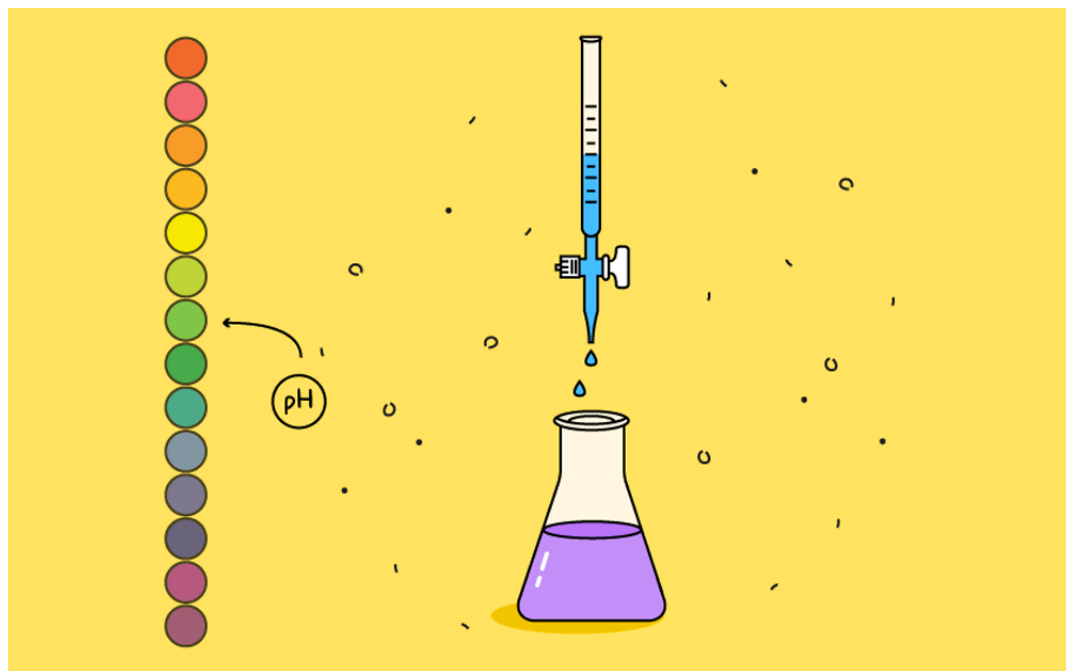




Chapter 17. Aqueous equilibria

Chapter outline

- Common ion effect
- Buffers
 - Henderson-Hasselbalch equation
- Acid-base titration
 - Strong acid by strong base
 - Weak acid by strong base
 - Weak base by strong acid
- pH indicators
- Salt solubility and K_{sp}
- Precipitation reactions
- Complex ions

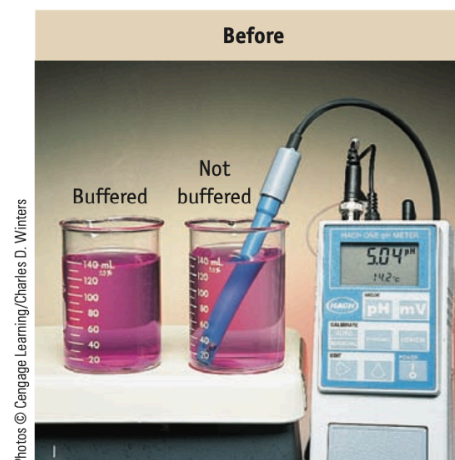


Common ion effect

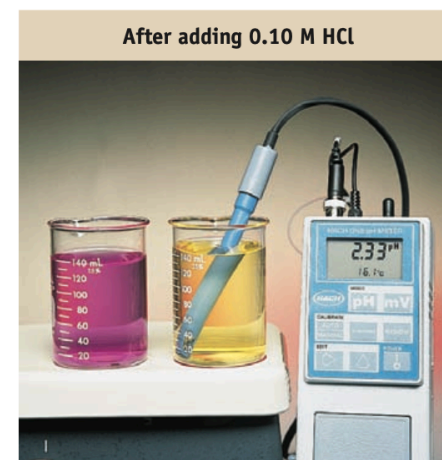
- Solutions where both HA and A⁻ are present
- pH of 0.25 M CH₃COOH (aq) = 2.67
 - $[H_3O^+] = \sqrt{K_a[HA]}$
- pH of 0.25 M CH₃COOH/0.10 M CH₃COO⁻?
- CH₃COOH (aq) + H₂O (l) ⇌ CH₃COO⁻ (aq) + H₃O⁺ (aq)
- Le Chatelier's principle

Buffers

- Add 0.010 mol HCl to 1.0 L H₂O
 - pH drops by 5 units (7 → 2)
- Add 0.010 mol HCl to 1.0 L human blood
 - pH drops by 0.1 unit (7.4 → 7.3)
- Blood is buffered against pH change
 - **Acid** reacts with (neutralizes) added **OH⁻** ions
 - **Base** reacts with (neutralizes) added **H₃O⁺** ions
 - Acid and base don't react with each other
- Good way to prepare buffer: **from weak conjugate acid-base pair (**HA** and **A⁻**)**



(a) The pH electrode is indicating the pH of water that contains a trace of acid (and bromphenol blue acid-base indicator). The solution at the left is a buffer solution with a pH of about 7. (It also contains bromphenol blue dye.)



(b) When 5 mL of 0.10 M HCl is added to each solution, the pH of the water drops several units, whereas the pH of the buffer stays essentially constant, as implied by the fact that the indicator color does not change.

