18.6 $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

$[H_3O^+] = 10^{-pH} = 10^{-5.0} = 1\times10^{-5}\,M = [NH_3]$

From reaction table, $K_a = \dfrac{[NH_3][H_3O^+]}{[NH_4^+]} = \dfrac{(x)(x)}{0.2 - x}$

$\approx \dfrac{(1\times10^{-5})^2}{0.2} = 5\times10^{-10}$

18.7 $K_a = \dfrac{[H_3O^+][OCN^-]}{[HOCN]} = \dfrac{(x)(x)}{0.10 - x} = 3.5\times10^{-4}$

Since $\dfrac{[HOCN]_{init}}{K_a} = \dfrac{0.10}{3.5\times10^{-4}} = 286 < 400$, you must solve a quadratic equation: $x^2 + (3.5\times10^{-4})x - (3.5\times10^{-5}) = 0$

$x = [H_3O^+] = 5.7\times10^{-3}\,M$; pH = 2.24

18.8 $K_b = \dfrac{[C_5H_5NH^+][OH^-]}{[C_5H_5N]} = 10^{-8.77} = 1.7\times10^{-9}$

Assuming $0.10\,M - x \approx 0.10\,M$, $K_b = 1.7\times10^{-9} \approx \dfrac{(x)(x)}{0.10}$;

$x = [OH^-] \approx 1.3\times10^{-5}\,M$; $[H_3O^+] = 7.7\times10^{-10}\,M$;

pH = 9.11

18.9 K_b of $ClO^- = \dfrac{K_w}{K_a \text{ of HClO}} = \dfrac{1.0\times10^{-14}}{2.9\times10^{-8}} = 3.4\times10^{-7}$

Assuming $0.20\,M - x \approx 0.20\,M$,

$K_b = 3.4\times10^{-7} = \dfrac{[HClO][OH^-]}{[ClO^-]} \approx \dfrac{x^2}{0.20}$;

$x = [OH^-] \approx 2.6\times10^{-4}\,M$; $[H_3O^+] = 3.8\times10^{-11}\,M$; pH = 10.42

18.10 (a) Basic:

$ClO_2^-(aq) + H_2O(l) \rightleftharpoons HClO_2(aq) + OH^-(aq)$

K^+ is from strong base KOH.

(b) Acidic:

$CH_3NH_3^+(aq) + H_2O(l) \rightleftharpoons CH_3NH_2(aq) + H_3O^+(aq)$

NO_3^- is from strong acid HNO_3.

(c) Neutral: Cs^+ is from strong base CsOH; I^- is from strong acid HI.

18.11 (a) K_a of $Cu(H_2O)_6^{2+} = 3\times10^{-8}$

K_b of $CH_3COO^- = \dfrac{K_w}{K_a \text{ of } CH_3COOH} = 5.6\times10^{-10}$

Since $K_a > K_b$, $Cu(CH_3COO)_2(aq)$ is acidic.

(b) K_a of $NH_4^+ = \dfrac{K_w}{K_b \text{ of } NH_3} = 5.7\times10^{-10}$

K_b of $F^- = \dfrac{K_w}{K_a \text{ of HF}} = 1.5\times10^{-11}$

Since $K_a > K_b$, $NH_4F(aq)$ is acidic.

18.12 (a) OH^- is the Lewis base; $Al(OH)_3$ is the Lewis acid.

(b) H_2O is the Lewis base; SO_3 is the Lewis acid.

(c) NH_3 is the Lewis base; Co^{3+} is the Lewis acid.

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 problems refer to aqueous solutions at 298 K (25°C).

Acids and Bases in Water

(Sample Problem 18.1)

18.1 Describe the role of water according to the Arrhenius acid-base definition.

18.2 What characteristics do all Arrhenius acids have in common? What characteristics do all Arrhenius bases have in common? Explain neutralization in terms of the Arrhenius acid-base definition. What quantitative finding led Arrhenius to propose this idea of neutralization?

18.3 Why is the Arrhenius acid-base definition considered too limited? Give an example of a case in which the Arrhenius definition does not apply.

18.4 What is meant by the words "strong" and "weak" in terms of acids and bases? Weak acids have K_a values that vary over more than 10 orders of magnitude. What do they have in common that classifies them as "weak"?

