Problems

Problems with **colored** numbers are answered in Appendix E. Sections match the text and provide the numbers of relevant sample problems. Bracketed problems are grouped in pairs (indicated by a short rule) that cover the same concept. Comprehensive Problems are based on material from any section or previous chapter.

Note: Unless stated otherwise, all of the problems for this chapter refer to aqueous solutions at 298 K (25°C).

Equilibria of Acid-Base Buffer Systems
(Sample Problems 19.1 and 19.2)

19.1 What is the purpose of an acid-base buffer?

19.2 How do the acid and base components of a buffer function? Why are they often a conjugate acid-base pair of a weak acid?

19.3 What is the common-ion effect? How is it related to Le Châtelier's principle? Explain with equations that include HF and NaF.

19.4 When a small amount of H_3O^+ is added to a buffer, does the pH remain constant? Explain.

19.5 What is the difference between buffers with high and low capacities? Will adding 0.01 mol of HCl produce a greater pH change in a buffer with a high or a low capacity? Explain.

19.6 Which of these factors influence buffer capacity? How?
(a) Conjugate acid-base pair   (b) pH of the buffer
(c) Concentration of buffer components   (d) Buffer range
(e) pK_a of the acid component

19.7 What is the relationship between the buffer range and the buffer-component concentration ratio?

19.8 A chemist needs a pH 3.5 buffer. Should she use NaOH with formic acid ($K_a = 1.8\times10^{-4}$) or with acetic acid ($K_a = 1.8\times10^{-5}$)? Why? What is the disadvantage of choosing the other acid? What is the role of the NaOH?

19.9 What are the $[H_3O^+]$ and the pH of a propanoic acid–propanoate buffer that consists of 0.25 M CH_3CH_2COONa and 0.15 M CH_3CH_2COOH (K_a of propanoic acid = 1.3×10^{-5})?

19.10 What are the $[H_3O^+]$ and the pH of a benzoic acid–benzoate buffer that consists of 0.33 M C_6H_5COOH and 0.28 M C_6H_5COONa (K_a of benzoic acid = 6.3×10^{-5})?

19.11 Find the pH of a buffer that consists of 1.0 M sodium phenolate (C_6H_5ONa) and 1.2 M phenol (C_6H_5OH) (pK_a of phenol = 10.00).

19.12 Find the pH of a buffer that consists of 0.12 M boric acid (H_3BO_3) and 0.82 M sodium borate (NaH_2BO_3) (pK_a of boric acid = 9.24).

19.13 Find the pH of a buffer that consists of 0.20 M NH_3 and 0.10 M NH_4Cl (pK_b of NH_3 = 4.75).

19.14 Find the pH of a buffer that consists of 0.50 M methylamine (CH_3NH_2) and 0.60 M CH_3NH_3Cl (pK_b of CH_3NH_2 = 3.35).

19.15 What is the buffer-component concentration ratio, $[Pr^-]/[HPr]$, of a buffer that has a pH of 5.11 (K_a of HPr = 1.3×10^{-5})?

19.16 What is the buffer-component concentration ratio, $[NO_2^-]/[HNO_2]$, of a buffer that has a pH of 2.95 (K_a of $HNO_2 = 7.1\times10^{-4}$)?

19.17 A buffer containing 0.2000 M of acid, HA, and 0.1500 M of its conjugate base, A^-, has a pH of 3.35. What is the pH after 0.0015 mol of NaOH is added to 0.5000 L of this solution?

19.18 A buffer that contains 0.40 M base, B, and 0.25 M of its conjugate acid, BH^+, has a pH of 8.88. What is the pH after 0.0020 mol of HCl is added to 0.25 L of this solution?

19.19 A buffer is prepared by mixing 184 mL of 0.442 M HCl and 0.500 L of 0.400 M sodium acetate. (See Appendix C.) (a) What is the pH? (b) How many grams of KOH must be added to 0.500 L of the buffer to change the pH by 0.15 units?

19.20 A buffer is prepared by mixing 50.0 mL of 0.050 M sodium bicarbonate and 10.7 mL of 0.10 M NaOH. (See Appendix C.) (a) What is the pH? (b) How many grams of HCl must be added to 25.0 mL of the buffer to change the pH by 0.07 units?

19.21 Choose specific acid-base conjugate pairs suitable for preparing the following buffers: (a) pH ≈ 4.0; (b) pH ≈ 7.0. (See Appendix C.)

