Problems Chapter 17 (Aqueous Equilibria)

1. For each of the following cases, decide whether the pH is less than 7, equal to 7, or greater than 7.
    a. Equal volumes of 0.10 M acetic acid ($CH_3COOH$) and 0.10 M KOH are mixed.
    b. 25 mL of 0.015 M $NH_3$ is mixed with 12 mL of 0.015 M HCl.
    c. 150 mL of 0.20 M $HNO_3$ is mixed with 75 mL of 0.40 M NaOH.
    d. 25 mL of 0.45 M $H_2SO_4$ is mixed with 25 mL of 0.90 M NaOH.

2. Calculate the hydronium ion concentration and the pH of the solution that results when 50.0 mL of 0.40 M $NH_3$ is mixed with 25.0 mL of 0.20 M HCl.

3. Rank the following compounds in order of increasing solubility in water: $Na_2CO_3$, $BaCO_3$, $Ag_2CO_3$.

4. A buffer solution is prepared by dissolving 1.50 g each of benzoic acid, $C_6H_5COOH$, and sodium benzoate, $NaC_6H_5COO$, in 150.0 mL of solution.
    a. What is the pH of this buffer solution?
    b. Which buffer component must be added, and in what quantity, to change the pH to 4.00?
    c. What quantity of 2.0 M NaOH or 2.0 M HCl must be added to the buffer to change the pH to 4.00?

5. What is the equilibrium constant for the following reaction?

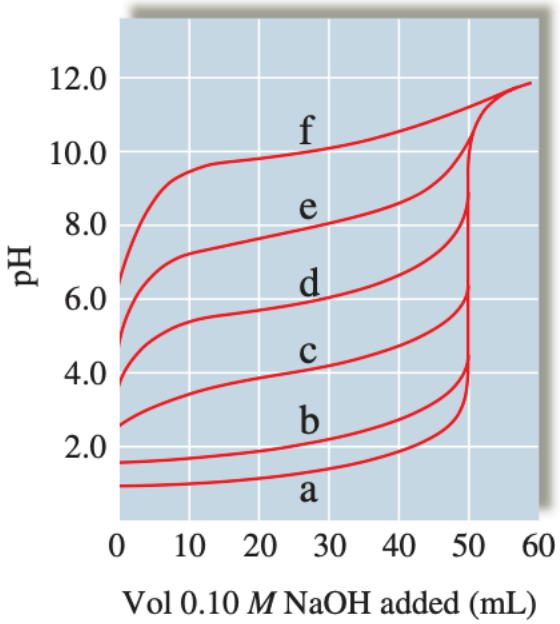
$$AgCl\ (s) + I^-\ (aq) \Leftrightarrow AgI\ (s) + Cl^-\ (aq)$$

    Does the equilibrium lie predominantly to the left or to the right? Will AgI form if iodide ion, $I^-$, is added to a saturated solution of AgCl?

6. A solution contains 0.10 M iodide ion, $I^-$, and 0.10 M carbonate ion, $CO_3^{2-}$.
    a. If solid $Pb(NO_3)_2$ is slowly added to the solution, which salt will precipitate first, $PbI_2$ or $PbCO_3$?
    b. What will be the concentration of the first ion that precipitates ($CO_3^{2-}$ or $I^-$) when the second, more soluble salt begins to precipitate?

7. For the titration of 50.0 mL of 0.150 M ethylamine, $C_2H_5NH_2$, with 0.100 M HCl, find the pH at each of the following points, and then use that information to sketch the titration curve and decide on an appropriate indicator ($K_b$ of ethylamine is $4.3 \times 10^{-4}$).
    a. At the beginning, before HCl is added.
    b. At the halfway point in the titration.
    c. When 75% of the required acid has been added.
    d. At the equivalence point.
    e. When 10.0 mL more HCl has been added than is required.
    f. Sketch the titration curve.
    g. Suggest an appropriate indicator for this titration.

