Basics of Materials Engineering
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Lecture – 13
Defects in Crystalline Materials – 1 (Equilibrium Concentration of Vacancies)

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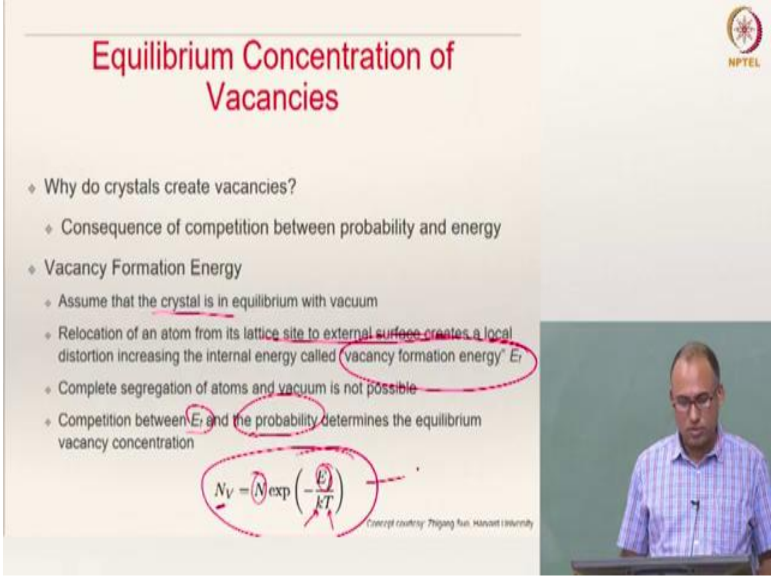

Equilibrium Concentration of Vacancies

- Why do crystals create vacancies?
  - Consequence of competition between probability and energy
- Vacancy Formation Energy
  - Assume that the crystal is in equilibrium with vacuum
  - Relocation of an atom from its lattice site to external surface creates a local distortion increasing the internal energy called "vacancy formation energy" E_f
  - Complete segregation of atoms and vacuum is not possible
  - Competition between E_f and the probability determines the equilibrium vacancy concentration

$$N_V = N \exp\left(-\frac{E_f}{kT}\right)$$

Concept courtesy: Zhigang Suo, Harvard University

While addressing this question, we will come across this concept of equilibrium concentration of vacancies or equilibrium number of vacancies in a crystal lattice. Why do crystals create vacancies? The creation of vacancies or point defects in crystals is due to the competition between the energy minimization and the probability. We will see what probability are we talking about. This competition is what creates the vacancies.

When you are creating a vacancy, there is an energy associated with this vacancy creation, which is called vacancy formation energy. For instance, let us assume that the given crystal for which we are actually trying to understand whether there are going to be any vacancies or not under equilibrium, is in equilibrium with vacuum. If you want to relocate an atom from one of its lattice sites from the bulk, what do you need to do? If you want to relocate, you need to break the bonds and then move the atom from the bulk to the surface, and hence there is an energy associated with that.

So, the relocation of atom from its lattice site to an external surface creates a local distortion in the crystal lattice, because suddenly this one atom is missing as you have broken the bonds, and these atoms find freedom to deform because there is no constraint here. As a result, the local movement of these atoms creates distortion in the crystal structure, and that is going to increase the internal energy of the system. The energy associated with moving an atom from its crystalline site to the surface where it is not having any interactions with other atoms is called vacancy formation energy.

The vacancy formation energy is a property of the material. For every material you will have some vacancy formation energy, because it depends on the bond strength of these materials. The complete segregation of atoms and vacuum is not possible. Since the atoms and vacuum are in equilibrium, you cannot segregate them.

The competition between the vacancy formation energy and the probability (we will talk about in a minute), determines the equilibrium vacancy concentration. And this is the expression:

$$N_V = N \exp\left(-\frac{E_f}{kT}\right)$$

where N_V is the number of vacancies in a crystal lattice, N is the number of lattice sites, E_f is the vacancy formation energy, T is the absolute temperature in Kelvin, and k is the Boltzmann's constant. We need to derive this equation.

