Diffusion in Multicomponent Solids
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Lecture 28
Energetics of Vacancy Formation

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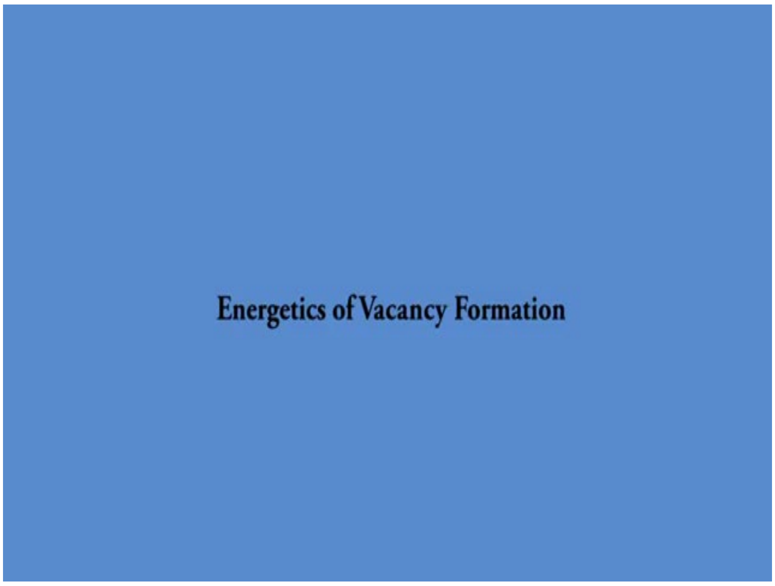

Energetics of Vacancy Formation

Welcome to the 7th week of the open course on Diffusion in Multicomponent Solids. This is 28th lecture in the series. In this lecture, I have talked about energetics of formation of vacancies and divacancies. Although, I have not talked about other point defects such as interstitials and impurity atoms, similar treatment can be extended to the other point defects too. Point defects play important role in governing the phenomenon of diffusion. Vacancy is probably the most important point defect in the study of diffusion, because it acts as a vehicle for diffusion. Vacancies mediate the atomic jumps and hence guide the diffusion.

In this class, we will discuss the energetics of vacancy formation. Similar treatment can be applied to other point defects including interstitials and impurity atoms. To start with, what is a vacancy?

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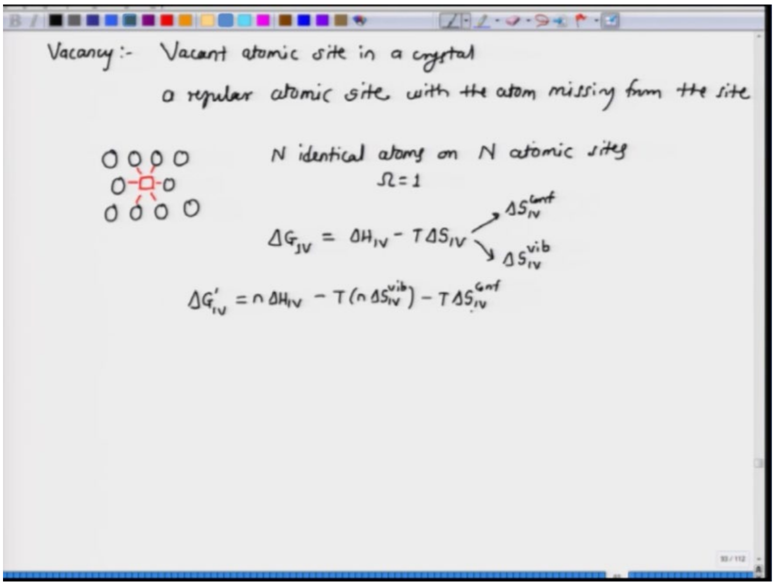

Vacancy :- Vacant atomic site in a crystal

a regular atomic site with the atom missing from the site

N identical atoms on N atomic sites

$\Omega = 1$

$$\begin{tikzcd} & \Delta S_{1V}^{conf} \\ \Delta G_{1V} = \Delta H_{1V} - T\Delta S_{1V} \arrow[ur] \arrow[dr] & \\ & \Delta S_{1V}^{vib} \end{tikzcd}$$

$$\Delta G'_{1V} = n\,\Delta H_{1V} - T(n\,\Delta S_{1V}^{vib}) - T\Delta S_{1V}^{conf}$$

A vacancy is just a vacant atomic site in a crystal or it is a regular atomic site with the atom missing from the site. Now it is easy to see that formation of a vacancy leads to increase in configurational entropy. For example, let us consider these two dimensional lattice in which atoms are arranged periodically. Now, if we have to arrange N identical atoms on N atomic sites, we know there is only one possible way because all the atoms are identical. Now, instead of N atoms, let us say you have to arrange $N - 1$ atoms and one vacancy on the N sites. Let us denote the vacancy by square. Now, obviously, there are N different ways in which the vacancy can be placed on N number of sites.

Formation of a vacancy leads to increase in configurational entropy and because of the entropic reason vacancy is a stable point defect. Now, there is an increase in entropy, but at the same time to form a vacancy, the atomic bonds have to be broken. That means, there is also an increase in enthalpy. There has to be certain equilibrium concentration of vacancies at any given temperature and pressure. And this equilibrium concentration is achieved as a compromise between increase in entropy and increase in enthalpy because of the formation of the vacancies.

