

6.4: Ion Distributions in Electrolyte Solution

To gain some insight into how ions in aqueous solution at physiological temperatures behave, we begin with the thermodynamics of homogeneous ionic solutions. Let's describe the distribution of ions relative to one another as a function of the concentration and charge of the ions. The free energy for an open system containing charged particles can be written

$$dG = -SdT + Vdp + \sum_{j=1}^{N_{\text{comp}}} \mu_j dN_j + \sum_{i=1}^{N_{\text{charges}}} \Phi(x) dq_i \quad (6.4.1)$$

μ_j and N_j are the chemical potential and the number of solutes of type j , in which the solute may or may not be charged and where the contribution of electrostatics is not included. This term primarily reflects the entropy of mixing in electrolyte solutions. The sum i only over charges q_i , under the influence of a spatially varying electrostatic potential. This reflects the enthalpic contribution to the free energy from ionic interactions.

In our case, we will assume that ions are the only solutes present, so that the sum over i and j are the same and this extends over all cations and anions in solution. We can relate the charge and number density through

$$q_i = z_i e N_i$$

where z is the valency of the ion ($\pm 1, 2, \dots$) and e is the fundamental unit of charge. Then expressing dq_i in terms of dN_i , we can write the free energy under constant temperature and pressure conditions as

$$dG|_{T,p} = \sum_i (\mu_i + z_i e \Phi) dN_i = \sum_i \mu'_i dN_i$$

Here μ'_i is known as the electrochemical potential.

To address the concentration dependence of the electrochemical potential, we remember that

$$\mu_i = \mu_i^\circ + k_B T \ln C_i$$

where C_i is the concentration of species i referenced to standard state, $C^\circ = 1M$. (Technically ionic solutions are not ideal and C_i is more accurately written as an activity.) Equivalently we can relate concentration to the number density of species i relative to standard state. Then the electrochemical potential of species i is

$$\mu'_i(x) = \mu_i^\circ + k_B T \ln C_i(x) + z_i e \Phi(x) \quad (6.4.2)$$

Here we write $C(x)$ to emphasize that there may be a spatial concentration profile. At equilibrium, the chemical potential must be the same at all points in space. Therefore, we equate the electrochemical potential at two points:

$$\mu'(x_2) = \mu'(x_1)$$

So from eq. (6.4.2)

$$\ln \frac{C(x_2)}{C(x_1)} = \frac{-ze\Delta\Phi}{k_B T} \quad (6.4.3)$$

where the potential difference is

$$\Delta\Phi = \Phi(x_2) - \Phi(x_1).$$

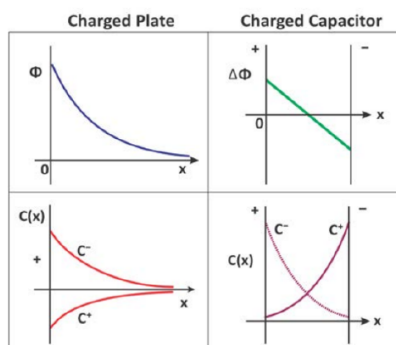
Equation (6.4.3) is one version of the Nernst Equation, which describes the interplay of the temperature-dependent entropy of mixing the ions and their electrostatic interactions. Rewriting it to describe $\Delta\Phi$ as a function of concentration is sometimes used to calculate the transmembrane potential as a function of ion concentrations on either side of the membrane.

The Nernst equation predicts Boltzmann statistics for the spatial distribution of charged species, i.e., that concentration gradients around charged objects drop away exponentially in space with in the interaction energy

$$\begin{aligned} \Delta U(x) &= ze\Delta\Phi(x) \\ C(x) &= C(x_0)e^{-\Delta U(x)/k_B T} \end{aligned} \quad (6.4.4)$$

This principle will hold whether we are discussing the ion concentration profile around a macroscopic object, like a charged plate, or for the average concentration profiles about a single ion. At short distances, oppositely charged particles will have their concentrations enhanced, whereas equally charged objects will be depleted. At short range, the system is dominated by the electrostatic interaction between charges, whereas at long distance, the entropy of mixing dominates.

For the case of charged plates:



Bjerrum Length, ℓ_B

The distance at which electrostatic interaction energy between two charges equals $k_B T$.

For ± 1 charges $\ell_B = \frac{1}{4\pi\epsilon} \frac{e^2}{k_B T}$

At $T = 300 \text{ K}$, $k_B T/e = 25 \text{ mV}$ and

For:	$\epsilon_r = 1 \quad \ell_B = 560 \text{ \AA}$ $\epsilon_r = 80 \quad \ell_B = 7.0 \text{ \AA}$
For $\ell > \ell_B$	Electrostatic interactions are largely screened, and motion is primarily Brownian
For $\ell < \ell_B$	Attractive and repulsive forces dominate. The Bjerrum length gives ion pairing threshold. For $\ell_B = 7.0 \text{ \AA}$, the ion concentrations are approximately, $6.9 \times 10^{26} \text{ m}^{-3}$ or $\sim 1 \text{ M}$.

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