

Chapter 17

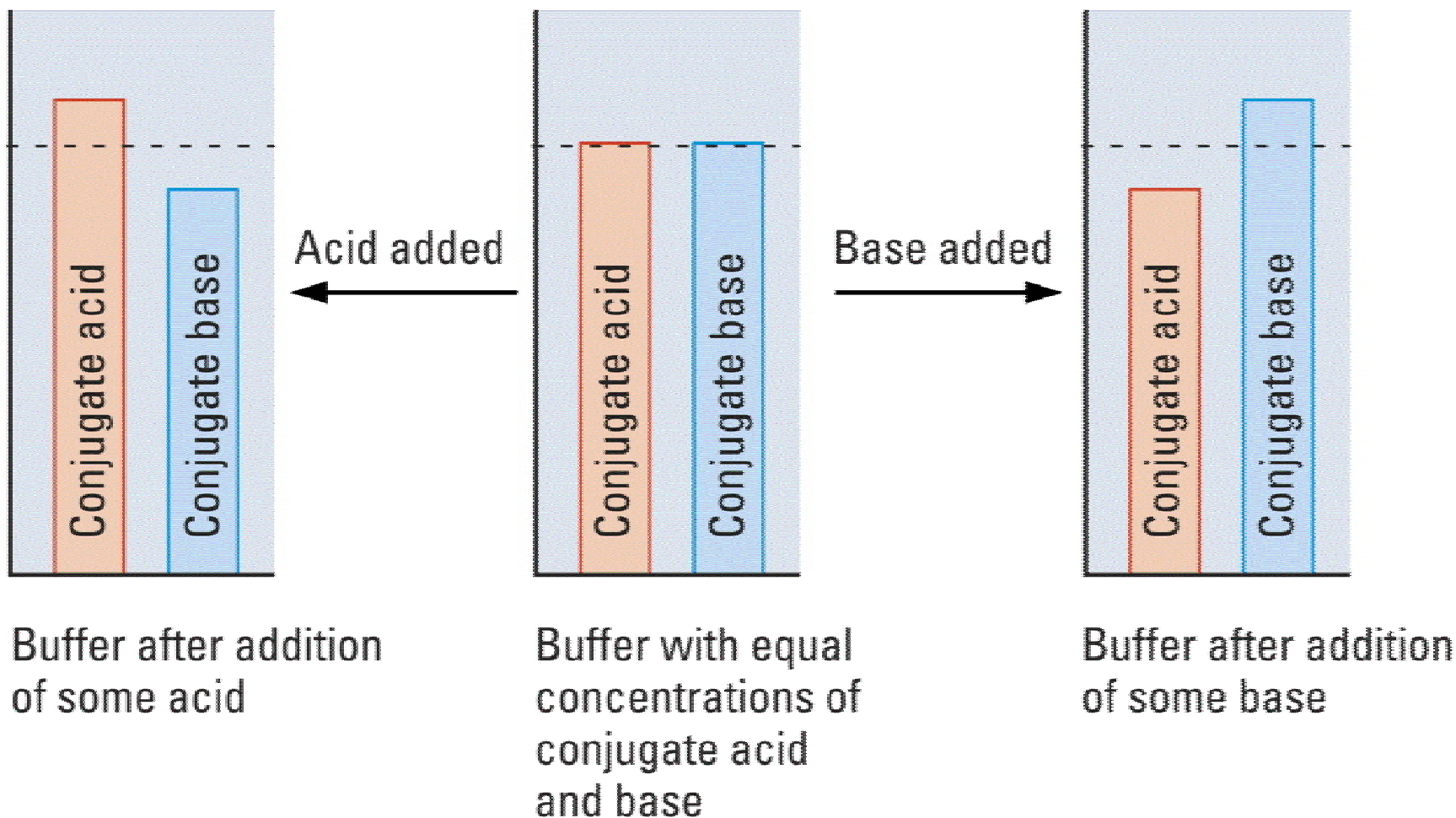
Additional Aqueous Equilibria

Buffers

A buffered solution resists changes in pH when small amounts of acids and bases are added or when dilution occurs.

Definition - a buffer solution is composed of:
a weak-acid and its salt (conjugate base) or
a weak-base and its salt (conjugate acid)

Adding an Acid or Base to a Buffer



Buffer Solution

Henderson-Hasselbalch Equation

$$[\text{H}_3\text{O}^+] = K_a \times ([\text{HA}]/[\text{A}^-])$$

$$\text{pH} = \text{pK}_a + \log([\text{A}^-]/[\text{HA}])$$

$$\text{when } [\text{A}^-] = [\text{HA}]$$

$$\text{pH} = \text{pK}_a$$

EXAMPLE: Describe how 1.00 L of a **pH 10.00 ammonia-ammonium chloride buffer** solution would be made using concentrated **NH₃ (14 M)** and **solid NH₄Cl**.

$$K_a = 5.6 \times 10^{-10} \text{ M} = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-10.00} = 1.0 \times 10^{-10} \text{ M}$$

$$\frac{[\text{NH}_4^+]}{[\text{NH}_3]} = \frac{[\text{H}_3\text{O}^+]}{K_a} = \frac{1.0 \times 10^{-10} \text{ M}}{5.6 \times 10^{-10} \text{ M}} = 0.18$$

if we use 1.00 L of concentrated NH₃, then

$$[\text{NH}_4^+] = 0.18 \times [\text{NH}_3] = 0.18 (14\text{M}) = 2.5\text{M}$$

$$\# \text{ g NH}_4\text{Cl} = (2.5 \text{ mol/L})(1.00 \text{ L})(54 \text{ g/mol}) = 1.3 \times 10^2 \text{ g}$$

Dissolve $1.3 \times 10^2 \text{ g}$ of NH₄Cl in 1.00 L of concentrated NH₃.