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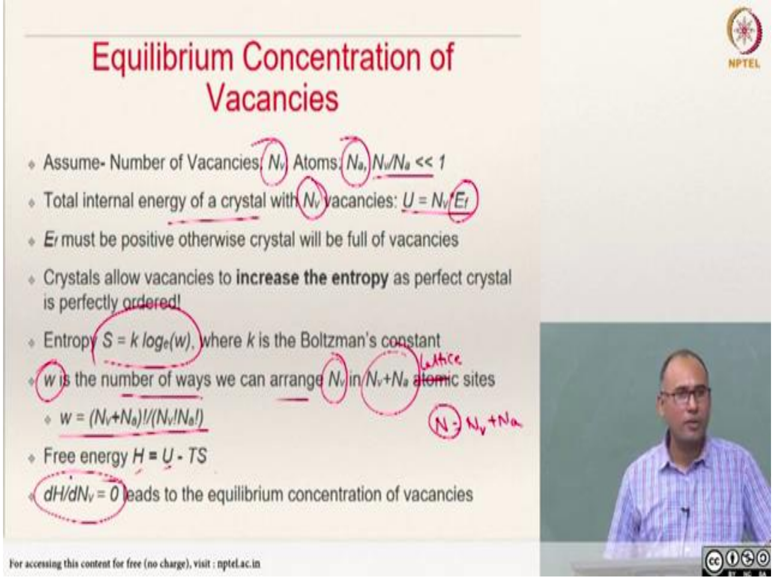

Equilibrium Concentration of Vacancies

- Assume- Number of Vacancies N_v Atoms N_a, $N_v/N_a << 1$
- Total internal energy of a crystal with N_v vacancies: $U = N_v E_f$
- E_f must be positive otherwise crystal will be full of vacancies
- Crystals allow vacancies to **increase the entropy** as perfect crystal is perfectly ordered!
- Entropy $S = k \log_e(w)$, where k is the Boltzman's constant
- w is the number of ways we can arrange N_v in N_v+N_a ~~atomic~~ lattice sites
  - $w = (N_v+N_a)!/(N_v!N_a!)$
- Free energy $H = U - TS$
- $dH/dN_v = 0$ leads to the equilibrium concentration of vacancies

$N = N_v + N_a$

Let us now assume there are N_V number of vacancies and N_a number of atoms in the crystal lattice. There are total $N_V + N_a$ number of lattice positions available. Out of all these lattice positions, N_a number of sites are occupied by atoms and N_V number of sites are not occupied by atoms i.e., N_V number of vacancies, N_a number of atoms are there.

In general, the number of vacancies should be much smaller than the number of atom sites. If you have a very few atoms, then you cannot call this as a material; you rather call it as defects, not everything is free space, right? So, the assumption is that

$$\frac{N_V}{N_a} \ll 1$$

Whenever you remove one atom from the bulk of the crystal lattice, then the vacancy formation energy is E_f. That is the amount of energy by which the internal energy of the system increases whenever you remove an atom. If you have N_V vacancies, the total internal energy of the crystal would have been $N_V \times E_f$. If the base internal energy is made 0, then the total energy would be $N_V \times E_f$ because each vacancy is created by providing a vacancy formation energy of E_f.

E_f must be positive. What happens if it is negative? You keep on forming vacancies and then eventually you will not have anything, you will have only nothing, you will have only vacuum. So, the crystals allow vacancies to increase the entropy of a perfect crystal. Entropy is nothing but a measure of disorder of the system.

So, the crystals allow the formation of vacancies, because it will increase the entropy. A perfect crystal is perfectly ordered and its entropy is 0. So, we have this expression for entropy

$$S = k \log_e(w)$$

where, S is the entropy, k is the Boltzmann's constant and w is the number of ways we can arrange N_V vacancies in $N_V + N_a$ lattice sites. There are only N_a positions occupied by atoms, and $N_V + N_a$ are the total positions available.

