University of Washington
Department of Chemistry
Chemistry 452/456
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Lecture 21 8/15/14

A. Equilibrium and the Electrochemical Potential

- For a two component system an both the Gibbs energy is given by

$$\begin{aligned} dG &= -SdT + VdP + \sum_i \left(\mu_i + z_i F\psi\right) dn_i \\ &= -SdT + VdP + \sum_i \tilde{\mu}_i dn_i \end{aligned} \qquad (21.1)$$

- Suppose we have a chemical reaction involving charged species. This chemical reaction has the form: $\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D$, where A, B, C, and D are all charged species. Integrating 21.1 the expression for the Gibbs energy at constant P and T is found to be

$$\Delta G = \nu_C \tilde{\mu}_C + \nu_D \tilde{\mu}_D - \nu_A \tilde{\mu}_A - \nu_B \tilde{\mu}_B \qquad (21.2)$$

- The criterion for equilibrium is:

$$\begin{aligned} &\Delta G = 0 = \nu_C \tilde{\mu}_C + \nu_D \tilde{\mu}_D - \nu_A \tilde{\mu}_A - \nu_B \tilde{\mu}_B \\ &or \ldots \nu_C \tilde{\mu}_C + \nu_D \tilde{\mu}_D = \nu_A \tilde{\mu}_A + \nu_B \tilde{\mu}_B \end{aligned} \qquad (21.3)$$

B. Electrochemical Cells

- In the figure at the right are some standard reduction potentials ψ_0 for various chemical species. In general, electrons move in oxidation-reduction reactions toward the species with the more positive reduction potentials. This means electrons move from species near the top of the table toward species near the bottom of the table.

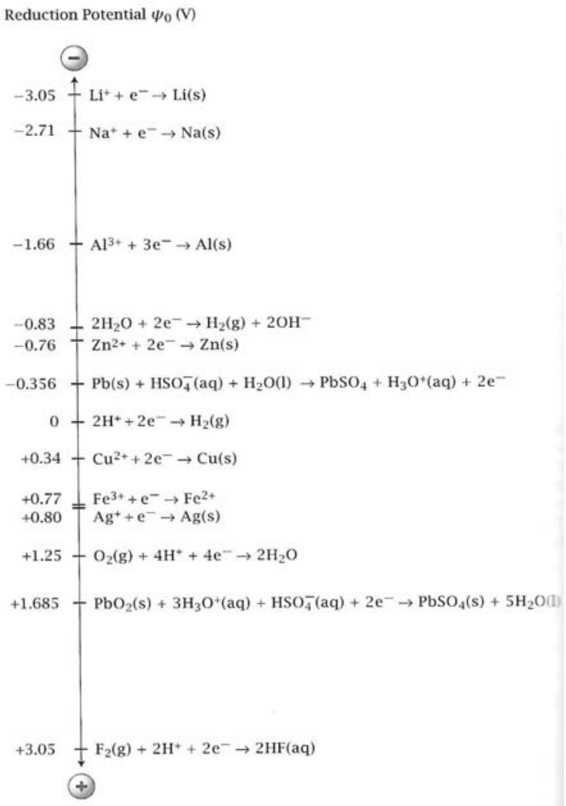
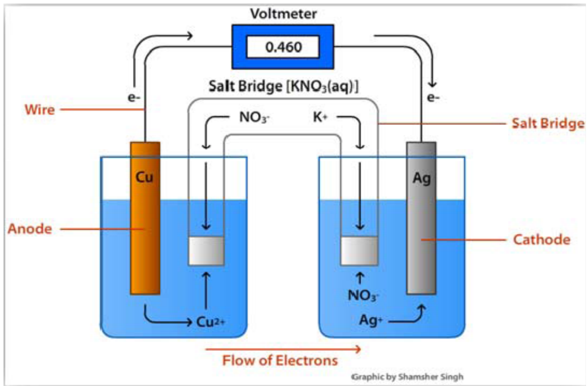


Figure 1: standard reduction potentials for various chemical species.

- The redox reaction $Cu(s)+2Ag^{+}(aq)\rightarrow Cu^{2+}(aq)+2Ag(s)$ runs toward the right because electrons will move from Cu, which is higher on the reduction potential table, resulting in the production of Cu^{2+}, toward Ag^{+} , resulting in the production of Ag.
- The figure at the right is the electrochemical cell within which the reaction shown above occurs. Let us suppose the Ag+ at the surface of the electrode is in equilibrium with the Ag+ in solution. Then the electrochemical potentials are equal:



Graphic by Shamsher Singh

$$\tilde{\mu}_{Ag^{+}}(s)=\tilde{\mu}_{Ag^{+}}(aq) \tag{21.4}$$

- The electrochemical potential expressions are:

$$\tilde{\mu}_{Ag^{+}}(aq)=\mu^{0}_{Ag^{+}}(aq)+RT\ln a_{Ag^{+}}(aq)+zF\psi_{aq} \tag{21.5}$$

$$\tilde{\mu}_{Ag^{+}}(s)=\mu^{0}_{Ag}(s)+RT\ln a_{Ag^{+}}(s)+zF\psi_{S} \tag{21.6}$$

where ψ_s and ψ_{aq} are the electrostatic potentials within the solid and the solution.