Buffer Capacity

- refers to the ability of the buffer to retard changes in pH when small amounts of acid or base are added
- the ratio of $[A^-]/[HA]$ determines the pH of the buffer whereas the magnitude of $[A^-]$ and $[HA]$ determine the **buffer capacity**

Buffer Systems

TABLE 17.1 Buffer Systems That Are Useful at Various pH Values*

Desired pH	Weak acid	Weak base	K_a (Weak acid)	pK_a
4	Lactic acid ($\text{CH}_3\text{CHOHCOOH}$)	Lactate ion ($\text{CH}_3\text{CHOHCOO}^-$)	1.4×10^{-4}	3.85
5	Acetic acid (CH_3COOH)	Acetate ion (CH_3COO^-)	1.8×10^{-5}	4.74
6	Carbonic acid (H_2CO_3)	Hydrogen carbonate ion (HCO_3^-)	4.2×10^{-7}	6.38
7	Dihydrogen phosphate ion (H_2PO_4^-)	Hydrogen phosphate ion (HPO_4^{2-})	6.2×10^{-8}	7.21
8	Hypochlorous acid (HClO)	Hypochlorite ion (ClO^-)	3.5×10^{-8}	7.46
9	Ammonium ion (NH_4^+)	Ammonia (NH_3)	5.6×10^{-10}	9.25
10	Hydrogen carbonate ion (HCO_3^-)	Carbonate ion (CO_3^{2-})	4.8×10^{-11}	10.32

*Adapted from Masterton, W. L., and Hurley, C. N. *Chemistry—Principles and Reactions*, 4th ed. Philadelphia: Saunders College Publishing, 2001; p. 416.

Titration Apparatus

analyte + titrant \Rightarrow products



Buret delivering base to a flask containing an acid. The pink color in the flask is due to the phenolphthalein indicator.

Photo by George Lisensky

Endpoint vs. Equivalence Point

Endpoint

point where there is a physical change, such as color change, with the *indicator*

Equivalence Point

moles titrant = # moles analyte

$$\text{\#moles}_{\text{titrant}} = (V \times M)_{\text{titrant}}$$

$$\text{\#moles}_{\text{analyte}} = (V \times M)_{\text{analyte}}$$

Acid-Base Indicator

Weak acid that changes color with changes in pH



acid

base

color

color

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]}$$

Acid-Base Indicator Behavior

acid color shows when

$$\frac{[\text{In}^-]}{[\text{HIn}]} \leq \frac{1}{10} \quad \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} = \frac{1}{10} \times [\text{H}_3\text{O}^+] = K_a$$

base color shows when

$$\frac{[\text{In}^-]}{[\text{HIn}]} \geq 10 \quad \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} = 10 \times [\text{H}_3\text{O}^+] = K_a$$

Indicator pH Range

acid color shows when

$$\text{pH} + 1 = \text{pK}_a$$

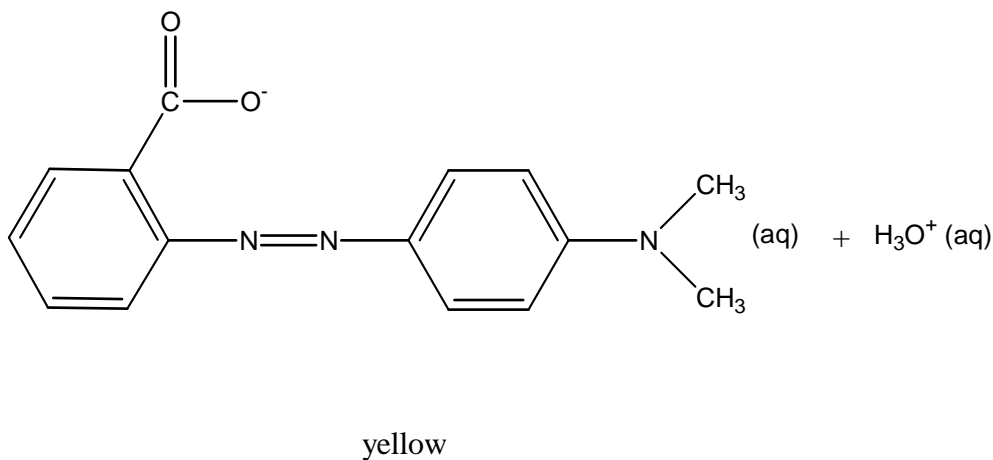
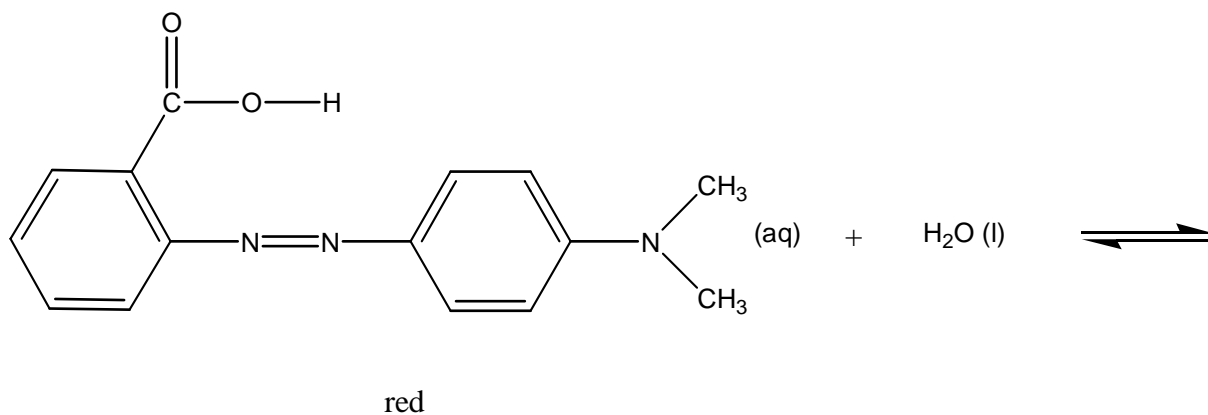
and base color shows when

