**CHEM 121**
**Supplemental Questions for Electrochemistry**

1a. Balance the following redox reaction that takes place in <u>acidic</u> solution. Identify the oxidant and the reductant.

$$FeO_4^{2-} (aq) + Ti^{2+} (aq) \rightarrow Fe^{3+} (aq) + TiO_2 (s)$$

**$2\ FeO_4^{2-} (aq) + 3\ Ti^{2+} (aq) + 4\ H^+ (aq) \rightarrow 2\ Fe^{3+} (aq) + 3\ TiO_2 (s) + 2\ H_2O (l)$**

**$FeO_4^{2-}$ gets reduced, so it is the oxidant**

**$Ti^{2+}$ gets oxidized, so it is the reductant**

b. Balance the following redox reaction that takes place in <u>basic</u> solution. Identify the chemical species that was reduced and the chemical species that was oxidized.

$$SeO_4^{2-} (aq) + S_2O_4^{2-} (aq) \rightarrow SeO_3^{2-} (aq) + SO_3^{2-} (aq)$$

**$SeO_4^{2-} (aq) + S_2O_4^{2-} (aq) + 2\ OH^- (aq) \rightarrow SeO_3^{2-} (aq) + SO_3^{2-} (aq) + H_2O (l)$**

**$SeO_4^{2-}$ is reduced.**

**$S_2O_4^{2-}$ is oxidized**

2. An electrochemical cell is constructed of one half-cell in which a silver wire is placed into a 1.00 m aqueous solution of $AgNO_3$, and the other half-cell consists of a zinc electrode in an aqueous solution of $Zn(NO_3)_2$ that is also is 1.00 m.

a. Write the balanced chemical equation for the spontaneous reaction that occurs in this cell under standard conditions.

**Standard reduction potentials for the half-reactions are**

| | |
|---|---|
| **$Ag^+ (aq) + e^- \rightarrow Ag (s)$** | **$E^0 = +0.80$ V** |
| **$Zn^{2+} (aq) + 2\ e^- \rightarrow Zn (s)$** | **$E^0 = -0.763$ V** |

**To get a spontaneous reaction we would need to flip the second reduction. Thus Zn will be oxidized and it will be the anode.**

| | |
|---|---|
| **$Ag^+ (aq) + e^- \rightarrow Ag (s)$** | **cathode (reduction)** |
| **$Zn (s) \rightarrow Zn^{2+} (aq) + 2\ e^-$** | **anode (oxidation)** |

**Balance the number of electrons and add to get overall net ionic equation.**

$$\begin{array}{l} \mathbf{2\ Ag^{+}\ (aq) + 2\ e^{-} \rightarrow 2\ Ag\ (s)} \\ \underline{\mathbf{Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2\ e^{-}}} \\ \mathbf{2\ Ag^{+}\ (aq) + Zn(s) \rightarrow 2\ Ag\ (s) + Zn^{2+}\ (aq)} \end{array}$$

**The overall chemical reaction is**

$$\mathbf{2\ AgNO_3\ (aq) + Zn\ (s) \rightarrow 2\ Ag\ (s) + Zn(NO_3)_2\ (aq)}$$

b. What is $E^0$ for this cell?

$$E^0_{cell} = E^0_{cathode} - E^0_{anode} = +0.80\ \text{V} - (-9.763\ \text{V}) = +\ 1.56\ \text{V}$$

**$E^0$ for this cell is +1.56 V.**

c. What is $\Delta G^0$ for this cell?

$$\Delta G^0 = -n \cdot F \cdot E^0 = -2(96485.309\ C \cdot mole^{-1})(+1.56\ J \cdot C^{-1})$$

$$\Delta G^0 = -301.\ kJ \cdot mole^{-1}$$

**For this cell $\Delta G^0$ is -301. k J·mole$^{-1}$.**

d. Write this cell in line notation (the short-hand way discussed in class).