- We put equations 21.6 and 21.5 into 21.4 and use the fact that for a pure solid $a_{Ag^{+}}(s)=1$

$$\mu^{0}_{Ag^{+}}(aq)+RT\ln a_{Ag^{+}}(aq)+zF\psi_{aq}=\mu^{0}_{Ag}(s)+zF\psi_{S} \tag{21.7}$$

- Equation 21.7 is rearranged to given the expression for a half-cell potential:

$$\mu^{0}_{Ag^{+}}(aq)+RT\ln a_{Ag^{+}}(aq)+zF\psi_{aq}=\mu^{0}_{Ag}(s)+zF\psi_{S}$$

$$\therefore \psi_{aq}=\frac{\mu^{0}_{Ag}(s)-\mu^{0}_{Ag^{+}}(aq)+zF\psi_{S}}{zF}-\frac{RT}{zF}\ln a_{Ag^{+}}(aq) \tag{21.8}$$

$$=\psi^{0}-\frac{RT}{zF}\ln a_{Ag^{+}}(aq)$$

- In equation 21.8 the term

$$\psi^{0}=\frac{\mu^{0}_{Ag}(s)-\mu^{0}_{Ag^{+}}(aq)+zF\psi_{S}}{zF} \tag{21.9}$$

  is called a standard half cell potential.
- Electrochemical cells are composed of two half-cells. The simplest electrochemical cell is a concentration cell, in which two solutions with the same ion at different concentrations are placed in contact with

electrodes. In this case the cell potential E is the difference between the two half cell potentials

$$E = \psi_{liq}(1) - \psi_{liq}(2) = \Delta\psi =$$

$$\psi^0 - \frac{RT}{zF}\ln a_{Ag^+}(1) - \psi^0 - \frac{RT}{zF}\ln a_{Ag^+}(2) = -\frac{RT}{zF}\ln\left(\frac{a_{Ag^+}(1)}{a_{Ag^+}(2)}\right) \quad (21.10)$$

C. Active & Passive Transport of ions Across Membranes

- We can use the equilibrium criterion in equation 21.3 to derive how ions move when subjected to an external electrostatic potential, which as we have seen is created by a charge configuration. Let us consider the equilibrium populations of the ion species at points x_1 and x_2 that result from this potential.
- At equilibrium equation 21.3 is applicable. But there is only one species of ion and it moves between two positions. When equilibrium is reached 21.3 has the form:

$$\tilde{\mu}(x_1) = \tilde{\mu}(x_2) \quad (21.11)$$

- Now put the expression for the electrochemical potential into 21.4:

$$\mu^*(x_1) + RT\ln(c(x_1)) + zF\psi(x_1) = \mu^*(x_2) + RT\ln(c(x_2)) + zF\psi(x_2) \quad (21.12)$$

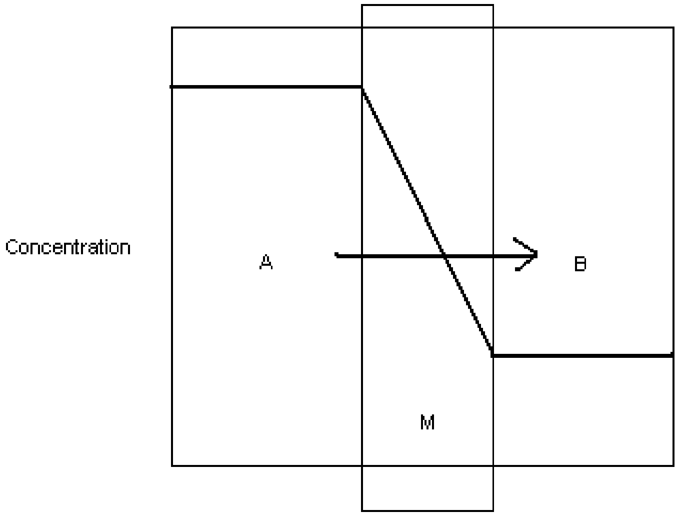
- We assume the standard chemical potentials are equal at x_1 and x_2:

$$\mu^*(x_1) = \mu^*(x_2) \quad (21.13)$$

- With assumption 21.6 we can rearrange 21.5:

$$\ln\left(\frac{c(x_2)}{c(x_1)}\right) = -\frac{zF(\psi(x_2) - \psi(x_1))}{RT} \quad (21.14)$$

- The transport of molecules across cell membranes is a fundamental requirement. There are three general types of transport: passive, active and facilitated..
  - Passive Transport: Consider the transport of a substance between two



compartments.

