Defects in Crystalline Solids (Part-I)
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Lecture - 03
Energy of Vacancy Formation

So, last lecture we were looking at formation energy of vacancies, we are looking at the simplest of point defects which is a mono vacancy. So, we looked at their energy delta free energy difference and also at the entropy, configurational entropy which arises, because of mixing. Now, like I said in the last lecture that today I will show how we get the equilibrium concentration ok.

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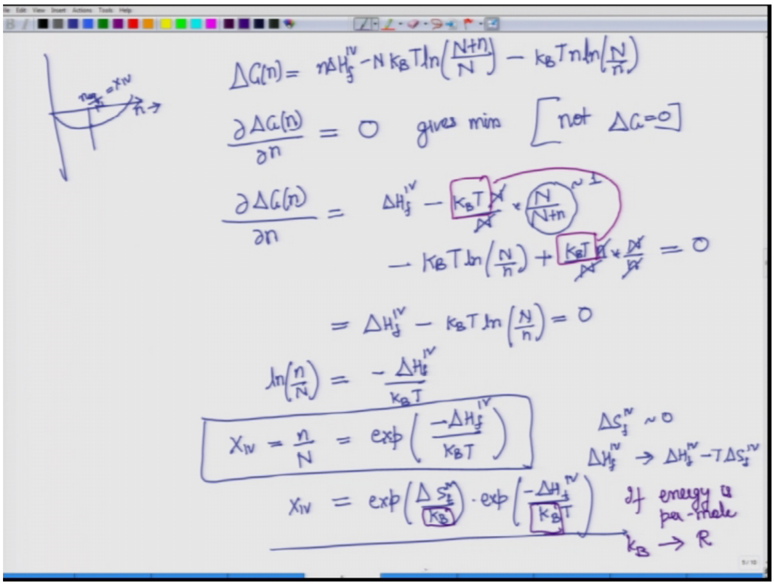

$$\Delta G(n) = n\Delta H_f^{1V} - N k_B T \ln\left(\frac{N+n}{N}\right) - k_B T n \ln\left(\frac{N}{n}\right)$$

$$\frac{\partial \Delta G(n)}{\partial n} = 0 \quad \text{gives min} \quad [\text{not } \Delta G = 0]$$

$$\frac{\partial \Delta G(n)}{\partial n} = \Delta H_f^{1V} - \boxed{k_B T}\,\cancel{N} \times \frac{N}{N+n} - k_B T \ln\left(\frac{N}{n}\right) + \boxed{k_B T}\,\cancel{n} \times \frac{\cancel{N}}{\cancel{N}} = 0$$

$$= \Delta H_f^{1V} - k_B T \ln\left(\frac{N}{n}\right) = 0$$

$$\ln\left(\frac{n}{N}\right) = -\frac{\Delta H_f^{1V}}{k_B T}$$

$$\boxed{X_{1V} = \frac{n}{N} = \exp\left(\frac{-\Delta H_f^{1V}}{k_B T}\right)}$$

$\Delta S_f^{1V} \sim 0$

$\Delta H_f^{1V} \rightarrow \Delta H_f^{1V} - T\Delta S_f^{1V}$

$$X_{1V} = \exp\left(\frac{\Delta S_f^{1V}}{\boxed{k_B}}\right) \cdot \exp\left(\frac{-\Delta H_f^{1V}}{\boxed{k_B} T}\right)$$

If energy is per-mole $k_B \rightarrow R$

So, we had the equation if you remember delta G where n is the number of vacancies equal to n H del that is delta H formation for one vacancy minus KB T this is the longer version of the equation. I am not using the simplified form of entropy equation, I am using the full form that we obtained, yes in the previous lecture and so there is still another term KB T and there is n over here and there is a N over here ok.

So, to find equilibrium concentration, what if you remember how does this plot go the delta G, we will come back to it later, but it is something like this. So, we want to find the minima this is the delta G this is the point where we have equal to n equilibrium of vacancies which we will which will wind when we divide by n would become equal to X 1v our equilibrium concentration. So, this is the point that we are looking at the minima. So, and this X axis is actually n increasing number of vacancies.

So, what we need to find to find the minima is simply take a differentiation of this with respect to n and the point, where we get 0 is the point which gives minima, it is not let me reiterate, it is not delta G equal to 0, but the differential of this delta G with respect to n that will that when gives 0 will lead the final value of equilibrium concentration.

