Chemistry 102 - Exam III Name____________________
22 November 2017

SHOW ALL WORK FOR CREDIT. STATE ANY ASSUMPTIONS MADE TO SOLVE A PROBLEM. STATE ALL ANSWERS WITH THE CORRECT NUMBER OF SIGNIFICANT FIGURES. ALL ANSWERS IN SCIENTIFIC NOTATION MUST BE IN PROPER SCIENTIFIC NOTATION (i.e., 6.02×10^{23} not 6.02E23 or 6.02e23). EACH INSTANCE OF IMPROPER SCIENTIFIC NOTATION WILL RESULT IN THE LOSS OF THREE (3) POINTS. ALL NUMBERS REQUIRING UNITS MUST HAVE THE UNITS INCLUDED. EACH INSTANCE OF NUMBERS WITHOUT UNITS WILL RESULT IN THE LOSS OF THREE (3) POINTS.

1. (25 points) A voltaic cell is constructed from the $Fe_3O_{4(s)} \mid Fe_{(s)}$ ($E^\circ = +0.085$ V) and the $H_2MoO_{4(aq)} \mid Mo_{(s)}$ ($E^\circ = +0.11$ V) in an acidic solution. The pH of the solution is 5.29 and the initial $[H_2MoO_4] = 1.635$ M.

   a. Write the balanced equation for the reaction.

   $H_2MoO_{4(aq)} \mid Mo_{(s)}$ is the cathode

$$\underset{+1\ +6\ -2}{H_2MoO_4} + \underset{0}{Fe} \rightarrow \underset{+8/3\ -2}{Fe_3O_4} + \underset{0}{Mo}$$

$$3(4\ H_2O + 3\ Fe \rightarrow Fe_3O_4 + 8\ H^+ + 8\ e^-)$$

$$4(6\ e^- + 6\ H^+ + H_2MoO_4 \rightarrow Mo + 4\ H_2O)$$

$$9\ Fe_{(s)} + 4\ H_2MoO_{4(aq)} \rightarrow 4\ Mo_{(s)} + 3\ Fe_3O_{4(s)} + 4\ H_2O_{(l)}$$

   b. What is the cell potential?

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.11\text{ V} - 0.085\text{ V} = 0.025\text{ V} = 0.03\text{ V}$$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln Q = E^\circ_{cell} - \frac{RT}{nF}\ln\frac{1}{[H_2MoO_4]^4}$$

$$= 0.03\text{ V} - \frac{(8.314472\text{ J mol}^{-1}\text{ K}^{-1})(298.15\text{ K})}{\left(24\,\frac{\text{mol e}^-}{\text{mol}}\right)\left(96485\,\frac{C}{\text{mol e}^-}\right)}\ln\frac{1}{(1.635)^4}$$

$$= 0.0\underline{3}2\text{ V} = 0.0\underline{3}\text{ V}$$

   c. What is the maximum amount of work the cell can do?

$$w = -nFE^\circ_{cell} = -(24\text{ mol e}^-)\left(\frac{96485\text{ C}}{\text{mol e}^-}\right)(0.03\text{ V}) = -6\times10^4\text{ J}$$

   d. How many grams of the cathode plate out if the cell is run at 6.53 A for 22.84 hours?

$$22.84\text{ h}\times\frac{3600\text{ s}}{1\text{ h}}\times\frac{6.53\text{ C}}{\text{s}}\times\frac{1\text{ mol e}^-}{96485\text{ C}}\times\frac{1\text{ mol Mo}}{6\text{ mol e}^-}\times\frac{95.94\text{ g Mo}}{1\text{ mol Mo}} = 89.0\text{ g Mo}$$

2. (30 points) A voltaic cell is constructed based on the following reaction and initial concentrations:

$[IrCl_6]^{3-}$ (0.0050 M) + H^+ + MnO_4^- (2.0 M) $\rightleftharpoons$ $[IrCl_6]^{2-}$ (0.0050 M) + $HMnO_4^-$ (0.0537 M)

Calculate $[[IrCl_6]^{2-}]$ when the cell reaction reaches equilibrium if the solution is buffered to a pH of 3.00.
$[IrCl_6]^{2-}$ | $[IrCl_6]^{3-}$ E° = + 0.87 V; MnO_4^- | $HMnO_4^-$ E° = + 0.90 V
Finding E_{cell} will allow us to determine the equilibrium constant. Comparing K to Q for the given values allows us to determine the direction of the reaction to get to equilibrium and to calculate the equilibrium values.

