

## Solutions to Even-Numbered Exercises:

- 9.2 In pure water  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$  and  $K_w = [\text{H}_3\text{O}^+] \times [\text{OH}^-]$ . Therefore,  $K_w = [\text{OH}^-]^2 = [\text{H}_3\text{O}^+]^2 = 2.51 \times 10^{-14}$ .  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = (K_w)^{1/2} = 1.58 \times 10^{-7}$ .
- 9.4 Water can act as an acid or a base, and, therefore, it is an amphoteric substance.
- 9.6 A strong acid is ionized 100% in aqueous solution. Two examples are HCl and  $\text{H}_2\text{SO}_4$ .
- 9.8 0.28 M  $\text{HClO}_3$  solution.  $\text{HClO}_3$  is a strong acid, which means that every  $\text{HClO}_3$  molecule dissociates into an  $\text{H}_3\text{O}^+$  ion and a  $\text{ClO}_3^-$  ion. Thus,  $[\text{H}_3\text{O}^+] = [\text{ClO}_3^-] = 0.28 \text{ M}$ .
- 9.10 0.025 M  $\text{Ca}(\text{OH})_2$  solution.  $\text{Ca}(\text{OH})_2$  is a strong base, which means that every  $\text{Ca}(\text{OH})_2$  molecule dissociates into a  $\text{Ca}^{2+}$  ion and 2  $\text{OH}^-$  ions. Thus,  $[\text{Ca}^{2+}] = 0.025 \text{ M}$ . Because there are twice as many  $\text{OH}^-$  ions in solution than  $\text{Ca}^{2+}$  ions, its concentration must be twice that of  $\text{Ca}^{2+}$ . Thus,  $[\text{OH}^-] = 0.025 \text{ M} \times 2 = 0.05 \text{ M}$ .
- 9.12 0.16 M KOH solution. KOH is a strong base, which means that every KOH molecule dissociates into a  $\text{K}^+$  ion and an  $\text{OH}^-$  ion. Thus,  $[\text{K}^+] = [\text{OH}^-] = 0.16 \text{ M}$ . It is also known that

$$[\text{H}_3\text{O}^+] \times [\text{OH}^-] = 1.0 \times 10^{-14} \rightarrow [\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14}}{0.16} = 6.3 \times 10^{-14}$$

- 9.14 0.285 M HCl solution. HCl is a strong acid, which means that every HCl molecule dissociates into an  $\text{H}_3\text{O}^+$  ion and a  $\text{Cl}^-$  ion. Thus,  $[\text{H}_3\text{O}^+] = [\text{Cl}^-] = 0.285 \text{ M}$ . It is also known that

$$[\text{H}_3\text{O}^+] \times [\text{OH}^-] = 1.00 \times 10^{-14} \rightarrow [\text{OH}^-] = \frac{1.00 \times 10^{-14}}{0.285} = 3.51 \times 10^{-14}$$

9.16 The pH of water at 37°C is 6.80. This is because the equilibrium reaction between two water molecules to form  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  changes with temperature, and at 37°C there is more  $\text{H}_3\text{O}^+$  formed than at 25°C where the pH is 7.00.

9.18  $\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.0026) = 2.59$

9.20  $\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.027) = 1.57$

$$[\text{H}_3\text{O}^+] \times [\text{OH}^-] = 1.00 \times 10^{-14} \rightarrow [\text{OH}^-] = \frac{1.00 \times 10^{-14}}{0.027} = 3.70 \times 10^{-13}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (3.70 \times 10^{-13}) = 12.43$$

Alternatively,  $\text{pH} + \text{pOH} = 14$ , thus  $\text{pH} = 14 - 1.57 = 12.43$

9.22 Each of the bases in this question is a strong base, which means that every base molecule dissociates into  $\text{OH}^-$  ions and a positive counter ion. Thus,  $[\text{OH}^-]$  will equal the concentration of the acid times the number of  $\text{OH}^-$  ions per molecules. Thus:

(a)  $[\text{OH}^-] = 0.0041 \times 1 = 0.0041$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(0.0041) = 2.39$$

$$\text{pH} = 14 - \text{pOH} = 14 - 2.39 = 11.61$$

(b)  $[\text{OH}^-] = .00094 \times 2 = 0.00188$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(0.00188) = 2.73$$

$$\text{pH} = 14 - \text{pOH} = 14 - 2.73 = 11.27$$

(c)  $[\text{OH}^-] = 0.035 \times 2 = 0.070$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(0.070) = 1.15$$

$$\text{pH} = 14 - \text{pOH} = 14 - 1.15 = 12.84$$

(d)  $[\text{OH}^-] = 0.0084 \times 1 = 0.0084$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(0.0084) = 2.08$$

$$\text{pH} = 14 - \text{pOH} = 14 - 2.08 = 11.92$$

9.24 A weak base is one that incompletely dissociates in water. Examples are given in table 9.4, aniline and morphine.

9.26 Formic acid dissociates more in aqueous solution ( $\text{p}K_a = 3.74$ ) than aniline does ( $\text{p}K_b = 9.38$ ). Therefore, the amount of  $[\text{H}_3\text{O}^+]$  ions created by formic acid will be much greater

than the amount of  $[\text{OH}^-]$  ions created by aniline. This excess amount of  $[\text{H}_3\text{O}^+]$  results in an acidic solution.

