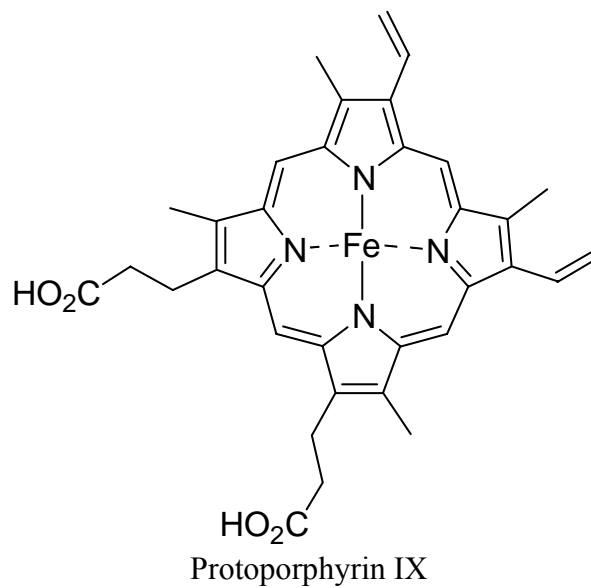


# Chemistry 212

## Final

March 17, 2004



100 (of 100)

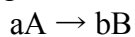
### KEY

\_\_\_\_\_  
Name

**Remember, just a number is not an acceptable answer, I must see your calculations for full credit! Do not forget to include units where appropriate.**

\_\_\_\_\_/\_\_\_\_

1. A certain reaction has the following general form:



At a particular temperature and  $[A]_0 = 2.00 \cdot 10^{-2} \text{ M}$ , concentration versus time data were collected for this reaction, and a plot of  $\ln[A]$  versus time resulted in a straight line with a slope value of  $-2.97 \cdot 10^{-2} \text{ min}^{-1}$ .

- a. Determine the rate law, the integrated rate law, and the value of the rate constant. (6 points)

**Since the  $\ln[A]$  vs. time plot was linear, the reaction is first order in A. The slope of  $\ln[A]$  vs. time plot equals  $-k$ .**

**Rate law:**

$$\text{Rate} = k[A]$$

**Integrated rate law:**

$$\ln[A]_t = -kt + \ln[A]_0$$

**Value of the rate constant:**

$$2.97 \cdot 10^{-2} \text{ min}^{-1}$$

- b. Calculate the half-life for this reaction. (2 points)

**The half-life expression for a first-order rate law is:**

$$t_{1/2} = \ln 2/k = 0.6931/k$$

$$t_{1/2} = 0.6931/(2.97 \cdot 10^{-2} \text{ min}^{-1}) = 23.3 \text{ min}$$

- c. How much time is required for the concentration of A to decrease to  $2.50 \cdot 10^{-3} \text{ M}$ ? (2 points)

**Using the integrated rate law:**

$$\ln([A]_t/[A]_0) = -kt$$

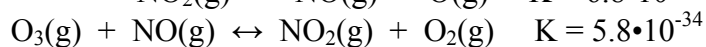
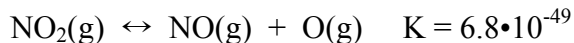
$$\ln(2.50 \cdot 10^{-3} \text{ M}/2.00 \cdot 10^{-2} \text{ M}) = -2.97 \cdot 10^{-2} \text{ min}^{-1} t$$

$$t = \ln(0.125)/-2.97 \cdot 10^{-2} \text{ min}^{-1} = 70.0 \text{ min}$$

2. Calculate a value for the equilibrium constant for the reaction

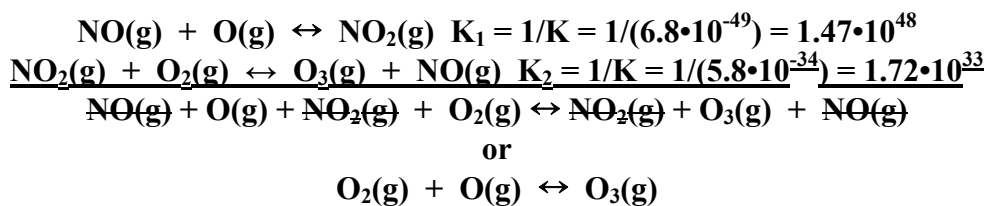


given



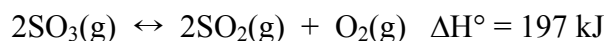
(5 points)

Reversing both reactions and adding them up results in:



$$K = ? = K_1 \cdot K_2 = 1.47 \cdot 10^{48} \times 1.72 \cdot 10^{33} = 2.53 \cdot 10^{81}$$

3. What will happen to the number of moles of  $\text{SO}_3$  in equilibrium with  $\text{SO}_2$  and  $\text{O}_2$  in the reaction



in each of the following cases? (1 points each)

a. Oxygen gas is added.

