Exercise #1: Acid-Base Equilibria and Buffer Solutions

1. Consider the ionization equilibrium of acetic acid in aqueous solution:

\[
\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{CO}_2^-(aq)
\]

(a) Does the equilibrium concentration of \(\text{H}_3\text{O}^+\) increase, decrease, or stay the same if some sodium acetate, NaCH\(_3\)CO\(_2\), is added to the acetic acid solution? Explain.

(b) Does the pH of the solution increase, decrease, or stay the same if some sodium acetate, NaCH\(_3\)CO\(_2\), is added to the acetic acid solution? Explain.

(c) Does the equilibrium concentration of acetate ion, \(\text{CH}_3\text{CO}_2^-\), increase, decrease, or stay the same if some sodium hydroxide is added to the solution? Explain. How will the pH change?

2. Given that \(K_a = 1.8 \times 10^{-5}\) for acetic acid, calculate the pH of each of the following solutions:

(a) A solution containing 0.10 M acetic acid (CH\(_3\)COOH) and 0.10 M sodium acetate (NaCH\(_3\)CO\(_2\)).

(b) A solution containing 0.10 M CH\(_3\)CO\(_2\)H and 0.050 M NaCH\(_3\)CO\(_2\).

(c) A solution containing 0.050 M CH\(_3\)CO\(_2\)H and 0.10 M NaCH\(_3\)CO\(_2\).

(Answer: (a) pH = 4.74; (b) pH = 4.44; (c) pH = 5.04)

3. Consider the ionization equilibrium of ammonia in aqueous solution.

\[
\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)
\]

(a) Does the equilibrium concentration of \(\text{OH}^-\) increase, decrease, or stay the same if ammonium chloride (NH\(_4\)Cl) is added to the ammonia solution? Explain.

(b) Does the pH of the solution increase, decrease, or stay the same if ammonium chloride (NH\(_4\)Cl) is added to the ammonia solution? Explain.

(c) In which direction does the equilibrium shift when HCl\(_{aq}\) is added to aqueous solution of ammonia? Does the equilibrium concentration of \(\text{NH}_4^+\) increase, decrease, or stay the same if some HCl\(_{aq}\) is added to the solution? Explain.
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4. (a) Calculate \([\text{H}_3\text{O}^+]\) and the pH of a solution that contains 0.10 \(M\) \(\text{NH}_3\) and 0.10 \(M\) \(\text{NH}_4\text{Cl}\).
\(K_a(\text{NH}_4^+) = 5.6 \times 10^{-10}\)  
(Answer: (a) \([\text{H}_3\text{O}^+] = 5.6 \times 10^{-10} \, \text{M}\), pH = 9.25)

(b) Calculate \([\text{H}_3\text{O}^+]\) and the pH a solution that contains 0.20 \(M\) \(\text{NH}_3\) and 0.10 \(M\) \(\text{NH}_4\text{Cl}\).
(Answers: \([\text{H}_3\text{O}^+] = 2.8 \times 10^{-10} \, \text{M}\), pH = 9.55)

5. Indicate whether each of the following solution combinations will make a buffer solution. Explain.
(a) 50.0 mL of 0.20 \(M\) \(\text{HCl}\) + 50.0 mL of 0.20 \(M\) \(\text{NaCl}\);
(b) 50.0 mL of 0.20 \(M\) \(\text{HNO}_2\) + 50.0 mL of 0.20 \(M\) \(\text{NaNO}_2\);
(c) 50.0 mL of 0.20 \(M\) \(\text{CH}_3\text{CO}_2\text{H}\) + 50.0 mL of 0.20 \(M\) \(\text{NaCH}_3\text{CO}_2\);
(d) 50.0 mL of 0.20 \(M\) \(\text{CH}_3\text{CO}_2\text{H}\) + 50.0 mL of 0.20 \(M\) \(\text{NaOH}\);
(e) 50.0 mL of 0.20 \(M\) \(\text{CH}_3\text{CO}_2\text{H}\) + 50.0 mL of 0.10 \(M\) \(\text{NaOH}\);
(f) 50.0 mL of 0.20 \(M\) \(\text{CH}_3\text{CO}_2\text{H}\) + 50.0 mL of deionized water;
(g) 50.0 mL of 0.20 \(M\) \(\text{NH}_3\) + 50.0 mL of 0.20 \(M\) \(\text{NH}_4\text{NO}_3\);
(h) 50.0 mL of 0.20 \(M\) \(\text{NH}_3\) + 50.0 mL of 0.20 \(M\) \(\text{HNO}_3\);
(i) 50.0 mL of 0.20 \(M\) \(\text{NH}_3\) + 50.0 mL of 0.10 \(M\) \(\text{HNO}_3\);
(j) 50.0 mL of 0.20 \(M\) \(\text{NH}_3\) + 50.0 mL of deionized water;
(k) 50.0 mL of 0.20 \(M\) \(\text{NH}_4\text{NO}_3\) + 50.0 mL of 0.20 \(M\) \(\text{NaOH}\);
(l) 50.0 mL of 0.20 \(M\) \(\text{NH}_4\text{NO}_3\) + 50.0 mL of 0.10 \(M\) \(\text{NaOH}\);