$$\text{pH} - 1 = \text{pK}_a$$

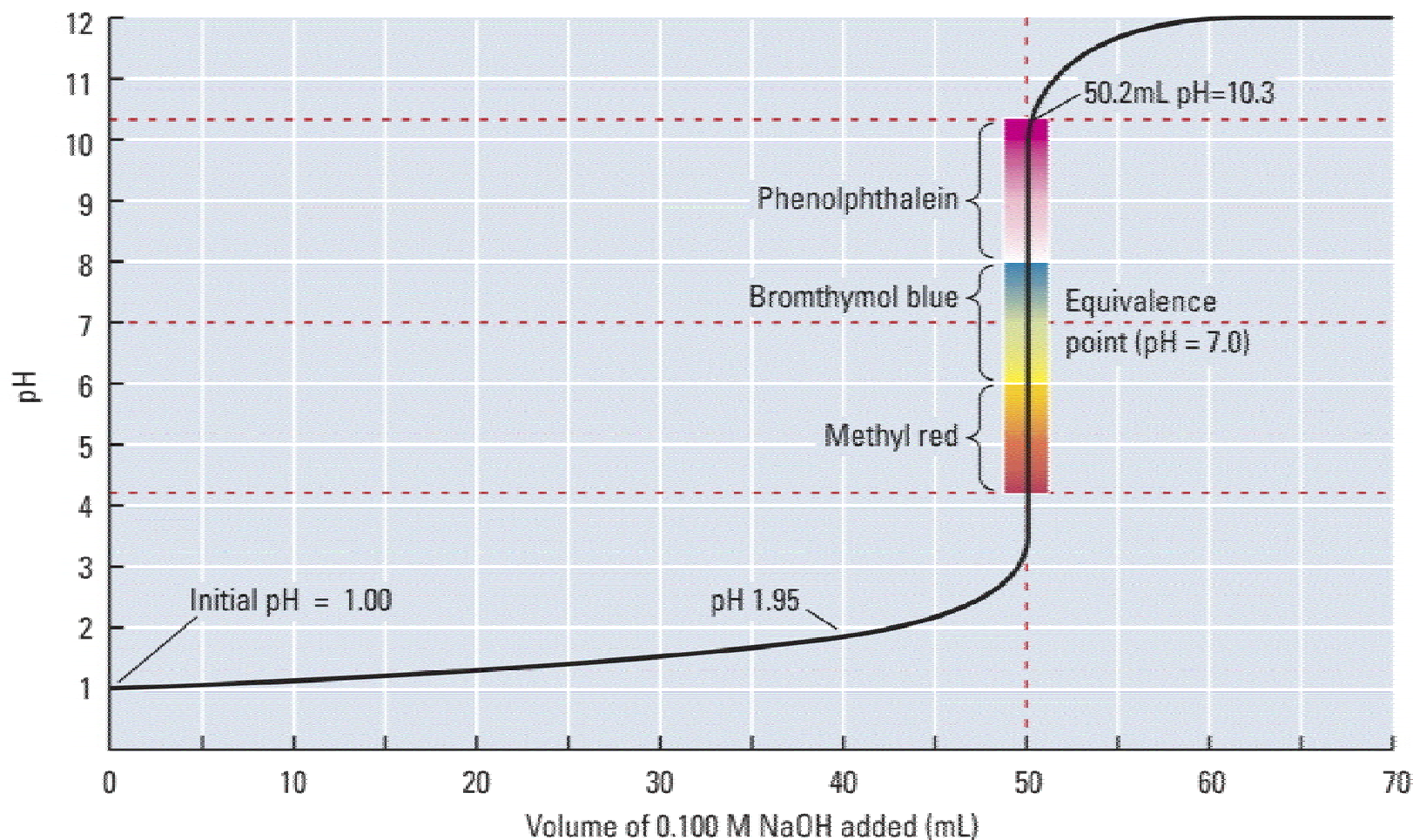
Color change range is

$$\text{pK}_a = \text{pH} \pm 1 \quad \text{or} \quad \text{pH} = \text{pK}_a \pm 1$$

