Chapter 6 - Answer Key

Page 333,Quick Check

1. Rb^+, Ca^{2+}, Cs^+, Ba^{2+}
2. ClO_2^-, Cl^-, NO_3^-
3. $RbClO_4$, BaI_2, $CaBr_2$

Page 334, Quick Check

1. $Fe(CH_3COO)_3$, KF, $Pb(NO_2)_2$, $Ba(CN)_2$
2. $Ca(HCOO)_2$, $SrCO_3$, $Mg(CN)_2$, $NaCH_3COO$, LiC_6H_5COO, K_3PO_4

Page 335, Practice Problems

1. $K_2CO_3 > RbCN > Na_2SO_3 > Na_2C_2O_4 > LiF > KNO_2$
2. 11.78
3. 4.5 M

Page 336, Quick Check

1.

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

$$K_a = \frac{[CH_3NH_2]\,[H_3O^+]}{[CH_3NH_3^+]}$$

b) $C_3H_7NH_3^+(aq) + H_2O(l) \rightleftharpoons C_3H_7NH_2(aq) + H_3O^+(aq)$

$$K_a = \frac{[C_3H_7NH_2]\,[H_3O^+]}{[C_3H_7NH_3^+]}$$

c) $(CH_3)_3NH^+(aq) + H_2O(l) \rightleftharpoons (CH_3)_3N(aq) + H_3O^+(aq)$

$$K_a = \frac{[(CH_3)_3N]\,[H_3O^+]}{[(CH_3)_3NH^+]}$$

2.

a) 2.3×10^{-11}

b) 2.9×10^{-11}

c) 1.6×10^{-10}

Page 337, Practice Problems

1. 4.82
2. 5.9×10^{-9}
3. 14 g

Page 338, Quick Check

1. NH_4I, $CrCl_3$, $Fe(NO_3)_3$
2.

(a). $Sn(H_2O)_4^{2+}(aq) + H_2O(l) \rightleftharpoons Sn(H_2O)_3(OH)^+(aq) + H_3O^+(aq)$

(b) $Cu(H_2O)_4^{2+}(aq) + H_2O(l) \rightleftharpoons Cu(H_2O)_3(OH)^+(aq) + H_3O^+(aq)$

(c) $Fe(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons Fe(H_2O)_5(OH)^{2+}(aq) + H_3O^+(aq)$

Page 339, Practice Problems

1. 0.72
2. 0.023 M
3. 3.45

Page 340, Quick Check

1. NH_4NO_2, $NaCH_3COO$, AlF_3
2. $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$
   $F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$
3. K_a for $NH_4^+ = 5.6 \times 10^{-10}$
   K_b for $F^- = 2.9 \times 10^{-11}$
   As the K_a for NH_4^+ is greater than the K_b for F^-, the hydrolysis of the ammonium ion will occur to a greater extent than the hydrolysis of the fluoride ion.

Page 341, Practice Problems

1. K_a for $NH_4^+ = 5.6 \times 10^{-10}$
   K_b for $CH_3COO^- = 5.6 \times 10^{-10}$
   As the K_a for NH_4^+ is equal to the K_b for CH_3COO^-, each hydrolysis reaction will occur to the same extent and so the approximate pH of the solution will be 7.
2.
   $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$
   $PO_4^{3-}(aq) + H_2O(l) \rightleftharpoons HPO_4^-(aq) + OH^-(aq)$
   K_a for $NH_4^+ = 5.6 \times 10^{-10}$

$$K_b \text{ for } PO_4^{3-} = \frac{K_w}{K_a \text{ for } HPO_4^-} = \frac{1.0 \times 10^{-14}}{2.2 \times 10^{-13}} = 0.045$$

   As the K_b for PO_4^{3-} is much greater than the K_a for NH_4^+, the anionic hydrolysis reaction will occur to a far greater extent and so the solution will be basic.
3. $(NH_4)_2CO_3 > NaNO_3 > Al(CH_3COO)_3 > FeCl_3$

Page 342, Practice Problems

1. K_a for $HPO_4^{2-} = 2.2 \times 10^{-13}$ K_b for HPO_4^{2-} 1.6×10^{-7}
   As the K_b for HPO_4^{2-} is greater than its K_a, the hydrolysis reaction involving the production of hydroxide ions will occur to a greater extent and so the solution will be basic.
2. $KHSO_4 < NaHSO_3 < LiHCO_3$
3. No calculations are required to determine if an aqueous solution of $KHSO_4$ will be acidic or basic because the bisulphate anion is *the conjugate base of a strong acid*. This means that the ion cannot accept protons from water and thus can only act as a weak acid. Therefore, an aqueous solution of $KHSO_4$ will be acidic.

Page 345, 6.1 Review Questions

1. Placing a few drops of universal indicator solution into each of the three beakers will identify the solutes.
   The $Al(NO_3)_3$ solution will be acidic because the hydrated Al^{3+} ion is a weak acid and the NO_3^- ion will not hydrolyze. Therefore, universal indicator will appear ***dark orange*** or ***red*** in this solution.
   The $Ca(NO_3)_2$ solution will be neutral because neither ion will hydrolyze. Therefore, universal indicator solution will appear ***light green*** in this solution.
   The K_3PO_4 solution will be basic because the PO_4^{3-} ion is a relatively strong weak base and the K^+ will not hydrolyze. Therefore, universal indicator will appear ***purple*** in this solution.
2.

