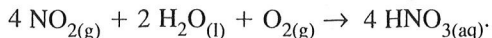


As ₂ O _{3(s)}	insoluble – no solution produced. The water remains neutral.
SiO _{2(s)}	insoluble – no solution produced. The water remains neutral.
P ₂ O _{3(s)}	acidic
SO _{3(g)}	acidic
Cl ₂ O _(g)	acidic

Extension

7. Rainwater containing dissolved NO_{2(g)} is acidic because of the formation of nitric acid in this reaction:



8.4 ACID-BASE TITRATION

PRACTICE

(Page 599)

Understanding Concepts

- pH 7
 - Since this is a titration of a strong acid with a strong base, the equivalence point occurs at pH 7. Any indicator with pH 7 within its range would be suitable, e.g., bromothymol blue, litmus, neutral red, phenol red.

$$\begin{aligned}
 2. \quad n_{\text{HI}} &= V_{\text{HI}} \times C_{\text{HI}} \\
 &= 11 \text{ mL} \times 0.18 \text{ mol/L} \\
 &= 1.98 \text{ mmol} \quad (\text{extra digits carried})
 \end{aligned}$$

$$n_{\text{HI}} = n_{\text{NaOH}} \text{ required}$$

$$C_{\text{NaOH}} = \frac{n_{\text{NaOH}}}{V_{\text{NaOH}}}$$

$$\begin{aligned}
 V_{\text{NaOH}} &= \frac{n_{\text{NaOH}}}{C_{\text{NaOH}}} \\
 &= \frac{1.98 \text{ mmol}}{0.23 \text{ mol/L}}
 \end{aligned}$$

$$V_{\text{NaOH}} = 8.6 \text{ mL}$$

8.6 mL of 0.23 mol/L sodium hydroxide is required to reach the equivalence point.

Applying Inquiry Skills

- The last drop is washed into the flask because the titrant volume level in the buret already includes the volume of the drop.
 - The results of the titration depend only on the moles of acid or base present, not their concentration. Adding water changes concentration but not the moles present.

PRACTICE

(Page 607)

Understanding Concepts

4. (a)

ICE Table for the Ionization of HCO ₂ H _(aq)			
	HCO ₂ H _(aq) ⇌	H _(aq) ⁺	CO ₂ H _(aq) ⁻
Initial concentration (mol/L)	0.20	0.00	0.00
Change in concentration (mol/L)	-x	+x	+x
Equilibrium concentration (mol/L)	0.20 - x	x	x

$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{CO}_2\text{H}_{(\text{aq})}^-]}{[\text{HCO}_2\text{H}_{(\text{aq})}]}$$

$$\frac{x^2}{0.20 - x} = 1.8 \times 10^{-4}$$

Predicting whether $0.20 - x \doteq 0.20 \dots$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{0.20 \text{ mol/L}}{1.8 \times 10^{-4}}$$

$$= 1100$$

Since $1100 > 100$, we assume that $0.20 - x \doteq 0.20$.

$$\frac{x^2}{(0.20)} \doteq 1.8 \times 10^{-4}$$

$$x^2 \doteq 3.6 \times 10^{-5}$$

$$x \doteq 6.0 \times 10^{-3}$$

Validating the assumption ...

$$\frac{6.0 \times 10^{-3}}{0.20} \times 100\% = 3.0\%$$

Since $3.0\% < 5.0\%$, the assumption is valid.

$$[\text{H}_{(\text{aq})}^+] = 6.0 \times 10^{-3} \text{ mol/L}$$

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

$$= -\log [6.0 \times 10^{-3}]$$

$$\text{pH} = 2.22$$

The pH of the 0.20 mol/L formic acid solution is 2.22.

(b) $V_{\text{HCO}_2\text{H}_{(\text{aq})}} = 25.00 \text{ mL}$

$$C_{\text{HCO}_2\text{H}_{(\text{aq})}} = 0.20 \text{ mol/L}$$

$$n_{\text{HCO}_2\text{H}_{(\text{aq})}} = V_{\text{HCO}_2\text{H}_{(\text{aq})}} \times C_{\text{HCO}_2\text{H}_{(\text{aq})}}$$

$$= 25.00 \text{ mL} \times 0.20 \text{ mol/L}$$

$$n_{\text{HCO}_2\text{H}_{(\text{aq})}} = 5.0 \text{ mmol}$$

$$V_{\text{NaOH}_{(\text{aq})}} = 10.00 \text{ mL}$$

$$C_{\text{NaOH}_{(\text{aq})}} = 0.20 \text{ mol/L}$$

$$n_{\text{NaOH}_{(\text{aq})}} = V_{\text{NaOH}_{(\text{aq})}} \times C_{\text{NaOH}_{(\text{aq})}}$$

