#### Exam 3 Review

## Distribution

- Describe how the molar concentrations of mono- and polyprotic weak acids and their conjugate bases vary with pH
- Identify the principal species resulting from the dissociation of a weak acid at a given pH
- $\bullet\,$  Sketch and interpret ionic distribution graphs given appropriate  $pK_a$  values
- 1. Sketch the acid-base distribution plot for sulfuric acid  $(H_2SO_4)$  below. Make sure to label the axes and identify the principal species at each point. The second  $K_a$  is 0.012. (This one is tricky!)
- 2. Calculate the pH of a 0.010 M sulfuric acid solution, given the fact that its second  $K_a$  is 0.012.
- 3. Sketch the acid-base distribution plot for arsenic acid (H<sub>3</sub>AsO<sub>4</sub>), given its three K<sub>a</sub> values,  $5.8 \times 10^{-3}$ ,  $1.1 \times 10^{-7}$ , and  $3.2 \times 10^{-12}$ .
- 4. Given the distribution plot below, determine which of the following acids it belongs to.
  - (a) Periodic acid,  $K_{a1} = 2.00 \times 10^{-2}$ ,  $K_{a2} = 5.00 \times 10^{-9}$
  - (b) Carbonic acid,  $K_{a1} = 4.45 \times 10^{-7}$ ,  $K_{a2} = 4.69 \times 10^{-11}$
  - (c) Fumaric acid,  $K_{a1} = 8.85 \times 10^{-4}$ ,  $K_{a2} = 3.21 \times 10^{-10}$



## Buffers

- Recognize how the molar concentrations of a weak acid and its conjugate base influence pH calculations
- Calculate the pH of a buffer solution or the conjugate acid/base ratio based on the buffer pH
- 1. Describe two typical ways to make a buffer.
- 2. Show how the Henderson-Hasselbalch equation can be derived from the  $K_a$  expression for the dissociation of the weak acid HA.
- 3. Over what range is the Henderson-Hasselbalch approximation valid?
- 4. Calculate the pH of a buffer solution made by adding 0.12 moles of sodium lactate to 0.10 moles of lactic acid. The  $K_a$  of lactic acid is  $1.4 \times 10^{-4}$ .
- 5. True or False. Given two buffer solutions with equal concentrations of a weak acid and its conjugate base, the solution with the lower concentrations of the two components will be able to neutralize more hydrochloric acid.
- 6. What ratio of ammonium chloride to ammonia should be used to form a buffer with a pH of 9.27? The  $K_b$  of ammonia is  $1.75 \times 10^{-5}$ .

## Titration

- Understand why titration curves have a particular shape and recognize the difference in the titration curves of acid/base titrations
- Describe how molar concentrations of a weak acid and its conjugate base vary with pH
- Identify the major species in solution and calculate the pH at various points during the titration
- 1. Sketch a general curve for the titration of a weak acid with a strong base. Be sure to label the axes correctly. How would the curve be different for the titration of a weak base with a strong acid?
- 2. On your graph above, circle the region where the Henderson-Hasselbalch equation is a useful approximation.

- 3. The following problems refer to the titration of 100 mL of the 0.10 M diprotic weak acid, malonic acid, with 0.20 M sodium hydroxide.  $K_{a1}$  for malonic acid is  $1.5 \times 10^{-3}$ , and  $K_{a2}$  is  $2.0 \times 10^{-6}$ .
  - (a) Calculate the pH before the addition of any sodium hydroxide.
  - (b) Calculate the pH after teh addition of 10 mL of sodium hydroxide.
  - (c) Calculate the pH after the addition of 25 mL of sodium hydroxide.
  - (d) Calculate the pH after the addition of 50 mL of sodium hydroxide.
  - (e) Calculate the pH after the addition of 65 mL of sodium hydroxide.
  - (f) Calculate the pH after the addition of 100 mL of sodium hydroxide.
  - (g) Calculate the pH after the addition of 150 mL of sodium hydroxide.