Salt Formula	**Ion(s) Which Hydrolyze(s)**	**Result for Aqueous Solution (Acidic, Basic, or Neutral)**	**Equation(s) for Hydrolysis Reaction(s) (if any)**
$(NH_4)_2SO_3$	both	basic as $K_b > K_a$	$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ $SO_3^{2-} + H_2O \rightleftharpoons HSO_3^- + OH^-$
$Al(IO_3)_3$	both	acidic as $K_a > K_b$	$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons Al(H_2O)_5(OH)^{2+} + H_3O^+$ $IO_3^- + H_2O \rightleftharpoons HIO_3 + OH^-$
RbF	F^-	basic	$F^- + H_2O \rightleftharpoons HF + OH^-$
SrI_2	neither	neutral	N/A
KHC_2O_4	$HC_2O_4^-$	acidic as $K_a > K_b$	$HC_2O_4^- + H_2O \rightleftharpoons C_2O_4^{2-} + H_3O^{3+}$ $HC_2O_4^- + H_2O \rightleftharpoons H_2C_2O_4 + OH^-$
$Fe_2(SO_4)_3$	both	acidic as $K_a > K_b$	$Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons Fe(H_2O)_5(OH)^{2+} + H_3O^+$ $SO_4^{2-} + H_2O \rightleftharpoons HSO_4^- + OH^-$

3. a) $CH_3COOH(aq) + KOH(aq) \rightarrow KCH_3COO(aq) + H_2O(l)$
   b) The salt solution that exists in the reaction vessel is 0.25 M KCH_3COO
   c) 9.07
4. 10.30
5. 0.43 g
6. 0.0012 g
7. 4.67
8. $NaHSO_4 < FeCl_3 < Cr(NO_3)_3 < NH_4Br < RbI < KCN < Li_2CO_3 < Na_3PO_4$
9. a)14 g
   b) The pH of the solution will increase as evaporation proceeds because the concentration of the basic anion is increasing.
10. 4.27

Page 350, Quick Check

1. Equal concentrations of a weak acid and its conjugate base allow the buffer to resist changes to its pH *equally well* following the addition of relatively small amounts of *both* strong acid and strong base.
2. In a buffer containing HA and A^-, the conjugate base, A^-, will react to neutralize added acid. As a result, following the addition of a small amount of strong acid to a buffer solution, the $[HA]/[A^-]$ ratio will increase, the $[H_3O^+]$ will increase slightly, and the pH will decrease slightly.
3. KF and HF + HCOOH and LiHCOO
   $NaHSO_4$ and Na_2SO_4 + KH_2PO_4 and K_2HPO_4

Page 353, Practice Problems

1. a) Following the addition of a small amount of strong base to a buffer solution, the $[HA]/[A^-]$ decreases, the $[H_3O^+]$ decreases slightly, and the pH increases slightly.
   b) $HNO_2(aq) + OH^-(aq) \rightarrow NO_2^-(aq) + OH^-(aq)$
   c) Following the addition of this strong base, the $[HNO_2]/[NO_2^-]$ ratio will decrease, the $[H_3O^+]$ will decrease slightly, and the pH of this solution will increase slightly.
2.(a) In 1.0 L of the diluted buffer solution, only 0.10 moles of HNO_2 and NO_2^- are available to neutralize added H_3O^+ and OH^-. However, in the undiluted solution, 1.0 mol of each of these buffer components is available.
   (b) Because only 0.10 mole of NO_2^- is available to neutralize added acid, the addition of 0.11 mol of strong acid will exceed the diluted *buffer's capacity* to neutralize acid by 0.01 moles and thus result in the pH of the diluted buffer decreasing significantly. The undiluted buffer, however, has 1.0 mole of NO_2^- available and can easily neutralize the added acid. The pH of the undiluted buffer solution will therefore not drop appreciably.
3. a) The combination of 0.10 M HI and 0.10 M NaI does not qualify as a buffer because although the HI is capable of neutralizing added base, the iodide ion is the conjugate base of a strong acid. This means that I^- cannot neutralize added acid because it cannot accept protons.
   b) The combination of 0.50 M NaF and 0.50 M NaCN does not qualify as a buffer because although sufficient quantities of weak base (F^- and CN^-) are available to neutralize added acid, no weak acid is present in the solution. This means that the solution has no ability to neutralize added base.
   c) The combination of 1.0 M $K_2C_2O_4$ / 1.0 M KHC_2O_4 does qualify as a buffer because this solution has appreciable (and in this case equal) quantities of both a weak acid ($HC_2O_4^-$) and its conjugate base ($C_2O_4^{2-}$). Therefore, both added acid and base can be neutralized by this solution.
   d) The combination of 0.20 M HF and 0.20 M HCN does not qualify as a buffer because although sufficient quantities of weak acid (HF and HCN) are available to neutralize added base, no weak base is present in the solution. This means that the solution has no ability to neutralize added acid.

Page 356, Practice Problems

1.

Weak Base	**Added Compound**
a) 1.0 M CH_3NH_2	1.0 M CH_3NH_3Cl
b) 0.80 M N_2H_4	0.80 M $N_2H_5NO_3$
c) 0.20 M $(CH_3)_2NH$	0.20 M $(CH_3)_2NH_2Br$

(*Note that in the above table, the anions present in the added compounds are the conjugate bases of strong acids. This ensures their role as spectator ions in the solution.*)

2.