9.28 (a) An acid is a compound that donates a proton; its conjugate base is the compound that is formed upon loss of a hydrogen. Both  $\text{HCOOH}$  and  $\text{NH}_4^+$  give up a proton to form  $\text{HCOO}^-$  and  $\text{NH}_3$  respectively. Therefore  $\text{HCOOH}$  and  $\text{HCOO}^-$  are one conjugate acid–base pair, while  $\text{NH}_4^+$  and  $\text{NH}_3$  are another.

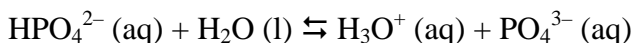
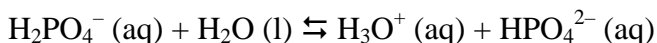
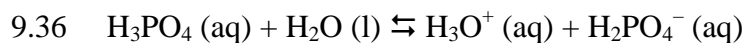
(b) An acid is a compound that donates a proton; its conjugate base is the compound that is formed upon loss of a hydrogen. Both  $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$  give up a proton to form  $\text{OH}^-$  and  $\text{H}_2\text{O}$  respectively. Therefore  $\text{H}_2\text{O}$  and  $\text{OH}^-$  are one conjugate acid–base pair, while  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{O}$  are another.

9.30 The equilibrium constant for the reaction of nitrous acid with water is  $K_a = 4.47 \times 10^{-4}$ .

$$9.32 \quad \text{p}K_a = -\log(K_a) = -\log(4.47 \times 10^{-4}) = 3.35$$

$$\text{p}K_b = -\log(K_b) = -\log(2.24 \times 10^{-11}) = 10.65$$

$$9.34 \quad \text{From 9.32, } \text{p}K_a + \text{p}K_b = 3.35 + 10.65 = 14.0$$



$$9.38 \quad K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = 5.93 \times 10^{-3}$$

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 6.32 \times 10^{-8}$$

$$K_{a3} = \frac{[\text{H}_3\text{O}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 4.84 \times 10^{-13}$$

9.40 From the equations in 9.38, the amount of  $\text{H}_3\text{O}^+$  contributed by  $\text{H}_2\text{PO}_4^-$  is a factor of 100,000 less than that contributed by  $\text{H}_3\text{PO}_4$  ( $10^{-8}/10^{-3} = 1/100,000$ ). Thus, it will be of minor significance.

9.42 Salts composed of cations and anions of strong acids and bases form neutral solutions, while salts having anions of weak acids form basic solutions and salts having cations of weak bases form acidic solutions, thus,

(a)  $\text{NH}_4\text{NO}_3$  is the salt of the cation of a weak base ( $\text{NH}_3$ ), thus the solution is acidic.

- (b)  $\text{Al}_2(\text{SO}_4)_3$  is the salt of the cation of a weak base, thus the solution is acidic.
- (c)  $\text{KI}$  is a salt of a strong base and a strong acid ( $\text{KOH}$  and  $\text{HI}$ ), thus the solution is neutral.
- (d)  $\text{NaHCO}_3$  is the salt of the anion of a weak acid ( $\text{H}_2\text{CO}_3$ ), thus the solution is basic.
- (e)  $\text{K}_2\text{HPO}_4$  is the salt of the anion of a weak acid ( $\text{H}_2\text{PO}_4$ ), thus the solution is basic.
- 9.44 Salts composed of cations and anions of strong acids and bases form neutral solutions, while salts having anions of weak acids form basic solutions and salts having cations of weak bases form acidic solutions, thus,
- (a)  $\text{Fe}(\text{NO}_3)_3$  is the salt of the cation of a weak base, thus the solution is acidic.
- (b)  $\text{Mg}(\text{NO}_2)_2$  is the salt of the anion of a weak acid ( $\text{HNO}_2$ ), thus the solution is basic.
- (c)  $\text{KBr}$  is a salt of a strong base and a strong acid ( $\text{KOH}$  and  $\text{HBr}$ ), thus the solution is neutral.
- (d)  $\text{CH}_3\text{COOCa}$  is the salt of the anion of a weak acid ( $\text{CH}_3\text{COOH}$ ), thus the solution is basic.
- (e)  $\text{MgCO}_3$  is the salt of the anion of a weak acid ( $\text{H}_2\text{CO}_3$ ), thus the solution is basic.
- 9.46 When the concentration of the conjugate acid and base are equal, the pH remains close to  $\text{p}K_a$ .
- 9.48 
$$\text{pH} = \text{p}K_a + \log\left(\frac{\text{proton acceptor}}{\text{proton donor}}\right) = \log\left(\frac{0.070}{0.070}\right) = 3.75 + 0 = 3.75$$
- 9.50 
$$\text{pH} = \text{p}K_a + \log\left(\frac{\text{proton acceptor}}{\text{proton donor}}\right) = \log\left(\frac{0.050}{0.075}\right) = 7.20 - 0.18 = 7.02$$
- 9.52 
$$32.0 \text{ mL} \times \frac{1\text{L}}{1000\text{mL}} \times \frac{0.0180 \text{ mol}}{\text{L}} = 0.000576 \text{ mol KOH}$$
- $0.000576 \text{ mol KOH} = 0.000576 \text{ mol HNO}_3$  when neutral
- $$\frac{0.000576 \text{ mol}}{0.0250\text{L}} = 0.0230\text{M}$$
- 9.54 
$$42.3 \text{ mL} \times \frac{1\text{L}}{1000\text{mL}} \times \frac{0.0850 \text{ mol}}{\text{L}} = 0.00360 \text{ mol KOH}$$

