Salts shield charges.

Poisson-Boltzmann Equation.

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SBU: CHE/PHY/BME 558, Physical & Quantitative Biology
Rutgers University: Chemical Thermodynamics
Lecturer: Gábor Balázsi
Nerve cell electrophysiology

Recording electrode inside axon

Nerves with giant axons

Brain

Mantle

Eye

Arm

Action potential

The Nobel Prize in Physiology or Medicine, 1963
Semipermeable membranes can create voltage

Many biological membranes have ion channels that let some ions pass through, but not others.

Assume that KCl concentration is high on the left, but low on the right of a membrane.

Only $K^+$ can cross the membrane: $K^+$ accumulates on the right. $\mu'_{K^+}(\text{Left}) = \mu'_{K^+}(\text{Right})$

\[
\mu_L^0 + kT \ln([K^+]_L) + e\psi_L = \mu_R^0 + kT \ln([K^+]_R) + e\psi_R
\]

\[
\Delta \psi = \psi_L - \psi_R = \frac{kT}{e} \ln \left( \frac{[K^+]_R}{[K^+]_L} \right)
\]

A voltage builds up across the membrane.

For skeletal muscle, the potential is -98 mV.
The Goldman Equation gives the potential difference across a neuronal membrane:

$$\Delta \psi = \frac{RT}{F} \ln \left( \frac{p_K [K^+]_o + p_{Na} [Na^+]_o + p_{Cl} [Cl^-]_i}{p_K [K^+]_i + p_{Na} [Na^+]_i + p_{Cl} [Cl^-]_o} \right) \approx -70 \text{ mV}$$

For squid giant axon:

<table>
<thead>
<tr>
<th></th>
<th>Concentration in axoplasm</th>
<th>Concentration in sea water</th>
<th>$[C]<em>{out}/[C]</em>{in}$</th>
<th>Relative permeability of membrane</th>
<th>Equilibrium potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium:</td>
<td>Na$^+$ 50 mM</td>
<td>460 mM</td>
<td>9/1</td>
<td>1/30</td>
<td>+55 mV</td>
</tr>
<tr>
<td></td>
<td>K$^+$ 400 mM</td>
<td>10 mM</td>
<td>1/40</td>
<td>1</td>
<td>-92 mV</td>
</tr>
<tr>
<td></td>
<td>Cl$^-$ 40 mM</td>
<td>540 mM</td>
<td>14/1</td>
<td>1/10</td>
<td>-67 mV</td>
</tr>
<tr>
<td>Anion:</td>
<td>A$^-$ 400 mM</td>
<td>—</td>
<td>—</td>
<td>0</td>
<td>—</td>
</tr>
</tbody>
</table>

At resting state, the nerve membrane is practically impermeable to Na$^+$ and the anion A$^-$. This keeps the inside negative, the outside positive.

K$^+$ and Cl$^-$ flow in and out relatively freely according to the Nernst Equation. The resulting equilibrium potential is about -70 mV.
How neurons work: Action potential

1. Upon depolarization, Na\(^+\) channels open up:

\[
\Delta \psi = \Delta \psi_{Na} = \frac{RT}{F} \ln \left( \frac{[Na^+]_o}{[Na^+]_i} \right) = +55 \text{ mV}
\]

2. Then Na\(^+\) inflow slows and K\(^+\) channels open:

\[
\Delta \psi = \Delta \psi_K = \frac{RT}{F} \ln \left( \frac{[K^+]_i}{[K^+]_o} \right) = -92 \text{ mV}
\]

3. Everything returns to the resting state.
Nerve impulses from semipermeable membranes

If an appropriate voltage is applied, the ions flow back, against the gradient.
The Nerst-Planck Equation: ion flows

The flux of particles in an electrostatic potential is given by diffusion + drift:

\[
J_p = -D \left( \frac{\partial c}{\partial x} \right) + c \frac{f}{\xi} \quad u = \frac{1}{\xi} : \text{mobility}
\]

\[
f = -ze \left( \frac{\partial \psi}{\partial x} \right)
\]

The flux of charges (rather than particles):

\[
J_c = ezJ_p = -zecu \left[ kT \frac{\partial \ln(c)}{\partial x} + \left( \frac{\partial \psi}{\partial x} \right) \right]
\]

For two ions with different mobilities, a voltage can transiently build up across a membrane:

\[
\Delta \psi = \psi_L - \psi_R = \frac{kT}{e} \frac{u_- - u_+}{u_- + u_+} \ln \left( \frac{c_L}{c_R} \right)
\]
Creating charge distributions

Van der Graaf generator

Cell phone charging
The free energy of creating charge distributions

Goal: assemble a charge distribution, one charged object at a time.