19.22 Choose specific acid-base conjugate pairs suitable for preparing the following buffers: (a) $[H_3O^+] \approx 1\times10^{-9}$ M; (b) $[OH^-] \approx 3\times10^{-5}$ M. (See Appendix C.)

19.23 An industrial chemist studying the effect of pH on bleaching and sterilizing processes prepares several hypochlorite buffers. Calculate the pH of each of the following buffers:
(a) 0.100 M HClO and 0.100 M NaClO
(b) 0.100 M HClO and 0.150 M NaClO
(c) 0.150 M HClO and 0.100 M NaClO
(d) One liter of the solution in part (a) after 0.0050 mol of NaOH has been added

19.24 Oxoanions of phosphorus are buffer components in blood. For a KH_2PO_4-Na_2HPO_4 solution with pH = 7.40 (pH of normal arterial blood), what is the buffer-component concentration ratio?

Acid-Base Titration Curves
(Sample Problem 19.3)

19.25 How can you estimate the pH range of an indicator's color change? Why do some indicators have two separate pH ranges?

19.26 Why does the color change of an indicator take place over a range of about 2 pH units?

19.27 Why doesn't the addition of an acid-base indicator affect the pH of the test solution?

19.28 What is the difference between the end point of a titration and the equivalence point? Is the equivalence point always reached first? Explain.

19.29 Some automatic titrators measure the slope of a titration curve to determine the equivalence point. What happens to the slope that enables the instrument to recognize this point?

19.30 Explain how *strong acid*–strong base, *weak acid*–strong base, and *weak base*–strong acid titrations using the same concentrations differ in terms of (a) the initial pH and (b) the pH at the equivalence point. (The component in italics is in the flask.)

19.31 What species are in the buffer region of a weak acid–strong base titration? How are they different from the species at the equivalence point? How are they different from the species in the buffer region of a weak base–strong acid titration?

19.32 Why is the center of the buffer region of a weak acid–strong base titration significant?

19.33 The indicator cresol red has $K_a = 5.0\times10^{-9}$. Over what approximate pH range does it change color?

19.34 The indicator thymolphthalein has $K_a = 7.9\times10^{-11}$. Over what approximate pH range does it change color?

19.35 Use Figure 19.5 to find an indicator for these titrations:
(a) 0.10 M HCl with 0.10 M NaOH
(b) 0.10 M HCOOH (Appendix C) with 0.10 M NaOH

19.36 Use Figure 19.5 to find an indicator for these titrations:
(a) 0.10 M CH$_3$NH$_2$ (Appendix C) with 0.10 M HCl
(b) 0.50 M HI with 0.10 M KOH

19.37 Calculate the pH during the titration of 50.00 mL of 0.1000 M HCl with 0.1000 M NaOH solution after the following additions of base: (a) 0 mL; (b) 25.00 mL; (c) 49.00 mL; (d) 49.90 mL; (e) 50.00 mL; (f) 50.10 mL; (g) 60.00 mL.

19.38 Calculate the pH during the titration of 30.00 mL of 0.1000 M KOH with 0.1000 M HBr solution after the following additions of acid: (a) 0 mL; (b) 15.00 mL; (c) 29.00 mL; (d) 29.90 mL; (e) 30.00 mL; (f) 30.10 mL; (g) 40.00 mL.

19.39 Find the pH during the titration of 20.00 mL of 0.1000 M butanoic acid, CH$_3$CH$_2$CH$_2$COOH ($K_a = 1.54\times10^{-5}$), with 0.1000 M NaOH solution after the following additions of titrant: (a) 0 mL; (b) 10.00 mL; (c) 15.00 mL; (d) 19.00 mL; (e) 19.95 mL; (f) 20.00 mL; (g) 20.05 mL; (h) 25.00 mL.

19.40 Find the pH during the titration of 20.00 mL of 0.1000 M triethylamine, (CH$_3$CH$_2$)$_3$N ($K_b = 5.2\times10^{-4}$), with 0.1000 M HCl solution after the following additions of titrant: (a) 0 mL; (b) 10.00 mL; (c) 15.00 mL; (d) 19.00 mL; (e) 19.95 mL; (f) 20.00 mL; (g) 20.05 mL; (h) 25.00 mL.