So, w is the number of ways that we can arrange the number of N_V vacancies in this total number of $N_V + N_a$ sites, or I will also call $N = N_V + N_a$. N is the total number of lattice sites. So, that probability can be written as

$$w = \frac{(N_V + N_a)!}{N_V!\, N_a!}$$

We know how to define Helmholtz free energy H of a system.

$$H = U - TS$$

where, U is the internal energy, S is the entropy, and T is the absolute temperature. When you want to seek equilibrium in the presence of vacancies, what you need to do? You need to find the stationery value of this Helmholtz free energy, i.e.,

$$\frac{dH}{dN_V} = 0$$

That is the condition that needs to be employed in order to find equilibrium in the presence of vacancies.

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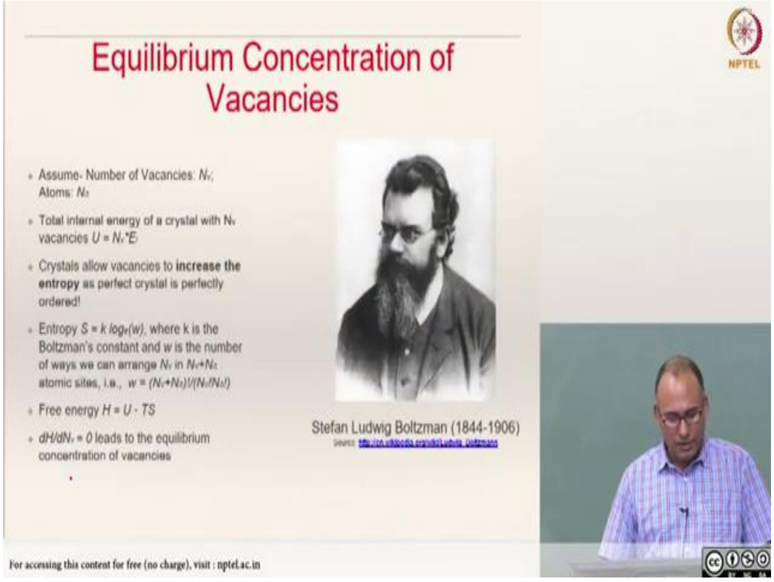

Equilibrium Concentration of Vacancies

- Assume- Number of Vacancies: N_v; Atoms: N_a
- Total internal energy of a crystal with N_v vacancies $U = N_v{}^*E_i$
- Crystals allow vacancies to **increase the entropy** as perfect crystal is perfectly ordered!
- Entropy $S = k\ log_e(w)$, where k is the Boltzman's constant and w is the number of ways we can arrange N_v in N_v+N_a atomic sites, i.e., $w = (N_v+N_a)!/(N_v!N_a!)$
- Free energy $H = U - TS$
- $dH/dN_v = 0$ leads to the equilibrium concentration of vacancies

Stefan Ludwig Boltzman (1844-1906)

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So, he is Boltzmann. This concept of entropy as a disorder was put forward by Boltzmann. I think you must have studied this in your thermodynamics class, right?

Student: (Refer Time: 08:06).

Alright.

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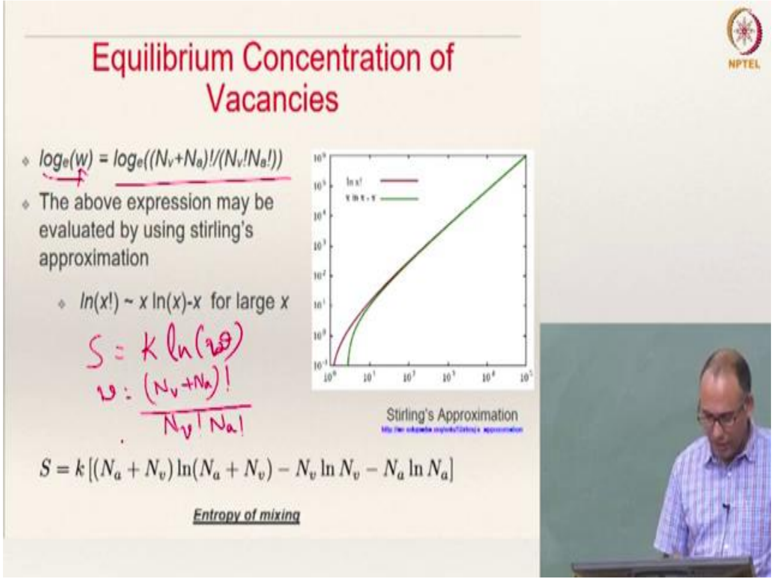

