

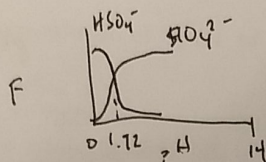
Exam 3 Review

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
 - Sketch and interpret ionic distribution graphs given appropriate pK_a values
- 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!)

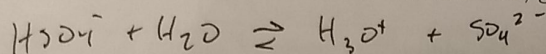
one pK_a between $pH=0$ and $pH=14$

$K_{a1} \gg 1$ because H_2SO_4 is strong



$$pK_2 = 1.92$$

- Calculate the pH of a 0.010 M sulfuric acid solution, given the fact that its second K_a is 0.012.



0.010

-x

0.010-x

0

+x

x

0

+x

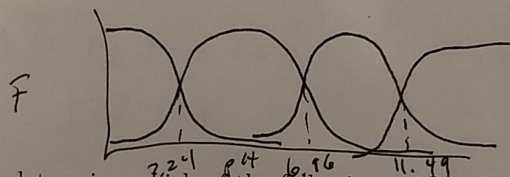
x

$$\frac{x^2}{0.010-x} = 0.012$$

$$x = 0.00649$$

$$pH = 2.19$$

- Sketch the acid-base distribution plot for arsenic acid (H_3AsO_4), given its three K_a values, 5.8×10^{-3} , 1.1×10^{-7} , and 3.2×10^{-12} .



- Given the distribution plot below, determine which of the following acids it belongs to.

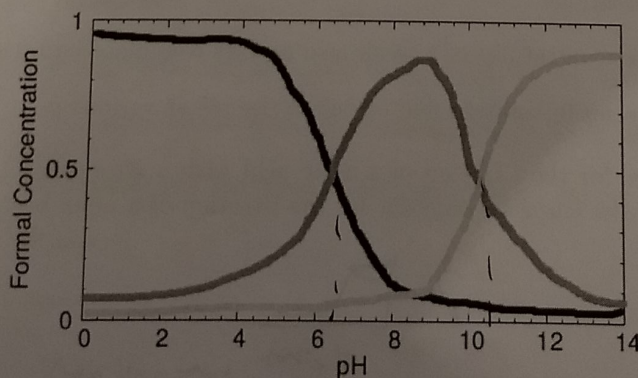
(a) Periodic acid, $K_{a1} = 2.00 \times 10^{-2}$, $K_{a2} = 5.00 \times 10^{-9}$

(b) Carbonic acid, $K_{a1} = 4.45 \times 10^{-7}$, $K_{a2} = 4.69 \times 10^{-11}$

(c) Fumaric acid, $K_{a1} = 8.85 \times 10^{-4}$, $K_{a2} = 3.21 \times 10^{-10}$

$$pK_{a1} = 6.35$$

$$pK_{a2} = 10.33$$



Buffers

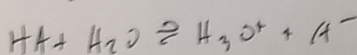
- Recognize how the molar concentrations of a weak acid and its conjugate base influence pH calculations
- Calculate the pH of a buffer solution or the conjugate acid/base ratio based on the buffer pH

1. Describe two typical ways to make a buffer.

Weak acid or base + salt of the conjugate

add strong acid or base to slightly more than a weak acid

2. Show how the Henderson-Hasselbalch equation can be derived from the K_a expression for the dissociation of the weak acid HA.



$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$pK_a = pH - \log \frac{[A^-]}{[HA]}$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

3. Over what range is the Henderson-Hasselbalch approximation valid?

$$0.1 < \frac{[A^-]}{[HA]} < 10$$

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 1.4×10^{-4} .

$$pH = 3.77 \text{ from Henderson-Hasselbalch}$$

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.

higher

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 1.75×10^{-5} .

$$9.27 = 9.24 + \log \frac{[NH_3]}{[NH_4^+]}$$

$$10^{9.27-9.24} = \frac{[NH_3]}{[NH_4^+]} = 1.07$$

$$\frac{[NH_4^+]}{[NH_3]} = 0.93$$

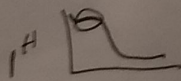
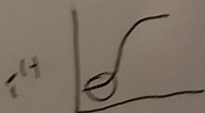
Titration

- 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?