**The number of moles of  $\text{SO}_3$  will increase.**

b. The pressure is increased.

**The number of moles of  $\text{SO}_3$  will increase.**

c. The volume is increased.

**The number of moles of  $\text{SO}_3$  will decrease.**

d. The temperature is decreased.

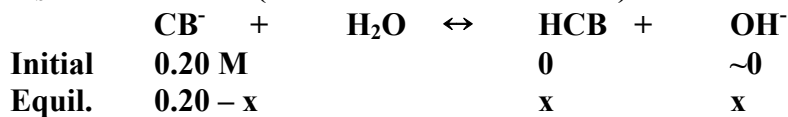
**The number of moles of  $\text{SO}_3$  will increase.**

e. Gaseous sulfur dioxide is removed.

**The number of moles of  $\text{SO}_3$  will decrease.**

4. A 0.20 M sodium chlorobenzoate ( $\text{NaC}_7\text{H}_4\text{ClO}_2$ ) solution has a pH of 8.65. Calculate the pH of a 0.20 M chlorobenzoic acid ( $\text{HC}_7\text{H}_4\text{ClO}_2$ ) solution. (10 points)

From the pH,  $\text{C}_7\text{H}_4\text{ClO}_2^-$  is a weak base. Use the weak base data to determine  $K_b$  for  $\text{C}_7\text{H}_4\text{ClO}_2^-$  (which I abbreviate as  $\text{CB}^-$ )



Since  $\text{pH} = 8.65$ ,  $\text{pOH} = 5.35$  and  $[\text{OH}^-] = 10^{-5.35} = 4.5 \cdot 10^{-6} \text{ M} = x$

$$K_b = [\text{HCB}][\text{OH}^-]/[\text{CB}^-] = x^2/(0.20 - x) = (4.5 \cdot 10^{-6})^2/(0.20 - 4.5 \cdot 10^{-6}) = 1.0 \cdot 10^{-10}$$

Since  $\text{CB}^-$  is a weak base,  $\text{HCB}$ , chlorobenzoic acid, is a weak acid. Solving the weak acid problem:



$$K_a = K_w/K_b = 1.0 \cdot 10^{-14}/1.0 \cdot 10^{-10} = 1.0 \cdot 10^{-4} = x^2/(0.20 - x) \approx x^2/(0.20)$$

$$x = [\text{H}^+] = 4.5 \cdot 10^{-3} \text{ M}; \text{pH} = 2.35$$

5. A 25.0 mL sample of 0.100 M lactic acid ( $\text{HC}_3\text{H}_5\text{O}_3$ ,  $\text{pK}_a = 3.86$ ) is titrated with 0.100 M NaOH solution. Calculate the pH of the resulting solution after the following volumes of NaOH have been added.

a. 0.00 mL (2 points)

**Only a weak acid is present. Solving the weak acid problem:**

$$K_a = 10^{-3.86} = 1.38 \cdot 10^{-4} = x^2 / (0.100 - x) \approx x^2 / (0.100), x = [\text{H}_3\text{O}^+] = 3.72 \cdot 10^{-3} \text{ M}$$

$$\text{pH} = 2.43$$

b. 12.5 mL (2 points)

**The added base will react completely with the best acid present,  $\text{HC}_3\text{H}_5\text{O}_3$ .**

$$\text{mmol HC}_3\text{H}_5\text{O}_3 \text{ present} = 0.025 \text{ L} \cdot (0.100 \text{ mol/L}) = 0.0025 \text{ mol}$$

$$\text{mmol OH}^- \text{ added} = 0.0125 \text{ L} \cdot (0.100 \text{ mol/L}) = 0.00125 \text{ mol}$$

$$\text{mmol HC}_3\text{H}_5\text{O}_3 \text{ present after reaction: } 0.0025 \text{ mol} - 0.00125 \text{ mol} = 0.00125 \text{ mol}$$