Buffers

- K values for $\text{HA} + \text{OH}^-$ and $\text{A}^- + \text{H}_3\text{O}^+$ reactions are typically very large
 - These reactions are essentially forward-only
 - OH^- and H_3O^+ are effectively removed

Table 18.1 Some Commonly Used Buffer Systems

Weak Acid	Conjugate Base	Acid K_a ($\text{p}K_a$)	Useful pH Range
Phthalic acid, $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$	Hydrogen phthalate ion, $\text{C}_6\text{H}_4(\text{CO}_2\text{H})(\text{CO}_2)^-$	1.3×10^{-3} (2.89)	1.9–3.9
Acetic acid, $\text{CH}_3\text{CO}_2\text{H}$	Acetate ion, CH_3CO_2^-	1.8×10^{-5} (4.74)	3.7–5.8
Dihydrogen phosphate ion, H_2PO_4^-	Hydrogen phosphate ion, HPO_4^{2-}	6.2×10^{-8} (7.21)	6.2–8.2
Hydrogen phosphate ion, HPO_4^{2-}	Phosphate ion, PO_4^{3-}	3.6×10^{-13} (12.44)	11.4–13.4

pH of a buffer solution

What is the pH of an $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ buffer with $[\text{CH}_3\text{COOH}] = 0.700 \text{ M}$ and $[\text{CH}_3\text{COO}^-] = 0.600 \text{ M}$?

pH of a buffer solution: Henderson-Hasselbalch equation

- From previous example: $[H_3O^+] = \frac{(K_a)[CH_3COOH]}{[CH_3COO^-]}$
- General expression: $[H_3O^+] = \frac{(K_a)[HA]}{[A^-]}$
- $-\log[H_3O^+] = -\log K_a - \log \frac{[HA]}{[A^-]}$
- $-\log[H_3O^+] = -\log K_a + \log \frac{[A^-]}{[HA]}$
- $pH = pK_a + \log \frac{[A^-]}{[HA]}$

Henderson-Hasselbalch equation

- $pH = pK_a + \log \frac{[A^-]}{[HA]}$
- Can use H-H expression when:
 - $3 \leq pH \leq 11$
 - pH close to pK_a of HA
 - HA with $K_a > 10^{-3}$ and A^- with $K_b > 10^{-3}$ are not weak enough to serve as buffers
 - $[HA]_0$ and $[A^-]_0$ are **relatively large**
- pH primarily established by pK_a
 - $[HA] = [A^-]$: $pH = pK_a$
 - $[HA] > [A^-]$: $pH < pK_a$
 - $[HA] < [A^-]$: $pH > pK_a$

Henderson-Hasselbalch equation

Benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$, 2.00 g) and sodium benzoate ($\text{C}_6\text{H}_5\text{COONa}$, 2.00 g) are dissolved in enough water to make 1.00 L of solution. Calculate the pH of the solution using the Henderson-Hasselbalch equation.

Preparing buffer solutions of desired pH

- Choose HA with pKa close to desired pH
- Get exact pH value by adjusting HA/A⁻ ratio
- To maintain adequate buffer capacity: $0.10 \text{ M} \leq [\text{HA}], [\text{A}^-] \leq 1.0 \text{ M}$
- Buffers lose buffering capacity when too much OH⁻ or H₃O⁺ is added
- Both HA and A⁻ are dissolved in the same solution
 - $V_{\text{HA}} = V_{\text{A}^-}$
 - We are concerned only about the **moles** of HA and A⁻ when preparing a buffer
 - Diluting a buffer doesn't change its pH

Preparing a buffer solution

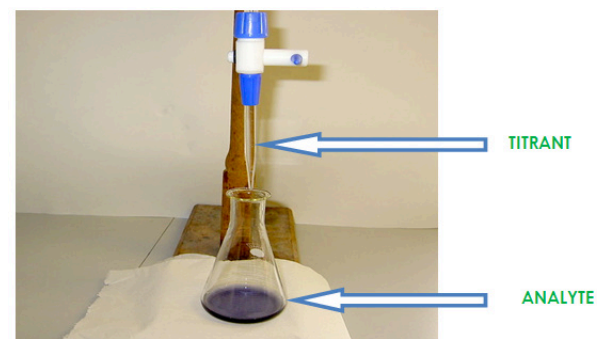
Describe how to prepare a buffer solution from Na_2HPO_4 and NaH_2PO_4 to have a pH of 7.5
(pK_a of H_2PO_4^- is 7.21)

How does a buffer maintain constant pH?

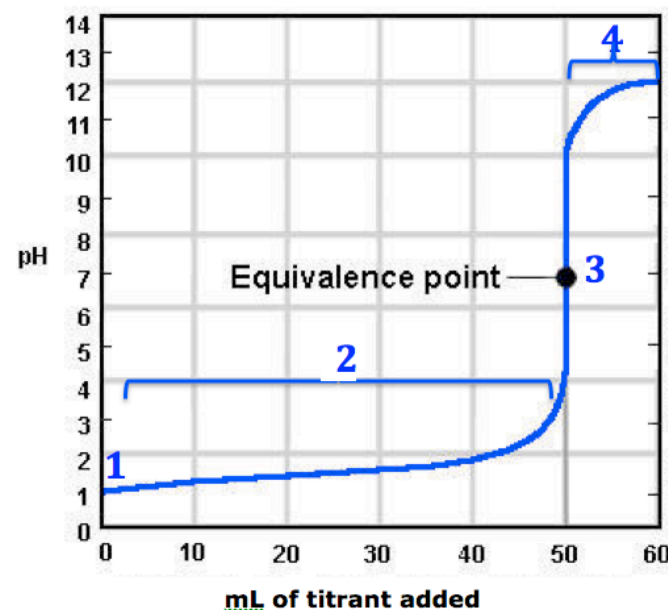
What is the change in pH when 1.00 mL of 1.00 M HCl is added to (1) 1.000 L of pure water, and (2) 1.000 L of $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$ buffer with $[\text{CH}_3\text{COOH}] = 0.700 \text{ M}$ and $[\text{CH}_3\text{COO}^-] = 0.600 \text{ M}$?