In general, if we denote the Gibbs free energy of formation of vacancy or more particularly a monovacancy (because we are considering only one vacancy at a time for now) we denote it aΔG_{1V}, $1V$ denotes the Gibbs free energy of formation of monovacancy. It can be given as:

$$\Delta G_{1V} = \Delta H_{1V} - T\Delta S_{1V}$$

Now, this ΔS_{1V}term includes two entropy terms. One is obviously, the configurational entropy, let us call it $\Delta {S_{1V}}^{conf}$ and the other one is the vibrational entropy. Let us call it delta $\Delta {S_{1V}}^{vib}$:

$$\Delta S_{1V} = \Delta {S_{1V}}^{conf} + \Delta {S_{1V}}^{vib}$$

Now we can understand the configurational entropy. About the vibrational entropy, since the atom is missing from the vacancy site, the neighbouring atoms experience change in the mode of vibrations and it leads to a positive change in vibrational entropy. In general, if there are n vacancies on the lattice we can write $\Delta G'_{IV}$. The prime denotes the total change in Gibbs free energy due to formation of n vacancies. It can be written as:

$$\Delta G'_{1V} = n\Delta H_{1V} - T\left(n\Delta {S_{1V}}^{vib}\right) - T\Delta {S_{1V}}^{conf}$$

Now it is easy to see that the enthalpy change per vacancy and the vibrational entropy change per vacancy are independent of the number of vacancies. For n vacancies we multiply by number n, but the quantity $\Delta {S_{1V}}^{conf}$ depends on the number of vacancies. So, we need to express this $\Delta {S_{1V}}^{conf}$ in terms of the number of vacancies, n.

How do we go about finding the equilibrium vacancy concentration? We need to carefully create the vacancy thermodynamically in order to study the energetics of it. When I create the vacancy thermodynamically, it has to be a reversible process and the mass has to be conserved.

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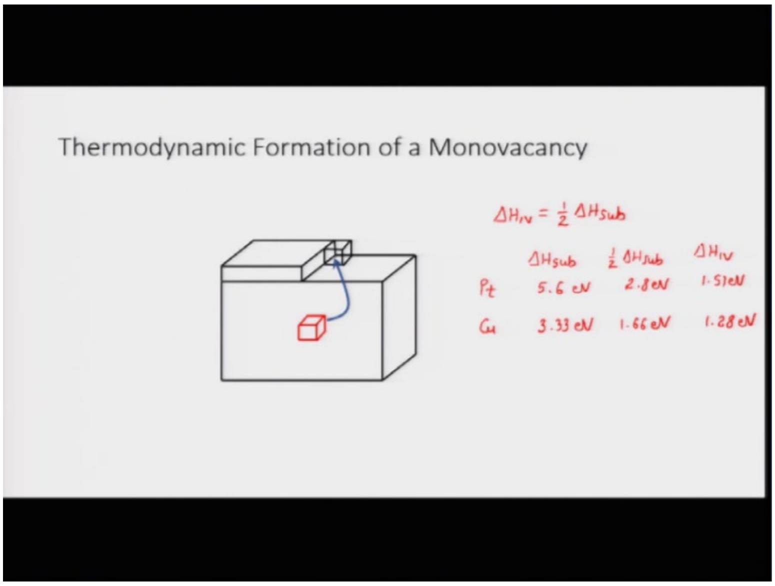

Thermodynamic Formation of a Monovacancy

$$\Delta H_{1V} = \frac{1}{2}\Delta H_{sub}$$

	ΔH_{sub}	$\frac{1}{2}\Delta H_{sub}$	ΔH_{1V}
Pt	5.6 eV	2.8 eV	1.51 eV
Cu	3.33 eV	1.66 eV	1.28 eV

What we do in order to create a vacancy is: Let us consider this crystal and each atom is denoted by this cubic box here. We have to remove one atom from the interior and we cannot just let it evaporate, because then there will be loss of mass. what we do? We place it back on the surface. Now when we place it back on the surface, the number of open bonds on the surface should not change. So, the ideal location for placing the atom back onto the surface is at a surface step edge like the one shown here. If you place this atom back on the surface at a surface step edge, we can see it will conserve the number of open bonds on the surface.

Here, we are conserving mass as well as number of open bonds on the surface. This is how we should create the vacancy in order to study its energetic. To create the vacancy, we are removing one atom from the interior, which means we are breaking Z number of bonds. Z here is the coordination number. And when we place it back on the surface, roughly half of the bonds are recovered.

So, it seems that the enthalpy of vacancy formation should be about half of the enthalpy of sublimation.

$$\Delta H_{1V} = \frac{1}{2}\Delta H_{Sub}$$

However, this is not true. Let us consider a couple of example:

	ΔH_{Sub}	$\frac{1}{2}\Delta H_{Sub}$	ΔH_{IV}
Pt	$5.6\ eV$	$2.8\ eV$	$1.51\ eV$
Cu	$5.33\ eV$	$1.66\ eV$	$1.28\ eV$

First one is platinum, ΔH_{Sub} for platinum is about 5.6 electron volt $\frac{1}{2}\Delta H_{Sub}$ is about 2.8 electron volt but experimentally determined value for ΔH_{IV}, enthalpy of formation of a monovacancy for platinum is 1.51 electron volts. Similarly values are also given for Copper. So, we can see that $\Delta H_{IV} < \frac{1}{2}\Delta H_{Sub}$. And the reason is, when we form a vacancy, there is an electronic and elastic rearrangement that the crystal experiences in the region surrounding the vacant site. Now, when we remove an atom from its regular site, the adjacent atoms tend to fall into that vacant site. The effective volume of a vacant site is not same as the effective volume of an atom in an otherwise perfect crystal. Similarly, the electronic charge density changes because of the removal of an atom from the metal. There will be electronic rearrangement in order to maintain the charge neutrality and because of that the enthalpy of monovacancy formation is actually less than half the enthalpy of sublimation. Swalin has discussed a nice model for this.