**Zn | $Zn(NO_3)_2$ (aq) || $AgNO_3$ (aq) | Ag**

e. What would be E for the cell at 35.0 °C when $[Ag^{+}]$ is 0.50 m and $[Zn^{2+}]$ = 1.00 m?

$$E = E^0 - \frac{RT}{nF}\ln Q = +1.56V - \frac{\left(8.314510\frac{J}{K \cdot mole}\right)(308.1_5 K)}{(2)\left(96485.309\frac{C}{mole}\right)}\ln\left(\frac{[Zn^{2+}]}{[Ag^{+}]^2}\right)$$

$$E = +1.56V - 1.327_{72}x10^{-2}\ln\left(\frac{1.00}{(0.50)^2}\right)V$$

$$E = +1.53V$$

**Under the stated conditions, this cell has a potential of + 1.53 V.**

3. We have learned that the ionization energy decreases down a group. So, for the elements of Group 1, it should be easier to remove an electron from K than it is to remove an electron from Na and this is easier than removing an electron from Li. In other words, ΔG for the reaction: M (g) → $M^+$ (g) + $e^-$ (where M is Li, Na, or K) should be more negative for K than Na, which is more negative than that of Li.

Consult the table of standard reduction potentials, and give the order of ΔG that it predicts for the reaction M(s) → $M^+$ (aq) + $e^-$ (where M is Li, Na, or K). What have we forgotten to take into account that might fix the apparent incongruity between the order predicted by the ionization energies and that predicted by the $E^0$?

**The $E^0$ (and therefore $\Delta G^0$) for the reaction M(s) → $M^+$ (aq) + $e^-$ (where M is Li, Na, or K) is in the opposite order than that shown in the table. So, Li has the most negative $\Delta G^0$, followed by K and with Na being the least negative $\Delta G^0$.**

**The problem is that the ionization energies are measured in the gaseous state; while the $E^0$ are measured in condensed states (fancy physics term for solids and liquids). In both the solid and the solution we need to account for the interactions between the particles (in the solid this is the metallic bonding, while in solution it is primarily an ion-dipole interaction between the ion and the polar water). These will affect ΔH. We don't expect ΔS to be very different between Li, Na and K because the reactions are identical. So, the difference in $\Delta G^0$ must arise from ΔH (remember, ΔG = ΔH – TΔS).**

*FYI The difference between the ionization energy and $E^0$ is attributed to $\Delta H_{hydration}$. Because $Li^+$ is so small the water molecules can not pack around it has effectively as with the larger $Na^+$ and $K^+$.*

4. An electrochemical cell is constructed consisting of a saturated calomel electrode (SCE) in one compartment and a silver wire coated with $Ag_2CrO_4$ in the other compartment. The SCE is an electrode that is composed of liquid mercury in contact with a saturated solution of $Hg_2Cl_2$ (calomel), which is also saturated with KCl. The SCE is described by the half-reaction that is shown below, and it has $E^0$ of +0.2412 V versus SHE.

$$Hg_2Cl_2\ (s) + 2\ e^- \leftrightharpoons 2\ Hg\ (l) + 2\ Cl^-\ (aq)$$

The $E^0$ for the following half-reaction is +0.466 V relative to SHE.

$$Ag_2CrO_4\ (s) + 2\ e^- \leftrightharpoons 2\ Ag\ (s) + CrO_4^{2-}\ (aq)$$

a. Combine the two half-reactions to get the overall balanced chemical equation for the cell. Calculate $E^0$ and $\Delta G^0$ for this cell (25.0 °C, $[CrO_4^{2-}]$ = 1.00 M).

**For a spontaneous reaction we need to reverse the first reaction making the Hg electrode the anode (*Hg is oxidized*).**

$$2\ Hg\ (l) + 2\ Cl^-\ (aq) \rightleftharpoons Hg_2Cl_2\ (s) + 2\ e^-$$
$$Ag_2CrO_4\ (s) + 2\ e^- \rightleftharpoons 2\ Ag\ (s) + CrO_4^{2-}\ (aq)$$
$$2\ Hg\ (l) + 2\ Cl^-\ (aq) + Ag_2CrO_4\ (s) + 2\ e^- \rightleftharpoons 2\ Ag\ (s) + CrO_4^{2-}\ (aq) + Hg_2Cl_2\ (s)$$

$$E^0_{cell} = E^0_{cathode} - E^0_{anode} = +0.466\ V - (+0.2412\ V) = +0.225\ V$$

$$\Delta G^0 = -nFE^0$$
$$\Delta G^0 = -(2)\left(9.6485309x104\frac{C}{mole}\right)\left(+0.225\frac{J}{C}\right)$$
$$\Delta G^0 = -43.4\frac{kJ}{mole}$$

**For this reaction $E^0$ is +0.225 V and $\Delta G^0$ is -43.4 kJ/mole.**

b. Write the Nernst equation for this cell. Assume that all of the concentrations associated with the SCE are 1.00 m.

