Chemistry 192
Problem Set 4
Spring, 2018

1. The ionization constant of benzoic acid in water associated with the reaction

$$C_6H_5COOH_{(aq)} + H_2O_{(\ell)} \rightleftharpoons C_6H_5COO^-_{(aq)} + H_3O^+_{(aq)}$$

is $K_a = 6.3 \times 10^{-5}$. Calculate the value of K_b associated with the reaction

$$C_6H_5COO^-_{(aq)} + H_2O_{(\ell)} \rightleftharpoons C_6H_5COOH_{(aq)} + OH^-_{(aq)}.$$

Answer: $K_b = 1.6 \times 10^{-10}$

2. Use the data and/or results from problem 1 to calculate the pH of a 0.100 M solution of sodium benzoate, NaC_6H_5COO.
Answer: pH=8.60

3. The ionization constant of hydroxylamine producing the hydroxylammonium ion via the reaction

$$HONH_{2(aq)} + H_2O_{(\ell)} \rightleftharpoons HONH^+_{3(aq)} + OH^-_{(aq)}$$

is $K_b = 9.1 \times 10^{-9}$. Calculate the pH of a 0.0100 M solution of hydroxylammonium chloride.
Answer: pH=3.96

4. Using the ionization constant of acetic acid

$$CH_3COOH_{(aq)} + H_2O_{(\ell)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)} \qquad K_a = 1.8 \times 10^{-5}$$

calculate the mass of sodium acetate that must be added to 100. mL of water to produce a solution with pH=8.00.
Answer:0.015 g

5. The ionization reaction of hypochlorous acid with water

$$HOCl_{(aq)} + H_2O_{(\ell)} \rightleftharpoons OCl^-_{(aq)} + H_3O^+_{(aq)}$$

has a $pK_a = 7.54$. Consider a 0.100 M NaOCl (sodium hypochlorite) solution.

(a) Do you expect the pH of the NaOCl solution to be less than or greater than 7.00? Explain your reasoning.

(b) Calculate the pH of a 0.100 M NaOCl solution given sodium hypochlorite is completely ionized in water.
Answer: pH=10.27

6. The ionization constant for hydrofluoric acid via the reaction

$$HF_{(aq)} + H_2O_{(\ell)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)}$$

is $K_a = 6.6 \times 10^{-4}$. Calculate the concentration of fluoride ion in a 0.100 M hydrofluoric acid solution and an aqueous mixture 0.100 M aqueous HF and 0.0100 M HCl. Recall that HCl is completely ionized in water.
Answer $[F^-]=4.4 \times 10^{-3}$ M

7. Aqueous methylamine is a weak base with the reaction

$$CH_3NH_{2(aq)} + H_2O_{(\ell)} \rightleftharpoons OH^-_{(aq)} + CH_3NH^+_{3(aq)}$$

having ionization constant $K_b = 4.2 \times 10^{-4}$. A 0.0100 M solution of mehtylamine is mixed with sufficient sodium hydroxide to yield a solution having pH=9.30. Calculate the concentration of the methylammonium ions and methylamine in the solution.
Answer: $[CH_3NH_3^+] = 9.5 \times 10^{-3}$ M, $[CH_3NH_2] = 5.0 \times 10^{-4}$ M

8. The value of K_a for the dissociation of benzoic acid

$$C_6H_5COOH_{(aq)} + H_2O_{(\ell)} \rightleftharpoons H_3O^+_{(aq)} + C_6H_5COO^-_{(aq)}$$

is 6.3×10^{-5}. Calculate the pH of a solution that is 0.0100 M in benzoic acid and 0.0100 M in sodium benzoate.
Answer:pH=4.20

9. For benzoic acid as in problem 8, calculate the pH of a solution that is 0.0100 M in benzoic acid and 0.0500 M in sodium benzoate.
Answer: pH=4.87

10. Sodium azide (NaN_3) is a highly toxic and highly water soluble salt made from sodium hydroxide (NaOH, a strong base) and hydrazoic acid (HN_3, a weak acid). Sodium azide solutions are completely ionized in water. It is found that a 0.100 M aqueous solution of sodium azide has a pH=8.80. Calculate the pK_a of the reaction

$$HN_{3(aq)} + H_2O_{(\ell)} \rightleftharpoons N^-_{3(aq)} + H_3O^+_{(aq)}.$$

Answer: pK_a= 4.60

11. For aqueous ammonia using the reaction

$$NH_{3(aq)} + H_2O_{(\ell)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)} \qquad K_b = 1.8 \times 10^{-5}$$

calculate the pH of a solution that is 0.0100 M in ammonia and 0.0500 M in ammonium chloride.
Answer: pH=8.56

