Chapter 5 – Applications of Acid-Base Reactions Answer Key
September 20, 2012

Section 5.1 Hydrolysis of Salts – The Reactions of Ions with Water

Warm Up

1. (a) A **0.050 M KNO₃** solution exists in the reaction vessel.

   (b) The potassium ion is not on the Table and the nitrate ion is located near the top right corner of the Table. Because the nitrate ion is the conjugate base of a strong acid, it cannot accept protons from water. As neither ion is likely to react with water, we would predict that **the pH of this salt solution will be approximately 7**.

2. (a) A **0.050 M NaCH₃COO** solution exists in the reaction vessel.

   (b) The sodium ion is not located on the Table, but the acetate ion is located on the right side of the middle portion of the Table. The acetate ion is the conjugate base of a weak acid and therefore functions as a weak base in water. As a result, we would predict that **the pH of this salt solution will be above 7**.

Quick Check

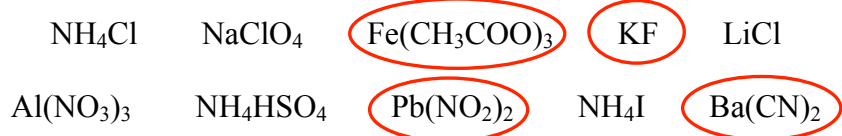1. Circle the ions in the following list that represent cations of strong bases.

Al^{3+} ⬭Rb^+⬭ Fe^{3+} Cr^{3+} ⬭Ca^{2+}⬭ Sn^{4+} ⬭Cs^+⬭ ⬭Ba^{2+}⬭

2. Circle the ions in the following list that represent the conjugate bases of strong acids.

F^- ClO_2^- ⬭ClO_4^-⬭ SO_4^{2-} ⬭Cl^-⬭ NO_2^- CH_3COO^- CN^- ⬭NO_3^-⬭

3. Circle the following salts whose ions will not hydrolyze when dissociated in water.

NH_4Cl Na_2CO_3 ⬭$RbClO_4$⬭ Li_2SO_3 ⬭BaI_2⬭ NH_4HCOO KIO_3 CsF ⬭$CaBr_2$⬭

Quick Check 1. Which of the following salts contain the anion of a weak acid?

NH_4Cl $NaClO_4$ ⬭$Fe(CH_3COO)_3$⬭ ⬭KF⬭ $LiCl$

$Al(NO_3)_3$ NH_4HSO_4 ⬭$Pb(NO_2)_2$⬭ NH_4I ⬭$Ba(CN)_2$⬭

2. Which of the following salts will produce a basic aqueous solution due to anionic hydrolysis?

$AlBr_3$ ⬭$Ca(HCOO)_2$⬭ $RbClO_4$ ⬭$SrCO_3$⬭ ⬭$Mg(CN)_2$⬭

$$\boxed{NaCH_3COO} \qquad Cr(NO_3)_3 \qquad \boxed{LiC_6H_5COO} \qquad FeI_3 \qquad \boxed{K_3PO_4}$$

Practice Problems

1. $\qquad K_2CO_3 \;>\; RbCN \;>\; Na_2SO_3 \;>\; Na_2C_2O_4 \;>\; LiF \;>\; KNO_2$

2. $[Na_2CO_3]_{dil} = \dfrac{(0.50 \text{ M}) \,(200.0 \text{ mL})}{(500.0 \text{ mL})} = 0.20$ M $\qquad Na_2CO_3(s) \rightarrow 2Na^+(aq) + CO_3^{2-}(aq)$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad$ 0.20 M $\qquad$ 0.40 M $\qquad$ 0.20 M
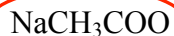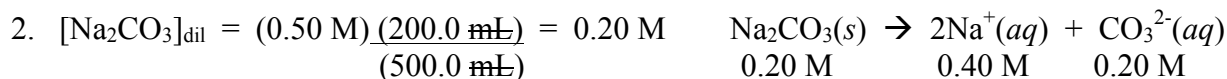
Na^+ will not hydrolyze, but CO_3^{2-} is a weak base and will thus accept protons from water according to following equilibrium: $\qquad CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$
Let $x = [OH^-]_{eq}$
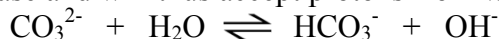
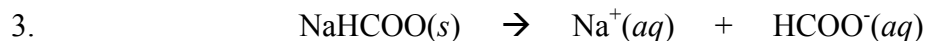|	CO_3^{2-} +	$H_2O \rightleftharpoons$	HCO_3^- +	OH^-
I	0.20		0	0
C	- x		+ x	+ x
E	0.20 - x		x	x

Assume $0.20 - x \approx 0.20$

K_b for $CO_3^{2-} = \dfrac{K_w}{K_a \text{ for } HCO_3^-} = \dfrac{1.0 \times 10^{-14}}{5.6 \times 10^{-11}} = 1.79 \times 10^{-4}$

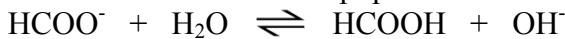$K_b = \dfrac{[HCO_3^-]\,[OH^-]}{[CO_3^{2-}]} = \dfrac{x^2}{0.20} = 1.79 \times 10^{-4} \qquad x = \sqrt{(1.79 \times 10^{-4})\,(0.20)}$

$x = 5.98 \times 10^{-3}$ M $\qquad pOH = -\log(5.98 \times 10^{-3}) = 2.223 \qquad pH = 14.000 - 2.223 = \textbf{11.78}$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (2 sig. digits)

3. $\qquad\qquad\qquad NaHCOO(s) \;\rightarrow\; Na^+(aq) \;+\; HCOO^-(aq)$

Na^+ will not hydrolyze, but $HCOO^-$ is a weak base and will thus accept protons from water according to the following equilibrium: $\qquad HCOO^- + H_2O \rightleftharpoons HCOOH + OH^-$

$\qquad\qquad pOH = 14.00 - 9.20 = 4.80 \qquad\qquad$ so $[OH]_{eq} = 10^{-4.80} = 1.58 \times 10^{-5}$ M

$\qquad\qquad\qquad$ Let $x = [HCOO^-]_{initial} = [NaHCOO]$

	$HCOO^-$ +	$H_2O \rightleftharpoons$	$HCOOH$ +	OH^-
I	x		0	0
C	- 1.58 x 10⁻⁵		+ 1.58 x 10⁻⁵	+ 1.58 x 10⁻⁵
E	x - 1.58 x 10⁻⁵		1.58 x 10⁻⁵	1.58 x 10⁻⁵

K_b for $HCOO^- = \dfrac{K_w}{K_a \text{ for } HCOOH} = \dfrac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.56 \times 10^{-11}$
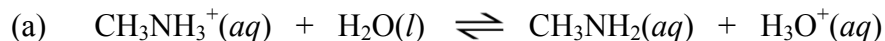
$K_b = \dfrac{[HCOOH]\,[OH^-]}{[HCOO^-]} = \dfrac{(1.58 \times 10^{-5})^2}{(x - 1.58 \times 10^{-5})} = 5.56 \times 10^{-11}$

$x - 1.58 \times 10^{-5} = \dfrac{(1.58 \times 10^{-5})^2}{5.56 \times 10^{-11}}$ $x = [HCOO^-]_{initial} = [NaHCOO] = \textbf{4.5 M}$
(2 sig. digits)

Quick Check

1.
(a) $CH_3NH_3^+(aq) + H_2O(l) \rightleftharpoons CH_3NH_2(aq) + H_3O^+(aq)$

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

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

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

(c) $(CH_3)_3NH^+(aq) + H_2O(l) \rightleftharpoons (CH_3)_3N(aq) + H_3O^+(aq)$
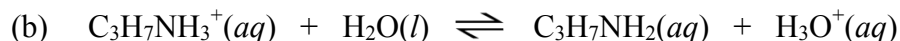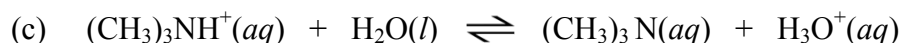
$K_a = \dfrac{[(CH_3)_3N][H_3O^+]}{[(CH_3)_3NH^+]}$

2.
(a) K_a for $CH_3NH_3^+ = \dfrac{K_w}{K_b \text{ for } CH_3NH_2} = \dfrac{1.0 \times 10^{-14}}{4.4 \times 10^{-10}} = \textbf{2.3 x 10}^{\textbf{-11}}$

(b) K_a for $C_3H_7NH_3^+ = \dfrac{K_w}{K_b \text{ for } C_3H_7NH_2} = \dfrac{1.0 \times 10^{-14}}{3.5 \times 10^{-4}} = \textbf{2.9 x 10}^{\textbf{-11}}$

(c) K_a for $(CH_3)_3NH^+ = \dfrac{K_w}{K_b \text{ for } (CH_3)_3N} = \dfrac{1.0 \times 10^{-14}}{6.3 \times 10^{-5}} = \textbf{1.6 x 10}^{\textbf{-10}}$
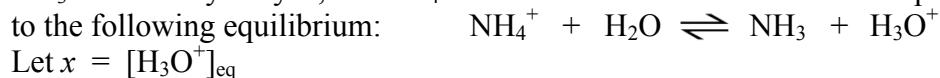
Practice Problems

1.
$\dfrac{16.0 \text{ g } NH_4NO_3}{0.5000 \text{ L}} \times \dfrac{1 \text{ mol}}{80.0 \text{ g}} = 0.400 \text{ M } NH_4NO_3$

$$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$$

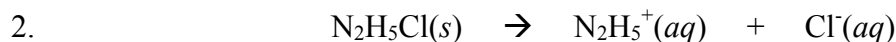NO_3^- will not hydrolyze, but NH_4^+ is a weak acid and will thus donate protons to water according to the following equilibrium: $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$
Let $x = [H_3O^+]_{eq}$

	NH_4^+	$+ H_2O \rightleftharpoons$	NH_3	$+$	H_3O^+
I	0.400		0		0
C	- x		+ x		+ x
E	0.400 - x		x		x

Assume $0.400 - x \approx 0.400$

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$K_a = \dfrac{[NH_3][H_3O^+]}{[NH_4^+]} = \dfrac{x^2}{0.400} = 5.6 \times 10^{-10}$ $x = \sqrt{(5.6 \times 10^{-10})(0.400)} = 1.50 \times 10^{-5}$ M

$$pH = -\log(1.50 \times 10^{-5}) = \mathbf{4.82} \quad \text{(2 sig digits)}$$

2. $N_2H_5Cl(s) \rightarrow N_2H_5^+(aq) + Cl^-(aq)$

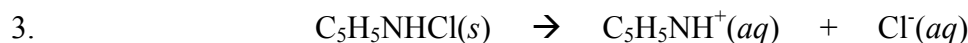Cl^- will not hydrolyze, but $N_2H_5^+$ is a weak acid and will thus donate protons to water according to the following equilibrium: $N_2H_5^+ + H_2O \rightleftharpoons N_2H_4 + H_3O^+$
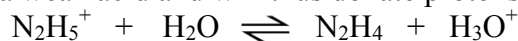
$[H_3O^+]_{eq} = 10^{-4.266} = 5.420 \times 10^{-5}$ M

	$N_2H_5^+$ +	$H_2O \rightleftharpoons$	N_2H_4 +	H_3O^+
I	0.50		0	0
C	-5.420×10^{-5}		$+5.420 \times 10^{-5}$	$+5.420 \times 10^{-5}$
E	≈ 0.50		5.420×10^{-5}	5.420×10^{-5}

$K_a = \dfrac{[N_2H_4][H_3O^+]}{[N_2H_5^+]} = \dfrac{(5.420 \times 10^{-5})^2}{0.50} = \mathbf{5.9 \times 10^{-9}}$ (2 sig digits)

$(K_a$ for $N_2H_5^+)$ $(K_b$ for $N_2H_4) = (5.9 \times 10^{-9})(1.7 \times 10^{-6}) = \mathbf{1.0 \times 10^{-14}}$ (Answer checks)

3. $C_5H_5NHCl(s) \rightarrow C_5H_5NH^+(aq) + Cl^-(aq)$

Cl^- will not hydrolyze, but $C_5H_5NH^+$ (pyridinium) is a weak acid and will thus donate protons to water according to the following equilibrium: $C_5H_5NH^+ + H_2O \rightleftharpoons C_5H_5N + H_3O^+$
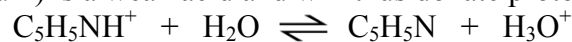
$pH = 3.00$ so $[H_3O^+]_{eq} = 10^{-3.00} = 0.00100$ M

Let $x = [C_5H_5NH^+]_{initial} = [C_5H_5NHCl]$

	$C_5H_5NH^+$ +	$H_2O \rightleftharpoons$	C_5H_5N +	H_3O^+
I	x		0	0
C	-0.00100		$+0.00100$	$+0.00100$
E	$x - 0.00100$		0.00100	0.00100

$K_a = \dfrac{[C_5H_5N][H_3O^+]}{[C_5H_5NH^+]} = \dfrac{(0.00100)^2}{(x - 0.00100)} = 2.13 \times 10^{-6}$ so $x - 0.00100 = \dfrac{(0.00100)^2}{2.13 \times 10^{-6}}$

$x = [C_5H_5NH^+]_{initial} = [C_5H_5NHCl] = 0.470$ M

0.470 ~~mol~~ C_5H_5NHCl x 115.5 g x 0.250 ~~L~~ = **14 g** (2 sig. digits)
                    ~~L~~   ~~mol~~

Quick Check

1. Circle the following salts that will produce acidic aqueous solutions.

$NaNO_2$ ⟮NH_4I⟯ $CaBr_2$ ⟮$CrCl_3$⟯ $Sr(CN)_2$ $RbCH_3COO$ ⟮$Fe(NO_3)_3$⟯ Li_2SO_3

2.

