# AP Chemistry
# Electrochemistry Sample Problems 2

1. The following oxidation-reduction reaction is spontaneous:

$$Cr_2O_7^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + 6I^-{}_{(aq)} \rightarrow 2Cr^{3+}{}_{(aq)} + 3I_{2(s)} + 7H_2O_{(l)}$$

A solution containing $K_2Cr_2O_7$ and $H_2SO_4$ is poured into one beaker, and a solution of KI is poured into another. A salt bridge is used to join the beakers. A metallic conductor that will not react with either solution (such as platinum foil) is suspended in each solution, and the two conductors are connected with wires through a voltmeter or some other device to detect an electric current. The resultant voltaic cell generates an electric current. Indicate the reaction occurring at the anode, the reaction at the cathode, the direction of electron and ion migrations, and the signs of the electrodes.

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ reduction, cathode,

$6I^-(aq) \rightarrow 3I_2(s) + 6e^-$ Oxidation, anode, negative electrode

electrons flow from anode to cathode

Cations move towards cathode / anions move towards anode

Positive electrode

2. For the voltaic cell $Zn|Zn^{2+}||Cu^{2+}|Cu$ $E^o_{cell} = 1.10V$ and the Zn electrode is the anode. Given that the standard reduction potential of $Zn^{2+}$ is $-0.76V$, calculate the $E^o_{red}$ for the reduction of $Cu^{2+}$ to Cu.

$E^o_{cell} = E^o_{red}(\text{cathode}) - E^o_{red}(\text{anode})$ $\quad 1.10V = E^o_{red}(\text{cathode}) - (-0.76V)$

$E^o_{red}(\text{cathode}) = 1.10V - 0.76V = \boxed{0.34V}$

3. Using a table of standard reduction potentials, calculate the standard emf for the cell reaction given in question 1.

$$Cr_2O_7^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + 6I^-{}_{(aq)} \rightarrow 2Cr^{3+}{}_{(aq)} + 3I_{2(s)} + 7H_2O_{(l)}$$

$I_2 \rightarrow I^- = +0.54V$

$Cr_2O_7^{2-} \rightarrow Cr^{3+} = +1.33V$

Cathode $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

anode $6I^-(aq) \rightarrow 3I_2(s) + 6e^-$

$E^o_{cell} = 1.33V - 0.54V = \boxed{0.79V}$

Note this value is not changed by stoichiometry

4. A voltaic cell is based on the following two standard half-reactions:

$Cd^{2+}{}_{(aq)} + 2e^- \rightarrow Cd_{(s)}$

$Sn^{2+}{}_{(aq)} + 2e^- \rightarrow Sn_{(s)}$

Using a table of SRP, determine (a) the half-reactions that occur at the cathode and the anode, and (b) the standard cell potential.

$E^o_{red}(Cd^{2+}/Cd) = -0.403V$ $\quad E^o_{red}(Sn^{2+}/Sn) = -0.136V$

Sn reduction occurs at the cathode

Cd oxidation occurs at the anode

$E^o_{cell} = (-0.136V) - (-0.403V) = \boxed{0.267V}$

5. Which of the following species is the strongest oxidizing agent: $NO_3^-{}_{(aq)}$, $Ag^+{}_{(aq)}$, $Cr_2O_7^{2-}{}_{(aq)}$?

