Chem 10123, Quiz 8 **Answer Key**

April 8, 2020

1. (2 points) Write balanced ionic equations for the half reactions that occur at the anode and cathode for the electrolysis of an aqueous solution of $Cu(NO_3)_2$.

Anode:

$2\ H_2O \longrightarrow O_{2(g)} + 4\ H^+ + 4\ e^-$

Cathode:

$Cu^{2+}{}_{(aq)} + 2\ e^- \longrightarrow Cu_{(s)}$ see note below*

2. Consider the following galvanic cell in which the volume of each half-cell is 0.500 L.

$$Pb_{(s)}\ |\ PbO_{(s)}\ |\ OH^-\ (3.00\ M)\ ||\ Au^{3+}\ (1.00\ M)\ |\ Au_{(s)}$$

(a) (3 points) Write balanced chemical equations for the two half-reactions and for the overall cell reaction.

Anode:

$Pb_{(s)} + 2\ OH^-{}_{(aq)} \longrightarrow PbO_{(s)} + H_2O + 2\ e^-$ E° = - 0.58 v

Cathode:

$Au^{3+}{}_{(aq)} + 3\ e^- \longrightarrow Au_{(s)}$ E° = 1.50 v

Cell:

$3\ Pb_{(s)} + 6\ OH^-{}_{(aq)} + 2\ Au^{3+}{}_{(aq)} \longrightarrow 3\ PbO_{(s)} + 3\ H_2O + 2\ Au_{(s)}$

(b) (5 points) Determine the ***cell potential*** (E_{cell}) for the cell as described above.

$E°_{cell} = E°_{red} + E°_{oxid} = 1.50\ v + (0.58\ v) = 2.08\ v$

$E_{cell} = E°_{cell} - (0.0592/n) \log Q$

$Q = 1 / [OH^-]^6 [Au^{3+}]^2 = 1 / (3.00)^6 (1.00)^2 = 0.001372$

$E_{cell} = 2.08\ v - (0.0592/6) \log(0.001372) = 2.08 - (-0.028) = 2.11\ v$

*Credit was also given for the possible reduction of NO_3^- instead of Cu^{2+}:

$NO_3^- + 4\ H^+ + 3\ e^- \longrightarrow NO + 2\ H_2O$ E° = 0.96 v

Although this reduction has a higher potential than Cu^{2+}, it requires an acidic solution (to supply the H^+ reactant). $Cu(NO_3)_{2(aq)}$ is neutral, so the Cu^{2+} reduction actually occurs at the cathode.

2. continued…..

(c) (5 points) **SHOW ALL WORK.** If current is drawn from the above cell at a constant rate of 0.50 amp, determine the pH of the solution in the Pb half-cell after 72 hours.

(0.50 amp) (72 hr) (3600 sec / hr) = 129,600 amp·sec

(129,600 amp·sec) (1 coul / amp·sec) (1 mole e^- / 96,485 coul) = 1.343 mole e^-

(1.343 mole e^-) (2 mole OH^- / 2 mole e^-) = 1.343 mole OH^- consumed

initial mole OH^- = (0.500 L) (3.00 mole/L) = 1.50 mole

OH^- remaining = 1.50 mole - 1.343 mole = 0.157 moles OH^-

$[OH^-]$ = 0.157 mole / 0.50 L = 0.314 M

pOH = - log(0.314) = 0.503 pH = 13.50

3. (5 points) **SHOW ALL WORK.** Use appropriate electrochemical data to determine the ***formation constant*** **(K_f)** for $AuCl_4^-{}_{(aq)}$. ***Include balanced chemical equations for all relevant reactions***.

$Au^{3+}{}_{(aq)} + 3\,e^- \longrightarrow Au_{(s)}$ E°_{red} = 1.50 v

$Au_{(s)} + 4\,Cl^-{}_{(aq)} \longrightarrow AuCl_4^-{}_{(aq)} + 3\,e^-$ E°_{oxid} = - 1.00 v

$Au^{3+}{}_{(aq)} + 4\,Cl^-{}_{(aq)} \rightleftharpoons AuCl_4^{2-}{}_{(aq)}$

E°_{cell} = 1.50 - 1.00 = 0.50 v

log K_f = n E°_{cell} / 0.0592 = 3 (0.50) / 0.0592 = 25.33

K_f = 2.2 x 10^{25}