

increases. Acidic solutions are those that contain more $H^+(aq)$ than $OH^-(aq)$; basic solutions contain more $OH^-(aq)$ than $H^+(aq)$.

Section 16.4 The concentration of $H^+(aq)$ can be expressed in terms of pH: $pH = -\log [H^+]$. At 25°C the pH of a neutral solution is 7.00, whereas the pH of an acidic solution is below 7.00, and the pH of a basic solution is above 7.00. The pX notation is also used to represent the negative log of other small quantities, as in pOH and pK_w . The pH of a solution can be measured using a pH meter, or it can be estimated using acid-base indicators.

Section 16.5 Strong acids are strong electrolytes, ionizing completely in aqueous solution. The common strong acids are HCl, HBr, HI, HNO_3 , $HClO_3$, $HClO_4$, and H_2SO_4 . The conjugate bases of strong acids have negligible basicity. Common strong bases are the ionic hydroxides of alkali metals and the heavy alkaline earth metals. The cations of strong bases have negligible acidity.

Section 16.6 Weak acids are weak electrolytes; only part of the molecules exist in solution in ionized form. The extent of ionization is expressed by the acid-dissociation constant, K_a , which is the equilibrium constant for the reaction $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$, which can also be written $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$. The larger the value of K_a , the stronger the acid. The concentration of a weak acid and its K_a value can be used to calculate the pH of a solution.

Section 16.7 Polyprotic acids, such as H_2SO_3 , have more than one ionizable proton. These acids have acid-dissociation constants that decrease in magnitude in the order $K_{a1} > K_{a2} > K_{a3}$. Because nearly all the $H^+(aq)$ in a polyprotic acid solution comes from the first dissociation step, the pH can usually be estimated satisfactorily by considering only K_{a1} .

Sections 16.7 and 16.8 Weak bases include NH_3 , amines, and the anions of weak acids. The extent to which a weak base reacts with water to generate the corresponding conjugate acid and OH^- is measured by the base-dissociation constant, K_b . This is the equilibrium constant for the reaction $B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$ where B is the base.

The relationship between the strength of an acid and the strength of its conjugate base is expressed quantitatively by the equation $K_a \times K_b = K_w$, where K_a and K_b are dissociation constants for conjugate acid-base pairs.

Section 16.9 The acid-base properties of salts can be ascribed to the behavior of their respective cations and anions. The reaction of ions with water, with a resultant change in pH, is called hydrolysis. The cations of the alkali metals and the alkaline earth metals and the anions of strong acids do not undergo hydrolysis. They are always spectator ions in acid-base chemistry.

Section 16.10 The tendency of a substance to show acidic or basic characteristics in water can be correlated with its chemical structure. Acid character requires the presence of a highly polar H—X bond. Acidity is also favored when the H—X bond is weak and when the X^- ion is very stable.

For oxyacids with the same number of OH groups and the same number of O atoms, acid strength increases with increasing electronegativity of the central atom. For oxyacids with the same central atom, acid strength increases as the number of oxygen atoms attached to the central atom increases. The structures of carboxylic acids, which are organic acids containing the COOH group, also help us to understand their acidity.

Section 16.11 The Lewis concept of acids and bases emphasizes the shared electron pair rather than the proton. A Lewis acid is an electron-pair acceptor, and a Lewis base is an electron-pair donor. The Lewis concept is more general than the Brønsted-Lowry concept because it can apply to cases in which the acid is some substance other than H^+ . The Lewis concept helps to explain why many hydrated metal cations form acidic aqueous solutions. The acidity of these cations generally increases as their charge increases and as the size of the metal ion decreases.