The work for bringing in the 2\textsuperscript{nd} object from infinity: \( w_2 = q_2 \psi_1 = q_2 \frac{q_1}{4\pi\varepsilon_0 D r_{12}} \)

The work for bringing in the \( i \)\textsuperscript{th} object from infinity: \( w_i = q_i \psi_{1,2,...,(i-1)} = q_i \sum_{j=1}^{i-1} \frac{q_j}{4\pi\varepsilon_0 D r_{ij}} \)

The free energy of the whole system: \( \Delta G_{el} = \frac{1}{2} \sum_{i=1}^{N} q_i \psi_{1,2,...,(i-1),(i+1),...,N} = \frac{1}{8\pi\varepsilon_0 D} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{j\neq i} q_i q_j r_{ij} \)
Continuous charge distributions

If the charge is distributed 3-dimensionally:

\[ \Delta G_{el} = \frac{1}{2} \int_{V} \rho \psi_{V} dV \]

If the charge is distributed 2-dimensionally:

\[ \Delta G_{el} = \frac{1}{2} \int_{S} \sigma \psi_{S} dS \]

If the charge is distributed 1-dimensionally:

\[ \Delta G_{el} = \frac{1}{2} \int_{L} \lambda \psi_{l} dl \]

Example 1: Charging the surface of a sphere:

\[ \Delta G_{el} = \frac{1}{2} \int_{S} \sigma \psi_{S} dS = \frac{qS}{2S} \frac{q}{4\pi \varepsilon_{0} DR} = \frac{q^{2}}{8\pi \varepsilon_{0} DR} \]

Example 2: Charging two parallel planes:

\[ \Delta G_{el} = 2 \frac{1}{2} \int_{S} \sigma \frac{\sigma d}{\varepsilon_{0} D} dS = \frac{\sigma^{2} dA}{2\varepsilon_{0} D} \]
Ion solvation: Born energy

Consider an ion that moves from water into oil. This type of ion partitioning has an electrostatic contribution to the Gibbs free energy.

To calculate this energy, we take a 3-step process:

1) discharge:  \( \Delta G_{el, \text{dis}} = -\frac{q^2}{8\pi\varepsilon_0 D_1 R} \)

2) transfer:  \( \Delta G_{el, \text{trans}} = 0 \)

3) recharge:  \( \Delta G_{el, \text{chg}} = \frac{q^2}{8\pi\varepsilon_0 D_2 R} \)

\[
\Delta G_{el} = \frac{q^2}{8\pi\varepsilon_0 R} \left( \frac{1}{D_2} - \frac{1}{D_1} \right)
\]

Charges transfer between media if \( \Delta G_{el} < 0 \) (or \( D_1 < D_2 \)).

Does an ion transfer from water into oil?
No, because \( D_{\text{water}} = 80 > D_{\text{oil}} = 2 \).
Oil actually repels charged particles that are in water.
Salts shield charges
Salt ions shield charged objects in solution

Charged objects or molecules can change their shape in the presence of salt ions. This happens because salt ions shield charges.

A charged molecule P:
- attracts salt ions of opposite charge (counterions);
- repels salt ions of identical charge (co-ions).

The counterions shield charges on P. The interface around P is the electrical double layer.
Salt ions cause colloid aggregation: River Deltas

Colloid particles often carry charge and repel each other in pure water. However, salt ions can shield their charges, causing aggregation and sedimentation. This is how a river delta forms: silt particles aggregate and sediment down.
The Poisson-Boltzmann equation

Assume that a charged particle \( P \) produces a potential \( \psi \) that depends only on \( x \). Submerge this particle into a salt solution where co- and counter-ions have the same valency. The concentrations of positive and negative ions are given by the Nernst equation:

\[
    n_+(x) = n_\infty e^{-\frac{ze\psi(x)}{kT}} \quad n_-(x) = n_\infty e^{\frac{ze\psi(x)}{kT}}
\]

