

Diffusion 2

Primer Materials
Spring 2021

Nernst Einstein Equation

$$J_i = g_i C_i E e z$$

where g_i is mobility of ions,
 C_i is the concentration of
ions and E is electric field.

$$g_i = -\frac{Dez}{kT}$$

$$E e z e \lll kT$$

$$\vec{J} = \sigma \vec{E}$$

Example 5.1

Ag_2S is one of the most known mixed (ionic and electronic) conductors.

At room temperature, the diffusion coefficient of Ag exceeds $10^{-10} \text{ cm}^2/\text{s}$, which is higher than that for Ag^+ in some water solutions! However, the most intriguing feature of this compound is a strong deviation from the Nernst-Einstein equation. Already, if the electric field reaches 10 kV/cm , the mobility of Ag ions exceeds that expected from the self-diffusion coefficient by more than 5 times, indicating that the activation energy for electro-migration essentially disappears. Estimate the activation energy of self-diffusion.

To make the activation energy for electro migration disappear, the applied electric field should create an energy difference between two neighboring sites equal to the activation energy of self-diffusion. The distance between two ion sites in the lattice is $0.1\text{-}1 \text{ \AA}$. Taking as an estimate 0.5 \AA , one can get:

$$Q = E \cdot a \cdot e = 0.5 \cdot 10^{-8} \cdot 10^4 = 5 \cdot 10^{-5} \text{ eV}$$

Example 5.2

Consider a layer containing mobile ions, for instance a layer of SiO_2 with trapped Na ions in it ($D = 10^{-16} \text{ cm}^2/\text{sec}$ at room temperature).

Application of external voltage for a sufficiently long time causes the ion drift to one of the layer surfaces. After the voltage is switched off the ions will diffuse back to assume homogenous distribution. Prove that **a)** the ratio between the time necessary to displace the ions to the time necessary for the ions to diffuse back is independent from the thickness of the layer. **b)** Does this ratio depend on the diffusion coefficient? **c)** What is this ratio at room temperature if the applied voltage is 5V?

$$\text{a) } g_i = \frac{Dez}{kT}; v_i = Eg_i = \frac{EDez}{kT}; E = U/d; t_{\text{migration}} = d/v_i = \frac{d^2kT}{UDez};$$
$$t_{\text{diffusion}} = \frac{d^2}{\beta D}; r = t_{\text{migration}}/t_{\text{diffusion}} = \frac{d^2kT}{UDez} \frac{\beta D}{d^2} = \frac{\beta kT}{Uez}$$

g_i is the mobility E is electric field, U is applied voltage, d is thickness and v_i is the velocity. **b)** No, The result is just the ratio between the thermal energy and the electrical energy. **c)** At room temperature, kT is $\approx 0.025 \text{ V}$, thus $0.025\text{V}/5\text{V}=1/200$.

Example 5.3

You are a processing engineer at a semiconductor factory. It turns out that the metal contact on top of the 10 nm thick insulating layer is contaminated by an unknown impurity. The expected lifetime of the device is 5 years, the operating voltage is 4 V. You estimated operating temperature as being below 350 K. Furthermore, with a series of tests, you have found out that the diffusion coefficient of this impurity is 10^{-14} cm²/sec at 1007 K and $5 \cdot 10^{-16}$ cm²/sec at 799 K. Will you take responsibility and guarantee that the device will last for 5 years?

$$D1 := 10^{-14} \frac{\text{cm}^2}{\text{s}} \quad D2 := 5 \cdot 10^{-16} \frac{\text{cm}^2}{\text{s}} \quad T1 := 1007 \cdot \text{K} \quad T2 := 799 \cdot \text{K}$$

$$Q := \frac{k \cdot \ln\left(\frac{D1}{D2}\right)}{\left(\frac{1}{T2} - \frac{1}{T1}\right)} \quad Q = 0.999 \text{ eV} \quad D0 := \frac{D1}{\exp\left(-\frac{Q}{k \cdot T1}\right)} \quad D0 = 0.995 \cdot 10^{-9} \frac{\text{cm}^2}{\text{s}}$$

at 350 K $T3 := 350 \cdot \text{K}$

$$D3 := D0 \cdot \exp\left(-\frac{Q}{k \cdot T3}\right) \quad D3 = 0.416 \cdot 10^{-23} \frac{\text{cm}^2}{\text{s}}$$

$$d := 10 \cdot 10^{-9} \cdot \text{m} \quad U := 4 \cdot \text{V}$$

$$t := \frac{k \cdot T3 \cdot d^2}{e \cdot U \cdot D3} \quad t = 1.816 \times 10^9 \text{ s} \quad \frac{t}{\text{year}} = 57.593$$

Example 5.4

Activation energy of Na diffusion in a window glass is about 1.05 eV. a) How many times the diffusion coefficient jumps up during heating from 100 ° C to 200 ° C? b) how many times the ionic conductivity of Na increases during the same procedure?

a)
$$\frac{D_1}{D_2} = \frac{\exp\left(-\frac{Q}{KT_1}\right)}{\exp\left(-\frac{Q}{KT_2}\right)} = \frac{\exp\left(-\frac{1.05}{8.617 \cdot 10^{-5} \cdot 473}\right)}{\exp\left(-\frac{1.05}{8.617 \cdot 10^{-5} \cdot 373}\right)} = 1000$$

b)
$$\sigma = \frac{(ze)^2 CD}{KT}$$
$$\frac{\sigma_1}{\sigma_2} = \frac{T_2 D_1}{T_1 D_2} = 1000 \cdot \frac{373}{473} = 789$$