8. The following plot shows the pH curves for the titrations of various acids by 0.10 M NaOH (all of the acids were 50.0-mL samples of 0.10 M concentration).




   a. Which pH curve corresponds to the weakest acid?
   b. Which pH curve corresponds to the strongest acid? Which point on the pH curve would you examine to see if this acid is a strong acid or a weak acid (assuming you did not know the initial concentration of the acid)?
   c. Which pH curve corresponds to an acid with $K_a \approx 1 \times 10^{-6}$?

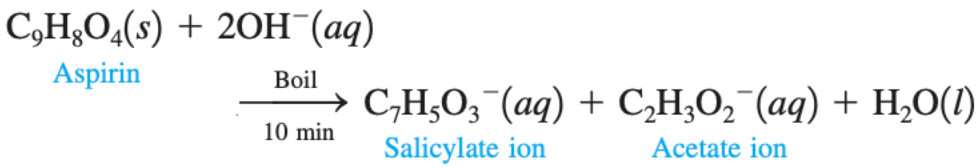
9. Tris(hydroxymethyl)aminomethane, commonly called TRIS or Trizma, is often used as a buffer in biochemical studies. Its buffering range is pH 7 to 9, and $K_b$ is $1.19 \times 10^{-6}$ for the aqueous reaction.

$$\underset{\text{TRIS}}{(HOCH_2)_3CNH_2} + H_2O \Leftrightarrow \underset{\text{TRISH}^+}{(HOCH_2)_3CNH_3^+} + OH^-$$

a. What is the optimal pH for TRIS buffers?
b. Calculate the ratio [TRIS]/[TRISH$^+$] at pH = 7.00 and at pH = 9.00.
c. A buffer is prepared by diluting 50.0 g TRIS base and 65.0 g TRIS hydrochloride (written as TRISHCl) to a total volume of 2.0 L. What is the pH of this buffer? What is the pH after 0.50 mL of 12 M HCl is added to a 200.0-mL portion of the buffer?

10. Calculate the solubility of $Mg(OH)_2$ in 0.50 M $NH_4Cl$.

11. One method for determining the purity of aspirin (molecular formula $C_9H_8O_4$) is to hydrolyze it with NaOH solution and then to titrate the remaining NaOH. The reaction of aspirin with NaOH is as follows:




A sample of aspirin with a mass of 1.427 g was boiled in 50.00 mL of 0.500 M NaOH. After the solution was cooled, it took 31.92 mL of 0.289 M HCl to titrate the excess NaOH. Calculate the purity of the aspirin. What indicator should be used for this titration? Why?

12. You are asked to prepare a $KH_2PO_4$ – $Na_2HPO_4$ solution that has the same pH as human blood, 7.40.
    a. What should be the ratio of concentrations $[HPO_4^{2-}]/[H_2PO_4^-]$ in this solution?
    b. Suppose you have to prepare 1.00 L of the solution described in part (a) and that this solution must be isotonic with blood (have the same osmotic pressure as blood). What masses of $KH_2PO_4$ and of $Na_2HPO_4 \cdot 12\ H_2O$ would you use? (A solution of NaCl with 9.2 g NaCl/L solution is isotonic with blood. Assume that NaCl is completely ionized in aqueous solution)

13. Because an acid-base indicator is a weak acid, it can be titrated with a strong base. Suppose you titrate 25.00 mL of a 0.0100 M solution of the indicator p-nitrophenol $HOC_6H_4NO_2$, with 0.0200 M NaOH. The $pK_a$ of p-nitrophenol is 7.15, and it changes from colorless to yellow in the pH range from 5.6 to 7.6.
    a. Sketch the titration curve for this titration.
    b. Show the pH range over which p-nitrophenol changes color.
    c. Explain why p-nitrophenol cannot serve as its own indicator in this titration.