$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$ $\quad E^o_{red} = +0.96V$

$Ag^+(aq) + e^- \rightarrow Ag(s)$ $\quad E^o_{red} = +0.80V$

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ $\quad E^o_{red} = +1.33V$

[$Cr_2O_7^{2-}$ is the Strongest Oxidizing Agent]

6. Using standard reduction potentials, determine whether the following reactions are spontaneous under standard conditions:

$$Cu_{(s)} + 2H^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + H_{2(g)}$$

$$Cl_{2(g)} + 2I^-_{(aq)} \rightarrow 2Cl^-_{(aq)} + I_{2(s)}$$

$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$ $E^\circ_{red} = 0V$

$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$ $E^\circ_{red} = +0.34V$

$0V - (0.34V) = -0.34V$ Not spontaneous

$Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$ $E^\circ_{red} = +1.36V$

$2I^-_{(aq)} \rightarrow I_{2(s)} + 2e^-$ $E^\circ_{red} = +0.54V$ $1.36 - 0.54 = +0.82V$ Spontaneous

7. a. Use standard reduction potentials to calculate the standard free-energy change, $\Delta G^\circ$, for the following reaction:

$$4Ag_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 4Ag^+_{(aq)} + 2H_2O_{(l)}$$

$E^\circ_{cell} = 1.23V - 0.80V = 0.43V$

b. Suppose the reaction in part "a" were written as

$$2Ag_{(s)} + ½\,O_{2(g)} + 2H^+_{(aq)} \rightarrow 2Ag^+_{(aq)} + H_2O_{(l)}$$

What are the values of E° and $\Delta G^\circ$ when the reaction is written this way?

a. $O_{2}(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ $E^\circ_{red} = +1.23V$ red

$4Ag(s) \rightarrow 4Ag^+(aq) + 4e^-$ $E^\circ_{red} = +0.80V$ oxi

$\Delta G^\circ = -nFE^\circ = -(4)(96,500\ J/V\text{-}mol)(+0.43V) = \underline{-170kJ/mol}$

b. $E^\circ_{cell}$ doesn't change $(=0.43V)$ but $\Delta G^\circ = -(2)(96,500\ J/V\text{-}mol)(+0.43V) = \underline{-83kJ/mol}$

8. Calculate the emf at 298K generated by the cell described in question 1 when $[Cr_2O_7^{2-}] = 2.0M$, $[H^+] = 1.0M$, $[I^-] = 1.0M$, and $[Cr^{3+}] = 1.0x10^{-5}M$:

$$Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} + 6I^-_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 3I_{2(s)} + 7H_2O_{(l)}$$

$$Q = \frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}[I^-]^6} = \frac{(1.0\times10^{-5})^2}{(2.0)(1.0)^{14}(1.0)^6} = 5.0\times10^{-11}$$

$$E = 0.79V - \frac{0.0592V}{6}\log(5.0\times10^{-11})$$

$$= 0.79 - \frac{0.0592V}{6}(-10.30) = \boxed{0.89V}$$

9. If the voltage of a Zn-H$^+$ cell is 0.45V at 25°C when $[Zn^{2+}] = 1.0M$ and $P(H_2) = 1atm$, what is the concentration of H$^+$?

$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

$$0.45 = 0.76 - \frac{0.0592}{2}\log\frac{[Zn^{2+}]P_{H_2}}{[H^+]^2} = 0.76 - \frac{0.0592}{2}\log\frac{1.0}{[H^+]^2}$$

$$[H^+] = 10^{-5.2} = \boxed{6\times10^{-6}M}$$

10. Consider a cell with one compartment consisting of a strip of nickel metal immersed in a 1.00M solution of $Ni^{2+}_{(aq)}$ and the other compartment also with a nickel metal electrode and a $1.00x10^{-3}M$ solution of $Ni^{2+}_{(aq)}$. The two compartments are connected by a salt bridge and by and external wire with a voltmeter. Calculate the cell potential of this system. $E^\circ_{cell} = 0$ but this is NOT Standard Conditions

Anode $Ni(s) \rightarrow Ni^{2+}(aq;\text{dilute}) + 2e^-$

Cathode $Ni^{2+}(aq;\text{concen}) + 2e^- \rightarrow Ni(s)$

$$E = 0 - \frac{0.0592}{2}\log\frac{1.00\times10^{-3}M}{1.00M} = \boxed{+0.0888V}$$