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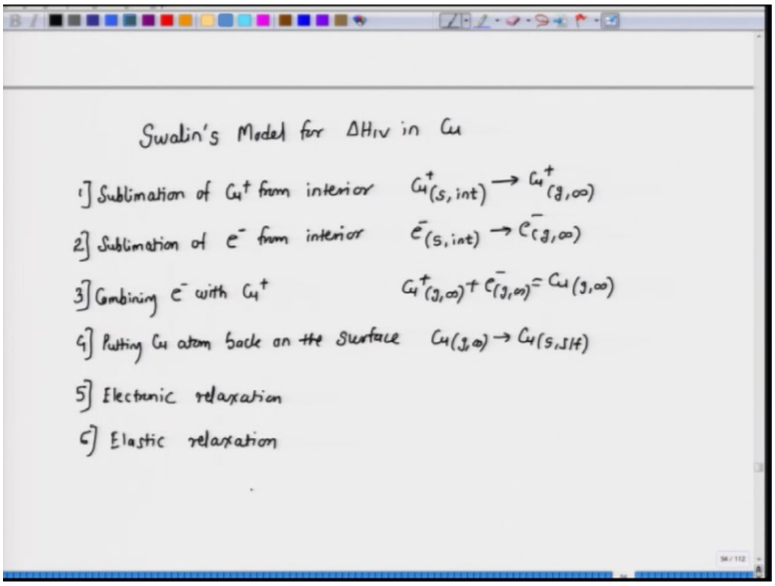


Swalin's Model for ΔH_{1V} in Cu

1] Sublimation of Cu^+ from interior $Cu^+_{(s,int)} \rightarrow Cu^+_{(g,\infty)}$

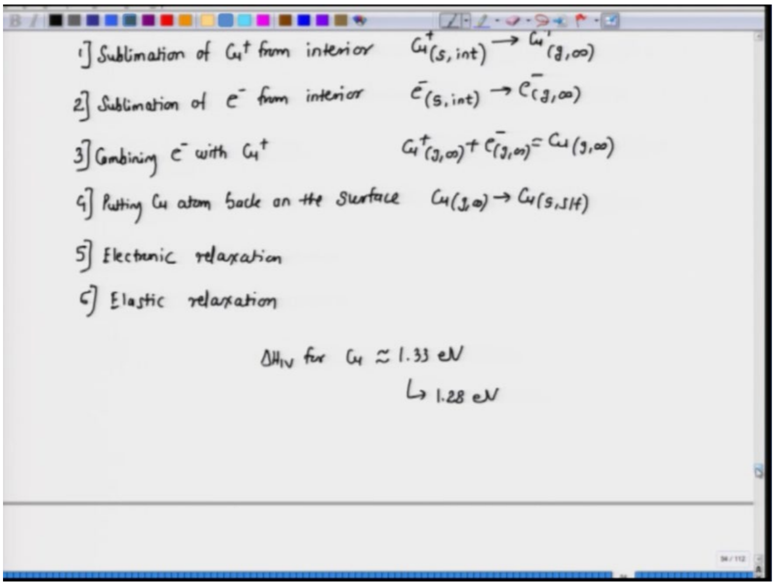
2] Sublimation of e^- from interior $e^-_{(s,int)} \rightarrow e^-_{(g,\infty)}$

3] Combining e^- with Cu^+ $Cu^+_{(g,\infty)} + e^-_{(g,\infty)} = Cu(g,\infty)$

4] Putting Cu atom back on the surface $Cu(g,\infty) \rightarrow Cu(s,SH)$

5] Electronic relaxation

6] Elastic relaxation



1] Sublimation of Cu^+ from interior $Cu^+_{(s,int)} \rightarrow Cu^+_{(g,\infty)}$

2] Sublimation of e^- from interior $e^-_{(s,int)} \rightarrow e^-_{(g,\infty)}$

3] Combining e^- with Cu^+ $Cu^+_{(g,\infty)} + e^-_{(g,\infty)} = Cu(g,\infty)$

4] Putting Cu atom back on the surface $Cu(g,\infty) \rightarrow Cu(s,SH)$

5] Electronic relaxation

6] Elastic relaxation

ΔH_{1V} for Cu $\simeq$ 1.33 eV

$\hookrightarrow$ 1.28 eV

He considered the monovacancy formation in copper and he split the process in 6 different steps. In a metal, metal ions are held together at their regular lattice positions by the cloud of electrons. The first step he considered was sublimation of one copper ion from the interior. He denoted this as Cu^+ from solid and the interior of the solid to Cu^+ in gas state to infinity:

$$Cu^+_{(S,int)} \rightarrow Cu^+_{(g,\infty)}$$

And once the copper ion is removed to maintain the charge neutrality, you need to remove one electron. So, the second step is sublimation of one electron from the interior. Electron from this interior of the solid to gaseous infinity:

$$e^-_{(S,int)} \rightarrow e^-_{(g,\infty)}$$

Then combining the electron with copper ion:

$$Cu^+_{(S,int)} + e^-_{(S,int)} \rightarrow Cu_{(g,\infty)}$$

Copper ion at infinity plus electron at infinity gives a copper atom at infinity. And then, putting that copper atom back on the surface. That is the copper at infinity is placed back on the solid surface:

$$Cu_{(g,\infty)} \rightarrow Cu_{(S,Sf)}$$

After this, a vacant site is created in the interior and there will be electronic relaxation as well as elastic relaxations. With these steps he estimated:

$$\varDelta H_{1V}\ for\ Cu \sim 1.33\ eV\ = 1.28\ eV$$

Where $1.28\ eV$ is the experimentally determined value. The gist is, once the vacancy is created, there will be electronic and elastic relaxations in the region around the vacant lattice site. Now, let us try to develop an expression for the equilibrium vacancy concentration in a metal.