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

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

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

Practice Problems

1.
$$Fe(NO_3)_3(s) \rightarrow Fe^{3+}(aq) + 3NO_3^-(aq)$$
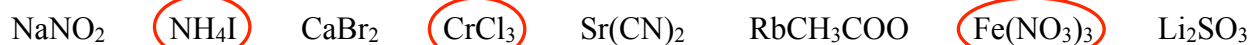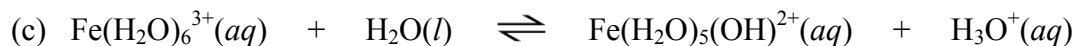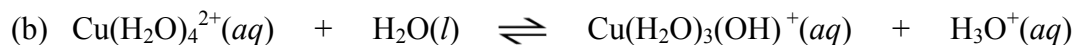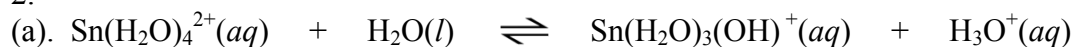
NO_3^- will not hydrolyze, but the hydrated Fe^{3+} is a weak acid and will thus donate protons to water according to the following equilibrium:
$$Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons Fe(H_2O)_5(OH)^{2+} + H_3O^+$$

Let $x = [H_3O^+]_{eq}$

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

	$Fe(H_2O)_6^{3+}$		$Fe(H_2O)_5(OH)^{2+}$	H_3O^+
I	6.0		0	0
C	- x		+ x	+ x
E	6.0 - x		x	x

Assume $6.0 - x \approx 6.0$

$K_a = \dfrac{[Fe(H_2O)_5(OH)^{2+}] [H_3O^+]}{[Fe(H_2O)_6^{3+}]} = \dfrac{x^2}{6.0} = 6.0 \times 10^{-3}$ $x = \sqrt{(6.0 \times 10^{-3})(6.0)} = 0.190\,M$

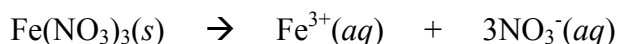pH $= -\log (0.190) = $ **0.72** (2 sig digits)
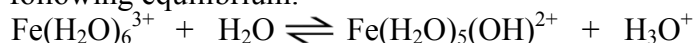

2.
$$AlBr_3(s) \rightarrow Al^{3+}(aq) + 3Br^-(aq)$$
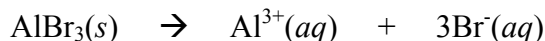
Br^- will not hydrolyze, but the hydrated Al^{3+} is a weak acid and will thus donate protons to water according to the following equilibrium: $Al(H_2O)_6^{3+} + H_2O \rightleftharpoons Al(H_2O)_5(OH)^{2+} + H_3O^+$

pH $= 3.25$ so $[H_3O^+] = 10^{-3.25} = 5.62 \times 10^{-4}\,M$

Let $x = [Al(H_2O)_6^{3+}]_{initial} = [AlBr_3]$

$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons Al(H_2O)_5(OH)^{2+} + H_3O^+$

	$Al(H_2O)_6^{3+}$		$Al(H_2O)_5(OH)^{2+}$	H_3O^+
I	x		0	0
C	$- 5.62 \times 10^{-4}$		$+ 5.62 \times 10^{-4}$	$+5.62 \times 10^{-4}$
E	$x - 5.62 \times 10^{-4}$		5.62×10^{-4}	5.62×10^{-4}

$K_a = \dfrac{[Al(H_2O)_5(OH)^{2+}] [H_3O^+]}{[Al(H_2O)_6^{3+}]} = \dfrac{(5.62 \times 10^{-4})^2}{(x - 5.62 \times 10^{-4})} = 1.4 \times 10^{-5}$

$x - 5.62 \times 10^{-4} = \dfrac{(5.62 \times 10^{-4})^2}{1.4 \times 10^{-5}}$ $x = $ **0.023 M** (2 sig. digits)

3. $BeI_2(s)$ → $Be^{2+}(aq)$ + $2I^-(aq)$
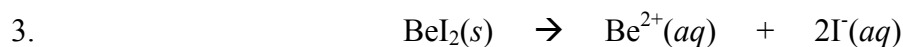
I^- will not hydrolyze, but the hydrated Be^{2+} is a weak acid and will thus donate protons to water according to the following equilibrium: $Be(H_2O)_4^{2+}$ + $H_2O \rightleftharpoons Be(H_2O)_3(OH)^+$ + H_3O^+

Let x = $[H_3O^+]_{eq}$

$Be(H_2O)_4^{2+}$ + $H_2O \rightleftharpoons Be(H_2O)_3(OH)^+$ + H_3O^+

	$Be(H_2O)_4^{2+}$		$Be(H_2O)_3(OH)^+$	H_3O^+
I	0.400		0	0
C	- x		+ x	+ x
E	0.400 - x		x	x

Assume $0.400 - x \approx 0.400$

K_a = $\dfrac{[Be(H_2O)_3(OH)^+]\,[H_3O^+]}{[Be(H_2O)_4^{2+}]}$ = $\dfrac{x^2}{0.400}$ = 3.2×10^{-7}

x = $\sqrt{(3.2 \times 10^{-7})(0.400)}$ = 3.58×10^{-4} M   pH = -log (3.58×10^{-4}) = **3.45** (2 sig digits)

Quick Check
1. Which of the following salts will dissociate into ions that will *both* react with water?

KI   (NH$_4$NO$_2$)   (Fe(CN)$_3$)   Sn(NO$_3$)$_2$ Rb$_2$C$_2$O$_4$ (CrBr$_3$)   NaCH$_3$COO   (AlF$_3$)

2.
$NH_4^+(aq)$ + $H_2O(l)$ $\rightleftharpoons$ $NH_3(aq)$ + $H_3O^+(aq)$

$F^-(aq)$ + $H_2O(l)$ $\rightleftharpoons$ $HF(aq)$ + $OH^-(aq)$
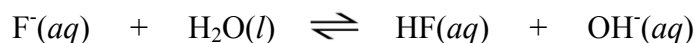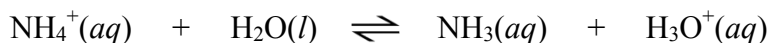
3.
K_a for NH_4^+ = 5.6×10^{-10}

K_b for F^- = $\dfrac{K_w}{K_a \text{ for HF}}$ = $\dfrac{1.0 \times 10^{-14}}{3.5 \times 10^{-4}}$ = 2.9×10^{-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.

Practice Problems
1.
K_a for NH_4^+ = 5.6×10^{-10}

K_b for CH_3COO^- = $\dfrac{K_w}{K_a \text{ for CH}_3\text{COOH}}$ = $\dfrac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$ = 5.6×10^{-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.

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

$PO_4^{3-}(aq) + H_2O(l) \rightleftharpoons HPO_4^-(aq) + OH^-(aq)$
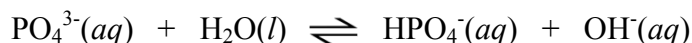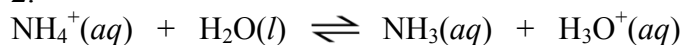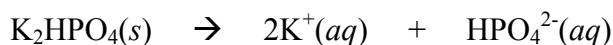
K_a for $NH_4^+ = 5.6 \times 10^{-10}$ K_b for $PO_4^{3-} = \dfrac{K_w}{K_a \text{ for } HPO_4^-} = \dfrac{1.0 \times 10^{-14}}{2.2 \times 10^{-13}} = 0.045$

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. $(NH_4)_2CO_3 > NaNO_2 > Al(CH_3COO)_3 > FeCl_3$

Practice Problems

1.
$$K_2HPO_4(s) \rightarrow 2K^+(aq) + HPO_4^{2-}(aq)$$

K^+ will not hydrolyze, but HPO^{2-} is an amphiprotic ion and will thus both donate protons to and accept protons from water according to the following equilibria:

$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+$

$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + OH^-(aq)$
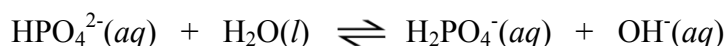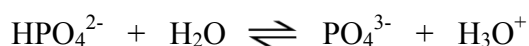
K_a for $HPO_4^{2-} = 2.2 \times 10^{-13}$ K_b for $HPO_4^{2-} = \dfrac{K_w}{K_a \text{ for } H_2PO_4^-} = \dfrac{1.0 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.6 \times 10^{-7}$

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. $KHSO_4 < NaHSO_3 < LiHCO_3$
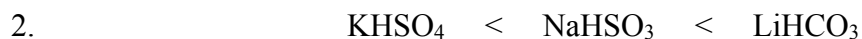
3. No calculations are required to determine if an aqueous solution of $KHSO_4$ will be acidic or basic because the bisulphate anion is *the conjugate base of a strong acid*. This means that the ion cannot accept protons from water and thus can only act as a weak acid. Therefore, an aqueous solution of $KHSO_4$ will be **acidic**.

5.1 Activity
(a) $NaHSO_4$ (pH $\leq$ 3)
(b) K_3PO_4 (pH $\geq$ 11)
(c) NH_4NO_3 (pH = **5.1**)
(d) $Na_2C_2O_4$ (pH = **8.6**)

(a) $(NH_4)_2CO_3$ (pH = **8.5**)
(b) $Fe_2(SO_4)_3$ (pH = **3.8**)
(c) $(NH_4)_2C_2O_4$ (pH = **6.5**)

(a) KH_2PO_4 (pH = **5.5**)
(b) $NaHSO_3$ (pH = **4.0**)
(c) $KHCO_3$ (pH = **9.0**)

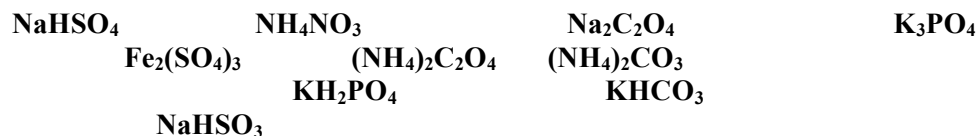| pH	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Colour	RED		ORANGE		YELLOW		GREEN			BLUE		PURPLE-VIOLET		

$NaHSO_4$ NH_4NO_3 $Na_2C_2O_4$ K_3PO_4
        $Fe_2(SO_4)_3$ $(NH_4)_2C_2O_4$ $(NH_4)_2CO_3$
                    KH_2PO_4 $KHCO_3$
        $NaHSO_3$

5.1 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) $CH_3COOH(aq) + KOH(aq) \rightarrow KCH_3COO(aq) + H_2O(l)$
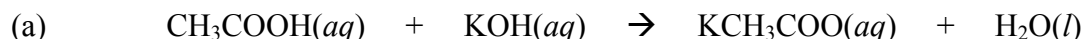
(b) The salt solution that exists in the reaction vessel is 0.25 M KCH_3COO

(c) $KCH_3COO(s) \rightarrow K^+(aq) + CH_3COO^-(aq)$
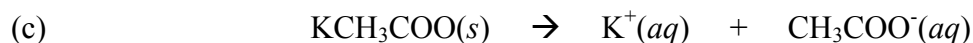
K^+ will not hydrolyze, but CH_3COO^- is a weak base and will thus accept protons from water according to the following equilibrium: $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$
Let $x = [OH^-]_{eq}$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

	CH_3COO^-	H_2O	CH_3COOH	OH^-
I	0.25		0	0
C	$-x$		$+x$	$+x$
E	$0.25 - x$		x	x

Assume $0.25 - x \approx 0.25$

K_b for $CH_3COO^- = \dfrac{K_w}{K_a \text{ for } CH_3COOH} = \dfrac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$

$K_b = \dfrac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \dfrac{x^2}{0.25} = 5.56 \times 10^{-10}$ $x = \sqrt{(5.56 \times 10^{-10})(0.25)}$

$x = 1.18 \times 10^{-5}$ M   pOH $= -\log(1.18 \times 10^{-5}) = 4.928$ pH $= 14.000 - 4.928 = \mathbf{9.07}$
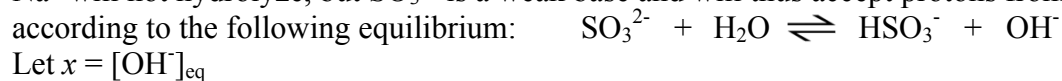
(2 sig. digits)

4.

$$\frac{25.2 \text{ g Na}_2\text{SO}_3}{0.5000 \text{ L}} \times \frac{1 \text{ mol}}{126.1 \text{ g}} = 0.3996 \text{ M} \qquad\qquad \text{Na}_2\text{SO}_3(s) \rightarrow 2\text{Na}^+(aq) + \text{SO}_3^{2-}(aq)$$

                                                                            0.3996 M   0.7994 M   0.3996 M

Na^+ will not hydrolyze, but SO_3^{2-} is a weak base and will thus accept protons from water according to the following equilibrium: $\text{SO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HSO}_3^- + \text{OH}^-$

Let $x = [\text{OH}^-]_{eq}$

|	SO_3^{2-} +	$\text{H}_2\text{O} \rightleftharpoons$	HSO_3^- +	OH^-
I	0.3996		0	0
C	$-x$		$+x$	$+x$
E	$0.3996 - x$		x	x

Assume $0.3996 - x \approx 0.3996$

$$K_b \text{ for SO}_3^{2-} = \frac{K_w}{K_a \text{ for HSO}_3^-} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-7}} = 1.0 \times 10^{-7}$$

$$K_b = \frac{[\text{HSO}_3^-][\text{OH}^-]}{[\text{SO}_3^{2-}]} = \frac{x^2}{0.3996} = 1.0 \times 10^{-7} \qquad x = \sqrt{(1.0 \times 10^{-7})(0.3996)}$$

$x = 1.999 \times 10^{-4}$ M   pOH $= -\log(1.999 \times 10^{-4}) = 3.6992$

pH $= 14.000 - 3.6992 = \mathbf{10.30}$ (2 sig. digits)

5. The Cl^- ion will not hydrolyze, but the hydrated Cu^{2+} ion is a weak acid and will thus donate protons to water according to the following equilibrium:

$$\text{Cu(H}_2\text{O)}_4^{2+} + \text{H}_2\text{O} \qquad \text{Cu(H}_2\text{O)}_3(\text{OH})^+ + \text{H}_3\text{O}^+$$
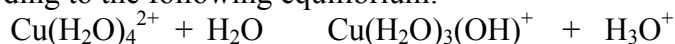
pH $= 5.00$ so $[\text{H}_3\text{O}^+] = 10^{-5.00} = 1.00 \times 10^{-5}$ M

Let $x = [\text{Cu(H}_2\text{O)}_4^{2+}]_{initial} = [\text{CuCl}_2 \cdot 2\text{H}_2\text{O}]$

	$\text{Cu(H}_2\text{O)}_4^{2+}$ +	$\text{H}_2\text{O} \rightleftharpoons$	$\text{Cu(H}_2\text{O)}_3(\text{OH})^+$ +	H_3O^+
I	x		0	0
C	-1.00×10^{-5}		$+1.00 \times 10^{-5}$	$+1.00 \times 10^{-5}$
E	$x - 1.00 \times 10^{-5}$		1.00×10^{-5}	1.00×10^{-5}

$$K_a = \frac{[\text{Cu(H}_2\text{O)}_3(\text{OH})^+][\text{H}_3\text{O}^+]}{[\text{Cu(H}_2\text{O)}_4^{2+}]} = \frac{(1.00 \times 10^{-5})^2}{(x - 1.00 \times 10^{-5})} = 1.0 \times 10^{-8}$$

$$x - 1.00 \times 10^{-5} = \frac{(1.00 \times 10^{-5})^2}{1.00 \times 10^{-8}} = 0.0100$$

$x = [\text{Cu(H}_2\text{O)}_4^{2+}]_{initial} = [\text{CuCl}_2 \cdot 2\text{H}_2\text{O}] = 0.0100$ M

$\dfrac{0.0100 \text{ mol CuCl}_2 \cdot 2\text{H}_2\text{O}}{\text{L}} \times \dfrac{170.5 \text{ g}}{\text{mol}} \times 0.250 \text{ L} = \mathbf{0.43 \text{ g}}$ (2 sig. digits)

