

CHEM 212, Exam 2
Fall 2014

Name: _____

1. (20 pts) For the forward reaction at 25°C $aA + bB \rightleftharpoons cC + dD$, the $\Delta H = 85 \text{ kJ mol}^{-1}$ and $\Delta S = 24 \text{ J mol}^{-1} \text{ K}^{-1}$.

a. Is this reaction **exothermic** or **endothermic**?

2 Is that favorable? Yes **No** not sure

b. Does disorder **increase** or **decrease**?

2 Is that favorable? **Yes** No not sure

c. Calculate Gibbs free energy of the reaction

$$\Delta G = \Delta H - T \Delta S = 85,000 \text{ J/mol} - \frac{298 \text{ K} \cdot 24 \text{ J/mol K}}{1} = 77,800 \text{ J/mol}$$

7
$$\Delta G = 77.8 \text{ kJ/mol}$$

d. Is this reaction spontaneous?

1 Yes **No** not sure

e. Determine the equilibrium constant for this reaction.

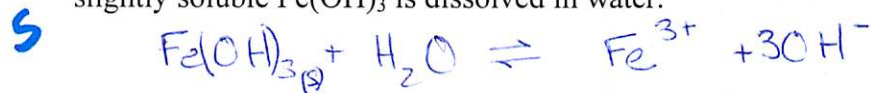
8
$$k = e^{-\frac{\Delta G}{RT}}$$

$$k = e^{\frac{-77.8 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol K} \cdot 298 \text{ K}}}$$

-31.40

$$k = 2.31 \times 10^{-14}$$

2. (20 pts, 5 ea) Write the reaction and solubility product equilibrium expression for slightly soluble $\text{Fe}(\text{OH})_3$ is dissolved in water.



$$K_{sp} = [\text{Fe}^{3+}][\text{OH}^-]^3$$

5 If the K_{sp} for the above reaction is 7.58×10^{-11} , calculate the $[\text{Fe}^{3+}]$ at equilibrium.

$$5 \quad K_{sp} = x \cdot 3x^3 = 27x^4 \quad x = [\text{Fe}^{3+}]$$

$$x = 1.29 \times 10^{-3}$$

5 If the species formed in solution include: Fe^{3+} , $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_2^{2+}$, H^+ , H_2O , and OH^- . Write a charge balance equation.

$$[\text{OH}^-] - 3[\text{Fe}^{3+}] + [\text{Fe}(\text{OH})_2^+] + 2[\text{Fe}(\text{OH})_2^{2+}] + [\text{H}^+] = 0$$

$$\text{or } 0 = 3[\text{Fe}^{3+}] + [\text{Fe}(\text{OH})_2^+] + 2[\text{Fe}(\text{OH})_2^{2+}] + [\text{H}^+] - [\text{OH}^-]$$

5 Write a mass balance expression for total iron (eg tot Fe=)

$$\text{tot Fe} = [\text{Fe}^{3+}] + [\text{Fe}(\text{OH})_2^+] + [\text{Fe}(\text{OH})_2^{2+}]$$

$$K_a = 6.31 \times 10^{-5}$$

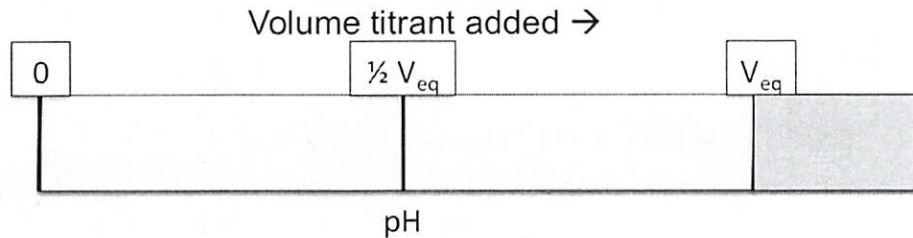
3. (45pts) A 50 ml solution of 0.057 M benzoic acid (C_6H_5COOH) was titrated with 0.0723 M KOH. $pK_a = 4.20$

a. (5) Determine the volume ^{base} acid added at the equivalence point.

$$0.057 \frac{\text{mol A}}{\text{L}} \times 0.05 \text{ L} \times \frac{\text{mol B}}{\text{mol A}} \times \frac{\text{L}}{0.0723 \text{ mol B}} \times \frac{1000 \text{ mL}}{\text{L}} =$$