Net Ionic Equation When Acid Added	**Net Ionic Equation When Base Added**
a) $CH_3NH_2(aq) + H_3O^+(aq) \rightarrow CH_3NH_3^+(aq) + H_2O(l)$	a) $CH_3NH_3^+(aq) + OH^-(aq) \rightarrow CH_3NH_2(aq) + H_2O(l)$
b) $N_2H_4(aq) + H_3O^+(aq) \rightarrow N_2H_5^+(aq) + H_2O(l)$	b) $N_2H_5^+(aq) + OH^-(aq) \rightarrow N_2H_4(aq) + H_2O(l)$
c) $(CH_3)_2NH(aq) + H_3O^+(aq) \rightarrow (CH_3)_2NH^+(aq) + H_2O(l)$	c) $(CH_3)_2NH^+(aq) + OH^-(aq) \rightarrow (CH_3)_2NH(aq) + H_2O(l)$

Page 359, Practice Problems

1. The four buffer solutions ranked in order from lowest to highest capacity are:

$$b < d < a < c$$

2. Because the $[A^-]/[HA]$ ratio should be no less than 0.1 and no more than 10 for a buffer to be effective, the Henderson-Hasselbalch equation shows us that buffers have a usable range within ± 1 pH unit of the pK_a of the acid component as shown by the following:

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$pH = pK_a + \log\left(\frac{1}{10}\right) = pK_a - 1 \quad \text{and} \quad pH = pK_a + \log\left(\frac{10}{1}\right) = pK_a + 1$$

$$\text{Buffer pH range} = pK_a \pm 1$$

3.

Desired pH	Weak Acid	Weak Acid pK_a	Salt of Conjugate Base
4.00	**benzoic**	**4.19**	**NaC_6H_5COO**
7.00	**bisulfphite ion**	**7.00**	**Na_2SO_3**
10.00	**phenol**	**9.89**	**NaC_6H_5O**

Page 360 Quick Check

1. a) $HPO_4^{2-}(aq) + H_3O^+(aq) \rightarrow H_2PO_4^-(aq) + H_2O(l)$
   b) $H_2PO_4^-(aq) + OH^-(aq) \rightarrow HPO_4^{2-}(aq) + H_2O(l)$
2. a) If the concentration of dissolved carbon dioxide in the blood is too low, the above equilibrium will shift to the left and so the concentration of hydrogen (hydronium) ions in the blood will drop. This will raise the blood pH level.
   (If the blood pH level gets too high, the $[HBO_2^-]$ will get too high to allow for adequate release of molecular oxygen from hemoglobin. This condition is called *alkalosis*.)
   b) Breathing into a paper bag means that exhaled breath containing CO_2 in continually re-inhaled. This raises the concentration of dissolved carbon dioxide in the blood which shifts the equilibrium described in 2(a) above to the right. This in turn increases the $[H^+]$ in the blood and thus lowers the blood pH level.

Page 363, 6.2 Review Questions

1. The purpose of a buffer is to resist significant pH changes following the addition of relatively small amounts of strong acid or strong base.
2. The components of a buffer solution are normally a conjugate acid-base pair because these components will not react with each other.
3. A buffer must be able to resist pH changes following the addition of either an acid or a base. Although HNO_3 is certainly capable of neutralizing added OH^- ions, its conjugate base, NO_3^-, cannot neutralize added acid. This is because the nitrate ion is the conjugate base of a strong acid and is thus incapable of accepting protons.
4. C_6H_5COOH / KC_6H_5COO
   $CH_3NH_3NO_3$ / CH_3NH_2 K_2SO_3 / $KHSO_3$
   KIO_3 / HIO_3 $NaHS$ / H_2S HF / LiF
   H_2O_2 / $RbHO_2$
5. a) As $[HCN] = [CN^-]$, then $[H_3O^+] = K_a$ for $HCN = 4.9 \times 10^{-10}$ M
   b) This solution considered to be a basic buffer because it buffers the solution in the basic region of the pH scale.
   c) $CN^-(aq) + H_3O^+(aq) \rightarrow HCN(aq) + H_2O(l)$
   Following the addition of a small amount of HCl, the pH of the buffer solution will decrease slightly.
   d) $HCN(aq) + OH^-(aq) \rightarrow CN^-(aq) + H_2O(l)$
   Following the addition of a small amount of NaOH, the pH of the buffer solution will increase slightly.

6.

Stress Applied	Net Ionic Equation	How $[HA]/[A^-]$ Changes	How pH Changes
H_3O^+ added	$A^-(aq) + H_3O^+(aq) \rightarrow HA(aq) + H_2O(l)$	$[HA]/[A^-]$ ratio increases	pH decreases slightly
OH^- added	$HA(aq) + OH^-(aq) \rightarrow A^-(aq) + H_2O(l)$	$[HA]/[A^-]$ ratio decreases	pH increases slightly

7. The buffer solutions listed in order from lowest $[H_3O^+]$ to highest $[H_3O^+]$ are:

$$b < a < c < d$$

8. Buffer Capacity is defined as the amount of acid or base a buffer can neutralize before its pH changes appreciably. Buffer Capacity depends on the absolute concentrations of the buffer components. A more concentrated, or *high-capacity* buffer will experience less of a pH change following the addition of a given amount of strong acid or strong base than a less concentrated or *low-capacity* buffer will. Therefore, buffer solution "d" listed above would have the highest capacity.

