CHAPTERS 13–17 BRINGING IT TOGETHER

Once again you have an opportunity to test your understanding of concepts, your knowledge of scientific terms, and your skills at solving chemistry problems. Read through the following questions carefully, and answer each as fully as possible. Review topics when necessary. When you are able to answer these questions correctly, you are ready to go on to the next group of chapters.

1. List the factors that affect the speed of a chemical reaction.

2. At 25° C and $[OH^-] = 1.00\ M$, the reaction

$$I^-(aq) + OCl^-(aq) \longrightarrow OI^-(aq) + Cl^-(aq)$$

has the following rate law

$$\text{Rate} = (0.60\ \text{L mol}^{-1}\ \text{s}^{-1})[I^-][OCl^-]$$

Calculate the rate of the reaction when $[OH^-] = 1.00\ M$ and

(a) $[I^-] = 0.0100\ M$ and $[OCl^-] = 0.0200\ M$

(b) $[I^-] = 0.100\ M$ and $[OCl^-] = 0.0400\ M$

3. A reaction has the stoichiometry: $3A + B \longrightarrow C + D$. The following data were obtained for the initial rate of formation of C at various concentrations of A and B.

Initial Concentrations		Initial Rate of Formation of C (mol L^{-1} s^{-1})
$[A]$	$[B]$	
0.010	0.010	2.0×10^{-4}
0.020	0.020	8.0×10^{-4}
0.020	0.010	8.0×10^{-4}

(a) What is the rate law for the reaction?

(b) What is the value of the rate constant?

(c) What is the rate at which C is formed if $[A] = 0.017\ M$ and $[B] = 0.033\ M$?

4. If the concentration of a particular reactant is doubled and the rate of the reaction is cut in half, what must be the order of the reaction with respect to that reactant?

5. Organic compounds that contain large proportions of nitrogen and oxygen tend to be unstable and are easily decomposed. Hexanitroethane, $C_2(NO_2)_6$, decomposes according to the equation

$$C_2(NO_2)_6 \longrightarrow 2NO_2 + 4NO + 2CO_2$$

The reaction in CCl_4 as a solvent is first order with respect to $C_2(NO_2)_6$. At 70 °C, $k = 2.41 \times 10^{-6}\ s^{-1}$ and at 100 °C $k = 2.22 \times 10^{-4}\ s^{-1}$.

(a) What is the half-life of $C_2(NO_2)_6$ at 70 °C? What is the half-life at 100 °C?

(b) If 0.100 mol of $C_2(NO_2)_6$ is dissolved in CCl_4 at 70 °C to give 1.00 L of solution, what will be the $C_2(NO_2)_6$ concentration after 500 minutes?

(c) What is the value of the activation energy of this reaction, expressed in kilojoules?

(d) What is the reaction's rate constant at 120 °C?

6. Radioactive strontium-90, ^{90}Sr, has a half-life of 28 years.

(a) What fraction of a sample of ^{90}Sr will remain after three half-lives?

(b) What fraction of a sample of ^{90}Sr will remain after 168 years?

(c) If the amount of ^{90}Sr remaining in a sample is only one-sixteenth of the amount originally present, how many years has the sample been undergoing radioactive decay?

(d) If the amount of ^{90}Sr remaining in a sample is only one-sixth of the amount originally present, how many years has the sample been undergoing radioactive decay?

7. The reaction $2A + 2B \longrightarrow M + N$ has this rate law: Rate $= k[A]^2$. At 25 °C, $k = 1.0 \times 10^{-4}$ L mol^{-1} s^{-1}. If the initial concentrations of A and B are 0.250 M and 0.150 M, respectively

(a) What is the half-life of the reaction?

(b) What will be the concentrations of A and B after 30 minutes?

8. Define *reaction mechanism, rate-determining step,* and *elementary process.*

9. The decomposition of ozone, O_3, is believed to occur by the two-step mechanism

$$\begin{aligned} O_3 &\longrightarrow O_2 + O && \text{(slow)} \\ O + O_3 &\longrightarrow 2O_2 && \text{(fast)} \\ \hline 2O_3 &\longrightarrow 3O_2 && \text{(net reaction)} \end{aligned}$$

If this is the mechanism, what is the reaction's rate law?

10. Draw a diagram showing how the potential energy varies during an exothermic reaction. Identify the activation energy for both the forward and reverse reactions. Also, identify the heat of reaction.

11. How does a heterogeneous catalyst increase the rate of a chemical reaction?

12. One possible mechanism for the decomposition of ethane, C_2H_6, into ethylene, C_2H_4, and hydrogen,

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

includes the following steps.

$$\begin{aligned} &(1) && C_2H_6 \longrightarrow 2CH_3\cdot \\ &(2) && CH_3\cdot + C_2H_6 \longrightarrow CH_4 + C_2H_5\cdot \\ &(3) && C_2H_5\cdot \longrightarrow C_2H_4 + H\cdot \\ &(4) && H\cdot + C_2H_6 \longrightarrow C_2H_5\cdot + H_2 \\ &(5) && H\cdot + C_2H_5\cdot \longrightarrow C_2H_6 \end{aligned}$$

(a) Which steps initiate the reaction?