18.5 Which of the following are Arrhenius acids?

(a) H_2O (b) $Ca(OH)_2$ (c) H_3PO_3 (d) HI

18.6 Which of the following are Arrhenius bases?

(a) CH_3COOH (b) HOH (c) CH_3OH (d) H_2NNH_2

18.7 Write the K_a expression for each of the following in water:

(a) HNO_2 (b) CH_3COOH (c) $HBrO_2$

18.8 Write the K_a expression for each of the following in water:

(a) $H_2PO_4^-$ (b) H_3PO_2 (c) HSO_4^-

18.9 Use Appendix C to rank the following in order of *increasing* acid strength: HIO_3, HI, CH_3COOH, HF.

18.10 Use Appendix C to rank the following in order of *decreasing* acid strength: HClO, HCl, HCN, HNO_2.

18.11 Classify each as a strong or weak acid or base:

(a) H_3AsO_4 (b) $Sr(OH)_2$ (c) HIO (d) $HClO_4$

18.12 Classify each as a strong or weak acid or base:

(a) CH_3NH_2 (b) K_2O (c) HI (d) HCOOH

Autoionization of Water and the pH Scale

(Sample Problems 18.2 and 18.3)

18.13 What is an autoionization reaction? Write equations for the autoionization reactions of H_2O and of H_2SO_4.

18.14 (a) What is the change in pH when $[OH^-]$ increases by a factor of 10?

(b) What is the change in $[H_3O^+]$ when the pH decreases by 2 units?

18.15 Which solution has the higher pH? Explain.

(a) A 0.1 *M* solution of an acid with $K_a = 1\times10^{-4}$ or one with $K_a = 4\times10^{-5}$

(b) A 0.1 *M* solution of an acid with $pK_a = 3.0$ or one with $pK_a = 3.5$

(c) A 0.1 *M* solution of a weak acid or a 0.01 *M* solution of the same acid

(d) A 0.1 *M* solution of a weak acid or a 0.1 *M* solution of a strong acid

(e) A 0.1 *M* solution of an acid or a 0.1 *M* solution of a base

(f) A solution of pOH 6.0 or one of pOH 8.0

18.16 (a) What is the pH of 0.0111 *M* NaOH? Is the solution neutral, acidic, or basic?
(b) What is the pOH of 1.23×10^{-3} *M* HCl? Is the solution neutral, acidic, or basic?

18.17 (a) What is the pH of 0.0333 *M* HNO_3? Is the solution neutral, acidic, or basic?
(b) What is the pOH of 0.0347 *M* KOH? Is the solution neutral, acidic, or basic?

18.18 (a) What are $[H_3O^+]$, $[OH^-]$, and pOH in a solution with a pH of 9.78?
(b) What are $[H_3O^+]$, $[OH^-]$, and pH in a solution with a pOH of 10.43?

18.19 (a) What are $[H_3O^+]$, $[OH^-]$, and pOH in a solution with a pH of 3.47?
(b) What are $[H_3O^+]$, $[OH^-]$, and pH in a solution with a pOH of 4.33?

18.20 How many moles of H_3O^+ or OH^- must you add to 6.5 L of HA solution to adjust its pH from 4.82 to 5.22? Assume a negligible volume change.

18.21 How many moles of H_3O^+ or OH^- must you add to 87.5 mL of HA solution to adjust its pH from 8.92 to 6.33? Assume a negligible volume change.

18.22 Although the text asserts that water is an extremely weak electrolyte, parents commonly warn their children of the danger of swimming in a pool or lake during a lightning storm. Explain.

18.23 Like any equilibrium constant, K_w changes with temperature.
(a) Given that autoionization is an endothermic process, does K_w increase or decrease with rising temperature? Explain with an equation that includes heat as reactant or product.
(b) In many medical applications, the value of K_w at 37°C (body temperature) may be more appropriate than the value at 25°C, 1.0×10^{-14}. The pH of pure water at 37°C is 6.80. Calculate K_w, pOH, and $[OH^-]$ at this temperature.

Proton Transfer and the Brønsted-Lowry Acid-Base Definition

(Sample Problems 18.4 and 18.5)

18.24 How do the Arrhenius and Brønsted-Lowry definitions of an acid and a base differ? How are they similar? Name two Brønsted-Lowry bases that are not considered Arrhenius bases. Can you do the same for acids? Explain.

18.25 What is a conjugate acid-base pair? What is the relationship between the two members of the pair?

18.26 A Brønsted-Lowry acid-base reaction proceeds in the net direction in which a stronger acid and stronger base form a weaker acid and weaker base. Explain.

