have N sites ok. So, there are a total of N sites ok. Now so this crystal has a total of N sites and now each if each of those is occupied by an atom ok, then you will have a configuration where there is no vacancy ok.

Now, suppose I say that there is one vacancy in the crystal. Now consider one vacancy; only one vacancy ok. Now immediately you will say that this vacancy can be in any of the N sites; can be at any of N sites ok. So, basically there are N possibilities; N

possibilities ok. I am using the word possibilities a little loosely in a more precise language of statistical mechanics we will say there are N configurations ok. So, actually let me use about configurations ok.

So, if you have just 2 vacancy, as you said it can be; it can be in any of these N sites. So, there are N configurations and you can see what will happen, if you have 2 vacancies ok. The you can choose; you can choose one of them from the N configurations; the other one from the remaining N minus 1 configurations and obviously, their order does not differ. So, you have total of N choose 2 configurations. So, it is a usual combinatorial factor and N choose 2 ok. The expression for N chose 1 is N factorial over 2 factorial N minus 2 factorial. So, let us continue.

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Defect formation energy
CONFIGURATIONAL ENTROPY
 m vacancies $N C_m$ configurations = $\frac{N!}{m!(N-m)!}$

$S = k_B \ln W$
 No of configurations

$S(m) = k_B \ln \frac{N!}{m!(N-m)!}$

Defect formation energy E_d
 = Energy of crystal with defect
 - Energy of perfect crystal

\Rightarrow No obvious way to calculate E_d
 \rightarrow More complicated for other defects

The slide also features a graph of $S(m)$ vs m showing a symmetric bell-shaped curve peaking at $m = N/2$, and a diagram of a 3x3 crystal lattice with one site occupied by a red dot representing a vacancy.

Now, suppose you have N vacancies ok, I am continuing the discussion on configurational entropy. Suppose, you have N vacancies, then the number of choices is number of configurations is N choose m configurations ok. This is equal to N factorial divided by m factorial N minus m factorial ok.

So, now the entropy the Boltzmann entropy expression S is equal to k times natural log of ω which is the number of configurations. And so, basically if you have a configuration with m vacancies ok, a configuration with m vacancies will have an

entropy of I should write this k_B ; this is Boltzmann constant. So, this is k_B natural log of now the number of configurations is N factorial divided by m factorial ok.

So now the Boltzmann formula for statistical mechanics ok; so, the Boltzmann expression for statistical mechanics is valid when you have a very large number of configurations ok. When the number of configurations is very large that means, the number of site is very large and the number of defects is also very large ok. So, when both N factorial and m factorial are both very large and in fact we also assume that N factorial is ok. So, both N factorial and m factorial are very large ok.

And in this case, you can write you can use something called the Sterling's approximation; well fine. Before we mention that, I will just; I will just show ok. So, if you just take this function, if you just take this function and you just make a plot of it. If you just plot S versus m ok, when m equal to 0; m equal to 0, then S is then basically you have natural log of one which is 0. So, entropy is 0 there is only one configuration ok.

So, you start at 0, then it increases with m ok. It keeps increasing with m and it reaches maximum when m equal to $N/2$ and it goes down and again goes to 0 when at $N - m$. In fact it is a perfectly symmetric its a usual binomial distribution ok. This is S of m as a function of m ok. Now usually the number of defects is very small, it is much less than N so, you are only; so, you are only in this region ok, you are only in this region of the graph ok.

So, you so, your m is usually very small much smaller than N ok. However, you can see that as you increase the number of defects, your entropy goes up and so this entropy is called the configurational entropy and that tells you why you know just based on number of configurations available, you can see why defects increase entropy.

Now, again let me emphasize that I took this for the particular example of I took it for one illustrative example of a you know defect occupy occupying a site, but this can be generalized for all kinds of defects ok. You might not be able to arrive at such simple expression for other kinds of defects ok, but in any case the entropy will increase as you increase the number of defects ok.

Now, the next point is the defect formation energy, I will call it E_d ok. This is the energy of crystal or you can say energy of crystal with defect minus energy of perfect crystal and this E_d is huge is greater than 0 because the crystal with a defect has higher energy than the perfect crystal ok. And now, if you take the particular case of this vacancy at a site then what you have to do is to so let me just take an example. If you have; if you have a crystal, I will just show a small piece of a crystal. This is the perfect crystal, I am just showing this set of 9 atoms and now let me say that now I have a defected crystal, where let us say one of these atoms is missing.

So, let me show the defected crystal in this way. So, I say that one of these atoms is missing. I am just showing a small piece of a crystal ok. So, you should imagine that the crystal is extending in all directions and this is just one part of the crystal. Here there is a defect ok. Now what I am showing in the red is the missing atom ok. Now obviously, because of this missing atom, there will be some you know the interactions of the crystal or that were there in the perfect crystal.

