CHEM465/865, 2006-3, 27th Sep., Dr. M. Eikerling, C9034, x4463

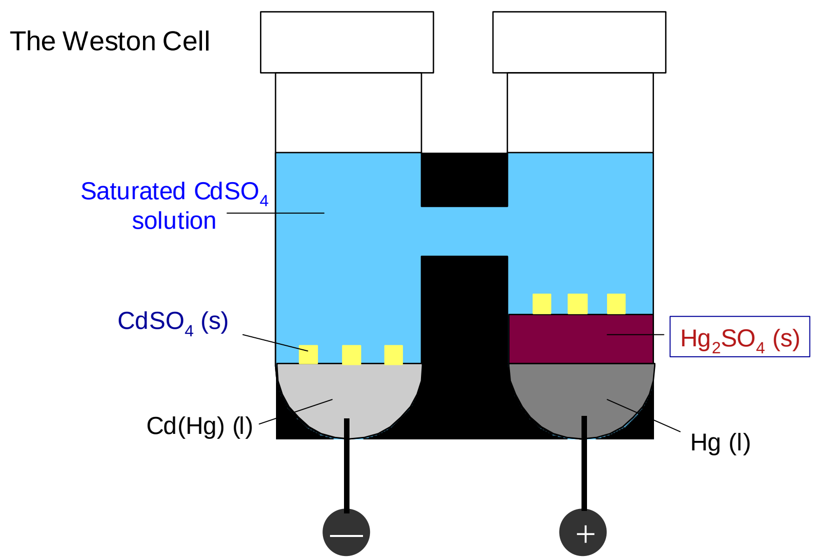
Exercise Series 2

Due date: Oct. 4, 2006

Ata Roudgar, aroudgar@sfu.ca, C8034, x3699

1. Write down explanations of the following terms or answers on the queries
   - (a) What is the EMF of a galvanic cell? Specify the relation between the maximum reversible work of a reaction and the EMF.
   - (b) Why can galvanic potentials between distinct phases not be measured?
   - (c) What are the properties of a good reference electrode?
   - (d) Specify the known “standard conditions” as complete as possible.
   - (e) What is an ideally polarizable electrode?

2. The **Weston cell**, invented by Edward Weston in 1893, is an electrochemical cell. Due to its highly stable voltage it is suitable as a laboratory standard for calibration of voltmeters. It was adopted as the Int. Standard for EMF in 1911.



The anode is an amalgam of cadmium with mercury, the cathode is of pure mercury, and the electrolyte is a solution of cadmium sulphate. The overall cell reaction is

$$\mathbf{Cd(Hg) + Hg_2SO_4(s) \leftrightarrow 2\,Hg(l) + Cd^{2+}(aq) + SO_4^{2-}(aq.)}$$

- (a) What are the half reactions of this cell?
- (b) Write the Nernst-equation for the cell reaction.
- (c) The EMF is $E = 1.0180$ **V (at 25°C)**. What is the corresponding reaction Gibbs free energy? What is the corresponding rate constant
- (d) The EMF given in (c) is not the standard EMF, but it is nevertheless very stable. Can you explain why (<u>hint</u>: you can assume that the solution remains saturated, what about other parameters)?

3. Consider the cell **Pt | H_2(g, 1 atm) | H^+(aq, a=1) | Fe^{3+}(aq),Fe^{2+} | Pt,** given that **Fe^{3+} + e^-** $\leftrightarrow$ **Fe^{2+}** and $E^0 = 0.771$ **V**.

(a) If the cell potential is $E = 0.712$ **V (at 25°C)**, what is the ratio of concentrations of Fe^{3+}(aq) and Fe^{2+}(aq)? Could you determine the absolute values of concentrations or just their ratio?

(b) What is the ratio of these concentrations if the cell potential is $E = 0.830$ **V (at 25°C)**?

4. Nernst equation demonstrates that the electrode potential depends upon concentration. A cell made of the same materials, but with different concentrations, will also produce a potential difference. Consider a cell

Cu | Cu^{2+} (0.001 M) || Cu^{2+} (1.00 M) | Cu

(a) What is standard potential of this cell?

(b) Write down the Nernst-equation (using for simplicity concentrations of ions in solution instead of activities). What is the number ν_e of electrons being transferred?

(c) Calculate E at 25°C for the specified concentrations.

5. Living cells maintain a small voltage drop across their membrane in its resting state due to the directed transport of sodium ions from inside to outside and the transport of potassium ions in the opposite direction (driven by pumping mechanisms). The inside of the cell is negative with respect to the outside. Consider a mammalian muscle cell with the internal and external ion concentrations:

outside	**inside**
$[K]_o$ = 2.5 mM	$[K]_i$ = 140 mM
$[Na]_o$ = 115 mM	$[Na]_i$ = 10 mM
$[Cl]_o$ = 140 mM	$[Cl]_i$ = 15 mM

(a) What are the equilibrium potentials for each of these ions?

(b) Calculate the total molar Gibbs free energy of reaction and the corresponding voltage across the cell membrane.