(b) Which are propagation steps?

(c) Which is a termination step?

13. Write the appropriate mass action expression, using molar concentrations, for these reactions.

(a) $NO_2(g) + N_2O(g) \rightleftharpoons 3NO(g)$

(b) $CaSO_3(s) \rightleftharpoons CaO(s) + SO_2(g)$

(c) $NiCO_3(s) \rightleftharpoons Ni^{2+}(aq) + CO_3^{2-}(aq)$

14. At a certain temperature, the reaction $2HF(g) \rightleftharpoons 2HF(g) + F_2(g)$ has $K_c = 1 \times 10^{-13}$. Does this reaction

proceed far toward completion when equilibrium is reached? If 0.010 mol HF was placed in a 1.00 L container and the system was permitted to come to equilibrium, what would be the concentrations of H_2 and F_2 in the container?

15. At 100°C, the reaction $2NO_2(g) \rightleftharpoons N_2O_4(g)$ has $K_P = 6.5 \times 10^{-2}$. What is the value of K_c at that temperature?

16. At 1000°C, the reaction $NO_2(g) + SO_2(g) \rightleftharpoons NO(g) + SO_3(g)$ has $K_c = 3.60$. If 0.100 mol NO_2 and 0.100 mol SO_2 are placed in a 5.00 L container and allowed to react, what will all the concentrations be when equilibrium is reached? What will the new equilibrium concentrations be if 0.010 mol NO and 0.010 mol SO_3 are added to the original equilibrium mixture?

17. For the reaction in the preceding question, $\Delta H° = -41.8$ kJ. How will the equilibrium concentration of NO be affected if
(a) More NO_2 is added to the container?
(b) Some SO_3 is removed from the container?
(c) The temperature of the reaction mixture is raised?
(d) Some SO_2 is removed from the mixture?
(e) The pressure of the gas mixture is lowered by expanding the volume to 10.0 L?

18. At 60°C, $K_w = 9.5 \times 10^{-14}$. What is the pH of pure water at that temperature? Why can we say that the water is neither acidic nor basic?

19. At 25 °C, the water in a natural pool of water in one of the western states was found to contain hydroxide ions at a concentration of 4.7×10^{-7} g OH^- per liter. Calculate the pH of the water and state if it is acidic, basic, or neutral.

20. Which is the stronger acid, H_3AsO_3 or H_3AsO_4? How can one tell without a table of weak and strong acids?

21. Which is the stronger acid, H_2S or H_2Te?

22. What are the conjugate acids of (a) HSO_3^- and (b) N_2H_4?

23. What are the conjugate bases of (a) HSO_3^-, (b) N_2H_4, and (c) $C_5H_5NH^+$?

24. Identify the conjugate acid–base pairs in the reaction

$$CH_3NH_2 + NH_4^+ \rightleftharpoons CH_3NH_3^+ + NH_3$$

25. What is the definition of an *amphoteric substance*? What is a *Lewis acid?* What is a *Lewis base*?

26. Use Lewis structures to diagram the reaction between the Lewis base OH^- and the Lewis acid SO_3.

27. *X, Y,* and *Z* are all nonmetallic elements in the same period of the periodic table where they occur, left to right, in the order given. Which would be a stronger binary acid than the binary acid of *Y*, the binary acid of *X* or the binary acid of *Z*? Explain.

28. The first antiseptic to be used in surgical operating rooms was phenol, C_6H_5OH, a weak acid and a potent bactericide. A 0.550 *M* solution of phenol in water was found to have a pH of 5.07.
(a) Write the chemical equation for the equilibrium involving C_6H_5OH in the solution.
(b) Write the equilibrium law corresponding to K_a for C_6H_5OH.
(c) Calculate the values of K_a and pK_a for phenol.
(d) Calculate the values of K_b and pK_b for the phenoxide ion, $C_6H_5O^-$.

29. The pK_a of saccharin, $HC_7H_3SO_3$, a sweetening agent, is 11.68.
(a) What is the pK_b of the saccharinate ion, $C_7H_3SO_3^-$?
(b) Does a solution of sodium saccharinate in water have a pH of 7, or is the solution acidic or basic? If the pH is not 7, calculate the pH of a 0.010 *M* solution of sodium saccharinate in water.

30. At 25 °C the value of K_b for codeine, a pain-killing drug, is 1.6×10^{-6}. Calculate the pH of a 0.0115 *M* solution of codeine in water.

31. Methylamine, CH_3NH_2, is a weak base. Write the chemical equation for the equilibrium that occurs in an aqueous solution of this solute. Write the equilibrium law corresponding to K_b for CH_3NH_2.