**After the reaction, both weak acid and its conjugate base are present. Using Henderson-Hasselbach equation to solve for pH:**

$$\text{pH} = \text{pK}_a + \log\left[\frac{[\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]}\right] = 3.86 + \log(0.00125/0.00125)$$

$$\text{pH} = 3.86 + 0 = 3.86$$

c. 20.0 mL (2 points)

$$\text{mmol HC}_3\text{H}_5\text{O}_3 \text{ present} = 0.025 \text{ L} \cdot (0.100 \text{ mol/L}) = 0.0025 \text{ mol}$$

$$\text{mmol OH}^- \text{ added} = 0.0200 \text{ L} \cdot (0.100 \text{ mol/L}) = 0.00200 \text{ mol}$$

$$\text{mmol HC}_3\text{H}_5\text{O}_3 \text{ present after reaction: } 0.0025 \text{ mol} - 0.00200 \text{ mol} = 0.0005 \text{ mol}$$

$$\text{pH} = \text{pK}_a + \log\left[\frac{[\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]}\right] = 3.86 + \log(0.00200/0.0005)$$

$$\text{pH} = 3.86 + 0.602 = 4.46$$

d. 25.0 mL (2 points)

$$\text{mmol HC}_3\text{H}_5\text{O}_3 \text{ present} = 0.025 \text{ L} \cdot (0.100 \text{ mol/L}) = 0.0025 \text{ mol}$$

$$\text{mmol OH}^- \text{ added} = 0.0250 \text{ L} \cdot (0.100 \text{ mol/L}) = 0.0025 \text{ mol}$$

$$\text{mmol HC}_3\text{H}_5\text{O}_3 \text{ present after reaction: } 0.0025 \text{ mol} - 0.0025 \text{ mol} = 0 \text{ mol}$$

**This is the equivalence point. Enough base has been added to convert all acid into its conjugate base. This is therefore a weak base problem. The total volume of the solution has to be considered: 25 mL original solution + 25 mL added solution = 50 mL. Conc. of weak conj. base = 0.0025 mol/0.050 L = 0.05 M**

$$K_b = K_w/K_a = 7.25 \cdot 10^{-11} = x^2 / (0.05 - x) \approx x^2 / 0.05, x = [\text{OH}^-] = 1.9 \cdot 10^{-6} \text{ M}$$

$$\text{pOH} = 5.72; \text{pH} = 8.28$$

e. 28.0 mL (2 points)

**An excess of strong base has been added. The excess of strong base will determine the pH. 25 mL of the 28 mL added reacted with the weak acid  $\text{HC}_3\text{H}_5\text{O}_3$ , therefore, 3 mL of 0.100 M base in the new total volume of 25 mL + 28 mL = 53 mL will determine the pH.**

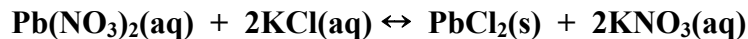
$$(0.003 \text{ L} \times 0.100 \text{ M}) / 0.052 \text{ L} = 0.00577 \text{ M OH}^- \text{ solution. pOH} = 2.24$$

$$\text{pH} = 11.76$$

\_\_\_\_\_ / \_\_\_\_\_

6. A solution is prepared by mixing 50.0 mL of aqueous 0.10 M  $\text{Pb}(\text{NO}_3)_2$  with 50.0 mL of aqueous 1.0 M KCl.
- a. Write the molecular equation (2 points), the total ionic equation (2 points), and the net ionic equation (2 points) for this reaction.

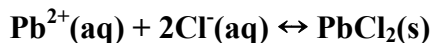
**Molecular equation:**



**Total ionic equation:**



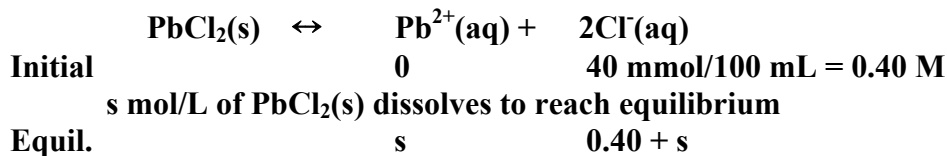
**Net ionic equation:**



- b. Calculate the concentrations of  $\text{Pb}^{2+}$  and  $\text{Cl}^-$  at equilibrium. The  $K_{\text{sp}}$  for  $\text{PbCl}_2(\text{s})$  is  $1.6 \cdot 10^{-5}$ . (4 points)

$$K_{\text{sp}}(\text{PbCl}_2) = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