- The free energy change in transporting a substance from compartment A, where it has concentration C_A to compartment B where it has concentration C_B, through the membrane M is given by the difference between the electrochemical chemical potentials

$$\Delta\bar{G} = \tilde{\mu}_B - \tilde{\mu}_A = \mu_B^* - \mu_A^* + RT\ln\left(\frac{a_B}{a_A}\right) + zF\left(\psi_B - \psi_A\right)$$
$$= \mu_B^0 - \mu_A^0 + RT\ln\left(\frac{\gamma_\pm^B C_B}{\gamma_\pm^A C_A}\right) + zF\Delta\psi \approx RT\ln\left(\frac{C_B}{C_A}\right) + zF\Delta\psi \qquad (21.15)$$

where we assumed $\mu_B^* \approx \mu_A^*$ and $\gamma_\pm^A \approx \gamma_\pm^B$. For the transport to be passive

$$\Delta\bar{G} = RT\ln\left(\frac{C_B}{C_A}\right) + zF\Delta\psi < 0 \qquad (21.16)$$

Because both chemical and electrical effects enter the transport equation it is not sufficient that $C_B<C_A$ for the free energy change to be negative . The transport of charge must also be favorable.

- Active Transport: This type of transport occurs in order to maintain large concentration gradients across membranes. It is especially important to maintain electrical gradients across membranes and this is accomplished by keeping ion concentrations inside versus outside the membrane unequal. Therefore, transport of ions must out of necessity occur against a concentration gradient.
  - Typical active transport processes are the movement of sodium and potassium ions across a cell membrane against their respective concentration gradients. The electrostatic potential across a membrane results from unequal distribution of sodium, potassium, and chloride ions inside versus outside the cell. Typical ion concentrations are given in the table below:

Ion	Intracellular	Extracellular
Na+	15 mM	150 mM
K+	150 mM	5 mM
Cl-	10 mM	110 mM

  - The work required to reversibly move sodium ions from within the cell to the outside is given by the chemical potential difference

$$\Delta\bar{G}\left(Na^+ : in \to out\right) = \tilde{\mu}_{out} - \tilde{\mu}_{in} = \mu_{out}^* - \mu_{in}^* + RT\ln\left(\frac{a_{out}}{a_{in}}\right) + z\Im\left(\psi_{out} - \psi_{in}\right)$$
$$= RT\ln\left(\frac{a_{out}}{a_{in}}\right) + z\Im\Delta\psi \qquad (21.17)$$

- The term $RT\ln\left(\frac{a_{out}}{a_{in}}\right)$ involves the activities of the ions. For the activities we have $a_{out} = \gamma_{\pm}^{out} c_{out} \; and \; a_{in} = \gamma_{\pm}^{in} c_{in}$. Assume
- Assume for simplicity that $\gamma_{\pm}^{A} \approx \gamma_{\pm}^{B}$. Then equation 21.17 simplifies to:

$$\Delta\overline{G}\left(Na^{+} : in \to out\right) = RT\ln\left(\frac{c_{out}^{Na^{+}}}{c_{in}^{Na^{+}}}\right) + z\Im\Delta\psi \tag{21.18}$$

- Because for sodium the extracellular concentrationis much higher than the intracellular concentration $c_{out}^{Na^{+}} >> c_{in}^{Na^{+}}$, the first term on the right of equation 21.18 is positive. But to get the sign of $\Delta\overline{G}\left(Na^{+} : in \to out\right)$ we must also know the value $\Delta\psi = \psi_{out} - \psi_{in}$. A typical value is $\Delta\psi = +0.07V$.
- Using the data in the table above $\frac{c_{out}^{Na^{+}}}{c_{in}^{Na^{+}}} = \frac{\left[Na^{+}\right]_{out}}{\left[Na^{+}\right]_{in}} = \frac{150mM}{15mM} = 10$ and with $\Delta\psi$=0.07V, we find that at T=310K.

$$\begin{aligned}
&\Delta\overline{G}\left(Na^{+} : in \to out\right) = RT\ln(10) + z\Im(0.07V) \\
&= \left(8.31JK^{-1}mol^{-1}\right)(310K)\ln(10) + (+1)\left(96485Cmol^{-1}\right)(0.070V) \\
&= 5932Jmol^{-1} + 6754Jmol^{-1} = 12686Jmol^{-1}
\end{aligned} \tag{21.19}$$

This means that 12686 J of work must be performed to transport a mole of sodium ion from inside to the outside of the cell.