14. A series of titrations of lactic acid, $CH_3CH(OH)COOH$ ($pK_a = 3.86$) is planned. About 1.00 mmol of the acid will be titrated with NaOH (aq) to a final volume of about 100 mL at the equivalence point.
    a. Which acid-base indicator would you select for the titration?
    b. To assist in locating the equivalence point in the titration, a buffer solution is to be prepared having the same pH as that at the equivalence point. A few drops of the indicator in this buffer will produce the color to be matched in the titrations. Which of the following combinations would be suitable for the buffer solutions?
        i. $CH_3COOH/CH_3COO^-$
        ii. $H_2PO_4^-/HPO_4^{2-}$
        iii. $NH_4^+/NH_3$
    c. What ratio of conjugate base to acid is required in the buffer?

15. Two buffers are prepared by adding an equal number of moles of formic acid (HCOOH) and sodium formate (HCOONa) to enough water to make 1.00 L of solution. Buffer A is prepared using 1.00 mol each of formic acid and sodium formate. Buffer B is prepared by using 0.010 mol of each.
    a. Calculate the pH of each buffer.
    b. Which buffer will have the greater buffer capacity?
    c. Calculate the change in pH for each buffer upon the addition of 1.0 mL of 1.00 M HCl.
    d. Calculate the change in pH for each buffer upon the addition of 10. mL of 1.00 M HCl.

16. A biochemist needs 750 mL of an acetic acid – sodium acetate buffer with pH 4.50. Solid sodium acetate ($CH_3COONa$) and glacial acetic acid ($CH_3COOH$) are available. Glacial acetic acid is 99% $CH_3COOH$ by mass and has a density of 1.05 g/mL. If the buffer is to be 0.15 M in $CH_3COOH$, how many grams of $CH_3COONa$ and how many milliliters of glacia acetic acid must be used?

17. The solubility of $CaCO_3$ is pH dependent.
    a. Calculate the molar solubility of $CaCO_3$ ($K_{sp} = 4.5 \times 10^{-9}$) neglecting the acid-base character of the carbonate ion.
    b. Use the $K_b$ expression for the $CO_3^{2-}$ ion to determine the equilibrium constant for the reaction

$$CaCO_3\,(s) + H_2O\,(l) \Leftrightarrow Ca^{2+}\,(aq) + HCO_3^-\,(aq) + OH^-\,(aq)$$

    c. If we assume that the only sources of $Ca^{2+}$, $HCO_3^-$ and $OH^-$ ions are from the dissolution of $CaCO_3$, what is the molar solubility of $CaCO_3$ using the equilibrium expression from part (b)?
    d. What is the molar solubility of $CaCO_3$ at the pH of the ocean (8.3)?
    e. If the pH is buffered at 7.5, what is the molar solubility of $CaCO_3$?

18. The value of $K_{sp}$ for $Cd(OH)_2$ is $2.5 \times 10^{-14}$.
    a. What is the molar solubility of $Cd(OH)_2$?
    b. The solubility of $Cd(OH)_2$ can be increased through formation of the complex ion $[CdBr_4]^{2-}$ ($K_f = 5 \times 10^3$). If solid $Cd(OH)_2$ is added to a NaBr solution, what is the initial concentration of NaBr needed to increase the molar solubility of $Cd(OH)_2$ to $1.0 \times 10^{-3}$ M?

19. Gout – a condition that results in join swelling and pain – is caused by the formation of sodium urate ($NaC_5H_3N_4O_3$) crystals within tendons, cartilage, and ligaments. Sodium urate precipitates out of blood plasma when uric acid levels become abnormally high. This sometimes happens as a result of eating too many rich foods and consuming too much alcohol, which is why gout is sometimes referred to as the “disease of kings”. If the sodium concentration in blood plasma is 0.140 M, and $K_{sp}$ for sodium urate is $5.76 \times 10^{-8}$, what minimum concentration of urate would result in precipitation?

20.

