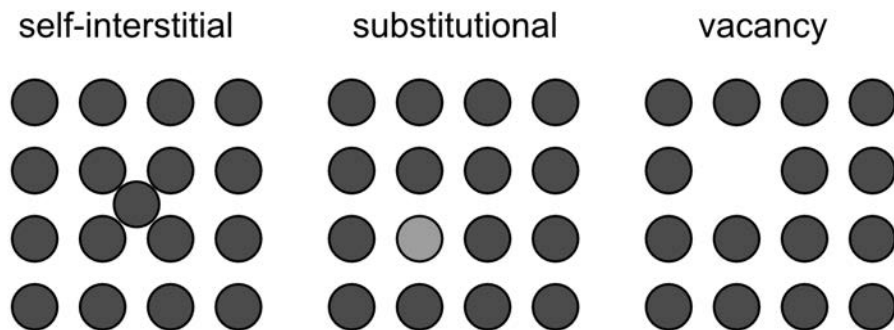


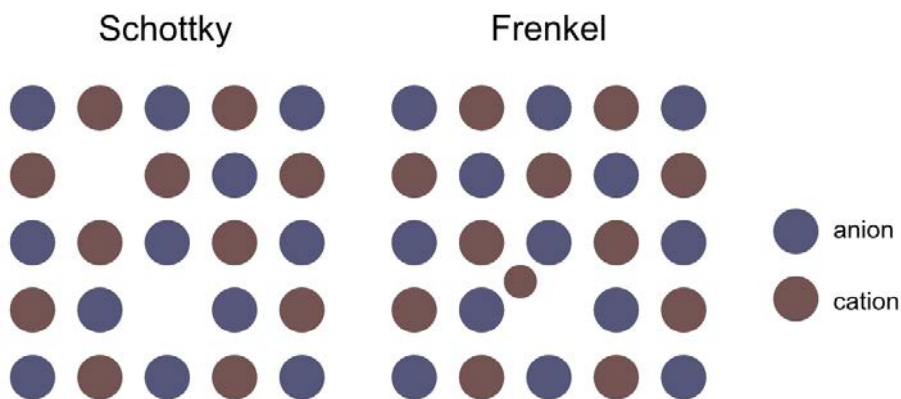
1 Point defects

Point defects are local, so-called zero-dimensional defects in a lattice. They consist of an atom and its immediate surroundings, no more than a few atomic layers away. In 3.091, we'll talk about three types of defects that occur in covalent solids, and two that occur in ionic solids. As a reminder, the individual atoms in a covalent solid have no charge relative to each other. The three defects are pictured below:



A *self-interstitial* occurs in crystals with atoms that are reasonably small compared to their spacing: it is sometimes possible for an atom to squeeze in between the atoms that are in their correct lattice position. A *substitutional defect* occurs when an atom in the homogeneous crystal is replaced by something else- think Ge in Si, for example. Finally, a *vacancy* occurs when one of the atoms in the crystal is missing from its standard lattice site. Remember also - though these are shown in 2D here, the real crystals they occur in are 3D Bravais lattices!

In an ionic crystal, all of the atoms have a relative charge: usually they are arranged to alternate, so the material retains both local and global charge neutrality. Therefore, it is important to account for charge neutrality when thinking about defects. Two ionic defects are shown below.



A *Schottky defect* occurs when there are two simultaneous vacancies – one anion and one cation – in close proximity. A *Frenkel defect* occurs when a cation vacancy neighbors an interstitial cation. Realistically, this occurs when a cation leaves its spot in the crystal lattice and becomes an interstitial. Recall that cations

have a much smaller atomic radius than anions: it is much more practical for this sort of atomic migration to occur with a small cation than a huge anion!

Many, many defects occur in even the purest of crystals. In fact, they are entropically favorable! They can interact with each other, and even move around through the lattice in a thermally-activated process. In 3.091, it is sufficient to be able to identify them.

Example: How many oxygen vacancies are generated if you dope ZrO_2 with 0.5g of Sc_2O_3 ?

In zirconia, each zirconium is stoichiometrically matched with two oxygen atoms. Therefore, the charge on the zirconium atom must be Zr^{4+} . In scandium oxide, there are two scandium ions per three oxygen ions, so it must be coordinated as Sc^{3+} . If we dope zirconia with scandium oxide, the scandium will substitute for the zirconium, and the oxygen will just go on oxygen sites. But each Zr^{4+} that is replaced by Sc^{3+} leaves a local charge imbalance in the lattice of one missing positive charge. This can be counteracted with *oxygen vacancies* in the lattice, effectively creating missing negative charge to balance things out. For every 2 Sc^{3+} atoms added, one V_O'' must be generated in order to maintain charge neutrality.

$$0.5 \text{ g Sc}_2\text{O}_3 \left(\frac{1 \text{ mol Sc}_2\text{O}_3}{137.9 \text{ g}} \right) = 0.0036 \text{ mol Sc}_2\text{O}_3$$

$$0.0072 \text{ mol Sc}^{3+} \text{ added} \times \frac{1 \text{ mol V}_\text{O}''}{2 \text{ mol Sc}^{3+}} = 0.0036 \text{ mol V}_\text{O}''$$

$$\# \text{ oxygen vacancies} = (0.0036 \text{ mol V}_\text{O}'') \left(6.022 \times 10^{23} \frac{\text{vacancies}}{\text{mol vacancies}} \right) = 2.18 \times 10^{21}$$

2 Arrhenius-like vacancy activation

Arrhenius provided a mathematical description for *thermally activated processes* which relates the rate at which a process occurs to temperature. The dependence is exponential and parameterized by energy: you can think of it as an "activation energy" to achieve a state.