50.0 mL x 0.10 M = 5.0 mmol  $\text{Pb}^{2+}$ ; 50.0 mL x 1.0 M = 50 mmol  $\text{Cl}^-$ . For this solution,  $Q > K_{\text{sp}}$ , so  $\text{PbCl}_2$  precipitates. Assume precipitation of  $\text{PbCl}_2(\text{s})$  is complete. 5.0 mmol  $\text{Pb}^{2+}$  requires 10 mmol of  $\text{Cl}^-$  for complete precipitation, which leaves 40 mmol  $\text{Cl}^-$  in excess. Now, let some of the  $\text{PbCl}_2(\text{s})$  redissolve to establish equilibrium

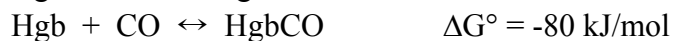


$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = s \cdot (0.40 + 2s)^2 \approx s(0.40)^2$$

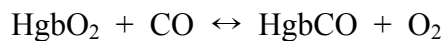
$$s = 1.0 \cdot 10^{-4} \text{ mol/L. Assumption good}$$

**At equilibrium:**  $[\text{Pb}^{2+}] = s = 1.0 \cdot 10^{-4} \text{ mol/L}$   
 $[\text{Cl}^-] = 0.40 + 2s = 0.40 + 2(1.0 \cdot 10^{-4}) = 0.40 \text{ M}$

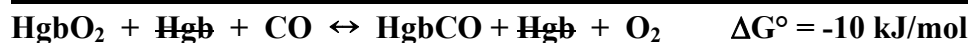
7. Carbon monoxide is toxic because it bonds much more strongly to the iron in hemoglobin (Hgb) than does O<sub>2</sub>. Consider the following reactions and approximate standard free energy changes:



Using these data, calculate the equilibrium constant value at 25 °C for the following reaction:



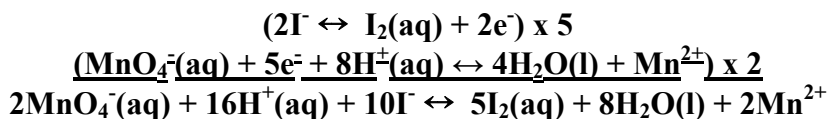
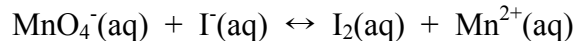
You will need  $R = 8.3145 \text{ J/K}\cdot\text{mol}$  for your calculation. (10 points)



$$\Delta G^\circ = -RT \ln K, K = \exp(-\Delta G^\circ/RT) = \exp[-(-10 \cdot 10^3 \text{ J})/(8.3145 \text{ J/K}\cdot\text{mol})(298 \text{ K})]$$

$$K = 60$$

8. a. Balance the following redox reaction: (6 points)



- b. Now, calculate  $E^\circ$  for the above cell, using the following half-cell potentials:  
 $E^\circ_{\text{MnO}_4/\text{Mn}^{2+}} = 1.51 \text{ V}$ ,  $E^\circ_{\text{I}_2/\text{I}^-} = 0.54 \text{ V}$ . (2 points)

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 1.51 \text{ V} - 0.54 \text{ V} = 0.97 \text{ V}$$

- c. Calculate the cell potential at 25 °C and pH = 3 (Hint: I provide this number because you need it!) when the concentrations are as follows:  
 $[\text{MnO}_4^-] = 0.1 \text{ M}$ ;  $[\text{Mn}^{2+}] = 2 \cdot 10^{-6} \text{ M}$ ;  $[\text{I}^-] = 0.01 \text{ M}$ ;  $[\text{I}_2] = 3 \cdot 10^{-4} \text{ M}$ . (2 points)

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log Q = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Mn}^{2+}]^2 [\text{I}_2]^5}{[\text{MnO}_4^-]^2 [\text{H}^+]^{16} [\text{I}^-]^{10}}$$

Using the concentrations and converting pH to  $[\text{H}^+] = 10^{-3}$ :

$$E_{\text{cell}} = 0.97 \text{ V} - \frac{0.0591}{10} \log \frac{(2.6 \times 10^{-6})^2 (3.0 \times 10^{-4})^5}{(0.1)^2 (10^{-3})^{16} (0.01)^{10}}$$