6. $$NaCN(s) \rightarrow Na^+(aq) + CN^-(aq)$$
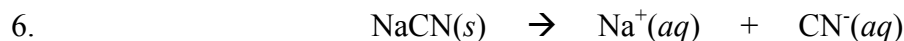
Na^+ will not hydrolyze, but CN^- is a weak base and will thus accept protons from water
according to the following equilibrium: $CN^- + H_2O \rightleftharpoons HCN + OH^-$

$$pOH = 14.00 - 9.50 = 4.50 \qquad so\ [OH]_{eq} = 10^{-4.50} = 3.16 \times 10^{-5}\ M$$

Let $x = [CN^-]_{initial} = [NaCN]$

	CN^-	$+$	$H_2O \rightleftharpoons$	HCN	$+$	OH^-
I	x			0		0
C	$- 3.16 \times 10^{-5}$			$+ 3.16 \times 10^{-5}$		$+ 3.16 \times 10^{-5}$
E	$x - 3.16 \times 10^{-5}$			3.16×10^{-5}		3.16×10^{-5}

$$K_b \text{ for } CN^- = \frac{K_w}{K_a \text{ for } HCN} = \frac{1.0 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.04 \times 10^{-5}$$

$$K_b = \frac{[HCN][OH^-]}{[CN^-]} = \frac{(3.16 \times 10^{-5})^2}{(x - 3.16 \times 10^{-5})} = 2.04 \times 10^{-5}$$

$$x - 3.16 \times 10^{-5} = \frac{(3.16 \times 10^{-5})^2}{2.04 \times 10^{-5}} \qquad x = [CN^-]_{initial} = [NaCN] = 8.05 \times 10^{-5}\ M$$

8.05×10^{-5} ~~mol~~ $NaCN$ $\times$ $\dfrac{49.0\ g}{\text{~~mol~~}}$ $\times$ 0.3000 ~~L~~ $= $ **0.0012 g** (2 sig. digits)

$\dfrac{}{\text{~~L~~}}$

7. $$NH_4ClO_4(s) \rightarrow NH_4(aq) + ClO_4^-(aq)$$
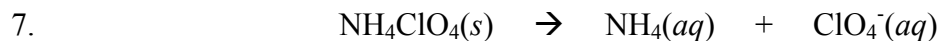
ClO_4^- will not hydrolyze, but NH_4^+ is a weak acid and will thus donate protons to water
according to the following equilibrium: $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

$$\frac{470\ g\ NH_4ClO_4}{5.0\ L} \times \frac{1\ mol}{117.5\ g} = 0.800\ M$$

let $x = [H_3O^+]_{eq}$

	NH_4^+	$+ H_2O \rightleftharpoons$	NH_3	$+$	H_3O^+
I	0.800		0		0
C	$- x$		$+ x$		$+ x$
E	$0.800 - x$		x		x

Assume $0.800 - x \approx 0.800$

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{x^2}{0.800} = 5.6 \times 10^{-10} \qquad x = \sqrt{(5.6 \times 10^{-10})(0.800)} = 2.12 \times 10^{-5}\ M$$

$$pH = -\log(2.12 \times 10^{-5}) = \textbf{4.67} \quad (2 \text{ sig digits})$$

8.
$$NaHSO_4 < FeCl_3 < Cr(NO_3)_3 < NH_4Br < RbI < KCN < Li_2CO_3 < Na_3PO_4$$

9. (a) $KNO_2(s)$ → $K^+(aq)$ + $NO_2^-(aq)$
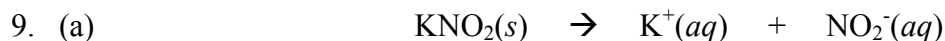
K^+ will not hydrolyze, but NO_2^- is a weak base and will thus accept protons from water
according to the following equilibrium: $NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$

$pOH = 14.00 – 8.50 = 5.50$ so $[OH]_{eq} = 10^{-5.50} = 3.16 \times 10^{-6}$ M

Let $x = [NO_2^-]_{initial} = [KNO_2]$

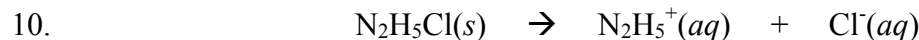|	NO_2^-	$+ H_2O \rightleftharpoons$	HNO_2	$+$	OH^-
I	x		0		0
C	$- 3.16 \times 10^{-6}$		$+ 3.16 \times 10^{-6}$		$+ 3.16 \times 10^{-6}$
E	$\approx x$		3.16×10^{-6}		3.16×10^{-6}

K_b for $NO_2^- = \dfrac{K_w}{K_a \text{ for } HNO_2} = \dfrac{1.0 \times 10^{-14}}{4.6 \times 10^{-4}} = 2.17 \times 10^{-11}$

$K_b = \dfrac{[HNO_2][OH^-]}{[NO_2^-]} = \dfrac{(3.16 \times 10^{-6})^2}{x} = 2.17 \times 10^{-11}$

$x = \dfrac{(3.16 \times 10^{-6})^2}{2.17 \times 10^{-11}}$ $x = [NO_2^-]_{initial} = [KNO_2] = 0.460$ M

0.460 ~~mol~~ KNO_2 x $\dfrac{85.1 \text{ g}}{\cancel{L}}$ x 0.350 ~~L~~ = **14 g** (2 sig. digits)
                          ~~mol~~

   (b) The pH of the solution will increase as evaporation proceeds because the concentration of
the basic anion is increasing.

10. $N_2H_5Cl(s)$ → $N_2H_5^+(aq)$ + $Cl^-(aq)$

Cl^- will not hydrolyze, but $N_2H_5^+$ is a weak acid and will thus donate protons to water according
to the following equilibrium: $N_2H_5^+ + H_2O \rightleftharpoons N_2H_4 + H_3O^+$

Let $x = [H_3O^+]_{initial}$

	$N_2H_5^+$	$+ H_2O \rightleftharpoons$	N_2H_4	$+$	H_3O^+
I	0.500		0		0
C	$- x$		$+$		$+$
E	$0.500 - x$		x		x

Assume $0.500 – x \approx 0.500$

K_a for $N_2H_5^+ = \dfrac{K_w}{K_b \text{ for } N_2H_4} = \dfrac{1.0 \times 10^{-14}}{1.7 \times 10^{-6}} = 5.88 \times 10^{-9}$

$K_a = \dfrac{[N_2H_4][H_3O^+]}{[N_2H_5^+]} = \dfrac{x^2}{0.500} = 5.88 \times 10^{-9}$

$x = \sqrt{(5.88 \times 10^{-9})(0.500)} = 5.42 \times 10^{-5}$ M $pH = -\log(5.42 \times 10^{-5}) = $ **4.27**
                                                                                    (2 sig digits)

Section 5.2 The Chemistry of Buffers

Warm Up

1.

Let $x = [H_3O^+]_{eq}$

$$CH_3\ COOH + H_2O \rightleftharpoons CH_3\ COO^- + H_3O^+$$

	CH₃ COOH		CH₃ COO⁻	H₃O⁺
I	0.10		0	0
C	- x		+ x	+ x
E	0.10 - x		x	x

Assume $0.10 - x \approx 0.10$

$$K_a = \frac{[CH_3COO^-]\,[H_3O^+]}{[CH_3COOH]} = \frac{x^2}{0.10} = 1.8 \times 10^{-5}$$

$$x = \sqrt{(1.8 \times 10^{-5})\,(0.10)} = 0.00134\ M$$

$$pH = -\log(0.00134) = \mathbf{2.87}\quad (2\ \text{sig. digits})$$

2. Percent ionization $= \dfrac{[H_3O^+]_{eq}}{[HA]_{initial}} \times 100\ \%$

$= \dfrac{0.00134}{0.10} \times 100\ \% = \mathbf{1.3\ \%}\quad (2\ \text{sig. digits})$

3.

(a) The equilibrium described in question #1 above would **shift to the left** if 0.10 mole of NaCH₃COO is added to the solution.

(b) This is called the **common ion effect**.

(c) Because the equilibrium shifts to the left, **the hydronium concentration will decrease and the pH will increase.** Therefore, **the percent ionization will decrease**.

(d) Following the addition of NaCH₃COO, the two predominate chemical species in the solution participating in the equilibrium are **CH₃COOH** and **CH₃COO⁻**. Because they are members of a conjugate acid-base pair, **they cannot react with each other**.

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. Circle the following pairs of chemical species that could be used to prepare a buffer solution:

HNO_3 and $NaNO_3$ (KF and HF) HNO_2 and HNO_3 (HCOOH and LiHCOO)

(NaHSO$_4$ and Na$_2$SO$_4$) K_2CO_3 and $K_2C_2O_4$ HCl and NaCl   (KH$_2$PO$_4$ and K$_2$HPO$_4$)

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) $HNO_2(aq)$ + $OH^-(aq)$ → $NO_2^-(aq)$ + $OH^-(aq)$

(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.

Practice Problems

1. Each of the following solutions contains a weak base. What compounds (in what concentrations ideally) would make each a buffer solution?

|	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. Write the six net ionic equations representing the reactions occurring when a small amount of strong acid and also a small amount of strong base are added to each of the above basic buffer solutions.

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) $(CH_3)_2NH^+(aq) + OH^-(aq) \rightarrow (CH_3)_2NH(aq) + H_2O(l)$

Practice Problems

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

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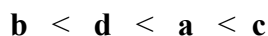
2. Because the $[A^-]/[HA]$ ratio should be no less than 0.1 and no more than 10 for a buffer to be effective, the Henderson-Hasselbalch equation shows us that **buffers have a usable range within ± 1 pH unit of the pK_a of the acid component** as shown by the following:

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

$$pH = pK_a + \log \left[\frac{1}{10} \right] = pK_a - 1 \quad \text{and} \quad pH = pK_a + \log \left[\frac{10}{1} \right] = pK_a + 1$$
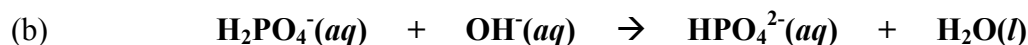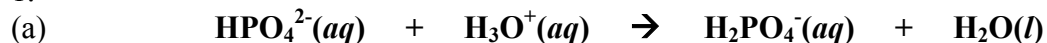
$$\textbf{Buffer pH range} = pK_a \pm 1$$

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

Practice Problems

1.

(a) $HPO_4^{2-}(aq)$ + $H_3O^+(aq)$ → $H_2PO_4^-(aq)$ + $H_2O(l)$

(b) $H_2PO_4^-(aq)$ + $OH^-(aq)$ → $HPO_4^{2-}(aq)$ + $H_2O(l)$

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**.
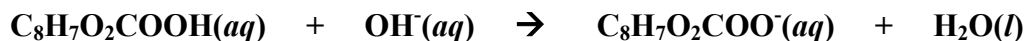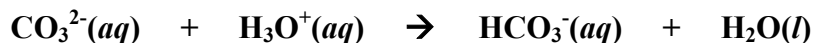(If the blood pH level gets too high, the $[HBO_2^-]$ will get too high to allow for adequate release of molecular oxygen from hemoglobin. This condition is called *alkalosis*.)

(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.**

5.2 Activity

Procedure

1. The ion that acts as the "acid neutralizer" is **the CO_3^{2-} ion**.

$$CO_3^{2-}(aq) + H_3O^+(aq) → HCO_3^-(aq) + H_2O(l)$$

$$C_8H_7O_2COOH(aq) + OH^-(aq) → C_8H_7O_2COO^-(aq) + H_2O(l)$$

A solution containing appreciable quantities of acetylsalicylic acid and the carbonate ion **would not function very well as a buffer solution** because the weak acid would react with carbonate ion and thus reduce the concentrations of each ion in the solution. The solution would qualify as a buffer, but its capacity would be compromised.
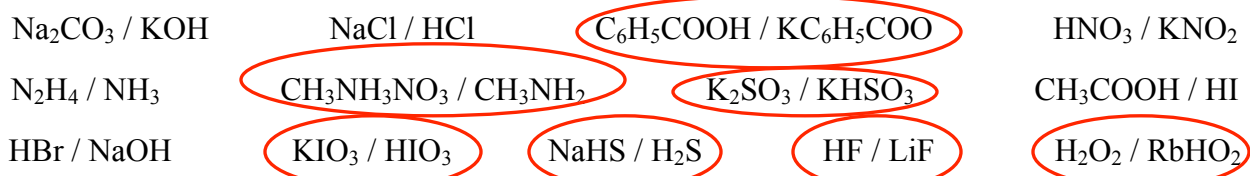
2. If the concentrations of the components of a buffer solution are equal, then the following relationship applies: $[H_3O^+] = K_a$ for the weak acid

Therefore: $[H_3O^+] = K_a$ for $HCO_3^- = 5.6 \times 10^{-11}$

So: pH = -log $(5.6 \times 10^{-11}) = $ **10.25** (This solution would be considered to be a **basic buffer**.)

5.2 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. Each of the following compound pairs exists at a concentration 0.50 M in their respective solutions. Circle the solutions that represent buffers:

Na_2CO_3 / KOH   NaCl / HCl C_6H_5COOH / KC_6H_5COO HNO_3 / KNO_2

N_2H_4 / NH_3 $CH_3NH_3NO_3$ / CH_3NH_2 K_2SO_3 / $KHSO_3$ CH_3COOH / HI

HBr / NaOH 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 x 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)   **$CN^-(aq)$ + $H_3O^+(aq)$ → $HCN(aq)$ + $H_2O(l)$**

Following the addition of a small amount of HCl, **the pH of the buffer solution will decrease slightly**.

d)   **$HCN(aq)$ + $OH^-(aq)$ → $CN^-(aq)$ + $H_2O(l)$**
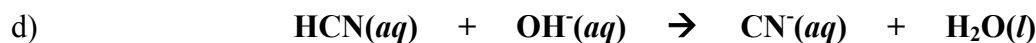
Following the addition of a small amount of NaOH, **the pH of the buffer solution will increase slightly**.

6.

Stress Applied	Net Ionic Equation	How [HA]/[A⁻] Changes	How pH Changes
H_3O^+ added	$A^-(aq)$ + $H_3O^+(aq)$ → $HA(aq)$ + $H_2O(l)$	**[HA]/[A⁻] ratio increases**	**pH decreases slightly**
OH⁻ added	$HA(aq)$ + $OH^-(aq)$ → $A^-(aq)$ + $H_2O(l)$	**[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
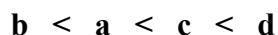
8. Buffer Capacity is defined as **the amount of acid or base a buffer can neutralize before its pH changes appreciably.** Buffer Capacity depends on **the absolute concentrations of the buffer components**. A more concentrated, or *high-capacity* buffer will experience less of a pH change following 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
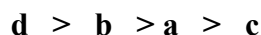
10. Buffer range is defined as **the pH range over which a buffer acts effectively**. That pH range is normally **from 1 pH unit below the pK_a value for the weak acid component of a buffer solution to 1 pH above the pK_a value**.