So, now differentiate the earlier equation to get this what we get is something like this. So, if we differentiate this equation over here this becomes delta. This is simply, sorry minus T N and since this is N over here this will be we will get a factor over here f a 1 by n and it is 1 over if you take the derivative of log some ln something that it becomes one over that. So, this becomes N by N plus n minus now let us go to the third term which is minus KB T. So, there is two n is at two places on the outside and the in inside. So, we will have to do it by parts.

So, first let us do the exterior part. So, this becomes ln N by n now for the log part this remains minus, but then we can take n in the smaller n in the numerator therefore, it becomes plus which is denoted here. So, it becomes KB the free factor is KBTn and the factor in the that has to be differentiate has 1 by n. So, it comes over here and then it is just inverse of this. So, ln X is 1 over X. So, that is what we are doing and this has to be equated to 0.

So, now what are the terms that cancel out, this cancel out, this cancels out and this is KB now over here if you look this term is approximately equal to 1 these two cancel out. So, again if you look at this term and this term they will also cancel out ok.

So, what we are left with is this delta H f 1v which is the enthalpy of formation of one vacancy minus KB T ln N by n equal to 0, therefore, from this what you will obtain is ln n by N equal to minus delta Hf 1v by KBT this is just rearranging and from here we have X 1v which is our equilibrium concentration we are denoting it by this which is nothing, but n by N we could have used a subscript e eq as it is in many places, but for now we will just let it be like this just keep in mind that what we have derived here is the equilibrium concentration. So, this becomes delta Hf 1v by KBT.

Now, remember this is using some approximation what was the approximation like I said even in the previous class towards the end that we had used delta S formation 1v approximately equal to 0, if not then what we will have to do is replace delta Hf 1v with delta Hf 1v minus T delta S f 1v. So, if you do that then the more accurate form of this equation would become.

So, if we if you put it over here minus this is this is an exponential we can just multiply it the two terms. So, the first term will have minus and minus. So, it becomes plus and it has T over here and in the denominator. So, it becomes independent of t and it becomes delta Sf by KB times exp the same term that is here. So, this is also 1v sometime I may miss it, but please keep in mind what terms are being taken forward.

So, this is the expanded form of equilibrium concentration and remember this derivation because in the next few cases when we will discuss this what we will be doing is we will show what is the energy of formation and in some cases just show what will be how it the entropy energy will change, but once we have those values we will directly insert it over here to get the final form of the equation. We need not go through all the derivation that we have shown you over here.

Another thing that you should note here is that this we are using here as KB let me, now let us say if I were using delta Hf which is energy instead of per atom as per mole. So, if the energy if energy is per mole basis then what happens to KB you convert KB to R which is the gas constant. So, K because why because we know that KB into n a which is Avogadro number is equal to R gas constant. So, this will this KB and this KB will convert to R and energy is given per mole. So, that is something that you should keep in mind. Now, another aspect that I want to go through is, now to begin with let me draw this what.

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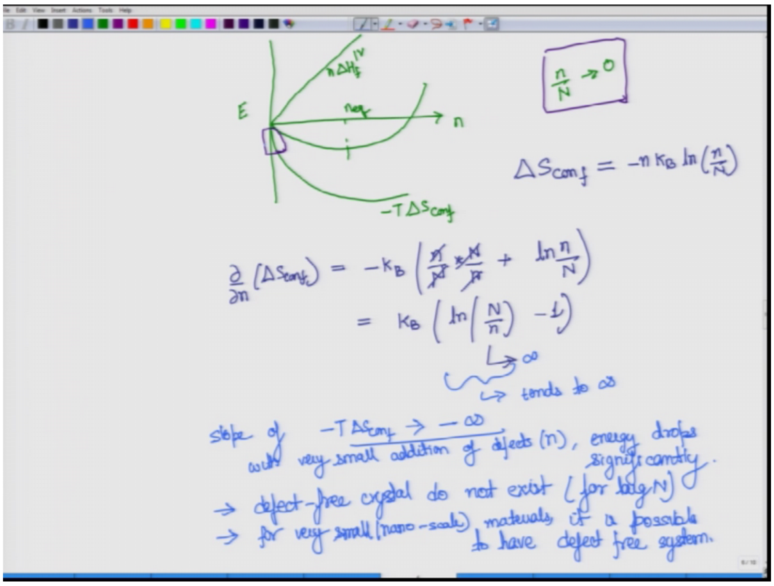

$$\frac{n}{N} \to 0$$

$$\Delta S_{conf} = -n k_B \ln\left(\frac{n}{N}\right)$$

$$\frac{\partial}{\partial n}(\Delta S_{conf}) = -k_B\left(\frac{\cancel{n}}{\cancel{N}} \times \frac{\cancel{N}}{\cancel{n}} + \ln\frac{n}{N}\right)$$

$$= k_B\left(\underbrace{\ln\left(\frac{N}{n}\right)}_{\to\infty} - 1\right)$$

↳ tends to ∞

slope of $\underline{-T\Delta S_{conf} \to -\infty}$ with very small addition of defects (n), energy drops significantly.

