Homework 10

1. Consider a hydrogen electrode in HBr(aq) at 25°C operating at 1.45 bar. Estimate the change in the electrode potential when the solution is changed from 5.0 mmol L^{-1} to 25.0 $mmol^{-1}$.

2. Write the cell reactions and electrode half-reactions for the following cells: (a) $Ag(s)|AgNO_3(aq,b_L)||AgNO_3(aq,b_R)|Ag(s)$
(b) $Pt(s)|H_2(g,p_L)|HCl(aq)|H_2(g,p_R)|Pt(s)$
(c) $Pt(s)|K_3[Fe(CN)_6](aq),K_4[Fe(CN)_6](aq)||Mn^{2+}(aq),H^+(aq)|MnO_2(s)|Pt(s)$
(d) $Pt(s)|Cl_2(g)|HCl(aq)||HBr(aq)|Br_2(l)|Pt(s)$
(e) $Pt(s)|Fe^{3+}(aq),Fe^{2+}(aq)||Sn^{4+}(aq),Sn^{2+}(aq)|Pt(s)$
(f) $Fe(s)|Fe^{2+}(aq)||Mn^{2+}(aq),H^+(aq)|MnO_2(s)|Pt(s)$
Write the Nernst equations for each of the above cells.

3. Calculate the standard Gibbs energies at 25°C of the following reactions from the standard potential data in Data Section.
(a) $Ca(s) + 2\ H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$
(b) $2\ Ca(s) + 4\ H_2O(l) \rightarrow 2\ Ca(OH)_2 + 2\ H_2(g)$
(c) $Fe(s) + 2\ H_2O(l) \rightarrow Fe(OH)_2(aq) + H_2(g)$
(d) $Na_2S_2O_8(aq) + 2\ NaI(aq) \rightarrow I_2(s) + 2\ Na_2SO_4(aq)$
(e) $Na_2S_2O_8(aq) + 2\ KI(aq) \rightarrow I_2(s) + Na_2SO_4(aq) + K_2SO_4(aq)$
(f) $Pb(s) + Na_2CO_3(aq) \rightarrow PbCO_3(aq) + 2\ Na(s)$

4. Calculate the equilibrium constants of the following reactions at 25°C from standard potential data:
(a) $Sn(s) + Sn^{4+}(aq) \leftrightarrows 2\ Sn^{2+}(aq)$
(b) $Sn(s) + 2\ AgBr(s) \leftrightarrows SnBr_2(aq) + 2\ Ag(s)$
(c) $Fe(s) + Hg(NO_3)_2(aq) \leftrightarrows Hg(l) + Fe(NO_3)_2(aq)$
(d) $Cd(s) + CuSO_4(aq) \leftrightarrows Cu(s) + CdSO_4(aq)$
(e) $Cu^+(aq) + Cu(s) \leftrightarrows 2\ Cu^+(aq)$
(f) $3Au^{2+}(aq) \leftrightarrows Au(s) + 2Au^{3+}$

5. The standard potential of the cell $Ag(s)|AgI(s)|AgI(aq)|Ag(s)$ is +0.9509 at 25°C. Calculate (a) the molar solubility of AgI and (b) its solubility constant.

6. Devise a cell in which the overall reaction is $Pb(s) + Hg_2SO_4(s) \rightarrow PbSO_4(s) + 2\ Hg\ (l)$. What is its potential when the electrolyte is saturated with both salts at 25°C?

The solubility constants of Hg_2SO_4 and $PbSO_4$ are 6.6×10^{-7} and 1.6×10^{-8}, respectively.

7. Given that $\Delta_r G^{\varnothing} = -212.7$ kJ mol^{-1} for the reaction in the Daniell cell at 25°C, and $b(CuSO_4) = 1.0\times10^{-3}$ mol kg^{-1} and $b(ZnSO_4) = 3.0\times10^{-3}$ mol kg^{-1}, calculate (a) the ionic strengths of the solutions, (b) the mean activity coefficients in the compartments, (c) the reaction quotient, (d) the standard cell emf, and (e) the cell emf. (Take $\gamma_+ = \gamma_- = \gamma_\pm$ in the respective compartments).