Section 8.7: Acid–Base Titration
Tutorial 1 Practice, page 547
1. Given: $[NaOH(aq)] = 0.50$ mol/L; $V_{NaOH} = 25.0$ mL; $[HCl(aq)] = 0.10$ mol/L

   Required: $V_{HCl(aq)}$ to reach equivalence point

   Solution: $n_{OH^-} = c_{OH^-} \times V_{OH^-}$

$$= \frac{0.50 \text{ mmol}}{\cancel{mL}} \times 25.0 \ \cancel{mL}$$

$$n_{OH^-} = 12.5 \text{ mmol}$$

$$V_{HCl(aq)} = \frac{n_{HCl(aq)}}{[HCl(aq)]}$$

$$= \frac{12.5 \ \cancel{mmol}}{0.10 \ \cancel{mmol}/mL}$$

$$V_{HCl(aq)} = 120 \text{ mL}$$

2. (a) Given: $V_{HCl(aq)} = 25.00$ mL; $[HCl(aq)] = 0.350$ mol/L;
   $V_{NaOH(aq)} = 5.0$ mL; $[NaOH(aq)] = 0.500$ mol/L;

   Required: $[H^+(aq)]$, pH

   Analysis: Before titration, amount of H^+ is:

$$n_{H^+(aq)} = c_{H^+(aq)} \times V_{H^+(aq)}$$

$$= \frac{0.350 \text{ mmol}}{\cancel{mL}} \times 25.00 \ \cancel{mL}$$

$$n_{H^+(aq)} = 8.75 \text{ mmol}$$

Added amount of OH^- is:

$$n_{OH^-(aq)} = c_{OH^-(aq)} \times V_{OH^-(aq)}$$

$$= \frac{0.500 \text{ mmol}}{\cancel{mL}} \times 5.0 \ \cancel{mL}$$

$$n_{OH^-(aq)} = 2.5 \text{ mmol}$$

   Solution: $[H^+(aq)] = \dfrac{n_{H^+(aq)} - n_{OH^-(aq)}}{V_{total}}$

$$= \frac{8.75 \text{ mmol} - 2.50 \text{ mmol}}{30.0 \text{ mL}}$$

$$= 0.208 \text{ mmol/mL}$$

$$[H^+(aq)] = 0.208 \text{ mol/L}$$

$$\text{pH} = -\log([H^+(aq)])$$
$$= -\log(0.208)$$
$$\text{pH} = 0.681$$

(b) Given: $V_{HCl(aq)} = 25.00$ mL; $[HCl(aq)] = 0.350$ mol/L;
   $V_{NaOH(aq)} = 20.0$ mL; $[NaOH(aq)] = 0.500$ mol/L;

   Required: $[H^+(aq)]$, pH

Analysis:
Before titration, amount of H$^+$ is
$$n_{\text{H}^+(aq)} = c_{\text{H}^+(aq)} \times V_{\text{H}^+(aq)}$$
$$= \frac{0.350 \text{ mmol}}{\text{mL}} \times 25.00 \text{ mL}$$
$$n_{\text{H}^+(aq)} = 8.75 \text{ mmol}$$
Added amount of OH$^-$ is:
$$n_{\text{OH}^-(aq)} = c_{\text{OH}^-(aq)} \times V_{\text{OH}^-(aq)}$$
$$= \frac{0.500 \text{ mmol}}{\text{mL}} \times 20.0 \text{ mL}$$
$$n_{\text{OH}^-(aq)} = 10.0 \text{ mmol}$$
Solution:

$$[\text{H}^+(aq)] = \frac{n_{\text{H}^+(aq)} - n_{\text{OH}^-(aq)}}{V_{\text{total}}}$$
$$= \frac{8.75 \text{ mmol} - 10.00 \text{ mmol}}{50.0 \text{ mL}}$$
$$= -0.025 \text{ mmol/mL}$$

$[\text{H}^+(aq)] = 0 \text{ mol/L}$
All the hydrochloric acid has been neutralized.

$[\text{OH}^-(aq)] = 0.025 \text{ mol/L}$
pOH $= -\log([\text{OH}^-(aq)])$
　　　$= -\log(0.025)$
pOH $= 1.602$
pH $= 14.000 - 1.602$
　　$= 12.398$

Tutorial 2 Practice, page 554
1. Given: $V_{\text{HC}_2\text{H}_3\text{O}_{2(aq)}} = 20.00 \text{ mL}$; $[\text{HC}_2\text{H}_3\text{O}_2(aq)] = 0.600 \text{ mol/L}$
(a) Required: Amount of unreacted ethanoic acid and pH when 10.00 mL of 0.300 mol/L NaOH(aq) is added
　Analysis: Before titration begins:
$$n_{\text{HC}_2\text{H}_3\text{O}_{2(aq)}} = [\text{HC}_2\text{H}_3\text{O}_2(aq)] \times V_{\text{HC}_2\text{H}_3\text{O}_2}(aq)$$
$$= (0.600 \text{ mmol/mL})(20.00 \text{ mL})$$
$$n_{\text{HC}_2\text{H}_3\text{O}_{2(aq)}} = 12.00 \text{ mmol}$$