→ defect-free crystal do not exist (for big N)

→ for very small (nano-scale) materials it is possible to have defect free system.

I have been what I had drew even the even in the previous lecture. So, this is some form of energy and here you have n delta H f 1v ok. So, depending and this is n. So, this slope is equal to delta H 1v and this is the total enthalpy because of formation of n number of vacancies and there is an entropy term that we remember ok.

Let me be more accurate that we will what I know beforehand what you will see in some time is this is minus T delta S configurational ok, this is not the formation entropy this is the configurational entropy that we have to keep in mind the difference between the two and the sum of these two would lead to our energy the delta G. So, somewhere over here is what we have is the n equilibrium this is where what we calculated in the previous equation.

Now, what I want to show here is what will happen when n by N tends to 0 or what we are talking about is what will happen to what happens to entropy over here what how is the slope in this particular region where n by N tends to 0. So, again we want to find the slope what we need to do is differentiate this delta S configuration with respect to n.

So, let us do that and see what happens when we have n by N tending to 0. So, let us go the usual way del by del n delta S configurational and we will. So, what was the delta S equal to we will use the simpler equation here without loss of generality, you can always go back and use the extended version I have shown you one equation which was differentiated delta G with using the extended form of delta S.

Now, here I am using the condensed version to show you this will ensure that both of times you can you will be able to do the same thing ok. So, this becomes n KB ln n by N, now what we have to do is differentiate. So, simply again there are n at two places. So, we have to do it by parts n by N into N by n plus ln and. So, these two get cancelled and what we are left with is KB, now when N by n tends to 0 what happens to uppercase N by small case n this quantity tends to this quantity tends to infinity.

Now, when this quantity tends to infinity this quantity overall which is the log of N by n this also tends to infinity, which would mean that this slope which is equal to minus T delta S slope of this particular quantity minus delta S configuration tends to minus infinity ok. So, it is very close to infinity, but in the with a negative value, this means that with a very small amount of increase in N by n or with a very small amount of increase in the vacancy the entropy would change very drastically or entropy that minus T delta S term will reduce the energy drastically.

So, let me write this with very small addition of defects which is vacancies energy drops significantly ok. So, what does this imply what as the what is the big implication of this, the implication of this is that if you add or in other words not add it is very difficult to find a defect free crystal; defect free crystals do not exist this is the implication this is what it is what it implies.

Particularly this is, particularly true when we are talking about for large N meaning the total number of lattice site is large because that is where N by n tends to infinity and that is where this slope becomes minus infinity. So, this is this is one important implication and a corollary of this is now you have seen that I have written large for very large N the corollary for this is that if you have a very small crystal ok. So, like whiskers or nano fibers then N is for small very small nano scale materials it is possible to have defect free system ok.

So, the first implication and the second one are kind of inverse of each other, but they are coming from the same equation or the same thing that we derived that when your n by N which is small n by is uppercase N this tends to 0 that is this the small region over here over there we saw that the entropy changes drastically which means that the minus T delta S which is there another component of Gibbs free energy that drops very drastically. And when that drops what it implies is that your energy is changes drastically meaning that even a small amount of addition of defect will reduce to reduction energy. So, the system or the component will have a tendency to absorb these defects.

And therefore, I have written defect free crystals do not exist and now this when we when I derived this we had assumed that small n by uppercase N is ten into 0 or in other words uppercase N is a very large number. So, the other corollary from this is that when this is not true that is the uppercase N is not very large then which is for very small nano scale materials it is possible to have defect free system.

For example our whiskers and nano crystals and that is where their special properties originate from now since they are defect free if you remember I told you that if your copper was defect free it did not have dislocations even dislocations this is not dislocation we are talking about, but let us say it is a dislocation free copper then with the strength would be 100 times higher than what we usually get. So, that is possible only when we are talking about nano scale. So, this is a very big implication and this also let us to know why there is so, much of work going on at nano length scale because you get some superior properties most of the time superior properties ok.

So, let us move on to an example problem, now that we have seen the equilibrium concentration how it is related to temperature let me ask you what. So, the question problem question would be something like that at what temperature does 1 vacancy per mole becomes stable in copper?

