Practice for Exam 3

1. Determine the emf of the following cell

   Pb(s) | $PbCl_2$ (s), Cl^-(0.250 M) | | H^+ (1.00 M) | H_2 (1.00 bar) | Pt(s)

   The anode is essentially a lead electrode, Pb(s) | Pb^{2+}(aq). However, the anode solution is saturated with lead(II) chloride, so that the lead(II) ion concentration is determined by the solubility product of lead(II) chloride ($K_{sp} = 1.6 \times 10^{-5}$)

$$E^\circ = 0.00\text{ V} - (-0.126\text{ V}) = 0.126\text{ V}$$

$$K_{sp} = \left[Pb^{2+}\right]\left[Cl^-\right]^2 \qquad \left[Pb^{2+}\right] = \frac{K_{sp}}{\left[Cl^-\right]^2} = \frac{1.6\times10^{-5}}{(0.250)^2} = 2.6\times10^{-4}$$

$$E = E^\circ - \frac{RT}{nF}\ln Q = E^\circ - \frac{RT}{nF}\ln\frac{P_{H_2}\left[Pb^{2+}\right]}{\left[H^+\right]^2} = E^\circ - \frac{RT}{nF}\ln\left[Pb^{2+}\right]$$

$$= 0.126\text{ V} - \frac{\left(8.314\text{ J mol}^{-1}\text{ K}^{-1}\right)(298.15\text{ K})}{\left(\frac{2\text{ mol e}^-}{\text{mol}}\right)\left(\frac{96485\text{ C}}{\text{mol e}^-}\right)}\ln\left(2.6\times10^{-4}\right) = 0.232\text{ V}$$

2. A study of the gas–phase oxidation of nitrogen monoxide at 25°C and 1.00 bar pressure gave the following results:

$$2\,NO_{(g)} + O_{2\,(g)} \rightarrow NO_{2\,(g)}$$

	Conc. NO, mol/L	*Conc. O2, mol/L*	*Initial Rate, mol/(L·s)*
Exp. 1	4.5×10^{-2}	2.2×10^{-2}	0.80×10^{-2}
Exp. 2	4.5×10^{-2}	6.8×10^{-2}	2.47×10^{-2}
Exp. 3	6.1×10^{-2}	6.8×10^{-2}	6.15×10^{-2}
Exp. 4	3.8×10^{-1}	4.6×10^{-3}	?

a**.** What is the experimental rate law for the reaction above? Include the value for the rate constant with the appropriate units.

$$\frac{R_2}{R_1} = \frac{2.47\times10^{-2}}{0.80\times10^{-2}} = 3.0875 = \frac{\cancel{k}\,\cancel{[NO]_2^m}\,[O_2]_2^n}{\cancel{k}\,\cancel{[NO]_1^m}\,[O_2]_1^n} = \left(\frac{6.8\times10^{-2}}{2.2\times10^{-2}}\right)^n = (3.0909\ldots)^n$$

$$n = \frac{\log 3.0875}{\log 3.0909\ldots} = 0.99902 \approx 1$$

$$\frac{R_3}{R_2} = \frac{6.15\times10^{-2}}{2.47\times10^{-2}} = 2.489878 = \frac{\cancel{k}\,[NO]_3^m\,\cancel{[O_2]_3^1}}{\cancel{k}\,[NO]_2^m\,\cancel{[O_2]_2^1}} = \left(\frac{6.1\times10^{-2}}{4.5\times10^{-2}}\right)^n = (1.3555\ldots)^n$$

$$n = \frac{\log 2.489878}{\log 1.3555\ldots} = 2.998683 \approx 3$$

$$k = \frac{Rate}{[NO]^3[O_2]^1} = \frac{0.80\times10^{-2}\ \text{mol/L s}}{(4.5\times10^{-2}\ \text{mol/L})^3(2.2\times10^{-2}\ \text{mol/L})} = 4.0\times10^{3}\ \text{L}^{-3}\ \text{mol}^{-3}\ \text{s}^{-1}$$

$$Rate = (4.0\times10^{3}\ \text{L}^{-3}\ \text{mol}^{-3}\ \text{s}^{-1})[NO]^3[O_2]$$

b. What is the initial rate of the reaction in Experiment 4?

$$Rate = (4.0\times10^{3}\ \text{L}^{-3}\ \text{mol}^{-3}\ \text{s}^{-1})[NO]^3[O_2] = (4.0\times10^{3}\ \text{L}^{-3}\ \text{mol}^{-3}\ \text{s}^{-1})[3.8\times10^{-1}\ \text{mol/L}]^3[4.6\times10^{-3}\ \text{mol/L}]$$
$$= 1.0\ \text{mol/L s}$$