$$0.00360 \text{ moles KOH} \times \frac{1 \text{ mol H}_3\text{PO}_4}{3 \text{ mol KOH}} = 0.00120 \text{ mol HNO}_3 \text{ when neutral}$$

$$\frac{0.00120 \text{ mol}}{0.0200 \text{ L}} = 0.0600 \text{ M}$$

- 9.56 0.200 N solution denotes 0.200 equivalents of acid/liter. An equivalent is defined as the number of moles of dissociable  $\text{H}^+$ /mole of acid. In  $\text{H}_2\text{SO}_4$ , 2  $\text{H}^+$  ions can come from a single  $\text{H}_2\text{SO}_4$  molecule, thus

$$\frac{0.200 \text{ equivalent}}{\text{L}} = \frac{x \text{ mol}}{\text{L}} \times \frac{2 \text{ mol H}^+}{\text{mol}} \quad x = 0.100 \text{ mol H}_2\text{SO}_4 \text{ per liter}$$

$$0.100 \text{ mol H}_2\text{SO}_4 \times 98.1 \text{ g/mol} = 9.81 \text{ g H}_2\text{SO}_4$$

Thus, 9.81 g of  $\text{H}_2\text{SO}_4$  must be dissolved in sufficient water to make 1.00 L of solution.

9.58  $0.016 \text{ M H}_2\text{SO}_4 \times \frac{2 \text{ mol H}^+}{\text{mol H}_2\text{SO}_4} = 0.032 \text{ N solution}$

9.60 (a)  $\frac{27.4 \text{ mmol}}{54.7 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} \times \frac{1 \text{ mol}}{1000 \text{ mmol}} \times \frac{1 \text{ eq}}{\text{L}} = 0.500 \text{ N}$

(b)  $\frac{7.81 \text{ mmol}}{54.7 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} \times \frac{1 \text{ mol}}{1000 \text{ mmol}} \times \frac{2 \text{ eq}}{\text{L}} = 0.286 \text{ N}$

(c)  $\frac{6.08 \text{ mmol}}{54.7 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} \times \frac{1 \text{ mol}}{1000 \text{ mmol}} \times \frac{3 \text{ eq}}{\text{L}} = 0.333 \text{ N}$

9.62  $\text{pOH} + \text{pH} = 14.00$ , thus  $\text{pOH} = 14.00 - \text{pH}$

(a)  $14.00 - 2.50 = 11.50$       (b)  $14.00 - 0.00 = 14.0$       (c)  $14.00 - 2.16 = 11.84$

(d)  $14.00 - 1.72 = 12.28$       (e)  $14.00 - 1.64 = 12.36$

9.64  $\text{pOH} + \text{pH} = 14.00$ , thus  $\text{pH} = 14.00 - \text{pOH}$

(a)  $14.00 - 2.21 = 11.79$       (b)  $14.00 - 2.09 = 11.91$       (c)  $14.00 - 1.25 = 12.75$

(d)  $14.00 - 0.00 = 14.00$       (e)  $14.00 - 2.00 = 12.00$

- 9.66 The combination of a weak acid and the salt of its conjugate base is a buffer solution. The pH of a buffer is

$$\text{pH} = \text{pK}_a + \log\left(\frac{\text{proton acceptor}}{\text{proton donor}}\right) = \log\left(\frac{0.075}{0.050}\right) = 6.35 + 0.18 = 6.53$$

$$9.68 \quad 35.9 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.048 \text{ mol}}{\text{L}} = 0.00172 \text{ mol of KOH}$$

