FYS4715 2021 Lectures 6,7

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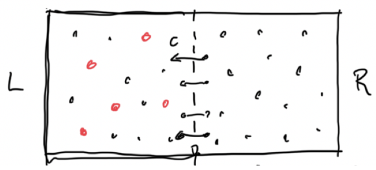
1 Osmosis



A fixed volume, V where the left and right subvolume $V_L = V_R = V/2$ are separated by a semipermeable membrane that only the black particles can cross. The red particles are stuck on the left side. The number of red solute particles N_2 is much smaller than the number of black solvent particles N_1: $N_2 \ll N_1$. In a biological system black particles are water, red particles are proteins, ions...

- What will happen?
- How will the water particles $N_{1,L}$, $N_{1,R}$ distribute?
- From intuition and ideal gas: Entropy S is maximized when concentration is even, $N_{1,L} = N_{1,R}$.
- P_L, P_R?
- For ideal solutions $N_{1,L} = N_{1,R} \Rightarrow P_{1,L} = P_{1,R}$.
- What is the effect of the excess of particles on left side?
- Basic assumption: Dilute solution $\Rightarrow$ non-interacting particles $\Rightarrow$ Ideal gas model

The ideal gas is a collection of non-interacting particles *in thermal motion* which our solute particles are. Ideal gas EOS on the left side:

$$P_2 V_L = N_2 kT \tag{1}$$

$$\Delta P = P_L - P_R = P_2 = C_2 kT = c_2 RT, \qquad C_2 = \frac{N_2}{V_L} \tag{2}$$

Can this shockingly simple argument be true?

1.1 Van't Hoff equation

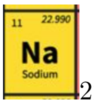
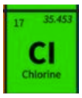
$$\Delta P = \sum_i \phi_i c_i RT, \tag{3}$$

where c_i are the molar solute concentrations and ϕ_i *the number of particles in solution from one solute particles.*

- NaCl $\rightarrow$ Na$^+$+ Cl$^-$ $\Rightarrow \phi = 2$
- Glucose $\rightarrow$ glucose $\Rightarrow \phi = 1$
- Carboxylic acid $\rightarrow$ dimer of carboxylic acid $\Rightarrow \phi = 1/2$

It's the number of "ideal gas" particles that counts.

1.2 Numbers

- Physiological saline solution: 9g Nacl/1000 g H2O
- How do we calculate molar concentration?
-  22  35
- Units? g/mol, R=8.3 J/(K mol)
- $c_2 = \frac{9g}{(23+35)g/mol1l}$ = 0.15mol/l=150 mol/m^3

$$\Delta P = 2cRT = 2 * 150 * 8.3 * 300 = 7.2 \cdot 10^5 Pa = 7.2 bar$$

More than in the tyres of a racing bike!

2 Sidestep: Chemical potential

The equilibrium conditions at constant T and P and V are given by the Gibbs G and Helmholtz F free energies. Equilibrium with respect to number of particles is defined by the equality of chemical potential

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T} = \left(\frac{\partial F}{\partial N}\right)_{V,T} = T\left(\frac{\partial S}{\partial N}\right)_{E,V} \tag{4}$$

This is the fundamental equilibrium condition, not equality of concentration.

2.1 The Gibbs-Duhem relation

When there are I components in a system only I-1 components have independent values for the chemical potential. The Gibbs-Duhem relation is a relation between changes in chemical potential for the different components:

$$\sum_i n_i d\mu_i = -SdT + VdP \tag{5}$$

Using the sum $\sum_i V_i n_i = V$ of partial molar volumes $V_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}}$ we can rewrite the Gibbs-Duhem relation as

$$\sum_i n_i(d\mu_i - V_i dP) = -SdT \tag{6}$$

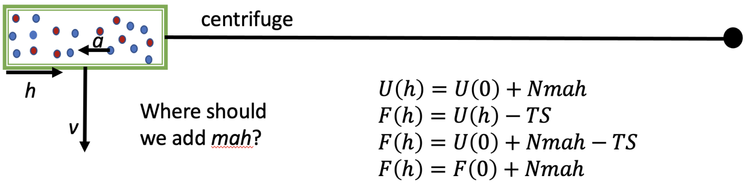
2.2 Chemical potential of ideal solutions