19.41 Find the pH and volume (mL) of 0.0372 M NaOH needed to reach the equivalence point in titrations of
(a) 42.2 mL of 0.0520 M CH$_3$COOH
(b) 23.4 mL of 0.0390 M HNO$_2$

19.42 Find the pH and the volume (mL) of 0.135 M HCl needed to reach the equivalence point(s) in titrations of the following:
(a) 55.5 mL of 0.234 M NH$_3$
(b) 17.8 mL of 1.11 M CH$_3$NH$_2$

Equilibria of Slightly Soluble Ionic Compounds
(Sample Problems 19.4 to 19.9)

19.43 The molar solubility of M$_2$X is 5×10^{-5} M. What is the molarity of each ion? How do you set up the calculation to find K_{sp}? What assumption must you make about the dissociation of M$_2$X into ions? Why is the calculated K_{sp} higher than the actual value?

19.44 Why does pH affect the solubility of CaF$_2$ but not of CaCl$_2$?

19.45 In a gaseous equilibrium, the reverse reaction occurs when $Q_c > K_c$. What occurs in aqueous solution when $Q_{sp} > K_{sp}$?

19.46 Write the ion-product expressions for (a) silver carbonate; (b) barium fluoride; (c) copper(II) sulfide.

19.47 Write the ion-product expressions for (a) iron(III) hydroxide; (b) barium phosphate; (c) tin(II) sulfide.

19.48 The solubility of silver carbonate is 0.032 M at 20°C. Calculate its K_{sp}.

19.49 The solubility of zinc oxalate is 7.9×10^{-3} M at 18°C. Calculate its K_{sp}.

19.50 The solubility of silver dichromate at 15°C is 8.3×10^{-3} g/100 mL solution. Calculate its K_{sp}.

19.51 The solubility of calcium sulfate at 30°C is 0.209 g/100 mL solution. Calculate its K_{sp}.

19.52 Find the molar solubility of SrCO$_3$ ($K_{sp} = 5.4\times10^{-10}$) in (a) pure water and (b) 0.13 M Sr(NO$_3$)$_2$.

19.53 Find the molar solubility of BaCrO$_4$ ($K_{sp} = 2.1\times10^{-10}$) in (a) pure water and (b) 1.5×10^{-3} M Na$_2$CrO$_4$.

19.54 Calculate the molar solubility of Ca(IO$_3$)$_2$ in (a) 0.060 M Ca(NO$_3$)$_2$ and (b) 0.060 M NaIO$_3$. (See Appendix C.)

19.55 Calculate the molar solubility of Ag$_2$SO$_4$ in (a) 0.22 M AgNO$_3$ and (b) 0.22 M Na$_2$SO$_4$. (See Appendix C.)

19.56 Which compound in each pair is more soluble in water?
(a) Magnesium hydroxide or nickel(II) hydroxide
(b) Lead(II) sulfide or copper(II) sulfide
(c) Silver sulfate or magnesium fluoride

19.57 Which compound in each pair is more soluble in water?
(a) Strontium sulfate or barium chromate
(b) Calcium carbonate or copper(II) carbonate
(c) Barium iodate or silver chromate

19.58 Write equations to show whether the solubility of either of the following is affected by pH: (a) AgCl; (b) SrCO$_3$.

19.59 Write equations to show whether the solubility of either of the following is affected by pH: (a) CuBr; (b) Ca$_3$(PO$_4$)$_2$.

19.60 Does any solid Cu(OH)$_2$ form when 0.075 g of KOH is dissolved in 1.0 L of 1.0×10^{-3} M Cu(NO$_3$)$_2$?

19.61 Does any solid PbCl$_2$ form when 3.5 mg of NaCl is dissolved in 0.250 L of 0.12 M Pb(NO$_3$)$_2$?

19.62 When blood is donated, sodium oxalate solution is used to precipitate Ca^{2+}, which triggers clotting. A 104-mL sample of blood contains 9.7×10^{-5} g Ca^{2+}/mL. A technologist treats the sample with 100.0 mL of 0.1550 M Na$_2$C$_2$O$_4$. Calculate [Ca^{2+}] after the treatment. (See Appendix C for K_{sp} of CaC$_2$O$_4$·H$_2$O.)
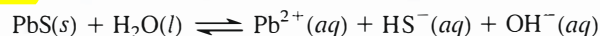
Equilibria Involving Complex Ions
(Sample Problem 19.10)

19.63 How can a positive metal ion be at the center of a negative complex ion?

19.64 Write equations to show the stepwise reaction of Cd(H$_2$O)$_4^{2+}$ in an aqueous solution of KI to form CdI$_4^{2-}$. Show that $K_{f(overall)} = K_{f1} \times K_{f2} \times K_{f3} \times K_{f4}$.