Exercises

Arrhenius and Brønsted-Lowry Acids and Bases

1. Although HCl and H_2SO_4 have very different properties as pure substances, their aqueous solutions possess many common properties. List some general properties of these solutions, and explain their common behavior in terms of the species present.
2. Although pure NaOH and CaO have very different properties, their aqueous solutions possess many common properties. List some general properties of these solutions, and explain their common behavior in terms of the species present.
3. (a) What is the difference between the Arrhenius and the Brønsted-Lowry definitions of an acid? (b) $NH_3(g)$ and

- HCl(g) react to form the ionic solid $NH_4Cl(s)$ (Figure 16.3). Which substance is the Brønsted-Lowry acid in this reaction? Which is the Brønsted-Lowry base?
- 16.4 (a) What is the difference between the Arrhenius and the Brønsted-Lowry definitions of a base? (b) When ammonia is dissolved in water, it behaves both as an Arrhenius base and as a Brønsted-Lowry base. Explain.
 - 16.5 Give the conjugate base of the following Brønsted-Lowry acids: (a) H_2SO_3 ; (b) $HC_2H_3O_2$; (c) $H_2AsO_4^-$; (d) NH_4^+
 - 16.6 Give the conjugate acid of the following Brønsted-Lowry bases: (a) HSO_4^{2-} ; (b) CH_3NH_2 ; (c) SO_4^{2-} ; (d) $H_2PO_4^-$
 - 16.7 Designate the Brønsted-Lowry acid and the Brønsted-Lowry base on the left side of each of the following

- 16.28 Complete the following table by calculating the missing entries. In each case indicate whether the solution is acidic or basic.

pH	pOH	$[H^+]$	$[OH^-]$	acidic or basic?
6.21				
	10.13			
		$3.5 \times 10^{-3} M$		
			$5.6 \times 10^{-4} M$	

- 16.29 The average pH of normal arterial blood is 7.40. At normal body temperature ($37^\circ C$), $K_w = 2.4 \times 10^{-14}$. Calculate $[H^+]$ and $[OH^-]$ for blood at this temperature.
- 16.30 Carbon dioxide in the atmosphere dissolves in rain to produce carbonic acid (H_2CO_3), causing the pH of clean, unpolluted rain to range from about 5.2 to 5.6. What are the ranges of $[H^+]$ and $[OH^-]$ in the rain?

Strong Acids and Bases

- 16.31 (a) What is a strong acid? (b) A solution is labeled 0.500 M HCl. What is $[H^+]$ for the solution? (c) Which of the following are strong acids: HF, HCl, HBr, HI?
- 16.32 (a) What is a strong base? (b) A solution is labeled 0.125 M $Sr(OH)_2$. What is $[OH^-]$ for the solution? (c) Is the following statement true or false? Because $Mg(OH)_2$ is not very soluble, it cannot be a strong base. Explain.
- 16.33 Calculate the pH of each of the following strong acid solutions: (a) $8.5 \times 10^{-3} M$ HBr; (b) 1.52 g of HNO_3 in 575 mL of solution; (c) 5.00 mL of 0.250 M $HClO_4$ diluted to 50.0 mL; (d) a solution formed by mixing 10.0 mL of 0.100 M HBr with 20.0 mL of 0.200 M HCl.
- 16.34 Calculate the pH of each of the following strong acid solutions: (a) 0.0575 M HNO_3 ; (b) 0.723 g of $HClO_4$ in 2.00 L of solution; (c) 5.00 mL of 1.00 M HCl diluted to 0.750 L; (d) a mixture formed by adding 50.0 mL of 0.020 M HCl to 125 mL of 0.010 M HI.
- 16.35 Calculate $[OH^-]$ and pH for (a) $1.5 \times 10^{-3} M$ $Sr(OH)_2$; (b) 2.250 g of LiOH in 250.0 mL of solution; (c) 1.00 mL

of 0.175 M NaOH diluted to 2.00 L; (d) a solution formed by adding 5.00 mL of 0.105 M KOH to 15.0 mL of $9.5 \times 10^{-2} M$ $Ca(OH)_2$.

- 16.36 Calculate $[OH^-]$ and pH for each of the following strong base solutions: (a) 0.0050 M KOH; (b) 2.055 g of KC in 500.0 mL of solution; (c) 10.0 mL of 0.250 M Ca(OH)₂ diluted to 500.0 mL; (d) a solution formed by mixing 10.0 mL of 0.015 M $Ba(OH)_2$ with 30.0 mL of $7.5 \times 10^{-3} M$ NaOH.
- 16.37 Calculate the concentration of an aqueous solution of NaOH that has a pH of 11.50.
- 16.38 Calculate the concentration of an aqueous solution of $Ca(OH)_2$ that has a pH of 12.00.
- 16.39 Calculate the pH of a solution made by adding 15.0 g of sodium hydride (NaH) to enough water to make 2.00 L of solution.
- 16.40 Calculate the pH of a solution made by adding 2.50 g of lithium oxide (Li_2O) to enough water to make 1.20 L of solution.