Amount of NaOH(aq) added:
$$n_{\text{NaOH(aq)}} = [\text{NaOH(aq)}] \times V_{\text{NaOH(aq)}}$$
$$= (0.300 \text{ mmol/mL})(10.00 \text{ mL})$$
$$n_{\text{NaOH(aq)}} = 3.00 \text{ mmol}$$

Since NaOH(aq) reacts completely with ethanoic acid:

Unreacted ethanoic acid $= n_{HC_2H_3O_{2(aq)}} - n_{NaOH(aq)}$

$\qquad\qquad\qquad\qquad = 12 \text{ mmol} - 3.0 \text{ mmol}$

Unreacted ethanoic acid $= 9.0 \text{ mmol}$

Since 10.00 mL of NaOH(aq) was added to 20.00 mL of ethanoic acid solution, the total volume is now 30.00 mL.

Solution: The concentration of unreacted ethanoic acid, $[HC_2H_3O_2(aq)]$, can be determined:

$$[HC_2H_3O_2(aq)] = \frac{n_{HC_2H_3O_2(aq)}}{V_{HC_2H_3O_2(aq)}}$$

$$= \frac{(9.00 \text{ mmol})}{(30.00 \text{ mL})}$$

$$[HC_2H_3O_2(aq)] = 0.300 \text{ mol/L}$$

Similarly, the concentration of the conjugate base of ethanoic acid, $[C_2H_3O_2^-(aq)]$, is determined:

$$[C_2H_3O_2^-(aq)] = \frac{n_{C_2H_3O_2^-(aq)}}{V_{C_2H_3O_2^-(aq)}}$$

$$= \frac{(3.00 \text{ mmol})}{(30.00 \text{ mL})}$$

$$[C_2H_3O_2^-(aq)] = 0.100 \text{ mol/L}$$

For the ethanoic acid/ethanoate solution:

	$HC_2H_3O_2$ (aq)	$\rightleftharpoons$	H^+(aq)	+	$C_2H_3O_2^-$(aq)
I	0.300		0		0.100
C	$-x$		$+x$		$+x$
E	$0.300 - x$		$+x$		$0.100 + x$

The values can now be substituted into the equilibrium equation for the ionization of a weak acid, where $K_a = 1.8 \times 10^{-5}$.

$$K_a = \frac{[H^+(aq)][C_2H_3O_2^-(aq)]}{[HC_2H_3O_2(aq)]}$$

$$1.8 \times 10^{-5} = \frac{(x)(0.100 + x)}{(0.300 - x)}$$

Using simplifying assumptions, $0.100 + x \approx 0.100$ and $0.300 - x \approx 0.300$ (valid by the hundred rule),

$$1.8 \times 10^{-5} \approx (x)\frac{(0.100)}{(0.300)}$$

$$x \approx \frac{(1.8 \times 10^{-5})(0.300)}{(0.100)}$$

$$x \approx 5.40 \times 10^{-5}$$

Therefore $[H^+(aq)] = x \approx 5.40 \times 10^{-5}$ and the pH can be determined:

$$pH = -\log[H^+(aq)]$$
$$\approx -\log(5.40 \times 10^{-5})$$
$$pH \approx 4.267$$

Statement: The amount of unreacted ethanoic acid is 9.0 mmol. The pH of the solution is 4.267.

(b) Required: Amount of unreacted ethanoic acid and pH when 18.00 mL of 0.300 mol/L NaOH(aq) is added

Analysis: Before titration begins:

$$n_{HC_2H_3O_{2(aq)}} = [HC_2H_3O_2(aq)] \times V_{HC_2H_3O_{2(aq)}}$$
$$= (0.600 \text{ mmol/mL})(20.00 \text{ mL})$$
$$n_{HC_2H_3O_{2(aq)}} = 12.00 \text{ mmol}$$

The amount of NaOH(aq) added is also determined:

$$n_{NaOH(aq)} = [NaOH(aq)] \times V_{NaOH(aq)}$$
$$= (0.300 \text{ mmol/mL})(18.00 \text{ mL})$$
$$n_{NaOH(aq)} = 5.40 \text{ mmol}$$

Unreacted ethanoic acid $= n_{HC_2H_3O_{2(aq)}} - n_{NaOH(aq)}$
$$= 12.00 \text{ mmol} - 5.40 \text{ mmol}$$

Unreacted ethanoic acid $= 6.60$ mmol

Since 18.00 mL of NaOH(aq) was added to 20.00 mL of ethanoic acid solution, the total volume is now 38.00 mL.