So, in the perfect crystal, this atom these two atoms were interacting with each other; these were interacting with each other; these were interacting with each other and that would that was what was holding the crystal together ok. Now when you do not have this ok; you do not have all those attractive interactions. So, it its actually energetically less stable and its energy is higher and now you can see that you know how do you know simple way to calculate defect formation energy ok.

So, no obvious way; calculate E_d ok, but you can imagine; you can imagine that if there is some way you could calculate the energy and for those who are familiar with quantum mechanics, you can think that I can do a calculation and I can calculate the energy of a configuration with a defect and a configuration without a defect and I can take their difference ok.

But in any case there is no obvious way ok, but and this is only for the case of point defects. You can imagine that for line defects and you will get more complicated for other defects ok. So, but then having this idea of defect formation energy is extremely useful ok. You know just way to calculate it nor is there an obvious way to measure it ok, but there is something that you can get from this defect formation energy; something that you can read that you can relate the defect formation energy to ok. That is the following.

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Boltzmann factor and defect concentrations

$E_d \longrightarrow \frac{N_d}{N}$ (number of defects) fraction

$N_1 \rightarrow E_1$
 $N_2 \rightarrow E_2$ ⇒ At Equilibrium at temperature T

then $\frac{N_1}{N_2} = \frac{e^{-\frac{E_1}{k_B T}}}{e^{-\frac{E_2}{k_B T}}} = e^{-\frac{E_1 - E_2}{k_B T}}$

$\frac{N_d}{N - N_d} = e^{-\frac{E_d}{k_B T}}$ Usually $N_d \ll N$

$\frac{N_d}{N} = e^{-\frac{E_d}{k_B T}}$ → Did not explicitly use entropy

You can relate you can use something called a Boltzmann factor and relate this and connect this defect formation energy to defect concentration ok. So, the idea is that your defect formation energy. So, E_d is from here you go to number of defects, this is number of defects. Actually it is not the number ok. So, it is the fractional number ok; it is the number fraction.

So, I will say it N_d by total N . So, this is a number fraction of defects ok. So, this is something that you can do using the Boltzmann factor alright. So, how is this done ok? So, the idea is very straightforward ok. What the Boltzmann factor says is that if you have two if you have a configuration of energy E_d higher ok. So, if you have; if you have two configurations and if you have N_1 of energy E_1 and N_2 of energy E_2 ok.

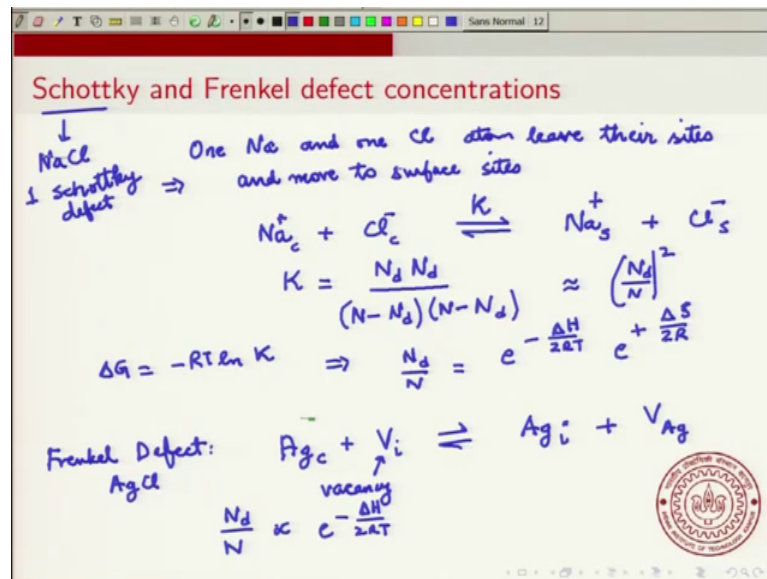
So, let us say you have N_1 is the number of configurations with energy E_1 and N_2 is a number of configurations at energy E_2 and let us say the whole thing is at equilibrium at temperature T ok. Then, N_1 by N_2 is equal to $e^{-\frac{E_1 - E_2}{k_B T}}$ ok. So, essence let me write it in a slightly different way. So, it is equal to this divided by $e^{-\frac{E_2}{k_B T}}$ and you can expand you can write this as $e^{-\frac{E_1 - E_2}{k_B T}}$ ok. So, this is a Boltzmann factor that comes from thermodynamics from statistical mechanics. So, N_1 by N_2 equal to $e^{-\frac{E_1 - E_2}{k_B T}}$ ok.