Equilibrium Concentration of Vacancies

- $\log_e(w) = \log_e((N_v+N_a)!/(N_v!N_a!))$
- The above expression may be evaluated by using stirling's approximation
  - $\ln(x!) \sim x\ln(x)-x$ for large x

$S = k\ln(w)$

$w = \frac{(N_v+N_a)!}{N_v!\,N_a!}$

$S = k\,[(N_a+N_v)\ln(N_a+N_v) - N_v\ln N_v - N_a\ln N_a]$

Entropy of mixing

$$S = k\ln w$$

$$w = \frac{(N_V + N_a)!}{N_V!\,N_a!}$$

$$\ln w = \ln\ [(N_V + N_a)\,!] - \ \ln\ (N_V\,!) - \ln\ (N_a\,!)$$

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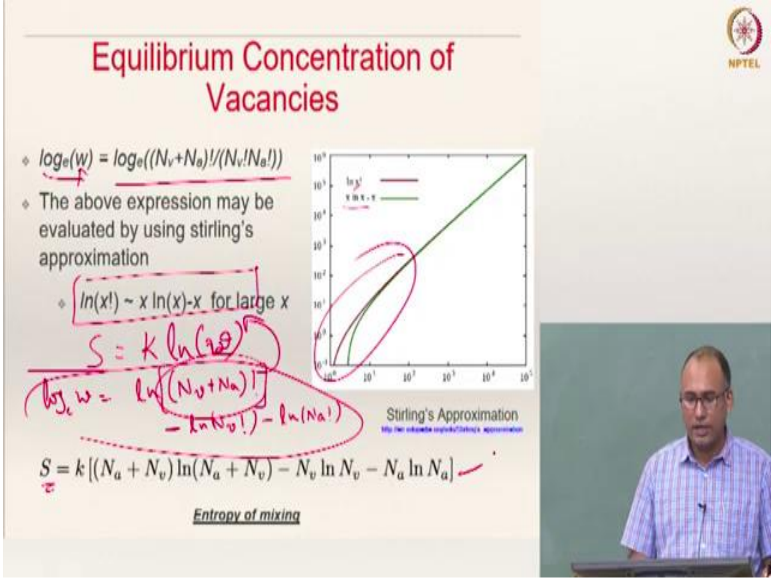

Equilibrium Concentration of Vacancies

- $\log_e(w) = \log_e((N_v+N_a)!/(N_v!N_a!))$
- The above expression may be evaluated by using stirling's approximation
  - $\ln(x!) \sim x\ln(x)-x$ for large x

$S = k\ln(w)$

$\log_e w = \ln[(N_v+N_a)!] - \ln(N_v!) - \ln(N_a!)$

$S = k\,[(N_a+N_v)\ln(N_a+N_v) - N_v\ln N_v - N_a\ln N_a]$

Entropy of mixing

For large values of x,

$$\ln(x!) \sim x\ln x - x$$

The number of atom sites N_a and vacancies N_V are usually going to be much larger than 1, and hence, the Stirling's approximation makes a reasonable sense. Employing these approximations, we get