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} = 0.90\text{ V} - 0.87\text{ V} = 0.03\text{ V}$$

$$K = e^{-nFE^{\circ}_{cell}/RT} = e^{\left(1\frac{\text{mol e}^-}{\text{mol}}\right)\left(96485\frac{C}{\text{mol e}-}\right)(0.03\text{ V})\Big/\left(8.314472\text{ J mol}^{-1}\text{ K}^{-1}\right)(298.15\text{ K})} = 3.\underline{2}1442019598$$

$$Q = \frac{\left[[IrCl_6]^{2-}\right]\left[HMnO_4^-\right]}{\left[[IrCl_6]^{3-}\right]\left[H^+\right]\left[MnO_4^-\right]} = \frac{(0.0050)(0.0537)}{(0.0050)\left(1.0\times10^{-3}\right)(2.00)} = 26.85$$

$K < Q$ so reaction goes to the left to get to equilibrium.

	$[IrCl_6]^{3-}$	H^+	MnO_4^-	$HMnO_4^-$	$[IrCl_6]^{2-}$
I	0.0050	1.0×10^{-3}	0.0537	2.0	0.0050
C	+x	~0	+x	−x	−x
E	0.0050+x	1.0×10^{-3}	0.0537+x	2.0−x	0.0050−x

$$K = \frac{\left[[IrCl_6]^{2-}\right]\left[MnO_4^-\right]}{\left[[IrCl_6]^{3-}\right]\left[H^+\right]\left[HMnO_4^-\right]} = \frac{(0.0050-x)(2.0-x)}{(0.0050+x)\left(1.0\times10^{-3}\right)(0.0537+x)} = 3.2$$

$$x^2 - 2.0050x + 0.010 = (3.2)\left(1.0\times10^{-3}\right)\left(x^2 + .0587x + 0.0002685\right) = 0.0032x^2 + 0.00018784x + 0.0000008592$$

$$0.9968x^2 - 2.00518784x + 0.0099991408 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} : a = 0.9968; b = -2.00518784; c = +0.0099991408$$

$$x = 0.00499906, \cancel{2.00663}$$

$$\left[[IrCl_6]^{2-}\right] = 0.0050 - x = 0.00000094\text{ M}$$

3. (30 points) Nitrogen reacts with oxygen gas at high temperatures and pressures to produce nitrogen monoxide. The following data regarding the rate of the reaction at 1250 K and 1.50 bar were collected:

Experiment #	$[N_2]_0$, mol L^{-1}	$[O_2]_0$, mol L^{-1}	Initial Rate, M s^{-1}
1	0.253	0.557	1.573×10^{-2}
2	0.253	0.279	0.393×10^{-2}
3	0.506	0.557	3.146×10^{-2}

From these data, determine the rate law for the reaction including the value for k with units.

$$\frac{Exp2}{Exp1}=\frac{R_2}{R_1}=\frac{0.393\times10^{-2}}{1.573\times10^{-2}}=\frac{\cancel{k}\cancel{[N_2]_2^m}[O_2]_2^n}{\cancel{k}\cancel{[N_2]_1^m}[O_2]_1^n}=\left(\frac{0.279}{0.557}\right)^n=(0.48947368)^n=0.24984106$$

$$\ln(0.48947368)^n=n\ln(0.48947368)=\ln(0.24984106)$$

$$n=\frac{\ln(0.24984106)}{\ln(0.48947368)}=1.94132499\approx2$$

$$\frac{Exp3}{Exp1}=\frac{R_3}{R_1}=\frac{3.146\times10^{-2}}{1.573\times10^{-2}}=\frac{\cancel{k}[N_2]_2^m\cancel{[O_2]_2^n}}{\cancel{k}[N_2]_1^m\cancel{[O_2]_1^n}}=\left(\frac{0.506}{0.253}\right)^m=(2.)^m=2$$

$$\ln(2)^n=n\ln(2)=\ln(2)$$

$$n=\frac{\ln(2)}{\ln(2)}=1$$

$$Rate=k[N_2]^1[O_2]^2$$

$$k=\frac{Rate}{[N_2][O_2]^2}=\frac{1.573\times10^{-2}\text{ M s}^{-1}}{(0.253\text{ M})(0.557\text{ M})^2}=0.200\text{ M}^{-2}\text{ s}^{-1}$$

$$Rate=\left(0.200\text{ M}^{-2}\text{ s}^{-1}\right)[N_2][O_2]^2$$

What is the rate of the reaction at 1000. K if the initial $[N_2]$ = 1.443 M, $[O_2]$ = 3.564 M and the activation energy is 75.9 kJ mol^{-1}?

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

$$\ln k_2=\frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)+\ln k_1=\frac{75.9\times10^3\text{ J mol}^{-1}}{8.314472\text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{1250.\text{ K}}-\frac{1}{1000.\text{ K}}\right)+\ln 0.200$$

$$=-3.43517020186$$

$$k_2=e^{-3.43517020186}=0.0322\text{ M}^{-2}\text{ s}^{-1}$$

$$Rate=\left(0.0322\text{ M}^{-2}\text{ s}^{-1}\right)(1.443\text{ M})(3.564\text{ M})^2=0.591\text{ M s}^{-1}$$

4. (20 points) The molar mass of a metal (M) is 183.84 g/mol; it forms a chloride of unknown composition. Electrolysis of a sample of the molten chloride with a current of 12.43 A for 23.6 minutes produces 5.59 g of M at the cathode. Determine the empirical formula of the chloride.

