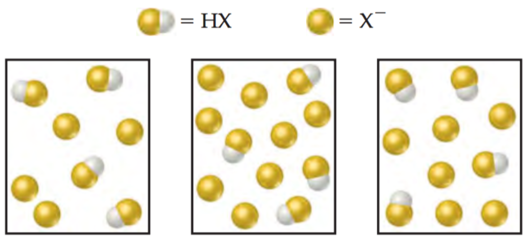
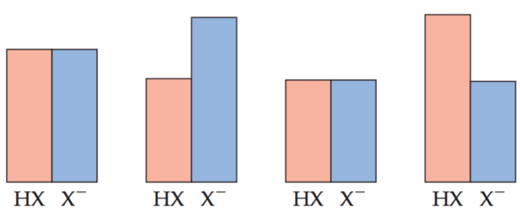
Aqueous Ionic Equilibria
Problem Set

17.1 The following boxes represent aqueous solutions containing a weak acid, HX, and its conjugate base, X^-. Water molecules, hydronium ions and cations are not shown. Which solution has the highest pH? Explain. [Section 17.1]

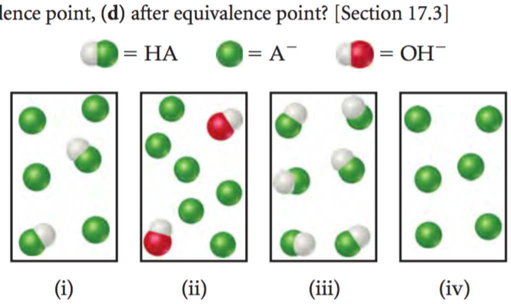


17.3 A buffer contains a weak acid, HX, and its conjugate base. The weak acid has a pK_a of 4.5, and the buffer has a pH of 4.3. Without doing a calculation, predict whether $[HX] = [X^-]$, $[HX] > [X^-]$, or $[HX] < [X^-]$. Explain. [Section 17.2]

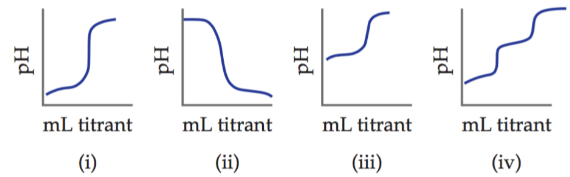
17.4 The drawing on the left represents a buffer composed of equal concentrations of a weak acid, HX, and its conjugate base, X^-. The heights of the columns are proportional to the concentrations of the components of the buffer. **(a)** Which of the three drawings, (1), (2), or (3), represents the buffer after the addition of a strong acid? **(b)** Which of the three represents the buffer after the addition of a strong base? **(c)** Which of the three represents a situation that cannot arise from the addition of either an acid or a base? [Section 17.2]



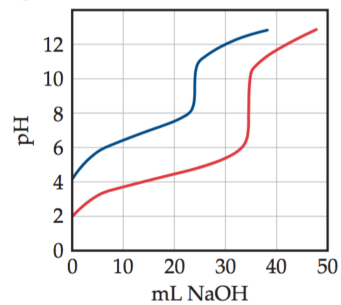
17.5 The following drawings represent solutions at various stages of the titration of a weak acid, HA, with NaOH. (The Na^+ ions and water molecules have been omitted for clarity.) To which of the following regions of the titration curve does each drawing correspond: **(a)** before addition of NaOH, **(b)** after addition of NaOH but before equivalence point, **(c)** at equivalence point, **(d)** after equivalence point? [Section 17.3]



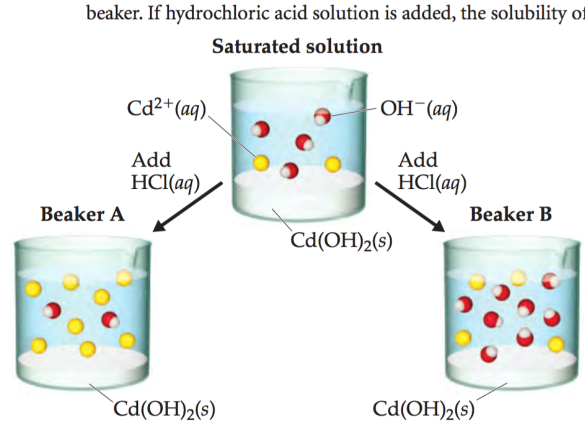
17.6 Match the following descriptions of titration curves with the diagrams: **(a)** strong acid added to strong base, **(b)** strong base added to weak acid, **(c)** strong base added to strong acid, **(d)** strong base added to polyprotic acid. [Section 17.3]



17.7 Equal volumes of two acids are titrated with 0.10 *M* NaOH resulting in the two titration curves shown in the following figure. **(a)** Which curve corresponds to the more concentrated acid solution? **(b)** Which corresponds to the acid with the larger K_a? Explain. [Section 17.3]

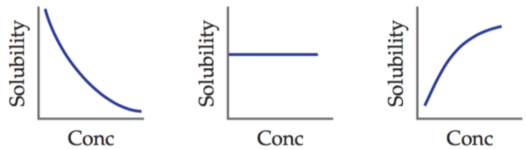


17.8 A saturated solution of $Cd(OH)_2$ is shown in the middle beaker. If hydrochloric acid solution is added, the solubility of