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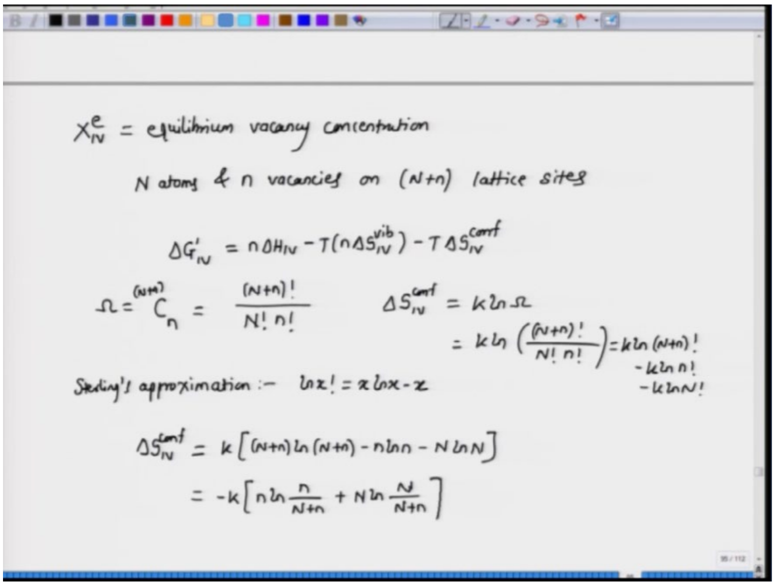


X^e_{1V} = equilibrium vacancy concentration

N atoms & n vacancies on (N+n) lattice sites

$$\Delta G'_{1V} = n\Delta H_{1V} - T(n\Delta S^{vib}_{1V}) - T\Delta S^{conf}_{1V}$$

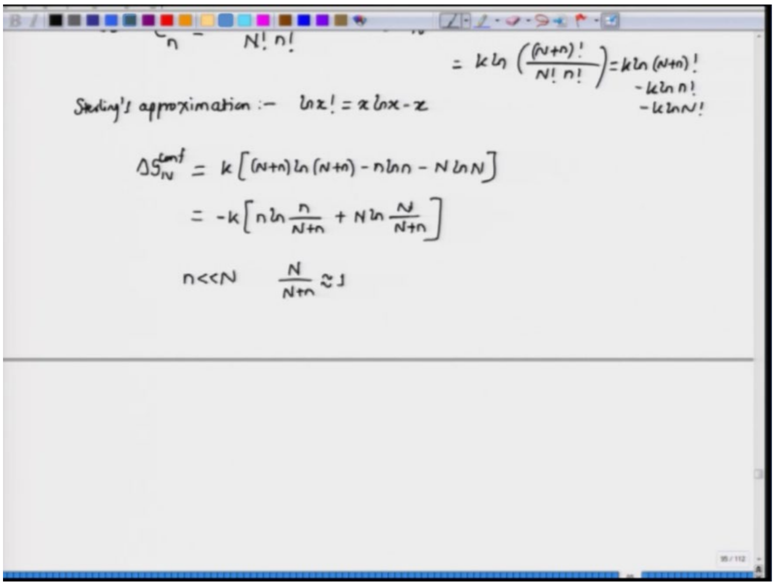
$$\Omega = {}^{(N+n)}C_n = \frac{(N+n)!}{N!\,n!} \qquad \Delta S^{conf}_{1V} = k\ln\Omega$$

$$= k\ln\left(\frac{(N+n)!}{N!\,n!}\right) = k\ln(N+n)! - k\ln n! - k\ln N!$$

Sterling's approximation :- $\ln x! = x\ln x - x$

$$\Delta S^{conf}_{1V} = k\left[(N+n)\ln(N+n) - n\ln n - N\ln N\right]$$

$$= -k\left[n\ln\frac{n}{N+n} + N\ln\frac{N}{N+n}\right]$$



$$C_n = \frac{}{N!\,n!}$$

$$= k\ln\left(\frac{(N+n)!}{N!\,n!}\right) = k\ln(N+n)! - k\ln n! - k\ln N!$$

Sterling's approximation :- $\ln x! = x\ln x - x$

$$\Delta S_{IV}^{conf} = k\left[(N+n)\ln(N+n) - n\ln n - N\ln N\right]$$

$$= -k\left[n\ln\frac{n}{N+n} + N\ln\frac{N}{N+n}\right]$$

$n << N \qquad \frac{N}{N+n} \simeq 1$

Let us denote it as X_{1V}^{e}. This denotes the equilibrium vacancy concentration. Let us consider there are N number of atoms and n number of vacancies on total of $N + n$ lattice sites. And the Gibbs free energy change because of formation of n vacancies, as we have seen earlier, would be:

$$\Delta G'_{1V} = n\Delta H_{1V} - T\left(n\Delta S_{1V}{}^{vib}\right) - T\Delta S_{1V}{}^{conf}$$