Solution: The concentration of unreacted ethanoic acid, $[HC_2H_3O_2(aq)]$, can be determined:

$$[HC_2H_3O_2(aq)] = \frac{n_{HC_2H_3O_2(aq)}}{V_{HC_2H_3O_2(aq)}}$$

$$= \frac{(6.60 \text{ mmol})}{38.00 \text{ mL}}$$

$$[HC_2H_3O_2(aq)] = 0.174 \text{ mol/L}$$

Similarly, the concentration of the conjugate base of ethanoic acid, $[C_2H_3O_2^-(aq)]$, is determined based on the amount of NaOH(aq) added:

$$[C_2H_3O_2^-(aq)] = \frac{n_{C_2H_3O_2^-(aq)}}{V_{C_2H_3O_2^-(aq)}}$$

$$= \frac{(5.40\ mmol)}{(38.00\ mL)}$$

$$[C_2H_3O_2^-(aq)] = 0.142\ mol/L$$

For the ethanoic acid/ethanoate solution:

	$HC_2H_3O_2$ (aq) $\rightleftharpoons$	H^+(aq)	+ $C_2H_3O_2^-$ (aq)
I	0.174	≈ 0	0.142
C	$-x$	$+x$	$+x$
E	$0.174 - x$	$+x$	$0.142 + x$

The values can now be substituted into the equilibrium equation for the ionization of a weak acid, where $K_a = 1.8 \times 10^{-5}$.

$$K_a = \frac{[H^+(aq)][C_2H_3O_2^-(aq)]}{[HC_2H_3O_2(aq)]}$$

$$1.8 \times 10^{-5} = \frac{(x)(0.142 + x)}{(0.174 - x)}$$

Using simplifying assumptions, $0.142 + x \approx 0.142$ and $0.174 - x \approx 0.174$ (valid by the hundred rule).

$$1.8 \times 10^{-5} \approx \frac{(x)(0.142)}{(0.174)}$$

$$x \approx \frac{(1.8 \times 10^{-5})(0.174)}{(0.142)}$$

$$x \approx 2.21 \times 10^{-5}$$

Therefore $[H^+(aq)] = x \approx 2.21 \times 10^{-5}$ and the pH can be determined:

pH $= -\log[H^+(aq)]$

$\approx -\log(2.21\ x\ 10^{-5})$

pH ≈ 4.656

Statement: The amount of unreacted ethanoic acid is 6.6 mmol and the pH is 4.545.

2. a) Given: $V_{HClO(aq)} = 25.00\ mL$; $V_{KOH(aq)} = 19.3\ mL$; $[KOH(aq)] = 0.100\ mol/L$

  Required: $[HClO(aq)]$

  Analysis: Added amount of OH^- is:

$n_{OH^-} = c_{OH^-} \times V_{OH^-}$

$= 0.100\ mmol/mL \times 19.3\ mL$

$n_{OH^-} = 1.93\ mmol$

Solution: H^+ and OH^- react in a 1:1 ratio, so $n_{H^+} = 1.93$ mmol
$n_{H^+} = n_{HClO} = 1.93$ mmol
$[HClO(aq)] = n_{HClO(aq)} / V_{HClO(aq)}$
$\quad = 1.93$ mmol $/ 25.00$ mL
$\quad = 0.0772$ mol/L

b) $ClO^-(aq)$ oxidizes water
$ClO^-(aq) + H_2O(aq) \rightleftharpoons HClO(aq) + OH^-(aq)$
$K_b = K_w / K_a$
$\quad = 1.0 \times 10^{-14} / 3.5 \times 10^{-8}$
$\quad = 2.85 \times 10^{-7}$
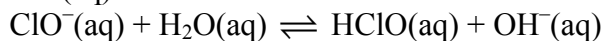
$V_{tot} = 25.00$ mL $+ 19.3$ mL	$n_{ClO^-} = n_{HClO}$	$c_{ClO^-} = n_{ClO^-} / V_{ClO^-}$
$\quad = 44.3$ mL	$\quad = 1.93$ mmol	$\quad = 1.93$ mol$/ 44.3$ L
		$\quad = 0.0436$ mol/L

$$K_b = \frac{[HClO(aq)][OH^-(aq)]}{[ClO^-(aq)]}$$

$$2.85 \times 10^{-7} = \frac{(x)(x)}{0.0436}$$
$$x^2 = 1.2 \times 10^{-8}$$
$$x \approx 1.12 \times 10^{-4}$$
$pOH \approx {}^-log[OH^-(aq)]$
$\quad \approx {}^-log(1.12 \times 10^{-4})$
$\quad \approx 3.95$
$pH \approx 14 - pOH$
$\quad \approx 14 - 3.95$
$\quad \approx 10.05$

Section 8.7 Questions, page 557

1. Given: $V_{HCl(aq)} = 25.0$ mL; $V_{NaOH(aq)} = 67.2$ mL; $[NaOH(aq)] = 0.125$ mol/L;
Required: $[HCl(aq)]$
Analysis: Added amount of $OH^-(aq)$ is:
$$n_{OH^-} = c_{OH^-} \times V_{OH^-}$$
$$= \frac{0.125 \text{ mmol}}{\cancel{mL}} \times 67.2 \cancel{mL}$$
$$n_{OH^-} = 8.4 \text{ mmol}$$