18.27 What is an amphoteric species? Name one and write balanced equations that show why it is amphoteric.

18.28 Give the formula of the conjugate base:
(a) HCl (b) H_2CO_3 (c) H_2O

18.29 Give the formula of the conjugate base:
(a) HPO_4^{2-} (b) NH_4^+ (c) HS^-

18.30 Give the formula of the conjugate acid:
(a) NH_3 (b) NH_2^- (c) nicotine, $C_{10}H_{14}N_2$

18.31 Give the formula of the conjugate acid:
(a) O^{2-} (b) SO_4^{2-} (c) H_2O

18.32 In each equation, label the acids, bases, and conjugate acid-base pairs:
(a) $NH_3 + H_3PO_4 \rightleftharpoons NH_4^+ + H_2PO_4^-$
(b) $CH_3O^- + NH_3 \rightleftharpoons CH_3OH + NH_2^-$
(c) $HPO_4^{2-} + HSO_4^- \rightleftharpoons H_2PO_4^- + SO_4^{2-}$

18.33 In each equation, label the acids, bases, and conjugate acid-base pairs:
(a) $NH_4^+ + CN^- \rightleftharpoons NH_3 + HCN$
(b) $H_2O + HS^- \rightleftharpoons OH^- + H_2S$
(c) $HSO_3^- + CH_3NH_2 \rightleftharpoons SO_3^{2-} + CH_3NH_3^+$

18.34 Write balanced net ionic equations for the following reactions, and label the conjugate acid-base pairs:
(a) $NaOH(aq) + NaH_2PO_4(aq) \rightleftharpoons H_2O(l) + Na_2HPO_4(aq)$
(b) $KHSO_4(aq) + K_2CO_3(aq) \rightleftharpoons K_2SO_4(aq) + KHCO_3(aq)$

18.35 Write balanced net ionic equations for the following reactions, and label the conjugate acid-base pairs:
(a) $HNO_3(aq) + Li_2CO_3(aq) \rightleftharpoons LiNO_3(aq) + LiHCO_3(aq)$
(b) $2NH_4Cl(aq) + Ba(OH)_2(aq) \rightleftharpoons 2H_2O(l) + BaCl_2(aq) + 2NH_3(aq)$

18.36 The following aqueous species constitute two conjugate acid-base pairs. Use them to write one acid-base reaction with $K_c > 1$ and another with $K_c < 1$: HS^-, Cl^-, HCl, H_2S.

18.37 The following aqueous species constitute two conjugate acid-base pairs. Use them to write one acid-base reaction with $K_c > 1$ and another with $K_c < 1$: NO_3^-, F^-, HF, HNO_3.

18.38 Use Figure 18.9 to determine whether $K_c > 1$ for
(a) $HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$
(b) $H_2SO_3 + NH_3 \rightleftharpoons HSO_3^- + NH_4^+$

18.39 Use Figure 18.9 to determine whether $K_c < 1$ for
(a) $H_2PO_4^- + F^- \rightleftharpoons HPO_4^{2-} + HF$
(b) $CH_3COO^- + HSO_4^- \rightleftharpoons CH_3COOH + SO_4^{2-}$

Solving Problems Involving Weak-Acid Equilibria

(Sample Problems 18.6 and 18.7)

18.40 In each of the following cases, would you expect the concentration of acid before and after dissociation to be nearly the same or very different? Explain your reasoning.
(a) A concentrated solution of a strong acid
(b) A concentrated solution of a weak acid
(c) A dilute solution of a weak acid
(d) A dilute solution of a strong acid

18.41 In which of the following solutions will $[H_3O^+]$ be approximately equal to $[CH_3COO^-]$: (a) 0.1 *M* CH_3COOH; (b) 1×10^{-7} *M* CH_3COOH; (c) a solution containing both 0.1 *M* CH_3COOH and 0.1 *M* CH_3COONa? Explain.

18.42 Why do successive K_a's decrease for all polyprotic acids?

18.43 A 0.15 *M* solution of butanoic acid, $CH_3CH_2CH_2COOH$, contains 1.51×10^{-3} *M* H_3O^+. What is the K_a of butanoic acid?

18.44 A 0.035 *M* solution of a weak acid (HA) has a pH of 4.88. What is the K_a of the acid?

18.45 Nitrous acid, HNO_2, has a K_a of 7.1×10^{-4}. What are $[H_3O^+]$, $[NO_2^-]$, and $[OH^-]$ in 0.50 *M* HNO_2?

18.46 Hydrofluoric acid, HF, has a K_a of 6.8×10^{-4}. What are $[H_3O^+]$, $[F^-]$, and $[OH^-]$ in 0.75 *M* HF?

18.47 Chloroacetic acid, $ClCH_2COOH$, has a pK_a of 2.87. What are $[H_3O^+]$, pH, $[ClCH_2COO^-]$, and $[ClCH_2COOH]$ in 1.05 *M* $ClCH_2COOH$?