3. You have decided to take a job as an electroplater because this class just didn't work out for you as you had planned. A person with a hot rod comes in and wants you to plate his bumper, which has an area of 672 in^2 (1 in = 2.540 cm), with chromium (density = 7.14 g/cm^3). The thickness of the plating is to be 0.01 cm. Your apparatus can generate only 8.50 amps and you have a solution of chromium(VI) chloride. In how many hours should the person return to pick up his bumper?

$$? \text{ h} = \left(672 \text{ in}^2\right)\left(\frac{2.540 \text{ cm}}{1 \text{ in}}\right)^2 \left(0.01 \text{ cm}\right) \times \frac{7.14 \text{ g}}{cm^3} \times \frac{1 \text{ mol Cr}}{51.996 \text{ g}} \times \frac{6 \text{ mol e}^-}{1 \text{ mol Cr}} \times \frac{96485 \text{ C}}{\text{mol e}^-} \times \frac{1 \text{ s}}{8.50 \text{ C}} \times \frac{1 \text{ h}}{3600 \text{ s}}$$

$$= 1 \times 10^2 \text{ h}$$

4. Using half-cell potentials, calculate the equilibrium constant at 25°C for

$$6 \quad Hg^{2+}{}_{(aq)} + 2\ Au_{(s)} \leftrightharpoons 3\ Hg_2{}^{2+}{}_{(aq)} + 2\ Au^{3+}{}_{(aq)}.$$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.920 \text{ V} - 1.498 \text{ V} = -0.578 \text{ V}$$

$$K = e^{\frac{nFE^\circ}{RT}} = 2.4 \times 10^{-59}$$

If 100.00 g of gold is added to 1.00 L of a 1.00 M $Hg(NO_3)_2$ solution, calculate the concentrations of mercury(II), mercury(I), and gold(III) at equilibrium.

	Hg^{2+}	$Hg_2{}^{2+}$	Au^{3+}
I	1.00	0	0
C	-6x	+3x	+2x
E	1.00-6x	3x	2x

$$K_c = \frac{\left[Hg_2^{2+}\right]^3 \left[Au^{3+}\right]^2}{\left[Hg^{2+}\right]^6} = \frac{(3x)^3 (2x)^2}{(1.00 - 6x)^6} = 2.4 \times 10^{-59} \approx \frac{(3x)^3 (2x)^2}{(1.00)^6} = 108x^5$$

$$x = \sqrt[5]{\frac{2.4 \times 10^{-59}}{108}} = 7.5 \times 10^{-13}$$

$[Hg^{2+}]$ = 1.00 M

$[Hg_2{}^{2+}]$ = 2.2×10^{-12} M

$[Au^{3+}]$ = $1.5\times10^{-}$ M

5. A reaction has a rate constant of 83.46 s^{-1} at 15.8 °C. The same reaction has a rate constant of 1534 s^{-1} at 62.4 °C. What is the rate constant when the temperature is 33.4 °C?

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$E_a = \frac{R\ln\frac{k_2}{k_1}}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} = \frac{\left(8.314472\text{ J mol}^{-1}\text{ K}^{-1}\right)\ln\frac{1534\text{ s}^{-1}}{83.46\text{ s}^{-1}}}{\left(\frac{1}{289.0\text{ K}} - \frac{1}{335.6\text{ K}}\right)} = 5.04910725\times10^{4}\text{ J mol}^{-1}$$

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln k_2 = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \ln k_1 = \frac{5.04910725\times10^{4}\text{ J mol}^{-1}}{8.314472\text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{289.0\text{ K}} - \frac{1}{306.6\text{ K}}\right) + \ln 83.46 = 5.6305765$$

$$k_2 = e^{5.6305765} = 278.8\text{ s}^{-1}$$

6. The following is a possible mechanism for a reaction involving hydrogen peroxide in aqueous solution;

$$H_2O_2 + Br^- \rightarrow BrO^- + H_2O$$
$$H_2O_2 + BrO^- \rightarrow Br^- + H_2O + O_2$$

only a small amount of sodium bromide was added to the reaction mixture. What is the overall reaction? What species is acting as a catalyst? Are there any reaction intermediates? If the second reaction is the slow one, what is the overall order of the reaction with respect to hydrogen peroxide?

Overall reaction:

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$$

Catalyst: Br^-

Intermediate: BrO^-

Overall order with respect to H_2O_2 is 2 because we use 2 molecules of H_2O_2 by the time finish the slow step.