An ideal solution has no volume change upon mixing and the enthalpy of mixing is zero. Thus in a binary solution $c = \frac{N}{V}$ is constant independent of $x_1 = \frac{N_1}{N} = \frac{N_1}{N_1+N_2}$. The chemical potential of an ideal solution is

$$\mu(P,T,c_1) = \mu^0(P,T) + RT\ln c_1 \tag{7}$$

2.3 Chemical potential of external fields

The chemical potential measures the energy required to insert a particle into the system. The "internal" chemical potential concerns concentrations in different systems without any differences external potentials. The "external" chemical potential includes the differences in pressure or external potentials. For example



$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = \mu(c) + mah \tag{8}$$

$$\mu_{tot} = \mu_{int} + \mu_{ext} \tag{9}$$

This can be used in order to derive the barometric pressure formula. In equilibrium the chemical potential of air is independent of height:

$$\mu(z) = \mu_0 = \mu_0 + kT\ln\frac{P(z)}{P_0} + mgz$$

$$\Rightarrow \frac{P(z)}{P_0} = e^{-mgz/kT} \tag{10}$$

For ions in an electrical field ε the potential energy is $U(x) = -q\varepsilon x$ and thus $\mu_{ext} = U(x)$.

3 Osmotic flow

The simplistic derivation of osmotic pressure was done for constant N and V and we only found the equilibrium pressure. We would like to know how the pressure, chemical potentials, concentrations and particle flux over the membrane evolve with time when the two sides start at the same pressure and the right hand side is open.

3.1 Formalism of irreversible thermodynamics

We will introduce the formalism of irreversible thermodynamics which concerns linear transport. The basic idea is that the flux of particles, J_p ,and heat, J_q are linearly dependent on the thermodynamic driving forces K that are $\nabla\mu$ and ∇T:

$$J_i = -\sum_{ij} l_{ij} K_j$$

For an isothermal 2 component system this can be written:

$$\begin{aligned} J_1 &= -l_{11}\nabla\mu_1 - l_{12}\nabla\mu_2 \\ J_2 &= -l_{21}\nabla\mu_1 - l_{22}\nabla\mu_2 \end{aligned} \tag{11}$$

The l_{ij} are called linear transport coefficients. The transport coefficients with equal indices $l_{11} = D\left(\frac{\partial\mu}{\partial c}\right)$ are proportional to the diffusion coefficients we know from Fick's law of diffusion $J = -D\nabla c$. The off-diagonal transport coefficients are related to non-ideal solutions where different species attract or repel and tend to be affected by each other's gradients. Onsager showed that the coefficient matrix is symmetric: $l_{ij} = l_{ji}$.

3.2 General derivation of osmotic flux and pressure

For osmosis we want to calculate the fluxes across the semipermeable membrane. We will therefore only use differences Δ instead of gradients ∇.

$$\begin{aligned} J_1 &= -l_{11}\Delta\mu_1 - l_{12}\Delta\mu_2 \\ J_2 &= -l_{21}\Delta\mu_1 - l_{22}\Delta\mu_2, \end{aligned} \tag{12}$$

where water is species 1 and solute particles are species 2. Since species 2 cannot traverse the membrane $l_{22} = l_{2,1} = 0$ and because of the Onsager symmetry relation $l_{12} = l_{21} = 0$. This shows that even though there is a difference in concentration of species 2 that will not affect the flow or equilibrium condition of species 1: only the chemical potential of species 1 matters. We already assumed as much for the ideal case, but now it is proven in general.