11. Using a table of standard reduction potentials, calculate the equilibrium constant for the oxidation of $Fe^{2+}$ by $O_2$ in acidic solution, according to the following reaction:

$$O_{2(g)} + 4H^+_{(aq)} + 4Fe^{2+}_{(aq)} \rightarrow 4Fe^{3+}_{(aq)} + 2H_2O_{(l)}$$

reduction $O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O(l)$ $E^\circ_{red} = +1.23V$

Oxidation $4Fe^{2+}(aq) \rightarrow 4Fe^{3+}(aq) + 4e^-$ $E^\circ_{red} = +0.77V$

$E^\circ = 1.23 - 0.77 = 0.46V$ $n = 4$

$$E^\circ_{cell} = \frac{0.025693V}{n}\ln K_{eq} \quad \ln K_{eq} = \frac{(4)(0.46V)}{0.025693V} = 71.61 \quad K_{eq} = e^{71.61} = \underline{1.3\times10^{31}}$$

# AP Chemistry
# Oxidation-Reduction Example Problems

1. Assign oxidation numbers to all the atoms in the following compounds and ions:

   a. $Na_2SO_4$ $Na = 1+$ $O = 2-$ $S = +6$
   b. $CuCl$ $Cl = 1-$ $Cu = 1+$
   c. $SO_3^{2-}$ $O = 2-$ $S = +4$
   d. $Na_2S_2O_3$ $O = -2$ $Na = +1$ $S = +2$
   e. $S_4O_6^{2-}$ $O = -2$ $S = +2.5$

2. Determine whether Fe is oxidized or reduced during the following reactions:

   a. $2Fe + 3/2\ O_2 + xH_2O \rightarrow Fe_2O_3 \bullet xH_2O$ (Rust) Oxidized
   b. $FeO + CO \rightarrow Fe + CO_2$ Reduced
   c. $2Hg + 2Fe^{3+} + 2Cl^- \rightarrow Hg_2Cl_2 + 2Fe^{2+}$ Reduced

3. Balance the following redox reaction by the ion-electron (half-reaction) method:

   a. $Cu + HNO_3 \rightarrow Cu^{2+} + NO_2$ (in acidic solution)
   b. $H_2C_2O_4 + MnO_4^- \rightarrow Mn^{2+} + CO_2$ (acidic solution)

4. Balance the following redox reaction involving bromine in basic solution using the ion-electron method:

   a. $Br_{2(aq)} \rightarrow BrO_3^-{}_{(aq)} + Br^-{}_{(aq)}$
   b. $P_4 \rightarrow PH_3 + HPO_3^{2-}$

3a. $Cu \rightarrow Cu^{2+}$ $HNO_3 \rightarrow NO_2$

$H^+ + HNO_3 \rightarrow NO_2 + H_2O$

$Cu \rightarrow Cu^{2+} + 2e^-$ $e^- + H^+ + HNO_3 \rightarrow NO_2 + H_2O$

add $2e^- + 2H^+ + 2HNO_3 \rightarrow 2NO_2 + 2H_2O$

[$Cu + 2H^+ + 2HNO_3 \rightarrow Cu^{2+} + 2NO_2 + 2H_2O$]