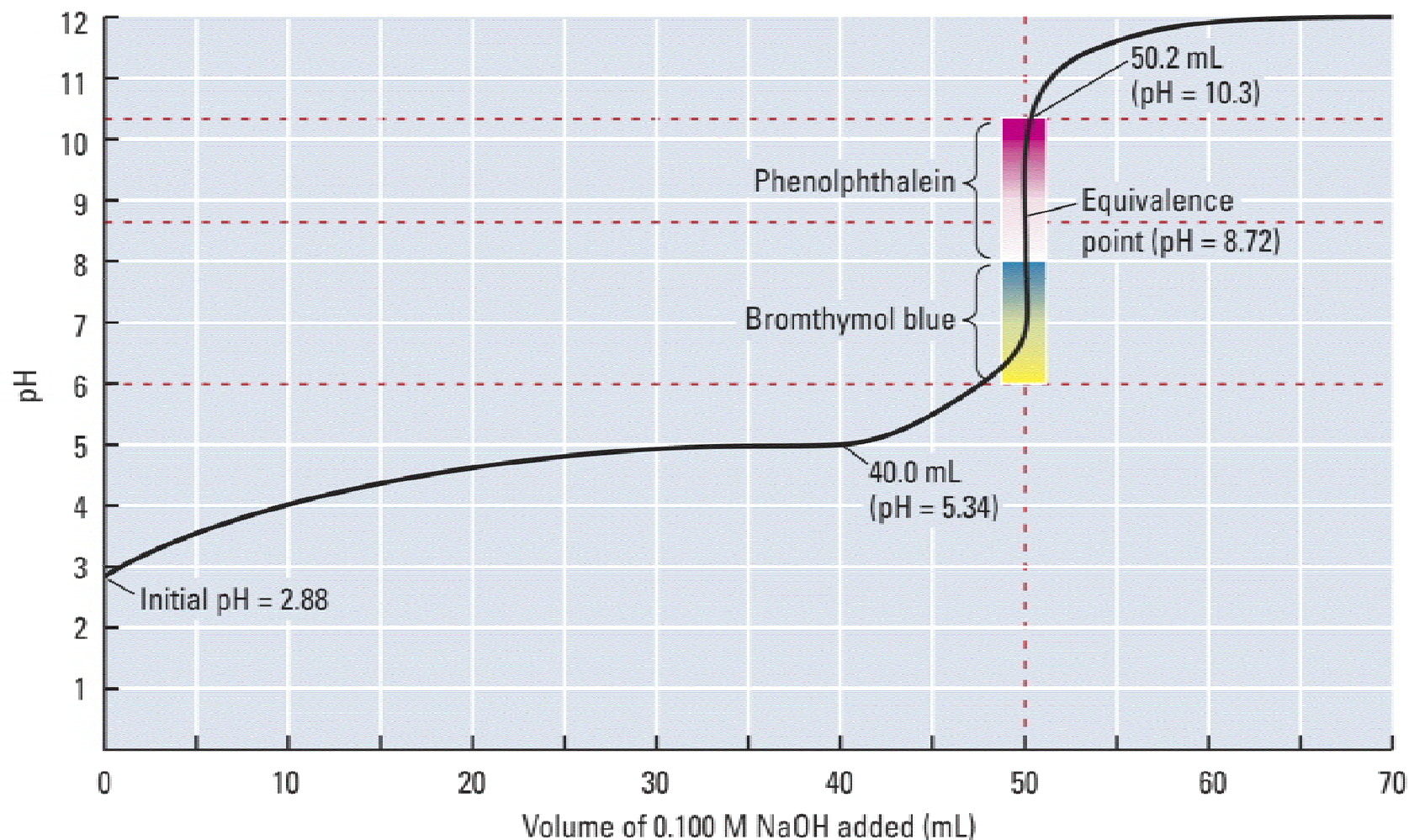
Red Cabbage as Indicator



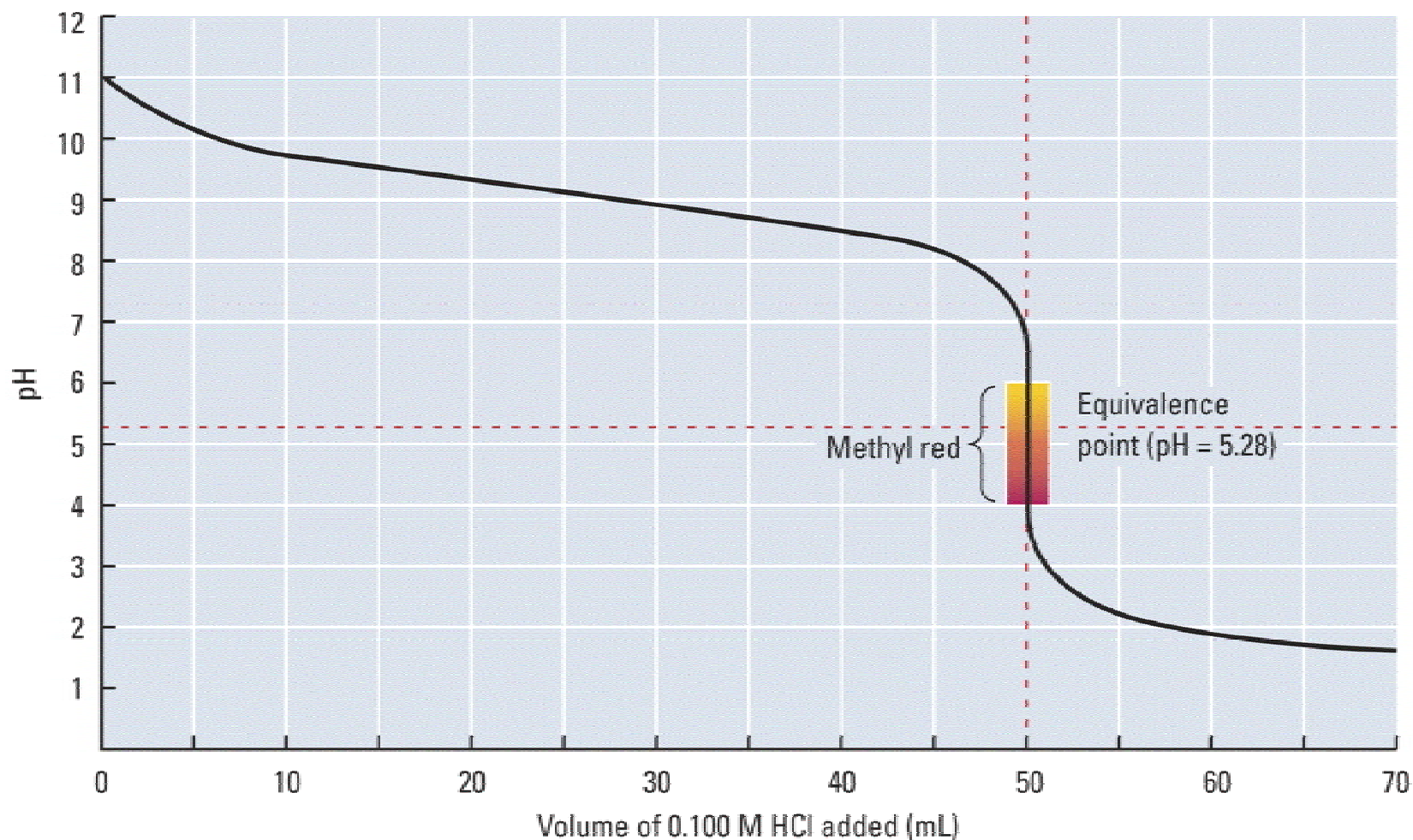
Indicator and Titration Curve



Titration of Weak Acid with Strong Base



Titration of Weak Base with Strong Acid



EXAMPLE: Derive the titration curve for the titration of 35.00 mL of 0.1000 M HCl with 0.00, 15.00, 35.00, and 50.00 mL of 0.1000 M NaOH.

At 0.00 mL of NaOH added, initial point

$$[\text{H}_3\text{O}^+] = C_{\text{HCl}} = 0.1000 \text{ M}; \text{ pH} = 1.00$$

At 15.00 mL of NaOH added, $V_a \times M_a > V_b \times M_b$ thus

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \frac{(V_a \times M_a) - (V_b \times M_b)}{(V_a + V_b)} \\ &= \frac{((35.00\text{mL}) \times (0.1000\text{M})) - ((15.00\text{mL}) \times (0.1000\text{M}))}{(35.00 + 15.00)\text{mL}} \\ &= 4.000 \times 10^{-2} \text{ M} \quad \text{pH} = 1.40 \end{aligned}$$