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:

$$HNO_2(aq) \ + \ OH^-(aq) \ \rightarrow \ NO_2^-(aq) \ + \ H_2O(l)$$
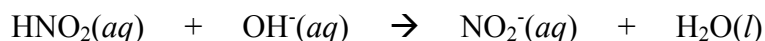
This shows us that if we add 0.50 mol NaOH to 1.0 L of 1.0 M HNO_2, the 0.50 mol NaOH will be totally consumed and in the process stoichiometrically convert 0.50 mol HNO_2 into 0.50 mol NO_2^-. We will therefore have a buffer solution containing equal concentrations of the weak acid HNO_2 and its conjugate 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 $\quad \text{pH} = pK_a + \log\left[\dfrac{[A^-]}{[HA]}\right]$ $\qquad\qquad$ If $[A^-] = [HA]$, then $\quad \textbf{pH} = \textbf{\textit{pK}}_{\textbf{\textit{a}}}$

(a) $\text{pH} = pK_a$ for $HNO_2 = -\log(4.6 \times 10^{-4}) = \textbf{3.34}$

(b) $\text{pH} = pK_a$ for $CH_3COOH = -\log(1.8 \times 10^{-5}) = \textbf{4.74}$

(c) $\text{pH} = pK_a$ for $NH_4^+ = -\log(5.6 \times 10^{-10}) = \textbf{9.25}$

(d) $\text{pH} = pK_a$ for $HF = -\log(3.5 \times 10^{-4}) = \textbf{3.46}$

16. *Extension*

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

Therefore:

$\qquad 10.00 = pK_a$ for $HCO_3^- + \log\left[\dfrac{[CO_3^{2-}]}{[HCO_3^-]}\right]$

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

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

$\qquad \dfrac{[CO_3^{2-}]}{(0.20)} = 10^{-0.25} = 0.562$ $\qquad$ so: $\quad [CO_3^{2-}] = (0.20)(0.562) = 0.112$ M

$\qquad [CO_3^{2-}] = [Na_2CO_3] = \dfrac{0.112 \;\text{mol}}{\text{L}} \times \dfrac{106.0 \text{ g } Na_2CO_3}{\text{mol}} \times 1.0 \;\text{L} = \textbf{12 g}$ (2 sig. digits)

b) The addition of 0.0010 mol HCl to the 1.0 L buffer solution will reduce the $[CO_3^{2-}]$ by 0.0010 M and increase the $[HCO_3^-]$ by 0.0010 M according to the following net ionic equation:

$\qquad\qquad CO_3^{2-}(aq) + H_3O^+(aq) \rightarrow HCO_3^-(aq) + H_2O(l)$
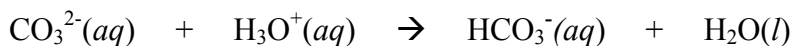
As a result, the pH of the buffer solution will now be given by:

$\qquad \text{pH} = 10.25 + \log\left[\dfrac{(0.112 - 0.0010)}{(0.200 + 0.0010)}\right] = 10.25 + \log\left[\dfrac{0.111}{0.201}\right]$

$\qquad\qquad = 10.25 + -0.258 = \textbf{9.99}$ (2 sig. digits)

Section 5.3 Acid-Base Titrations – Analyzing with Volume

Warm Up

1. The typical purpose of a titration is to determine the solute concentration of a solution.

2.

0.10 M HCl	0.10 M HCN
Hydrochloric acid is a strong monoprotic acid and so the hydronium ion concentration is equal to the acid concentration. Therefore: pH - log (0.10) = **1.00**	Let $x = [H_3O^+]_{eq}$ $HCN + H_2O \rightleftharpoons CN^- + H_3O^+$ <table><tr><td>I</td><td>0.10</td><td></td><td>0</td><td>0</td></tr><tr><td>C</td><td>- x</td><td></td><td>+ x</td><td>+ x</td></tr><tr><td>E</td><td>0.10 - x</td><td></td><td>x</td><td>x</td></tr></table> Assume $0.10 - x \approx 0.10$ $K_a = \dfrac{[CN^-][H_3O^+]}{[HCN]} = \dfrac{x^2}{0.10} = 4.9 \times 10^{-10}$ $x = \sqrt{(4.9 \times 10^{-10})(0.10)} = 7.0 \times 10^{-6}$ M $pH = - \log (7.0 \times 10^{-6}) = $ **5.15** (2 sig. digits)

3. In 25.0 mL each of the above solutions, there are *equal molar amounts* of each acid present as given by:

$$0.0250 \; \cancel{L} \; \times \; \frac{0.10 \text{ mol acid}}{\cancel{L}} \; = \; 0.0025 \text{ mol acid}$$

Therefore, **each solution will require the same number of moles of NaOH *and therefore the same volume of a 0.10 M NaOH solution* to neutralize all of the acid present**. The strength of the acid has *no bearing* on the volume of basic solution required to neutralize it.

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 1 does not agree to within 0.1 mL of the volumes from either trial 2 or trial 3. Trial 1 is 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 $= \dfrac{23.67 \text{ mL} + 23.59 \text{ mL}}{2} = $ **23.63 mL**

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.

Practice Problems

1. $2NaOH(aq) + H_2C_2O_4(aq) \rightarrow Na_2C_2O_4(aq) + 2H_2O(l)$
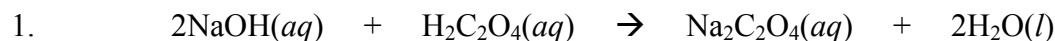
Step 1:   mol $H_2C_2O_4$ = 0.02500 ~~L~~ x $\dfrac{0.0521 \text{ mol } H_2C_2O_4}{\text{~~L~~}}$ = 0.001303 mol $H_2C_2O_4$

Step 2:   mol NaOH = 0.001303 ~~mol $H_2C_2O_4$~~ x $\dfrac{2 \text{ mol NaOH}}{\text{~~mol $H_2C_2O_4$~~}}$ = 0.002606 mol NaOH

Step 3:   [NaOH] = $\dfrac{0.002606 \text{ mol NaOH}}{0.02156 \text{ L}}$ = **0.121 M NaOH** (3 sig. digits)

2. $Na_2CO_3(aq) + 2HNO_3(aq) \rightarrow 2NaNO_3(aq) + CO_2(g) + 2H_2O(l)$

$[Na_2CO_3]$ = $\dfrac{1.546 \text{ ~~g Na_2CO_3~~}}{0.2500 \text{ L}}$ x $\dfrac{1 \text{ mol } Na_2CO_3}{106.0 \text{ ~~g~~}}$ = 0.058340 M Na_2CO_3

mol Na$_2$CO$_3$ = 0.02500 ~~L~~ x 0.058340 <u>mol Na$_2$CO$_3$</u> = 0.0014585 mol Na$_2$CO$_3$

                                              ~~L~~

mol HNO$_3$ = 0.0014585 ~~mol Na$_2$CO$_3$~~ x <u>2 mol HNO$_3$</u> = 0.0029170 mol HNO$_3$

                                                      ~~mol Na$_2$CO$_3$~~

[HNO$_3$] = <u>0.0029170 mol HNO$_3$</u> = **0.1259 M HNO$_3$** (4 sig. digits)

                     0.02317 L

Practice Problems

1.   KOH(*aq*) + CH$_3$COOH (*aq*) → KCH$_3$COO(*aq*) + H$_2$O(*l*)

mol KOH = 0.02564 ~~L~~ x <u>0.1175 mol KOH</u> = 0.003013 mol KOH

                                        ~~L~~

mol CH$_3$COOH = mol KOH = 0.003013 mol

[CH$_3$COOH] = <u>0.003013 mol CH$_3$COOH</u> = **0.0603 M** (3 sig. digits)

                          0.0500 L

2.   NaOH(*aq*) + C$_2$H$_5$OCOOH(*aq*) → NaC$_2$H$_5$OCOO(*aq*) + H$_2$O(*l*)
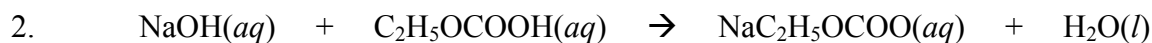
mol NaOH = (avg. trials 2 & 3) 0.03360 ~~L~~ x <u>0.153 mol NaOH</u> = 0.005141 mol NaOH

                                                        ~~L~~

mol C$_2$H$_5$OCOOH = mol NaOH = 0.005141 mol

[C$_2$H$_5$OCOOH] = <u>0.005141 mol C$_2$H$_5$OCOOH</u> = **0.206 M** (3 sig. digits)

                                 0.02500 L

3.   CH$_3$NH$_2$(*aq*) + HCl(*aq*) → CH$_3$NH$_3$Cl(*aq*)
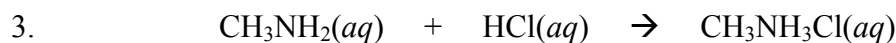
mol HCl = (avg. trials 2 & 3) 0.02730 ~~L~~ x <u>0.185 mol HCl</u> = 0.005051 mol HCl

                                                    ~~L~~

mol CH$_3$NH$_2$ = mol HCl = 0.005051 mol

[CH$_3$NH$_2$] = <u>0.005051 mol CH$_3$NH$_2$</u> = **0.101 M** (3 sig. digits)

                           0.0500 L

Practice Problems

1.   2KOH(aq) + H$_2$SO$_4$(aq) → K$_2$SO$_4$(*aq*) + 2H$_2$O(*l*)

mol H$_2$SO$_4$ = 0.0150 ~~L~~ x <u>0.178 mol H$_2$SO$_4$</u> = 0.002595 mol H$_2$SO$_4$

                                   ~~L~~

mol KOH $=$ 0.002595 ~~mol H₂SO₄~~ x $\dfrac{\text{2 mol KOH}}{\text{mol H}_2\text{SO}_4}$ $=$ 0.005190 mol KOH

volume KOH solution $=$ 0.005190 ~~mol KOH~~ x $\dfrac{1.00 \text{ L}}{0.215 \text{ mol}}$ $=$ 0.0241 L $=$ **24.1 mL**
(3 sig. digits)

2. $Sr(OH)_2(aq)$ $+$ $2HCl(aq)$ → $SrCl_2(aq)$ $+$ $2H_2O(l)$

mol Sr(OH)₂ $=$ 0.0250 ~~L~~ x $\dfrac{0.285 \text{ mol Sr(OH)}_2}{\text{L}}$ $=$ 0.007125 mol Sr(OH)₂

mol HCl $=$ 0.007125 ~~mol Sr(OH)₂~~ x $\dfrac{\text{2 mol HCl}}{\text{mol Sr(OH)}_2}$ x 0.01425 mol HCl

[HCl] $=$ [H₃O⁺] $=$ $10^{-0.432}$ $=$ 0.3698 M

volume HCl solution $=$ 0.01425 mol HCl x $\dfrac{1.00 \text{ L}}{0.03698 \text{ mol}}$ $=$ 0.0385 L $=$ **38.5 mL**
(3 sig. digits)

3. $NH_3(aq)$ $+$ $HNO_3(aq)$ → $NH_4Cl(aq)$
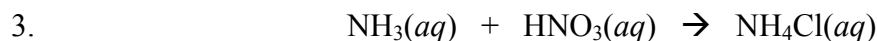
[NH₃] $=$ $\dfrac{5.60 \text{ ~~L NH₃ gas~~}}{0.5000 \text{ L soln.}}$ x $\dfrac{\text{1 mol NH}_3}{22.4 \text{ ~~L gas~~}}$ $=$ 0.5000 M

mol NH₃ $=$ 0.0200 ~~L~~ x $\dfrac{0.5000 \text{ mol NH}_3}{\text{L}}$ $=$ 0.01000 mol NH₃

mol HNO₃ $=$ NH₃ $=$ 0.01000 mol

volume HNO₃ solution $=$ 0.01000 ~~mol HNO₃~~ x $\dfrac{1.00 \text{ L}}{0.368 \text{ ~~mol~~}}$ $=$ 0.0272 L $=$ **27.2 mL**
(3 sig digits)

Practice Problems

1. $NaOH(aq)$ $+$ $HA(aq)$ → $NaA(aq)$ $+$ $H_2O(l)$

mol NaOH $=$ 0.01250 ~~L~~ x $\dfrac{0.01104 \text{ mol NaOH}}{\text{L}}$ $=$ 0.001380 mol NaOH

mol HA $=$ mol NaOH $=$ 0.001380 mol

[HA] $=$ $\dfrac{0.00138 \text{ mol HA}}{0.0250 \text{ L}}$ $=$ 0.05520 M

mol HA in original 750 mL solution $=$ 0.7500 ~~L~~ x $\dfrac{0.05520 \text{ mol HA}}{\text{L}}$ $=$ 0.04140 mol HA

molar mass of HA $=$ $\dfrac{3.648 \text{ g HA}}{0.04140 \text{ mol}}$ $=$ **88.1 g /mol** (3 sig. digits)

2. $2NaOH(aq)$ + $H_2A(aq)$ → $Na_2A(aq)$ + $2H_2O(l)$
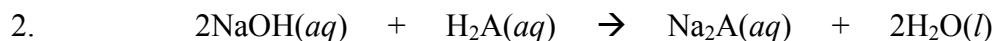
mol NaOH = (avg. trials 2 & 3) 0.03735 L̶ x $\underline{0.2115\ mol\ NaOH}$ = 0.007900 mol NaOH
                                                                    L̶

mol H_2A = 0.007900 m̶o̶l̶ ̶N̶a̶O̶H̶ x $\underline{1\ mol\ H_2A}$ x 0.003950 mol H_2A
                                                    2 m̶o̶l̶ ̶N̶a̶O̶H̶

molar mass of H_2A = $\underline{0.375\ g\ H_2A}$ = **94.9 g/mol** (3 sig. digits)
                                   0.003950 mol

3. $B(aq)$ + $HCl(aq)$ → $BHCl(aq)$
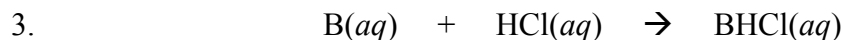
mol HCl = 0.01749 L̶ x $\underline{0.05115\ mol\ HCl}$ = 8.9461×10^{-4} mol HCl
                                          L̶

mol B = mol HCl = 8.9461×10^{-4} mol

$[B]$ = $\underline{8.9461 \times 10^{-4}\ mol\ B}$ = 0.035784 M
              0.0250 L

mol B in original 250.0 mL = 0.250 L̶ x $\underline{0.035784\ mol\ B}$ = 0.0089461 mol B
                                                            L̶

molar mass of B = $\underline{\quad 2.552\ g\ B \quad}$ = **285 g/mol** (3 sig. digits)
                              0.0089461 mol

Practice Problems

1. $NaOH(aq)$ + $C_6H_5COOH(aq)$ → $NaC_6H_5COO(aq)$ + $H_2O(l)$

mol NaOH = 0.02376 L̶ x $\underline{0.1052\ mol\ NaOH}$ = 0.0024996 mol NaOH
                                          L̶

mol pure C_6H_5COOH = mol NaOH = 0.0024996 mol

Actual mass pure C_6H_5COOH =

0.0024996 m̶o̶l̶ x $\underline{122.0\ g\ C_6H_5COOH}$ = 0.30495 g C_6H_5COOH
                                    m̶o̶l̶