So, now you can say number of configurations with the defect divided by number of configurations without the defect. So, number of configurations without the defect is N minus N_d ok. This is equal to $e^{-\frac{E_d}{k_B T}}$ now the difference in energy of a configuration with a defect and without the defect is just E_d . And so, basically this is a factor that tells you how the number of defects changes with temperature that means, at very low temperatures when temperature is very small, then $e^{-\frac{E_d}{k_B T}}$ will be very large. So, you have $e^{-\frac{E_d}{k_B T}}$ a very large number and it will be very small.

When temperature is very large, $e^{-\frac{E_d}{k_B T}}$ this will go to 0. So, this will go to 1, so, the number of defects will be large. In fact, we usually work. So, usually N_d is much much less than N ok. So, the defects are very few ok. They are usually in parts per million or even smaller parts per billion and so, because N_d is much less than N , you can just write this as N_d by N ok. This $N - N_d$, I just replace it by N that is very close to N ok. So, this is equal to $e^{-\frac{E_d}{k_B T}}$ ok.

So, the fractional population of defects is proportional to $e^{-\frac{E_d}{k_B T}}$ ok. So, this Boltzmann factor actually relates the defect formation energy to the defect concentrations and notice that this way we so, we did not we did not explicitly use entropy. So, did not explicitly use entropy use entropy and in fact, the fact that we are using the Boltzmann distribution automatically implies that we that we are using entropy, but we did not have to go through that entropy calculation that we did in the other case. So, we could just use a defect formation energy and use temperature to estimate the fraction of defects ok.

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So, now let me use this for one particular for two particular examples. We use it for the Schottky defect and the Frenkel defect ok. Now you should keep in mind that each of these defects ok, have slightly different origin ok. And in a Schottky defect, so let us take then heads first take the example of a Schottky defect ok. So, if you take the short key defect and let us take an example in NaCl. So, then what would happen is that a sodium atom at a crystal site and a chlorine atom also at a crystals site will have to leave their crystal sites and go to the surface ok. So, one sodium and one Cl atom leaves its site, leaves their sites in the leave one Cl once here leave their sites and move to the surface sites; I will just say surface sites ok.

So, this corresponds to 1 Schottky defect ok. So, 1 Schottky defect, so, this corresponds to 1 Schottky defect. So, 1 Schottky defect corresponds to 1 sodium defect and 1 chloride to defect ok. So, now if you look at this in the following way you look at this as a sodium at the lattice site plus a chloride at the lattice site ok. So, I will just say crystal ok. So, this is sodium and chloride at their proper crystal sites and these are going to sodium plus at the surface and chloride minus at the surface ok.

So, this is what is happening and then, you form those two defects all right and if you look at this; if you look at this as an as an equilibrium reaction ok, then the equilibrium constant K; K is given by number of sodium at the surface which is the number of vacancies ok. So, number of defects number of chloride at the surface which is it is also

the number of defects divided by number of sodium plus at crystal site which is just which is just $N - N_d$ and $N - N_d$ is a number of chlorides at the at their crystal sites ok.

So, the equilibrium constant can be written in this way and again, if we assume that N_d is less than 1 less and N_d is much smaller than N this is approximately N_d by N square. And you can use the relation that. So, what this will eventually lead to I mean if you can work you can work this out in the following way, you can write that ΔG is equal to $-\ln K$ and you can use this to write N_d by N is equal to $e^{-\frac{\Delta H}{2RT}}$ plus $e^{-\frac{\Delta S}{2R}}$ ok.

So, all I did was I wrote I just inverted this relation, I wrote I replace K by N_d by N square and I took; and I took $R T$ to the bottom here, I took this factor of a. So, we see that there is a factor of two that comes with the ΔH in the case of Schottky defect and again, you can do for the Frenkel defect and also calculate the same ok. So, you can do the same for the Frenkel defects. Again, in this case; in this case you will get; you will get exactly the same factor, but in this case you have a let me take the case of AgCl . So, you have an Ag which is in the lattice in the crystal site and you have a vacancy in the interstitial site ok.

So, this is a vacancy or a vacancy interstitial site and this is going to; this is going to Ag in the interstitial site and vacant Ag site ok. So, this so there is an Ag site that is empty ok. This is another vacancy in the Ag side and again you can do the same analysis ok. I will not go into this detail ok, but again you will get that number of defects divided by total number of sites is proportional to $e^{-\frac{\Delta H}{2RT}}$ ok.

So, there is a factor of two that appears with the ΔH and the constant is this entropy with the constant of proportionality is this entropy factor ok. So, with this, I will conclude this lecture and you can actually use thermodynamics very effectively to calculate the fraction of defects and we will see this in some exercise exercises.

So, in the last lecture I will summarize what we learnt in the 7th week and do some practice problems.

Thank you.