Solution: $H^+(aq)$ and $OH^-(aq)$ react in a 1:1 ratio, so $n_{H^+} = 8.4$ mmol

1 mol of acid produces 1 mol of HCl, so $n_{HCl} = 8.4$ mmol

$$[HCl(aq)] = \frac{n_{HCl(aq)}}{V_{HCl(aq)}}$$

$$= \frac{16.8 \text{ mmol}}{25.00 \text{ mL}} \qquad [HCl(aq)] = 8.4 \text{ mmol} / 25.0 \text{ mL} = 0.336 \text{ mmol/mL}$$

$$= 0.672 \text{ mmol/mL}$$

$$[HCl(aq)] = 0.672 \text{ mol/L}$$

2. (a) Given: $V_{HCl(aq)} = 15.00$ mL; $[HCl(aq)] = 0.250$ mol/L;

Required: n_{H^+}, pH

Solution:

$$n_{H^+(aq)} = c_{H^+(aq)} \times V_{H^+(aq)}$$

$$= \frac{0.250 \text{ mmol}}{\text{mL}} \times 15.00 \text{ mL}$$

$$= 3.75 \text{ mmol}$$

$$n_{H^+(aq)} = 0.00375 \text{ mol}$$

$$pH = -\log([H^+(aq)]$$

$$= -\log(0.250)$$

$$pH = 0.602$$

(b) Given: $V_{HCl(aq)} = 25.00$ mL; $[HCl(aq)] = 0.350$ mol/L

$V_{NaOH(aq)} = 10.0$ mL; $[NaOH(aq)] = 0.500$ mol/L

Required: n_{H^+}, pH

Analysis: Before titration, amount of H^+ is

$$n_{H^+(aq)} = c_{H^+(aq)} \times V_{H^+(aq)}$$

$$= \frac{0.250 \text{ mmol}}{\text{mL}} \times 15.00 \text{ mL}$$

$$= 3.75 \text{ mmol}$$

Added amount of $OH^-(aq)$ is:

$$n_{OH^-(aq)} = c_{OH^-(aq)} \times V_{OH^-(aq)}$$

$$= \frac{0.250 \text{ mmol}}{\text{mL}} \times 10.0 \text{ mL}$$

$$n_{OH^-(aq)} = 2.50 \text{ mmol}$$

Solution: $[H^+(aq)] = \dfrac{n_{H^+(aq)} - n_{OH^-(aq)}}{V_{total}}$

$$= \dfrac{3.75 \text{ mmol} - 2.50 \text{ mmol}}{35 \text{ mL}}$$

$$= 0.0357 \text{ mmol/mL}$$

$$[H^+(aq)] = 0.0357 \text{ mol/L}$$

$$\begin{aligned}
pH &= -\log([H^+(aq)]) \\
&= -\log(0.0357) \\
pH &= 1.447
\end{aligned}$$

(c) pH = 7.00 because a strong acid is titrated with a strong base.

3. Given:

$V_{NH_3} = 40.0 \text{ mL}$

$V_{HCl} = 25.0 \text{ mL}; \left[HCl(aq) \right] = 0.50 \text{ mol / L};$

Required: $[NH_3(aq)]$

Analysis: Added amount of H^+ is:

$n_{H^+(aq)} = c_{H^+(aq)} \times V_{H^+(aq)}$

$$= \dfrac{0.50 \text{ mmol}}{\cancel{mL}} \times 25.0 \,\cancel{mL}$$

$n_{H^+(aq)} = 12.5 \text{ mmol}$

Solution: $H^+(aq)$ and $NH_3(aq)$ react in a 1:1 ratio, so $n_{NH_3} = 12.5$ mmol

$[NH_3(aq)] = \dfrac{n_{NH_3(aq)}}{V_{NH_3(aq)}}$

$$= \dfrac{12.5 \text{ mmol}}{40.0 \text{ mL}}$$

$$= 0.313 \text{ mmol/mL}$$

$[NH_3(aq)] = 0.31 \text{ mol/L}$

(b) Given: $[NH_4^+(aq)] = 0.31$ mol/L; $K_b = 1.8 \times 10^{-5}$

Required: pH

Analysis:

	NH_4^+(aq)	$\rightleftharpoons$	NH_3(aq)	+	H^+ (aq)
I	0.31		0		0
C	$-x$		$+x$		$+x$
E	$0.31 - x$		x		x

$$K_a = \frac{K_w}{K_b}$$

$$K_a = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}}$$

$$K_a = 5.55 \times 10^{-10}$$

$$K_a = \frac{[NH_3(aq)][H^+(aq)]}{[NH_4^+(aq)]}$$

Solution: $5.55 \times 10^{-10} = \dfrac{(x)(x)}{(0.31 - x)}$

$$5.55 \times 10^{-10} \approx \frac{(x)(x)}{0.31}$$

$$x^2 \approx 1.70 \times 10^{-10}$$

$$x = [H^+(aq)] \approx 1.31 \times 10^{-5} \text{ mol/L}$$

pH $= -\log(1.30 \times 10^{-5})$

pH $= 4.88$

4. (a) Given: $V_{ASA(aq)} = 25.0$ mL; $V_{NaOH(aq)} = 98.3$ mL; $[NaOH(aq)] = 0.15$ mol/L