% purity = $\underline{actual\ mass\ pure\ C_6H_5COOH}$ x 100 % = $\underline{0.30495\ g̶}$ x 100 % = **93.40 %**
                given mass impure C_6H_5COOH 0.3265 g̶   (4 sig. digits)

2. $Ca(OH)_2(aq)$ + $2HCl(aq)$ → $CaCl_2(aq)$ + $2H_2O(l)$

mol HCl = 0.01772 ~~L~~ x $\underline{0.0615 \text{ mol HCl}}$ = 0.0010898 mol HCl
                                                    ~~L~~

mol $Ca(OH)_2$ = 0.0010898 ~~mol HCl~~ x $\dfrac{1 \text{ mol } Ca(OH)_2}{2 \text{ ~~mol HCl~~}}$ = 5.4489×10^{-4} mol $Ca(OH)_2$

Actual $[Ca(OH)_2]$ = $\dfrac{5.4489 \times 10^{-4} \text{ mol } Ca(OH)_2}{0.0250 \text{ L}}$ = 0.021796 M

Expected $[Ca(OH)_2]$ = $\dfrac{1.309 \text{ ~~g Ca(OH)}_2}{0.7500 \text{ L}}$ x $\dfrac{1 \text{ mol } Ca(OH)_2}{74.1 \text{ ~~g~~}}$ = 0.023554 M

% purity = $\dfrac{\text{actual } [Ca(OH)_2]}{\text{expected } [Ca(OH)_2]}$ x 100 % = $\dfrac{0.021796 \text{ ~~M~~}}{0.023554 \text{ ~~M~~}}$ x 100 % = **92.5 %**
                                                                                (3 sig. digits)

3. $NaOH(aq)$ + $C_5H_4NCOOH(aq)$ → $NaC_5H_4NCOO(aq)$ + $H_2O(l)$
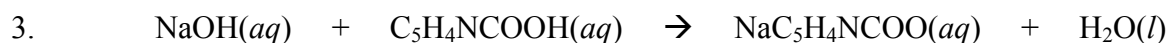
mol NaOH = 0.02096 ~~L~~ x $\underline{0.501 \text{ mol NaOH}}$ = 0.01050 mol NaOH
                                                    ~~L~~

mol pure C_5H_4NCOOH = mol NaOH = 0.01050 mol

Actual mass pure C_5H_4NCOOH =

0.01050 ~~mol C₅H₄NCOOH~~ x $\dfrac{123.0 \text{ g } C_5H_4NCOOH}{\text{~~mol~~}}$ = 1.292 g C_5H_4NCOOH

% purity = $\dfrac{\text{actual mass } C_5H_4NCOOH}{\text{given mass impure } C_5H_4NCOOH}$ x 100 % = $\dfrac{1.292 \text{ ~~g~~}}{1.361 \text{ ~~g~~}}$ x 100 % = **94.9 %**
                                                                                (3 sig. digits)

5.3 Activity

Procedure
1.
(a) A burette ensures the accurate and precise measurement of the volume of titrant required during a titration.

(b) A pipette ensures the accurate and precise measurement of the volume of solution dispensed into the Erlenmeyer flask for analysis in a titration.

(c) An Erlenmeyer flask allows for swirling of the aqueous reaction mixture during a titration without any loss of solution.

(d) A correctly-chosen indicator signals when a titration reaction has just gone to completion by changing colour at (or very near to) the equivalence point.

(e) A standard (or standardized) solution is a solution whose concentration is known to a high level of precision. This ensures that the volume of standard solution required in a titration can be used to accurately determine the number of moles of solute added from the burette. This in turn ensures the accurate determination of the number of moles of reactant present in the solution being analyzed.

(f) An acidic or basic primary standard allows the concentration of the solution in the burette to be determined to a high level of precision.

2. Because a titration is an analytical procedure, accuracy is paramount. Therefore, every titration must be repeated to ensure accurate results. Incomplete mixing of solutions, improper pipetting techniques, and errors made when reading burette volumes (particularly for beginning students) can all contribute to inaccurate results.

Titration Procedure

Part A: Standardizing the NaOH Solution

1. Determine the mass of $H_2C_2O_4 \cdot 2H_2O$ required to make up 250.0 mL of a 0.0500 M solution.

2. Put on the safety goggles and lab apron.

3. Place the 100 mL beaker on the analytical balance and determine the beaker's mass.

4. Add the calculated mass of oxalic acid dihydrate to the beaker. (As long as this mass is known accurately, dispensing a mass *close to* the calculated value is sufficient).

5. Remove the beaker and acid from the balance and add water to the beaker to dissolve the acid.

6. Pour the acid solution through the funnel into the volumetric flask. Wash the beaker a few times with water from the wash bottle to remove all of the acid and add the washings to the flask.

7. Fill the flask to the mark with water and stopper it. Shake the flask to ensure the solution is homogeneous. Calculate the concentration of this standard solution using the measured mass of oxalic acid present in the 250.0 mL volume.

8. Using the second funnel, add about 10 - 15 mL of NaOH solution to the burette, stopper it, and rinse it back and forth. Discard the NaOH solution by opening the stopcock over the sink. Fill the burette with NaOH solution using the same funnel and drain a small amount out of the bottom to eliminate any air bubbles in the bottom until the volume of solution is just below the "0 mL" mark on the burette. Withdraw the funnel.

9. Place the tip of the pipette into the volumetric flask (if it won't fit, pour some oxalic acid solution into a clean dry beaker) and withdraw about 5 – 10 mL of acid solution. Rinse the pipette back and forth and discard the acid solution. Withdraw 25.0 mL of acid solution into the pipette and transfer the solution to one of the Erlenmeyer flask. Add 3 or 4 drops of phenolphthalein indicator solution to the acid in the flask.

10. Record the initial volume of NaOH in the burette and titrate the oxalic acid solution with the basic solution until the first faint pink colour remains in the flask for about 15 seconds and close

the burette stopcock. Record the final volume reading on the burette.

11. Repeat step #10 until agreement within ± 0.10 mL is achieved. Average the two trials that agree and use that volume and the [$H_2C_2O_4$] calculated in step #7 above to determine the [NaOH]. This is now the standardized solution to be used to calculate the [$C_8H_7O_2COOH$].

Part B: Determining the Concentration of ASA Solution

1. Using the same funnel employed to fill the burette with NaOH solution, refill the burette with the basic solution and record the initial volume.

2. Using the second pipette, withdraw about 5 – 10 mL of ASA solution, rinse the pipette back and forth and discard the acid solution. Withdraw 25.0 mL of the ASA solution into the pipette and transfer the solution to the second Erlenmeyer flask. Add 3 or 4 drops of phenolphthalein indicator solution to the acid in the flask.

3. Titrate the ASA solution with the basic solution until the first faint pink colour remains in the flask for about 15 seconds and close the burette stopcock. Record the final volume reading on the burette.

4. Repeat step #3 until agreement within ± 0.10 mL is achieved. Average the two trials that agree and use that volume and the [NaOH] calculated in Part A above to determine the [$C_8H_7O_2COOH$].

Results and Discussion

1. $NaOH(aq)$ + $C_8H_7O_2COOH(aq)$ → $NaC_8H_7O_2COO(aq)$ + $H_2O(l)$
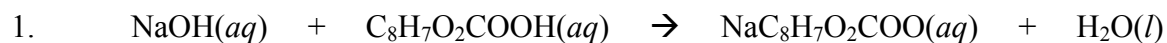
2. At the equivalence point, an aqueous solution of $NaC_8H_7O_2COO$ exists in the reaction flask. The pH of this solution will be above 7 because the anion of the salt is the conjugate base of a weak acid and will therefore hydrolyze by accepting protons from water and thus produce hydroxide ions.

3. A concentration of 0.0500 M is appropriate for the oxalic acid solution because the [NaOH] is approximately 0.1 M. A 2:1 mole ratio in the neutralization reaction means that a given volume of 0.0500 M solution of oxalic acid will require approximately the same volume 0.1 M NaOH to reach the equivalence point.

4. Some possible sources of error and their impact are:
- Non-homogeneity of the oxalic acid solution will cause each aliquot used in the standardization to have a different concentration. Thus, different volumes of NaOH solution will be required to neutralize it.
- Poor technique when filling and/or emptying the pipette will dispense different molar amounts of oxalic acid and/or ASA solution into the reactant flask. Once again, different volumes of NaOH solution will then be required to reach the equivalence points.
- Improper reading of initial and/or final volumes of standardized solution in the burette will result in incorrect mole amounts of NaOH being calculated.

- Errors made when interpreting the indicator colour change at the equivalence point will cause incorrect volumes, and thus moles (often too much) of NaOH to be added to the reaction flask.
- Improper operating of the burette stopcock as the equivalence point is approached will once again dispense incorrect volumes of NaOH into the reaction flask. An incorrect volume means an incorrect mole amount.

5.3 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:

$$0.0250 \text{ L} \quad \text{x} \quad \frac{0.2 \text{ mol } CH_3COOH}{L} \quad = \quad 0.005 \text{ mol } CH_3COOH$$

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

$$0.0500 \text{ L} \quad \text{x} \quad \frac{0.0650 \text{ mol NaOH}}{L} \quad = \quad 0.00325 \text{ mol NaOH}$$

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. $\qquad NaOH(aq) \quad + \quad KHC_8H_4O_4(aq) \quad \rightarrow \quad NaKHC_8H_4O_4(aq) \quad + \quad H_2O(l)$
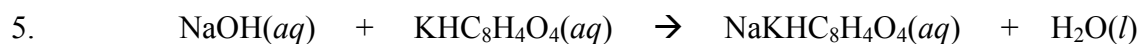
$$\text{mol KHP} \quad = \quad 0.835 \text{ g } KHC_8H_4O_4 \quad \text{x} \quad \frac{1 \text{ mol}}{204.1 \text{ g}} \quad = \quad 0.004091 \text{ mol KHP}$$

$$\text{mol NaOH} \quad = \quad \text{mol KHP} \quad = \quad 0.004091 \text{ mol}$$

$$[\text{NaOH}] \quad = \quad \frac{0.004091 \text{ mol NaOH}}{0.02524 \text{ L}} \quad = \quad \textbf{0.162 M} \text{ (3 sig. digits)}$$

6. $2NaOH(aq) + H_2C_2O_4(aq) \rightarrow Na_2C_2O_4(aq) + 2H_2O(l)$
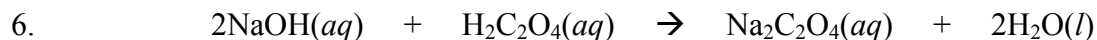
mol NaOH $= 0.02156$ ~~L~~ x $\dfrac{0.125 \text{ mol NaOH}}{L} = 0.002695$ mol NaOH

mol $H_2C_2O_4 = 0.002695$ ~~mol NaOH~~ x $\dfrac{1 \text{ mol } H_2C_2O_4}{2 \text{ mol NaOH}} = 0.001348$ mol $H_2C_2O_4$

mass $H_2C_2O_4 \cdot 2H_2O = 0.001348$ ~~mol $H_2C_2O_4$~~ x $\dfrac{126.0 \text{ g } H_2C_2O_4}{mol} = \textbf{0.170 g}$ (3 sig. digits)

7. $2NaOH(aq) + H_2C_2O_4(aq) \rightarrow Na_2C_2O_4(aq) + 2H_2O(l)$
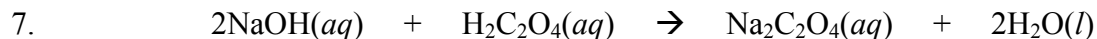
pOH $= 14.000 - 13.440 = 0.560$

$[OH^-] = [NaOH] = 10^{-0.560} = 0.2754$ M

mol $H_2C_2O_4 = 0.0250$ ~~L~~ x $\dfrac{0.156 \text{ mol } H_2C_2O_4}{L} = 0.003900$ mol $H_2C_2O_4$

mol NaOH $= 0.003900$ ~~mol $H_2C_2O_4$~~ x $\dfrac{2 \text{ mol NaOH}}{\text{mol } H_2C_2O_4} = 0.007800$ mol NaOH

volume NaOH solution $= 0.007800$ ~~mol NaOH~~ x $\dfrac{1.00 \text{ L}}{0.2754 \text{ ~~mol~~}} = 0.02832$ L $= \textbf{28.3 mL}$ (3 sig. digits)

8. $Sr(OH)_2(aq) + 2HCl(aq) \rightarrow SrCl_2(aq) + 2H_2O(l)$

$[HCl] = \dfrac{4.48 \text{ ~~L HCl gas~~}}{0.400 \text{ L soln.}}$ x $\dfrac{1 \text{ mol HCl}}{22.4 \text{ ~~L gas~~}} = 0.5000$ M

mol HCl $= 0.0250$ ~~L~~ x $\dfrac{0.5000 \text{ mol HCl}}{L} = 0.1250$ mol HCl

mol $Sr(OH)_2 = 0.1250$ ~~mol HCl~~ x $\dfrac{1 \text{ mol } Sr(OH)_2}{2 \text{ ~~mol HCl~~}} = 0.006250$ mol $Sr(OH)_2$

volume $Sr(OH)_2$ solution $= 0.006250$ ~~mol $Sr(OH)_2$~~ x $\dfrac{1.00 \text{ L}}{0.227 \text{ ~~mol~~}} = 0.02753$ L $= \textbf{27.5 mL}$ (3 sig. digits)

9. $KOH(aq) + HA(aq) \rightarrow KA(aq) + H_2O(l)$

mol KOH $= 0.02651$ ~~L~~ x $\dfrac{0.2055 \text{ mol KOH}}{L} = 0.0054478$ mol KOH

mol HA $=$ mol KOH $= 0.0054478$ mol

molar mass HA $= \dfrac{0.665 \text{ g HA}}{0.0054478 \text{ mol}} = \textbf{122 g/mol}$ (3 sig. digits)

10. $Sr(OH)_2(aq)$ + $H_2A(aq)$ → $SrA(aq)$ + $2H_2O(l)$

mol $Sr(OH)_2$ = 0.0236 L̶ x $\dfrac{0.2231 \text{ mol } Sr(OH)_2}{\text{L̶}}$ = 0.005265 mol $Sr(OH)_2$

mol H_2A = mol $Sr(OH)_2$ = 0.005265 mol

$[H_2A]$ = $\dfrac{0.005265 \text{ mol } H_2A}{0.0250 \text{ L}}$ = 0.2106 M

mol H_2A present in 250.0 mL = 0.2500 L̶ x $\dfrac{0.2106 \text{ mol } H_2A}{\text{L̶}}$ = 0.5265 mol H_2A

molar mass H_2A = $\dfrac{5.47 \text{ g } H_2A}{0.5265 \text{ mol}}$ = **104 g/mol** (3 sig. digits)