$$= 10.00 \text{ mL} \times 0.20 \text{ mol/L}$$

$$n_{\text{NaOH}_{(\text{aq})}} = 2.0 \text{ mmol}$$

$$n_{\text{HCO}_2\text{H}_{(\text{aq})}} \text{ remaining } \dots$$

$$n_{\text{HCO}_2\text{H}_{(\text{aq})}} = 5.0 \text{ mmol} - 2.0 \text{ mmol}$$

$$n_{\text{HCO}_2\text{H}_{(\text{aq})}} = 3.0 \text{ mmol}$$

$$\text{Total volume} = 25.00 \text{ mL} + 10.00 \text{ mL}$$

$$= 35.00 \text{ mL}$$

$$C_{\text{HCO}_2\text{H}_{(\text{aq})}} = \frac{3.0 \text{ mmol}}{35.00 \text{ mL}}$$

$$C_{\text{HCO}_2\text{H}_{(\text{aq})}} = 0.08571 \text{ mol/L} \quad (\text{extra digits carried})$$

$$C_{\text{CO}_2\text{H}_{(\text{aq})}^-} = \frac{2.0 \text{ mmol}}{35.00 \text{ mL}}$$

$$C_{\text{CO}_2\text{H}_{(\text{aq})}^-} = 0.05714 \text{ mol/L} \quad (\text{extra digits carried})$$

Let x represent the changes in concentration that occur as the system reestablishes equilibrium.

ICE Table for the ionization of $\text{HCO}_2\text{H}_{(\text{aq})}$			
	$\text{HCO}_2\text{H}_{(\text{aq})} \rightleftharpoons$	$\text{H}_{(\text{aq})}^+$ +	$\text{CO}_2\text{H}_{(\text{aq})}^-$
Initial concentration (mol/L)	0.08571	0.00	0.05714
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.08571 - x$	x	$0.05714 + x$

$$\frac{[\text{H}_{(\text{aq})}^+][\text{CO}_2\text{H}_{(\text{aq})}^-]}{[\text{HCO}_2\text{H}_{(\text{aq})}]} = K_a$$

$$\frac{x(0.05714 + x)}{0.08571 - x} = 1.8 \times 10^{-4}$$

Checking whether an approximation is warranted:

$$\frac{[\text{HCO}_2\text{H}_{(\text{aq})}]_{\text{initial}}}{K_a} = \frac{0.08571}{1.8 \times 10^{-4}}$$

$$\frac{[\text{HCO}_2\text{H}_{(\text{aq})}]_{\text{initial}}}{K_a} = 480$$

Since $480 > 100$, we can assume that

$$0.08571 - x \doteq 0.08571 \text{ and that}$$

$$0.05714 + x \doteq 0.05714$$

The equilibrium simplifies to

$$\frac{x(0.05714)}{0.08571} = 1.8 \times 10^{-4}$$

$$x = 2.70 \times 10^{-4}$$

Verifying the assumption with the 5% rule:

$$\frac{2.70 \times 10^{-4}}{0.20} \times 100\% = 0.14\%$$

Since $0.14\% < 5\%$, the simplifying assumption is justified.

$$[\text{H}_{(\text{aq})}^+] \doteq 2.70 \times 10^{-4} \text{ mol/L}$$

$$\text{pH} \doteq -\log[2.70 \times 10^{-4}]$$

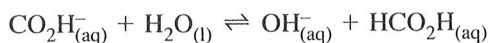
$$\text{pH} = 3.569$$

The pH after the addition of 10.00 mL of $\text{NaOH}_{(\text{aq})}$ is 3.57.

(c) At the equivalence point, 25.00 mL of 0.20 mol/L $\text{NaOH}_{(\text{aq})}$ were added.

Entities remaining in solution: $\text{Na}_{(\text{aq})}^+$, $\text{CO}_2\text{H}_{(\text{aq})}^-$, $\text{H}_2\text{O}_{(\text{l})}$

Since $\text{Na}_{(\text{aq})}^+$ does not hydrolyze, the pH of the solution is determined by the methanoate ion.



$$\frac{[\text{HCO}_2\text{H}_{(\text{aq})}][\text{OH}^-_{(\text{aq})}]}{[\text{CO}_2\text{H}^-_{(\text{aq})}]} = K_b$$

$$K_a = 1.8 \times 10^{-4}$$

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

$$= \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}}$$

$$K_b = 5.6 \times 10^{-11}$$

Therefore,

$$\frac{[\text{HCO}_2\text{H}_{(\text{aq})}][\text{OH}^-_{(\text{aq})}]}{[\text{CO}_2\text{H}^-_{(\text{aq})}]} = 5.6 \times 10^{-11}$$

At the equivalence point, the total volume = 50.00 mL.