At 35.00 mL of NaOH added

$$V_a \times M_a = V_b \times M_b, \text{ equivalence point}$$

**at equivalence point of a
strong acid - strong base titration**

$$\text{pH} \equiv 7.00$$

At 50.00 mL of NaOH added

$$V_b \times M_b > V_a \times M_a, \text{ post equivalence point}$$

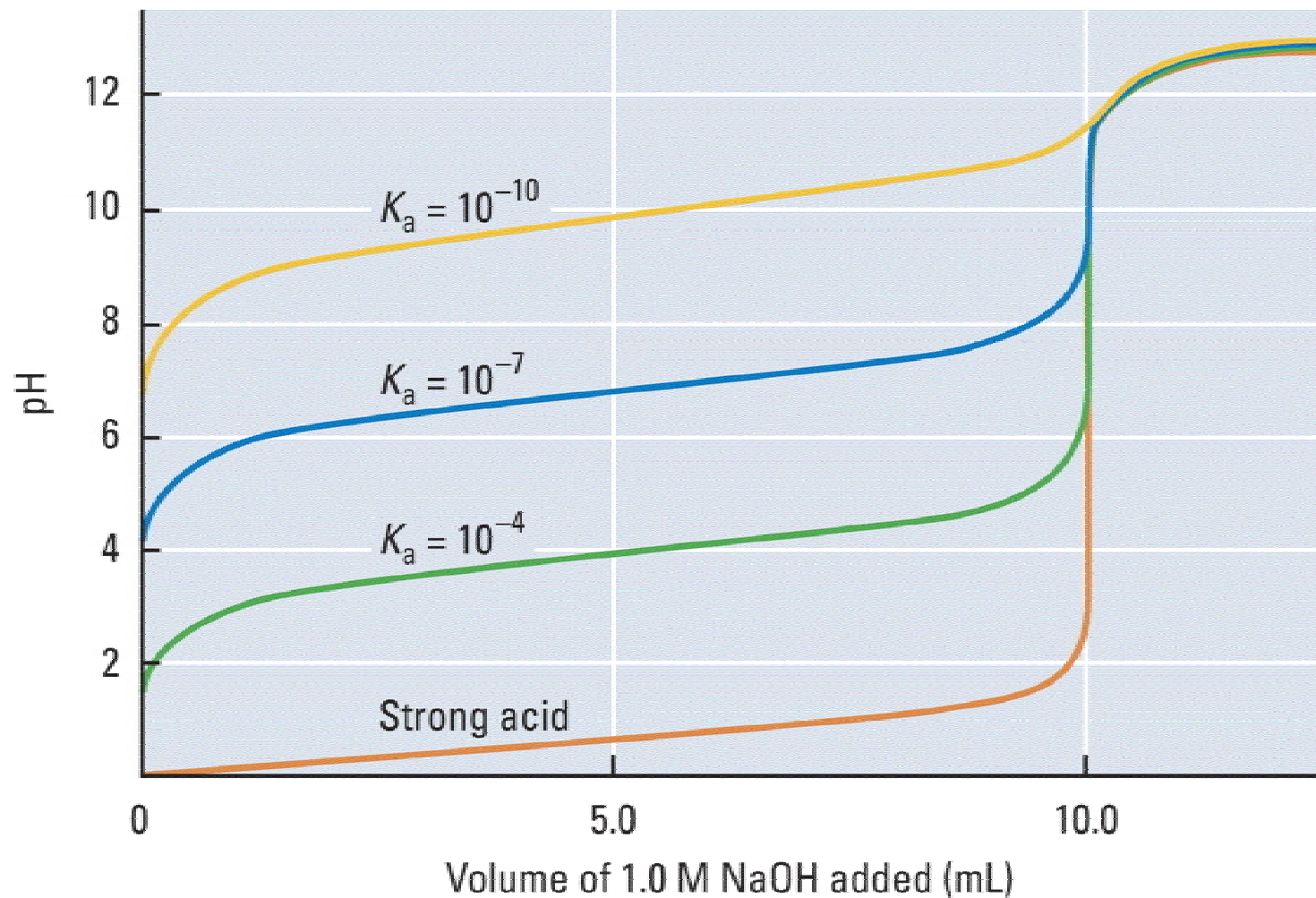
$$[\text{OH}^-] = \frac{(V_b \times M_b) - (V_a \times M_a)}{(V_a + V_b)}$$

$$= \frac{((50.00\text{mL}) \times (0.1000\text{M})) - ((35.00\text{mL}) \times (0.1000\text{M}))}{(35.00 + 50.00)\text{mL}}$$

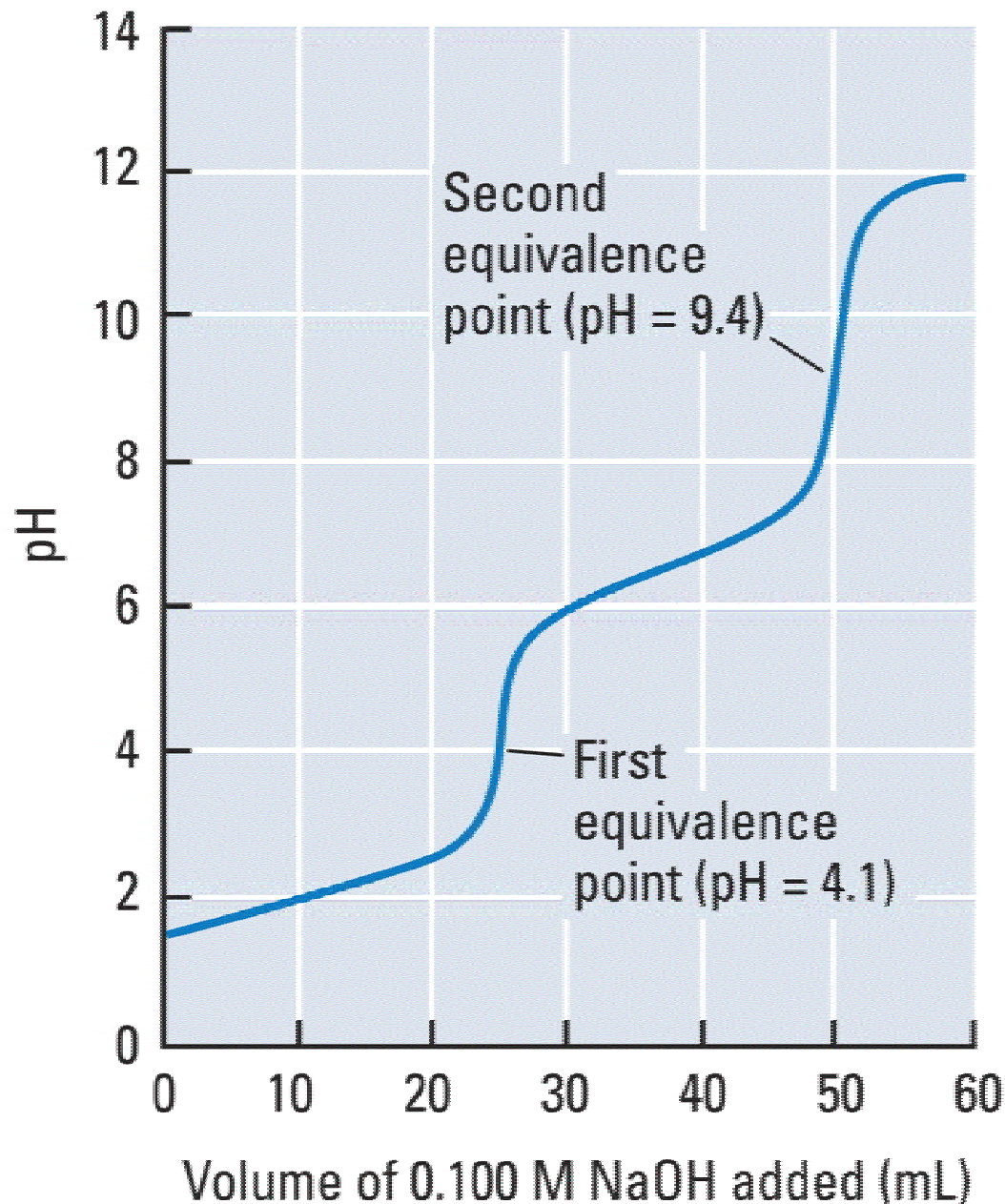
$$= 1.765 \times 10^{-2} \text{ M}; \text{ pOH} = 1.75$$