In order to get to the equilibrium number of vacancies, we need to differentiate with respect to n and where the derivative of $\Delta G'_{IV}$ with respect to n is zero that gives the equilibrium number of vacancies. Now, we first need to express this $\Delta S_{1V}{}^{conf}$ in terms of the number n and that is easy to do. We can consider this as a mixture of N number of atoms and n number of vacancies. And the number of ways, let us denote it by Ω in which N atoms and n vacancies can be arranged on $N + n$ number of sites would be:

$$\Omega = {}^{(N+n)}C_n$$

And this can be written as:

$$\Omega = {}^{(N+n)}C_n = \frac{(N+n)!}{N!\,n!}$$

We know the $\Delta S_{1V}{}^{conf}$ would be given by Boltzmann's equation:

$$\Delta S_{1V}{}^{conf} = kln\,\Omega$$

Which becomes:

$$\Delta {S_{1V}}^{conf} = k\ln\Omega \ = k\ln\left(\frac{(N+n)!}{N!\,n!}\right)$$

Now, if we use Sterling's approximation, which states that for large values of x:

$$\ln x! = x\ln x - x$$

Both the numbers N and small n are large numbers here. So, we can use Sterling's approximation. Before that if we simplify this further, this will be:

$$\Delta {S_{1V}}^{conf} = k\ln\Omega = kln\left(\frac{(N+n)!}{N!\,n!}\right) = kln(N+n)! - klnN! - klnn!$$

And if you apply Sterling's approximation to each of this logarithmic term we get

$$\Delta {S_{1V}}^{conf} = k[(N+n)ln(\,N+n) - nlnn - NlnN]$$

$$= -k\left[n\ln\frac{n}{N+n} + N\ln\frac{N}{N+n}\right]$$

Now both N and n are large numbers, but we should note that the n is typically much lesser than N. The number of vacancies in a crystal are typically much less than the number of atoms present in the crystal at any temperature:

$$n \ll N \quad so \quad \frac{N}{N+n} \sim 1$$

So, we can get rid of this second term here.

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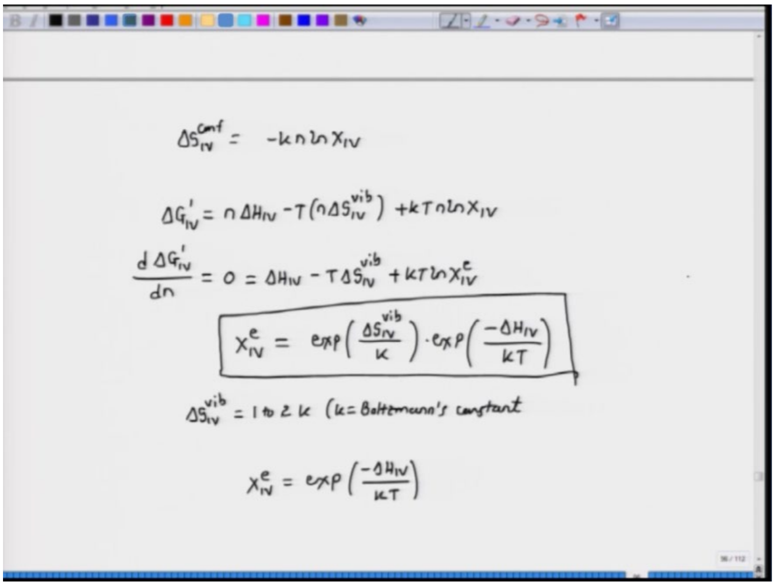


$$\Delta S_{1V}^{conf} = -kn\ln X_{1V}$$

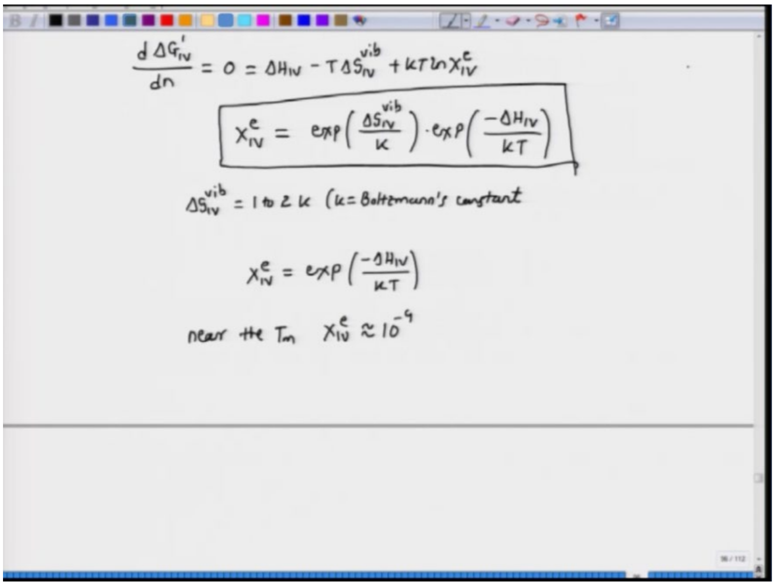
$$\Delta G_{1V}' = n\Delta H_{1V} - T(n\Delta S_{1V}^{vib}) + kTn\ln X_{1V}$$

$$\frac{d\Delta G_{1V}'}{dn} = 0 = \Delta H_{1V} - T\Delta S_{1V}^{vib} + kT\ln X_{1V}^{e}$$

$$\boxed{X_{1V}^{e} = exp\left(\frac{\Delta S_{1V}^{vib}}{k}\right)\cdot exp\left(\frac{-\Delta H_{1V}}{kT}\right)}$$

$\Delta S_{1V}^{vib} = 1$ to $2\,k$ (k = Boltzmann's constant

$$X_{1V}^{e} = exp\left(\frac{-\Delta H_{1V}}{kT}\right)$$



$$\frac{d\Delta G'_{1V}}{dn} = 0 = \Delta H_{1V} - T\Delta S_{1V}^{vib} + kT\ln X_{1V}^{e}$$

$$\boxed{X_{1V}^{e} = \exp\left(\frac{\Delta S_{1V}^{vib}}{k}\right)\cdot\exp\left(\frac{-\Delta H_{1V}}{kT}\right)}$$