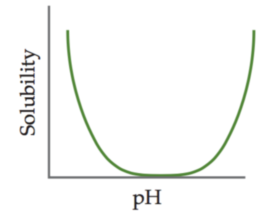


$Cd(OH)_2$ will increase, causing additional solid to dissolve. Which of the two choices, Beaker A or Beaker B, accurately represents the solution after equilibrium is reestablished? Explain. (The water molecules and Cl^- ions are omitted for clarity). [Sections 17.4 and 17.5]

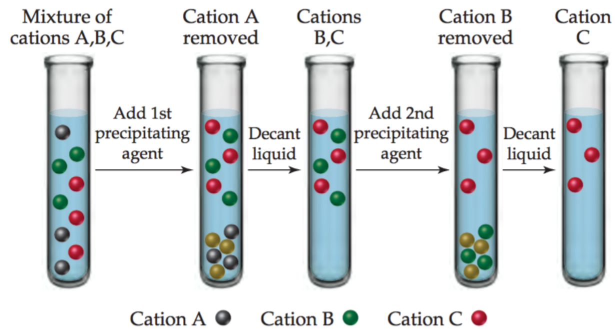
17.9 The following graphs represent the behavior of $BaCO_3$ under different circumstances. In each case the vertical axis indicates the solubility of the $BaCO_3$ and the horizontal axis represents the concentration of some other reagent. **(a)** Which graph represents what happens to the solubility of $BaCO_3$ as HNO_3 is added? **(b)** Which graph represents what happens to the $BaCO_3$ solubility as Na_2CO_3 is added? **(c)** Which represents what happens to the $BaCO_3$ solubility as $NaNO_3$ is added? [Section 17.5]



17.11 What is the name given to the kind of behavior demonstrated by a metal hydroxide in this graph? [Section 17.5]



17.12 Three cations, Ni^{2+}, Cu^{2+}, and Ag^{+}, are separated using two different precipitating agents. Based on Figure 17.23, what two precipitating agents could be used? Using these agents, indicate which of the cations is A, which is B, and which is C. [Section 17.7]



17.13 **(a)** What is the common-ion effect? **(b)** Give an example of a salt that can decrease the ionization of HNO_2 in solution.

17.18 **(a)** Calculate the percent ionization of 0.125 M lactic acid ($K_a = 1.4 \times 10^{-4}$). **(b)** Calculate the percent ionization of 0.125 M lactic acid in a solution containing 0.0075 M sodium lactate.

17.19 Explain why a mixture of CH_3COOH and CH_3COONa can act as a buffer while a mixture of HCl and NaCl cannot.

17.20 Explain why a mixture formed by mixing 100 mL of 0.100 M CH_3COOH and 50 mL of 0.100 M NaOH will act as a buffer.

17.22 **(a)** Calculate the pH of a buffer that is 0.105 M in $NaHCO_3$ and 0.125 M in Na_2CO_3. **(b)** Calculate the pH of a solution formed by mixing 65 mL of 0.20 M $NaHCO_3$ with 75 mL of 0.15 M Na_2CO_3.

17.23 A buffer is prepared by adding 20.0 g of sodium acetate (CH_3COONa) to 500 mL of a 0.150 M acetic acid (CH_3COOH) solution. **(a)** Determine the pH of the buffer. **(b)** Write the complete ionic equation for the reaction that occurs when a few drops of hydrochloric acid are added to the buffer. **(c)** Write the complete ionic equation for the reaction that occurs when a few drops of sodium hydroxide solution are added to the buffer.

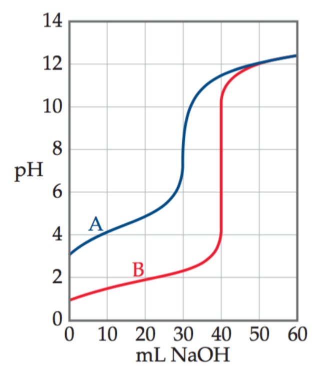
17.26 You are asked to prepare a pH = 4.00 buffer starting from 1.50 L of 0.0200 M solution of benzoic acid (C_6H_5COOH) and an excess of sodium benzoate (C_6H_5COONa). **(a)** What is the pH of the benzoic acid solution prior to adding sodium benzoate? **(b)** How many grams of sodium benzoate should be added to prepare the buffer? Neglect the small volume change that occurs when the sodium benzoate is added.

17.27 A buffer contains 0.10 mol of acetic acid and 0.13 mol of sodium acetate in 1.00 L. **(a)** What is the pH of this buffer? **(b)** What is the pH of the buffer after the addition of 0.02 mol of KOH? **(c)** What is the pH of the buffer after the addition of 0.02 mol of HNO_3?

17.29 **(a)** What is the ratio of HCO_3^- to H_2CO_3 in blood of pH 7.4? **(b)** What is the ratio of HCO_3^- to H_2CO_3 in an exhausted marathon runner whose blood pH is 7.1?