Weak Acids

- 16.41 Write the chemical equation and the K_a expression for the ionization of each of the following acids in aqueous solution. First show the reaction with $H^+(aq)$ as a product and then with the hydronium ion: (a) $HBrO_2$; (b) $HC_3H_5O_2$.
- 16.42 Write the chemical equation and the K_a expression for the acid dissociation of each of the following acids in aqueous solution. First show the reaction with $H^+(aq)$ as a product and then with the hydronium ion: (a) $HC_6H_5O_2$; (b) HCO_3^- .
- 16.43 Lactic acid ($HC_3H_5O_3$) has one acidic hydrogen. A 0.10 M solution of lactic acid has a pH of 2.44. Calculate K_a .
- 16.44 Phenylacetic acid ($HC_8H_7O_2$) is one of the substances that accumulates in the blood of people with phenylketonuria, an inherited disorder that can cause mental retardation or even death. A 0.085 M solution of $HC_8H_7O_2$ is found to have a pH of 2.68. Calculate the K_a value for this acid.
- 16.45 A 0.200 M solution of a weak acid HA is 9.4% ionized. Using this information, calculate $[H^+]$, $[A^-]$, $[HA]$, and K_a for HA.

- 16.46 A 0.100 M solution of chloroacetic acid ($ClCH_2COOH$) is 11.0% ionized. Using this information, calculate $[ClCH_2COO^-]$, $[H^+]$, $[ClCH_2COOH]$, and K_a for chloroacetic acid.
- 16.47 A particular sample of vinegar has a pH of 2.90. Assuming that acetic acid is the only acid that vinegar contains ($K_a = 1.8 \times 10^{-5}$), calculate the concentration of acetic acid in the vinegar.
- 16.48 How many moles of HF ($K_a = 6.8 \times 10^{-4}$) must be present in 0.500 L to form a solution with a pH of 2.70?
- 16.49 The acid-dissociation constant for benzoic acid ($HC_7H_5O_2$) is 6.3×10^{-5} . Calculate the equilibrium concentrations of H_3O^+ , $C_7H_5O_2^-$, and $HC_7H_5O_2$ in the solution if the initial concentration of $HC_7H_5O_2$ is 0.050 M.
- 16.50 The acid-dissociation constant for hypochlorous acid ($HClO$) is 3.0×10^{-8} . Calculate the concentrations of H_3O^+ , ClO^- , and $HClO$ at equilibrium if the initial concentration of $HClO$ is 0.0075 M.
- 16.51 Calculate the pH of each of the following solutions and K_b values are given in Appendix D: (a) 0.095 M picric acid ($HC_3H_2O_3$); (b) 0.100 M hydrogen chromate ion ($HCrO_4^-$); (c) 0.120 M pyridine (C_5H_5N).

