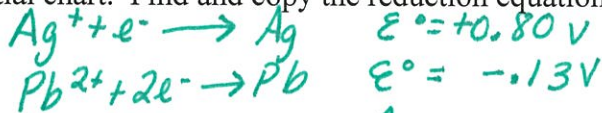


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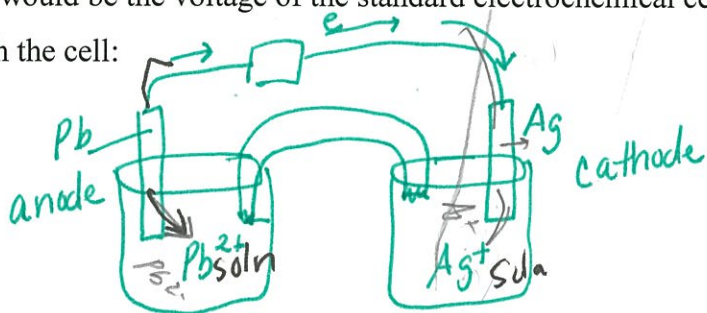
18 • Electron Transfer Reactions

A VISIT TO ELECTROCHEMISTRYLAND

Consider the reduction potential chart. Find and copy the reduction equations for $\text{Ag}^+ \rightarrow \text{Ag}^\circ$ and $\text{Pb}^{2+} \rightarrow \text{Pb}^\circ$.



- Which metal ion has the greater reduction potential? Ag
- If these two metals (and their solutions) were used to create a galvanic cell, which metal would be the anode? Pb smaller \mathcal{E}° value
- Write the reaction at the anode: $\text{Pb} \rightarrow \text{Pb}^{2+} + 2e^-$
- Write the reaction at the cathode: $\text{Ag}^+ + e^- \rightarrow \text{Ag}$
- What is the overall reaction? $2\text{Ag}^+ + \text{Pb} \rightarrow \text{Pb}^{2+} + 2\text{Ag}^\circ$
- What would be the voltage of the standard electrochemical cell? $.80 + .13 = .93 \text{ V}$
- Sketch the cell:



- Write the cell notation for the cell: $\text{Pb} \mid \text{Pb}^{2+} \parallel \text{Ag}^+ \mid \text{Ag}$
anode cathode
- How many moles of electrons are involved in this reaction? $n = 2$

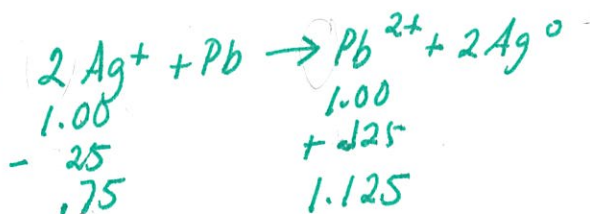
- Find and copy down the Nernst Equation: $\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{nF} \ln Q$

- If the standard cell is allowed to run until the $[\text{Ag}^+] = 0.75 \text{ M}$, the $[\text{Pb}^{2+}] = 1.125 \text{ M}$

- At these new concentrations, the cell voltage will be less (greater / less).

- Use the Nernst equation to calculate the cell voltage with these new concentrations.

$$E_{\text{cell}} = .93 \text{ V} - \frac{(8.31 \text{ V}\cdot\text{C})(298 \text{ K})}{(2 \text{ mole}) \times (96500 \text{ C}\cdot\text{mol}^{-1})} \ln \frac{1.125}{.75} = .927$$



ΔG, E°, and K_{eq}

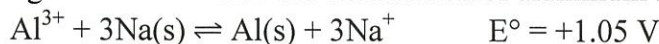
Variables that appear in these equations are R and F.

Values and units? R = 8.31 J/mol K F = 96500 coulombs/mole e⁻

E° and K	ΔG° and E°	ΔG° and K
log K = nE° / 0.0592 @ 25°C	ΔG° = -nF E°	ΔG° = - RTlnK
ln K = $\frac{nF E^\circ}{RT}$	Note: volt x coul = J	
	ΔG° in kJ	

Problems:

1. An early method of producing aluminum metal was the reaction of aluminum salts with sodium metal:



What is ΔG° for this reaction

- a) -304 kJ d) +202 kJ
 b) -101 kJ e) +304 kJ
 c) +101 kJ

$$\Delta G = -nFE^\circ$$

$$\Delta G = -(3 \text{ mol}) \left(\frac{96500 \text{ C}}{\text{mole e}^-} \right) (1.05 \text{ V}) \left(\frac{1 \text{ J}}{\text{C} \cdot \text{V}} \right) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) = -304 \text{ kJ}$$

2. Calculate K_{eq} for this reaction.

$$\log K = \frac{nE}{0.0592} = \frac{(3 \text{ mol})(1.05 \text{ V})}{0.0592} = 53.2$$

$$K = 10^{53.2} = 1.6 \times 10^{53}$$

3. Calculate E° for the following reaction:



$$-1.07 + 1.53 = -0.54 \text{ V}$$

4. Calculate ΔG for the above reaction

- a) +105 kJ d) +52 kJ
 b) -105 kJ e) -312 kJ
 c) +312 kJ

$$\Delta G = -nFE$$

$$-(2 \text{ mol}) \left(\frac{96500 \text{ C}}{\text{mole}} \right) (-0.54 \text{ V}) \left(\frac{1 \text{ J}}{\text{C} \cdot \text{V}} \right) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) = +105 \text{ kJ}$$