9. The buffer solutions listed in order from highest to lowest capacity are:

$$d > b > a > c$$

10. Buffer range is defined as the pH range over which a buffer acts effectively. That pH range is normally from 1 pH unit below the pK_a value for the weak acid component of a buffer solution to 1 pH above the pK_a value.

11. When the concentration of dissolved carbon dioxide in the blood decreases, the concentration of hydrogen (hydronium) ions in the blood also decreases. This raises the blood pH level.

12. Alkalosis occurs when the blood pH level gets too high. This causes the $[HbO_2^-]$ to increase to the point where the release of O_2 from hemoglobin molecules is compromised. In short, the hemoglobin will not release the oxygen molecules to which it has attached.

13. Acidosis occurs when the blood pH level gets too low. This causes the $[HbO_2^-]$ to decrease to the point where hemoglobin's affinity for oxygen is reduced. In short, hemoglobin and oxygen will no longer bind together.

14. By considering the net ionic equation for the neutralization of a strong base by the acidic component of a buffer, the answer to this question becomes clear. In this case, when NaOH is added to a solution of HNO_2, the following represents the net ionic equation:

$$HNO_2(aq) + OH^-(aq) \rightarrow NO_2^-(aq) + H_2O(l)$$

This shows us that if we add 0.50 mol NaOH to 1.0 L of 1.0 M HNO_2, the 0.50 mol NaOH will be totally consumed and in the process stoichiometrically convert 0.50 mol HNO_2 into 0.50 mol NO_2^-. We will therefore have a buffer solution containing equal concentrations of the weak acid HNO_2 and its conjugate base, NO_2^-.

15. The Henderson-Hasselbalch equation shows us that if the buffer component concentrations are equal, then the pH of the buffer solution simply equals the pK_a of the acid present in the buffer.

As $$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

If $[A^-] = [HA]$, then $pH = pK_a$

a) $pH = pK_a$ for $HNO_2 = -\log(4.6 \times 10^{-4}) = 3.34$
b) $pH = pK_a$ for $CH_3COOH = -\log(1.8 \times 10^{-5}) = 4.74$
c) $pH = pK_a$ for $NH_4^+ = -\log(5.6 \times 10^{-10}) = 9.25$
d) $pH = pK_a$ for $HF = -\log(3.5 \times 10^{-4}) = 3.46$

16.

a) The solution must be buffered to pH = 10.00 using CO_3^{2-} and HCO_3^-. Therefore:

$$10.00 = pK_a \text{ for } HCO_3^- + \log\left(\frac{[CO_3^{2-}]}{[HCO_3^-]}\right)$$

Because the $[HCO_3^-] = 0.20$ M, the above equation is written as the following:

$$10.00 = 10.25 + \log\left(\frac{[CO_3^{2-}]}{0.20}\right) \quad \text{so:} \quad \log\left(\frac{[CO_3^{2-}]}{(0.20}\right) = -0.25$$

$$\frac{[CO_3^{2-}]}{(0.20)} = 10^{-0.25} = 0.562$$

so: $[CO_3^{2-}] = (0.20)(0.562) = 0.112$ M

$$[CO_3^{2-}] = [Na_2CO_3] = \frac{0.112 \cancel{\text{mol}}}{\cancel{\text{L}}} \times \frac{106.0 \text{ g } Na_2CO_3}{\cancel{\text{mol}}} \times 1.0 \cancel{\text{L}}$$

$$= 12 \text{ g}$$

b) 9.99

17. a) pH = 4.92

b) pH =9.13

18. a) pH = 4.74
    b) pH = 4.64
    c) pH = 4.85
19. pH = 3.42
20. 6.2 to 1 (6.2:1)
21. 0.80 mol/L, 78g
22. a) pH = 4.79
    b) (i) 4.1 x 10^{-2} mol/L
       (ii) 0.200 mol/L

Page 370, Quick Check

1. To ensure that an acid-base titration reaction goes to completion, at least one of the two reacting species must be strong.
2. An "endpoint" or "transition point" in an acid-base titration is the point at which an indicator changes colour and is only dependent upon the chemical nature of the acid-base indicator.
   The "equivalence point" or "stoichiometric point" in an acid-base titration is the point at which the total number of moles of H_3O^+ from the acid equals the total number of moles of OH^- from the base. The equivalence point is only dependent upon the chemical nature of the reacting species.
3. The table shows that the volume from trial 1does not agree to within 0.1 mL of the volumes from either trial 2 or trial 3. Trial 1is therefore discarded and the volumes from trials 1 and 3 are averaged to obtain the correct volume of standard solution recorded by the student.

Titration Trial	Volume of Std. Solution
1	23.88 mL
2	23.67 mL
3	23.59 mL

Average volume of standard solution

$$= \frac{23.67\text{ mL} + 23.59\text{ mL}}{2} = 23.63\text{ mL}$$

Page 371, Quick Check

1. A 4.00 g sample of NaOH will contain less than 0.100 mol of the compound. A portion of the sample's mass will be due to absorbed water and also Na_2CO_3 produced from the reaction of the NaOH with atmospheric CO_2.
2. a) A volumetric pipette ensures the accurate and precise measurement of the volume of the solution being analyzed in the reaction flask.
   b) Standardizing the titrant against a primary standard ensures the accurate and precise determination of the titrant's concentration.
   c) A burette ensures the accurate and precise measurement of the volume of titrant required in the titration.
   d) An appropriate indicator signals the correct determination of the equivalence point during the titration.