Acid-base titrations

- Recall from Ch. 4: titration = slow addition of titrant to analyte
 - Titrant = strong acid or base
 - Analyte strong/weak acid or base
- Purpose of titration:
 - To determine quantity of unknown acid/base
 - To determine identity of unknown acid/base (molar mass, pK_a or pK_b)
- Learning goals:
 - How to draw and interpret a **titration curve**
 - How to **find pH** of analyte at any point of titration
 - How to **find pK_a or pK_b** from titration data



TITRATION PROCESS



Titration curve

- Plot of analyte pH vs. volume of titrant added
- Four important regions
 - pH of **initial analyte solution**
 - pH as titrant is added but **before equivalence point**
 - Buffer region
 - pH at **equivalence point**
 - Equivalence point: analyte completely consumed by titrant
 - pH **after equivalence point**
- Two examples
 - Titrating 50.0 mL of 0.100 M **HCl** (aq) with 0.100 M **NaOH** (aq)
 - Strong acid – strong base (SA – SB)
 - Titrating 100.0 mL of 0.100 M **CH₃COOH** (aq) with 0.100 M **NaOH** (aq)
 - Weak acid – strong base (WA – SB)

Titrating 50.0 mL of 0.100 M HCl with 0.100 M NaOH

1) **Initial HCl pH:** $-\log(0.100 \text{ M}) = 1.000$

2) After adding 10.00 mL 0.100 M NaOH (**before equivalence point**)

Titrating 50.0 mL of 0.100 M HCl with 0.100 M NaOH

2) After adding 10.00 mL 0.100 M NaOH (**before equivalence point**)

- SA-SB neutralization rxns have large K values: “one way” (\rightarrow)
- **Stoichiometry problem** (analyte in excess, titrant LR)
 - That means you need MOLES of titrant to calculate MOLES of excess analyte!
- **pH** controlled by the concentration of **excess analyte** (here HCl)
- Product salt is neutral and doesn't affect pH
- **Don't forget to add V analyte and V titrant to calculate final $[\text{H}_3\text{O}^+]$!**

Titrating 50.0 mL of 0.100 M HCl with 0.100 M NaOH

3) Equivalence point

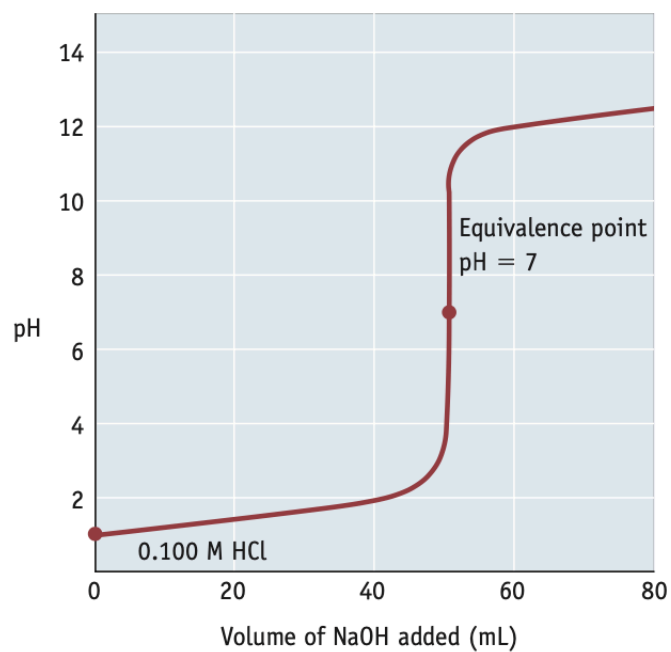
- At the equivalence point **moles HCl = moles NaOH**
- That means, it will occur when $5.00 \times 10^{-3} \text{ mol} \times \frac{1 \text{ L}}{0.100 \text{ mol}} = 50.0 \text{ mL NaOH}$ are added
- No excess $\text{H}_3\text{O}^+/\text{OH}^-$ present, as HCl and NaOH are fully neutralized
- NaCl does not contribute to pH (neutral salt)
- **pH = pH of neutral H_2O = 7.00**
 - This holds at the equivalence point of every strong acid – strong base titration!

Titrating 50.0 mL of 0.100 M HCl with 0.100 M NaOH

4) After equivalence point

- H_3O^+ is fully neutralized
- pH controlled by excess OH^- coming from the titrant
- After adding 55.0 mL of 0.100 M NaOH

Titration curve (0.100 M HCl with 0.100 M NaOH)



50.0 mL of 0.100 M HCl titrated
with 0.100 M NaOH

Volume of base added	pH
0.0	1.00
10.0	1.18
20.0	1.37
40.0	1.95
45.0	2.28
48.0	2.69
49.0	3.00
50.0	7.00
51.0	11.00
55.0	11.68
60.0	11.96
80.0	12.36
100.0	12.52
very large amount	13.00 (maximum)

Titrating 100.0 mL of 0.100 M CH_3COOH with 0.100 M NaOH

1) Initial CH_3COOH pH

- Equilibrium hydrolysis problem
 - $\text{CH}_3\text{COOH (aq)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{CH}_3\text{COO}^- \text{(aq)} + \text{H}_3\text{O}^+ \text{(aq)}$
- ICE table
- If $100K_a < [\text{A}]_0$ holds (which is usually the case), ICE table boils down to $[\text{H}_3\text{O}^+] = \sqrt{[\text{HA}]K_a}$

Titrating 100.0 mL of 0.100 M CH_3COOH with 0.100 M NaOH

2) After adding 90.0 mL 0.100 M NaOH (**before equivalence point**)

- CH_3COONa (specifically, the anion CH_3COO^-) **affects pH**
- Substantial amounts of CH_3COOH and CH_3COO^- (**conjugate weak acid – weak base pair**) are present = **BUFFER**
- **Buffer region**
- Can use **Henderson-Hasselbalch equation** ($\text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]}$) to get pH

Titrating 100.0 mL of 0.100 M CH_3COOH with 0.100 M NaOH

A special point in the buffer region: **half-equivalence point** (HEP)

- **Enough NaOH** has been added to **neutralize half the moles** of CH_3COOH that were originally present.
- So, from the original CH_3COOH :
 - 50% of the moles are still CH_3COOH
 - 50% have been converted to the conjugate base CH_3COO^-
 - **$[\text{HA}] = [\text{A}^-]$**
 - $pH = pK_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$ is reduced to **$pH = pK_a$**

Titrating 100.0 mL of 0.100 M CH_3COOH with 0.100 M NaOH

3) Equivalence point

- At the equivalence point moles CH_3COOH = moles NaOH
- That means, it will occur when $0.0100 \text{ mol} \times \frac{1 \text{ L}}{0.100 \text{ mol}} = 100. \text{ mL}$ NaOH are added
- CH_3COOH and NaOH (OH^-) are fully neutralized
- **pH controlled by CH_3COO^-** , a weak base (CB of CH_3COOH)