Since 5.00 mmol of $\text{HCO}_2\text{H}_{(\text{aq})}$ was present initially,

5.00 mmol of $\text{CO}_2\text{H}^-_{(\text{aq})}$ is present at the equivalence point.

$$[\text{CO}_2\text{H}^-_{(\text{aq})}] = \frac{5.00 \text{ mmol}}{50.00 \text{ mL}}$$

$$[\text{CO}_2\text{H}^-_{(\text{aq})}] = 0.100 \text{ mol/L}$$

ICE Table for the Hydrolysis of $\text{CO}_2\text{H}^-_{(\text{aq})}$				
	$\text{CO}_2\text{H}^-_{(\text{aq})} +$	$\text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$	$\text{HCO}_2\text{H}_{(\text{aq})} +$	$\text{OH}^-_{(\text{aq})}$
Initial concentration (mol/L)	0.100	–	0.000	0.000
Change in concentration (mol/L)	–x	–	+x	+x
Equilibrium concentration (mol/L)	0.100 – x	–	x	x

$$\frac{[\text{HCO}_2\text{H}_{(\text{aq})}][\text{OH}^-_{(\text{aq})}]}{[\text{CO}_2\text{H}^-_{(\text{aq})}]} = 5.6 \times 10^{-11}$$

$$\frac{x^2}{0.100 - x} = 5.6 \times 10^{-11}$$

Checking whether an approximation is warranted:

$$\frac{[\text{CO}_2\text{H}^-_{(\text{aq})}]_{\text{initial}}}{K} = \frac{0.10}{5.6 \times 10^{-11}}$$

$$\frac{[\text{CO}_2\text{H}^-_{(\text{aq})}]_{\text{initial}}}{K} = 1.8 \times 10^9$$

Since $1.8 \times 10^9 > 100$, we can assume that

$$0.100 - x \doteq 0.100$$

The equilibrium simplifies to $\frac{x^2}{0.100} = 5.6 \times 10^{-11}$

$$x = 2.37 \times 10^{-6}$$

Verifying the assumption with the 5% rule:

$$\frac{2.37 \times 10^{-6}}{0.100} \times 100\% = 2.4 \times 10^{-3}\%$$

Since $2.4 \times 10^{-3}\% < 5\%$, the simplifying assumption is justified.

$$[\text{OH}_{(\text{aq})}^-] \doteq 2.37 \times 10^{-6} \text{ mol/L}$$

$$\text{pOH} \doteq -\log[2.37 \times 10^{-6}]$$

$$\text{pOH} = 5.625$$

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

$$\text{pH} = 8.37$$

The pH at the equivalence point is 8.37.

$$\begin{aligned} 5. \quad V_{\text{HOCN}_{(\text{aq})}} &= 30.00 \text{ mL} \\ C_{\text{HOCN}_{(\text{aq})}} &= 0.17 \text{ mol/L} \\ n_{\text{HOCN}_{(\text{aq})}} &= V_{\text{HOCN}_{(\text{aq})}} \times C_{\text{HOCN}_{(\text{aq})}} \\ &= 30.00 \text{ mL} \times 0.17 \text{ mol/L} \\ n_{\text{HOCN}_{(\text{aq})}} &= 5.1 \text{ mmol} \\ V_{\text{NaOH}_{(\text{aq})}} &= 10.00 \text{ mL} \\ C_{\text{NaOH}_{(\text{aq})}} &= 0.250 \text{ mol/L} \\ n_{\text{NaOH}_{(\text{aq})}} &= V_{\text{NaOH}_{(\text{aq})}} \times C_{\text{NaOH}_{(\text{aq})}} \\ &= 10.00 \text{ mL} \times 0.250 \text{ mol/L} \\ n_{\text{NaOH}_{(\text{aq})}} &= 2.50 \text{ mmol} \\ n_{\text{HCON}_{(\text{aq})}} &\text{ remaining ...} \\ n_{\text{HOCN}_{(\text{aq})}} &= 5.1 \text{ mmol} - 2.50 \text{ mmol} \\ n_{\text{HOCN}_{(\text{aq})}} &= 2.6 \text{ mmol} \end{aligned}$$