Page 372, Practice Problems

1. 0.121 M NaOH
2. 0.1259 M HNO_3

Page 373, Practice Problems

1. 0.0603 M
2. 0.206 M
3. 0.101 M

Page 375, Practice Problems

1. 24.1 mL
2. 38.5 mL
3. 27.2 mL

Page 377, Practice Problems

1. 88.1 g /mol
2. 94.9 g/mol
3. 285 g/mol

Page 379, Practice Problems

1. 93.40 %
2. 92.5 %
3. 94.9 %

Page 382, 6.3 Review Questions

1. Disagree. Because a titration reaction goes to completion, the volume of standard solution required is only dependent upon the stoichiometry of the reaction and the moles of each species (acid or base) that it must neutralize. *It is not dependent upon the strength of those species*. Thus each acid solution will require approximately the same volume of standard NaOH solution to reach the equivalence point.
2. Agree. The volume of solution to be analyzed has been recorded and thus the number of reactant moles has been specified. Adding water to the reaction flask will not change the number of moles of reactant present and will thus not affect the volume standard solution required to reach the equivalence point.

3. Agree. A 25.0 mL of approximately 0.2 M acetic acid contains approximately 0.005 mol of acid as given by the following:

$$0.0250\,\cancel{L} \times \frac{0.2 \text{ mol } CH_3COOH}{\cancel{L}} = 0.005 \text{ mol } CH_3COOH$$

A 50.0 mL burette filled to capacity with 0.0650 M NaOH contains only 0.00325 mol NaOH as given by the following:

$$0.0500\,\cancel{L} \times \frac{0.0650 \text{ mol NaOH}}{\cancel{L}} = 0.00325 \text{ mol NaOH}$$

Thus there is insufficient standard solution available in the burette to reach the equivalence point.

4. Agree. NaOH is normally only 95 – 98 % pure and rapidly both absorbs water and reacts with CO_2 from the atmosphere. Therefore, any amount of NaOH will contain impurities and thus less than the measured mass of NaOH. This means that the calculated [NaOH] will be too high.
5. 0.162 M
6. 0.170 g
7. 28.3 mL
8. 27.5 mL
9. 122 g/mol
10. 104 g/mol
11. 91.6 %
12. 95.6 %
13. 89.5 %
14. The “analysis” process is always based on the volume of solution added from the burette. This determines the number of moles of one reagent required to reach the equivalence point and all subsequent calculations proceed from that data.

Page 389, Practice Problems

1. 3.8; $K_a = 2 \times 10^{-4}$

In a 1.8×10^{-4} M HCl solution:

$[H_3O^+] = [HCl] = 1.8 \times 10^{-4}$ M (This equals the approximate K_a of bromphenol blue.)

And $pH = -\log(1.8 \times 10^{-4}) = 3.74$

Because the solution pH corresponds to the transition point pH for bromphenol blue, an intermediate green colour will be seen.

2. $[H_3O^+] \approx 10^{-8.1} \approx 8 \times 10^{-9}$ M (1 sig. digit)

3. an intermediate orange colour is seen.

4. $K_{a1} = 4 \times 10^{-7}$

$K_{a2} = 2 \times 10^{-12}$

5. Solution A has a pH $\geq$ 10. This must be the Na_2CO_3 solution. The carbonate anion is a relatively strong weak base and the cation dos not hydrolyze.

Solution B has a pH $\approx$ 7. This must be the NH_4CH_3COO solution. Both the cation and the anion of salt hydrolyze, but because the K_a of the cation = K_b of the anion, the solution will be neutral.

Solution C has a pH between 4.4 and 7.0. This must be the NaH_2PO_4 solution. The cation of the salt does not hydrolyze, and the K_a of the amphiprotic anion (6.2×10^{-8}) is greater than its K_b (1.3×10^{-12}). Therefore the solution will be slightly acidic.

Solution D has a pH $\leq$ 3.2. This must be the $NaHSO_4$ solution. The cation does not hydrolyze and the anion (which can only donate protons to water) is a stronger weak acid than any ion present in the other salts. This solution will therefore be the most acidic.

Page 394, Quick Check

1. $H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$
2. Phenolphthalein is often chosen because the appearance of a pink colour in a colourless solution at the transition point is much easier to detect than a change in colour from one colour to another.
3. The pH at the equivalence point of a strong acid – strong base titration is equal to 7 because neither of the dissociated ions from the salt that exists at the equivalence point will undergo hydrolysis.

Page 395, Practice Problems

1. 4
2. 10
3. The solution at the equivalence point will be slightly basic. Although the cation (Na^+) of the dissociated salt will not hydrolyze, the anion (SO_4^{2-}) of the salt the conjugate base of a weak acid and will thus hydrolyze by accepting protons from water producing OH^- ions.