- 16.52 Determine the pH of each of the following solutions (K_a and K_b values are given in Appendix D): (a) 0.125 M hypochlorous acid; (b) 0.0085 M phenol; (c) 0.095 M hydroxylamine.
- 16.53 Saccharin, a sugar substitute, is a weak acid with $pK_a = 2.32$ at 25°C. It ionizes in aqueous solution as follows:
- $$\text{HNC}_7\text{H}_4\text{SO}_3(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{NC}_7\text{H}_4\text{SO}_3^-(\text{aq})$$
- What is the pH of a 0.10 M solution of this substance?
- 16.54 The active ingredient in aspirin is acetylsalicylic acid ($\text{HC}_9\text{H}_7\text{O}_4$), a monoprotic acid with $K_a = 3.3 \times 10^{-4}$ at 25°C. What is the pH of a solution obtained by dissolving two extra-strength aspirin tablets, containing 500 mg of acetylsalicylic acid each, in 250 mL of water?
- 16.55 Calculate the percent ionization of hydrazoic acid (HN_3) in solutions of each of the following concentrations (K_a is given in Appendix D): (a) 0.400 M; (b) 0.100 M; (c) 0.0400 M.
- 16.56 Calculate the percent ionization of HCrO_4^- in solutions of each of the following concentrations (K_a is given in Appendix D): (a) 0.250 M; (b) 0.0800 M; (c) 0.0200 M.
- [16.57] Show that for a weak acid, the percent ionization should vary as the inverse square root of the acid concentration.
- [16.58] For solutions of a weak acid, a graph of pH versus the log of the initial acid concentration should be a straight line. What is the magnitude of the slope of that line?
- [16.59] Citric acid, which is present in citrus fruits, is a triprotic acid (Table 16.3). Calculate the pH and the citrate ion ($\text{C}_6\text{H}_5\text{O}_7^{3-}$) concentration for a 0.050 M solution of citric acid. Explain any approximations or assumptions that you make in your calculations.
- [16.60] Tartaric acid is found in many fruits, including grapes. It is partly responsible for the dry texture of certain wines. Calculate the pH and the tartarate ion ($\text{C}_4\text{H}_4\text{O}_6^{2-}$) concentration for a 0.250 M solution of tartaric acid, for which the acid-dissociation constants are listed in Table 16.3. Explain any approximations or assumptions that you make in your calculation.

Weak Bases

- 16.61 What is the essential structural feature of all Brønsted-Lowry bases?
- 16.62 What are two kinds of molecules or ions that commonly function as weak bases?
- 16.63 Write the chemical equation and the K_b expression for the ionization of each of the following bases in aqueous solution: (a) dimethylamine, $(\text{CH}_3)_2\text{NH}$; (b) carbonate ion, CO_3^{2-} ; (c) formate ion, CHO_2^- .
- 16.64 Write the chemical equation and the K_b expression for the reaction of each of the following bases with water: (a) propylamine, $\text{C}_3\text{H}_7\text{NH}_2$; (b) monohydrogen phosphate ion, HPO_4^{2-} ; (c) benzoate ion, $\text{C}_6\text{H}_5\text{CO}_2^-$.
- 16.65 Calculate the molar concentration of OH^- ions in a 0.075 M solution of ethylamine ($\text{C}_2\text{H}_5\text{NH}_2$) ($K_b = 6.4 \times 10^{-4}$). Calculate the pH of this solution.
- 16.66 Calculate the molar concentration of OH^- ions in a 1.15 M solution of hypobromite ion (BrO^- ; $K_b = 4.0 \times 10^{-6}$). What is the pH of this solution?
- 16.67 Ephedrine, a central nervous system stimulant, is used in nasal sprays as a decongestant. This compound is a weak organic base:
- $$\text{C}_{10}\text{H}_{15}\text{ON}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{C}_{10}\text{H}_{15}\text{ONH}^+(\text{aq}) + \text{OH}^-(\text{aq})$$
- A 0.035 M solution of ephedrine has a pH of 11.38.
- (a) What are the equilibrium concentrations of $\text{C}_{10}\text{H}_{15}\text{ON}$, $\text{C}_{10}\text{H}_{15}\text{ONH}^+$, and OH^- ? (b) Calculate K_b for ephedrine.
- 16.68 Codeine ($\text{C}_{18}\text{H}_{21}\text{NO}_3$) is a weak organic base. A 5.0×10^{-3} M solution of codeine has a pH of 9.95. Calculate the value of K_b for this substance. What is the pH for this base?