18.48 Hypochlorous acid, HClO, has a pK_a of 7.54. What are $[H_3O^+]$, pH, $[ClO^-]$, and [HClO] in 0.115 *M* HClO?

18.49 In a 0.25 *M* solution, a weak acid is 3.0% dissociated.
(a) Calculate the $[H_3O^+]$, pH, $[OH^-]$, and pOH of the solution.
(b) Calculate K_a of the acid.

18.50 In a 0.735 *M* solution, a weak acid is 12.5% dissociated.
(a) Calculate the $[H_3O^+]$, pH, $[OH^-]$, and pOH of the solution.
(b) Calculate K_a of the acid.

18.51 The weak acid HZ has a K_a of 1.55×10^{-4}.
(a) Calculate the pH of 0.075 *M* HZ.
(b) Calculate the pOH of 0.045 *M* HZ.

18.52 The weak acid HQ has a pK_a of 4.89.
(a) Calculate the $[H_3O^+]$ of 3.5×10^{-2} *M* HQ.
(b) Calculate the $[OH^-]$ of 0.65 *M* HQ.

18.53 Acetylsalicylic acid (aspirin), $HC_9H_7O_4$, is the most widely used pain reliever and fever reducer. Find the pH of 0.018 *M* aqueous aspirin at body temperature (K_a at 37°C = 3.6×10^{-4}).

18.54 Formic acid, HCOOH, the simplest carboxylic acid, has many uses in the textile and rubber industries. It is an extremely caustic liquid that is secreted as a defense by many species of ants (family *Formicidae*). Calculate the percent dissociation of 0.50 *M* HCOOH.

Weak Bases and Their Relation to Weak Acids

(Sample Problems 18.8 and 18.9)

18.55 What is the key structural feature of all Brønsted-Lowry bases? How does this feature function in an acid-base reaction?

18.56 Why are most anions basic in H_2O? Give formulas of four anions that are not basic.

18.57 Except for the Na^+ spectator ion, aqueous solutions of CH_3COOH and CH_3COONa contain the same species. (a) What are the species (other than H_2O)? (b) Why is 0.1 *M* CH_3COOH acidic and 0.1 *M* CH_3COONa basic?

18.58 Write balanced equations and K_b expressions for these Brønsted-Lowry bases in water:
(a) Pyridine, C_5H_5N (b) CO_3^{2-}

18.59 Write balanced equations and K_b expressions for these Brønsted-Lowry bases in water:
(a) Benzoate ion, $C_6H_5COO^-$ (b) $(CH_3)_3N$

18.60 What is the pH of 0.050 *M* dimethylamine?

18.61 What is the pH of 0.12 *M* diethylamine?

18.62 (a) What is the pK_b of ClO_2^-?
(b) What is the pK_a of the dimethylammonium ion, $(CH_3)_2NH_2^+$?

18.63 (a) What is the pK_b of NO_2^-?
(b) What is the pK_a of the hydrazinium ion, $H_2N{-}NH_3^+$ (K_b of hydrazine = 8.5×10^{-7})?

18.64 (a) What is the pH of 0.050 *M* KCN?
(b) What is the pH of 0.30 *M* triethylammonium chloride, $(CH_3CH_2)_3NHCl$?

18.65 (a) What is the pH of 0.100 *M* sodium phenolate, C_6H_5ONa, the sodium salt of phenol?
(b) What is the pH of 0.15 *M* methylammonium bromide, CH_3NH_3Br (K_b of CH_3NH_2 = 4.4×10^{-4})?

18.66 Sodium hypochlorite solution, sold as "chlorine bleach," is recognized as a potentially dangerous household product. The dangers arise from its basicity and from ClO^-, the active bleaching ingredient. What is $[OH^-]$ in an aqueous solution that is 5.0% NaClO by mass? What is the pH of the solution? (Assume *d* of solution = 1.0 g/mL.)

18.67 Codeine ($C_{18}H_{21}NO_3$) is a narcotic pain reliever that forms a salt with HCl. What is the pH of 0.050 *M* codeine hydrochloride (pK_b of codeine = 5.80)?