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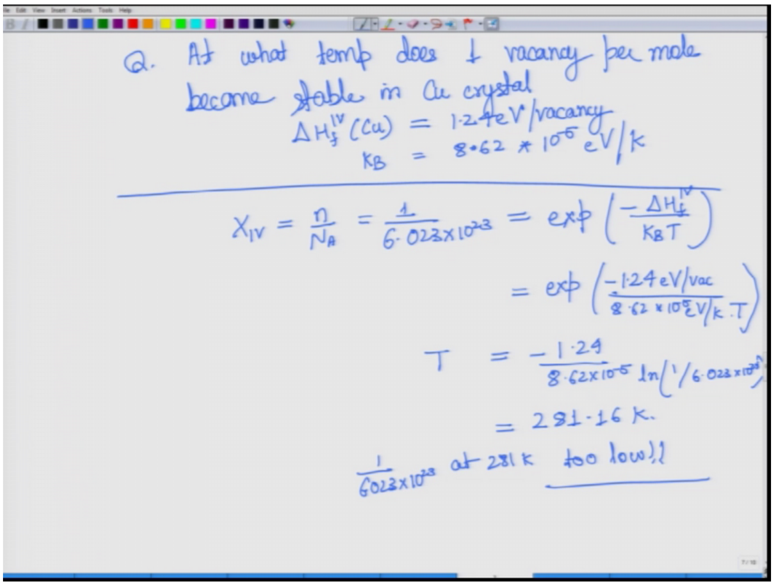

Q. At what temp does 1 vacancy per mole become stable in Cu crystal

$\Delta H_f^{1V}(Cu) = 1.24 eV/vacancy$

$K_B = 8.62 * 10^{-5} eV/K$

$$X_{1V} = \frac{n}{N_A} = \frac{1}{6.023\times10^{23}} = \exp\left(\frac{-\Delta H_f^{1V}}{K_B T}\right)$$

$$= \exp\left(\frac{-1.24 eV/vac}{8.62\times10^{-5} eV/K \cdot T}\right)$$

$$T = \frac{-1.24}{8.62\times10^{-5} \ln\left(1/6.023\times10^{23}\right)}$$

$$= 281.16 K.$$

$\frac{1}{6.023\times10^{23}}$ at 281 K too low!!

This is a question that I have taken from Prof Anandh Subramanyam sir lecture notes if you can access those from you can access those from it IIT website it is a very good collection of slides and it will be useful for you for this course also. So, what is given here it is given that delta H formation 1v for copper is equal to 1.24 electron volt per vacancy and KB is known to be 8.62 into 10 to the power minus electron volt per Kelvin. So, this is the problem statement how do we go about solving it ok. So, what we know we you know that this is talking about a equilibrium concentration and what temperature does one vacancy per mole become stable. So, thermodynamically stable. So, it is the equilibrium concentration what is the equation for equilibrium concentration, you remember it was X 1v is equal to n by N A why we are taking N A because we are talking about 1 vacancy in per mole.

So, n is equal to 1 NA is the Avogadro number and therefore, this becomes 1 over 6.023 into 10 to the power 23 and on the rhs right hand side what we have is minus delta H formation 1 vacancy by KBT, delta H formation is given in electron volt per vacancy. So, we need not convert the KB to R well let it be like this and therefore, this becomes. So, T is the unknown here d everything else is known except T.

So, you can very easily convert or transform this equation to this form and when you solve this you would see that this value comes out to be 281.16 Kelvin so, a little above room temperature. So, a little sorry not room temperature a little above 0 degree Celsius 273 is the 0 degree Celsius. So, it is just 8 degrees above that. So, around 8 degree Celsius it is saying that given this delta Hf you will have this vacancy concentration. So, that tells you how to solve it that is very well and good, but you should also note that this value does it sound right to you that at 8 degree Celsius you will have only 1 vacancy per mole there it does not I would I would think that this is a very low value this sounds. So, this is a little too low.

Now, what are what could be the possible reasons for it there may be several reasons it is to begin with the delta Hf value that is given here it may be a little on the higher side it is possible that at what you observe is not really the equilibrium concentration because we are talking about a very low temperature where mobility becomes very small. So, what you are, what you observe is not equal to what we have been given here and the there are possible several possible reasons for it. So, some of the reasons I discussed here and some of those I will leave up to you to think about it. So, now let us go to another aspect of our problem of our topic and this aspect is what is the energy of vacancy formation?