6. A phosphate buffer solution is prepared by dissolving 25.0 g of potassium hydrogen phosphate \((\text{K}_2\text{HPO}_4; \text{FM} = 174.18)\) and 12.0 g of potassium dihydrogen phosphate \((\text{KH}_2\text{PO}_4; \text{FM} = 136.09)\) in 250. mL of the buffer solution.
(a) Calculate the molar concentrations of \(\text{HPO}_4^{2-}\) and \(\text{H}_2\text{PO}_4^-\), respectively, and the pH of the buffer solution using the following equilibrium:
\[
\text{H}_2\text{PO}_4^- (aq) + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{HPO}_4^{2-} (aq) ; \quad (K_a = 6.2 \times 10^{-8})
\]
(b) Write an equation for the buffering reaction: (i) when a strong acid is added; (ii) when a strong base is added to the phosphate buffer solution.

(c) Calculate the final pH of the solution: (i) when 2.0 mL of 6.0 \(M\) \(\text{HCl}_{(aq)}\) is added to the buffer; (ii) when 2.0 mL of 6.0 \(M\) \(\text{NaOH}_{(aq)}\) is added to the buffer. (In each case, assume the final volume of the solution is 250. mL)
(Answer: (a) \([\text{HPO}_4^{2-}] = 0.574 \, \text{M}\); \([\text{H}_2\text{PO}_4^-] = 0.353 \, \text{M}\), and pH = 7.42; (c) (i) pH = 7.33; (ii) pH = 7.52)
7. (a) Calculate the pH of the resulting solutions when (i) 2.0 mL of 6.0 M HCl(aq) is added to pure water; (ii) 2.0 mL of 6.0 M NaOH is added to pure water. In each case the final volume of the solution is 250 mL. (Answer: (a) (i) pH = 1.32; (ii) pH = 12.68)

(b) How do changes in pH caused by the addition of a small amount of strong acid or strong base to a buffer solution compare to that added to pure water?

(c) Explain the much smaller change in pH caused by the addition of strong acid or strong base observed/calculated for the buffer solution. Illustrate your explanation with relevant equations.

8. How many grams of sodium hydroxide must be added to a 500.-mL solution of 1.0 M acetic acid to produce a buffer solution buffered with pH = 5.00? (Assume the final volume is 500. mL, and for acetic acid, $K_a = 1.8 \times 10^{-5}$) (Answer: 12.5 g of NaOH)

9. (a) Explain buffering range and buffer capacity. (b) Can you change the buffering range of a given buffer solution? (c) How would you increase the buffering capacity of a buffer solution?

10. The $K_a$ values of some acids are given below:
    - Formic acid, HCOOH, $K_a = 1.8 \times 10^{-4}$; Acetic acid, CH$_3$COOH, $K_a = 1.8 \times 10^{-5}$;
    - Lactic acid, HC$_3$H$_5$O$_3$, $K_a = 1.4 \times 10^{-4}$; dihydrogenphosphate, H$_2$PO$_4^-$, $K_a = 6.2 \times 10^{-8}$;
    - Ammonia, NH$_3$, $K_b = 1.8 \times 10^{-5}$, and hydrogen carbonate, HCO$_3^-$, $K_a = 5.6 \times 10^{-11}$.
    (a) Which acids and base solutions will you use to make buffers with the following pH? (i) pH = 3.50; (ii) pH = 5.00; (iii) pH = 7.50; (iv) pH = 9.00; (v) pH = 10.50.
    (b) Indicate the composition and the molar ratio of the conjugate base to the acid in each of the above buffer solutions.
    (Answers to (b): (i) $\frac{[\text{NaHCO}_3]}{[\text{HCOOH}]} = 0.57$; (ii) $\frac{[\text{NaC}_2\text{H}_5\text{O}_2]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.82$; (iii) $\frac{[\text{KH}_2\text{PO}_4]}{[\text{K}_2\text{HPO}_4]} = 1.95$; (iv) $\frac{[\text{NH}_3]}{[\text{NH}_4\text{Cl}]} = 0.56$; (v) $\frac{[\text{Na}_2\text{CO}_3]}{[\text{NaHCO}_3]} = 1.77$)
Exercise #2: Acid-Base Titrations