$\Delta S_{1V}^{vib} = 1$ to $2\,k$ (k= Boltzmann's constant

$$X_{1V}^{e} = \exp\left(\frac{-\Delta H_{1V}}{kT}\right)$$

near the T_m $X_{1V}^{e} \approx 10^{-4}$

So, we will get $\Delta S_{1V}{}^{conf}$ equal to:

$$\Delta S_{1V}{}^{conf} = -k\left[n\ln\frac{n}{N+n}\right]$$

$$\Delta S_{1V}{}^{conf} = -k\, n\ln X_{1V}$$

The term $\frac{n}{N+n}$ is the site fraction of the vacancies given by X_{1V}. If you substitute back in our expression for $\Delta G'_{1V}$, we get:

$$\Delta G'_{1V} = n\Delta H_{1V} - T\left(n\Delta S_{1V}{}^{vib}\right) + kT\,n\,\ln X_{1V}$$

And to get to the equilibrium vacancy concentration, we differentiate $\Delta G'_{1V}$ with respect to n, which should be equal to 0 for equilibrium concentration:

$$\frac{d\Delta G'_{IV}}{dn} = 0 = \Delta H_{1V} - T\Delta S_{1V}{}^{vib} + kT\ln X_{1V}^{e}$$

We have denoted the equilibrium vacancy concentration more specifically as X_{1V}^{e}. And if we rearrange we get the equilibrium vacancy concentration X_{1V}^{e} to be equal to:

$$X_{1V}^{e} = exp\left(\frac{\Delta S_{1V}{}^{vib}}{k}\right).exp\left(\frac{-\Delta H_{1V}}{kT}\right)$$

This is the expression for equilibrium vacancy concentration in terms of the enthalpy of formation of a monovacancy and the vibrational entropy change due to formation of a monovacancy. Now, the first term $\Delta S_{1V}{}^{vib}$ is typically between 1 to 2 k, where k is the Boltzmann constant.

$$\Delta S_{1V}{}^{vib} = 1\ to\ 2\ k\ \ (k = Boltzmann's\ \ constant)$$

The factor $\left(\frac{\Delta S_{1V}{}^{vib}}{k}\right)$ will be typically between 2 to 5 and most of the time this is ignored. The main reason for this is that factor of 2 to 5 typically comes within the experimental errors. When we determine the vacancy concentrations experimentally, the experimentally errors involved are larger than this factor. So, typically you will see very often the first term is ignored and we write:

$$X_{1V}^{e} = exp\left(\frac{-\Delta H_{1V}}{kT}\right)$$

Obviously, when we write ΔH_{1V} in terms of Joule per atom, this constant in the denominator here is K. But if we express the enthalpy of vacancy formation in terms of joule per mole, this should be replaced appropriately by the gas constant R. We can see the equilibrium vacancy concentration increases exponentially with temperature and near the melting point:

$$near\ T_m \quad X_{1V}^{e} \sim 10^{-4}$$

If we consider one mole of the crystal, there are roughly 10^{23} atoms and there will be around 10^{19} vacancies present in the crystal at equilibrium near the melting temperature.

Now there can be multiple vacancies formed on adjacent lattice sites. These are referred to as vacancy clusters. If there are two adjacent vacancies it is denoted as divacancies, the three adjacent vacancies will form a trivacancy and on. Their concentration typically will be much smaller than the individual vacancies. However, the divacancies may become important. So, let us look into the energetics of divacancies.

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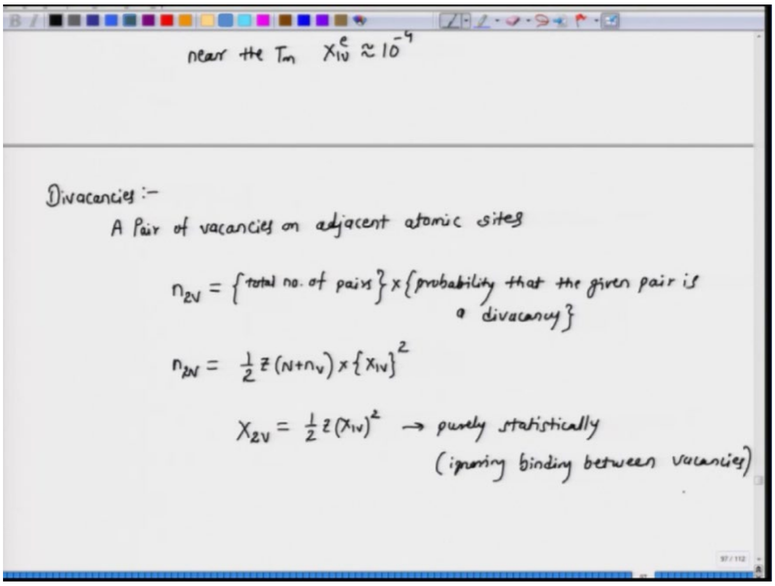