$K_a = 3.2 \times 10^{-4}$

Required: $[ASA(aq)]$

Solution:

$$n_{OH^-(aq)} = c_{OH^-(aq)} \times V_{OH^-(aq)}$$

$$= \frac{0.15 \text{ mmol}}{\cancel{mL}} \times 98.3 \ \cancel{mL}$$

$$n_{OH^-(aq)} = 14.7 \text{ mmol}$$

$$n_{OH^-(aq)} = n_{H^+(aq)} = n_{ASA(aq)}$$

$$[ASA(aq)] = \frac{n_{ASA(aq)}}{V_{ASA(aq)}}$$

$$= \frac{14.7 \text{ mmol}}{25.00 \text{ mL}}$$

$$= 0.588 \text{ mmol/mL}$$

$$[ASA(aq)] = 0.59 \text{ mol/L}$$

(b) amount of ASA (calculated in part A) = 14.7 mmol, or 0.015 mol

(c) Given: $V_{ASA}(aq) = 25.0$ mL; $[ASA(aq)] = 0.59$ mol/L (from part (a))

$K_a = 3.2 \times 10^{-4}$

Required: pH at equivalence point

Analysis:

	ASA⁻(aq)	+ H₂O(l) ⇌	ASA (aq)	+	OH⁻(aq)
I	0.59	−	0		0
C	− x	−	+ x		+ x
E	0.59 − x	−	x		x

$$K_b = \frac{K_w}{K_a}$$

$$K_b = \frac{1 \times 10^{-14}}{3.2 \times 10^{-4}}$$

$$K_b = 3.12 \times 10^{-11}$$

$$K_b = \frac{[ASA(aq))][OH^-(aq)]}{[ASA^-(aq)]}$$

Solution:
$$3.12 \times 10^{-11} = \frac{(x)(x)}{(0.59 - x)}$$

$$3.12 \times 10^{-11} \approx \frac{(x)(x)}{0.59}$$

$$x^2 \approx 1.84 \times 10^{-11}$$

$$x = [OH^-(aq)] \approx 4.29 \times 10^{-6} \text{ mol/L}$$

pOH = −log(4.29 × 10⁻⁶)

pOH = 5.37

pH = 14.0 − 5.37

pH = 8.63

5. (a) Given: $V_{HCO_2H(aq)} = 50.00$ mL; $\left[HCO_2H(aq)\right] = 0.30$ mol / L

$\left[NaOH(aq)\right] = 0.30$ mol / L;

Required: $V_{NaOH(aq)}$

Solution:

$$n_{H^+(aq)} = c_{H^+(aq)} \times V_{H^+(aq)}$$

$$= \frac{0.30 \text{ mmol}}{\text{mL}} \times 50.0 \text{ mL}$$

$$n_{H^+(aq)} = 15.0 \text{ mmol}$$

$$n_{OH^-(aq)} = n_{H^+(aq)}$$

$$V_{NaOH(aq)} = \frac{n_{NaOH(aq)}}{c_{NaOH(aq)}}$$

$$= \frac{15.0 \text{ mmol}}{0.30 \text{ mmol/mL}}$$

$$= 5.00$$

$$V_{NaOH(aq)} = 50.0 \text{ mL}$$

(b) Given: $V_{HCO_2H(aq)} = 50.00 \text{ mL};\ [HCO_2H(aq)] = 0.30 \text{ mol/L}$

$\quad\quad K_a = 3.2 \times 10^{-4}$ (from table)

	HCO$_2$H(aq) $\rightleftharpoons$	HCO$_2^-$ (aq) +	H$^+$(aq)
I	0.30	0	0
C	$-x$	$+x$	$+x$
E	$0.30 - x$	x	x

$$K_a = \frac{[HCO_2^-(aq)][H^+(aq)]}{[HCO_2H(aq)]}$$

Solution: $\quad 3.2 \times 10^{-4} = \frac{(x)(x)}{(0.30 - x)}$

$$3.2 \times 10^{-4} \approx \frac{(x)(x)}{0.30}$$

$$x^2 \approx 9.6 \times 10^{-5}$$

$$x = [H^+(aq)] \approx 9.80 \times 10^{-3} \text{ mol/L}$$

$$pH = -\log(9.80 \times 10^{-3})$$

$$pH = 2.01$$

(c) Given: $V_{HCO_2H(aq)} = 50.00 \text{ mL};\ [HCO_2H(aq)] = 0.30 \text{ mol/L}$

$\quad\quad K_a = 3.2 \times 10^{-4}$ (from table)

Required: pH at equivalence point

Analysis:

	HCO$_2^-$ (aq)	+ H$_2$O(l) $\rightleftharpoons$	HCO$_2$H (aq) +	OH$^-$(aq)
I	0.30	$-$	0	0
C	$-x$	$-$	$+x$	$+x$
E	$0.30 - x$	$-$	x	x

$$K_b = \frac{K_w}{K_a}$$

$$K_b = \frac{1 \times 10^{-14}}{3.2 \times 10^{-4}}$$

$$K_b = 3.12 \times 10^{-11}$$

$$K_{b} = \frac{[\text{ASA}(\text{aq}))][\text{OH}^{-}(\text{aq})]}{[\text{ASA}^{-}(\text{aq})]}$$

Solution: $3.12 \times 10^{-11} = \dfrac{(x)(x)}{(0.30 - x)}$

$3.12 \times 10^{-11} \approx \dfrac{(x)(x)}{0.30}$

$x^2 \approx 9.36 \times 10^{-12}$

$x = [OH^-(aq)]$

$\approx 3.06 \times 10^{-6}$ mol/L

pOH = $-\log(3.06 \times 10^{-6})$
pOH = 5.51
pH = 14.0 − 5.51
pH = 8.46

6. (a) Given: $V_{HCN(aq)}$ = 30.0 mL; [HCN(aq)] = 0.340 mol/L

$V_{NaOH(aq)}$ = 10.0 mL; [NaOH(aq)] = 0.500 mol/L

$K_a = 6.2 \times 10^{-10}$ (from table)

Required: pH

Analysis:

$n_{HCN(aq)} = c_{HCN(aq)} \times V_{HCN(aq)}$

$= \dfrac{0.340 \text{ mmol}}{\text{mL}} \times 30.0 \text{ mL}$

$n_{HCN(aq)} = 10.2$ mmol

V_{total} = 40.0 mL so [HCN(aq)] = 10.2 mmol/40 mL

$= 0.255$ mol/L

$n_{OH^-(aq)} = c_{OH^-(aq)} \times V_{OH^-(aq)}$

$= \dfrac{0.500 \text{ mmol}}{\text{mL}} \times 10.0 \text{ mL}$

$n_{OH^-(aq)} = 5.0$ mmol

The equivalence point has not been reached, so H^+ predominates.

	HCN(aq) $\rightleftharpoons$	**CN$^-$ (aq)** +	**H$^+$(aq)**
I	0.255	0	0
C	$-x$	$+x$	$+x$
E	$0.255 - x$	x	x

$K_a = \dfrac{[CN^-(aq)][H^+(aq)]}{[HCN(aq)]}$

Solution: $6.2 \times 10^{-10} = \dfrac{(x)(x)}{(0.255 - x)}$

$$6.2 \times 10^{-10} \approx \dfrac{(x)(x)}{0.255}$$

$$x^2 \approx 1.58 \times 10^{-10}$$

$$x = [H^+(aq)]$$

$$\approx 1.26 \times 10^{-5} \text{ mol/L}$$

$pH = -\log(1.26 \times 10^{-5})$

$pH = 4.90$

7. Yes, cresol red changes colour between pH = 1 and pH = 2. For a strong acid and a strong base, this range occurs very close to the endpoint.

8. Given: $V_{HC2H3O2(aq)} = 50.00$ mL; $[HC_2H_3O_2(aq)] = 0.100$ mol/L; $[KOH(aq)] = 0.100$ mol/L

(a) Required: Amount of unreacted ethanoic acid and pH before titration

Analysis: $n_{HC2H3O2} = [HC_2H_3O_2(aq)] \times V_{HC_2H_3O_{2(aq)}}$

$$= (0.100 \text{ mmol/mL})(50.00 \text{ mL})$$

$$n_{HC2H3O2} = 5.0 \text{ mmol}$$

Solution: The ionization of ethanoic acid prior to titration can be represented in an ICE table:

	$HC_2H_3O_2$ (aq) $\rightleftharpoons$ H^+(aq) + $C_2H_3O_2^-$ (aq)		
I	0.100	0	0
C	$-x$	$+x$	$+x$
E	$0.100 - x$	$+x$	$+x$

$$K_a = \dfrac{[H^+(aq)][C_2H_3O_2^-(aq)]}{[HC_2H_3O_2(aq)]}$$

$$1.8 \times 10^{-5} = \dfrac{x^2}{(0.100 - x)}$$

$$1.8 \times 10^{-5} = \dfrac{x^2}{0.100}$$

(Assuming $0.100 - x \approx 0.100$; valid by the hundred rule.)

$$x^2 \approx 0.100 \times 1.8 \times 10^{-5}$$

$$x \approx 1.34 \times 10^{-3}$$

$[H+(aq)] = x \approx 1.34 \times 10^{-3}$ mol/L

$pH = -\log[H^+(aq)]$

$pH \approx -\log(1.34 \times 10^{-3} \text{ mol/L})$

$pH \approx 2.873$

Statement: Before titration the amount of unreacted ethanoic acid is 5.0 mmol and the pH of the sample is 2.873.