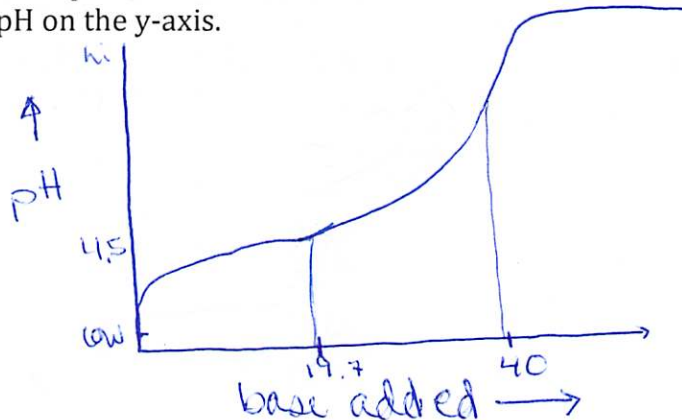
39.42 mL

b. (5) Label the volumes and pH's or range of pH you would expect to calculate at each point on the diagram below.



	0	$0 < V < \frac{1}{2}V_{eq}$	$V = \frac{1}{2}V_{eq}$	$\frac{1}{2}V_{eq} < V < V_{eq}$	$V = V_{eq}$	$V > V_{eq}$
Volume (or range) titrant added	0 ml	14	19.71	X	39.42	45
Expected value or range of pH	$\ll 4.20$		4.20		> 7	$\gg 7$
Calculated pH	2.72	3.95	4.20	X	8.35	11.54

c. (5) Sketch the shape of the titration curve with volume of titrant added on the x-axis and the pH on the y-axis.



Begin by writing the reaction governing the solution and equilibrium expression in each case:

d. (5) Determine the pH of the initial solution before the titration begins



$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{F-x} \quad \text{assume } F \gg x$$

$$x = [H^+] = \sqrt{6.309 \times 10^{-5} \cdot 0.057} = \sqrt{3.60 \times 10^{-6}} = 1.896 \times 10^{-3}$$

$$x = 3.3 \% F$$

$$0 = x^2 - K_a x + F K_a$$

$$x =$$

$$pH = 2.73$$

assumption not valid
must use quadratic

e. (5) Determine the pH after 14 mL of base is added

$$pH = pK_a + \log \frac{A^-}{HA} \quad OH^- + HA \rightleftharpoons H_2O + A^-$$

$$pH = 4.20 + \log \frac{1.022 \times 10^{-3}}{1.828 \times 10^{-3}}$$

0.559

$$pH = 4.20 - 0.25$$

$$pH = 3.95$$

$$\text{mols } OH^- = \frac{0.073 \text{ mol}}{L} \cdot 0.014 L = 1.022 \times 10^{-3} \text{ mol}$$

$$F = \text{mols } HA + A^- = \frac{0.057 \text{ mol}}{L} \cdot 0.05 L = 2.85 \times 10^{-3} \text{ mol}$$

all OH^- added converts HA to A^-

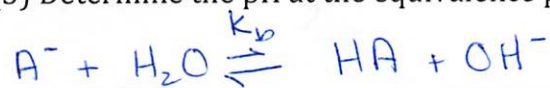
$$[A^-] = [OH^-]_{\text{added}} \quad F - [OH^-] = [HA] = 1.828 \times 10^{-3}$$

f. (5) Determine the pH of the solution at $\frac{1}{2} V_{eq}$ ml base is added

$$pH = pK_a = 4.20$$

$$pK_b = 9.8 \quad K_b = 1.58 \times 10^{-10}$$

- g. (5) Determine the pH at the equivalence point



$$M_1 V_1 = M_2 V_2$$

$$F' = 0.057 M \cdot \frac{50 \text{ mL}}{89.42 \text{ mL}} = 0.032 M$$

$$K_b = \frac{[HA][OH^-]}{[A^-]} = \frac{x^2}{F' - x}$$

assume $F' \gg x$
assumption good

$$\sqrt{K_b \cdot 0.032 M} = x = [HA] = [OH^-]$$

$$x = 2.248 \times 10^{-6}$$

$$pOH = 5.6$$

$$pH = 8.35$$

- h. (5) Calculate the pH after 45 ml of base is added.