$$\text{pH} = 14.00 - 1.75 = 12.25$$

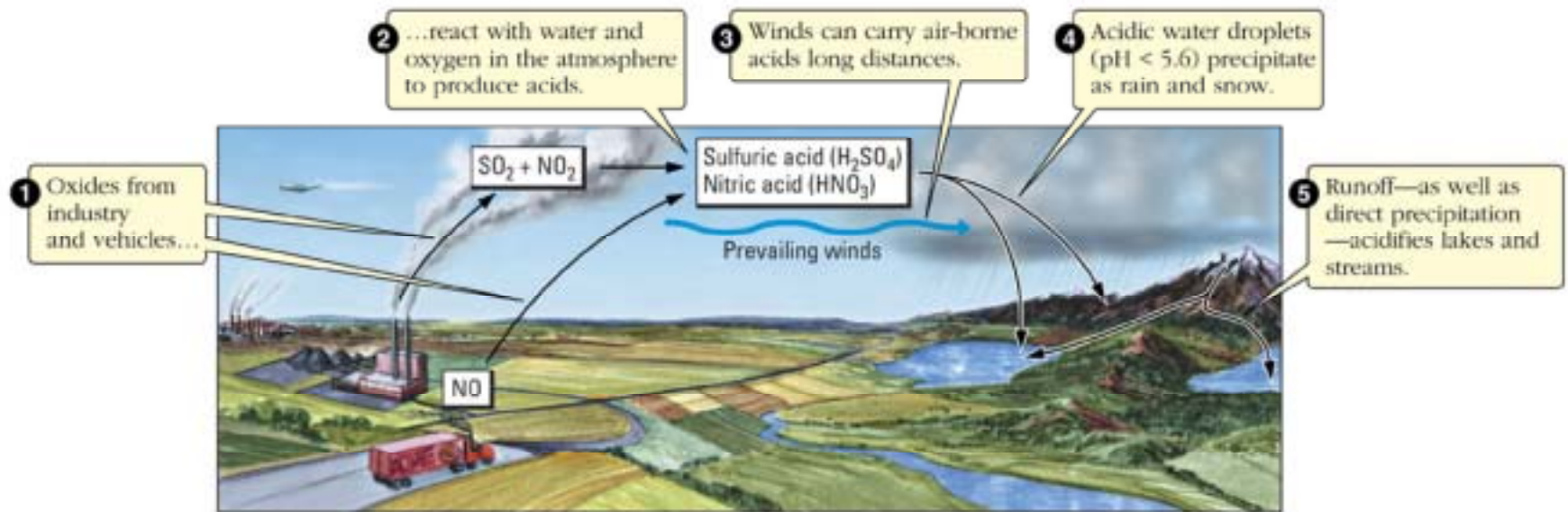
Effect of Acid Strength on Titration Curve



Titration of Diprotic Weak Acid with Strong Base



How Acid Precipitation Forms



Solubility Product Constant

Solubility-product constant $\Rightarrow K_{sp}$

constant that is equal to the solubilities of the ions produced when a substance dissolves



$$K = \frac{[A^{+y}]^x [B^{-x}]^y}{[A_xB_y]} \quad [A_xB_y] K = K_{sp} = [A^{+y}]^x [B^{-x}]^y$$

$$K_{sp} = [A^{+y}]^x [B^{-x}]^y$$

For silver sulfate



$$K_{sp} = [Ag^+]^2[SO_4^{2-}]$$

Solubility Product Constant Values

TABLE 17.2 K_{sp} Values
for Some
Slightly
Soluble Salts

Compound	K_{sp} at 25 °C
AgBr	3.3×10^{-15}
AuBr	5.0×10^{-17}
AuBr ₃	4.0×10^{-36}
CuBr	5.3×10^{-9}
Hg ₂ Br ₂ *	1.3×10^{-22}
PbBr ₂	6.3×10^{-6}
AgCl	1.8×10^{-10}
AuCl	2.0×10^{-23}
AuCl ₃	3.2×10^{-25}
CuCl	1.9×10^{-7}
Hg ₂ Cl ₂ *	1.1×10^{-18}
PbCl ₂	1.7×10^{-5}
AgI	1.5×10^{-15}
AuI	1.6×10^{-13}
AuI ₃	1.0×10^{-46}
CuI	5.1×10^{-12}
Hg ₂ I ₂ *	4.5×10^{-29}
HgI ₂	4.0×10^{-29}
PbI ₂	8.7×10^{-9}
Ag ₂ SO ₄	1.7×10^{-5}
BaSO ₄	1.1×10^{-10}
PbSO ₄	1.8×10^{-8}
Hg ₂ SO ₄ *	6.8×10^{-7}
SrSO ₄	2.8×10^{-7}

*These compounds contain the diatomic ion Hg₂²⁺.