Importantly, the ions contribute to \( \psi(x) \). We will use Poisson’s equation to see how. The charge density at position \( x \) is:

\[
    \rho(x) = ze[n_+(x) - n_-(x)]
\]

\[
    \nabla^2 \psi = -\frac{\rho}{\varepsilon_0 D} = \frac{ze n_\infty}{\varepsilon_0 D} \left[ e^{\frac{ze\psi(x)}{kT}} - e^{-\frac{ze\psi(x)}{kT}} \right]
\]

This is the Poisson-Boltzmann equation. It cannot be solved analytically.
Approximation: Poisson-Boltzmann equation

A common approximation for exponentials if $x \ll 1$ is:

$$ e^{-x} \approx 1 - x \quad e^{x} \approx 1 + x $$

$$ \nabla^2 \psi \approx 2 \frac{ze n_\infty}{\varepsilon_0 D} \frac{ze \psi(x)}{kT} = \kappa^2 \psi(x) $$

The "Debye length" is

$$ \frac{1}{\kappa} = \frac{1}{ze} \sqrt{\frac{\varepsilon_0 D kT}{2n_\infty}} $$

"Linearized Poisson-Boltzmann" or "Debye-Hückel" equation.

Charges closer than $1/\kappa$ can "see" the charged object P.

For monovalent ions: $1/\kappa \approx 9.62\text{Å}$

For ions with unequal co- and counterion valencies:

$$ I = \frac{c_+ z_+^2 + c_- z_-^2}{2} $$

is the ionic strength, and...

$$ \kappa^2 = \frac{(z_+^2 + z_-^2)e^2 n_\infty}{\varepsilon_0 D kT} = \frac{2e^2 I}{\varepsilon_0 D kT} $$
A uniformly charged plane with ions present

We use the Debye-Hückel equation: \( \nabla^2 \psi = \kappa^2 \psi(x) \)

Solutions that work look like: \( \psi(x) = A_1 e^{\kappa x} + A_2 e^{-\kappa x} \)

Now we use boundary conditions to find \( A_1 \) and \( A_2 \):

\[ \psi(\infty) = A_1 e^{\kappa x} = 0 \Rightarrow A_1 = 0 \]

\[ \psi(x) = \psi_0 e^{-\kappa x} \]

\[ \frac{d\psi}{dx} = -\kappa \psi_0 e^{-\kappa x} = -E_x = -\frac{\sigma}{\varepsilon_0 D} \]

For very small \( x \):

\[ \psi_0 = \frac{\sigma}{\varepsilon_0 \kappa D} \]

\[ \psi(x) = \frac{\sigma}{\varepsilon_0 \kappa D} e^{-\kappa x} \]
Spherical charge in salt solution

Consider a uniformly charged sphere (Q) of radius R in a salt solution.

\[ \nabla^2 \psi = \kappa^2 \psi(r) \quad \Rightarrow \quad \frac{1}{r^2} \left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) \right] = \kappa^2 \psi(r) \quad \Rightarrow \quad \psi(r) = A_1 \frac{e^{\kappa r}}{r} + A_2 \frac{e^{-\kappa r}}{r} \]

is a solution (try it!)

Boundary conditions:

\[ \psi(\infty) = A_1 \frac{e^{\kappa r}}{r} = 0 \Rightarrow A_1 = 0 \quad \psi(R) = A_2 \frac{e^{-\kappa R}}{R} \Rightarrow A_2 = R e^{\kappa R} \psi(R) \]

\[ \psi(r) = \frac{e^{-\kappa(r-R)}}{r} R \psi(R) \]

\[ \left. \frac{d\psi}{dr} \right|_{r=R} = - \left[ \frac{e^{-\kappa r}}{r^2} + \kappa \frac{e^{-\kappa r}}{r} \right]_{r=R} \]

\[ R \psi(R) e^{\kappa R} = -\psi(R) \frac{\kappa R + 1}{R} \]

\[ \Rightarrow \quad \psi(R) = \frac{Q}{4\pi\varepsilon_0 DR(\kappa R + 1)} \quad \Rightarrow \quad \psi(r) = \frac{Q}{4\pi\varepsilon_0 D(\kappa R + 1)} \frac{e^{-\kappa(r-R)}}{r} \]
Weak and strong electrolytes

Salts in solution dissociate according to the reaction:

$$AC \overset{K}{\rightarrow} A^- + C^+$$

The equilibrium constant is:

$$K = \frac{[A^-][C^+]}{[AC]}$$

Strong electrolytes have large $K$, typically $K>0.1$. We define $pK=-\log_{10}(K)$.