5. If ΔG of the following reaction is -203 kJ, what is E°? $2\text{Ag}^+(\text{aq}) + \text{Ni(s)} \rightarrow 2\text{Ag(s)} + \text{Ni}^{2+}(\text{aq})$

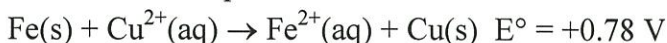
- a) -1.05 V d) -0.011 V
 b) +2.10 V e) +1.05 V
 c) +0.0011 V

$$\Delta G = -nFE^\circ$$

$$-203 \text{ kJ} \left(\frac{1000 \text{ J}}{1 \text{ kJ}} \right) = -(2 \text{ mol}) \left(\frac{96500 \text{ C}}{\text{mole e}^-} \right) (E^\circ)$$

$$E^\circ = +1.05 \text{ V}$$

6. What is the equilibrium constant for the following reaction at 20°C?



- a) 2.3×10^{26} d) 1.8×10^{28}
 b) 6.9×10^{26} e) 1.2×10^{-21}
 c) 1.4×10^{27}

$$\Delta G = -RT \ln K = -nFE$$

$$\ln K = \frac{nFE}{RT}$$

$$\ln K = \frac{(2 \text{ mol}) \left(\frac{96500 \text{ C}}{\text{mole}} \right) (+0.78 \text{ V})}{8.31 \frac{\text{V} \cdot \text{C}}{\text{mole} \cdot \text{K}} (293 \text{ K})} = 6.9 \times 10^{26}$$

$$\ln K = 66.8$$

$$C/s = \text{AMP}$$

$$96500 \text{ C/mole } e^-$$



Stoichiometry

1. Calculate the quantity of electricity (Coulombs) necessary to deposit 100.00g of copper from a $CuSO_4$ solution.

$$\frac{100.00 \text{ g Cu}}{63.546 \text{ g}} \times \frac{1 \text{ mol Cu}}{1 \text{ mol Cu}} \times \frac{2 \text{ mole } e^-}{1 \text{ mole } e^-} \times \frac{96500 \text{ C}}{1 \text{ mole } e^-} = \boxed{3.04 \times 10^5 \text{ C}}$$

2. How many minutes will it take to plate out 40.00 g of Ni from a solution of $NiSO_4$ using a current of 3.450 amp?

$$\frac{40.00 \text{ g Ni}}{58.7 \text{ g Ni}} \times \frac{1 \text{ mol Ni}}{1 \text{ mol Ni}} \times \frac{2e^-}{1 \text{ mole } e^-} \times \frac{96500 \text{ C}}{3.450 \text{ C}} \times \frac{1 \text{ sec}}{60 \text{ sec}} \times \frac{1 \text{ min}}{60 \text{ sec}} = \boxed{635.3 \text{ min}}$$

$$3.450 \text{ Amp} = 3.450 \text{ C/s}$$

3. What is the equivalent weight of a metal if a current of 0.2500 amp causes 0.5240g of metal to plate out a solution undergoing electrolysis in 1 hour? ** One mole of electrons will plate out one equivalent weight of metal

$$0.2500 \text{ AMP} = \frac{0.2500 \text{ C}}{\text{sec}} \times \frac{3600 \text{ sec}}{1 \text{ mole } e^-} \times \frac{1 \text{ mole } e^-}{96500 \text{ C}} = 9.33 \times 10^{-3} \text{ mol}$$

$$\frac{0.5240 \text{ g}}{9.33 \times 10^{-3} \text{ mol}} = \boxed{56.2 \text{ g/mol}}$$

4. How many hours will it take to plate out copper in 200.00ml of 0.15M Cu^{2+} solution using a current of 0.200 amp?

$$0.15 \text{ M} = \frac{x}{0.200 \text{ L}} = 0.0300 \text{ mol Cu} \times \frac{2 \text{ mole } e^-}{1 \text{ Cu}} \times \frac{96500 \text{ C}}{1 \text{ mole } e^-} \times \frac{1 \text{ sec}}{3600 \text{ sec}} \times \frac{1 \text{ hr}}{3600 \text{ sec}} = \boxed{8.04 \text{ hrs}}$$

5. A constant electric current deposits 0.3650g of silver metal in 12960 seconds from a solution of silver nitrate. What is the current? What is the half reaction for the deposition of silver?



$$\frac{0.3650 \text{ g Ag}}{107.87 \text{ g Ag}} \times \frac{1 \text{ mol Ag}}{1 \text{ mol Ag}} \times \frac{1 \text{ mole } e^-}{1 \text{ mole } e^-} \times \frac{96500 \text{ C}}{12960 \text{ sec}} = \boxed{0.252 \text{ AMP}}$$