Oxidation

4a. $Br_2 \rightarrow BrO_3^-$

$Br_2 \rightarrow 2BrO_3^-$

$6H_2O + Br_2 \rightarrow 2BrO_3^-$

$6H_2O + Br_2 \rightarrow 2BrO_3^- + 12H^+ + 10e^-$

$12OH^- + 6H_2O + Br_2 \rightarrow 2BrO_3^- + 12H^+ + 12OH^- + 10e^-$

$12OH^- + Br_2 \rightarrow 2BrO_3^- + 6H_2O + 10e^-$

$12OH^- + Br_2 \rightarrow 2BrO_3^- + 6H_2O + \cancel{10e^-}$

Reduction

$Br_2 \rightarrow Br^-$

$Br_2 \rightarrow 2Br^-$

$2e^- + Br_2 \rightarrow 2Br^-$

$5\times(2e^- + Br_2 \rightarrow 2Br^-) =$

add

$10e^- + 5Br^2 \rightarrow 10Br^-$

$$12OH^- + 6Br_2 \rightarrow 2BrO_3^- + 10Br^- + 6H_2O$$

3b. $5H_2C_2O_4 + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

4b. $P_4 + 4OH^- + 2H_2O \rightarrow 2PH_3 + 2HPO_3^{2-}$

Review Questions

#1

$$H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2e^-$$

$$2Ag^+_{(aq)} + 2e^- \longrightarrow 2Ag_{(s)}$$

$$2Ag^+_{(aq)} + H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2Ag_{(s)}$$

#2 Chlorine is reduced (cathode)

$E^\circ_{cell} = E^\circ_{cath} - E^\circ_{anode}$ Note: cell potential does not depend on stoichiometry

$0.35V = 1.36V - (X)$

$[X = 1.01V]$ $Pu^{4+} + e^- \rightarrow Pu^{3+}$

#3

a. Fe $Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$ $E^\circ_{ox} = +0.440$ yes. Reducing agent

b. Ag $Ag_{(s)} \rightarrow Ag^+_{(aq)} + 1e^-$ $E^\circ_{ox} = -0.800$ No.

c. Cu $Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$ $E^\circ_{ox} = -0.340$ NO.

d. Sn $Sn_{(s)} \rightarrow Sn^{2+}_{(aq)} + 2e^-$ $E_{ox} = +0.137$ yes Oxidizing Agent

#4 a) $O_2$ most highly reducible

b) $H_2O$ $E^\circ = -1.23V$ (highly oxidizable)

c) $O_2$ $E^\circ = +1.23V$

d) $Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$ $E^\circ_{red} = +0.13V$

$Zn \longrightarrow Zn^{2+} + 2e^-$ $E^\circ_{ox} = +0.76V$

$E^\circ = 0.89V$

$Zn + Sn^{4+} \longrightarrow Sn^{2+} + Zn^{2+}$

#5 $E^\circ_{cell} = \frac{RT}{nF} \ln K_{eq}$ $E^\circ_{cell} = +0.771V - +0.695V = .076V$

$n = 2e^-$

$$.076V = \frac{(8.314\ J/molK)(298K)}{(2)(96485\ C/mol)} \ln K_{eq}$$

$\ln K_{eq} = 5.92$ $K_{eq} = e^{5.92} = \boxed{3.72 \times 10^2}$

#6 a) $Al^{3+} + 3e^- \longrightarrow Al$ $\frac{-6.50 \times 10^3 C}{-1.602 \times 10^{-19} C/e} = 4.057 \times 10^{22} e^- \left(\frac{1\ Al}{3e^-}\right) = 1.35 \times 10^{22} Al$

$\text{mol Al} = \frac{1.35 \times 10^{22}}{6.022 \times 10^{23}} = .022 \text{ mol Al } (26.98\ g/mol) = \boxed{.61g}$

b) $\frac{10g\ Al}{26.98\ g/mol} = .3706\ mol\ Al \times \frac{3e^-}{atom} = 1.11\ mol\ e^- \left(96,485\ C/mol\right)\left(\frac{1 sec}{30C}\right) = \boxed{59.5\ min}$

30 Amps

#7 Nernst equation

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592}{n} \log Q \qquad n=2$$

$$[H^+] = 10^{-pH} = 10^{-6.0}$$

$$E^{\circ}_{cell} = \underset{Ag}{+0.800V} - \underset{SHE}{0V} = 0.800V$$

$$E_{cell} = 0.800 - \frac{0.0592}{2} \underbrace{\log\left(\frac{(1\times10^{-6})^2}{(0.010)^2}\right)}_{-8}$$

$$= 0.800 - (-.2368)$$

$$= \boxed{1.04\,V}$$

#8 $K_{sp} = [Ag^+][Br^-] \qquad AgBr_{(s)} \rightleftharpoons Ag^+_{(aq)} + Br^-_{(aq)}$

