

Exam 1
Chem 311
Fall 2007

Name:

Pick 5 of the 8 problems. Each problem is worth 20 pts.

1. A buffer is prepared by adding 66.3 g K_2HPO_4 and 32.4 g NaH_2PO_4 to 200. mL of water and completely dissolving the salts. Calculate the pH of this buffer.

$$\text{Moles } \text{HPO}_4^{2-} = (66.3 \text{ g/1}) \cdot (1 \text{ mol}/174.17554 \text{ g}) = 0.38065 \text{ mol}$$

$$\text{Moles } \text{H}_2\text{PO}_4^- = (32.4 \text{ g/1}) \cdot (1 \text{ mol}/119.97648 \text{ g}) = 0.27005 \text{ mol}$$

$$\text{pH} = 7.199 + \log(.38065/.27005) = 7.348$$

2. Estimate (no extensive calculations required) the amount in which the pH will change, if 0.245 g of malonic acid (H_2M) is dissolved in the buffer described in problem 1. Based on your estimate, determine the concentration of the HM^- species of malonic acid. (Hint: use the alpha fraction equations)

$$\text{Moles malonic acid} = (0.245 \text{ g/1}) \cdot (1 \text{ mol}/104.06146 \text{ g}) = 0.002354 \text{ mol}$$

This would have practically no influence on the pH.

$$[\text{H}_3\text{O}^+] = 4.48665 \cdot 10^{-8} \text{ M}$$

$$K_{a1} = 0.00142$$

$$K_{a2} = 2.01 \cdot 10^{-6}$$

$$F_{\text{H}_2\text{M}} = (0.002354 \text{ mol}/.200 \text{ L}) = 0.01177 \text{ M}$$

$$\alpha_{\text{HM}^-} = K_{a1}[\text{H}^+] / ([\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}) = 0.021834$$

$$[\text{HM}^-] = (.021834) \cdot (0.01177) = 2.57 \cdot 10^{-4} \text{ M}$$

3. Determine the pH of a 0.0500 M solution of phenylacetic acid solution.

$$K_a = x^2/F$$

$$4.90 \cdot 10^{-5} = [\text{H}^+]^2/.05$$

$$[\text{H}^+] = 0.001565 \text{ M}$$

$$\text{pH} = 2.805$$

3 % dissociation, so assumption 2 is valid.

4. A 25.00-mL aliquot of 0.200 M solution of formic acid is titrated with 0.1007 M solution of NaOH. Calculate the pH at the equivalence point of this titration.

$$V^* = (25.00 \text{ mL})(0.200)/0.1007 = 49.65 \text{ mL}$$

At equiv. pt. all of the formic acid has been converted to formate.

$$Ff^- = (25.00 \text{ mL})(0.200)/(25.00+49.65) = 0.06698 \text{ M}$$

$$K_b = K_w/K_a = 5.611 \cdot 10^{-11}$$

$$K_b = [\text{OH}^-]^2/Ff^-$$

$$[\text{OH}^-] = 1.9386 \cdot 10^{-6} \text{ M}$$

$$[\text{H}_3\text{O}^+] = 5.20995 \cdot 10^{-9}$$

$$\text{pH} = 8.283$$

5. Calculate the ionic strength of a 0.01667 M solution of calcium hydroxide. Why is the actual pH of a 0.01667 M solution of $\text{Ca}(\text{OH})_2$ less than 12.52? Estimate the actual pH from the tables in Chapter 8.

This problem is flawed. I wrote this problem as if $\text{Ca}(\text{OH})_2$ was a soluble salt. It is not. If we treat it as a soluble salt...

$$\mu = \frac{1}{2}[(0.01667)(2)^2 + (2)(0.01667)(-1)^2] = 0.050 \text{ M}$$

The Activity of the OH^- is always less than its concentration, which makes the pH less than if you simply ignore the effects of activities.

Activity coefficient for OH^- from table is 0.81

$$\text{pH} = -\log a_{\text{H}^+} = -\log K_w/\gamma[\text{OH}^-] = 12.43$$

Alternatively, I gave credit for treating the problem as if it were a saturated solution of $\text{Ca}(\text{OH})_2$, which if done correctly is much more difficult. As, it turns out, a 0.01667 M solution is very close to a saturated solution of $\text{Ca}(\text{OH})_2$, if you take into account the activities. So, the pH also is approximately 12.44.

Most of you lost points for using the pH or the K_w equations in terms of concentration and not activities.

6. Calculate the maximum amount Co^{2+} in an aqueous solution at a pH of 10.00 (ignoring any effects from activities)

$$[\text{OH}^-] = 1.00 \cdot 10^{-4} \text{ M}$$

$$K_{sp}(\text{Co}(\text{OH})_2) = 1.3 \cdot 10^{-15} = [\text{Co}^{2+}]_{\text{max}}[\text{OH}^-]^2$$

$$[\text{Co}^{2+}] = 1.30 \cdot 10^{-7} \text{ M}$$

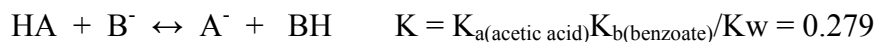
7. The Kjeldahl procedure was used to analyze 9.82 mg of protein. The sample was digested liberating NH_3 . The ammonia was collected in 20.00 mL of 0.0100 M HCl. The excess HCl required 8.62 mL of 0.0100 M NaOH to complete the titration. Determine the weight percent of nitrogen in the protein.

$$\text{mmol N} = (20.00 \text{ mL})(0.0100) - (8.62 \text{ mL})(0.0100) = 0.1138 \text{ mmol N}$$
$$(0.1138 \text{ mmol N})(14.0067 \text{ g/mol}) = 1.59396 \text{ mg N}$$

$$(1.59396 \text{ mg N} / 9.82 \text{ mg})(100) = 16.2 \%$$

8. Write the reaction that occurs when acetic acid is added to a solution of sodium benzoate. Determine the equilibrium constant of this reaction using Hess's law, $K_a(\text{acetic acid})$, $K_b(\text{benzoate})$, and K_w .

Let HA be acetic acid, A⁻ be the acetate ion, B⁻ be the benzoate ion, and BH be benzoic acid.



100.0 mL of 0.200 M acetic acid is mixed with 100.0 mL of 0.200 M sodium benzoate. Write an expression for the equilibrium concentrations of acetic acid, the benzoate ion, the acetate ion, and benzoic acid in terms of one variable. Which answer below best represents the equilibrium concentration of acetic acid.

$$F_{\text{HA}} = F_{\text{B}^-} = 0.100 \text{ M (due to dilution upon mixing)}$$

$$K = x^2 / \{(0.1-x)(0.1-x)\}$$

Since $[\text{HA}] = 0.1-x$, subtract each choice from 0.1, and plug it in to the equation. Answer b gives you K.

- a. 0.051 M
- b. 0.065 M**
- c. 0.035 M
- d. 0.100 M