Titrating 100.0 mL of 0.100 M CH_3COOH with 0.100 M NaOH

3) Equivalence point

- Equilibrium hydrolysis problem
 - $\text{CH}_3\text{COO}^- (\text{aq}) + \text{H}_2\text{O} (\text{l}) \rightleftharpoons \text{CH}_3\text{COOH} (\text{aq}) + \text{OH}^- (\text{aq})$
- ICE table
- If $100K_b < [A]_0$ holds (which is usually the case), ICE table boils down to

$$[\text{OH}^-] = \sqrt{[A^-]K_b}$$

Titrating 100.0 mL of 0.100 M CH_3COOH with 0.100 M NaOH

4) After equivalence point

- H_3O^+ is fully neutralized
- pH controlled by excess OH^- coming from the titrant
- After adding 110.0 mL of 0.100 M NaOH

Titration curve (0.100 M CH_3COOH with 0.100 M NaOH)

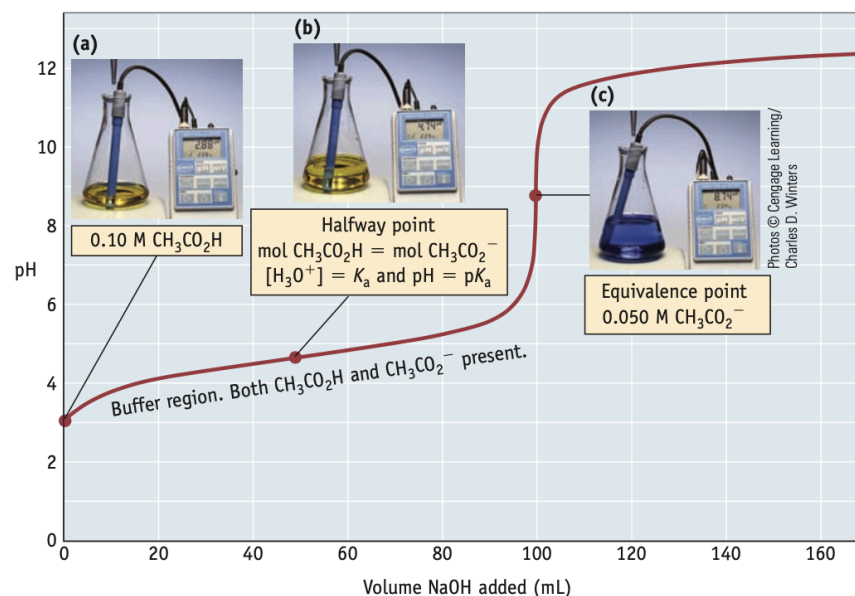


FIGURE 18.5 The change in pH during the titration of a weak acid with a strong base.

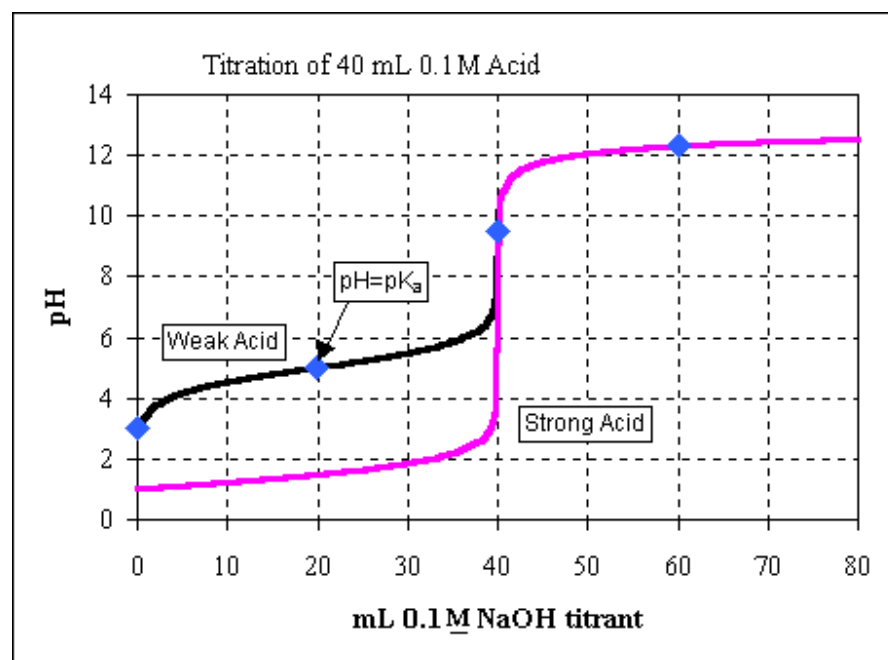
Here, 100.0 mL of 0.100 M acetic acid is titrated with 0.100 M NaOH. Note especially the following:

(a) Before titration. A 0.100 M solution of acetic acid has a pH of 2.87. **(b) Halfway point.** The pH at the point at which half the acid has reacted with base is equal to the pK_a for the acid ($\text{pH} = \text{pK}_a = 4.74$).

(c) Equivalence point. The solution contains the acetate ion, a weak base. Therefore, the solution is basic, with a pH of 8.72.

Summary: titration of strong vs. weak acid (equimolar)

- Major species present at each point of weak acid titration (besides H_2O)
 - 1) HA
 - 2) HA , A^-
 - 3) A^-
 - 4) OH^-
- Neutralization: stoichiometry problem
- Hydrolysis: equilibrium problem



What about titration of a weak base with a strong acid?