11. $2NaOH(aq)$ + $C_4H_6O_6(aq)$ → $Na_2C_4H_4O_6(aq)$ + $2H_2O(l)$
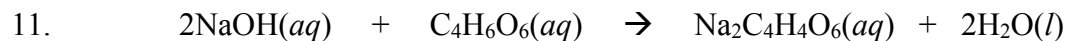
mol NaOH = 0.04031 L̶ x $\dfrac{0.223 \text{ mol NaOH}}{\text{L̶}}$ = 0.008989 mol NaOH

mol $C_4H_6O_6$ = 0.008989 m̶o̶l̶ ̶N̶a̶O̶H̶ x $\dfrac{1 \text{ mol } C_4H_6O_6}{2 \text{ m̶o̶l̶ ̶N̶a̶O̶H̶}}$ = 0.004495 mol $C_4H_6O_6$

Actual $[C_4H_6O_6]$ = $\dfrac{0.004495 \text{ mol } C_4H_6O_6}{0.02500 \text{ L}}$ = 0.1798 M

Expected $[C_4H_6O_6]$ = $\dfrac{7.36 \text{ g̶ } C̶_4H̶_6O̶_6}{0.2500 \text{ L}}$ x $\dfrac{1 \text{ mol } C_4H_6O_6}{150.0 \text{ g̶}}$ = 0.1963 M

% purity = $\dfrac{\text{actual } [C_4H_6O_6]}{\text{expected } [C_4H_6O_6]}$ x 100 % = $\dfrac{0.1798 \text{ M̶}}{0.1963 \text{ M̶}}$ x 100% = **91.6 %** (3 sig. digits)

12. $KOH(aq)$ + $C_5H_7COOH(aq)$ → $KC_5H_7COO(aq)$ + $H_2O(l)$
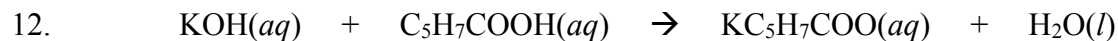
mol KOH = 0.02734 L̶ x $\dfrac{0.178 \text{ mol KOH}}{\text{L̶}}$ = 0.004867 mol KOH

mol C_5H_7COOH = mol KOH = 0.004867 mol

Actual mass C_5H_7COOH = 0.004867 m̶o̶l̶ x $\dfrac{112.0 \text{ g } C_5H_7COOH}{\text{m̶o̶l̶}}$ = 0.5451 g C_5H_7COOH

% purity = $\dfrac{\text{actual mass } C_5H_7COOH}{\text{expected mass } C_5H_7COOH}$ x 100 % = $\dfrac{0.5451 \text{ g̶}}{0.570 \text{ g̶}}$ x 100 % = **95.6 %**
(3 sig. digits)

13. $Sr(OH)_2(aq)$ + $2C_7H_7COOH(aq)$ → $Sr(C_7H_7COO)_2(aq)$ + $2H_2O(aq)$
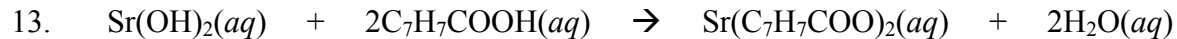
mol $Sr(OH)_2$ = 0.03107 ~~L~~ x $\underline{0.105\ mol\ Sr(OH)_2}$ = 0.003262 mol $Sr(OH)_2$
                                             ~~L~~

mol C_7H_7COOH = 0.003262 ~~mol Sr(OH)₂~~ x $\underline{2\ mol\ C_7H_7COOH}$ = 0.006252 mol C_7H_7COOH
                                                       ~~mol Sr(OH)₂~~

Actual mass C_7H_7COOH =

0.006252 ~~mol C₇H₇COOH~~   x $\underline{136.0\ g\ C_7H_7COOH}$ =   0.8874 g C_7H_7COOH
                                          ~~mol~~

% purity = $\underline{\text{actual mass } C_7H_7COOH}$ x   100 %   = $\underline{0.8874\ \cancel{g}}$ x   100 %   =   **89.5 %**
                  expected mass C_7H_7COOH 0.992 $\cancel{g}$ (3 sig. digits)

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.

Section 5.4 A Closer Look at Titrations

Warm Up

1.
Titration 1: $NaOH(aq)$ + $HCl(aq)$ → $NaCl(aq)$ + $H_2O(l)$

Titration 2: $NaOH(aq)$ + $CH_3COOH(aq)$ → $NaCH_3COO(aq)$ + $H_2O(l)$

Titration 3: $NH_3(aq)$ + $HCl(aq)$ → $NH_4Cl(aq)$
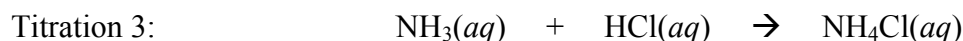
2.
Titration 1: An aqueous solution of **NaCl** exists in the reaction flask at the equivalence point.

Titration 2: An aqueous solution of **NaCH₃COO** exists in the reaction flask at the equivalence point.

Titration 3: An aqueous solution of **NH₄Cl** exists in the reaction flask at the equivalence point.

3.
Titration 1: At the equivalence point, the pH of this solution should be **equal to 7 because neither the Na⁺ nor the Cl⁻ ion will undergo hydrolysis**.

Titration 2: At the equivalence point, the pH of this solution should be **above 7 because the CH$_3$COO$^-$ ion is the conjugate base of a weak acid and will thus undergo hydrolysis producing OH$^-$ ions.**

Titration 3: At the equivalence point, the pH of this solution should be **below 7 because the NH$_4^+$ is the conjugate acid of a weak base and will thus undergo hydrolysis producing H$_3$O$^+$ ions**.

Practice Problems

1.   The pK_a (which also equals the transition point pH) for the indicator can be estimated by averaging the two pH values between which the colour change occurs:

$$pK_a \; = \; \frac{3.0 \; + \; 4.5}{2} \; = \; 3.75 \; = \; \textbf{3.8} \text{ (1 sig. digit)}$$

$$K_a \; = \; 10^{-3.75} \; = \; 1.8 \times 10^{-4} \; = \; \textbf{2} \; \times \; \textbf{10}^{-4} \text{ (1 sig. digit)}$$

In a 1.8 x 10^{-4} M HCl solution:
[H$_3$O$^+$] = [HCl] = 1.8 x 10^{-4} M (This equals the approximate K_a of bromphenol blue.)

And pH = - log (1.8 x 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.

Indicator	Colour
Phenol Red	red
Phenolphthalein	colourless

The phenol red colour tells us that the pH $\geq$ 8.0.
The phenolphthalein colour that the pH $\leq$ 8.2.
We would estimate the pH to be approximately 8.1.

Therefore: [H$_3$O$^+$] $\approx$ 10$^{-8.1}$ $\approx$ **8 x 10^{-9} M** (1 sig. digit)

3. In a 0.0010 M NaOH solution:

   pOH = - log (1.0 x 10^{-3}) = 3.00   and so   pH = 14.00 - 3.00 = 11.00

Once again, the solution pH = the indicator pK_a and so **an intermediate orange colour is seen**.

4.

	Below pH 5.6	Above pH 7.3	Below pH 11	Above pH 12.4
Alizarin Colour	yellow	red	red	purple

$pK_{a\,1}$ = $\dfrac{5.6\ +\ 7.3}{2}$ = 6.4   so $K_{a\,1}$ = $10^{-6.4}$ = **4 x 10⁻⁷** (1 sig. digit)

$pK_{a\,2}$ = $\dfrac{11.0\ +\ 12.4}{2}$ = 11.7   so $K_{a\,2}$ = $10^{-11.4}$ = **2 x 10⁻¹²** (1 sig. digit)

5.

|	Bromthymol Blue	Methyl Orange	Phenolphthalein
Solution A	blue	yellow	pink
Solution B	green	yellow	colourless
Solution C	yellow	yellow	colourless
Solution D	yellow	red	colourless

Solution A has a pH ≥ 10. This must be the Na₂CO₃ solution. The carbonate anion is a relatively strong weak base and the cation dos not hydrolyze.

Solution B has a pH ≈ 7. This must be the NH₄CH₃COO 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 NaH₂PO₄ solution. The cation of the salt does not hydrolyze, and the K_a of the amphiprotic anion (6.2 x 10⁻⁸) is greater than its K_b (1.3 x 10⁻¹²). Therefore the solution will be slightly acidic.

Solution D has a pH ≤ 3.2. This must be the NaHSO₄ 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.

Quick Check

1.   H₃O⁺(*aq*)   +   OH⁻(*aq*)   →   2H₂O(*l*)
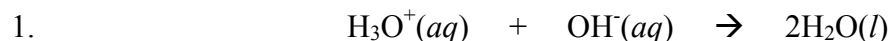
2. Phenolphthalein is often chosen because **the appearance of a pink colour in a colourless solution at the transition point is much easier to detect than a change in colour from one colour to another.**

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.**

Practice Problems

1.

$[HCl]_{IN}$ = 0.100 M x $\dfrac{25.00 \text{ mL}}{49.95 \text{ mL}}$ = 0.5005 M

$[NaOH]_{IN}$ = 0.100 M x $\dfrac{24.95 \text{ mL}}{49.95 \text{ mL}}$ = 0.4995 M

	HCl	NaOH	→	NaCl	+	H$_2$O
I	0.5005	0.4995		0		
C	- 0.4995	- 0.4995		+ 0.4995		
F	0.0001	≈ 0		0.4995		

Final [HCl] = $[H_3O^+]$ = 0.0001 M   so pH = - log (0.0001) = **4**

2.

$[HCl]_{IN}$ = 0.100 M x $\dfrac{25.00 \text{ mL}}{50.05 \text{ mL}}$ = 0.4995 M

$[NaOH]_{IN}$ = 0.100 M x $\dfrac{25.05 \text{ mL}}{50.05 \text{ mL}}$ = 0.5005 M

	HCl	NaOH	→	NaCl	+	H$_2$O
I	0.4995	0.5005		0		
C	- 0.4995	- 0.4995		+ 0.4995		
F	≈ 0	0.0001		0.4995		

Final [NaOH] = $[OH^-]$ = 0.0001 M

so pOH = - log (0.0001) = 4.00   pH = 14.00 - 4.00 = **10**

3. $H_2SO_4(aq)$ + $2NaOH(aq)$ → $Na_2SO_4(aq)$ + $2H_2O(l)$
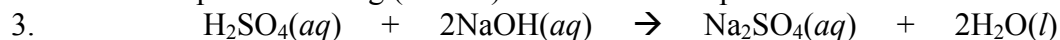
The solution at the equivalence point will be **slightly basic**. Although the cation (Na^+) of the dissociated salt will not hydrolyze, the **anion (SO_4^{2-}) of the salt the conjugate base of a weak acid and will thus hydrolyze by accepting protons from water producing OH⁻ ions**.

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:**

$$CH_3COO^- \ + \ H_2O \ \rightleftharpoons \ CH_3COOH \ + \ OH^-$$

4.
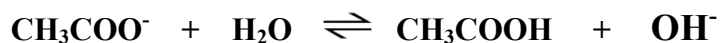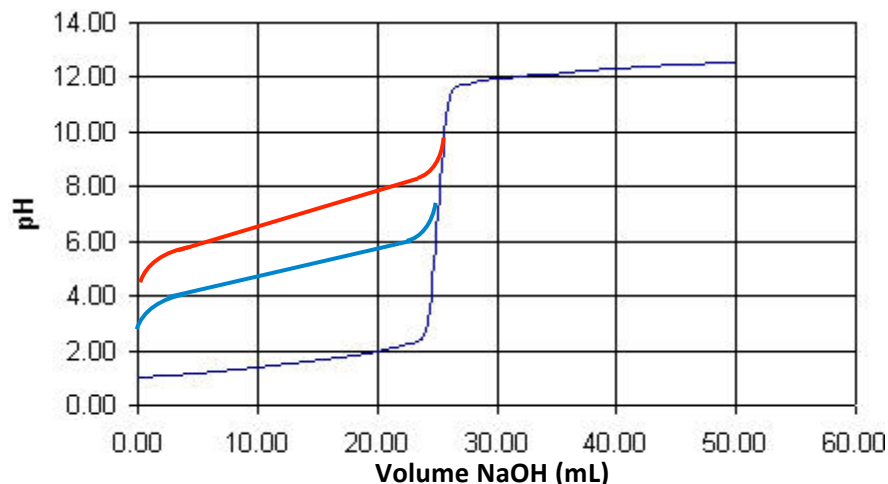
Practice Problems

1.
(a)

$[HCOOH]_{IN} \ = \ 0.200 \text{ M} \ \ \times \ \dfrac{20.00 \ \text{mL}}{29.00 \ \text{mL}} \ = \ 0.1379 \text{ M}$

$[NaOH]_{IN} \ = \ 0.200 \text{ M} \ \times \ \dfrac{9.00 \ \text{mL}}{29.00 \ \text{mL}} \ = \ 0.06207 \text{ M}$
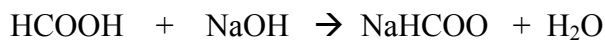
	HCOOH	+ NaOH	→ NaHCOO	+ H₂O
I	0.1379	0.06207	0	
C	- 0.06207	- 0.06207	+ 0.06207	
F	0.07583	≈ 0	0.06207	

$K_a \ = \ \dfrac{[H_3O^+]\,[HCOO^-]}{[HCOOH]}$ so $[H_3O^+] \ = \ \dfrac{K_a\,[HCOOH]}{[HCOO^-]}$

$[H_3O^+] \ = \ \dfrac{(1.8 \times 10^{-4})\,(0.07583)}{(0.06207)} \ = \ 2.199 \times 10^{-4} \text{ M}$

$pH \ = \ - \log (2.199 \times 10^{-4}) \ = \ \mathbf{3.66}$ (2 sig. digits)

(b)
Part 1

$[HCOOH]_{IN}$ = 0.200 M x $\dfrac{20.00 \text{ mL}}{40.00 \text{ mL}}$ = 0.1000 M

$[NaOH]_{IN}$ = 0.200 M x $\dfrac{20.00 \text{ mL}}{40.00 \text{ mL}}$ = 0.1000 M

	HCOOH	+ NaOH	→ NaHCOO	+ H$_2$O
I	0.1000	0.1000	0	
C	- 0.1000	- 0.1000	+ 0.1000	
F	≈ 0	≈ 0	0.1000	

Part 2
let $x = [OH^-]_{eq}$

	HCOO$^-$	+ H$_2$O ⇌	HCOOH	+ OH$^-$
I	0.1000		0	0
C	- x		+ x	+ x
E	0.1000 - x		x	x

Assume 0.1000 - x ≈ 0.1000

$$K_b = \dfrac{[HCOOH][OH^-]}{[HCOO^-]} = \dfrac{K_w}{K_a} = \dfrac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.56 \times 10^{-11}$$

$\dfrac{x^2}{0.1000} = 5.56 \times 10^{-11}$ so $x = \sqrt{(0.1000)(5.56 \times 10^{-11})}$

$x = [OH^-] = 2.36 \times 10^{-6}$ M   so   pOH = - log (2.36 $\times 10^{-6}$)

pOH = 5.628   and so   pH = 14.000 - 5.628 = **8.37** (2 sig. digits)

2. Halfway to the equivalence point in a weak acid – strong base titration:

pH of the solution = pK_a of the weak acid being titrated   and $[H_3O^+] = K_a$

Therefore:
$[H_3O^+]$ = $10^{4.187}$ = 6.50 $\times 10^{-5}$. This matches the K_a for benzoic acid. **Thus the weak acid being titrated is benzoic acid**.

