ELECTROCHEMICAL POTENTIAL (NERNST POTENTIAL)

The chemical potential is actually the work needed to remove dn particles from the system. When the particles are charged, an addional work is needed:

$$dW = \mu \cdot dn + V \cdot dq$$
$$= \underbrace{\mu \cdot dn + V \cdot (z \cdot F \cdot dn)}\,,$$

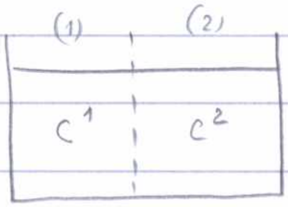
z; the ionization number
F; the Faraday constant; $F = N_A \cdot e$,

$$= (\mu + z \cdot F \cdot V) \cdot dn = \tilde{\mu}_i \cdot dn$$

$\tilde{\mu}_i = \mu + zF \cdot V$ is called the electrochemical potential,
V is the electric potential.

NERNST POTENTIAL

An ion exist in concentration c_1 and c_2 on either side of a permeable membrane.



p, T constant
At equilibrium the chemical potential of the component (i-th component, if several) is equally large on either side of the membrane;

$$dG = \mu^1 \cdot dn^1 + \mu^2 \cdot dn^2 = (\mu^1 - \mu^2) \cdot dn^1 = 0$$
$$(dn^2 = -dn^1) \quad \Rightarrow \quad \underline{\mu^1 = \mu_2}$$

$$\mu^0 + RT\ln c^1 + zFV_1 = \mu^0 + RT\ln c^2 + zF\cdot V_2,$$

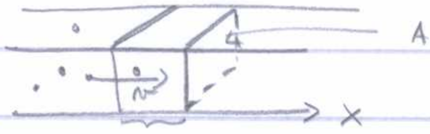
Hence: $\Delta V \equiv V_2 - V_1 = \dfrac{RT}{zF}\ln\left(c^1/c^2\right)$

ΔV is the potential difference across the membrane.

TRANSPORT ACROSS MEMBRANES; FLUXES AND FORCES

The particle current (J) is the number of particles (dn) passing through an area A in a time interval dt.

$$J = \frac{dn}{A\cdot dt} = \frac{1}{A}\cdot\left(dn/dt\right)$$



Suppose the particles move with velocity v,
then: $dn = c\cdot dx\cdot A$ (definition of concentration)
$= c\cdot v\cdot dt\cdot A \Rightarrow$

$$J = c\cdot v,$$

The particle flux is: $\Phi \equiv J\cdot A$

The force (X) on the particles (substance) is derived from the chemical potential as:

$$X = -\frac{\partial\mu}{\partial x},$$ because

$$\frac{\partial\mu}{\partial x} = -\frac{\partial}{\partial x}\left(\frac{\partial G}{\partial n}\right) = -\frac{\partial}{\partial n}\left(\frac{\partial G}{\partial x}\right) = -\frac{\partial}{\partial n}\left(-\frac{F\cdot\partial x}{\partial x}\right)$$

$$= \frac{\partial F}{\partial n}$$, which is

force pr. mole (∂m).

The force on an ion (i) when there is both a contration- and potential difference:

$$X_i = -\frac{d\mu_i}{dx} = -\frac{d}{dx}\left(\mu_0 + RT \ln c_i + z_i F \cdot V + \bar{V} \cdot p\right)$$

$$= -\left(RT \cdot \frac{1}{c_i} \cdot \frac{dc_i}{dx} + z_i F \frac{dV}{dx} + \bar{V} \cdot \frac{dp}{dx}\right)$$

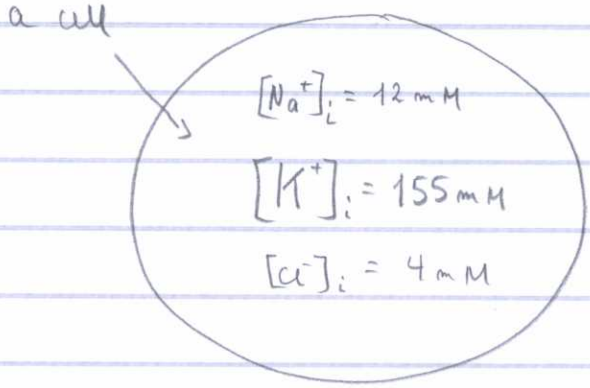
The ions will move with velocity v_i;

$f_i \cdot v_i = X_i$, and the particle flux is:

$$\underline{J_i} = c_i \cdot v_i = \left(1/f_i\right) \cdot \underline{\left\{RT \cdot \frac{dc_i}{dx} + z_i F \cdot c_i \cdot E + c_i \bar{V}\, dp/dx\right\}}$$

f_i is the friction coefficient of the i-th component. The inverse value of f_i; $u_i = 1/f_i$, is called particle mobility.

RESTING POTENTIAL OF CELLS



$[Na^+]_e = 145\ mM$

$[K^+]_e = 4\ mM$

$[Cl^-]_e = 120\ mM$

Across the cell membrane there is a potential difference of; $\Delta V = V_i - V_e = -90\ mV$, called the resting potential of the cell. As we will see, this is due to conditions of electroneutrality and ion fluxes caused by the chemical potential.

To start with: There can be no net transport of charges across the membrane:

$$\sum_i J_i \cdot z_i = 0, \quad \text{or}$$

$$J_{K^+} + J_{Na^+} - J_{Cl^-} = 0$$

Assume, for the moment, $J_{Cl^-} = 0$. Hence

$$u_{K^+} \cdot c_{K^+} \cdot \left\{ +RT \cdot \frac{d(\ln c_{K^+})}{dx} + F \cdot \frac{dV}{dx} \right\}$$

$$+ u_{Na^+} \cdot c_{Na^+} \cdot \left\{ +RT \cdot \frac{d(\ln Na^+)}{dx} + F \cdot \frac{dV}{dx} \right\} = 0$$

Rearranging:

$$\frac{dV}{dx} \left\{ u_{K^+} \cdot c_{K^+} + u_{Na^+} \cdot c_{Na^+} \right\} = -\frac{RT}{F} \cdot \frac{d}{dx} \left\{ u_{K^+} \cdot c_{K^+} + u_{Na^+} \cdot c_{Na^+} \right\}$$

$$\Rightarrow \frac{dV}{dx} = -\frac{RT}{F} \cdot \frac{d}{dx}\left\{ \ln\left(u_{K^+} C_{K^+} + u_{Na^+} \cdot C_{Na^+}\right)\right\}$$

Integration yields:

$$V_2 - V_1 = -\frac{RT}{F} \cdot \ln\left\{ \frac{\left(u_{K^+} C_{K^+} + u_{Na^+} \cdot C_{Na^+}\right)_2}{\left(u_{K^+} \cdot C_{K^+} + u_{Na^+} \cdot C_{Na^+}\right)_1} \right\}$$

Now we consider: $J_{K^+} + J_{Na^+} - J_{Cl^-} = 0$.

By adding the extra term, due to the flux of Cl^- ions, the above equation for the resting potential now becomes:

$$V_i - V_e = \frac{RT}{F} \cdot \ln\left\{ \frac{u_{K^+} \cdot C_{K^+}^{e} + u_{Na^+} \cdot C_{Na^+}^{e} + u_{Cl^-} \cdot C_{Cl^-}^{i}}{u_{K^+} \cdot C_{K^+}^{i} + u_{Na^+} \cdot C_{Na^+}^{i} + u_{Cl^-} \cdot C_{Cl^-}^{e}} \right\}$$

This is called the Goldmann equation