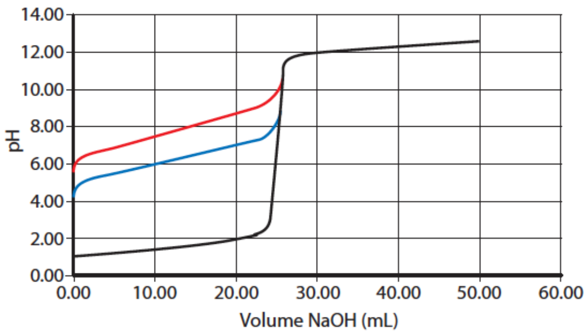
Page 402, Quick Check

1. The “buffer region” of a weak acid – strong base titration curve is so-named because during this part of the titration, appreciable quantities of both a weak acid and its conjugate base exist in the reaction flask.
2. The pH at the equivalence point of a weak acid – strong base titration is higher than 7 because the cation of the product salt will not hydrolyze, but the anion of the product salt is a weak base. Thus, the anion will accept protons from water producing OH^- ions.
3. Beyond the equivalence point, the contribution the acetate ion makes to the $[OH^-]$ is insignificant because excess NaOH is present in the solution.

Sodium hydroxide is a *strong base* and the excess hydroxide ions from this base suppress the hydrolysis of the weakly basic acetate ion by forcing that equilibrium further to the left as shown below:

$CH_3COO^- \quad + \quad H_2O \qquad CH_3COOH \quad + \quad OH^-$

4.



Page 402, Practice Problems

1. a) 3.66
   b) 8.37
2. The weak acid being titrated is benzoic acid.
3. a) 4.6×10^{-4} M
   b) 8.36

Page 408, Practice Problems

1. 9.22
2. Once the titration curve is drawn for the titration of a weak base by a strong acid, the pH, and thus the pOH, of the solution halfway to the equivalence point can be determined from the curve. The pOH of the solution halfway to the equivalence point equals the pK_b of the weak base being titrated. From that pK_b value, we can determine the K_b of the weak base.
3. 1.637; This calculated pH value does agree with the titration curve.

Page 408, Quick Check

1. The pH of a weak base – strong acid titration is lower than 7 because the anion of the product salt will not hydrolyze, but the cation of the product salt is a weak acid. Thus, the cation will donate protons to water producing H_3O^+ ions.
2. Phenolphthalein would be a poor choice for an indicator because as the strong acid is added to the weak base in the reaction flask, the indicator's pink colour will disappear at pH 8.2. This is in the basic range of the pH scale and well above the equivalence point pH which is below 7 in the acidic range of the pH scale. The result would be an incorrectly low volume recorded for an equivalence point and thus a calculation of too few moles of acid.
3. Beyond the equivalence point, the contribution the ammonium ion makes to the $[H_3O^+]$ is insignificant because excess HCl is present in the solution. The excess HCl is a *strong acid* and the increasing $[H_3O^+]$ from that acid forces the weak acid hydrolysis equilibrium even further to the left as shown below:

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

The result is that we can safely ignore any contribution to the $[H_3O^+]$ in the flask by the ammonium ion.

Page 411, 5.4 Review Questions

1. Given that: $\dfrac{K_a}{[H_3O^+]} = \dfrac{[In^-]}{[HIn]}$ and $K_a = 1.0 \times 10^{-7}$

Then:

Solution	$[In^-] / [HIn]$ Ratio in Solution	Solution Colour
0.0010 M HCl	$\dfrac{1.0 \times 10^{-7}}{1.0 \times 10^{-3}} = \dfrac{[In^-]}{[HIn]} = 1.0 \times 10^{-4}$	Yellow
Pure Water	$\dfrac{1.0 \times 10^{-7}}{1.0 \times 10^{-7}} = \dfrac{[In^-]}{[HIn]} = 1.0$	Green
0.0010 M NaOH	$\dfrac{1.0 \times 10^{-7}}{1.0 \times 10^{-11}} = \dfrac{[In^-]}{[HIn]} = 1.0 \times 10^{4}$	Blue

2. a) Because the yellow form of the indicator is seen in the presence of HA1, then HIn is a stronger acid than HA1.
   b) Because the red form of the indicator is seen in the presence of HA2, then HIn is a weaker acid than HA2.
   Thus: HA1 < HIn < HA2

3.

Solution →	0.10 M HCl	0.10 M NaOH	0.10 M $FeCl_3$	0.10 M NaCN
Indicator 1: methyl violet	*yellow/green*	blue	blue	blue
Indicator 2: bromthymol blue	yellow	blue	*yellow*	blue
Indicator 3: indigo carmine	blue	*yellow*	blue	*blue*

4.

	HNO_3 + KOH	NaOH + HCOOH	HBr + NH_3
pH at Equivalence Pt.	7	above 7	below 7
Indicator	phenolphthalein	phenolphthalein	methyl red

5. a) The K_a for bromcresol purple is slightly less than the K_a for acetic acid and so bromcresol purple is a slightly weaker acid than acetic acid.
b) Because the two weak acids are so close in strength, when both are present in a solution, the position of the equilibrium will not favour one side appreciably more than the other. This means that approximately equal [HIn] and [In^-] will exist in the solution resulting in an intermediate colour between yellow and purple. Thus, bromcresol purple would not be an ideal indicator to show that acetic acid is acidic.

6.

Solution A	Solution B	Solution C	Solution D	Solution E
HIO_3	**NaCl**	**K_3PO_4**	**CH_3COOH**	**LiHCOO**

7.