- Potassium transport from outside to the inside of the cell similarly must proceed against a concentration gradient. We similarly find

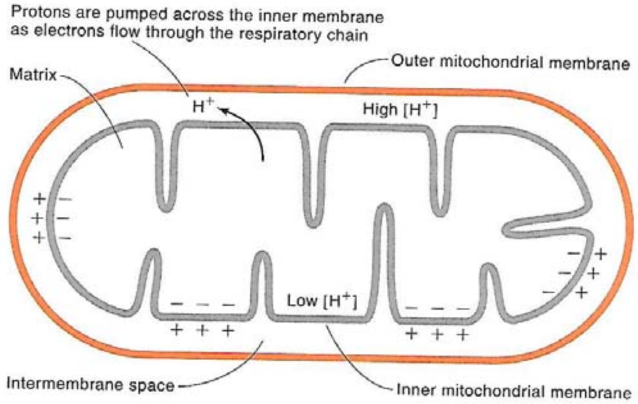
$$\begin{aligned}
&\Delta\tilde{G} = RT\ln\left(\frac{\left[K^{+}\right]_{in}}{\left[K^{+}\right]_{out}}\right) + \Im(-\Delta\psi) \\
&= (8.31J/mole)(310)\ln\left(\frac{150}{5}\right) + (96,485C/mole)(-0.07V) \\
&= 8.76kJ/mole - 6.75kJ/mole = 2.01kJ/mole
\end{aligned}$$

- In reality, a complex of membrane-associated proteins called the sodium-potassium pump transports 2 K^{+} ions into the cell for every three Na^{+} ions transported out of the cell. The total work required on a moles basis is

$$\begin{aligned}
&\Delta G_{T} = 3\Delta G_{in\to out}^{Na} + 2\Delta G_{out\to in}^{K} \\
&= (3moles)(12.7kJ/mole) + (2moles)(2kJ/mole) \approx 42kJ
\end{aligned}$$

D. Chemiosmotic Theory

- Chemiosmotic theory states that the source of work required to accomplish the oxidative phosphorylation of ADP to ATP is obtain from a transmembrane pH gradient.
- ADP is phosphorylated according to the equation $ADP + P_i \rightleftharpoons ATP$. Under standard conditions and at T=310K this requires about $\Delta G_{reac} \approx 31.3 kJmol^{-1}$.



- In the respiratory transport chain the flow of electrons is coupled to the "pumping" of protons from the inner membrane of the mitochondrion into the inter-membrane space.

- We can write the electrochemical potential of a proton inside the inner membrane of the mitochondrion:

$$\tilde{\mu}_{H^+}^{in} = \mu_{H^+}^{0,in} + RT\ln a_{H^+}^{in} + F\psi_{in} \approx \mu_{H^+}^{0,in} + RT\ln C_{H^+}^{in} + F\psi_{in} \tag{21.20}$$

- We can also write the electrochemical potential of a proton otside the inner membrane of the mitochondrion:

$$\tilde{\mu}_{H^+}^{out} = \mu_{H^+}^{0,out} + RT\ln a_{H^+}^{out} + F\psi_{out} \approx \mu_{H^+}^{0,out} + RT\ln C_{H^+}^{out} + F\psi_{out} \tag{21.21}$$

- The Gibbs energy that we obtain by moving a mole of protons from the inter-membrane space to the inner membrane region is obtained by simply subtracting 21.21 from 21.20:

$$\begin{aligned} \Delta\bar{G}_{H^+}(out \to in) &= \tilde{\mu}_{H^+}^{in} - \tilde{\mu}_{H^+}^{out} = RT\ln C_{H^+}^{in} - RT\ln C_{H^+}^{out} + F\psi_{in} - F\psi_{out} \\ &= 2.30RT\left(\log C_{H^+}^{in} - \log C_{H^+}^{out}\right) + F\left(\psi_{in} - \psi_{out}\right) \\ &= -2.30RT\left(pH_{in} - pH_{out}\right) + F\left(\psi_{in} - \psi_{out}\right) \\ &= -2.30RT\Delta pH + F\Delta\psi \end{aligned} \tag{21.22}$$

- Typical Values: At T=310K, ΔpH=0.5 and Δψ=-0.15V so the Gibbs energy change per mole of proton movement is:

$$\begin{aligned} &\Delta\bar{G}(out \to in) = -2.30RT\Delta pH + F\Delta\psi \\ &= (-2.30)\left(8.31JK^{-1}mol^{-1}\right)(310K)(0.5) + \left(96485Cmol^{-1}\right)(-0.15V) \\ &= -17.5kJmol^{-1} \end{aligned} \tag{21.23}$$

- It is observed that about four protons moves across the inner mitochondrial membrane for every ATP that is produced. Under standard conditions to phosphorylate ADP requires about 31.3kJmol^{-1}. Therefore the transport of four moles of protons provides over twice the Gibbs energy required to phosphorylate a mole of ADP.