

Solution to Exercise 3.2-1 "Crystal Identity"

Illustration

The jump rate of a vacancy is identical to that of an atom next to the vacancy. It was given by

$$v = v_0 \cdot \exp - \frac{G_m}{kT} \approx v_0 \cdot \exp - \frac{H_m}{kT}$$

The time t_a needed so that all the atoms with a vacancy next to them will make *one* jump thus is

$$t_a = \frac{1}{v} = \frac{1}{v_0} \cdot \exp \frac{H_m}{kT}$$

After *that* time t_a , the fraction of all atoms that had a vacancy a a neighbor, has made *one* jump.

- If you now wait another t_a , a *second* set of atoms can now make a jump. This second set may include atoms from the first set which simply jump back to their old position, but we ignore this effect for a rough estimate.
- If all atoms of the crystal are supposed to make one jump, you have to wait for a time t_c that is a defined multiple of t_a . It is simply

$$t_c = m \cdot t_a = \frac{t_a}{c_v}$$

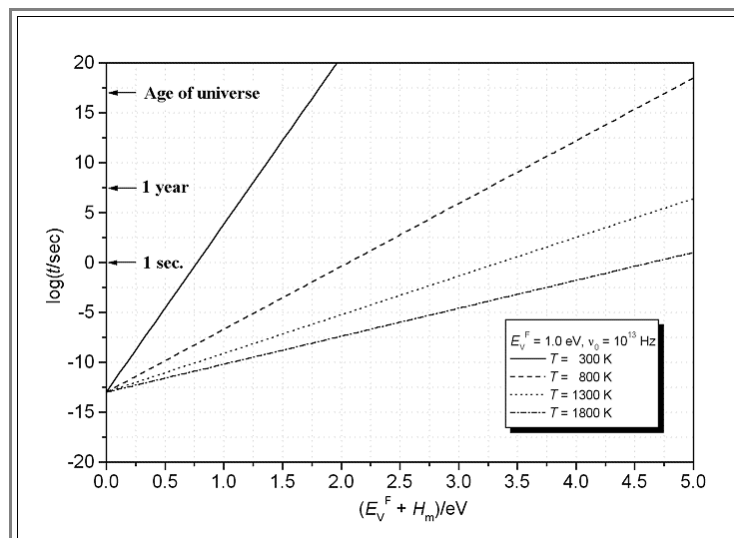
Because the multiplier m is of course the inverse of the vacancy concentration $c_v = \exp - (H_f)/kT$

t_c is the quantity we we are looking for, it is

$$t_c = \frac{1}{v_0} \cdot \exp \frac{H_m}{kT} \cdot \exp \frac{H_f}{kT} = \frac{1}{v_0} \cdot \exp \frac{H_m + H_f}{kT} = \frac{1}{v_0} \cdot \exp \frac{H_{SD}}{kT}$$

With H_{SD} = enthalpy of self diffusion.

We may replace $1/v_0$ by $1/v_0 = g \cdot a^2 / D_{SD}$ and use the diffusion coefficient for self-diffusion to obtain values for specific materials, but lets just look at what we get in a very simple approximation with $v_0 = 10^{13}$ Hz



Shown is t_c on a (rather far-reaching) **log** scale versus $H_m + H_f = H_{SD}$, i.e. the self-diffusion enthalpy H_{SD} , with the temperature as a parameter.

For $H_m + H_f = 0$, t_c is 10^{-13} s - as it should be.

● For sensible values. e.g. $H_{SD} = 2 \text{ eV}$, you must be very patient at room temperature, but at $800 \text{ }^\circ\text{C}$, your crystal has a different identity after **1 second!** Take **Si**, with $H_{SD} \approx 5 \text{ eV}$ and a melting point of roughly **1700 K**, and again no atom will be where it was after a rather short time.

▮ Using better values for v_0 from the self-diffusion coefficient as stated above, just shifts the whole set of curves a "little bit" on the t - axis and thus t_c by the same (logarithmic) amount