The flux equation reduces to

$$J_1 = -l_{11}\Delta\mu_1 \tag{13}$$

Now we would like to relate $\Delta\mu_1$ to the concentration of solute particles. In order to do so we use the Gibbs-Duhem relation which for isothermal changes can be written:

$$\sum_i c_i\Delta\mu_i = \Delta P \tag{14}$$

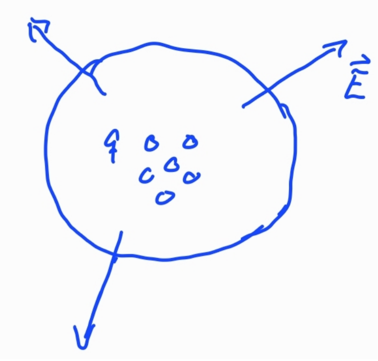


Figure 1: charges, surface and electric field

or

$$\Delta\mu_1 = \frac{1}{c_1}(\Delta P - c_2\Delta\mu_2) \tag{15}$$

We insert this into equation (13):

$$J_1 = -\frac{l_{11}}{c_1}(\Delta P - c_2\Delta\mu_2) \tag{16}$$

Now we will simplify assuming that the solutions are ideal:

$$\begin{aligned} \mu_2 &= \mu_{2,0} + RT\ln c_2 \\ \frac{d\mu_2}{dc_2} &= RT\frac{d\ln c_2}{dc_2} = RT\frac{1}{c_2} \\ \Rightarrow \Delta\mu_2 &= RT\frac{\Delta c_2}{c_2} \end{aligned} \tag{17}$$

With this we can find a version of equation (16) for ideal solutions:

$$J_1 = -\frac{l_{11}}{c_1}(\Delta P - RT\Delta c_2) \tag{18}$$

which has the same equilibrium state ($J_1 = 0$) as before:

$$\Delta P = RT\Delta c_2. \tag{19}$$

4 Charges and electric field

Gauss law

$$\nabla\vec{E} = \frac{\rho}{\varepsilon}, \tag{20}$$

where $\rho = q/V$, where q is the charge and V the volume and $\varepsilon = \varepsilon_0\varepsilon_r$ is the permittivity, subscript zero is for vacuum and r for relative permittivity. Ordinary solids and liquids have $\varepsilon_r \sim 1-10$, water has $\varepsilon_r \sim 1-10$. Permittivity is the degree of polarization of a medium in the electric field.

Electrical potential $\mathcal{V}$ from

$$\vec{E} = -\nabla\mathcal{V} \tag{21}$$

which leads to Poisson's equation

$$\nabla\vec{E} = -\nabla^2\mathcal{V} = \frac{\rho}{\varepsilon} \tag{22}$$

4.1 1-particle relations

Force F on a charged particle:

$$\vec{F} = q\vec{E} \tag{23}$$

Electrical field around 1 particle can be deduced from dimensional analysis: The total electrical field around a charge does not depend on distance (the surface integral around the charge is the same for all radii):

$$\vec{E}(r) = \frac{q}{\varepsilon A} = \frac{q\hat{r}}{4\pi\varepsilon r^2} \tag{24}$$

Electrical potential:

$$\mathcal{V}(r) = \frac{q\hat{r}}{4\pi\varepsilon r} \tag{25}$$

and Coulombs law:

$$\vec{F}(r) = q\vec{E} == \frac{q_1 q_2\hat{r}}{4\pi\varepsilon r^2} \tag{26}$$

4.2 Screening

Boltzmann distribution of of ions in an external potential $\mathcal{V}(\vec{r})$:

$$n_i(\vec{r}) = n_i^\infty \exp\left(\frac{-z_i e\mathcal{V}(\vec{r})}{kT}\right), \tag{27}$$

where n_i is the number concentration of species i, the energy of particle of species i with charge z_i is $\epsilon_i = z_i e\mathcal{V}$ and $n_i^\infty = n_i(r \to \infty)$. The charge distribution is

$$\rho(\vec{r}) = \sum_i n_i(\vec{r}) z_i e \tag{28}$$

that we can put into the Poisson equation

$$\nabla^2\mathcal{V} = -\frac{\rho}{\varepsilon} = \sum_i \frac{-n_i^\infty z_i e}{\varepsilon} \exp\left(\frac{-z_i e\mathcal{V}(\vec{r})}{kT}\right) \tag{29}$$

