

# Practice for Exam 3

1. Determine the emf of the following cell



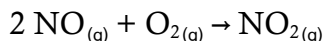
The anode is essentially a lead electrode,  $\text{Pb(s)} \mid \text{Pb}^{2+}(\text{aq})$ . However, the anode solution is saturated with lead(II) chloride, so that the lead(II) ion concentration is determined by the solubility product of lead(II) chloride ( $K_{\text{sp}} = 1.6 \times 10^{-5}$ )

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

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^-]^2 \quad [\text{Pb}^{2+}] = \frac{K_{\text{sp}}}{[\text{Cl}^-]^2} = \frac{1.6 \times 10^{-5}}{(0.250)^2} = 2.6 \times 10^{-4}$$

$$\begin{aligned} E &= E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{RT}{nF} \ln \frac{P_{\text{H}_2} [\text{Pb}^{2+}]}{[\text{H}^+]^2} = E^\circ - \frac{RT}{nF} \ln [\text{Pb}^{2+}] \\ &= 0.126 \text{ V} - \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{\left(\frac{2 \text{ mol e}^-}{\text{mol}}\right)\left(\frac{96485 \text{ C}}{\text{mol e}^-}\right)} \ln(2.6 \times 10^{-4}) = 0.232 \text{ V} \end{aligned}$$

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



	<i>Conc. NO, mol/L</i>	<i>Conc. O<sub>2</sub>, mol/L</i>	<i>Initial Rate, mol/(L·s)</i>
Exp. 1	$4.5 \times 10^{-2}$	$2.2 \times 10^{-2}$	$0.80 \times 10^{-2}$
Exp. 2	$4.5 \times 10^{-2}$	$6.8 \times 10^{-2}$	$2.47 \times 10^{-2}$
Exp. 3	$6.1 \times 10^{-2}$	$6.8 \times 10^{-2}$	$6.15 \times 10^{-2}$
Exp. 4	$3.8 \times 10^{-1}$	$4.6 \times 10^{-3}$	?

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

$$\frac{R_2}{R_1} = \frac{2.47 \times 10^{-2}}{0.80 \times 10^{-2}} = 3.0875 = \frac{\cancel{k} [\text{NO}]_2^m [\text{O}_2]_2^n}{\cancel{k} [\text{NO}]_1^m [\text{O}_2]_1^n} = \left( \frac{6.8 \times 10^{-2}}{2.2 \times 10^{-2}} \right)^n = (3.0909\dots)^n$$

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

$$\frac{R_3}{R_2} = \frac{6.15 \times 10^{-2}}{2.47 \times 10^{-2}} = 2.489878 = \frac{\cancel{k} [\text{NO}]_3^m \cancel{[\text{O}_2]_3^n}}{\cancel{k} [\text{NO}]_2^m \cancel{[\text{O}_2]_2^n}} = \left( \frac{6.1 \times 10^{-2}}{4.5 \times 10^{-2}} \right)^n = (1.3555\dots)^n$$

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

$$k = \frac{\text{Rate}}{[\text{NO}]^3 [\text{O}_2]^1} = \frac{0.80 \times 10^{-2} \text{ mol/L s}}{(4.5 \times 10^{-2} \text{ mol/L})^3 (2.2 \times 10^{-2} \text{ mol/L})} = 4.0 \times 10^3 \text{ L}^{-3} \text{ mol}^{-3} \text{ s}^{-1}$$

$$\text{Rate} = (4.0 \times 10^3 \text{ L}^{-3} \text{ mol}^{-3} \text{ s}^{-1}) [\text{NO}]^3 [\text{O}_2]$$

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

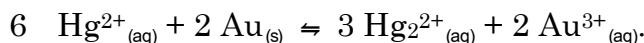
$$\begin{aligned} \text{Rate} &= (4.0 \times 10^3 \text{ L}^{-3} \text{ mol}^{-3} \text{ s}^{-1}) [\text{NO}]^3 [\text{O}_2] = (4.0 \times 10^3 \text{ L}^{-3} \text{ mol}^{-3} \text{ s}^{-1}) [3.8 \times 10^{-1} \text{ mol/L}]^3 [4.6 \times 10^{-3} \text{ mol/L}] \\ &= 1.0 \text{ mol/L s} \end{aligned}$$

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<sup>2</sup> (1 in = 2.540 cm), with chromium (density = 7.14 g/cm<sup>3</sup>). 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?

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

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

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



$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 0.920 \text{ V} - 1.498 \text{ V} = -0.578 \text{ V}$$

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

If 100.00 g of gold is added to 1.00 L of a 1.00 M Hg(NO<sub>3</sub>)<sub>2</sub> solution, calculate the concentrations of mercury(II), mercury(I), and gold(III) at equilibrium.

	Hg <sup>2+</sup>	Hg <sub>2</sub> <sup>2+</sup>	Au <sup>3+</sup>
I	1.00	0	0
C	-6x	+3x	+2x
E	1.00-6x	3x	2x

$$K_c = \frac{[\text{Hg}_2^{2+}]^3 [\text{Au}^{3+}]^2}{[\text{Hg}^{2+}]^6} = \frac{(3x)^3 (2x)^2}{(1.00 - 6x)^6} = 2.4 \times 10^{-59} \approx \frac{(3x)^3 (2x)^2}{(1.00)^6} = 108x^5$$

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

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

$$[\text{Hg}_2^{2+}] = 2.2 \times 10^{-12} \text{ M}$$

$$[\text{Au}^{3+}] = 1.5 \times 10^{-12} \text{ M}$$

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

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

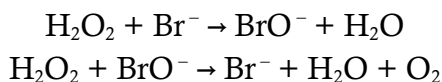
$$E_a = \frac{R \ln \frac{k_2}{k_1}}{\left( \frac{1}{T_1} - \frac{1}{T_2} \right)} = \frac{(8.314472 \text{ J mol}^{-1} \text{ K}^{-1}) \ln \frac{1534 \text{ s}^{-1}}{83.46 \text{ s}^{-1}}}{\left( \frac{1}{289.0 \text{ K}} - \frac{1}{335.6 \text{ K}} \right)} = 5.04910725 \times 10^4 \text{ J mol}^{-1}$$

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

$$\ln k_2 = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) + \ln k_1 = \frac{5.04910725 \times 10^4 \text{ J mol}^{-1}}{8.314472 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{289.0 \text{ K}} - \frac{1}{306.6 \text{ K}} \right) + \ln 83.46 = 5.6305765$$

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

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



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:



Catalyst:  $\text{Br}^-$

Intermediate:  $\text{BrO}^-$

Overall order with respect to  $\text{H}_2\text{O}_2$  is 2 because we use 2 molecules of  $\text{H}_2\text{O}_2$  by the time finish the slow step.