Exercise 18.4

E, ΔG, & Concentration

Name: _____

Date: _____ Per: _____

EMF, Free Energy, & K

A positive cell potential ($E°_{cell}$) also referred to as a positive electromotive force (EMF) indicates a spontaneous chemical process (ΔG is negative). The available usable energy of the system decreases as the redox reaction occurs. Available energy (Gibbs energy) is related to EMF by the equation:

$$\Delta G° = -nFE°$$

where: n = the moles of electrons transferred in the reaction
F = Faraday's constant (the charge on 1 mole of e^-) = 96485 C/mol
E = electromotive force (recall 1V = 1 J/C)

A positive value of $E°$ results in a negative value of $G°$. Because $\Delta G° = -RT \ln K$, the formulas may be combined to get:

$$E° = \frac{RT}{nF} \ln K$$

1. Consider only the species (standard conditions)

   Ce^{4+}, Ce^{3+}, Fe^{2+}, Fe^{3+}, Fe, Mg^{2+}, Mg, Ni^{2+}, Sn

   in answering the following questions. Give reasons for your answers.

   a. Which is the strongest oxidizing agent? _____

   b. Which is the strongest reducing agent? _____

   c. Will iron dissolve in a 1.0 *M* solution of Ce^{4+}? _____

      (i) If so, will there be Fe^{2+}or Fe^{3+} ions resulting in the solution? _____

   d. Which of the species can be oxidized by $H^+(aq)$? _____

   e. Which of the species can be reduced by $H_2(g)$? _____

   f. Would you use Mg or Sn to reduce Fe^{3+} to Fe^{2+}? _____

2. Use the table of standard reduction potentials to pick a reagent that is capable of each of the following oxidations (under standard conditions in acid solution).

   a. Oxidize Hg to Hg_2^{2+} but not oxidize Hg_2^{2+} to Hg^{2+}: _____

   b. Oxidize Br^- to Br_2 by not oxidize Cl^- to Cl_2: _____

   c. Oxidize Mn to Mn^{2+} but not oxidize Ni to Ni^{2+}: _____

3. Chlorine dioxide which is produced by the reaction

   $$2\ NaClO_2(aq) + Cl_2(g) \rightarrow 2\ ClO_2(g) + 2\ NaCl(aq)$$

   has been tested as a disinfectant for municipal water treatment.

   a. Using reduction potential tables, calculate $E°$, $\Delta G°$, and K at 25°C for the production of ClO_2.

   b. One of the concerns in using ClO_2 as a disinfectant is that carcinogenic chlorate ion (ClO_3^-) might be a by-product. It can be formed from the reaction

      $$ClO_2(g) \rightleftarrows ClO_3^-(aq) + Cl^-(aq)$$

      Balance the equation for the decomposition of ClO_2.

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4. Use the half-reactions

   $PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$ $E° = -0.35$ V
   $Pb + 2e^- \rightarrow Pb$ $E° = -0.13$ V

   to calculate the value of the solubility product for $PbSO_4(s)$.

5. Estimate $E°$ for the half-reaction

   $$2\ H_2O + 2e^- \rightarrow H_2 + OH^-$$

   given the following values of $\Delta G_f°$: $H_2O(l) = -237$ kJ/mol, $H_2(g) = 0.0$, $OH^- = -157$ kJ/mol. Compare this value of $E°$ with the value of $E°$ give in the reduction potential table.

6. The amount of manganese in steel is determined by changing it to permanganate ion. The steel is first dissolved in nitric acid, producing Mn^{2+} ions. These ions are then oxidized to the deeply colored MnO_4^- ions by periodate ions (IO_4^-) in acid solution.

   a. Complete and balance an equation describing each of the above redox reactions.

   b. Calculate $E°$, $\Delta G°$, and K at 25°C for reaction.

7. Consider the galvanic cell based on the following half-reactions:

   $Zn^{2+} + 2e^- \rightarrow Zn$ $E° = -0.76$ V
   $Fe^{2+} + 2e^- \rightarrow Fe$ $E° = -0.44$ V

   a. Determine the overall cell reactions and calculate $E°_{cell}$.

   b. Calculate $\Delta G°$ and K for the cell reaction at 25°C.

   c. Calculate E_{cell} at 25°C when $[Zn^{2+}] = 0.10$ M and $[Fe^{2+}] = 1.0 \times 10^{-5}$ M.