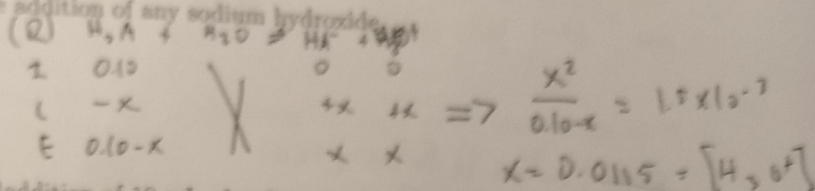


buffer region

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 1.5×10^{-3} , and K_{a2} is 2.0×10^{-6} .

(a) Calculate the pH before the addition of any sodium hydroxide.



(b) Calculate the pH after the addition of 10 mL of sodium hydroxide.

buffer region, use Henderson-Hasselbalch

$pH = 2.22$

(c) Calculate the pH after the addition of 25 mL of sodium hydroxide.

pK_{a1}

(d) Calculate the pH after the addition of 50 mL of sodium hydroxide.

equivalence point

$pH = 4.26$

between two half-equivalence points \Rightarrow average pK_{a1} and pK_{a2}

(e) Calculate the pH after the addition of 65 mL of sodium hydroxide.

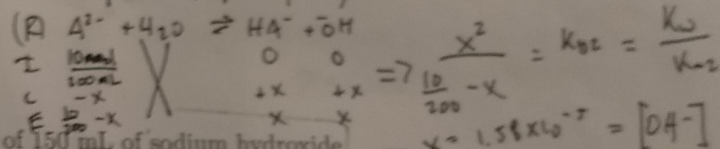
$pH = 5.33$

second buffer region \Rightarrow Henderson-Hasselbalch

(f) Calculate the pH after the addition of 100 mL of sodium hydroxide.

$pH = 9.20$

1st equivalence point, only A^{2-} left



(g) Calculate the pH after the addition of 150 mL of sodium hydroxide.

30 mmol OH^- total, used up 20, 10 mmol excess

$10 \text{ mmol} / 250 \text{ mL} = [OH^-]$

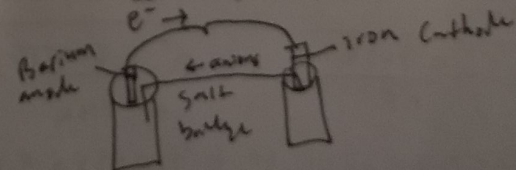
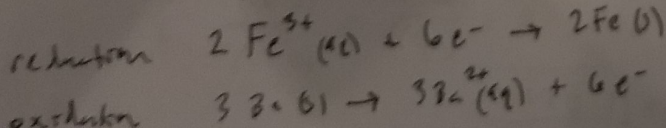
$14 - pOH = pH = 12.6$

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.

See Lab manual

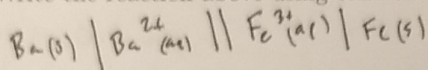
2. For the redox reaction $2Fe^{3+}(aq) + 3Ba(s) \rightarrow 3Ba^{2+}(aq) + 2Fe(s)$, write the half-reactions and label them as oxidation or reduction. Also, sketch the galvanic cell suggested by this reaction and label its necessary components.



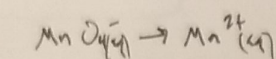
3. What is the oxidizing agent in the reaction above? Explain.

oxidizing agent facilitates oxidation for something else \Rightarrow it is the one that gets reduced so Fe^{3+}

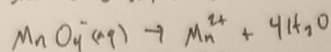
4. Write the reaction above using cell notation.