	Weak acid titration with strong base	Weak base titration with strong acid
Neutralization reaction	$\text{HA} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{A}^-$	$\text{B} + \text{H}_3\text{O}^+ \rightarrow \text{H}_2\text{O} + \text{BH}^+$
Reaction with H_2O before titration begins	$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$ (K_a , $\text{p}K_a$)	$\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^-$ (K_b , $\text{p}K_b$)
Reaction with H_2O at equivalence point	$\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{HA}$ (K_b , $\text{p}K_b$)	$\text{BH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{B} + \text{H}_3\text{O}^+$ (K_a , $\text{p}K_a$)

Remember, $\text{pH} + \text{pOH} = 14.00$
 $\text{p}K_a + \text{p}K_b = 14.00$

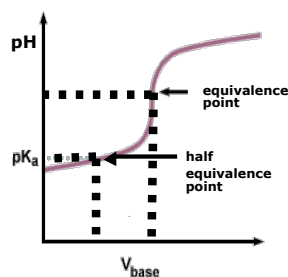


Figure (2): Titration curve for the weak acid HA with NaOH

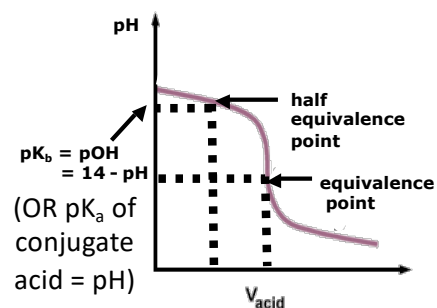


Figure (3): Titration curve for the weak base B with HCl

What about titration of a weak base with a strong acid?

- As a consequence:
- Initial pH < initial pH of equimolar strong base
 - $B + H_2O \rightleftharpoons BH^+ + OH^-$
 - $[OH^-] = \sqrt{[B]K_b}$
- Buffer region: pH only changes slightly; both B and BH^+ are present.
 - $pH = pK_a + \log \frac{[B]}{[BH^+]}$ (or $pOH = pK_b + \log \frac{[BH^+]}{[B]}$)
- At HEP: $pK_b = pOH$ (or $pK_a = pH$)
- At EP: $pH < 7$ (hydrolysis of BH^+)
 - $[H_3O^+] = \sqrt{[BH^+]K_a}$
- Past EP: pH changes due to excess H^+

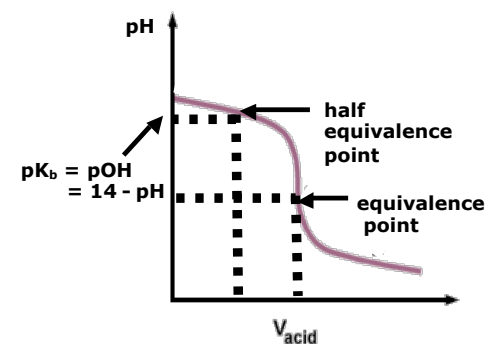


Figure (3): Titration curve for the weak base B with HCl

pH indicators

- Usually a compound that is itself a weak acid/base (HInd/Ind^-)
- Important property
 - HInd form has one color
 - Ind^- form has another color
- Phenolphthalein
 - $\text{HPhen (aq)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{Phen}^- \text{ (aq)} + \text{H}_3\text{O}^+ \text{ (aq)}$
 - $\text{pK}_a = 9.4$
- Bromthymol blue
 - $\text{HBrom (aq)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{Brom}^- \text{ (aq)} + \text{H}_3\text{O}^+ \text{ (aq)}$
 - $\text{pK}_a = 7.0$

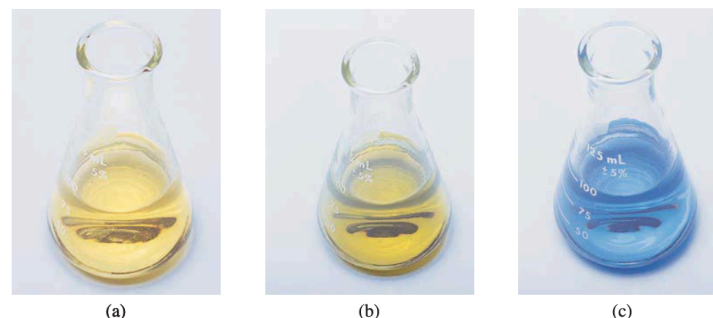
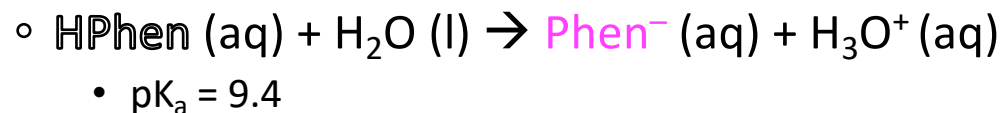


FIGURE 15.7

(a) Yellow acid form of bromthymol blue; (b) a greenish tint is seen when the solution contains 1 part blue and 10 parts yellow; (c) blue basic form.

pH indicators

- Phenolphthalein



- Henderson-Hasselbalch equation:

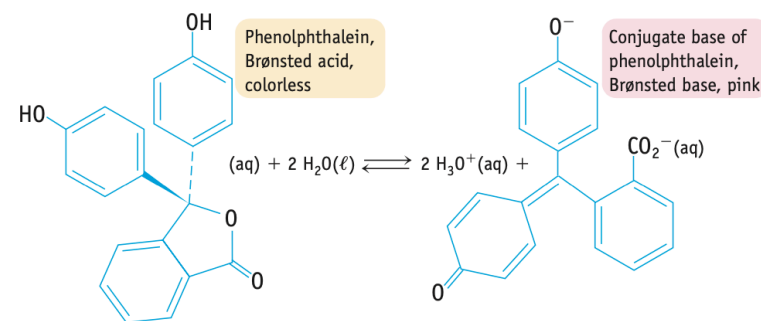
- $\text{pH} = 9.4 + \log \frac{[\text{Phen}^-]}{[\text{HPhen}]}$