This differential equation can be linearised by Taylor expanding $\exp(-x) \sim 1-x$ to yield the Debye-Hückel equation (or linearized Poisson-Boltzmann equation):

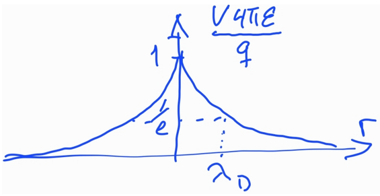
$$\nabla^2\mathcal{V}(r) = \lambda^{-2}\mathcal{V} - \frac{\rho_{ext}(r)}{\varepsilon} \tag{30}$$

where the characteristic length scale is the Debye length:

$$\lambda_D = \sqrt{\sum_i \frac{\varepsilon kT}{n_i^\infty z_i e^2}} = \frac{1}{4\pi\lambda_B \sum_i n_i^\infty z_i}, \tag{31}$$

where λ_B is the Bjerrum length $\lambda_B = e^2/(4\pi\varepsilon kT)$. Solution for the charge distribution around a point charge (for example a negatively charged protein) where $\rho_{ext}(r) = q\delta(r)$

$$\nabla^2\mathcal{V}(r) = \frac{q}{4\pi\varepsilon r}\exp(-r/\lambda_D) \tag{32}$$

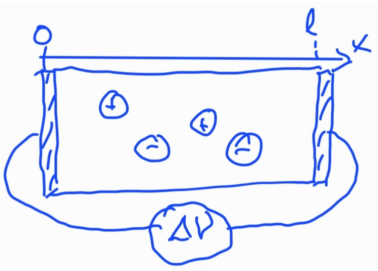


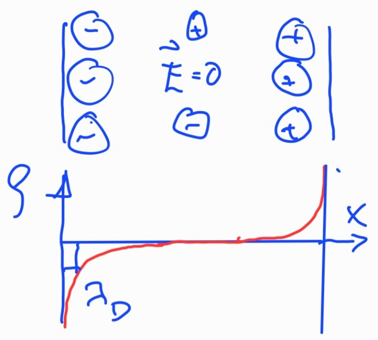
For a flat surface the solution is similar:

$$V(x) \propto V_0\exp(-x/\lambda_D) \tag{33}$$

5 Charges at surfaces (membranes)

5.1 Electrolyte in a cell with an electric potential field





While drawing ask:

- What happens?
- How do the ions distribute?
- What does the electrical field look like?

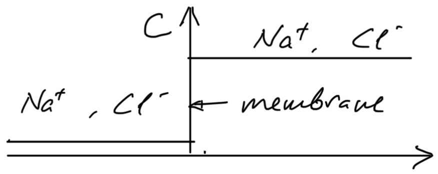
We will use the chemical potential to find the equilibrium distribution of ions.

$$\mu_{tot} = \mu_{int} + \mu_{ext} = \mu_0 + kT\ln\frac{c}{c_0} - \epsilon_i, \tag{34}$$

where $\epsilon_i = z_i e\mathcal{V} = -z_i eEx$.
How do we define equilibrium? $\frac{\partial\mu}{\partial x} = 0$, thus:

$$\begin{aligned} 0 &= kT\frac{d\ln c}{dx} - z_i eE && (35)\\ &= kT\Delta c = qEl = -q\Delta\mathcal{V} && (36)\\ \Delta\mathcal{V} &= \mathcal{V}_{Nernst} = \frac{kT}{q}\ln\frac{c_1}{c_2} && (37) \end{aligned}$$

5.2 Charges at membranes

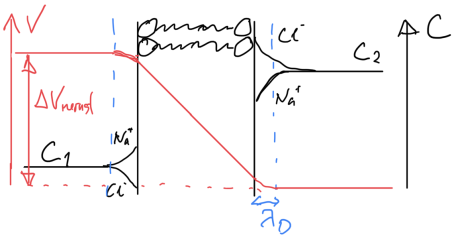


What happens when

- no ion species permeate?
- only one ion species permeates?
- both ion species permeate?