near the T_m $X_{1V}^e \approx 10^{-4}$

Divacancies :-

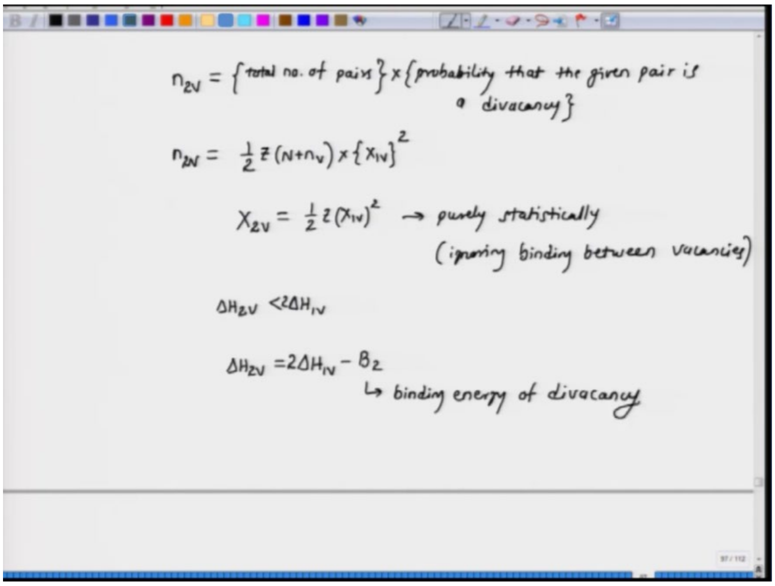
A Pair of vacancies on adjacent atomic sites

$n_{2V} = \{\text{total no. of pairs}\} \times \{\text{probability that the given pair is a divacancy}\}$

$n_{2V} = \frac{1}{2} z (N+n_V) \times \{X_{1V}\}^2$

$X_{2V} = \frac{1}{2} z (X_{1V})^2$ → purely statistically

(ignoring binding between vacancies)



$n_{2V} = \{\text{total no. of pairs}\} \times \{\text{probability that the given pair is a divacancy}\}$

$n_{2V} = \frac{1}{2} z (N+n_V) \times \{X_{1V}\}^2$

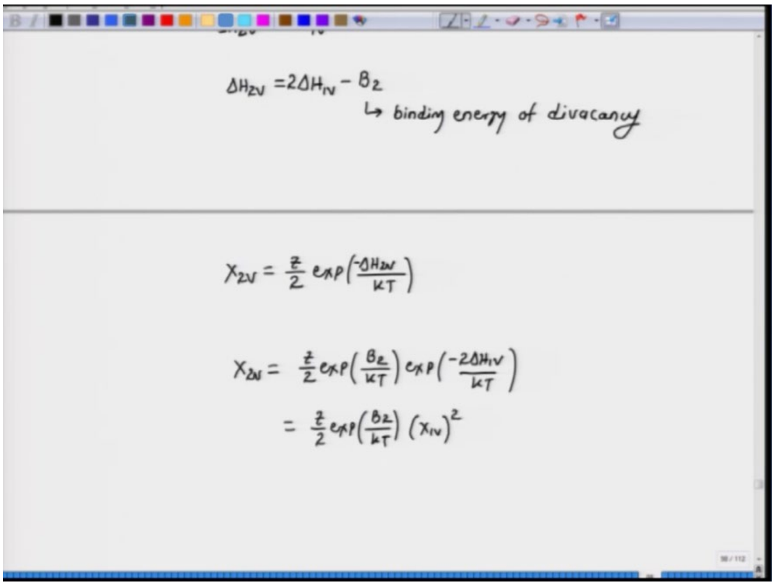
$X_{2V} = \frac{1}{2} z (X_{1V})^2$ → purely statistically

(ignoring binding between vacancies)

$\Delta H_{2V} < 2\Delta H_{1V}$

$\Delta H_{2V} = 2\Delta H_{1V} - B_2$

↳ binding energy of divacancy



$$\Delta H_{2V} = 2\Delta H_{1V} - B_2$$

$\hookrightarrow$ binding energy of divacancy

$$X_{2V} = \frac{Z}{2}\exp\left(\frac{-\Delta H_{2V}}{kT}\right)$$

$$X_{2V} = \frac{Z}{2}\exp\left(\frac{B_2}{kT}\right)\exp\left(-\frac{2\Delta H_{1V}}{kT}\right)$$

$$= \frac{Z}{2}\exp\left(\frac{B_2}{kT}\right)(X_{1V})^2$$

A divacancy is nothing but a pair of vacancies on adjacent atomic sites. If we consider through purely statistical point of view, that means, if we ignore the binding energy between two adjacent vacancies, then the number of divacancies can be given as:

$$n_{2V} = \{total\ no.of\ pairs\} \times \{probability\ that\ a\ given\ pair\ is\ a\ divacancy\}$$

First term here, the total number of pairs, can be given as number of bonds per atom times the total number of lattice sites, which in this case would be $(N + n_v)$. n_v is the number of individual vacancies. And since, we are counting each bond twice this way, we apply a factor of half. Now what is the probability that a given pair is a divacancy? That means, the first selected lattice site is a vacancy and also the next selected site is a vacancy. The probability that a given site is a vacancy is its concentration X_{1V}. So, this is simply ${X_{1V}}^2$. So we get:

$$n_{2V} = \frac{1}{2}Z(N + n_v) \times {X_{1V}}^2$$

And the fraction of divacancies is given as:

$$X_{2V} = \frac{1}{2}Z{X_{1V}}^2$$

This is purely statistical that is ignoring binding between vacancies. However, there will always be a binding energy associated with two adjacent vacancies. And it is easy to see why, because to form the first vacancy, Z number of bonds have to be broken, but to form a vacancy on an adjacent lattice site, we need to break one less bond. So, this is a simple reason.