- At $\text{pH} > 9.4$, $[\text{Phen}^-] > [\text{HPhen}]$

- Solution looks pink/magenta

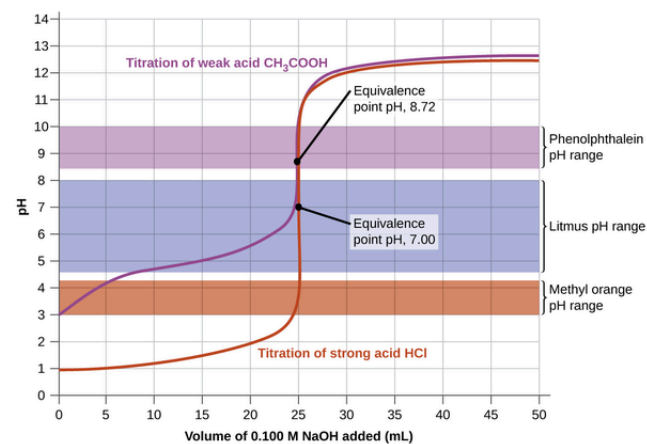
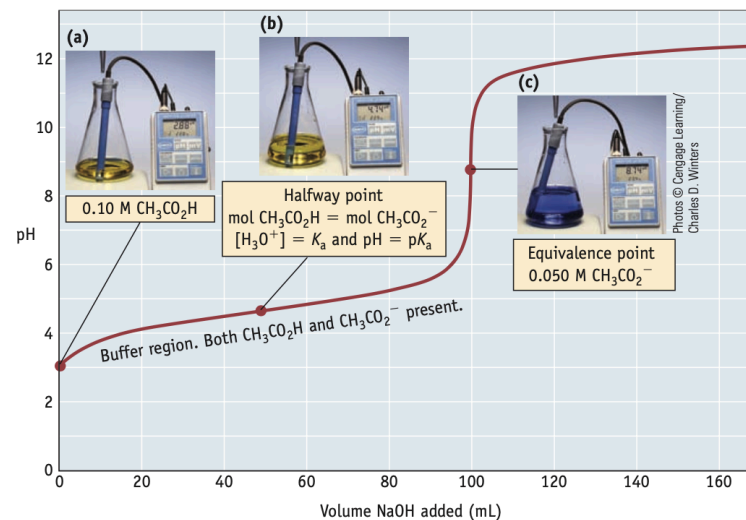
- At $\text{pH} < 9.4$, $[\text{HPhen}] > [\text{Phen}^-]$

- Solution looks clear



pH indicators

- Phenolphthalein
- If an acid-base titration has an equivalence point around pH 9, this equivalence point can be detected with phenolphthalein
 - pH @ equivalence point doesn't have to be EXACTLY 9.4 (since pH changes by many units around equivalence point)
- Endpoint = pH at which indicator changes color
- Equivalence point = analyte completely neutralized by titrant



pH indicators

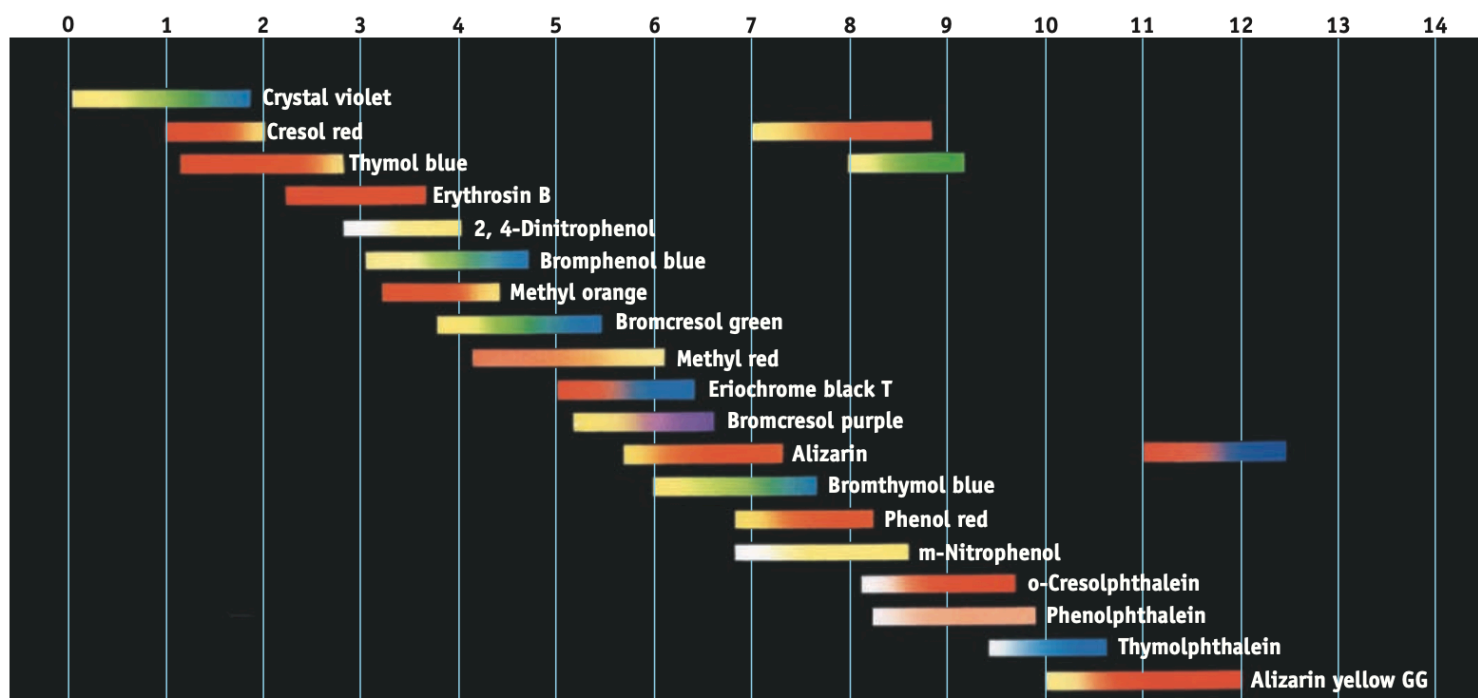


FIGURE 18.10 Common acid–base indicators. The color changes occur over a range of pH values. Notice that a few indicators have color changes over two different pH ranges.

Solubility of salts



Crocoite, lead(II) chromate, PbCrO_4



Rhodochrosite, manganese(II) carbonate, MnCO_3



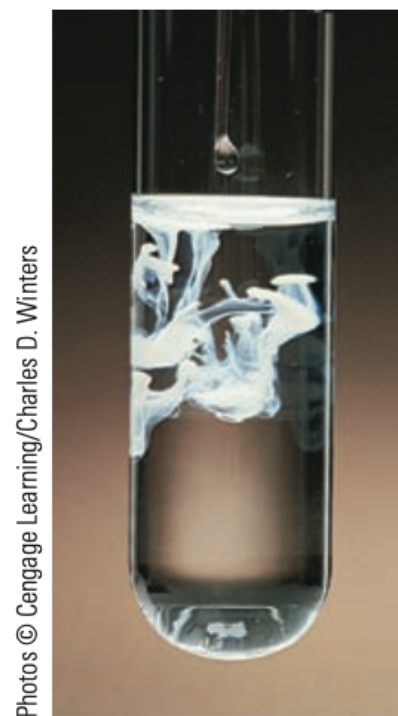
Copper(II) minerals: green malachite, $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$, and blue azurite, $2 \text{CuCO}_3 \cdot \text{Cu(OH)}_2$

FIGURE 18.11 Some insoluble substances.