12. Calculate the pH when 100. mL of the solution discussed in problem 8 is combined with 20.0 mL of 0.0100 M hydrochloric acid.
Answer: pH=4.02

13. Calculate the pH when 100. mL of the solution discussed in problem 11 is combined with 20.0 mL of 0.0100 M hydrochloric acid.
Answer: pH=8.44

14. Calculate the pH when 100. mL of the solution discussed in problem 8 is combined with 20.0 mL of a 0.0100 M aqueous sodium hydroxide solution.
Answer: pH=4.37

15. From the dissociation constant of benzoic acid given in problem 8, calculate the number of grams of sodium benzoate that must be added to 100. mL of 0.0100 M benzoic acid to produce a solution buffered to pH = 4.00.
Answer: 0.91 g

16. The weak base diethylamine reacts with water according to the reaction

$$(C_2H_5)_2NH_{(aq)} + H_2O_{(\ell)} \rightleftharpoons (C_2H_5)_2NH^+_{2(aq)} + OH^-_{(aq)},$$

and the equilibrium constant for the reaction is $K_b = 6.9 \times 10^{-4}$. A buffer solution is formed by mixing diethylamine and diethylammonium chloride having concentrations $[(C_2H_5)_2NH]$=0.124 M and $[(C_2H_5)_2NH^+_2]$=0.224 M. Calculate the pH of the final solution when 0.400 L of the buffer are mixed with 0.1500 L of 0.0150 M NaOH (a strong base).
Answer: pH=10.61

17. Pyridine (C_5H_5N) reacts with water as a weak base according to the reaction

$$C_5H_5N_{(aq)} + H_2O_{(\ell)} \rightleftharpoons C_5H_5NH^+_{(aq)} + HO^-_{(aq)}$$

with associate base ionization constant $K_b = 1.5 \times 10^{-9}$. A buffer is made by combining aqueous pyridine and pyridinium chloride (C_5H_5NHCl) of concentrations $[C_5H_5N]$=0.200 M and $[C_5H_5NH^+]$=0.300 M. A 0.100 L sample of the buffer is then mixed with 0.0100 L of 0.235 M aqueous hydrochloric acid (HCl, a strong acid). Calculate the pH of the mixture of the buffer and hydrochloric acid.
Answer: pH=4.92

18. The base dissociation constant of phenylamine ($C_6H_5NH_2$) is $K_b = 5.0 \times 10^{-10}$. A solution is prepared that is 0.100 M in phenylamine and 0.200 M in phenylammonium cation ($C_6H_5NH_3^+$). A 0.100 L sample of the buffer is then mixed with 0.100 L of 0.0100 M sodium hydroxide (a stong base). Calculate a) the pH of the initial buffer solution, and 2) the pH of the buffer/sodium hydroxide mixture.
Answer: Buffer, pH=4.40, mixture pH=4.46.

19. A buffer of volume 0.400 L is 0.250 M in formic acid (HCOOH) and 0.350 M in the formate ($HCOO^-$) anion. The buffer is then combined with 0.100 L of 0.0250 M sodium hydroxide. Given the pK_a of formic acid is 3.74, calculate the pH of the mixture of the buffer with the NaOH solution. Approximations work for this problem.
Answer: pH=3.90

20. Ethanolamine, $HO(CH_2)_2NH_2$ is a weak base in aqueous solutions, and its conjugate acid, $HO(CH_2)_2NH_3^+$ is called the ethanolammonium ion. The pK_b of ethanolamine is 4.50. A buffer is formed by mixing 0.10 moles of $HO(CH_2)_2NH_2$ with 0.20 moles of $HO(CH_2)_2NH_3^+$ to make an aqueous solution having a final total volume of 0.500 L. Calculate a) the pH of the buffer, and b) the pH if the buffer is mixed with 0.100 L of 0.050 M hydrochloric acid (a strong acid). Approximations work for this problem.
Answer: a) Original buffer, pH=9.20; b) after mixing, pH=9.17

21. Ethyl amine ($C_2H_5NH_2$) is a weak base with p$K_b = 3.37$. A buffer is made by combining 0.025 moles of ethyl amine and 0.050 moles of an ethyl ammonium salt ($C_2H_5NH_3^+$) with water so that the total volume is 0.25 L. The buffer is then combined with 0.020 L of 0.100 M hydrochloric acid (HCl). Calculate 1) the initial pH of the buffer, and 2) the pH of the buffer after the addition of the hydrochloric acid. **Answer**: pH 1= 10.33, pH2 = 10.28