The strength of electrolytes is given by the ion concentrations. They can be estimated from changes in melting points, or from conductivity measurements.

Strong electrolytes: (1) colligative properties indicating full dissociation;
(2) doubling electrolyte concentration doubles the conductivity.
This is Kohlrausch’s law.

Electrolytes can deviate in two ways from Kohlrausch’s law:
(1) if they do not dissociate completely;
(2) if they dissociate, but start clustering.
The chemical potential of neutral salts

For the next part we will need the chemical potential of neutral salts. Assume that we dissolve a neutral salt in a solution. There it splits into ions.

\[ \mu_{NaCl} = \mu_{Na^+} + \mu_{Cl^-} \]

\[ \mu_{NaCl} = \mu_{Na^+} + kT \ln c_{Na^+} + e\psi z_{Na^+} + \mu_{Cl^-} + kT \ln c_{Cl^-} + e\psi z_{Cl^-} \]

\[ \mu_{NaCl} = \mu_{Na^+} + kT \ln c_{Na^+} + e\psi_{Na^+} + \mu_{Cl^-} + kT \ln c_{Cl^-} - e\psi_{Cl^-} \]

\[ \mu_{NaCl} = \mu_{NaCl} + kT \ln(c_{Na^+}c_{Cl^-}) + e(\psi_{Na^+} - \psi_{Cl^-}) \]

(\(\psi=\text{const.}\))

\[ \mu_{NaCl} = \mu_{NaCl} + kT \ln(c_{Na^+}c_{Cl^-}) \]

\[ c_{Na^+} = c_{Cl^-} = c_{NaCl} \]

\[ \mu_{NaCl} = \mu_{NaCl} + 2kT \ln(c_{NaCl}) \]
Debye-Hückel theory of nonidealities

In solution, positive ions aggregate around negative ions and vice versa. This alters the chemical potential. Nonidealities can be described by the activity coefficient $\gamma$:

$$
\mu_{\text{NaCl}} = \mu^\circ + 2kT \ln c_{\text{NaCl}} + 2kT \ln \gamma \quad , \quad \text{activity coefficient: } \gamma = \sqrt{\gamma_{\text{Na}} \gamma_{\text{Cl}}}
$$

The activity coefficient describes how much Na and Cl ions “like” each other.

Debye and Hückel assumed that all nonideality arises from electrostatic clustering energy. This is the energy difference to charge up a sphere (ion) of radius $b$ with and without salt.

$$
\psi_{\text{dist}} = \psi_b - \psi_{\text{no-salt}} = \frac{z_+ e}{4\pi\varepsilon_0Db(\kappa b + 1)} - \frac{z_+ e}{4\pi\varepsilon_0Db} = -\frac{z_+ e}{4\pi\varepsilon_0D} \frac{\kappa}{kb + 1}
$$
Debye-Hückel theory of nonidealities

What is the effect of the salt on the charge distribution? Nonidealities are described by:

\[ \Psi_{\text{dist}}(\lambda) = -\lambda \frac{z_+e}{4\pi\varepsilon_0 D} \frac{\kappa}{\kappa b + 1} \]

In terms of energies, this relates to charging:

\[ kT \ln \gamma_+ = -\frac{(z_+e)^2}{8\pi\varepsilon_0 D} \frac{\kappa}{\kappa b + 1} \]

From here we obtain the activity coefficient:

\[ \ln \gamma = \ln \gamma_+ \gamma_- \propto \frac{\kappa}{\kappa b + 1} \approx \kappa \propto \sqrt{I} \]

(for \( \kappa b << 1 \))
Salts affect the rates of chemical reactions

Consider the reaction:

\[ A + B \xrightarrow{k_0} P \]

In the absence of salts:

\[ k_0 = \text{const}[A][B] \]

In the presence of salts:

\[ k_0 = \text{const}[A][B] \frac{\gamma_A \gamma_B}{\gamma_P} \]

\[ \ln \left( \frac{k_s}{k_0} \right) = \text{const} + \ln \left( \frac{\gamma_A \gamma_B}{\gamma_P} \right) \]

Applying the Debye-Hückel theory, we get:

\[ \ln \left( \frac{k_s}{k_0} \right) \approx 2A_0 z_A z_B \sqrt{I} \]