- “Insoluble” salt = less than 0.01 mol dissolves in 1 L of solution
- Quantifying solubility
- Conditions that affect solubility

Solubility product constant (K_{sp})

- $\text{AgBr (s)} \rightleftharpoons \text{Ag}^+ \text{ (aq)} + \text{Br}^- \text{ (aq)}$
- Equilibrium – saturated solution (25 °C)
 - $[\text{Ag}^+] = [\text{Br}^-] = 7.35 \times 10^{-7} \text{ M}$
- $K_{sp} = [\text{Ag}^+][\text{Br}^-] = (7.35 \times 10^{-7})^2 = 5.40 \times 10^{-13}$
 - AgBr not in equilibrium expression because (s)
 - K_{sp} values often very small
- In general
 - $\text{A}_x\text{B}_y \text{ (s)} \rightarrow x \text{ A}^{y+} \text{ (aq)} + y \text{ B}^{x-} \text{ (aq)}$
 - $K_{sp} = (\text{A}^{y+})^x (\text{B}^{x-})^y$



Photos © Cengage Learning/Charles D. Winters

Calculating K_{sp}

- CaF_2 , the main component of the mineral fluorite, dissolves to a slight extent in water. Calculate the K_{sp} value for CaF_2 if $[\text{Ca}^{2+}]$ has been found to be $2.3 \times 10^{-4} \text{ M}$.

Insoluble salts and their K_{sp} values

Table 18.2 Some Common Insoluble Compounds and Their K_{sp} Values*

Formula	Name	K_{sp} (25 °C)	Common Names/Uses
CaCO_3	Calcium carbonate	3.4×10^{-9}	Calcite, iceland spar
MnCO_3	Manganese(II) carbonate	2.3×10^{-11}	Rhodochrosite (forms rose-colored crystals)
FeCO_3	Iron(II) carbonate	3.1×10^{-11}	Siderite
CaF_2	Calcium fluoride	5.3×10^{-11}	Fluorite (source of HF and other inorganic fluorides)
AgCl	Silver chloride	1.8×10^{-10}	Chlorargyrite
AgBr	Silver bromide	5.4×10^{-13}	Used in photographic film
CaSO_4	Calcium sulfate	4.9×10^{-5}	Hydrated form is commonly called <i>gypsum</i>
BaSO_4	Barium sulfate	1.1×10^{-10}	Barite (used in "drilling mud" and as a component of paints)
SrSO_4	Strontium sulfate	3.4×10^{-7}	Celestite
Ca(OH)_2	Calcium hydroxide	5.5×10^{-5}	Slaked lime

* The values in this table were taken from *Lange's Handbook of Chemistry*, 15th edition, McGraw-Hill Publishers, New York, NY (1999). Additional K_{sp} values are given in Appendix J.

Solubility from K_{sp}

The K_{sp} value for MgF_2 is 5.2×10^{-11} . Calculate the solubility of MgF_2 in (a) M, and (b) g/L

Solubility from K_{sp}

- Relative solubilities can be deduced by comparing K_{sp} values ONLY if salts have the same cation to anion ratio
 - The smaller the K_{sp} , the less soluble the salt
- $\text{AgCl (s)} \rightleftharpoons \text{Ag}^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)}$
 - $K_{sp} = 1.8 \times 10^{-10}$
 - Solubility = $\sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5} \text{ M}$
- $\text{Ag}_2\text{CrO}_4 \text{ (s)} \rightleftharpoons 2 \text{Ag}^+ \text{ (aq)} + \text{CrO}_4^{2-} \text{ (aq)}$
 - $K_{sp} = 9.0 \times 10^{-12}$
 - Solubility = $\sqrt[3]{\frac{9.0 \times 10^{-12}}{4}} = 1.3 \times 10^{-4} \text{ M}$

Solubility and common ion effect

- Le Chatelier's principle
- When 1.0 M AgNO_3 (aq) is added to saturated AgCH_3COO (aq), more AgCH_3COO (s) forms

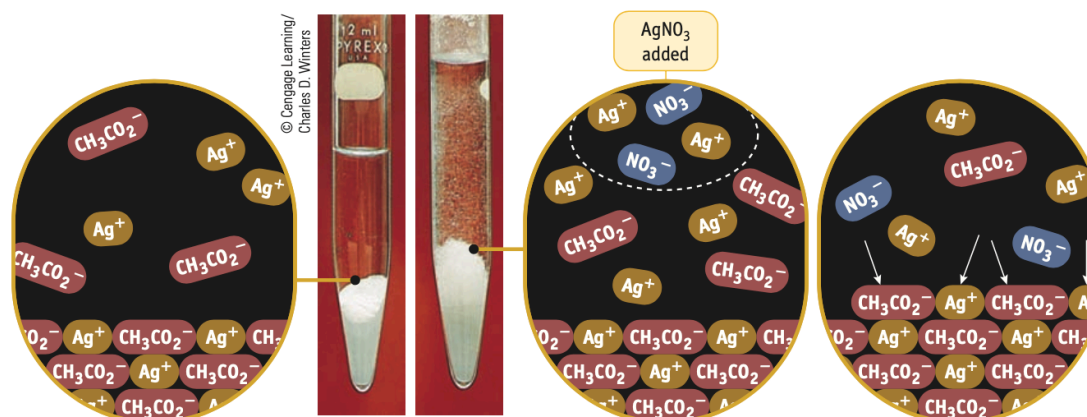


FIGURE 18.13 The common ion effect. The tube at the *left* contains a saturated solution of silver acetate, AgCH_3CO_2 . When 1.0 M AgNO_3 is added to the tube (*right*), more solid silver acetate forms.