19.65 Consider the dissolution of PbS in water:
$$PbS(s) + H_2O(l) \rightleftharpoons Pb^{2+}(aq) + HS^-(aq) + OH^-(aq)$$
Adding aqueous NaOH causes more PbS to dissolve. Does this violate Le Châtelier's principle? Explain.

19.66 Write a balanced equation for the reaction of Hg(H$_2$O)$_4^{2+}$ in aqueous KCN.

19.67 Write a balanced equation for the reaction of Zn(H$_2$O)$_4^{2+}$ in aqueous NaCN.

19.68 Write a balanced equation for the reaction of Ag(H$_2$O)$_2^+$ in aqueous Na$_2$S$_2$O$_3$.

19.69 Write a balanced equation for the reaction of Al(H$_2$O)$_6^{3+}$ in aqueous KF.

19.70 Find the solubility of AgI in 2.5 M NH$_3$ [K_{sp} of AgI = 8.3×10^{-17}; K_f of Ag(NH$_3$)$_2^+$ = 1.7×10^7].

19.71 Find the solubility of Cr(OH)$_3$ in a buffer of pH 13.0 [K_{sp} of Cr(OH)$_3$ = 6.3×10^{-31}; K_f of Cr(OH)$_4^-$ = 8.0×10^{29}].

Comprehensive Problems

Problems with an asterisk (*) are more challenging.

19.72 A microbiologist is preparing a medium on which to culture *E. coli* bacteria. She buffers the medium at pH 7.00 to minimize the effect of acid-producing fermentation. What volumes of equimolar aqueous solutions of K_2HPO_4 and KH_2PO_4 must she combine to make 100. mL of the pH 7.00 buffer?

19.73 Tris(hydroxymethyl)aminomethane [(HOCH$_2$)$_3$CNH$_2$, known as TRIS or THAM] is a weak base widely used in biochemical experiments to make buffer solutions in the pH range of 7 to 9. A certain TRIS buffer has a pH of 8.10 at 25°C and a pH of 7.80 at 37°C. Why does the pH change with temperature?

19.74 Gout is caused by an error in nucleic acid metabolism that leads to a buildup of uric acid in body fluids, which is deposited as slightly soluble sodium urate ($C_5H_3N_4O_3Na$) in the soft tissues of joints. If the extracellular $[Na^+]$ is 0.15 M and the solubility in water of sodium urate is 0.085 g/100. mL, what is the minimum urate ion concentration (abbreviated [Ur⁻]) that will cause a deposit of sodium urate?

19.75 Cadmium ion in solution is analyzed by being precipitated as the sulfide, a yellow compound used as a pigment in everything from artists' oil paints to glass and rubber. Calculate the molar solubility of cadmium sulfide at 25°C.

19.76 The solubility of KCl is 3.7 M at 20°C. Two beakers contain 100. mL of saturated KCl solution: 100. mL of 6.0 M HCl is added to the first beaker and 100. mL of 12 M HCl to the second. (a) Find the ion-product constant of KCl at 20°C. (b) What mass, if any, of KCl will precipitate from each beaker?

19.77 Manganese(II) sulfide is one of the compounds found in the nodules on the ocean floor that may eventually be a primary source of many transition metals. The solubility of MnS is 4.7×10^{-4} g/100 mL solution. Estimate the K_{sp} of MnS.

19.78 The normal pH of blood is 7.40 ± 0.05 and is controlled in part by the H_2CO_3-HCO_3^- buffer system.
(a) Assuming that the K_a value for carbonic acid at 25°C applies to blood, what is the $[H_2CO_3]/[HCO_3^-]$ ratio in normal blood?
(b) In a condition called *acidosis*, the blood is too acidic. What is the $[H_2CO_3]/[HCO_3^-]$ ratio in a patient whose blood pH is 7.20 (severe acidosis)?

19.79 Tooth enamel consists of hydroxyapatite, $Ca_5(PO_4)_3OH$ ($K_{sp} = 6.8 \times 10^{-37}$). Fluoride ion added to drinking water reacts with $Ca_5(PO_4)_3OH$ to form the more tooth decay–resistant fluorapatite, $Ca_5(PO_4)_3F$ ($K_{sp} = 1.0 \times 10^{-60}$). Fluoridated water has dramatically decreased cavities among children. Calculate the solubility of $Ca_5(PO_4)_3OH$ and of $Ca_5(PO_4)_3F$ in water.

