CHEM 361A - Lecture 14 Activity Electrochemistry

In Class

1. The conversion of NADH to NAD⁺ releases two electrons which are eventually used to reduce molecular oxygen to water in the terminal respiratory chain:

 $\begin{aligned} \mathrm{NAD}^+ + \mathrm{H}^+ + 2\,\mathrm{e}^- &\longrightarrow \mathrm{NADH} \ E^{\leftrightarrow\prime} = -0.32 \ \mathrm{V} \\ &\frac{1}{2}\,\mathrm{O}_2 + 2\,\mathrm{H}^+ + 2\,\mathrm{e}^- &\longrightarrow \mathrm{H}_2\mathrm{O} \ E^{\leftrightarrow\prime} = 0.816 \ \mathrm{V} \end{aligned}$

What is the change in the standard biochemical Gibbs Free Energy as a pair of electrons pass through the terminal respiratory chain?

- 2. One way to prevent a buried iron pipe from rusting is to connect it with a piece of wire to a magnesium or zinc rod. What is the electrochemical principle for this action?
- 3. For the reaction

$$NAD^{+}(aq) + H_{3}O^{+}(aq) + 2e^{-} \longrightarrow NADH(aq)$$

 $E^{*'} = -0.320$ V at 25°C. Calculate the value of E' at pH = 1 and [NAD⁺]=[NADH]=1. Recall that the prime means that we are using the biochemical standard state meaning that m^* for H₃O⁺ is 1×10^{-7} . Assume $\gamma_{\pm} = 1$.

4. A sodium ion channel which transports Na⁺-ions across a cell membrane can be described by the following reaction:

$$Na_{outside}^{+} \longrightarrow Na_{inside}^{+} \qquad E^{*\prime} = -0.062 V$$

At equilibrium, if the $[Na^+_{outside}]=0.143$ M, what is $[Na^+_{inside}]$ at 37°C?

Homework

5. You have a electrochemical cell setup with the following Daniell Cell

$$\operatorname{Sn}(s)|\operatorname{Sn}^{2+}(aq)||\operatorname{Pb}^{2+}(aq)|\operatorname{Pb}(s)|$$

At $25^{\circ}C$, determine

- (a) E° (0.0113 V)
- (b) ΔG° (-2180.9 J mol⁻¹)

- (c) K (2.4)
- (d) The ratio of $[\operatorname{Sn}^{2+}]/[\operatorname{Pb}^{2+}]$ at equilibrium. Assume $\gamma_{\pm} = 1$ Recall that when writing a chemical reaction for redox chemistry that the anode half-cell reaction is the forward reaction, and the cathode half-cell reaction is the reverse reaction. Assume γ_{\pm} is the same for all ionic species. (2.4)
- 6. Calculate the EMF of the Daniell Cell below at 25°C. Assume $\gamma_{\pm} = 1.$ (0.010 V)

$$Mg(s)|Mg^{2+}(aq) (0.24 M)||Mg^{2+}(aq) (0.53 M)|Mg(s)|$$

7. Flavin Adenine Dinucleotide (FAD) participates in several biological redox reactions according to the half-reaction

$$FAD + 2 H^+ + 2 e^- \longrightarrow FADH_2$$

If the value of $E^{*'}$ of this reaction is -0.219 V at 25°C, and pH 7, calculate its reduction potential at this temperature and pH when the solution contains

- (a) 85% of the oxidized form (-0.197 V)
- (b) 15% of the oxidized form (-0.241 V)

For both cases, assume $\gamma_{\pm} = 1$.