Molecular Properties and Acid Strength

18.68 Across a period, how does the electronegativity of a nonmetal affect the acidity of its binary hydride?

18.69 How does the atomic size of a nonmetal affect the acidity of its binary hydride?

18.70 A strong acid has a weak bond to its acidic proton, whereas a weak acid has a strong bond to its acidic proton. Explain.

18.71 Perchloric acid, $HClO_4$, is the strongest of the halogen oxoacids, and hypoiodous acid, HIO, is the weakest. What two factors govern this difference in acid strength?

18.72 Choose the *stronger* acid in each of the following pairs:
(a) H_2Se or H_3As (b) $B(OH)_3$ or $Al(OH)_3$ (c) $HBrO_2$ or HBrO

18.73 Choose the *weaker* acid in each of the following pairs:
(a) HI or HBr (b) H_3AsO_4 or H_2SeO_4 (c) HNO_3 or HNO_2

18.74 Use Appendix C to choose the solution with the *lower* pH:
(a) 0.1 *M* $CuSO_4$ or 0.05 *M* $Al_2(SO_4)_3$
(b) 0.1 *M* $ZnCl_2$ or 0.1 *M* $PbCl_2$

18.75 Use Appendix C to choose the solution with the *higher* pH:
(a) 0.1 *M* $NiCl_2$ or 0.1 *M* NaCl
(b) 0.1 *M* $Sn(NO_3)_2$ or 0.1 *M* $Co(NO_3)_2$

Acid-Base Properties of Salt Solutions

(Sample Problems 18.10 and 18.11)

18.76 What determines whether an aqueous solution of a salt will be acidic, basic, or neutral? Give an example of each type of salt.

18.77 Why is aqueous NaF basic but aqueous NaCl neutral?

18.78 The NH_4^+ ion forms acidic solutions, and the CH_3COO^- ion forms basic solutions. However, a solution of ammonium acetate is almost neutral. Do all of the ammonium salts of weak acids form neutral solutions? Explain your answer.

18.79 Explain with equations and calculations, when necessary, whether an aqueous solution of each of these salts is acidic, basic, or neutral: (a) KBr; (b) NH_4I; (c) KCN.

18.80 Explain with equations and calculations, when necessary, whether an aqueous solution of each of these salts is acidic, basic, or neutral: (a) $Cr(NO_3)_3$; (b) NaHS; (c) $Zn(CH_3COO)_2$.

18.81 Rank the following salts in order of *increasing* pH of their 0.1 *M* aqueous solutions:
(a) KNO_3, K_2SO_3, K_2S
(b) NH_4NO_3, $NaHSO_4$, $NaHCO_3$, Na_2CO_3

18.82 Rank the following salts in order of *decreasing* pH of their 0.1 *M* aqueous solutions:
(a) NH_4Cl, $MgCl_2$, $KClO_2$
(b) NH_4Br, $NaBrO_2$, NaBr, $NaClO_2$

Electron-Pair Donation and the Lewis Acid-Base Definition

(Sample Problem 18.12)

18.83 What feature must a molecule or ion have for it to act as a Lewis base? A Lewis acid? Explain the roles of these features.

18.84 How do Lewis acids differ from Brønsted-Lowry acids? How are they similar? Do Lewis bases differ from Brønsted-Lowry bases? Explain.

18.85 (a) Is a weak Brønsted-Lowry base necessarily a weak Lewis base? Explain with an example.
(b) Identify the Lewis bases in the following reaction:

$$Cu(H_2O)_4^{2+}(aq) + 4CN^-(aq) \rightleftharpoons Cu(CN)_4^{2-}(aq) + 4H_2O(l)$$

(c) Given that $K_c > 1$ for the reaction in part (b), which Lewis base is stronger?

18.86 In which of the three concepts of acid-base behavior discussed in the text can water be a product of an acid-base reaction? In which is it the only product?

18.87 (a) Give an example of a *substance* that is a base in two of the three acid-base definitions, but not in the third.
(b) Give an example of a *substance* that is an acid in one of the three acid-base definitions, but not in the other two.