The Common Ion Effect

common ion

- second source which is completely dissociated
- In the presence of a second source of the ion, there will be less dissolved than in its absence

common ion effect

- a salt will be less soluble if one of its constituent ions is already present in the solution

EXAMPLE: What is the **molar solubility** of **AgCl in pure water** and in **1.0 M NaCl**?



$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = 1.82 \times 10^{-10} \text{M}^2$$

$$\text{let } x = \text{molar solubility} = [\text{Ag}^+] = [\text{Cl}^-]$$

$$(x)(x) = K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = 1.82 \times 10^{-10} \text{M}^2$$

$$x = 1.35 \times 10^{-5} \text{M}$$



$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = 1.82 \times 10^{-10} \text{M}^2$$

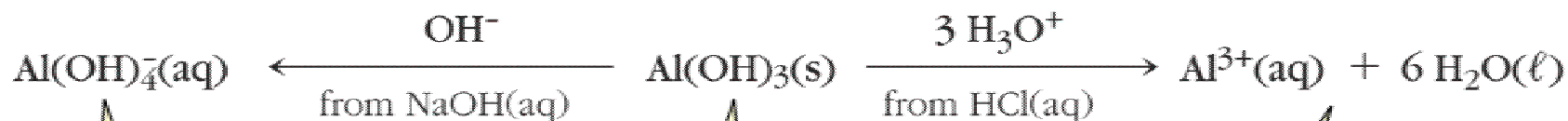
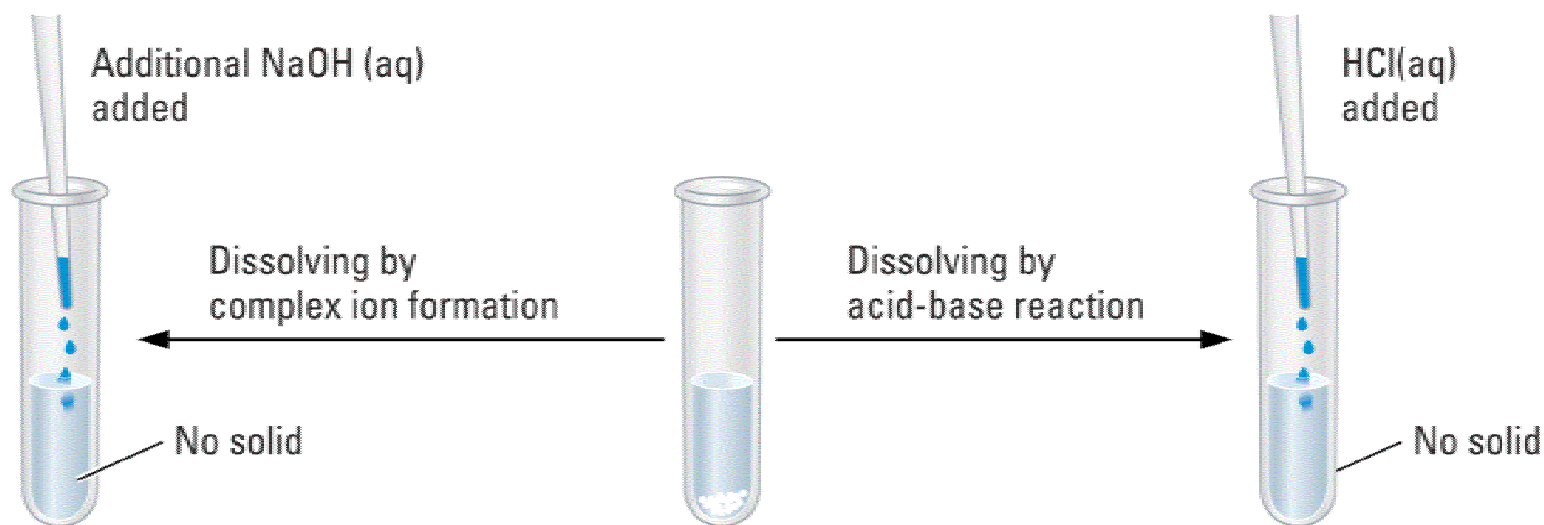
$$\text{let } x = \text{molar solubility} = [\text{Ag}^+]$$

$$[\text{Cl}^-] = 1.0 \text{ M}$$

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = (x)(1.0 \text{M}) = 1.82 \times 10^{-10} \text{M}^2$$

$$x = 1.82 \times 10^{-10} \text{M}$$

Amphoterism



The Al(OH)_3 precipitate dissolves by forming Al(OH)_4^- when additional NaOH is added.

Adding NaOH solution to a solution containing Al^{3+} ions has precipitated Al(OH)_3 .

The Al(OH)_3 precipitate dissolves when it reacts with hydrochloric acid.

Reactant Quotient, Q

Reactant Quotient, Q

- ion product of the initial concentration
- same form as solubility product constant

$Q < K_{sp}$ - no precipitate forms

unsaturated solution

$Q > K_{sp}$ - precipitate may form to restore
condition of saturated solution

$Q = K_{sp}$ - no precipitate forms, saturated solution

Will Precipitation Occur?