$$\begin{aligned} \text{Total volume} &= 30.00 \text{ mL} + 10.00 \text{ mL} \\ &= 40.00 \text{ mL} \end{aligned}$$

$$C_{\text{HOCN}_{(\text{aq})}} = \frac{2.6 \text{ mmol}}{40.00 \text{ mL}}$$

$$C_{\text{HOCN}_{(\text{aq})}} = 0.0625 \text{ mol/L}$$

$$C_{\text{OCN}_{(\text{aq})}^-} = \frac{2.5 \text{ mmol}}{40.00 \text{ mL}}$$

$$C_{\text{OCN}_{(\text{aq})}^-} = 0.0625 \text{ mol/L}$$

Let x represent the changes in concentration that occur as the system reestablishes equilibrium.

ICE Table for the Ionization of $\text{HOCN}_{(\text{aq})}$			
	$\text{HOCN}_{(\text{aq})} \rightleftharpoons$	$\text{H}_{(\text{aq})}^+ +$	$\text{OCN}_{(\text{aq})}^-$
Initial concentration (mol/L)	0.0625	0.00	0.0625
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.0625 - x$	x	$0.0625 + x$

$$\frac{[\text{H}^+_{(\text{aq})}][\text{OCN}^-_{(\text{aq})}]}{[\text{HOCN}_{(\text{aq})}]} = K_a$$

$$\frac{x(0.0625 + x)}{0.0625 - x} = 3.5 \times 10^{-4}$$

Checking whether an approximation is warranted:

$$\frac{[\text{HOCN}_{(\text{aq})}]_{\text{initial}}}{K_a} = \frac{0.0625}{3.5 \times 10^{-4}}$$

$$\frac{[\text{HOCN}_{(\text{aq})}]_{\text{initial}}}{K_a} = 180$$

Since $180 > 100$, we can assume that

$$0.0625 + x \doteq 0.0625 \text{ and that } 0.0625 - x \doteq 0.0625$$

The equilibrium simplifies to

$$\frac{x(0.0625)}{0.0625} = 1.8 \times 10^{-4}$$

$$x = 1.8 \times 10^{-4}$$

Verifying the assumption with the 5% rule:

$$\frac{1.8 \times 10^{-4}}{0.0625} \times 100\% = 0.29\%$$

Since $0.29\% < 5\%$, the simplifying assumption is justified.

$$[\text{H}^+_{(\text{aq})}] \doteq 1.8 \times 10^{-4} \text{ mol/L}$$

$$\text{pH} \doteq -\log[1.8 \times 10^{-4}]$$

$$\text{pH} = 3.74$$

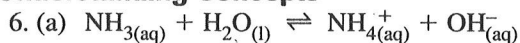
The $\text{OCN}_{(\text{aq})}$ is such a weak base ($K_b = 2.10 \times 10^{-12}$) that any hydrolysis to produce $\text{OH}^-_{(\text{aq})}$ is insignificant.

The pH of the resulting solution is 3.74. *3.44*

PRACTICE

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Understanding Concepts



$$K_b = \frac{[\text{NH}_4^+_{(\text{aq})}][\text{OH}^-_{(\text{aq})}]}{[\text{NH}_{3(\text{aq})}]}$$

$$K_b = 1.8 \times 10^{-5}$$

ICE Table for the Ionization of Ammonia				
	$\text{NH}_{3(\text{aq})} +$	$\text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$	$\text{NH}_4^+_{(\text{aq})} +$	$\text{OH}^-_{(\text{aq})}$
Initial concentration (mol/L)	0.15	–	0.00	0.00
Change in concentration (mol/L)	–x	–	+x	+x
Equilibrium concentration (mol/L)	$0.15 - x$	–	x	x

$$K_b = \frac{[\text{NH}_4^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{NH}_3(\text{aq})]}$$

$$K_b = 1.8 \times 10^{-5}$$

$$\frac{x^2}{0.15 - x} = 1.8 \times 10^{-5}$$

Predicting the validity of the assumption ...

$$\frac{0.15}{1.8 \times 10^{-5}} = 8300$$

Since $8300 > 100$, we may assume that $0.15 - x \doteq 0.15$.

The equilibrium expression becomes

$$\frac{x^2}{0.15} \doteq 1.8 \times 10^{-5}$$

which yields

$$x^2 \doteq 2.7 \times 10^{-6}$$

$$x \doteq 1.643 \times 10^{-3} \quad (\text{extra digits carried})$$

Justifying the simplification assumption ...

$$\frac{1.643 \times 10^{-3}}{0.15} \times 100\% = 1.1\%$$

Since $1.1\% < 5\%$, the assumption is justified.