Also, there will be other changes associated with the formation of second vacancies and there will be a binding energy associated with the formation of a second vacancy. Therefore, ΔH_{2V} that is the enthalpy of formation of a divacancy will always be:

$$\Delta H_{2V} < 2\Delta H_{1V}$$

The enthalpy of formation of a divacancy is not same as enthalpy of formation of two monovacancies. And ΔH_{2V} is typically given by:

$$\Delta H_{2V} = 2\Delta H_{1V} - B_2$$

Here B_2 indicates the binding energy of the divacancy. And X_{2V} is given by:

$$X_{2V} = \frac{Z}{2} exp\left(\frac{-\Delta H_{2V}}{kT}\right)$$

OR

$$X_{2V} = \frac{Z}{2} exp\left(\frac{B_2}{kT}\right) exp\left(\frac{-2\Delta H_{1V}}{kT}\right)$$

OR

$$X_{2V} = \frac{Z}{2} exp\left(\frac{B_2}{kT}\right) {X_{1V}}^2$$

Now the question arises, if the enthalpy of formation of second vacancy is less than that for the formation of an individual mono vacancy, then why is the second vacancy not forming always adjacent to an existing vacancy? The answer again lies in the compromise between enthalpy and entropy. Although the formation of second vacancy adjacent to an existing vacancy requires less enthalpy but by doing this, by putting the second vacancy adjacent to an existing vacancy, we are also reducing the number of possible configuration in which the second vacancy can exist. And it causes a reduction in entropy. That is why the second vacancy will not always exist as a neighbour to an existing vacancy. In fact, the number of divacancies at equilibrium are typically much less than the number of monovacancies. Let us look into an example that I have plotted for platinum.

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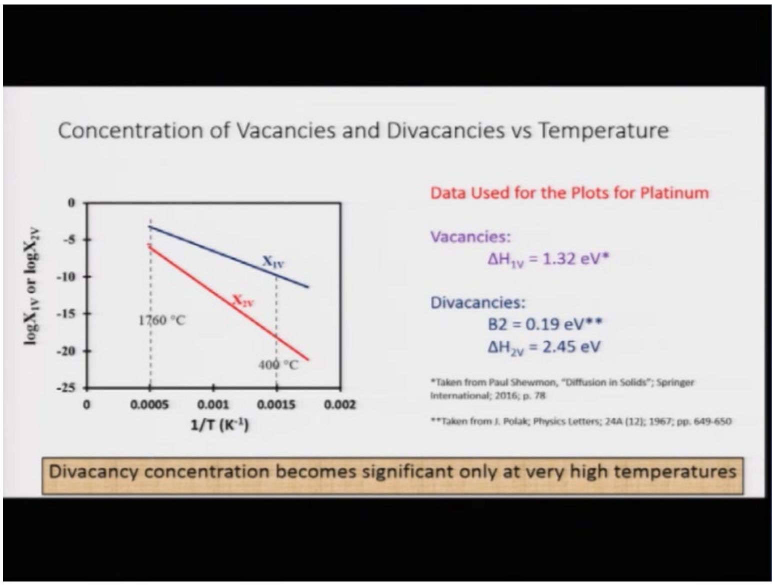

Concentration of Vacancies and Divacancies vs Temperature

Data Used for the Plots for Platinum

Vacancies:

$\Delta H_{1V} = 1.32$ eV*

Divacancies:

B2 = 0.19 eV**

$\Delta H_{2V} = 2.45$ eV

*Taken from Paul Shewmon, "Diffusion in Solids"; Springer International; 2016; p. 78

**Taken from J. Polak; Physics Letters; 24A (12); 1967; pp. 649-650

Divacancy concentration becomes significant only at very high temperatures

Here I have plotted the log of concentration of monovacancies and divacancies for platinum. Enthalpy parameters are for the platinum are:

$$\Delta H_{1V} = 1.32\ eV$$

and for divacancy, the binding energy is about:

$$B_2 = 0.19\ eV$$

Using:

$$\Delta H_{2V} = 2\Delta H_{1V} - B_2$$

We get:

$$\Delta H_{2V} = 2.45\ eV$$

Obviously, the magnitude of the slope of $\log X_{2V}$ versus $\frac{1}{T}$ should be larger than that for $\log X_{1V}$ versus $\frac{1}{T}$. We can see at smaller temperatures or at larger values of $\frac{1}{T}$, the difference between X_{1V} and X_{2V} is much large and the difference reduces as the temperature increases. If we consider two temperatures at 400 degree centigrade, the difference is about 9 order of magnitudes.

As we go to 1760, which is very close to the melting point of platinum the difference is about 3 orders of magnitude. The divacancy concentration becomes significant if at all only at very high temperatures close to the melting temperature. Typically at lower temperatures, the divacancies would not contribute much to the diffusion, although divacancies can diffuse very fast. But, these divacancies do play important role in quenched alloys. For example, the age-hardenable aluminium alloys during solutionizing are quenched from a very high temperature close to the melting temperature. Now at high temperature there is large fraction of divacancies and because of the quenching those fractions of divacancies are also retained at room temperature. It is generally not desirable that the ageing starts at room temperature, but because of these retained divacancies, and since the divacancies diffuse very fast, in many aluminium alloys the ageing will start at room temperature that is referred to as natural ageing and it is not desirable because the precipitates, which are formed during natural ageing do not give the best properties to the age hardened alloys.

The divacancies at normal temperatures are not considerable, they do not contribute much to the diffusion. But at higher temperatures their fraction may become significant. We can apply similar treatment to higher vacancy clusters like trivacancies and higher order clusters. As we increase the number of vacancies in a cluster, their contribution or their fraction would keep decreasing. It is only sufficient to consider monovacancies, which is very important and in some cases, the divacancies. Okay, that is all for this lecture. Thank you.