Example: Only Na^+ permeates.

- At equilibrium $\frac{\partial \mu}{\partial x} = 0$,
- Bulk concentrations of Na^+ and Cl^- are equal far from membrane due to charge neutrality.
- Sodium diffuses from high to low concentration until the resulting electrical potential difference equals the Nernst potential.
- Cloride distributes to shield the potential

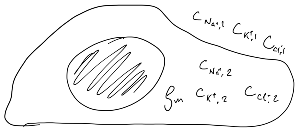


$$\Delta \mathcal{V} = \mathcal{V}_{Nernst} = \frac{kT}{q} \ln \frac{c_1}{c_2} \tag{38}$$

Typical thermal potential: $kT/e = 1/40$ V (Volt).

5.3 Multicomponent electrolytes, Donnan equilibrium

If we assume that inside a cell we have negatively charged macromolecules (eg. proteins) that can not permeate the semipermeable cell membrane. The small ions Na^+, Cl^- and K^+ can permeate.



$\rho_m/e = 125\,mM$
$c_{K^+,1} = 10\,mM$
$c_{Na^+,1} = 140\,mM$
$c_{Cl,1} = 150\,mM$

For all species that can permeate the membrane the concentration difference over the membrane must be given by the same Nernst potential:

$$\frac{e\Delta\mathcal{V}_{Nernst}}{kT} = \ln\frac{c_{Na^+,2}}{c_{Na^+,1}} = \ln\frac{c_{K^+,2}}{c_{K^+,1}} = \ln\frac{c_{Cl^-,1}}{c_{Cl^-,2}} \tag{39}$$

Exponentiating we get the so-called Donnan equilibrium:

$$\frac{c_{Na^+,2}}{c_{Na^+,1}} = \frac{c_{K^+,2}}{c_{K^+,1}} = \frac{c_{Cl^-,1}}{c_{Cl^-,2}} \tag{40}$$

With the 2 equations of the Donnan equilibrium and the equation for charge balance inside the cell

$$0 = c_{Na^+,2} + c_{K^+,2} + c_{Cl^-,2} + \frac{\rho_m}{e} \tag{41}$$

we have 3 equations and 3 unknown concentrations and can solve to find the ion concentrations inside the cell: $c_{Na^+,2} = 210$ mM, $c_{K^+,2} = 15$ mM and $c_{Cl^-,2} = 100$ mM. The proteins are few and highly charged and do not contribute to the total number of osmotic particles inside the cell $c_{tot,2} = 325$ mM. The total number of osmotic particles outside the cell is $c_{tot,1} = 300$ mM. The resulting osmotic pressure is

$$\Delta P = RT\Delta c = 8.3 \cdot 310 \cdot 25 \cdot 10^{-3} = 64 \text{ Pa} \tag{42}$$

5.4 Ion pumping

In order to control the ion concentrations and the electrical potential over the cell membrane the cells pump ions. The cells reach a dissipative steady state where the entropy production rate is

$$\sigma = \sum_i J_i \Delta\mu_i \tag{43}$$

and the energy dissipation rate is

$$\frac{dQ}{dt} = T\sigma = Tsum_i J_i \Delta\mu_i \tag{44}$$

In order to do this there are ion channels that hydrolyse ATP to ADP as an energy source for the pumping.

5.5 Steady state with ion pumping