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

$$\nu = \nu_0 \cdot \exp - \frac{G_m}{kT} \approx \nu_0 \cdot \exp - \frac{H_m}{kT}$$

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

$$t_a = \frac{1}{\nu} = \frac{1}{\nu_0} \cdot \exp \frac{H_m}{kT}$$

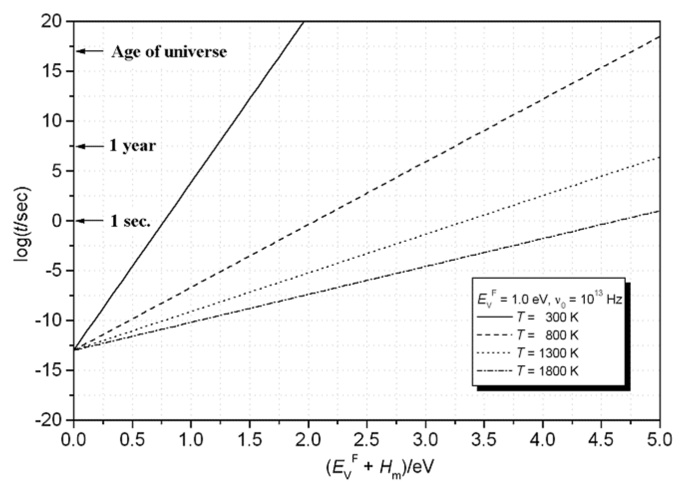
- After *that* time t_a, the fraction of all atoms that had a vacancy a a neighbor, has made *one* jump.
  - If you now wait another t_a, a *second* set of atoms can now make a jump. This second set may include atoms from the first set which simply jump back to their old position, but we ignore this 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

$$t_c = \frac{1}{\nu_0} \cdot \exp \frac{H_m}{kT} \cdot \exp \frac{H_F}{kT} = \frac{1}{\nu_0} \cdot \exp \frac{H_m + H_F}{kT} = \frac{1}{\nu_0} \cdot \exp \frac{H_{SD}}{kT}$$

  - With H_{SD} = enthalpy of self diffusion.
- We may replace $1/\nu_0$ by $1/\nu_0 = g \cdot a^2 / D_{SD}$ 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 $\nu_0 = 10^{13}$ 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 eV**, you must be very patient at room temperature, but at **800 ^{o}C**, your crystal has a different identity after **1 second**! Take **Si**, with **H_{SD}** ≈ **5 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 ν_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