$$M_1 V_1 = M_2 V_2$$

$$[OH^-] = 0.0723 M \cdot \frac{(45 - 39.42 \text{ mL})}{(45 + 50 \text{ mL})} = 0.0723 M \cdot \frac{4.58 \text{ mL}}{95 \text{ mL}}$$

volume excess base
total volume

$$[OH^-] = 0.00348$$

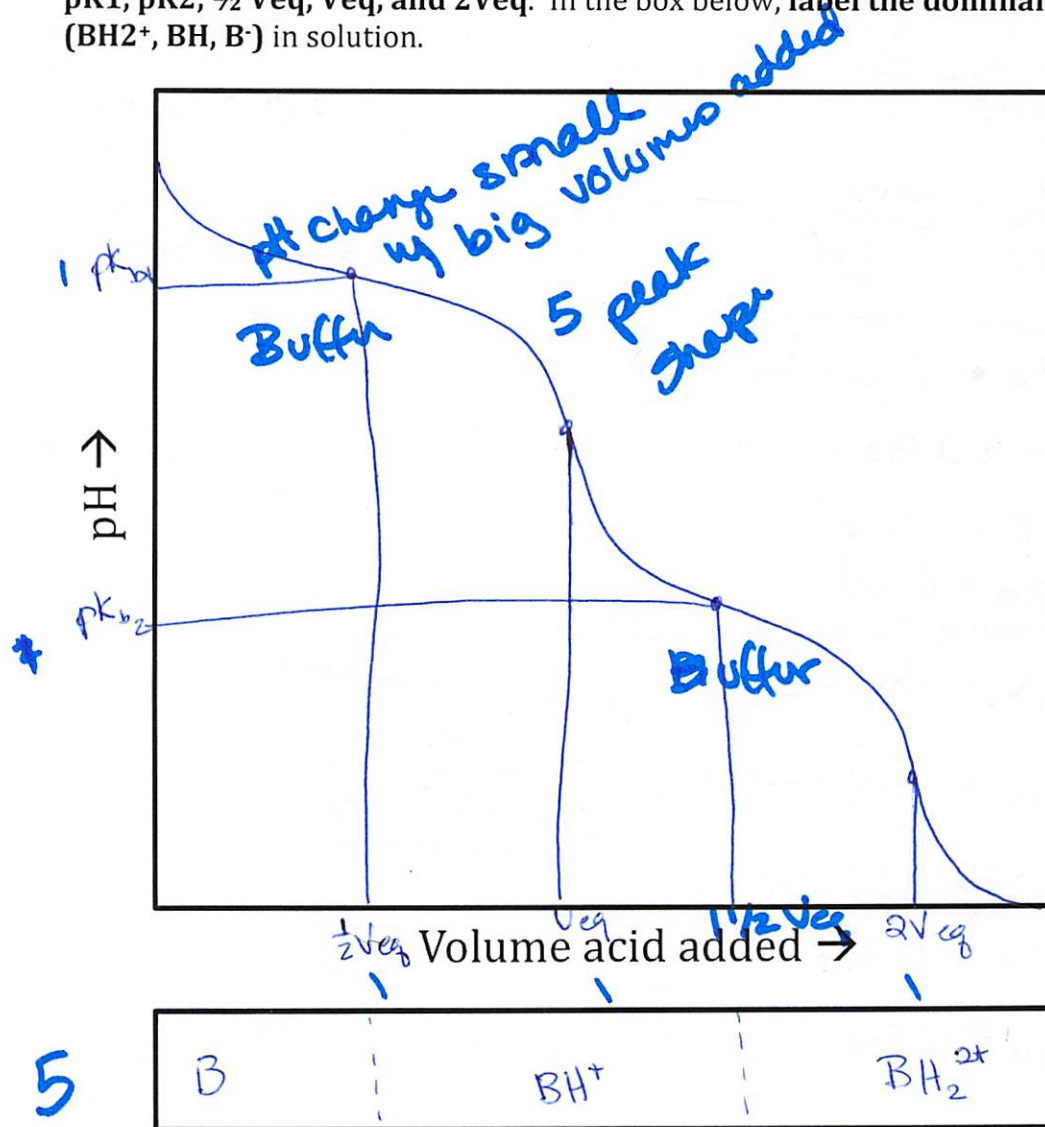
$$pOH = 2.46$$

$$pH = 11.54$$

- i. (5) Examine the figure you annotated in part B. Add your calculated values to the figure. Do the values you calculated agree with your expectations? Explain briefly.

yup.

4. (15 pts) Draw a titration curve for a diprotic base ~~acid~~ with a strong acid. Label **pK1**, **pK2**, $\frac{1}{2}$ **Ve_q**, **Ve_q**, and **2Ve_q**. In the box below, label the dominant phase (**BH₂⁺**, **BH**, **B⁻**) in solution.



What is the dominant species in solution?