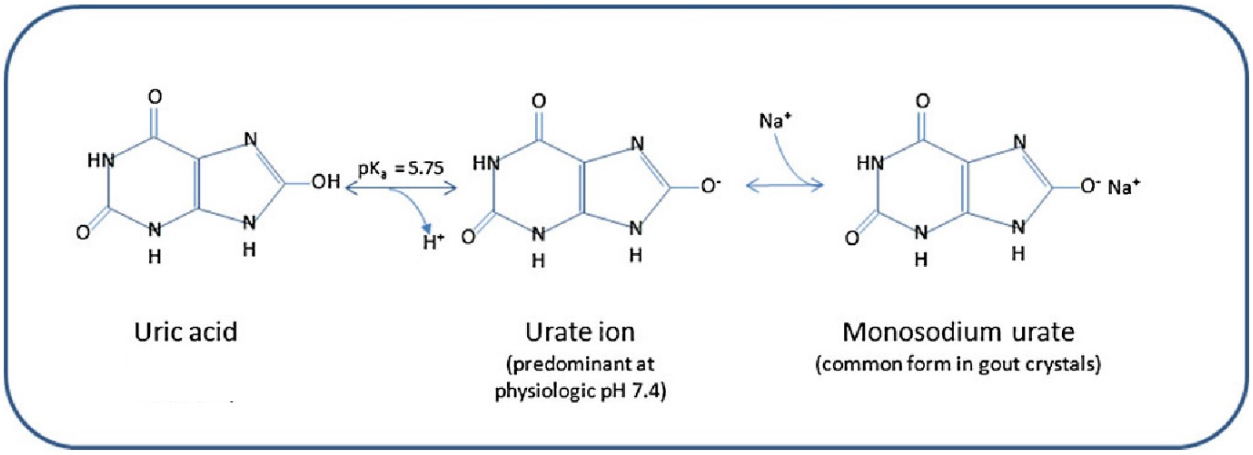
a. Using the $K_{sp}$ value for $Cu(OH)_2$ ($1.6 \times 10^{-19}$) and the overall formation constant for $[Cu(NH_3)_4]^{2+}$ ($1.0 \times 10^{13}$), calculate the value for the equilibrium constant for the following reaction:

$$Cu(OH)_2\ (s) + 4\ NH_3\ (aq) \Leftrightarrow [Cu(NH_3)_4]^{2+}\ (aq) + 2\ OH^-\ (aq)$$

b. Use the value of the equilibrium constant you calculated in part (a) to calculate the solubility (in M) of $Cu(OH)_2$ in 5.0 M $NH_3$. In 5.0 M $NH_3$, the concentration of $OH^-$ is 0.0095 M.

**Tsai-Fan Yu: a pioneer in elucidating and curing gout**

Gout (Problem 19) is a type of inflammatory arthritis resulting in painful, swollen joints, often at the base of the big toe. It is caused by the presence of excessive uric acid in blood and the resulting deposition of poorly soluble urate (conjugate base of uric acid) salt crystals around joints. Uric acid is a metabolic product of many rich foods such as organ meat, shellfish or beer; because of that, gout is often called “rich man’s disease”. Approximately 1–2% of the Western population suffer from gout during the course of their lives.




Tsai-Fan Yu was instrumental in providing an explanation for the cause of gout and developing therapies that are currently used for the treatment of gout. Yu was born in Shanghai, China and lost her mother at the age of 13; her father worked three jobs to ensure his daughter could afford an education. She immigrated to USA in 1947 and eventually became the first female professor to teach at Mount Sinai School of Medicine, one of the oldest and largest teaching hospitals in the country. In the 1950s Yu helped found an innovative clinic for treating gout and engaged in studying the mechanism of the development of gout, which led to connecting the cause of the disease to elevated levels of uric acid. Along with colleagues, Yu performed studies of various drugs that reduce levels of uric acid in the body (for example, by facilitating its

excretion), such as probenecid, colchicine and allopurinol. Yu's legacy in alleviating symptoms of gout – resulting from her exceptional ability to translate laboratory research into effective patient treatment – lives on.

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