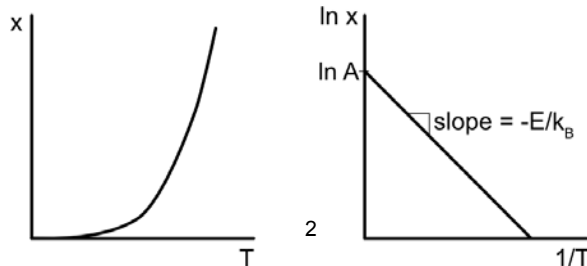
$$x \propto e^{-\frac{E_a}{k_B T}}$$

Here, E is the relevant activation energy in [J] or [eV], k_B is the Boltzmann constant (with units [J/k] or [eV/k] to match the energy), and T is temperature in Kelvin. If we call the constant of proportionality A, we can write this equation in a convenient linear form by taking the log of both sides:

$$\ln(x) = \ln(Ae^{-\frac{E}{k_B T}}) = \ln A - \frac{E}{k_B T}$$

$$\ln x = -\frac{E}{k_B} \frac{1}{T} + \ln A$$

Here we have a convenient slope-intercept form that allows us to read off the exponential rate and constant from a simple plot.



We'll come back to Arrhenius later in the course, but for now we will apply this exponential relationship to calculating the thermally-activated process of vacancy creation. Let's call the rate of vacancy formation r_{form} and the rate of vacancy annihilation $r_{destroy}$. We can describe these rates as Arrhenius processes:

$$r_{form} = A_{form} e^{-\frac{E_{a,form}}{k_B T}} \quad r_{destroy} = A_{destroy} e^{-\frac{E_{a,destroy}}{k_B T}}$$

In equilibrium, the flux of vacancies that form must be equal to the flux of vacancies are destroyed. The flux of vacancies formed is simply the number of sites available to form a vacancy times the rate at which vacancies form, and the flux of vacancies destroyed is the number of sites already having a vacancy times the rate at which vacancies are destroyed. Let's say our crystal has N atoms and N_V vacancies, then in equilibrium:

$$N * r_{form} = N_V * r_{destroy}$$

$$\frac{N_V}{N} = \frac{r_{form}}{r_{destroy}} = \frac{A_{form}}{A_{destroy}} e^{-\frac{E_{form} - E_{destroy}}{k_B T}}$$

We can wrap the difference in formation and annihilation activation energies into a ΔE that we'll call E_V . Then finally, the fraction of vacancies as a function of temperature is

$$\frac{N_V}{N} = \frac{A_{form}}{A_{destroy}} e^{-\frac{E_V}{k_B T}}$$

Example: At room temperature (295 k), a piece of Si has 3 vacancies per 10 million atoms. When it is heated to 400 k, there are 15 vacancies per 10 million atoms. What is E_V ?

Let's start up by setting up the equations for the fraction of vacancies at each temperature:

$$\frac{N_{V,295}}{N} = \frac{A_{form}}{A_{destroy}} e^{-\frac{E_V}{295 * k_B}} \quad \frac{N_{V,400}}{N} = \frac{A_{form}}{A_{destroy}} e^{-\frac{E_V}{295 * k_B}}$$

Here we essentially have two equations with two unknowns: one is E_V , the quantity we are looking for, and the other is $N \frac{A_{form}}{A_{destroy}}$, which we can treat as a constant. Here we are making an assumption that $\frac{A_{form}}{A_{destroy}}$ is temperature independent. We can divide the two equations to get rid of the constant we don't care about, and then solve for E_V :

$$\frac{\frac{N_{V,295}}{N}}{\frac{N_{V,400}}{N}} = \frac{\frac{A_{form}}{A_{destroy}} e^{-\frac{E_V}{295 k_B}}}{\frac{A_{form}}{A_{destroy}} e^{-\frac{E_V}{400 T}}}$$

$$\frac{N_{V,295}}{N_{V,400}} = e^{\frac{E_V}{k_B} \left(\frac{1}{400} - \frac{1}{295} \right)} = \frac{3}{15}$$

Taking the log of both sides:

$$\ln\left(\frac{3}{15}\right) = \frac{E_V}{8.617 \times 10^{-5} \text{ eV/k}} \left(\frac{1}{400} - \frac{1}{295} \right)$$

$$E_V = 0.16 \text{ eV}$$

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