#### **Redox and Electrochemistry**

- For a given redox reaction, draw a galvanic cell and identify the cathode and anode
- Describe an experiment that will determine the relative strengths of a series of oxidizing agents
- 1. Propose an experiment for determining the strongest oxidizing agent of copper, zinc, mercury, and aluminum.
- 2. For the redox reaction  $2 \operatorname{Fe}^{3+}(\operatorname{aq}) + 3 \operatorname{Ba}(\operatorname{s}) \longrightarrow 3 \operatorname{Ba}^{2+}(\operatorname{aq}) + 2 \operatorname{Fe}(\operatorname{s})$ , write the half-reactions and label them as oxidation or reduction. Also, sketch the galvanic cell suggested by this reaction and label its necessary components.

- 3. What is the oxidizing agent in the reaction above? Explain.
- 4. Write the reaction above using cell notation.
- 5. Balance the redox reaction  $MnO_4^{-}(aq) + C_2O_4^{2-}(aq) \longrightarrow Mn^{2+}(aq) + CO_2(aq)$ .

### Cell Potential and the Nernst Equation

- Identify the oxidizing and reducing agents based on their standard reduction potential
- Calculate the cell voltage
- Relate cell voltage to  $\Delta G$  and equilibrium constant K
- Use Q to adjust cell voltage or reduction potential
- 1. As the reduction potential for a compound decreases, what happens to the oxidation potential of its reduced form?
- 2. What conditions define standard conditions, denoted by the  $^{\circ}$  symbol?
- 3. Based on the cell potential measured for the cells below, what potential would you expect for the cell  $Fe(s) | Fe^{2+}(aq) || Co^{2+}(aq) | Co(s)?$   $Co(s) | Co^{2+}(aq) || Cu^{2+}(aq) | Cu(s), E^{\circ} = 0.614 V$  $Fe(s) | Fe^{2+}(aq) || Cu^{2+}(aq) | Cu(s), E^{\circ} = 0.777 V$
- 4. Use the Nernst equation to calculate the cell potential of the cell  $2 \operatorname{Ag}^+ + \operatorname{Ni}(s) \longrightarrow 2 \operatorname{Ag}(s) + \operatorname{Ni}^{2+}(aq)$ . The concentration of silver is 0.50 M and that of nickel is 0.20 M at 298 K.
- 5. Which of the following reactions are spontaneous as written under standard conditions?
  - (a)  $\operatorname{Zn}(s) + 2\operatorname{Fe}^{3+}(\operatorname{aq}) \longrightarrow \operatorname{Zn}^{2+}(\operatorname{aq}) + 2\operatorname{Fe}^{2+}$
  - (b)  $\operatorname{Cu}(s) + 2 \operatorname{H}^+(aq) \longrightarrow \operatorname{Cu}^{2+}(aq) + \operatorname{H}_2(g)$
  - $(c) \ 2 \operatorname{Br}^-(aq) + I_2(s) \longrightarrow \operatorname{Br}_2(l) + 2 \operatorname{I}^-(aq)$

# Selected Reduction Potentials

Half-Reaction	Standard Reduction Potential, $E^{\circ}$ (V)
$\operatorname{Zn}^{2+}(\operatorname{aq}) + 2 \operatorname{e}^{-} \longrightarrow \operatorname{Zn}(\operatorname{s})$	-0.763
$Ni^{2+}(aq) + 2e^{-} \longrightarrow Ni(s)$	-0.250
$2 \mathrm{H^+(aq)} + 2 \mathrm{e^-} \longrightarrow \mathrm{H}_2(\mathrm{g})$	$\pm 0.000$
$Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$	+0.337
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.535
$\mathrm{Fe}^{3+}(\mathrm{aq}) + \mathrm{e}^{-} \longrightarrow \mathrm{Fe}^{2+}(\mathrm{aq})$	+0.771
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.799
$\operatorname{Br}_2(l) + 2 e^- \longrightarrow 2 \operatorname{Br}^-(aq)$	+1.080