1. In a titration experiment, 40.0 mL of 0.100 M HCl is titrated with 0.100 M NaOH solution. Determine the pH of the solution:

   (a) before NaOH is added;

   (b) after 20.0 mL of NaOH is added;

   (c) after 30.0 mL of NaOH is added;

   (d) after 40.0 mL of NaOH is added;

   (e) after 45.0 mL of NaOH is added;

   (f) after 50.0 mL of NaOH is added.

   (Answers: (a) pH = 1.000; (b) pH = 1.48; (c) pH = 1.85; (d) pH = 7.00; (e) pH = 11.77; (f) pH = 12.05)

2. In another acid-base titration, 40.0 mL of 0.100 M acetic acid (CH₃COOH, $K_a = 1.8 \times 10^{-5}$) is titrated with 0.100 M NaOH solution. Determine the pH of the solution:

   (a) before NaOH solution is added;

   (b) after 20.0 mL of NaOH is added;

   (c) after 30.0 mL of NaOH is added;

   (d) after 40.0 mL of NaOH is added.

   (e) after 45.0 mL of NaOH is added.

   (f) after 50.0 mL of NaOH is added.

   (Answers: (a) pH = 2.87; (b) pH = 4.74; (c) pH = 5.22; (d) pH = 8.72; (e) pH = 11.77; (f) pH = 12.05)
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3. In a third acid-base titration, 40.0 mL of 0.100 M ammonia (NH₃, $K_b = 1.8 \times 10^{-5}$) is titrated with 0.100 M HCl solution. Determine the pH of the base solution:

(a) before HCl is added;
(b) after 20.0 mL of 0.100 M HCl is been added;
(c) after 30.0 mL of 0.100 M HCl is added;
(d) after 40.0 mL of 0.100 M HCl is added.
(e) after 45.0 mL of 0.100 M HCl is added.
(f) after 50.0 mL of 0.100 M HCl is added.

(Answers: (a) pH = 11.13; (b) pH = 9.25; (c) pH = 8.77; (d) pH = 5.28;
(e) pH = 2.23; (f) pH = 1.95)

4. What is the pH of the resulting solution if 40.0 mL of 0.100 M ammonia (NH₃, $K_b = 1.8 \times 10^{-5}$) is added to 40.0 mL of 0.100 M acetic acid (CH₃COOH, $K_a = 1.8 \times 10^{-5}$)?

(Answer: pH = 7.00)

5. 50.0 mL of 0.0500 M KHP (potassium hydrogen phthalate, KHC₈H₄O₄) was titrated with NaOH solution of unknown concentration and the pH of the solution was measured during titration. It required 23.20 mL of NaOH solution to reach equivalent point and the solution had a pH of 5.30 after 11.6 mL of NaOH was added. (a) Calculate the molar concentration of NaOH and the $K_a$ of KHP. (b) What is the $K_b$ of KHP? (c) What is the $K_b$ of the phthalate ion, C₈H₄O₄²⁻? (d) Calculate the expected pH at equivalent point.

(Answer: (a) [NaOH] = 0.108 M; (b) $K_a = 5.0 \times 10^{-6}$; (c) $K_b = 2.0 \times 10^{-9}$; (d) pH = 8.92)

6. Which indicator(s) is/are suitable for the titration of: (a) HCl with NaOH; (b) CH₃COOH with NaOH, and (c) NH₃ with HCl?

Available indicators are: Methyl Orange ($K_a \sim 10^{-4}$); Methyl Red ($K_a \sim 10^{-5}$); Phenol Red ($K_a \sim 10^{-8}$), and Phenolphthalein ($K_a \sim 10^{-9}$)