(b) Required: Amount of unreacted ethanoic acid and pH when 10.0 mL of 0.100 mol/L KOH(aq) is added

Solution:

n_{KOH} = [KOH(aq)] × $V_{KOH(aq)}$

    = (0.100 mmol/L)(10.0 mL)

n_{KOH} = 1.0 mol

Unreacted ethanoic acid = $n_{HC_2H_3O_2}$ − n_{NaOH}

                      = 5.00 mmol − 1.0 mmol

Unreacted ethanoic acid = 4.0 mmol

Since 10.0 mL of KOH(aq) was added to 50.00 mL of ethanoic acid solution, the total volume is now 60.0 mL.

The concentration of unreacted ethanoic acid, [$HC_2H_3O_2$], can be determined:

$$[HC_2H_3O_2(aq)] = \frac{n_{HC_2H_3O_2(aq)}}{V_{HC_2H_3O_2(aq)}}$$

$$= \frac{(4.0 \text{ mmol})}{(60.00 \text{ mL})}$$

$$[HC_2H_3O_2(aq)] = 0.0667 \text{ mol/L}$$

Similarly, the concentration of the conjugate base of ethanoic acid, [$C_2H_3O_2^-$], is determined based on the amount of KOH(aq) added:

$$[C_2H_3O_2^-(aq)] = \frac{n_{C_2H_3O_2^-(aq)}}{V_{C_2H_3O_2^-(aq)}}$$

$$= \frac{(1.0 \text{ mmol})}{(60.00 \text{ mL})}$$

$$[C_2H_3O_2^-(aq)] = 0.0167 \text{ mol/L}$$

For the ethanoic acid/ethanoate solution:

	$HC_2H_3O_2$ (aq)	$\rightleftharpoons$ H^+(aq)	+	$C_2H_3O_2^-$ (aq)
I	0.0667	≈ 0		0.0167
C	− x	+ x		+ x
E	0.0667 − x	+ x		0.0167 + x

The values can now be substituted into the equilibrium equation for the ionization of a weak acid, where K_a = 1.8 × 10^{-5}.

$$K_a = \frac{[H^+(aq)][C_2H_3O_2^-(aq)]}{[HC_2H_3O_2(aq)]}$$

$$1.8 \times 10^{-5} = \frac{(x)(0.0167 + x)}{(0.0667 - x)}$$

Using simplifying assumptions, $0.0167 + x \approx 0.0167$ and $0.0667 - x \approx 0.0667$ (valid by the hundred rule).

Chapter 8: Acid-Base Equilibrium

$$1.8\times10^{-5} \approx \frac{(x)(0.0167)}{(0.0667)}$$

$$x \approx \frac{(1.8\times10^{-5})(0.0667)}{(0.0167)}$$

$$x \approx 7.19\times10^{-5}$$

Therefore $[H^+(aq)] = x \approx 7.19 \times 10^{-5}$ and the pH can be determined:
$$pH = -\log[H^+(aq)]$$
$$\approx -\log(7.19 \times 10^{-5})$$
$$pH \approx 4.143$$
Statement: After 10.0 mL of KOH(aq) is added the amount of unreacted ethanoic acid is 4.0 mmol. The pH is 4.143.

(c) Required: pH when 30.0 mL of 0.100 mol/L KOH(aq) is added

Analysis: $n_{KOH} = [KOH(aq)] \times V_{KOH(aq)}$
$$= (0.100 \text{ mmol/L})(30.0 \text{ mL})$$
$$n_{KOH} = 3.0 \text{ mol}$$

Solution:
Unreacted ethanoic acid $= n_{HC_2H_3O_2} - n_{NaOH}$
$$= 5.0 \text{ mmol} - 3.0 \text{ mmol}$$
Unreacted ethanoic acid $= 2.0$ mmol

Since 30.00 mL of KOH(aq) were added to 50.00 mL of ethanoic acid solution, the total volume is now 80.00 mL.

The concentration of unreacted ethanoic acid, $[C_2H_3O_2^-]$, can be determined:

$$[HC_2H_3O_2(aq)] = \frac{n_{HC_2H_3O_2(aq)}}{V_{HC_2H_3O_2(aq)}}$$

$$= \frac{(2.0 \text{ mmol})}{(80.00 \text{ mL})}$$

$$[HC_2H_3O_2(aq)] = 0.0250 \text{ mol/L}$$

Similarly, the concentration of the conjugate base of ethanoic acid, $[C_2H_3O_2^-]$, is determined based on the amount of KOH(aq) added:

$$[C_2H_3O_2^-(aq)] = \frac{n_{C_2H_3O_2^-(aq)}}{V_{C_2H_3O_2^-(aq)}}$$

$$= \frac{(3.0 \text{ mmol})}{(80.00 \text{ mL})}$$

$$[C_2H_3O_2^-(aq)] = 0.0375 \text{ mol/L}$$

For the ethanoic acid/ethanoate solution:

	$HC_2H_3O_2$ (aq)	$\rightleftharpoons$ H^+(aq)	+ $C_2H_3O_2^-$ (aq)
I	0.0250	≈ 0	0.0375
C	$-x$	$+x$	$+x$
E	$0.0250 - x$	$+x$	$0.0375 + x$