Indicator	pK_a	K_a	Colour in Pure Water	Colour Displayed in 0.010 M NaOH	Colour Displayed in 0.010 M HCl
Phenol Red	7.3	5×10^{-8}	yellow/orange	red	yellow
Methyl Orange	3.8	2×10^{-4}	yellow	yellow	red
Alizarin Yellow	11.1	9×10^{-12}	yellow	red	yellow

8. a) In a weak acid – strong base titration, the weaker the acid being titrated, the or higher the initial pH of the solution will be, and the higher the pH at the equivalence point will be.
b) In a weak base – strong acid titration, the weaker the base being titrated, the lower the initial pH of the solution will be, and the lower the pH at the equivalence point will be.

9.

	Calculating pH Halfway to the Equivalence Point (Chemistry of Buffers)	Calculating pH at the Equivalence Point (Hydrolysis of Salts)
Titration of a Weak Acid by a Strong Base	A buffer solution exists at this point in the titration such that [weak acid] = [conjugate base] in the reaction flask. Thus, the [H_3O^+] = K_a for the weak acid and pH = pK_a.	At the equivalence point for this type of titration, the anion of the salt that exists at the equivalence point is the conjugate base of a weak acid. Being a weak base, it will thus hydrolyze by accepting protons from water producing OH^-.
Titration of a Weak Base by a Strong Acid	A buffer solution exists at this point in the titration such that [weak base] = [conjugate acid] in the reaction flask. Thus, the [H_3O^+] = K_a for the conjugate acid and pH = pK_a.	At the equivalence point for this type of titration, the cation of the salt that exists at the equivalence point is the conjugate acid of a weak acid. Being a weak acid, it will thus hydrolyze by donating protons to water producing H_3O^+.

10. For each type of titration described in question 8 above:

Step 1 in calculating the equivalence point pH involves calculating the final concentrations of the reacting species resulting from the titration reaction which goes to completion. This is most conveniently done by employing an IC*F* table in the solution process.

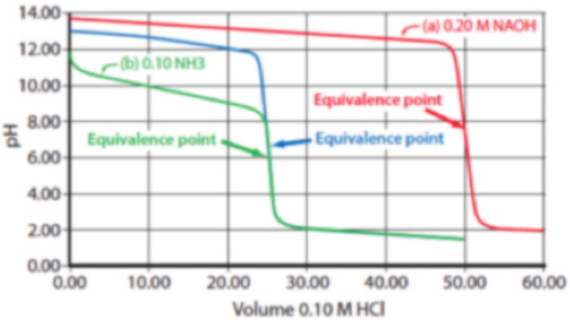
Step 2 then involves using the concentrations calculated in step 1 above as the initial concentrations in either a weak base pH calculation (due to anionic hydrolysis in #8. (a)) or a weak acid pH calculation (due to cationic hydrolysis in #8. (b)). This is most conveniently done by employing an IC*E* table in the solution process.

11. a) 3.74
    b) 25.0 mL
    c) 8.40

12. Thus pK_a for weak acid = 3.456 and so K_a = $10^{-3.456}$ = 3.50×10^{-4}; This matches the K_a for hydrofluoric acid.

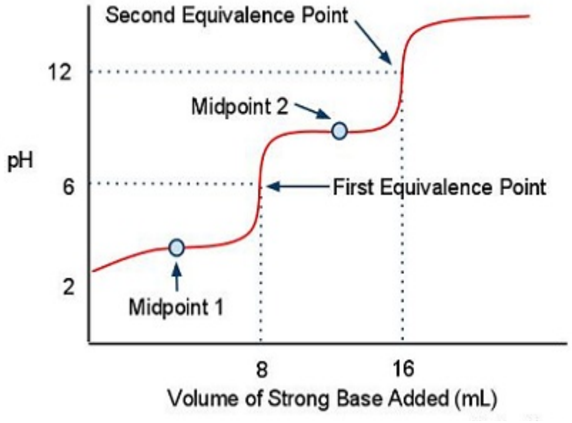
13. Thus pK_b for weak base = 14.00 - 9.50 = 4.50 and so K_b = $10^{-4.50}$ = 3.2×10^{-5}

14.



Appropriate indicators for titration (a) would be bromthymol blue or phenol red.
An appropriate indicator for titration (b) would be methyl red.

15. a)



(b) Selecting a diprotic indicator with $pK_{a\,1}$ and $pK_{a\,2}$ values close to the first and second equivalence point pH values respectively would be appropriate. Alternatively, monitoring the pH during the titration with a pH meter would be advisable.

Page 417, Quick Check

1. For a metal oxide to react with water to produce a basic solution and thus be considered a basic anhydride, the metal oxide must be both highly ionic and soluble.
2. The elements in Groups 1 and 2 (except beryllium) are the metals that satisfy these criteria.
3. The calcium oxide in the cement is a basic anhydride that will react with moisture on the skin to produce hydroxide ions. This strong base is corrosive and will cause irritation to the skin.

Page 418, Quick Check

1. The exhaled breath contains CO_2 which reacts with the water in the beaker to form H_3O^+ions. This lowers the pH of the solution causing the universal indicator to change colour.
2. No hydroxide ions are formed when covalent oxides react with water because no oxide ions are released into water during the hydrolysis.

Page 419, Practice Problems

1. a) $K_2O(s) + H_2O(l) \rightarrow 2KOH(aq)$
   b) $MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(aq)$
2. a) $Al_2O_3 < SiO_2 < P_4O_{10} < SO_3 < Cl_2O_7$
   b) $Cl_2O_7(aq) + H_2O(l) \rightarrow 2HClO_4(aq)$
   $SO_3(aq) + H_2O(l) \rightarrow H_2SO_4(aq)$
3. a) In general, *ionic oxides* react with water to produce ionic bases.
   b) In general, *molecular oxides* that react with water produce acids. Acids are molecular compounds.