32. The pK_b of methylamine, CH_3NH_2, is 3.43. Calculate the pK_a of its conjugate acid, $CH_3NH_3^+$.

33. Ascorbic acid, $H_2C_6H_6O_6$, is a diprotic acid usually known as vitamin C. For this acid, pK_{a_1} is 4.10 and pK_{a_2} is 11.79. When 125 mL of a solution of ascorbic acid was evaporated to dryness, the residue of pure ascorbic acid had a mass of 3.12 g.
(a) Calculate the molar concentration of ascorbic acid in the solution before it was evaporated.
(b) Calculate the pH of the solution and the molar concentration of the ascorbate ion, $C_6H_6O_6^{2-}$, before the solution was evaporated.

34. What ratio of molar concentrations of sodium acetate to acetic acid can buffer a solution at a pH of 4.50?

35. Write a chemical equation for the reaction that would occur in a buffer composed of sodium acetate and acetic acid if
(a) Some HCl were added.
(b) Some NaOH were added.

36. If 0.020 mol of NaOH were added to 0.500 L of a sodium acetate–acetic acid buffer that contains 0.10 *M* $NaC_2H_3O_2$ and 0.15 *M* $HC_2H_3O_2$, by how many pH units will the pH of the buffer change?

37. A biology experiment requires the use of a nutrient fluid buffered at a pH of 4.85, and 625 mL of the solution is needed. It has to be buffered to be able to hold the pH to within ±0.10 pH unit of 5.00 even if 5.00×10^{-3} mol of OH^- or 5.00×10^{-3} mol of H^+ ion enter the buffer.
(a) Using tabulated data, pick the best acid and its sodium salt that could be used to prepare the solution.
(b) Calculate the minimum number of grams of the pure acid and its salt that are needed to prepare the buffer solution.
(c) What are the molar concentrations of the acid and of its salt in the solution?

38. How would each of the following aqueous solutions test, acidic, basic, or neutral? (Assume that each is at least 0.2 *M*.) (a) potassium nitrate, (b) chromium(III) chloride, (c) ammonium iodide, (d) potassium dihydrogen phosphate.

39. When 50.00 mL of an acid with a concentration of 0.115 *M* (for which $pK_a = 4.87$) is titrated with 0.100 *M* NaOH, what is the pH at the equivalence point? What would be a good indicator for the titration?

40. Calculate the pH of a 0.050 *M* solution of sodium ascorbate, $Na_2C_6H_6O_6$. For ascorbic acid, $H_2C_6H_6O_6$, $K_{a_1} = 7.9 \times 10^{-5}$ and $K_{a_2} = 1.6 \times 10^{-12}$.

41. When 25.0 mL of 0.100 *M* NaOH was added to 50.0 mL of a 0.100 *M* solution of a weak acid, HX, the pH of the mixture reached a value of 3.56. What is the value of K_a for the weak acid?

42. How many grams of solid NaOH would have to be added to 0.100 L of a 0.100 *M* solution of NH_4Cl to give a mixture with a pH of 9.26?

43. The molar solubility of silver chromate, Ag_2CrO_4, in water is 6.7×10^{-5} *M*. What is K_{sp} for Ag_2CrO_4?

44. What is the pH of a saturated solution of magnesium hydroxide?

45. What is the solubility of iron(II) hydroxide in grams per liter if the solution is buffered to a pH of 10.00?

46. Suppose 30.0 mL of 0.100 *M* $Pb(NO_3)_2$ is added to 20.0 mL of 0.500 *M* KI.

(a) How many grams of PbI_2 will be formed?

(b) What will the molar concentrations of all the ions be in the mixture after equilibrium has been reached?

47. How many moles of NH_3 must be added to 1.00 L of solution to dissolve 1.00 g of $CuCO_3$? For $CuCO_3$, $K_{sp} = 2.3 \times 10^{-10}$. Ignore hydrolysis of CO_3^{2-}, but consider the formation of the complex ion, $Cu(NH_3)_4^{2+}$.

48. Over what pH range must a solution be buffered to achieve a selective separation of the carbonates of barium, $BaCO_3$ ($K_{sp} = 5.0 \times 10^{-9}$), and lead, $PbCO_3$ ($K_{sp} = 7.4 \times 10^{-14}$)? The solution is initially 0.010 *M* in Ba^{2+} and 0.010 *M* in Pb^{2+}.

49. A solution containing 0.10 *M* Pb^{2+} and 0.10 *M* Ni^{2+} is to be saturated with H_2S. What range of pH values could the solution have so that when the procedure is completed one of the ions remains in solution while the other is precipitated as its sulfide?

50. A solution that contains 0.10 *M* Fe^{2+} and 0.10 *M* Sn^{2+} is maintained at a pH of 3.00 while H_2S is gradually added to it. What will be the concentration of Sn^{2+} in the solution when FeS just begins to precipitate?

51. A metal sulfide *M*S has a value of K_{sp} of 4.0×10^{-29}. (a) What is the value of K_{spa} for this compound? (b) Calculate the molar solubility of *M*S in 0.30 *M* HCl.