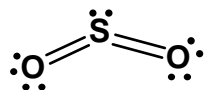
$$E_{\text{cell}} = 0.97 \text{ V} - 0.00591 \log (7.8 \times 10^{38})$$

$$E_{\text{cell}} = 0.97 \text{ V} - 0.23 \text{ V} = 0.74 \text{ V}$$

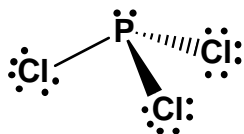


9. Draw Lewis structures for the following molecules. (2 points each)

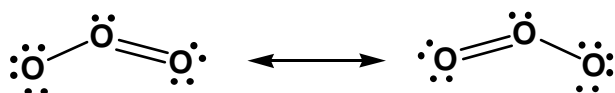
a. Sulfur dioxide



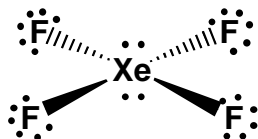
b.  $\text{PCl}_3$



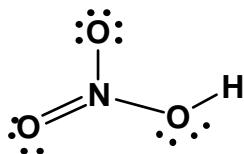
c.  $\text{O}_3$



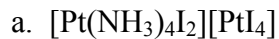
d. Xenon tetrafluoride



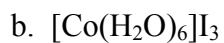
e. Nitric acid



10. Name the following inorganic complexes and organic molecules. (2 points each)

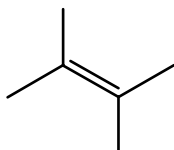


**tetraamminediiodoplatinum(IV) tetraiodoplatinate(II)**



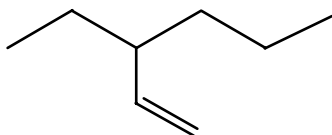
**hexaaquocobalt(III) iodide**

c.



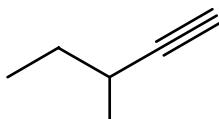
**2,3-dimethyl-2-butene**

d.



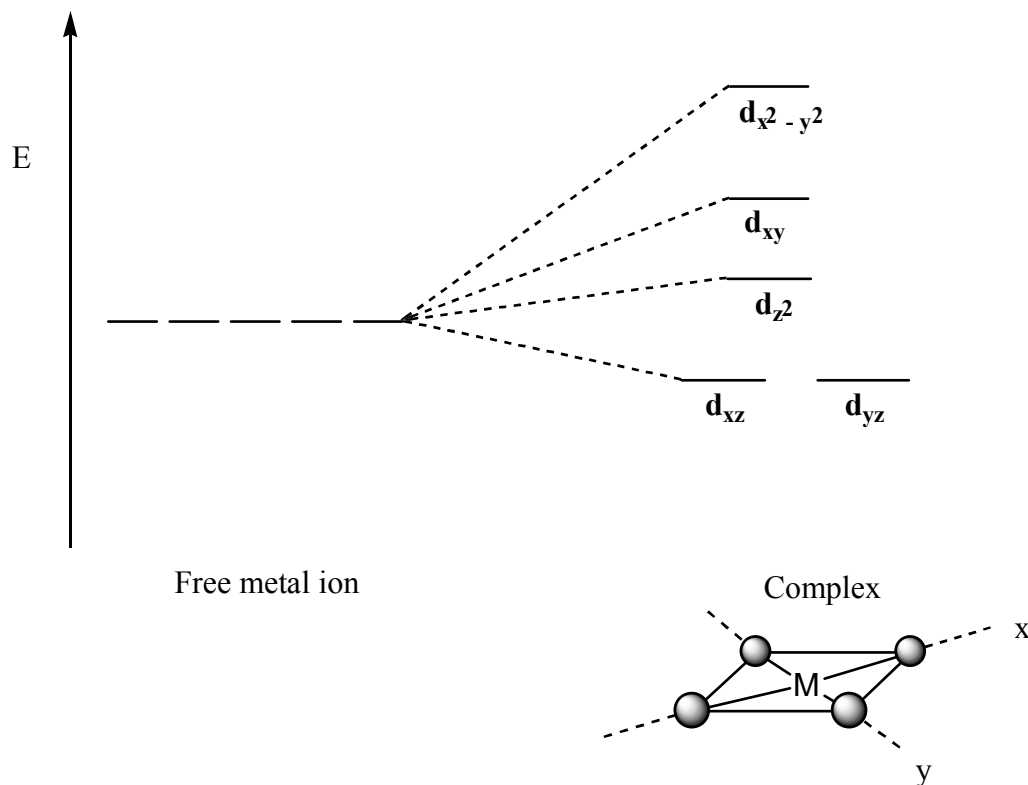
**3-ethyl-1-hexene**

e.



**3-methyl-1-pentyne**

11. Draw the crystal field diagram for a square planar complex oriented in the xy plane with ligands along the x and y axes. (4 points)



12. In each of the following nuclear reactions, supply the missing particle. (2 points each)