Page 421, Quick Check

1. NO_2, SO_2, and SO_3.
2. The combustion of impure coal containing pyrite produces SO_2 according to the following reaction:
   $4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$
3. In polluted air containing *ozone*, O_3, and *fine dust particles* (especially in the presence of *sunlight*), oxygen and ozone will oxidize some of the SO_2 to SO_3:

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

$$SO_2(g) + O_3(g) \rightarrow SO_3(g) + O_2(g)$$

Sulphur trioxide now reacts with water to form the *strong acid* sulphuric acid:

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

Page 424, Practice Problems

1. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
   $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$
   $2NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq)$
2. In water, hydrated aluminum ions function as weak acids according to the following:
   $Al(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons Al(H_2O)_5OH^{2+}(aq) + H_3O^+(aq)$.
   Thus aluminum ions entering aquatic ecosystems lower pH levels and threaten aquatic life.
3. Scrubbing involves first blowing powdered limestone ($CaCO_3$) into the combustion chamber where heat decomposes it to CaO and CO_2 according to the following:
   $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
   The calcium oxide (lime) then combines with the sulphur dioxide gas to produce solid calcium sulphite:
   $CaO(s) + SO_2(g) \rightarrow CaSO_3(s)$
   As a second step, to remove the $CaSO_3$ and any unreacted SO_2, an aqueous suspension of CaO is then sprayed into the exhaust gases before they reach the smokestack to produce a thick suspension of $CaSO_3$ called a slurry.

Page 427, 6.5 Review Questions

1. a) $Rb_2O(s) + H_2O(l) \rightarrow 2RbOH(aq)$
   b) $SrO(s) + H_2O(l) \rightarrow Sr(OH)_2(aq)$
   c) $SeO_2(s) + H_2O(l) \rightarrow H_2SeO_3(aq)$
   d) $N_2O_5(g) + H_2O(l) \rightarrow 2HNO_3(aq)$
2. $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$
   "Sweetening" the soil refers to increasing the alkalinity (the pH) of the soil. Moss thrives in acidic or "sour" soil, but doesn't grow as well in alkaline soil.
3. $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$
4. Oxygen gas and nitrogen gas will not react with each other under normal conditions of temperature and pressure because the activation energy for the reaction is far too high.
5. Several serious problems associated with acid precipitation are:

- Aquatic ecosystems are harmed because most species of fish will perish at pH levels below 5.
- Terrestrial plants are damaged and weakened when exposed to acidic precipitation.
- Acid precipitation contaminates the water supplies that human populations depend upon.
- The soils in many areas contain aluminum salts that are nearly insoluble in normal groundwater, but begin to dissolve in more acidic solutions. This dissolving soil releases the Al^{3+} ions into aquatic ecosystems where they lower the pH of the water and threaten fish.
- The dissolving soil also leaches out many valuable nutrients that are lost in the runoff.
- Many buildings, monuments, and even headstones contain $CaCO_3$ in the form of either marble or limestone. Carbonate salts dissolve in acids and long-term exposure to acid rain significantly degrades such structures.

6. a) $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$
   b) $2NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq)$
7. The oxides of sulphur and nitrogen that cause acid precipitation are gases that are carried into the atmosphere. Prevailing atmospheric winds can push clouds containing these oxides great distances from where the nonmetal oxides are actually produced.
8. Some lakes in regions where acid precipitation occurs are naturally protected because they are bounded by soils rich in limestone. As the limestone dissolves, the hydronium ions from acid rain cause more bicarbonate ions to form according to the following:
   $CO_3^{2-}(aq) + H_3O^+(aq) \rightleftharpoons HCO_3^-(aq) + H_2O(l)$
   Over time, as the $[HCO_3^-]$ increases, the lakes become effective bicarbonate / carbonate buffer systems and maintain a relatively constant pH. If a lake's soil *does not* contain sufficient limestone, a temporary solution is to add $CaCO_3$ or CaO directly to the lake.
9. a) The purpose of "scrubbers" in coal-burning electrical power plants and smelters is to remove sulphur dioxide gas from the exhaust stream before the exhaust stream is released into the atmosphere.
   b) Two problems associated with the process of scrubbing are:
   i) The process is expensive and consumes a great deal of energy.
   ii) Because no use has yet been found for the $CaSO_3$, the great quantities of this compound

that are produced by the process are usually buried in landfills.

10. A catalytic converter significantly reduces the levels of nitrogen oxides released into the atmosphere by using catalytic materials such as transition metal oxides and palladium or platinum metals to convert gaseous nitrogen oxides in the exhaust stream to nitrogen and oxygen gas before it leaves the tailpipe. The catalyzed reaction can be represented as follows:

$$2NO_x(g) \rightarrow xO_2(g) + N_2(g)$$

(The value of "x" is either "1" or "2")

11. Gaseous ammonia can lower NO_x emissions when it is reacted with the hot stack gases to produce nitrogen and water vapour according to the following reaction:

$$4NO(g) + 4NH_3(g) + O_2(g) \rightarrow 4N_2(g) + 6H_2O(l)$$