$$S = k[(N_a + N_V)\ln(N_a + N_V) - N_V \ln N_V - N_a \ln N_a]$$

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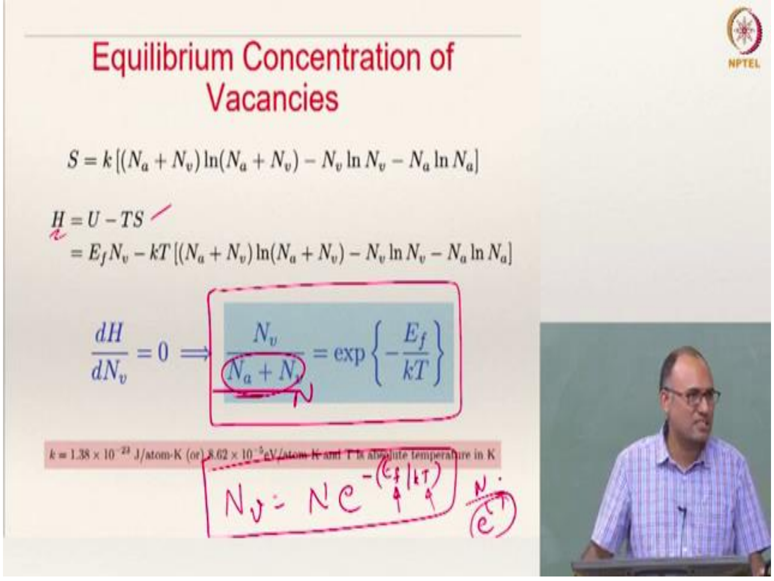

Equilibrium Concentration of Vacancies

$$S = k[(N_a + N_v)\ln(N_a + N_v) - N_v \ln N_v - N_a \ln N_a]$$

$$\begin{aligned} H &= U - TS \\ &= E_f N_v - kT[(N_a + N_v)\ln(N_a + N_v) - N_v \ln N_v - N_a \ln N_a] \end{aligned}$$

$$\frac{dH}{dN_v} = 0 \Longrightarrow \boxed{\frac{N_v}{N_a + N_v} = \exp\left\{-\frac{E_f}{kT}\right\}}$$

$k = 1.38 \times 10^{-23}$ J/atom-K (or) 8.62×10^{-5} eV/atom-K and T is absolute temperature in K

$$\boxed{N_v = N e^{-(E_f/kT)}}$$

$$H = U - TS$$
$$= E_f N_V - kT[(N_a + N_V)\ln(N_a + N_V) - N_V \ln N_V - N_a \ln N_a]$$
$$\frac{dH}{dN_V} = 0 \Rightarrow \frac{N_V}{N_V + N_a} = \exp\left\{-\frac{E_f}{kT}\right\}$$

This will tell you the equilibrium concentration of vacancies in a material, where if you know the vacancy formation energy of the material, you will be able to calculate the number of vacancies at a given temperature because it depends on the temperature. As you increase the temperature what happens?

Student: (Refer Time: 11:21).

As you increase the temperature this entire quantity will?

Student: (Refer Time: 11:34).

Decrease; as a result, N_V will increase. You can create vacancies by thermal activation, nicely described by this simple formula.

Let us try to calculate the number of vacancies in a material.

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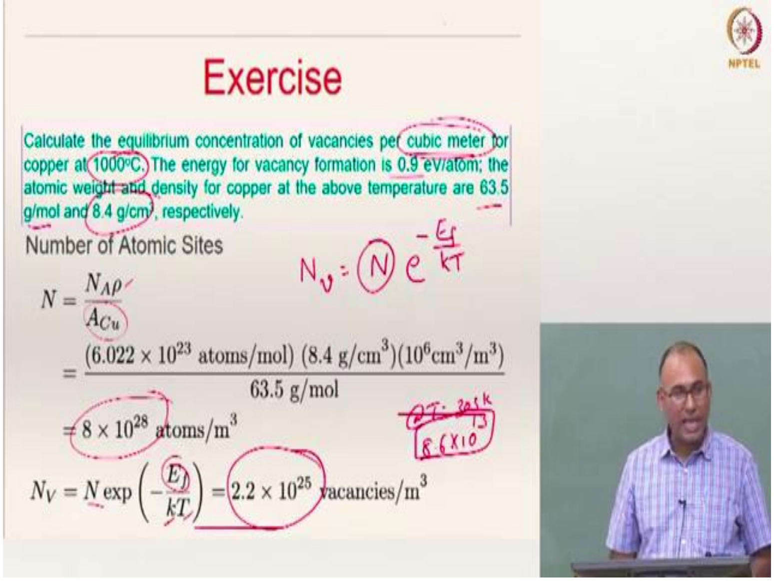