Solubility and common ion effect

If AgCl (s) is placed in 1.00 L of 0.55 M NaCl , what mass of AgCl will dissolve?

Effect of basic anions on salt solubility

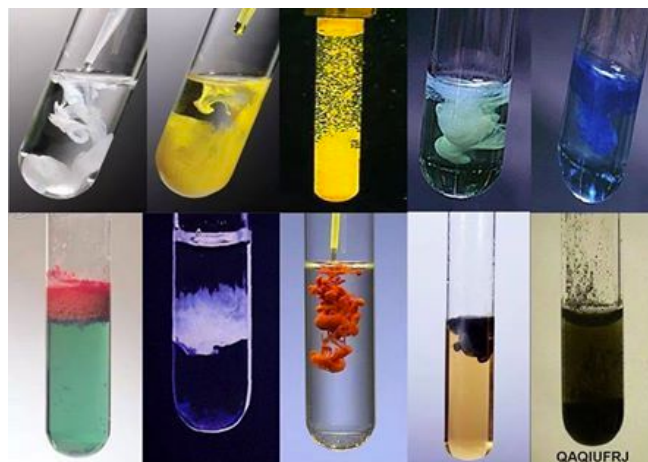
- Salts containing anions that are conjugate bases of a weak acid
- Anions are relatively strong bases and react with water
 - $\text{PbS (s)} \rightleftharpoons \text{Pb}^{2+} \text{ (aq)} + \text{S}^{2-} \text{ (aq)}$ K_{sp}
 - $\text{S}^{2-} \text{ (aq)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{HS}^- \text{ (aq)} + \text{OH}^- \text{ (aq)}$ $K_{\text{b}} = 1 \times 10^5$
 - Overall reaction
 - $\text{PbS (s)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{Pb}^{2+} \text{ (aq)} + \text{HS}^- \text{ (aq)} + \text{OH}^- \text{ (aq)}$ $K'_{\text{sp}} = K_{\text{sp}}K_{\text{b}} = 3 \times 10^{-28}$
- This increases solubility of salt
 - PO_4^{3-} , CH_3COO^- , CO_3^{2-} , CN^- , S^{2-}

Effect of basic anions on salt solubility

- Insoluble salts whose anion is a conjugate base of a weak acid dissolve in strong acids
 - CH_3COO^- , CO_3^{2-} , OH^- , PO_4^{3-} , S^{2-}
- $\text{Mg}(\text{OH})_2 (\text{s}) + 2 \text{H}_3\text{O}^+ (\text{aq}) \rightarrow 4 \text{H}_2\text{O} (\text{l}) + \text{Mg}^{2+} (\text{aq})$
 - $\text{Mg}(\text{OH})_2 (\text{s}) \rightleftharpoons \text{Mg}^{2+} (\text{aq}) + 2 \text{OH}^- (\text{aq})$ $K_{\text{sp}} = 5.6 \times 10^{-12}$
 - $2 \text{OH}^- + 2 \text{H}_3\text{O}^+ \rightleftharpoons 4 \text{H}_2\text{O}$ $K = (K_{\text{w}}^{-1})^2 = 1.0 \times 10^{28}$
 - $K_{\text{net}} = (K_{\text{sp}}) (K_{\text{w}}^{-1})^2 = 5.6 \times 10^{16}$

Precipitation reactions

- $\text{AgCl (s)} \rightleftharpoons \text{Ag}^+ \text{(aq)} + \text{Cl}^- \text{(aq)}$
 - $Q = K_{\text{sp}}$ saturated solution
 - $Q < K_{\text{sp}}$ more AgCl (s) will dissolve (until $Q = K_{\text{sp}}$)
 - $Q > K_{\text{sp}}$ AgCl (s) will precipitate (until $Q = K_{\text{sp}}$)



Precipitation reactions

The concentration of Ba^{2+} in a solution is 0.010 M. What concentration of SO_4^{2-} is required to begin the precipitation of BaSO_4 (s)?

Precipitation reactions

The concentration of Ba^{2+} in a solution is 0.010 M. When $[\text{SO}_4^{2-}]$ in the solution reaches 0.015 M, what $[\text{Ba}^{2+}]$ remains in the solution?

Precipitation reactions

Suppose you mix 100.0 mL of 0.0200 M BaCl_2 (aq) with 50.0 mL of 0.0300 M Na_2SO_4 (aq). Will BaSO_4 precipitate?

Complex ion equilibria

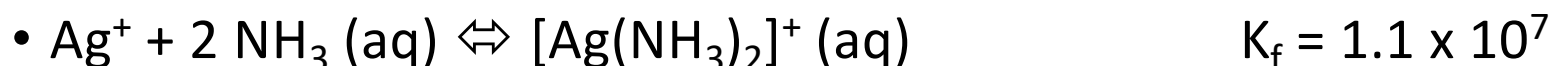
- Complex ions = metal ions bound to molecules/ions (Lewis bases)
- Ions/molecules bound to metal ion = **ligands**
- **Formation constant K_f** (often very large)
- $\text{Cu}^{2+} (\text{aq}) + 4 \text{NH}_3 (\text{aq}) \rightleftharpoons [\text{Cu}(\text{NH}_3)_4]^{2+} (\text{aq}) \quad K_f = 2.1 \times 10^{13}$

Complex ion equilibria

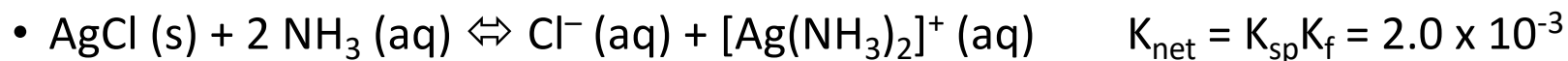
What is $[\text{Cu}^{2+}]$ in a solution prepared by adding 0.00100 mol of $\text{Cu}(\text{NO}_3)_2$ to 1.00 L of 1.50 M NH_3 (aq)?

Complex ions and solubility

- Low solubility salts dissolve better in solutions containing complex ions



- Net:



- $K_{\text{net}} = \frac{[\text{Cl}^-][[\text{Ag}(\text{NH}_3)_2]^+]}{[\text{NH}_3]^2}$