The K_a - K_b Relationship; Acid-Base Properties of Salts

- 16.69 Although the acid-dissociation constant for phenol ($\text{C}_6\text{H}_5\text{OH}$) is listed in Appendix D, the base-dissociation constant for the phenolate ion ($\text{C}_6\text{H}_5\text{O}^-$) is not.
- (a) Explain why it is not necessary to list both K_a for phenol and K_b for the phenolate ion. (b) Calculate the K_b for the phenolate ion. (c) Is the phenolate ion a weaker or stronger base than ammonia?
- 16.70 We can calculate K_b for the carbonate ion if we know the K_a values of carbonic acid (H_2CO_3). (a) Is K_{a1} or K_{a2} of carbonic acid used to calculate K_b for the carbonate ion? Explain. (b) Calculate K_b for the carbonate ion. (c) Is the carbonate ion a weaker or stronger base than ammonia?
- 16.71 (a) Given that K_a for acetic acid is 1.8×10^{-5} and that for hypochlorous acid is 3.0×10^{-8} , which is the stronger acid? (b) Which is the stronger base, the acetate ion or the hypochlorite ion? (c) Calculate K_b values for $\text{C}_2\text{H}_3\text{O}_2^-$ and ClO^- .
- 16.72 (a) Given that K_b for ammonia is 1.8×10^{-5} and that for hydroxylamine is 1.1×10^{-8} , which is the stronger base? (b) Which is the stronger acid, the ammonium ion or the hydroxylammonium ion? (c) Calculate K_a values for NH_4^+ and H_3NOH^+ .
- 16.73 Using data from Appendix D, calculate $[\text{OH}^-]$ and pH for each of the following solutions: (a) 0.10 M NaCN; (b) 0.080 M Na_2CO_3 ; (c) a mixture that is 0.10 M in NaNO_2 and 0.20 M in $\text{Ca}(\text{NO}_2)_2$.
- 16.74 Using data from Appendix D, calculate $[\text{OH}^-]$ and pH for each of the following solutions: (a) 0.036 M Na_2S ; (b) 0.127 M Na_2S ; (c) a mixture that is 0.035 M in $\text{NaC}_2\text{H}_3\text{O}_2$ and 0.055 M in $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$.
- 16.75 Predict whether aqueous solutions of the following compounds are acidic, basic, or neutral: (a) NH_4Br ; (b) FeCl_3 ; (c) Na_2CO_3 ; (d) KClO_4 ; (e) NaHC_2O_4 .

- 16.76 Predict whether aqueous solutions of the following substances are acidic, basic, or neutral: (a) CsBr; (b) $\text{Al}(\text{NO}_3)_3$; (c) KCN; (d) $[\text{CH}_3\text{NH}_3]\text{Cl}$; (e) KHSO_4 .
- 16.77 An unknown salt is either NaF, NaCl, or NaOCl. When 0.01 mol of the salt is dissolved in water to form 0.500 L of solution, the pH of the solution is 8.08. What is the identity of the salt?
- 16.78 An unknown salt is either KBr, NH_4Cl , KCN, or K_2CO_3 . If a 0.100 M solution of the salt is neutral, what is the identity of the salt?

Acid-Base Character and Chemical Structure

- 16.81 How does the acid strength of an oxyacid depend on (a) the electronegativity of the central atom; (b) the number of nonprotonated oxygen atoms in the molecule?
- 16.82 (a) How does the strength of an acid vary with the polarity and strength of the H—X bond? (b) How does the acidity of the binary acid of an element vary as a function of the electronegativity of the element? How does this relate to the position of the element in the periodic table?
- 16.83 Explain the following observations: (a) HNO_3 is a stronger acid than HNO_2 ; (b) H_2S is a stronger acid than H_2O ; (c) H_2SO_4 is a stronger acid than HSO_4^- ; (d) H_2SO_4 is a stronger acid than H_2SeO_4 ; (e) CCl_3COOH is a stronger acid than CH_3COOH .
- 16.84 Explain the following observations: (a) HCl is a stronger acid than H_2S ; (b) H_3PO_4 is a stronger acid than H_3AsO_4 ; (c) BrO_3^- is a stronger acid than HBrO_2 ; (d) $\text{H}_2\text{C}_2\text{O}_4$ is a stronger acid than HC_2O_4^- ; (e) benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) is a stronger acid than phenol ($\text{C}_6\text{H}_5\text{OH}$).
- 16.85 Based on their compositions and structures and on conjugate acid-base relationships, select the stronger base in each of the following pairs: (a) BrO^- or ClO^- ; (b) BrO_2^- or BrO_2^{2-} ; (c) HPO_4^{2-} or H_2PO_4^- .
- 16.86 Based on their compositions and structures and on conjugate acid-base relationships, select the stronger base in each of the following pairs: (a) NO_3^- or NO_2^- ; (b) PO_4^{3-} or AsO_4^{3-} ; (c) HCO_3^- or CO_3^{2-} .
- 16.87 Indicate whether each of the following statements is true or false. For each statement that is false, correct the statement so that it is true. (a) In general, the acidity of binary acids increases from left to right in a given row of the periodic table. (b) In a series of acids that have the same central atom, acid strength increases with the number of hydrogen atoms bonded to the central atom. (c) Hydrotelluric acid (H_2Te) is a stronger acid than H_2S because Te is more electronegative than S.
- 16.88 Indicate whether each of the following statements is true or false. For each statement that is false, correct the statement so that it is true. (a) Acid strength in a series of H—X molecules increases with increasing size of X. (b) For acids of the same general structure but differing electronegativities of the central atoms, acid strength decreases with increasing electronegativity of the central atom. (c) The strongest acid known is HF because fluorine is the most electronegative element.