$E^{\circ}_{Cu^{2+}/Cu} = +0.340\,V \qquad E^{\circ}_{Ag^+/Ag} = +0.800V$

Given Ag is Anode (oxidation)

$$2Ag_{(s)} + Cu^{2+}_{(aq)} \longrightarrow 2Ag^+_{(aq)} + Cu_{(s)} \qquad E^{\circ}_{cell} = +0.340 - (+0.800) = -.46$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592}{2} \log \frac{[Ag^+]^2}{[0.10]}$$

$$.28V = -.46V - \frac{0.0592}{2} \log \frac{[Ag^+]^2}{[0.10]}$$

$$-25 = \log \frac{[Ag^+]^2}{[0.10]} \qquad 1.0\times10^{-25} = \frac{[Ag^+]^2}{[0.10]} \qquad [Ag^+] = 1.0\times10^{-13}M$$

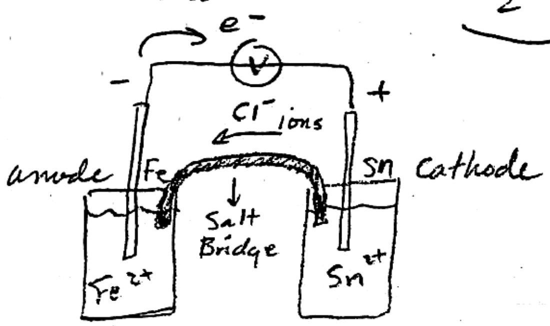
$$K_{sp} = [1.0\times10^{-13}M][\underset{Br^-}{.10M}] = 1\times10^{-14}$$

$K_{sp}$ published $= 5.0\times10^{-13}$

#9 $E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log K_{eq}$   $n = 2$   Fe is Oxidized
Sn is Reduced

$E^\circ_{cell} = (-0.14V) - (-0.44V) = \boxed{.30V = E^\circ_{cell}}$

$E_{cell} = .30V - \underbrace{\frac{.0591}{2} \log \frac{[1.0M]}{[10^{-3}M]}}_{.08865} = .21135V$




$Fe \rightarrow Fe^{2+} + 2e^-$   $Sn^{2+} + 2e^- \rightarrow Sn$

#10 $2.00 A = 2.00 \ C/s$   $20.0 min = 1200 sec$

$2.00 \ C/s \times 1200 \ sec = 2400 C$

$2400C / 96,485 \ C/mol = .02487 \ mol \ e^-$ / 2 electrons per atom

$.0124$ mol Cu reduced $\times 63.546 \ g/mol = \boxed{.790 g \ Cu}$

#11 $Cu^{2+} + 2e^- \rightarrow Cu$   $E^\circ_{red} = +0.34V$

$Pb^{2+} + 2e^- \rightarrow Pb$   $E^\circ_{red}$ $-0.13$

$Cu^{2+} + Pb \longrightarrow Cu + Pb^{2+}$   $E^\circ_{cell} = 0.34V - (-0.13V) = \boxed{+.47V}$

Precipitate will <u>increase</u> cell potential because it decreases $Pb^{2+}$ ion Disrupting equilibrium

#12 $4H_2O_{(l)} + 2MnO_4^-{}_{(aq)} + 6I^-_{(aq)} \rightarrow 3I_{2(s)} + 2MnO_{2(s)} + 8OH^-_{(aq)}$

#13 $10I^-_{(aq)} + 2MnO_4^-{}_{(aq)} + 16H^+_{(aq)} \rightarrow 5I_{2(s)} + 2Mn^{2+}_{(aq)} + 8H_2O_{(l)}$