18.88 Which are Lewis acids and which are Lewis bases?
(a) Cu^{2+} (b) Cl^- (c) $SnCl_2$ (d) OF_2

18.89 Which are Lewis acids and which are Lewis bases?
(a) Na^+ (b) NH_3 (c) CN^- (d) BF_3

18.90 Identify the Lewis acid and Lewis base in each equation:
(a) $Na^+ + 6H_2O \rightleftharpoons Na(H_2O)_6^+$
(b) $CO_2 + H_2O \rightleftharpoons H_2CO_3$
(c) $F^- + BF_3 \rightleftharpoons BF_4^-$

18.91 Identify the Lewis acid and Lewis base in each equation:
(a) $Fe^{3+} + 2H_2O \rightleftharpoons FeOH^{2+} + H_3O^+$
(b) $H_2O + H^- \rightleftharpoons OH^- + H_2$
(c) $4CO + Ni \rightleftharpoons Ni(CO)_4$

18.92 Classify the following as Arrhenius, Brønsted-Lowry, or Lewis acid-base reactions. A reaction may fit all, two, one, or none of the categories:
(a) $Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$
(b) $H_2SO_4 + NH_3 \rightleftharpoons HSO_4^- + NH_4^+$
(c) $2HCl \rightleftharpoons H_2 + Cl_2$
(d) $AlCl_3 + Cl^- \rightleftharpoons AlCl_4^-$

18.93 Classify the following as Arrhenius, Brønsted-Lowry, or Lewis acid-base reactions. A reaction may fit all, two, one, or none of the categories:
(a) $Cu^{2+} + 4Cl^- \rightleftharpoons CuCl_4^{2-}$
(b) $Al(OH)_3 + 3HNO_3 \rightleftharpoons Al^{3+} + 3H_2O + 3NO_3^-$
(c) $N_2 + 3H_2 \rightleftharpoons 2NH_3$
(d) $CN^- + H_2O \rightleftharpoons HCN + OH^-$

Comprehensive Problems

Problems with an asterisk (*) are more challenging.

18.94 Bodily processes in humans maintain the pH of blood within a narrow range. In fact, a condition called *acidosis* occurs if the blood pH goes below 7.35, and another called *alkalosis* occurs if the pH goes above 7.45. Given that the pK_w of blood is 13.63 at 37°C (body temperature), what is the normal range of $[H_3O^+]$ and of $[OH^-]$ in blood?

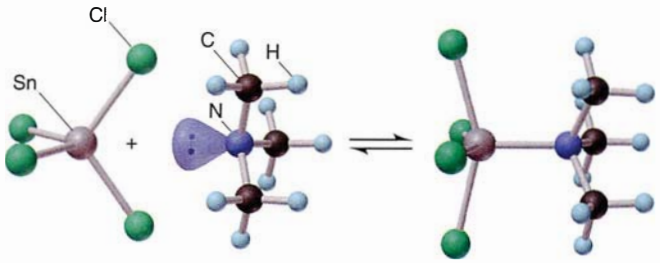
18.95 When carbon dioxide dissolves in water, it undergoes a multistep equilibrium process, with $K_{overall} = 4.5\times10^{-7}$, which is simplified to the following:

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$
$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

(a) Classify each step as a Lewis or a Brønsted-Lowry reaction.
(b) What is the pH of nonpolluted rainwater in equilibrium with clean air (P_{CO_2} in clean air $= 3.2\times10^{-4}$ atm; Henry's law constant for CO_2 at 25°C is 0.033 mol/L·atm)?
(c) What is $[CO_3^{2-}]$ in rainwater (K_a of $HCO_3^- = 4.7\times10^{-11}$)?
(d) If the partial pressure of CO_2 in clean air doubles in the next few decades, what will the pH of rainwater become?

* **18.96** Use Appendix C to calculate $[H_2C_2O_4]$, $[HC_2O_4^-]$, $[C_2O_4^{2-}]$, $[H_3O^+]$, pH, $[OH^-]$, and pOH in a 0.200 *M* solution of the diprotic acid oxalic acid. (*Hint:* Assume all the $[H_3O^+]$ comes from the first dissociation.)

18.97 Many molecules with central atoms from Period 3 or higher take part in Lewis acid-base reactions in which the central atom expands its valence shell. $SnCl_4$ reacts with $(CH_3)_3N$ as follows:

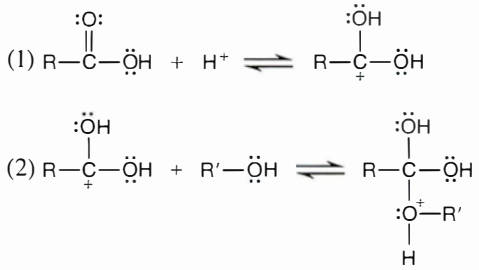


(a) Identify the Lewis acid and the Lewis base in the reaction.
(b) Give the *nl* designation of the sublevel of the central atom in the acid that accepts the lone pair.

