Homework 4 – Solution

1. (a) Calculate the activation energy for diffusion at 300 K given that \( D_0 = 10^{-3} \text{ m}^2/\text{s} \) and \( D = 10^{-17} \text{ m}^2/\text{s} \). (b) Estimate the value of \( D_0 \) for the diffusion of Na ions in NaCl and compare with the experimental value of \( D_0 = 0.0032 \text{ m}^2/\text{s} \). Assume that the \( \Delta S^* \) is about 10k in your calculation. (c) Calculate the electrical mobility of oxygen ions in UO\(_2\) at 700 °C. The diffusion coefficient of the oxygen ions at that temperature is \( 10^{-17} \text{ m}^2/\text{s} \). (d) Compare the mobility of question (c) with electron and hole mobilities in semiconductors (Table 3-4).

Solution:
(a) \( D = D_0 \exp(-Q/kT) \)
\[
10^{-17} = 10^{-3} \exp\left(-\frac{Q}{1.38 \times 10^{-23} \times 300}\right)
\]
Hence, \( Q = 1.34 \times 10^{-19} \text{ J/atom} = 0.83 \text{ eV/atom} = 80.4 \text{ kJ/mol} \)
(b) For NaCl. When diffusion is due to intrinsic vacancies:
\( \Delta S^* = k \frac{\mu}{b} \)
Given that the lattice parameter of NaCl = 0.564 nm, thus
\[
D_0 = \left(\frac{1}{12}\right) \left(\frac{\sqrt{2}}{2} \times 0.564 \times 10^{-9}\right)^2 \left(10^{13}\right)\exp\frac{10k}{k} = 2.9 \times 10^{-3} \text{ m}^2/\text{s}
\]
(c) Assume the diffusion is by interstitial mechanism, then applying Eq. (3.33)
\[
\mu_i = \frac{z_i e D_i}{kT} = 2 \cdot 1.6 \times 10^{-19} \times 10^{-17} = 2.4 \times 10^{-16} \text{ m}^2/\text{s} \cdot \text{V}
\]
(d) Given that the mobilities of electrons/holes are of the order of 0.1 m\(^2\)/s (c.f. Table 3.4) for most semiconductors, the difference is about 15 orders of magnitude slower for that of the ionic oxygen defects in Problem 1(c).

2. For a ceramic solid which exhibits predominately ionic conduction, why is the concentration of the mobile ions must be much greater than that of the electronic defects. Explain.

Solution:
Since the electrical conductivity \( \sigma \) is proportional to the product of \( e \mu \) (c.f. Eq. (3.36)), and the mobilities of electrons and holes are much greater than that of the
ions (see for example, the Problem 1(d)), it follows that for a ceramic solid to exhibit predominately ionic conduction, the concentration \( c \) of the Eq. (3.36) should be much greater than that of the electronic defects.

3. Estimate the number of vacant sites in an ionic ceramic conductor at room temperature in which the cations are the predominant charge carriers. Assume that at room temperature the electrical conductivity is \( 10^{-17} \, (\Omega \cdot m)^{-1} \) and the ionic mobility of \( 10^{-17} \, m^2 V^{-1} s^{-1} \). State your assumptions.

Solution:
Assume \( z_i = 2 \), and since

\[
\sigma_i = c_i z_i e \mu_i \quad \text{(c.f. Eq. (3.36))}
\]

\[
c_i = \frac{\sigma_i}{z_i e \mu_i} = \frac{10^{-17}}{2 \cdot 1.6 \cdot 10^{-19} \cdot 10^{-17}} = 3.1 \cdot 10^{18} \, m^{-3}
\]

4. A stoichiometric oxide, \( M_2O_3 \), has a band gap of 5 eV. The enthalpy of Frenkel defect formation is 2 eV, while that for Schottky defect formation is 7 eV. Further experiments have shown that the only mobile species are cation interstitials, with a diffusion coefficient \( D_{M, \text{int}} \) at 1000K equals to \( 1.42 \times 10^{-10} \, \text{cm}^2/\text{s} \). The mobility of the holes and electrons were found to be 2000 and 8000 \( \text{cm}^2/\text{V} \cdot \text{s} \), respectively. At 1000K, would you expect this oxide to be an ionic, electronic or mixed conductor? Show your calculation. Assume number of interstitial sites is equal to twice the number of atomic sites. Additionally, the molecular weight of the oxide is 40 g/mole, density \( \rho \) is 4 g/cm\(^3\). We also assume that the density of states for holes and electrons is of the order of \( 10^{22} \, \text{cm}^{-3} \).

Solution:
To solve this problem, the conductivities of the electrons, holes and ions have to be calculated.

i) For the electrons:

(Eq. (2.45)) \( n_e = N_e \exp \left( - \frac{E_g}{2kT} \right) = 10^{22} \cdot \exp \left( - \frac{5}{2 \cdot 8.62 \cdot 10^{-7} \cdot 1000} \right) = 2.5 \cdot 10^9 \, \text{cm}^{-3} \)

\[
\sigma_e = c_i z_i e \mu_e = 2.5 \cdot 10^9 \cdot 1.6 \cdot 10^{-19} \cdot 8000 = 3.2 \cdot 10^{-6} \, (\Omega \cdot cm)^{-1} = 3.2 \cdot 10^{-4} \, (\Omega \cdot m)^{-1}
\]

ii) For the holes:
The number of holes is the same as the number of electrons, but the holes
generally present a slower mobility than the electrons, i.e., $\mu_n \sim \mu_e/4$. Hence

$$\sigma_n \cong \sigma_e / 4 = 8 \cdot 10^{-5} \ (\Omega \cdot m)^{-1}$$

iii) For the ionic conduction:

The enthalpy of Frenkel defect formation (2 eV) is substantially smaller than that of the Schottky defect formation (7 eV). Therefore, number of Schottky defects would be negligibly small and can be reasonably ignored. Note that the only mobile species are the cation interstitials. Hence, in one mole of $\text{M}_2\text{O}_3$ there are

$$\frac{2 \cdot 6.02 \cdot 10^{23} \cdot 4}{40} = 1.2 \cdot 10^{23} \text{ atoms} / \text{cm}^3 = 1.2 \cdot 10^{29} \text{ atoms} / \text{m}^3$$

As stated in the problem, number of interstitial sites is double that number. Thus

$$c_i = 2 \cdot 1.2 \cdot 10^{29} \exp\left(-\frac{\Delta h}{2kT}\right) = 2.4 \cdot 10^{29} \exp\left(-\frac{2}{2 \cdot 8.62 \cdot 10^{-5} \cdot 1000}\right) = 2.2 \cdot 10^{24} \text{ m}^{-3}$$

Substituting this into Eq. 3.37

$$\sigma_{\text{ion}} = \frac{c_i z_i^2 e^2 D_i}{kT} = \frac{2.2 \cdot 10^{24} \cdot (3)^2 \cdot (1.6 \cdot 10^{-19})^2 \cdot 1.42 \cdot 10^{-10} \cdot 10^{-4}}{1.38 \cdot 10^{-23} \cdot 1000} = 5.2 \cdot 10^{-7} \ (\Omega \cdot m)^{-1}$$

Therefore, the oxide is an electronic conductor at this temperature since $\sigma_e \gg \sigma_{\text{ion}}$

(You need to be very careful about the unit in your calculation for the above problems.)

(Any queries about the solution or if you have any difficulties in understanding my lecture, feel free to come in and talk with me during the office hours.)