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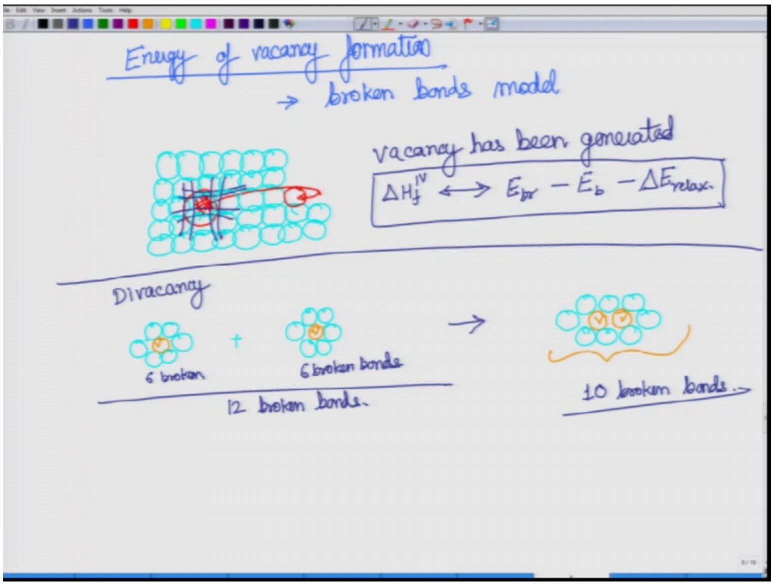

Energy of vacancy formation

→ broken bonds model

vacancy has been generated

$$\boxed{\Delta H_f^{1v} \longleftrightarrow E_{br} - E_b - \Delta E_{relax.}}$$

Divacancy

How do we usually estimate what is the amount of energy that is required for formation of vacancy formation energy, one of the simplest models is based on what is called as broken bonds; broken bonds model what does it do let us say we have. So, let us say these are the atoms in a original lattice where there is there were not effect and it need not always be a perfect flat system there would always be some atomic level hills and valleys. So, that is why I have drawn something like this. Now, let say I take one atom from here like this atom and move it over this place. So, this atom comes to this place and this place becomes vacant. So, this is a method of formation of vacancy and the you can say conceptual generation of vacancy. So, vacancy has been generated.

Now, what are the change in the energy because of this the delta Hf 1v can be related to the energy of broken bonds. So, what is the energy that you need one the number of bonds that you have breaking here. So, that is the total number of total amount of energy that was required, but at the same time when it goes to the surface because we are not reducing the number of atoms we cannot reduce the number of atom. So, the this is when it goes to the surface it will form some bonds over there. So, there will be energy bonding now this is that difference in the broke number of broken bonds when the atom was at this site to the number of broke bonds that has over here.

Apart from this there is also a relaxation term now when we are talking about a vacancy over here it will not stay there, atoms around it will not stay tight at its own place, there will be some relaxation like this. So, the atoms would move from the position a little bit and this relieves the energy somewhat and because of this there will also be some decrease in the energy which can be termed as E relaxation. So, this delta Hf which is the formation of 1 vacancy this can be obtained from this broken bond model by obtaining the broke number of broken energy because of broken bonds minus the energy that have minus the energy released because of the bonding at the surface minus energy released because of relaxation.

Now, using this concept what we will show is that your mono vacancies can actually merge to form dye vacancies. So, let us look at it a simple again the broken bond model how does it predict that mono vacancies should merge to form dye vacancies. So, let us say there says again and let us say there is. So, let me draw the vacancy at the end with a different colour. So, let us say there is a vacancy here let us say there is a vacancy over here. Now, in this simple model this 1 vacancy how many broken bonds do you see over here 1, 2, 3, 4, 5, 6, and we are talking about a 2 D plane ok. So, there is 6 broken bonds over here 6 broken bonds over here. So now, this is some amount of broken bonds over here some amount of broken bonds here, but what will happen what kind of structure do you see when both these vacancies combine.

So, let us say now bring the 2 bonds are the 2 vacancies together. So, it will look something like this the exact amount of difference in energy etcetera would depend on the crystal structure which orientation we are talking about, sorry not the orientation, just the crystal structure, but this is a simple model to explain the concept.

So, here there are 6 broken bonds plus 6 broken bonds which leads to how many 12 broken bonds, over here we have how many 1, 2, 3, 4, 5, 6, 7, 8. So, there are 8 plus there are bonds broken in between these two which is 9 plus 1, 10. So, there are 10 broken bonds at this site. So, there is a large amount of difference here ok. So, like I said that there are 12 broken bonds here and 10 broken bonds and how does this lead to the concentration difference between dye vacancy and mono vacancy we will discuss in the next lecture.

Thank you.