18.98 A chemist makes four successive 1:10 dilutions of 1.0×10^{-5} *M* HCl. Calculate the pH of the original solution and of each diluted solution (through 1.0×10^{-9} *M* HCl).

18.99 Hydrogen peroxide, H_2O_2 ($pK_a = 11.75$), is commonly used as a bleaching agent and an antiseptic. The product sold in stores is 3% H_2O_2 by mass and contains 0.001% phosphoric acid by mass to stabilize the solution. Which contributes more H_3O^+ to this commercial solution, the H_2O_2 or the H_3PO_4?

18.100 Esters, RCOOR′, are formed by the reaction of carboxylic acids, RCOOH, and alcohols, R′OH, where R and R′ are hydrocarbon groups. Many esters are responsible for the odors of fruit and, thus, have important uses in the food and cosmetics industries. The first two steps in the mechanism of ester formation are



Identify the Lewis acids and Lewis bases in these two steps.

18.101 Thiamine hydrochloride ($C_{12}H_{18}ON_4SCl_2$) is a water-soluble form of thiamine (vitamin B_1; $K_a = 3.37\times10^{-7}$). How many grams of the hydrochloride must be dissolved in 10.00 mL of water to give a pH of 3.50?

18.102 When Fe^{3+} salts are dissolved in water, the solution becomes acidic due to formation of $Fe(H_2O)_5OH^{2+}$ and H_3O^+. The overall process involves both Lewis and Brønsted-Lowry acid-base reactions. Write the equations for the process.

18.103 At 50°C and 1 atm, $K_w = 5.19\times10^{-14}$. Calculate parts (a)–(c) under these conditions:
(a) $[H_3O^+]$ in pure water
(b) $[H_3O^+]$ in 0.010 *M* NaOH

(c) $[OH^-]$ in 0.0010 M $HClO_4$

(d) Calculate $[H_3O^+]$ in 0.0100 M KOH at 100°C and 1000 atm pressure ($K_w = 1.10\times10^{-12}$).

(e) Calculate the pH of pure water at 100°C and 1000 atm.

* **18.104** A 1.000 m solution of chloroacetic acid ($ClCH_2COOH$) freezes at −1.93°C. Use these data to find the K_a of chloroacetic acid. (Assume the molarities equal the molalities.)

18.105 Calcium propionate [$Ca(CH_3CH_2COO)_2$] is a mold inhibitor used in food, tobacco, and pharmaceuticals. (a) Use balanced equations to show whether aqueous calcium propionate is acidic, basic, or neutral. (b) Use Appendix C to find the pH of a solution made by dissolving 7.05 g of $Ca(CH_3CH_2COO)_2$ in water to give 0.500 L of solution.

18.106 Carbon dioxide is less soluble in dilute HCl than in dilute NaOH. Explain.

18.107 (a) If $K_w = 1.139\times10^{-15}$ at 0°C and 5.474×10^{-14} at 50°C, find $[H_3O^+]$ and pH of water at 0°C and 50°C.

(b) The autoionization constant for heavy water (deuterium oxide, D_2O) is 3.64×10^{-16} at 0°C and 7.89×10^{-15} at 50°C. Find $[D_3O^+]$ and pD of heavy water at 0°C and 50°C.

(c) Suggest a reason for these differences.

* **18.108** HX ($\mathcal{M}$ = 150. g/mol) and HY ($\mathcal{M}$ = 50.0 g/mol) are weak acids. A solution of 12.0 g/L of HX has the same pH as one containing 6.00 g/L of HY. Which is the stronger acid? Why?

* **18.109** Nitrogen is discharged from wastewater treatment facilities into rivers and streams, usually as NH_3 and NH_4^+:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = 1.76\times10^{-5}$$

One strategy for removing it is to raise the pH and "strip" the NH_3 from solution by bubbling air through the water. (a) At pH 7.00, what fraction of the total nitrogen in solution is NH_3, defined as $[NH_3]/([NH_3] + [NH_4^+])$? (b) What is the fraction at pH 10.00? (c) Explain the basis of ammonia stripping.

18.110 Polymers and other large molecules are not very soluble in water, but their solubility increases if they have charged groups.

(a) Casein is a protein in milk that contains many carboxylic acid groups on its side chains. Explain how the solubility of casein in water varies with pH.

(b) Histones are proteins that are essential to the proper function of DNA. They are weakly basic due to the presence of side chains with $—NH_2$ and $=NH$ groups. Explain how the solubility of histones in water varies with pH.