Therefore,

$$[\text{OH}^-(\text{aq})] = 1.643 \times 10^{-3} \text{ mol/L}$$

$$\text{pOH} = -\log[1.643 \times 10^{-3}]$$

$$\text{pOH} = 2.7844 \quad (\text{extra digits carried})$$

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

$$= 14.0 - 2.7844$$

$$\text{pH} = 11.216$$

The pH before any $\text{HI}(\text{aq})$ is added is 11.22.

(b) At the equivalence point, the entities remaining in solution are $\text{NH}_4^+(\text{aq})$, $\text{I}^-(\text{aq})$, and $\text{H}_2\text{O}(\text{l})$.

Since $\text{I}^-(\text{aq})$ does not hydrolyze, the pH of the solution is determined by the ammonium ion.

$$C_{\text{NH}_3(\text{aq})} = 0.1500 \text{ mol/L}$$

$$n_{\text{NH}_3(\text{aq})} = V_{\text{NH}_3(\text{aq})} \times C_{\text{NH}_3(\text{aq})}$$

$$= 20.0 \text{ mL} \times 0.1500 \text{ mol/L}$$

$$n_{\text{NH}_3(\text{aq})} = 3.00 \text{ mmol (amount of } \text{NH}_4^+(\text{aq}) \text{ produced)}$$

Final volume = 40.0 mL

$$[\text{NH}_4^+(\text{aq})] = \frac{3.00 \text{ mmol}}{40.0 \text{ mL}}$$

$$[\text{NH}_4^+(\text{aq})] = 0.075 \text{ mol/L}$$

$$K_a = \frac{[\text{H}^+(\text{aq})][\text{NH}_3(\text{aq})]}{[\text{NH}_4^+(\text{aq})]}$$

$$\frac{x^2}{0.075 - x} = 5.8 \times 10^{-10}$$

Predicting whether $0.075 - x \doteq 0.075$:

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{0.075 \text{ mol/L}}{5.8 \times 10^{-10}}$$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = 1.3 \times 10^9$$

Since $1.3 \times 10^9 > 100$, we assume that $0.075 - x \doteq 0.075$.

$$\frac{x^2}{(0.075)} \doteq 5.8 \times 10^{-10}$$

$$x \doteq 6.595 \times 10^{-6} \quad (\text{extra digits carried})$$

$$[\text{H}_{(\text{aq})}^+] = 6.595 \times 10^{-6} \text{ mol/L}$$

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

$$= -\log[6.595 \times 10^{-6}]$$

$$\text{pH} = 5.181$$

The pH at the equivalence point is 5.18.

PRACTICE

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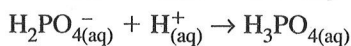
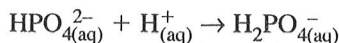
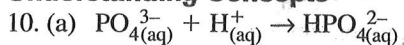
Understanding Concepts

- Since this is a titration of a weak base with a strong acid, the equivalence point will occur at pH less than 7. Alizarin yellow's pH range is 10.1–12.0, beyond the required equivalence point.
- Indicators are weak acids in equilibrium with their conjugate base. At the endpoint some titrant is required to "neutralize" the indicator. A small volume of indicator solution is used to keep the titrant volume required to produce the colour change insignificant to the results of the titration.
- Since this is a titration of a weak acid with a strong base, the equivalence point will occur at pH greater than 7. However, methyl red has a pH range of 4.8–6.0, well below the equivalence point. As a result, the endpoint of the titration occurs before the equivalence point is reached.

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Understanding Concepts



(b) 25 mL and 50 mL

(c) The hydrogen phosphate ion, $\text{HPO}_{4(\text{aq})}^{2-}$ is an extremely weak acid ($K_a = 4.2 \times 10^{-13}$) and does not lose its proton quantitatively. Only quantitative reactions produce detectable endpoints in an acid–base titration.

SECTION 8.4 QUESTIONS

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Understanding Concepts

- (a) The endpoint is at pH 9 and the equivalence point is at 26 mL.
(b) Phenolphthalein
(c) $\text{HC}_2\text{H}_3\text{O}_{2(\text{aq})} + \text{OH}_{(\text{aq})}^- \rightarrow \text{C}_2\text{H}_3\text{O}_{2(\text{aq})}^- + \text{H}_2\text{O}_{(\text{l})}$
- (a) 7
(b) >7