*Start with the general Nernst equation, and then substitute specific values (n = 2, and the only chemical species that appear will be $CrO_4^{2-}$ and $Cl^-$, because they are the only ones in solution).*

$$E = E^0 - \frac{RT}{nF}\ln(Q)$$
$$E = E^0 - \frac{RT}{2F}\ln\left(\frac{[CrO_4^{2-}]}{[Cl^-]^2}\right)$$

*Since the $[Cl^-]$ is 1.00 m, we can remove it from the Nernst equation for this cell. This leaves with the following Nernst equation for the cell.*

$$E = E^0 - \frac{RT}{2F}\ln([CrO_4^{2-}])$$

c. If the coated silver wire is placed in a solution at 25.0 °C in which $[CrO_4^{2-}]$ is $1.00x10^{-5}$ M, what is the expected cell potential?

*Start with the Nernst equation for the cell, found in part b, and substitute in the known values*

$$E = E^0 - \frac{RT}{2F}\ln\left([CrO_4^{2-}]\right) = +0.225V - \frac{\left(8.314510 J\cdot K^{-1}\cdot mole^{-1}\right)\left(298.1_5 K\right)}{(2)\left(96485.309 C\cdot mole^{-1}\right)}\ln\left(1.00x10^{-5}\right)$$

$$E = +0.373V$$

**Under these conditions the cell potential is +0.373 V.**

d. Using data from this problem and the half-reaction shown below ($E^0 = +0.7994$), calculate $K_{sp}$ for $Ag_2CrO_4$.

$$Ag^+ (aq) + e^- \leftrightharpoons Ag (s)$$

*Find $\Delta G^0$ for the reaction* $Ag_2CrO_4$ (s) + 2 $e^-$ ⇋ 2 Ag (s) + $CrO_4^{2-}$ (aq).

$$\Delta G^0 = -nFE^0 = -2\left(96485.309\frac{C}{mole}\right)\left(+0.466\frac{J}{C}\right) = +89.9_2\frac{kJ}{mole}$$

*Calculate $\Delta G^0$ for the reaction* Ag (s) ⇋ $Ag^+$ (aq) + $e^-$.

$$\Delta G^0 = -nFE^0 = -1\left(96485.309\frac{C}{mole}\right)\left(-0.7994\frac{J}{C}\right) = +77.13_0\frac{kJ}{mole}$$

*Combining these reactions and using Hess's Law gives $\Delta G^0$ for the desired reaction.*

| | |
|---|---|
| **$Ag_2CrO_4$ (s) + 2 $e^-$ ⇋ 2 Ag (s) + $CrO_4^{2-}$ (aq)** | **1 mole(–$89.9_2$ kJ/mole)** |
| **2 Ag (s) ⇋ 2 $Ag^+$ (aq) + 2 $e^-$** | **2 mole(+$77.13_0$ kJ/mole)** |
| **$Ag_2CrO_4$ (s) ⇋ 2 $Ag^+$ (aq) + $CrO_4^{2-}$ (aq)** | **+$64.3_4$ kJ/mole** |

*From $\Delta G^0$ for the desired reaction, calculate K.*

$$\Delta G^0 = -RT\, ln\, K$$

$$ln\, K = -\frac{\Delta G^0}{RT} = -\frac{+64.3_4 x10^3\ J\cdot mole^{-1}}{\left(8.31447\ J\cdot K^{-1}\cdot mole^{-1}\right)\left(298.15\ K\right)} = -25.9_5$$

$$K = e^{-25.9_5} = 5._3 x10^{-12}$$

**The $K_{sp}$ for this $Ag_2CrO_4$ is $5.x10^{-12}$.**