3.
(a) Halfway to the equivalence point, the hydronium ion concentration will equal the K_a of the weak acid being titrated. Therefore:
$$[H_3O^+] = K_a \text{ for HNO}_2 = \textbf{4.6} \times \textbf{10}^{\textbf{-4}} \textbf{ M}$$

(b)
Part 1

$[HNO_2]_{IN}$ = 0.450 M x $\dfrac{20.00 \text{ mL}}{38.00 \text{ mL}}$ = 0.2368 M

$[NaOH]_{IN}$ = 0.500 M x $\dfrac{18.00 \text{ mL}}{38.00 \text{ mL}}$ = 0..2368 M

	HNO$_2$	+	NaOH	→	NaNO$_2$	+	H$_2$O
I	0.2368		0.2368		0		╳
C	- 0.2368		- 0.2368		+ 0.2368		
F	≈ 0		≈ 0		0.2368		

Part 2
let $x = [OH^-]_{eq}$

	NO$_2^-$	+	H$_2$O	⇌	HNO$_2$	+	OH$^-$
I	0.2368		╳		0		0
C	- x				+ x		+ x
E	0.2368 - x				x		x

Assume 0.2368 - x ≈ 0.2368

$$K_b = \dfrac{[HNO_2][OH^-]}{[NO_2^-]} = \dfrac{K_w}{K_a} = \dfrac{1.0 \times 10^{-14}}{4.6 \times 10^{-4}} = 2.17 \times 10^{-11}$$

$\dfrac{x^2}{0.2368}$ = 2.17×10^{-11} so $x = \sqrt{(0.2368)(2.17 \times 10^{-11})}$

$x = [OH^-] = 2.27 \times 10^{-6}$ M   so pOH = - log (2.27×10^{-6})

pOH = 5.645   and so pH = 14.000 - 5.645 = **8.36** (2 sig. digits)

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$_3$O$^+$ 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:

$$NH_4^+(aq) \ + \ H_2O(l) \ \rightleftharpoons \ NH_3(aq) \ + \ H_3O^+(aq)$$
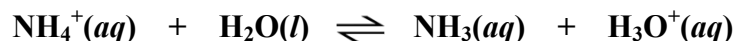
The result is that we can safely ignore any contribution to the $[H_3O^+]$ in the flask by the ammonium ion.

Practice Problems

1.
$[NH_3]_{IN} \ = \ 0.100 \text{ M} \ \times \ \dfrac{25.00 \text{ mL}}{38.00 \text{ mL}} \ = \ 0.06579 \text{ M}$

$[HCl]_{IN} \ = \ 0.100 \text{ M} \ \times \ \dfrac{13.00 \text{ mL}}{38.00 \text{ mL}} \ = \ 0.03421 \text{M}$

	NH$_3$	+ HCl	→ NH$_4^+$	+ Cl$^-$
I	0.06579	0.03421	0	0
C	- 0.03421	- 0.03421	+ 0.03421	+ 0.03421
F	0.03158	≈ 0	0.03421	0.03421

$K_b \ = \ \dfrac{[NH_4^+] \, [OH^-]}{[NH_3]}$ so $[OH^-] \ = \ \dfrac{K_b \, [NH_3]}{[NH_4^+]}$

$[OH^-] \ = \ \dfrac{(1.8 \times 10^{-5}) \, (0.03158)}{(0.03421)} \ = \ 1.66 \times 10^{-5} \text{ M}$

$pOH \ = \ - \log (1.66 \times 10^{-5}) \ = \ 4.779$ so $pH \ = \ 14.000 \ - \ 4.779 \ = \ \textbf{9.22}$ (2 sig. digits)

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.
$[NH_3]_{IN} \ = \ 0.100 \text{ M} \ \times \ \dfrac{25.00 \text{ mL}}{65.00 \text{ mL}} \ = \ 0.03846 \text{ M}$

$[HCl]_{IN} \ = \ 0.100 \text{ M} \ \times \ \dfrac{40.00 \text{ mL}}{65.00 \text{ mL}} \ = \ 0.06154 \text{ M}$

	NH$_3$	+ HCl	→ NH$_4^+$	+ Cl$^-$
I	0.03846	0.06154	0	0
C	- 0.03846	- 0.03846	+ 0.03846	+ 0.03846
F	≈ 0	0.02308	0.03846	0.03846

Final $[HCl] \ = \ $ Final $[H_3O^+] \ = \ 0.02308 \text{ M}$ $pH \ = \ - \log (0.02308) \ = \ \textbf{1.637}$ (3 sig. digits)

This calculated pH value does agree with the titration curve.

5.4 Activity: A Titration Curve Summary

Strong Acid + Strong Base Titration

Net Ionic Equation: $H_3O^+(aq)$ + $OH^-(aq)$ → $2 H_2O(l)$

Equivalence Point pH = 7

Volume | 0.100 M NaOH
Volume at Equivalence Point (25.00 mL)
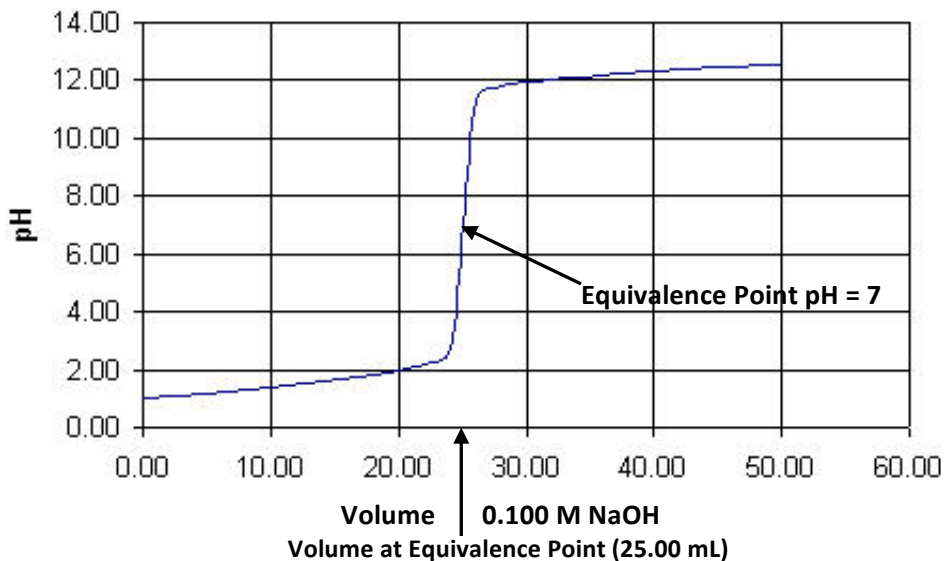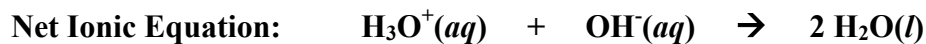
Reason for Equivalence Point pH
The titration of a strong monoprotic acid by a strong base will produce a solution with a pH of 7 at the equivalence point because **neither of the ions present in the product salt can undergo hydrolysis to affect the pH.**
.

Weak Acid + Strong Base Titration

Net Ionic Equation: HA(*aq*)   +   **OH⁻(*aq*)**   →   **A⁻(*aq*)**   +   **H₂O(*aq*)**

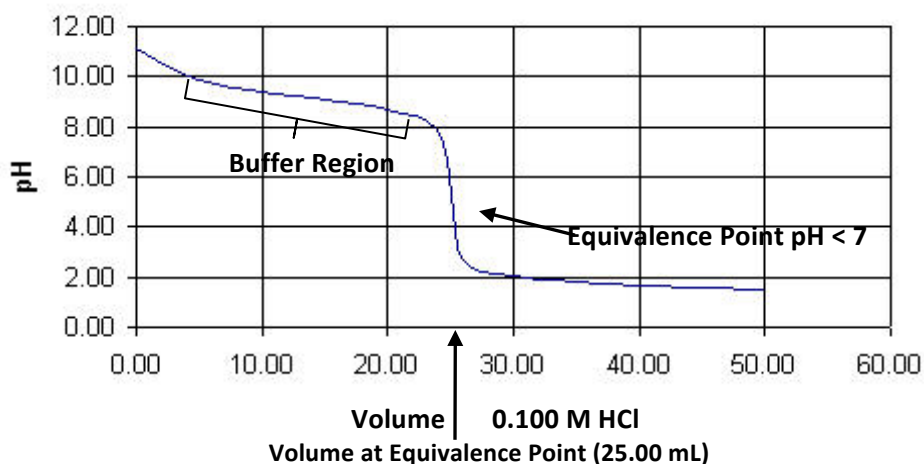Equivalence Point pH > 7

Buffer Region

Volume | 0.100 M NaOH
Volume at Equivalence Point (25.00 mL)
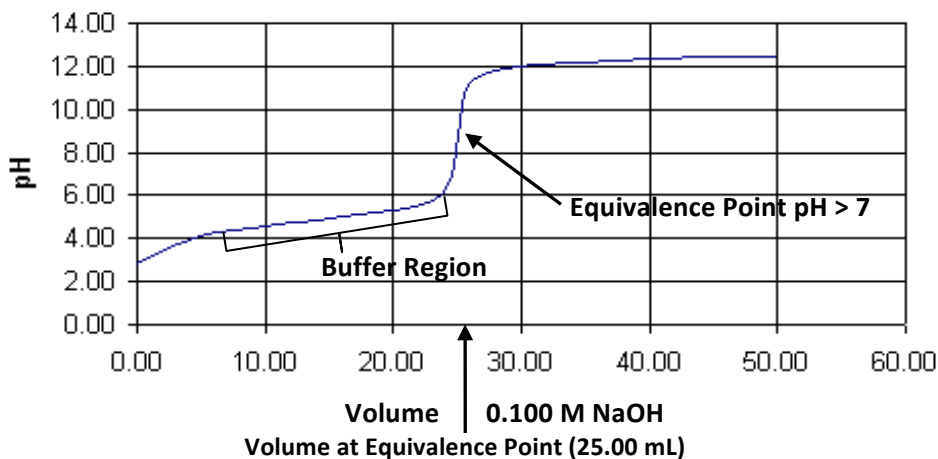
Reason for Equivalence Point pH
The titration of a weak acid by a strong base will produce a basic solution with a pH greater than 7 at the equivalence point **because the anion present in the product salt will undergo hydrolysis to produce OH⁻ ions and the cation will not hydrolyze.**

Weak Base + Strong Acid Titration

Net Ionic Equation: $B(aq)$ + $H_3O^+(aq)$ → $HB^+(aq)$ + $H_2O(l)$

Volume | 0.100 M HCl
Volume at Equivalence Point (25.00 mL)

Reason for Equivalence Point pH
The titration of a weak base by a strong acid will produce an acidic solution with a pH below 7 at the equivalence point because **the cation present in the product salt will undergo hydrolysis to produce H_3O^+ ions and the anion will not hydrolyze.**

Results and Discussion

1. The volume of titrant required to reach the equivalence point in each titration will be exactly the same because each titration reaction goes to completion and the volume of standard solution required is only dependent upon the stoichiometry of the reaction and the moles of the species (acid or base) that it must neutralize. **In each of the above titrations, the moles of each acid or base that must be neutralized by the 0.100 M standard solution is the same. Therefore, because the mole reacting ratio in each titration is 1:1, the volume of 0.100 M standard solution required to reach the equivalence point in each titration is the same.**

2. Explain how each of the two "Weak – Strong" titration curves can be used to determine one of either a K_a or a K_b value.

(a) Weak Acid – Strong Base Titration Curve
Halfway to the equivalence point, the pH of the solution in the reaction flask equals the pK_a of the weak acid being titrated. Therefore, the K_a for the acid can be determined.

(b) Weak Base – Strong Acid Titration Curve
Halfway to the equivalence point, the pOH of the solution in the reaction flask equals the pK_b of the weak base being titrated. This allows the K_b for the base to be determined.

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	$\dfrac{1.0 \times 10^{-7}}{1.0 \times 10^{-3}} = \dfrac{[In^-]}{[HIn]} = \mathbf{1.0 \times 10^{-4}}$	**Yellow**
Pure Water	$\dfrac{1.0 \times 10^{-7}}{1.0 \times 10^{-7}} = \dfrac{[In^-]}{[HIn]} = \mathbf{1.0}$	**Green**
0.0010 M NaOH	$\dfrac{1.0 \times 10^{-7}}{1.0 \times 10^{-11}} = \dfrac{[In^-]}{[HIn]} = \mathbf{1.0 \times 10^{4}}$	**Blue**

2. Acid – Base equilibria always favour the weaker species. When HIn exists in a solution with the strong acid, HNO_3, the acid colour of the indicator will be seen – which must be red – because HNO_3 is a stronger acid than HIn and so the following equilibrium lies effectively completely to the left:

$$\underset{\textbf{RED}}{\textbf{HIn}(aq)} \quad + \quad NO_3^-(aq) \rightleftharpoons \quad In^-(aq) \quad + \quad HNO_3(aq)$$
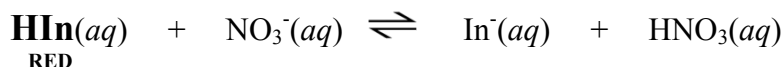
This tells us that if the colour red is seen in the presence of another acid, the other acid must be stronger than the indicator HIn.

Conversely, whenever the second colour for the indicator is seen (in this case yellow), it must mean that the basic form of the indicator, In⁻, is the predominant species. This would also mean that the acid present in the solution with the indicator (HA in this case) is a weaker acid than HIn and so the product side of the following equilibrium will be favoured:

$$HIn(aq) \quad + \quad A^-(aq) \rightleftharpoons \underset{\textbf{YELLOW}}{\textbf{In}^-(aq)} \quad + \quad HA(aq)$$
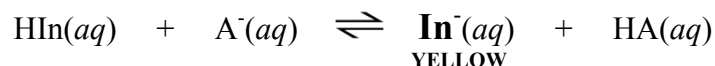
We thus make the following conclusions:

(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 FeCl₃	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.