19.80 The acid-base indicator ethyl orange turns from red to yellow over the pH range 3.4 to 4.8. Estimate K_a for ethyl orange.

* 19.81 Instrumental acid-base titrations use a pH meter to monitor the changes in pH and volume. The equivalence point is found from the volume at which the curve has the steepest slope.
(a) Use Figure 19.7 to calculate the slope $\Delta pH/\Delta V$ for all pairs of adjacent points and the average volume (V_{avg}) for each interval.

(b) Plot $\Delta pH/\Delta V$ vs. V_{avg} to find the steepest slope, and thus the volume at the equivalence point. (For example, the first pair of points gives $\Delta pH = 0.22$, $\Delta V = 10.00$ mL; hence, $\Delta pH/\Delta V = 0.022$ mL^{-1}, and $V_{avg} = 5.00$ mL.)

19.82 What is the pH of a solution of 6.5×10^{-9} mol of $Ca(OH)_2$ in 10.0 L of water [K_{sp} of $Ca(OH)_2 = 6.5 \times 10^{-6}$]?

19.83 A student wants to dissolve the maximum amount of CaF_2 ($K_{sp} = 3.2 \times 10^{-11}$) to make 1 L of aqueous solution.
(a) Into which of the following should she dissolve the salt?
(I) Pure water   (II) 0.01 M HF   (III) 0.01 M NaOH
(IV) 0.01 M HCl   (V) 0.01 M $Ca(OH)_2$
(b) Which would dissolve the least amount of salt?

19.84 The Henderson-Hasselbalch equation gives a relationship for obtaining the pH of a buffer solution consisting of HA and A⁻. Derive an analogous relationship for obtaining the pOH of a buffer solution consisting of B and BH$^+$.

19.85 Calculate the molar solubility of $Hg_2C_2O_4$ ($K_{sp} = 1.75 \times 10^{-13}$) in 0.13 M $Hg_2(NO_3)_2$.

19.86 The well water in an area is "hard" because it is in equilibrium with $CaCO_3$ in the surrounding rocks. What is the concentration of Ca^{2+} in the well water (assuming the water's pH is such that the CO_3^{2-} ion is not hydrolyzed)? (See Appendix C for K_{sp} of $CaCO_3$.)

19.87 An environmental technician collects a sample of rainwater. A light on her portable pH meter indicates low battery power, so she uses indicator solutions to estimate the pH. A piece of litmus paper turns red, indicating acidity, so she divides the sample into thirds and obtains the following results: thymol blue turns yellow; bromphenol blue turns green; and methyl red turns red. Estimate the pH of the rainwater.

* 19.88 Quantitative analysis of Cl⁻ ion is often performed by a titration with silver nitrate, using sodium chromate as an indicator. As standardized $AgNO_3$ is added, both white AgCl and red Ag_2CrO_4 precipitate, but so long as some Cl⁻ remains, the Ag_2CrO_4 redissolves as the mixture is stirred. When the red color is permanent, the equivalence point has been reached.
(a) Calculate the equilibrium constant for the reaction
$$2AgCl(s) + CrO_4^{2-}(aq) \rightleftharpoons Ag_2CrO_4(s) + 2Cl^-(aq)$$
(b) Explain why the silver chromate redissolves.

19.89 Some kidney stones form by the precipitation of calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$, $K_{sp} = 2.3 \times 10^{-9}$). The pH of urine varies from 5.5 to 7.0, and the average $[Ca^{2+}]$ in urine is 2.6×10^{-3} M.
(a) If the concentration of oxalic acid in urine is 3.0×10^{-13} M, will kidney stones form at pH = 5.5?
(b) At pH = 7.0?
(c) Vegetarians have a urine pH above 7. Are they more or less likely to form kidney stones?

19.90 A 35.00-mL solution of 0.2500 M HF is titrated with a standardized 0.1532 M solution of NaOH at 25°C.
(a) What is the pH of the HF solution before titrant is added?
(b) How many milliliters of titrant are required to reach the equivalence point?
(c) What is the pH at 0.50 mL before the equivalence point?
(d) What is the pH at the equivalence point?
(e) What is the pH at 0.50 mL after the equivalence point?