We need to find the number of moles of electrons transferred by the metal because that will be the charge on the metal which will give us the empirical formula.

$$?\frac{\text{mol e}^-}{\text{mol M}} = \frac{23.6\text{ min}}{5.59\text{ g M}} \times \frac{60\text{ s}}{1\text{ min}} \times \frac{12.43\text{ C}}{1\text{ s}} \times \frac{1\text{ mol e}^-}{96485\text{ C}} \times \frac{183.84\text{ g M}}{1\text{ mol M}} = 5.99933 \approx 6$$

The empirical formula of the chloride is MCl_6.

5. (25 points) The decomposition of nitric oxide occurs through two parallel reactions:

$$NO_{(g)} \rightarrow \tfrac{1}{2}\, N_{2(g)} + \tfrac{1}{2}\, O_{2(g)} \qquad k_1 = 25.7\ s^{-1}$$

$$NO_{(g)} \rightarrow \tfrac{1}{2}\, N_2O_{(g)} + \tfrac{1}{4}\, O_{2(g)} \qquad k_2 = 18.2\ s^{-1}$$

(a) What is the reaction order for these reactions?

Both reactions are first order because of the units on k.

(b) Which reaction is the slow reaction?

Reaction 2 is the slow reaction because it has the smaller rate constant.

(c) If the initial concentration of NO is 2.0 M, what is the concentration of N_2 after 0.1 seconds?

$$\ln\frac{[NO]_t}{[NO]_0} = -kt$$

$$\ln[NO]_t = -kt + \ln[NO]_0 = -\left(25.7\ \text{s}^{-1}\right)\left(0.1\ \text{s}\right) + \ln\left(2.0\right) = -1.8768528$$

$$[NO]_t = 0.15307$$

$$[N_2] = -\Delta[NO] \times \frac{\tfrac{1}{2}\ \text{mol N}_2}{1\ \text{mol NO}} = \left(0.15\ \text{M} - 2.0\ \text{M}\right) \times \frac{\tfrac{1}{2}\ \text{mol N}_2}{1\ \text{mol NO}} = 0.92\ \text{M}$$

(d) If the initial concentration of NO is 4.0 M, what is the concentration of N_2O after 0.025 seconds?

$$\ln\frac{[NO]_t}{[NO]_0} = -kt$$

$$\ln[NO]_t = -kt + \ln[NO]_0 = -\left(18.2\ \text{s}^{-1}\right)\left(0.025\ \text{s}\right) + \ln\left(4.0\right) = 0.93129436112$$

$$[NO]_t = 2.5\underline{3}1179187179$$

$$[N_2] = -\Delta[NO] \times \frac{\tfrac{1}{2}\ \text{mol N}_2\text{O}}{1\ \text{mol NO}} = \left(2.53\ \text{M} - 4.0\ \text{M}\right) \times \frac{\tfrac{1}{2}\ \text{mol N}_2\text{O}}{1\ \text{mol NO}} = 0.73\ \text{M}$$

6. (20 points) Determine the theoretical rate law for the reaction:

$$OCl^- + I^- \rightarrow OI^- + Cl^-$$

If the proposed mechanism is:

Fast:	$OCl^- + H_2O \rightleftharpoons HOCl + OH^-$	k_1, k_{-1}
Slow:	$I^- + HOCl \rightarrow HOI + Cl^-$	k_2
Fast:	$HOI + OH^- \rightleftharpoons OI^- + H_2O$	k_3, k_{-3}

What role does water play in the mechanism? Water is a catalyst

What role does hydroxide play in the mechanism? Hydroxide is an intermediate

$$Rate = k_2\left[I^-\right]\left[HOCl\right]$$

$$rate = k_1\left[OCl^-\right]\left[H_2O\right] = k_{-1}\left[HOCl\right]\left[OH^-\right]$$

$$\left[HOCl\right] = \frac{k_1\left[OCl^-\right]\left[H_2O\right]}{k_{-1}\left[OH^-\right]}$$

$$rate = k_2\frac{k_1}{k_{-1}}\left[I^-\right]\frac{\left[OCl^-\right]\left[H_2O\right]}{\left[OH^-\right]} = k\frac{\left[I^-\right]\left[OCl^-\right]\left[H_2O\right]}{\left[OH^-\right]} = k\frac{\left[I^-\right]\left[OCl^-\right]}{\left[OH^-\right]}$$

Where the water concentration is “absorbed” into the rate constant because its concentration is essentially constant.