Exercise

Calculate the equilibrium concentration of vacancies per cubic meter for copper at 1000°C. The energy for vacancy formation is 0.9 eV/atom; the atomic weight and density for copper at the above temperature are 63.5 g/mol and 8.4 g/cm³, respectively.

Number of Atomic Sites

$$N = \frac{N_A \rho}{A_{Cu}}$$

$$= \frac{(6.022 \times 10^{23}\ \text{atoms/mol})\ (8.4\ \text{g/cm}^3)(10^6\text{cm}^3/\text{m}^3)}{63.5\ \text{g/mol}}$$

$$= 8 \times 10^{28}\ \text{atoms/m}^3$$

$$N_V = N \exp\left(-\frac{E_f}{kT}\right) = 2.2 \times 10^{25}\ \text{vacancies/m}^3$$

$$N_v = N e^{-\frac{E_f}{kT}}$$

8.6×10

So, the formula is

$$N_V = N \exp\left\{-\frac{E_f}{kT}\right\}$$

What is the Boltzmann constant? 1.38×10^{-30}J K^{-1} or 8.6×10^{-5}eV K^{-1}. Please note down that part and then try to calculate that.

We are trying to calculate the number of vacancies in a copper crystal at 1000° C. At 1000° C, the energy of vacancy formation is given to be 0.9 eV/atom; the atomic weight and density for copper at the above temperature is 63.5 g/mol and 8.4 g/cm^3 respectively. Do you want to try this? First of all, you should know how many lattice sites are going to be there i.e., N. Can you calculate N?

You know the atomic weight, the density as well as the volume i.e., cubic meter of copper. If you have a cubic meter of copper and if you know Avogadro's number, then you can actually plug that in. The number of atomic sites is N_a; that is Avogadro's number, rho is the density, divided by atomic weight of copper in the consistent units.

And you find that to be 8×10^{28}atoms per cubic meter. We are asked to find per cubic meter, right? So, in 1 cubic meter of copper, you will have 8×10^{28} atoms. How many vacancies will be there at 1000° C? So, you just have to plug in; you are given E_f, you know k, and you know T and you know N, then plug in. How many vacancies are there? 2.2×10^{25}.

So, yes, there are vacancies everywhere, right? That is because it is almost close to? What is the melting temperature of copper? So, you please go back and check why there are so many vacancies. What will be the number of vacancies at room temperature, let us say 30° C? Can you calculate quickly using this formula? Is the density going to change as a function of temperature?

Student: (Refer Time: 15:24).

The density of a material changes as a function of temperature or not? But we do not have the information. So, use the same information as density and then just for the sake of understanding, can you tell me how many vacancies will be there if your temperature is 30° C, the room temperature in Chennai is little higher, right?

Student: 8.6×10^{13} (Refer Time: 16.10).

Significantly reduced right? 10^{25} to 10^{13} vacancies. So, the temperature plays a significant role in creating the number of vacancies. If you would calculate the percentage of vacancies here and percentage of vacancies with respect to the number of atom sites, you will realize that. So, even at room temperature, you will have some vacancies. When will you have zero vacancies?

Student: (Refer Time: 16:45).

Absolute zero. And now can you see why you cannot have a perfect crystal, right? Your thermodynamics prohibits you to go to absolute 0. So, no matter what you do, you cannot bring a material to 0 K, and hence you cannot have a material without few point defects. You will always have some point defects. As you increase the temperature, the concentration of vacancies keeps on increasing in a material.