Acid-Base Reactions

- 16.89 If a substance is an Arrhenius base, is it necessarily a Brønsted-Lowry base? Is it necessarily a Lewis base? Explain.
- 16.90 If a substance is a Lewis acid, is it necessarily a Brønsted-Lowry acid? Is it necessarily an Arrhenius acid? Explain.
- 16.91 Identify the Lewis acid and Lewis base among the reactants in each of the following reactions:
- (a) $\text{Fe}(\text{ClO}_4)_3(s) + 6\text{H}_2\text{O}(l) \rightleftharpoons \text{Fe}(\text{H}_2\text{O})_6^{3+}(aq) + 3\text{ClO}_4^-(aq)$
- (b) $\text{CN}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCN}(aq) + \text{OH}^-(aq)$
- (c) $(\text{CH}_3)_3\text{N}(g) + \text{BF}_3(g) \rightleftharpoons (\text{CH}_3)_3\text{NBF}_3(s)$
- (d) $\text{HIO}(lq) + \text{NH}_2^-(lq) \rightleftharpoons \text{NH}_3(lq) + \text{IO}^-(lq)$
(lq denotes liquid ammonia as solvent)
- 16.92 Identify the Lewis acid and Lewis base in each of the following reactions:
- (a) $\text{HNO}_2(aq) + \text{OH}^-(aq) \rightleftharpoons \text{NO}_2^-(aq) + \text{H}_2\text{O}(l)$
- (b) $\text{FeBr}_3(s) + \text{Br}^-(aq) \rightleftharpoons \text{FeBr}_4^-(aq)$
- (c) $\text{Zn}^{2+}(aq) + 4\text{NH}_3(aq) \rightleftharpoons \text{Zn}(\text{NH}_3)_4^{2+}(aq)$
- (d) $\text{SO}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{SO}_3(aq)$
- 16.93 Predict which member of each pair produces the more acidic aqueous solution: (a) K^+ or Cu^{2+} ; (b) Fe^{2+} or Fe^{3+} ; (c) Al^{3+} or Ga^{3+} . Explain.
- 16.94 Which member of each pair produces the more acidic aqueous solution: (a) ZnBr_2 or CdCl_2 ; (b) CuCl or $\text{Cu}(\text{NO}_3)_2$; (c) $\text{Ca}(\text{NO}_3)_2$ or NiBr_2 ? Explain.

Additional Exercises

- 16.95 Indicate whether each of the following statements is correct or incorrect. For those that are incorrect, explain why they are wrong.
- (a) Every Brønsted-Lowry acid is also a Lewis acid.
- (b) Every Lewis acid is also a Brønsted-Lowry acid.
- (c) Conjugate acids of weak bases produce more acidic solutions than conjugate acids of strong bases.
- (d) K^+ ion is acidic in water because it causes hydrating water molecules to become more acidic.
- (e) The percent ionization of a weak acid in water increases as the concentration of acid decreases.