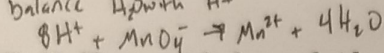
5. Balance the redox reaction $\text{MnO}_4^- (\text{aq}) + \text{C}_2\text{O}_4^{2-} (\text{aq}) \longrightarrow \text{Mn}^{2+} (\text{aq}) + \text{CO}_2 (\text{aq})$.



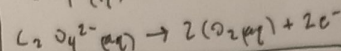
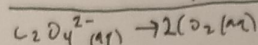
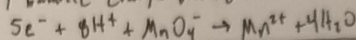
balance O with H_2O



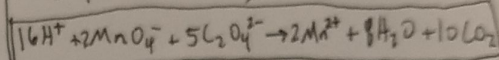
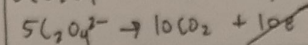
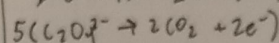
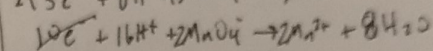
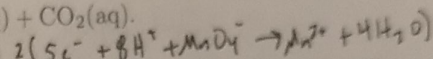
balance H with H^+



balance charge with electrons



Now multiply the first equation by 2 and the second by 5 to get equal # of e^- and add



Cell Potential and the Nernst Equation

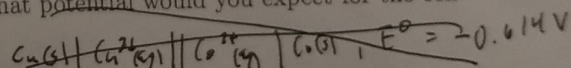
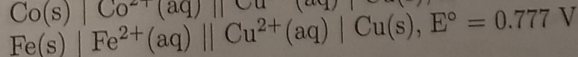
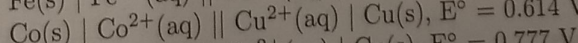
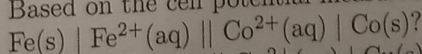
- Identify the oxidizing and reducing agents based on their standard reduction potential
- Calculate the cell voltage
- Relate cell voltage to ΔG and equilibrium constant K
- Use Q to adjust cell voltage or reduction potential

1. As the reduction potential for a compound decreases, what happens to the oxidation potential of its reduced form? *increases*

2. What conditions define standard conditions, denoted by the $^\circ$ symbol?

Solids must be pure, solutions at 1.0M concentration, gases at 1atm pressure, temperature is $25^\circ\text{C} = 298\text{K}$

3. Based on the cell potential measured for the cells below, what potential would you expect for the cell



need both to be reductions so

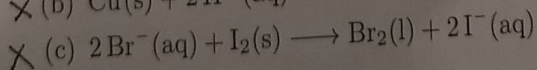
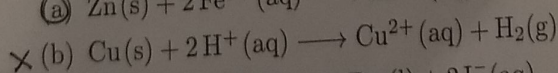
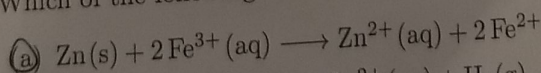
$$E_{\text{cell}} = -0.614 - 0.777 = -1.391\text{V}$$

$$+0.777\text{V} \rightarrow -0.777\text{V}$$

$$E_{\text{cell}} = -0.614 - (-0.777) = 0.163$$

4. Use the Nernst equation to calculate the cell potential of the cell $2\text{Ag}^+ + \text{Ni(s)} \longrightarrow 2\text{Ag(s)} + \text{Ni}^{2+}(\text{aq})$. 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?



check if $E_{\text{cell}} > 0$ using table

Nernst: $E = E^\circ - \frac{2.303RT}{nF} \log Q = E^\circ - \frac{0.0592}{n} \log Q$, $n=2$, $Q = \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2} = \frac{(0.20)}{(0.50)^2}$

$$E = E^\circ + 0.00296 \log 2 = 1.049\text{V} + 0.00296 \log 2 = 1.052\text{V}$$

$$E^\circ \text{ from table is } E^\circ = E^\circ(\text{Ag}) - E^\circ(\text{Ni}) = 0.799 - (-0.250) = +1.049\text{V}$$

Make them both to use $E_{\text{cell}} = E_{\text{red}}(\text{cathode}) - E_{\text{red}}(\text{anode})$

$$E_{\text{cell}} = 0.614$$