18.111 Hemoglobin (Hb) transports oxygen in the blood:

$$HbH^+(aq) + O_2(aq) + H_2O(l) \longrightarrow HbO_2(aq) + H_3O^+(aq)$$

In blood, $[H_3O^+]$ is held nearly constant at 4×10^{-8} M.

(a) How does the equilibrium position change in the lungs?

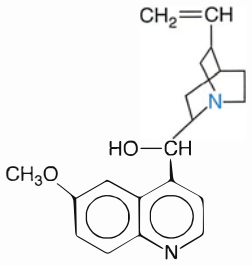
(b) How does it change in O_2-deficient cells?

(c) Excessive vomiting may lead to metabolic *alkalosis*, in which $[H_3O^+]$ in blood *decreases*. How does this condition affect the ability of Hb to transport O_2?

(d) Diabetes mellitus may lead to metabolic *acidosis*, in which $[H_3O^+]$ in blood *increases*. How does this condition affect the ability of Hb to transport O_2?

18.112 Vitamin C (ascorbic acid, $H_2C_6H_6O_6$) is a weak diprotic acid. It is essential for the synthesis of collagen, the major protein in connective tissue. If the pH of a 5.0% (w/v) solution of vitamin C in water is 2.77, calculate the K_{a1} of vitamin C.

* **18.113** Quinine ($C_{20}H_{24}N_2O_2$; *see below*) is a natural product with antimalarial properties that saved thousands of lives during construction of the Panama Canal. It stands as a classic example of the medicinal wealth of tropical forests. Both N atoms are basic, but the N (colored) of the 3° amine group is far more basic ($pK_b = 5.1$) than the N within the aromatic ring system ($pK_b = 9.7$).



(a) Quinine is not very soluble in water: a saturated solution is only 1.6×10^{-3} M. What is the pH of this solution?

(b) Show that the aromatic N contributes negligibly to the pH of the solution.

(c) Because of its low solubility as a free base in water, quinine is given as an amine salt. For instance, quinine hydrochloride ($C_{20}H_{24}N_2O_2\cdot HCl$) is about 120 times more soluble in water than quinine. What is the pH of 0.53 M quinine hydrochloride?

(d) An antimalarial concentration in water is 1.5% quinine hydrochloride by mass (d = 1.0 g/mL). What is the pH?

* **18.114** Drinking water is often disinfected with chlorine gas, which hydrolyzes to form hypochlorous acid (HClO), a weak acid but powerful disinfectant:

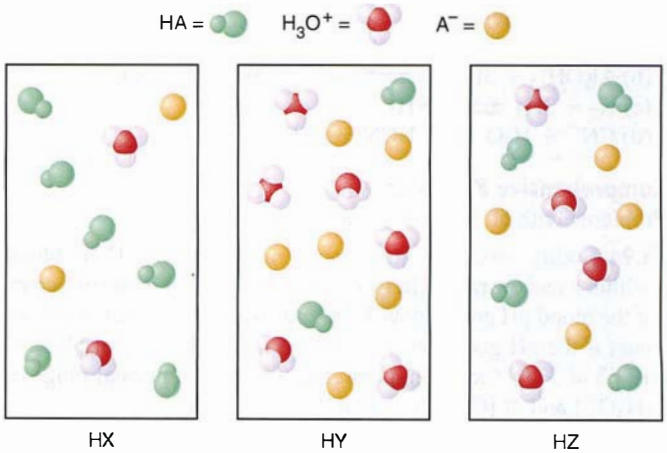
$$Cl_2(aq) + 2H_2O(l) \longrightarrow HClO(aq) + H_3O^+(aq) + Cl^-(aq)$$

The fraction of HClO in solution is defined as

$$\frac{[HClO]}{[HClO] + [ClO^-]}$$

(a) What is the fraction of HClO at pH 7.00 (K_a of HClO = 2.9×10^{-8})? (b) What is the fraction at pH 10.00?

* **18.115** The following scenes represent three weak acids HA (where A = X, Y, or Z) dissolved in water (H_2O is not shown):



(a) Rank the acids in order of increasing K_a.

(b) Rank the acids in order of increasing pK_a.

(c) Rank the conjugate bases in order of increasing pK_b.

(d) What is the percent dissociation of HX?

(e) If equimolar amounts of the sodium salts of the acids (NaX, NaY, and NaZ) were dissolved in water, which solution would have the highest pOH? The lowest pH?