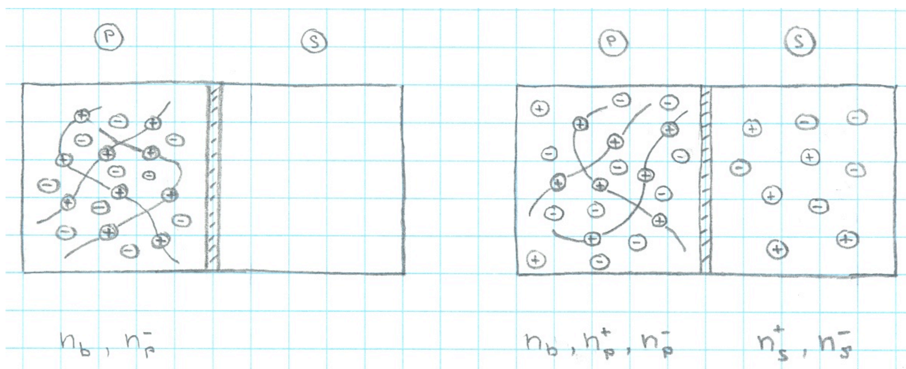
Donnan Equilibrium [pln62]

Here we investigate the chemical equilibrium in a region that contains a solvent on one side, possibly with salt in dilute solution, and a poly-electrolyte on the other side. The inhomogeneity is maintained by a semipermeable wall.

Within the space occupied by the poly-electrolyte, the bound charges are taken into account in the form of a continuous background. The Donnan equilibrium is being established by the mobility of small counter-ions and co-ions.



Situation depicted on the left:

Container with two chambers of equal volume separated by semi-permeable membrane.

- (s) contains solvent with no significant ion content,
- (p) contains a poly-electrolyte solution.

Positive charges are bound to polymers:[1] n_b, e_b^+. Negative charges are carried by small, mobile ions: n_p^-, e_p^-. Membrane is permeable to small ions only.

Local charge density:[2] $\rho_\mathrm{p}(\mathbf{r}) = n_\mathrm{b}(\mathbf{r})e_\mathrm{b}^+ + n_\mathrm{p}^-(\mathbf{r})e_\mathrm{p}^-$, $\quad \rho_\mathrm{s}(\mathbf{r}) = n_\mathrm{s}^-(\mathbf{r})e_\mathrm{s}^-$

Charge neutrality condition: $\rho_\mathrm{p}(\mathbf{r}) = \rho_\mathrm{s}(\mathbf{r}) = 0$

▷ Charge neutrality constraint prevents small ions from migrating through membrane in significant numbers.

▷ Osmotic pressure, $\pi = n_\mathrm{p}^- k_\mathrm{B}T$, depends on the density of ionic groups, which is much larger than the density of polymers.

[1] Scaled number density and charge of bound ionic groups or of small mobile ions.

[2] Averaged over suitably chosen mesoscopic distances.

Situation depicted on the right:

Salt is added to the solution and partially dissociates. Now small, mobile ions with positive or negative charges are present left (p) and right (s). These ions are free to migrate through the membrane until the (chemical) Donnan equilibrium is established.

Equilibrium condition:[3] $\mu_0 + k_\mathrm{B}T \ln n_\mathrm{p}^\pm + e_\mathrm{p}^\pm \psi_\mathrm{p} = \mu_0 + k_\mathrm{B}T \ln n_\mathrm{s}^\pm + e_\mathrm{s}^\pm \psi_\mathrm{s}$.

Charge neutrality condition implies $n_\mathrm{p}^+ + n_\mathrm{b} = n_\mathrm{p}^-$, $\quad n_\mathrm{s}^+ = n_\mathrm{s}^- \doteq n_\mathrm{s}$.

Results describing Donnan equilibrium, all expressed in terms of n_b (poly-electrolyte attribute) and n_s (controllable by salt concentration):

- density of mobile ions in the chamber with poly-electrolyte [pex56]:

$$n_\mathrm{p}^\pm = \frac{1}{2}\left[\sqrt{n_\mathrm{b}^2 + 4n_\mathrm{s}^2} \mp n_\mathrm{b}\right],$$

- Donnan potential:

$$\Delta\psi \doteq \psi_\mathrm{p} - \psi_\mathrm{s} = \frac{k_\mathrm{B}T}{e_0} \ln\left(\sqrt{1 + \left[\frac{n_\mathrm{b}}{2n_\mathrm{s}}\right]^2} + \frac{n_\mathrm{b}}{2n_\mathrm{s}}\right),$$

- osmotic pressure:

$$\Delta\pi \doteq k_\mathrm{B}T\Big[n_\mathrm{p}^+ + n_\mathrm{p}^- - 2n_\mathrm{s}\Big] = k_\mathrm{B}T\left[\sqrt{n_\mathrm{b}^2 + 4n_\mathrm{s}^2} - 2n_\mathrm{s}\right].$$

[gleaned from Doi 2013]

[3] The simplifying assumption $\mu_0^{(\mathrm{p})} = \mu_0^{(\mathrm{s})} \doteq \mu_0$ neglects the fact that the presence of polymers affects the chemical potential via a change in dielectric constant