17.32 You have to prepare a pH 5.00 buffer, and you have the following 0.10 M solutions available: HCOOH, HCOONa, CH_3COOH, CH_3COONa, HCN, and NaCN. Which solutions would you use? How many milliliters of each solution would you use to make approximately a liter of the buffer?

17.33 The accompanying graph shows the titration curves for two monoprotic acids. **(a)** Which curve is that of a strong acid? **(b)** What is the approximate pH at the equivalence point of each titration? **(c)** 40.0 mL of each acid was titrated with 0.100 M base. Which acid is more concentrated?



17.34 How does titration of a strong, monoprotic acid with a strong base differ from titration of a weak, monoprotic acid with a strong base with respect to the following: **(a)** quantity of base required to reach the equivalence point, **(b)** pH at the beginning of the titration, **(c)** pH at the equivalence point, **(d)** pH after addition of a slight excess of base, **(e)** choice of indicator for determining the equivalence point?

17.37 Predict whether the equivalence point of each of the following titrations is below, above, or at pH 7: **(a)** $NaHCO_3$ titrated with NaOH, **(b)** NH_3 titrated with HCl, **(c)** KOH titrated with HBr.

17.41 How many milliliters of 0.0850 M NaOH are required to titrate each of the following solutions to the equivalence point: **(a)** 40.0 mL of 0.0900 M HNO_3, **(b)** 35.0 mL of 0.0850 M CH_3COOH, **(c)** 50.0 mL of a solution that contains 1.85 g of HCl per liter?

17.42 How many milliliters of 0.105 M HCl are needed to titrate each of the following solutions to the equivalence point: **(a)** 45.0 mL of 0.0950 M NaOH, **(b)** 22.5 mL of 0.118 M NH_3, **(c)** 125.0 mL of a solution that contains 1.35 g of NaOH per liter?

17.43 A 20.0-mL sample of 0.200 M HBr solution is titrated with 0.200 M NaOH solution. Calculate the pH of the solution after the following volumes of base have been added: **(a)** 15.0 mL, **(b)** 19.9 mL, **(c)** 20.0 mL, **(d)** 20.1 mL, **(e)** 35.0 mL.

17.45 A 35.0-mL sample of 0.150 M acetic acid (CH_3COOH) is titrated with 0.150 M NaOH solution. Calculate the pH after the following volumes of base have been added: **(a)** 0 mL, **(b)** 17.5 mL, **(c)** 34.5 mL, **(d)** 35.0 mL, **(e)** 35.5 mL, **(f)** 50.0 mL.

17.49 **(a)** Why is the concentration of undissolved solid not explicitly included in the expression for the solubility-product constant? **(b)** Write the expression for the solubility-product constant for each of the following strong electrolytes: AgI, $SrSO_4$, $Fe(OH)_2$, and Hg_2Br_2.

17.54 A 1.00-L solution saturated at 25 °C with lead(II) iodide contains 0.54 g of PbI_2. Calculate the solubility-product constant for this salt at 25 °C.

17.56 Calculate the solubility of LaF_3 in grams per liter in **(a)** pure water, **(b)** 0.010 M KF solution, **(c)** 0.050 M $LaCl_3$ solution.

17.58 Consider a beaker containing a saturated solution of PbI_2 in equilibrium with undissolved $PbI_2(s)$. **(a)** If solid KI is added to this solution, will the amount of solid PbI_2 at the bottom of the beaker increase, decrease, or remain the same? **(b)** Will the concentration of Pb^{2+} ions in solution increase or decrease? **(c)** Will the concentration of I^- ions in solution increase or decrease?

17.59 Calculate the solubility of $Mn(OH)_2$ in grams per liter when buffered at pH **(a)** 7.0, **(b)** 9.5, **(c)** 11.8.

17.61 Which of the following salts will be substantially more soluble in acidic solution than in pure water: **(a)** $ZnCO_3$, **(b)** ZnS, **(c)** BiI_3, **(d)** AgCN, **(e)** $Ba_3(PO_4)_2$?

17.67 **(a)** Will $Ca(OH)_2$ precipitate from solution if the pH of a 0.050 M solution of $CaCl_2$ is adjusted to 8.0? **(b)** Will Ag_2SO_4 precipitate when 100 mL of 0.050 M $AgNO_3$ is mixed with 10 mL of 5.0×10^{-2} M Na_2SO_4 solution?

17.69 Calculate the minimum pH needed to precipitate $Mn(OH)_2$ so completely that the concentration of Mn^{2+} is less than 1 μg per liter [1 part per billion (ppb)].

17.72 A solution of Na_2SO_4 is added dropwise to a solution that is 0.010 M in Ba^{2+} and 0.010 M in Sr^{2+}. **(a)** What concentration of SO_4^{2-} is necessary to begin precipitation? (Neglect volume changes. $BaSO_4$: $K_{sp} = 1.1 \times 10^{-10}$; $SrSO_4$: $K_{sp} = 3.2 \times 10^{-7}$.) **(b)** Which cation precipitates first? **(c)** What is the concentration of SO_4^{2-} when the second cation begins to precipitate?