The values can now be substituted into the equilibrium equation for the ionization of a weak acid, where $K_a = 1.8 \times 10^{-5}$.

$$K_a = \frac{[H^+(aq)][C_2H_3O_2{}^-(aq)]}{[HC_2H_3O_2(aq)]}$$

$$1.8 \times 10^{-5} = \frac{(x)(0.0375 + x)}{(0.0250 - x)}$$

Using simplifying assumptions, $0.0375 + x \approx 0.0375$ and $0.0250 - x \approx 0.0250$ (valid by the hundred rule).

$$1.8 \times 10^{-5} \approx \frac{(x)(0.0375)}{(0.0250)}$$

$$x \approx \frac{(1.8 \times 10^{-5})(0.0375)}{(0.0250)}$$

$$x \approx 2.70 \times 10^{-5}$$

Therefore $[H^+(aq)] = x \approx 2.70 \times 10^{-5}$ and the pH can be determined:

$$pH = -\log[H^+(aq)]$$
$$\approx -\log(2.70 \times 10^{-5})$$
$$pH \approx 4.569$$

Statement: After adding 30.0 mL of base, the pH is 4.569.

(d) Required: Amount and volume of titrant added to reach the equivalence point

Analysis: At the equivalence point, enough base is added to react completely with the all the acid originally present. From part (a), 4.0 mmol of unreacted ethanoic acid was present originally. Therefore 4.0 mmol of titrant must be added to reach the equivalence point.

Solution: The volume needed to reach the equivalence point can be calculated:

$$V_{KOH} = \frac{n_{KOH}}{[KOH(aq)]}$$

$$= \frac{(4.0 \text{ mmol})}{(0.100 \text{ mmol/mL})}$$

$$= 40.0 \text{ mL}$$

Statement: 4.0 mmol, or 40.0 mL, of titrant must be added to reach the equivalence point.

(e) Required: Good indicator for this titration

Analysis: The indicator should change colour at a pH close to the equivalence point of the titration. Therefore, determine the pH at the equivalence point.

To reach the equivalence point, 40.0 mL of KOH(aq) was added to 50.00 mL of ethanoic acid solution; therefore, the total volume is now 90.0 mL. There are no unreacted $HC_2H_3O_2$ (aq) molecules left in the solution and $n_{C2H3O2^-} = 4.00$ mmol, equal to the amount of base added.

Solution:
The concentration of ethanoate $[C_2H_3O_2^-]$, can be determined:

$$[C_2H_3O_2^- (aq)] = \frac{n_{C_2H_3O_2^- (aq)}}{V_{C_2H_3O_2^- (aq)}}$$

$$= \frac{(4.0 \text{ mmol})}{(90.00 \text{ mL})}$$

$$[C_2H_3O_2^- (aq)] = 0.0444 \text{ mol/L}$$

For the hydrolysis equilibrium established at the equivalence point:

	$C_2H_3O_2^-$ (aq)	+ H_2O(l)	$\rightleftharpoons$ OH^-(aq)	+ $HC_2H_3O_2$ (aq)
I	0.0444	—	0	0
C	$-x$	—	$+x$	$+x$
E	$0.0444 - x$	—	$+x$	$+x$

The ionization constant equilibrium equation for a weak base is $K_b = \dfrac{[HA(aq)][OH^-(aq)]}{[A^-(aq)]}$.

K_b can be calculated from K_a and K_w:

$$K_b = \frac{K_w}{K_a}$$

$$= \frac{1.0 \times 10^{-14}}{3.5 \times 10^{-8}}$$

$$K_b = 2.9 \times 10^{-7}$$

The values can now be substituted into the equation:

$$K_b = \frac{[HC_2H_3O_2(aq)][OH^-(aq)]}{[C_2H_3O_2^- (aq)]}$$

$$2.9 \times 10^{-7} = \frac{x^2}{(0.0444 - x)}$$

$$2.9 \times 10^{-7} \approx \frac{x^2}{(0.0444)}$$

$$x^2 \approx 0.0444 \times 2.9 \times 10^{-7}$$

$$x \approx 1.13 \times 10^{-4}$$

Therefore $[OH^- (aq)] = x \approx 1.13 \times 10^{-4}$ and the pOH can be determined:
$$pOH = -\log[OH^- (aq)]$$
$$\approx -\log(1.13 \times 10^{-4})$$
$$pOH \approx 3.947$$

The pH can be determined from the pOH:

pH + pOH = 14

pH = 14 – pOH

≈ 14 – 3.947

pH ≈ 10.053

Statement: A good indicator for this titration is thymolphthalein, since its useful pH range is 9.3 to 10.5. Therefore the endpoint of the titration would be close to the equivalence point.

9. Answers may vary. Sample answer: A "digital titrator" is a computer controlled device that dispenses titrant while monitoring the pH. It can provide very accurate results using smaller sample volumes because the computer can monitor the pH continuously and adjust flow rates very precisely. Its main disadvantage over a traditional setup is the cost of the instrument.