	HNO₃ + KOH	NaOH + HCOOH	HBr + NH₃
pH at Equivalence Pt.	7	above 7	below 7
Indicator	phenolphthalein	phenolphthalein	methyl red

5.
(a) An indicator's transition point pH equals its pK_a. That value can be estimated by averaging the two pH values over which the colour changes occur. Therefore:

pK_a for bromcresol purple $= \dfrac{5.2 + 6.8}{2} = 6.0$ and so $K_a = 10^{-6.0} = 1 \times 10^{-6}$

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
HIO₃	**NaCl**	**K₃PO₄**	**CH₃COOH**	**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) Halfway to the equivalence point in a weak acid – strong base titration:

$$pH \text{ of the solution } = pK_a \text{ of the weak acid being titrated}$$

Therefore: pH = pK_a for methanoic acid = - log (1.8×10^{-4}) = **3.74** (2 sig. digits)

(b)   NaOH(aq)   +   HCOOH(aq)   →   NaHCOO(aq)   + H_2O(l)
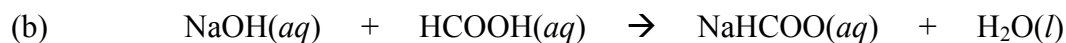
mol HCOOH = 0.0200 L̶ x $\underline{0.250 \text{ mol HCOOH}}$ = 0.005000 mol HCOOH
                                          L̶

mol NaOH = mol HCOOH =   0.005000 mol

volume NaOH solution = 0.005000 mol NaOH   x $\underline{1.00 \text{ L}}$ = 0.02500 L = **25.0 mL**
                                                                    0.200 mol   (3 sig. digits)

(c)
Part 1

$$[\text{HCOOH}]_{\text{IN}} = 0.250 \text{ M} \times \frac{20.00 \text{ m}\text{L}}{45.00 \text{ m}\text{L}} = 0.1111 \text{ M}$$

$$[\text{NaOH}]_{\text{IN}} = 0.200 \text{ M} \times \frac{25.00 \text{ m}\text{L}}{45.00 \text{ m}\text{L}} = 0.1111 \text{ M}$$

HCOOH + NaOH → NaHCOO + H₂O

	HCOOH	NaOH	NaHCOO	
I	0.1111	0.1111	0	
C	- 0.1111	- 0.1111	+ 0.1111	
F	≈ 0	≈ 0	0.1111	

Part 2
let $x = [\text{OH}^-]_{\text{eq}}$

HCOO⁻ + H₂O ⇌ HCOOH + OH⁻

	HCOO⁻	H₂O	HCOOH	OH⁻
I	0.1111		0	0
C	- x		+ x	+ x
E	0.1111 - x		x	x

Assume $0.1111 - x \approx 0.1111$

$$K_b = \frac{[\text{HCOOH}][\text{OH}^-]}{[\text{HCOO}^-]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.56 \times 10^{-11}$$

$$\frac{x^2}{0.1111} = 5.56 \times 10^{-11} \quad \text{so} \quad x = \sqrt{(0.1111)(5.56 \times 10^{-11})}$$

$$x = [\text{OH}^-] = 2.49 \times 10^{-6} \text{ M} \quad \text{so} \quad \text{pOH} = -\log(2.49 \times 10^{-6})$$

pOH = 5.605   and so   pH = 14.000 - 5.605 = **8.40** (2 sig. digits)

12. Halfway to the equivalence point in a weak acid – strong base titration:

pH of the solution = pK_a of the weak acid being titrated

Thus pK_a for weak acid = 3.456   and so K_a = $10^{-3.456}$ = 3.50 x 10⁻⁴
(3 sig. digits)

This matches the K_a for hydrofluoric acid.

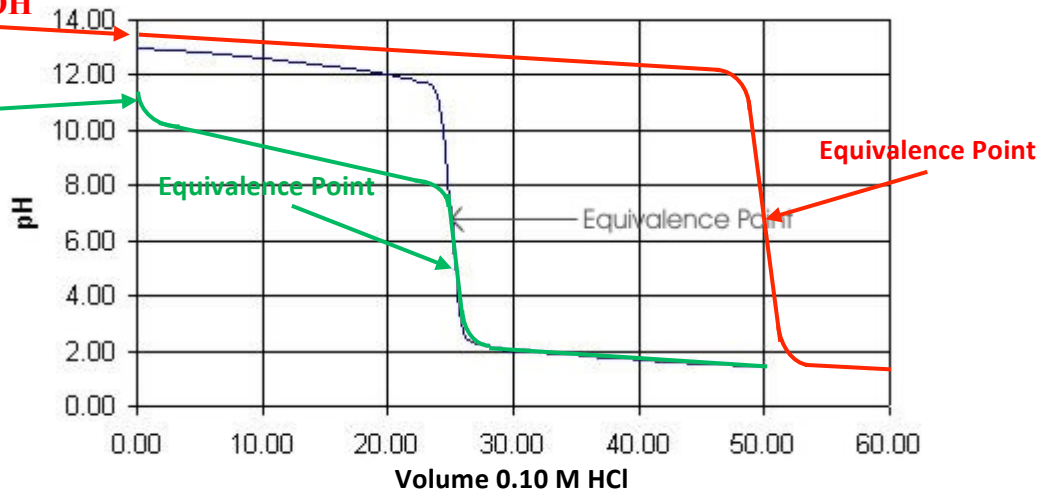13. Halfway to the equivalence point in a weak base – strong acid titration:

pOH of the solution = pK_b of the weak base being titrated

Thus pK_b for weak base = 14.00 - 9.50 = 4.50   and so K_b = $10^{-4.50}$ = 3.2 x 10⁻⁵
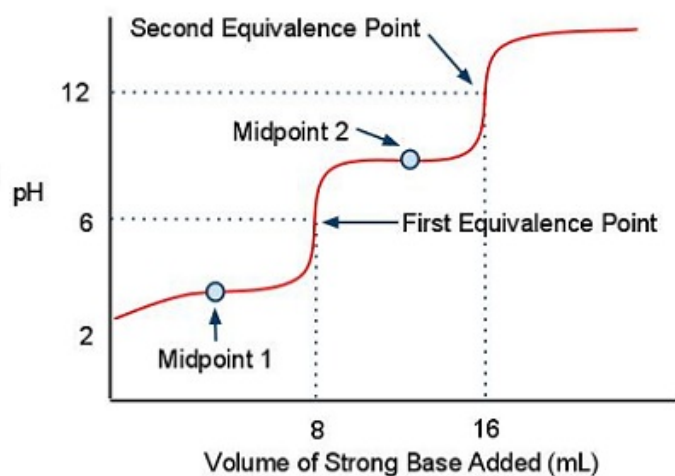(2. sig. digits)

14.

(a) **0.20 M NaOH**

(b) **0.10 NH₃**

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.**

Section 5.5 Non-metal and Metal Oxides in Water

Warm Up

1.
(a) **Elements from Groups 1 and 17 will form the most ionic compounds** because their electronegativity differences (ΔEN) are the greatest.

(b) **Elements from the upper right region of the periodic table will form the most covalent oxides** because the closer an element is to oxygen, the smaller ΔEN between that element and oxygen will be.

2.
(a) *In general*, the reaction of **ionic** oxides with water will produce *basic* solutions.

(b) *In general*, the reaction of **covalent** oxides with water will produce *acidic* solutions.

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.
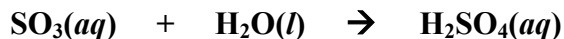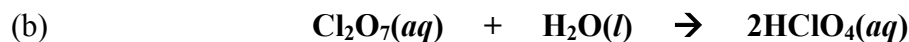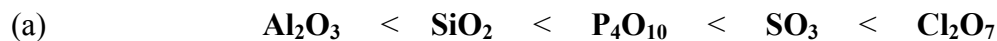
Quick Check

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**.

Practice Problems

1.
(a) $K_2O(s)$ + $H_2O(l)$ →   **$2KOH(aq)$**

(b) $MgO(s)$ + $H_2O(l)$ →   **$Mg(OH)_2(aq)$**

2.

(a) $\qquad$ Al_2O_3 < SiO_2 < P_4O_{10} < SO_3 < Cl_2O_7

(b) $\qquad$ $Cl_2O_7(aq)$ + $H_2O(l)$ → $2HClO_4(aq)$

$\qquad$ $SO_3(aq)$ + $H_2O(l)$ → $H_2SO_4(aq)$

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.

Quick Check

1. The three nonmetal oxides that react with water in the atmosphere to produce acid precipitation are NO_2, SO_2, and SO_3.
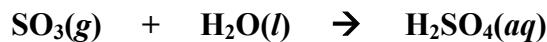
2. The **combustion of impure coal containing pyrite produces SO_2** according to the following reaction:

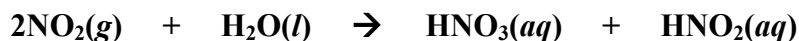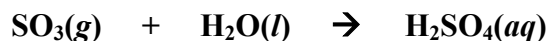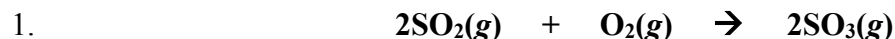$\qquad$ $4FeS_2(s)$ + $11O_2(g)$ → $2Fe_2O_3(s)$ + $8SO_2(g)$

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:
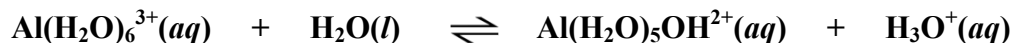
$\qquad$ $2SO_2(g)$ + $O_2(g)$ → $2SO_3(g)$

$\qquad$ $SO_2(g)$ + $O_3(g)$ → $SO_3(g)$ + $O_2(g)$

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

$\qquad$ $SO_3(g)$ + $H_2O(l)$ → $H_2SO_4(aq)$

Practice Problems

1. $\qquad$ $2SO_2(g)$ + $O_2(g)$ → $2SO_3(g)$

$\qquad$ $SO_3(g)$ + $H_2O(l)$ → $H_2SO_4(aq)$

$\qquad$ $2NO_2(g)$ + $H_2O(l)$ → $HNO_3(aq)$ + $HNO_2(aq)$

2. In water, hydrated aluminum ions function as weak acids according to the following:

$\qquad$ $Al(H_2O)_6^{3+}(aq)$ + $H_2O(l)$ ⇌ $Al(H_2O)_5OH^{2+}(aq)$ + $H_3O^+(aq)$

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:

$$CaO(s) + SO_2(g) \rightarrow CaSO_3(s)$$
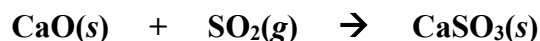
As a second step, to remove the $CaSO_3$ and any unreacted SO_2, an aqueous suspension of CaO is then sprayed into the exhaust gases before they reach the smokestack to produce a thick suspension of $CaSO_3$ called a slurry.

5.5 Activity

Part One: The Original Document

1. Sulphur Dioxide
A. For the United States
The target permanent national emissions cap for SO_2 produced by electrical utilities by the year 2010 was **8.95 million tons (8.14 million tonnes)**.

B. For Canada
The target total permanent national emissions cap for SO_2 by the year 2000 was **3.2 million tonnes**.

2. Nitrogen Oxides
A. For the United States
The ARP set the target level for total annual NO_x emissions to be **2 million tons (1.82 million tonnes)** below the 8.1 million tons (7.36 million tonnes) originally projected for the year 2000.

B. For Canada
The ARP set the target level for total annual NO_x emissions for the year 2000 to be **100 000 tonnes** below the 970 000 tonnes originally projected for the year 2000.

Part Two: The 2010 Progress Report

1. Sulphur Dioxide Emission Reductions
A. For Canada
(a) In 2008, Canada's total SO_2 emissions were **1.7 million tonnes. This represented 53% (or 47% below)** the national cap established by the ARP.

(b) The largest source of SO_2 emissions in Canada continues to be **the non-ferrous smelting and refining sector (which accounted of 39% of national SO_2 emissions in 2008)**.

B. For the United States
(a) In 2009, the total SO_2 emissions from the electric power sector were **5.7 million tons (5.18 million tonnes). This represents 63.7% of the 2010 cap of 8.95 million tons (8.17 million tonnes) established by the ARP**.

(b) The total SO_2 emissions from all sources in the U.S. in 1980 were **nearly 26 million tons (23.6 million tonnes)**. The total emissions from all sources in the U.S. in 2008 were **less than 11.4 million tons (10.4 million tonnes)**. The 2008 emissions from the electric power sector represent **65.8% of that total**.

2. Nitrogen Oxide Emission Reductions
A. For Canada
(a) In 2008, Canada's total NO_x emissions from stationary sources totaled **664 755 tonnes**. This represents **68.5% of the total 970 000 tonnes** projected for the year 2000.

(b) Transportation sources contribute to the majority of NO_x emissions and represent **nearly 53%** of total Canadian emissions.

B. For the United States
(a) In 2009, the total NO_x emissions from stationary sources (those covered by the ARP) were **2.0 million tons (1.82 million tonnes)**.
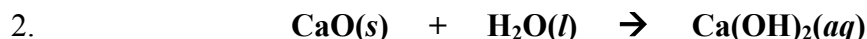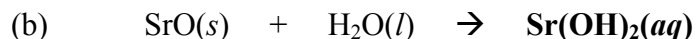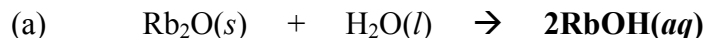
(b) The actual 2009 NO_x emissions of 2.0 million tons represent only **24.7%** of the 8.1 million tons projected annual NO_x emissions for the year 2000.
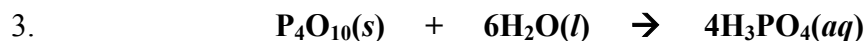
Results and Discussion
Student answers and solutions (hopefully).

Review Questions

1.
(a) $Rb_2O(s)$ + $H_2O(l)$ →   **$2RbOH(aq)$**

(b) $SrO(s)$ + $H_2O(l)$ →   **$Sr(OH)_2(aq)$**

(b) $SeO_2(s)$ + $H_2O(l)$ →   **$H_2SeO_3(aq)$**

(d) $N_2O_5(g)$ + $H_2O(l)$ →   **$2HNO_3(aq)$**

2.   **$CaO(s)$ + $H_2O(l)$ → $Ca(OH)_2(aq)$**

"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.

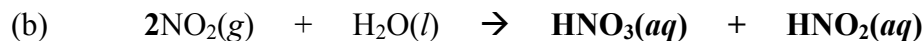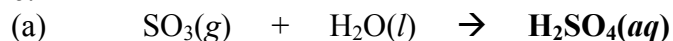3. $$P_4O_{10}(s) \quad + \quad 6H_2O(l) \quad \rightarrow \quad 4H_3PO_4(aq)$$

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

(b) $$2NO_2(g) \quad + \quad H_2O(l) \quad \rightarrow \quad HNO_3(aq) \quad + \quad HNO_2(aq)$$

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:

$$CO_3^{2-}(aq) \quad + \quad H_3O^+(aq) \quad \rightleftharpoons \quad HCO_3^-(aq) \quad + \quad H_2O(l)$$
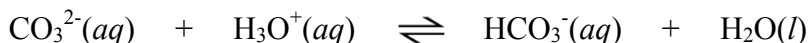
Over time, **as the $[HCO_3^-]$ increases, the lakes become effective bicarbonate / carbonate buffer systems** and maintain a relatively constant pH.
If a lake's soil *does not* contain sufficient limestone, a temporary solution is to **add $CaCO_3$ or CaO directly to the lake**.

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 CaSO₃, 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")
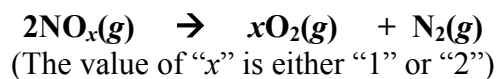
11. **Gaseous ammonia can lower NO$_x$ emissions when it is reacted with the hot stack gases to produce nitrogen and water vapour according to the following reaction:**

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