0.00172 mol KOH = 0.00172 mol HNO<sub>3</sub> when neutral

$$\frac{0.00172 \text{ mol}}{0.0150 \text{ L}} = 0.115 \text{ M}$$

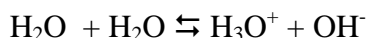
$$9.70 \quad \text{pH} = -\log [\text{H}_3\text{O}^+] = 3.20 \rightarrow [\text{H}_3\text{O}^+] = 6.31 \times 10^{-4}$$

HCl is a strong acid, which means that every HCl molecule dissociates into an H<sub>3</sub>O<sup>+</sup> ion and a Cl<sup>-</sup> ion. Thus, [H<sub>3</sub>O<sup>+</sup>] = [HCl] = 6.31 × 10<sup>-4</sup> M.

9.72 A polyprotic acid is one in which more than one H<sup>+</sup> ion can dissociate.

9.74 A combination of a weak acid and the salt of its conjugate base is a buffer solution. Thus, examples include acetic acid and potassium acetate, formic acid and sodium formate, and carbonic acid and sodium hydrogen carbonate.

9.76 The ionization of water is an equilibrium reaction



The fact that the ion product of water increases with temperature means that this equilibrium is shifted to the right (products) with an increase in temperature. According to Le Chatelier's principle, when an equilibrium is perturbed, it will shift to bring the equilibrium back to its initial conditions. Therefore, when the temperature is increased, this reaction will shift to lower the temperature, which in this reaction is towards the products. As an endothermic reaction will lower the temperature as it goes towards its products, this reaction is endothermic.

9.78 pH is a quantitative measure of acidity. Mathematically, it is equal to  $-\log[\text{H}_3\text{O}^+]$ .

9.80 The pH of a buffer solution equals the pK<sub>a</sub> of the weak acid if the concentrations of the acid and conjugate base are equal. Inspection of Table 9.5 shows that acetic acid has a pK<sub>a</sub> value of 4.76, close to 5. Thus, if a solution of equimolar amounts of acetic acid and sodium acetate is prepared, it will have a pH of 4.76, close to 5.

$$9.82 \quad 5.71 \times 10^{-10} = [x]^2/0.0100 \text{ [From Table 9.5]}$$

$$x = [\text{H}_3\text{O}^+] = 2.38 \times 10^{-6}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 5.62$$

9.84 Osmotic pressure of solution = molarity × R × absolute temperature

$$98.2 \text{ torr} \times 1 \text{ atm}/760 \text{ torr} = \text{molarity} \times 0.0821 \text{ liter-atm/mole K} \times 298 \text{ K}$$

molarity of solution = 0.00528



Thus, in one liter, 0.00028 mol of  $\text{HN}_3$  dissociates into 0.00028 mol of  $\text{H}_3\text{O}^+$  and 0.00028 mol of  $\text{N}_3^-$

$$K_a = [\text{H}_3\text{O}^+][\text{N}_3^-] / [\text{HN}_3]$$

$$[\text{HN}_3] = 0.00500 - 0.00028 = 0.00472 \text{ M}$$

$$[\text{H}_3\text{O}^+] = [\text{N}_3^-] = 0.00028 \text{ M}$$

$K_a = (0.00028)(0.00028) / (0.00472) = 1.66 \times 10^{-5}$ , which is very close to the value in the table,  $1.91 \times 10^{-5}$ .

- 9.86 The pH at the equivalence point of the titration in question 9.85 could not be 7.00. At the equivalence point, the acid has been completely neutralized and the resulting solution is that of its salt. Because the salt consists of a basic anion, hydrolysis of the anion will cause the solution to be basic. The solution's pH will be greater than 7.00.
- 9.88  $\text{pH} = -\log[\text{H}_3\text{O}^+]$ , therefore, the larger the pH, the smaller the concentration of hydronium ion. As the concentration of hydronium ion increases with dissociation constant, the compound with the smallest dissociation constant will have the highest pH and the dissociation constants will increase with decreasing pH.

$$6.65 > 4.82 > 3.41 > 2.85$$

- 9.90 (a)  $\text{H}_2\text{O} + \text{NH}_2^- \rightleftharpoons \text{NH}_3 + \text{OH}^-$
- (b)  $\text{H}_2\text{O} + \text{HS}^- \rightleftharpoons \text{H}_2\text{S} + \text{OH}^-$
- (c)  $\text{HCNO} + \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{CNO}^-$
- (d)  $\text{HNO}_2 + \text{CH}_3\text{COO}^- \rightleftharpoons \text{CH}_3\text{COOH} + \text{NO}_2^-$
- 9.92 A solution with a pH of 12 is basic, which will turn Nile blue red, thus the solution's color will become red.