* **19.91** Because of the toxicity of mercury compounds, mercury(I) chloride is used in antibacterial salves. The mercury(I) ion (Hg_2^{2+}) consists of two bound Hg^+ ions.
(a) What is the empirical formula of mercury(I) chloride?
(b) Calculate $[Hg_2^{2+}]$ in a saturated solution of mercury(I) chloride ($K_{sp} = 1.5 \times 10^{-18}$).
(c) A seawater sample contains 0.20 lb of NaCl per gallon. Find $[Hg_2^{2+}]$ if the seawater is saturated with mercury(I) chloride.
(d) How many grams of mercury(I) chloride are needed to saturate 4900 km^3 of water (the volume of Lake Michigan)?
(e) How many grams of mercury(I) chloride are needed to saturate 4900 km^3 of seawater?

* **19.92** A lake that has a surface area of 10.0 acres (1 acre = 4.840×10^3 yd^2) receives 1.00 in. of rain of pH 4.20. (Assume the acidity of the rain is due to a strong, monoprotic acid.)
(a) How many moles of H_3O^+ are in the rain falling on the lake?
(b) If the lake is unbuffered (pH = 7.00) and its average depth is 10.0 ft before the rain, find the pH after the rain has been mixed with lake water. (Ignore runoff from the surrounding land.)
(c) If the lake contains hydrogen carbonate ions (HCO_3^-), what mass of HCO_3^- would neutralize the acid in the rain?

19.93 Sodium chloride is purified for use as table salt by adding HCl to a saturated solution of NaCl (317 g/L). When 25.5 mL of 7.85 M HCl is added to 0.100 L of saturated solution, how many grams of purified NaCl precipitate?

19.94 Calcium ion present in water supplies is easily precipitated as calcite ($CaCO_3$):

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s)$$
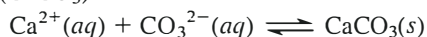
Because the K_{sp} decreases with temperature, heating hard water forms a calcite "scale," which clogs pipes and water heaters. Find the solubility of calcite in water (a) at 10°C ($K_{sp} = 4.4 \times 10^{-9}$) and (b) at 30°C ($K_{sp} = 3.1 \times 10^{-9}$).

19.95 Scenes A to D represent tiny portions of 0.10 M aqueous solutions of a weak acid HA ($K_a = 4.5 \times 10^{-5}$), its conjugate base A$^-$, or a mixture of the two (only these species are shown):
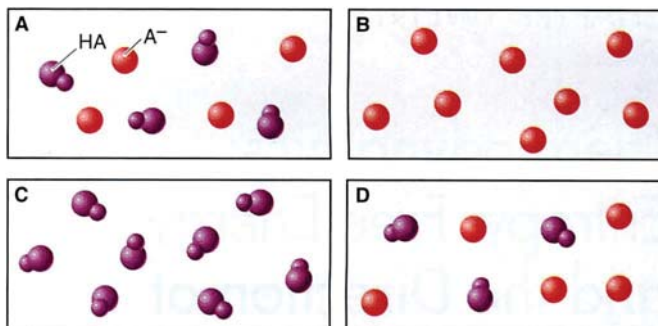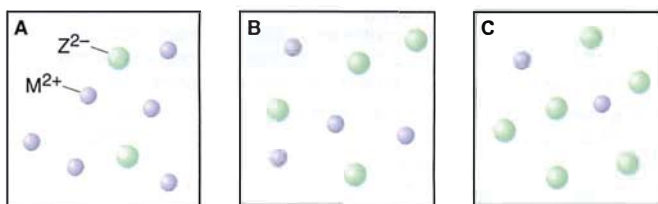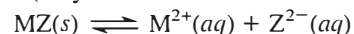

(a) Which scene(s) show(s) a buffer?
(b) What is the pH of each solution?
(c) Arrange the scenes in sequence, assuming that they represent stages in a weak acid–strong base titration.
(d) Which scene represents the titration at its equivalence point?

19.96 Scenes A to C represent aqueous solutions of the slightly soluble salt MZ (only the ions of this salt are shown):

$$MZ(s) \rightleftharpoons M^{2+}(aq) + Z^{2-}(aq)$$

(a) Which scene represents the solution just after solid MZ is stirred thoroughly in distilled water?
(b) If each sphere represents 2.5×10^{-6} M of ions, what is the K_{sp} of MZ?
(c) Which scene represents the solution after $Na_2Z(aq)$ is added?
(d) If Z^{2-} is CO_3^{2-}, which scene represents the solution after the pH has been lowered?