Chapter 15:

Applications of Aqueous Equilibria

Acid-Base Equlibria

15.1 Solutions of Acids or Bases Containing a Common Ion

Common Ion Effect

共同離子效應: The shift in equilibrium that occurs because of the addition of an ion already involved in the equilibrium reaction.

$$AgCl(s) \leftrightarrow Ag^{+}(aq) + Cl^{-}(aq)$$

$\xleftarrow{\text{adding NaCl}(aq)\text{ shifts equilibrium position}}$

對多質子酸而言, the common ion effect **亦是其** $K_{a1} > K_{a2} > K_{a3}$ .. **之因素**

Sample exercise 15.1

15.2 Buffered Solutions

A Buffered Solution

緩衝溶液: resists change in its pH when either H^+ or OH^- are added.

如:

1.0 L of 0.50 M H_3CCOOH

+ 0.50 M $H_3CCOONa$

pH = 4.74

Adding 0.010 mol solid NaOH raises the pH of the solution to 4.76, a very minor change.

(left) Pure water at pH 7.000. (right) When 0.01 mol NaOH is added to 1.0 L of pure water, the pH jumps to 12.000.

Key Points on Buffered Solutions

1. They are weak acids or bases containing a common ion.
2. After addition of strong acid or base, deal with stoichiometry first, then equilibrium.

Henderson-Hasselbalch Equation

- Useful for calculating pH when the $[A^-]/[HA]$ ratios are known.

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\left[A^-\right]/[HA]\right) = \mathrm{p}K_a + \log([\text{base}]/[\text{acid}])$$

Buffered Solution Characteristics

- Buffers contain relatively large amounts of weak acid and corresponding base.
- Added H^+ reacts to completion with the weak base.
- Added OH^- reacts to completion with the weak acid.
- The pH is determined by the ratio of the concentrations of the weak acid and weak base.

15.3 Buffering Capacity

Buffering Capacity

represents the amount of H^+ or OH^- the buffer can absorb without a significant change in pH

TABLE 15.1 Change in $[C_2H_3O_2^-]/[HC_2H_3O_2^-]$ for Two Solutions When 0.01 mol H^+ Is Added to 1.0 L of Each

Solution	$\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)_{orig}$	$\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)_{new}$	Change	Percent Change
A	$\frac{1.00\ M}{1.00\ M} = 1.00$	$\frac{0.99\ M}{1.01\ M} = 0.98$	$1.00 \rightarrow 0.98$	2.00%
B	$\frac{1.00\ M}{0.01\ M} = 100$	$\frac{0.99\ M}{0.02\ M} = 49.5$	$100 \rightarrow 49.5$	50.5%

15.4 Titrations and pH Curves

Titration (pH) Curve

酸鹼滴定曲線: A plot of pH of the solution being analyzed as a function of the amount of titrant added.

當量點: Equivalence (stoichiometric) point: Enough titrant has been added to react exactly with the solution being analyzed.

Strong Acid – Strong Base Titration

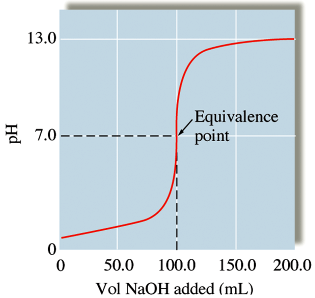


Fig. 15.1: The pH curve for the titration of 50.0 mL of 0.200 *M* HNO_3 with 0.100 *M* NaOH.

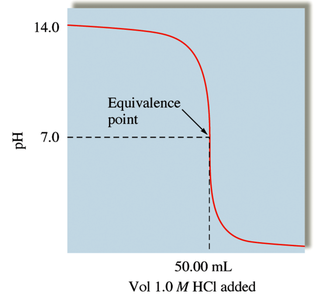


Fig. 15.2: The pH curve for the titration of 100.0 mL of 0.50 *M* NaOH with 1.0 *M* HCl.

Weak Acid – Strong Base Titration or Weak Base – Strong Acid Titration

Step 1 - A stoichiometry problem
reaction is assumed to run to completion - then determine remaining species.

Step 2 - An equilibrium problem
determine position of weak acid equilibrium and calculate pH.

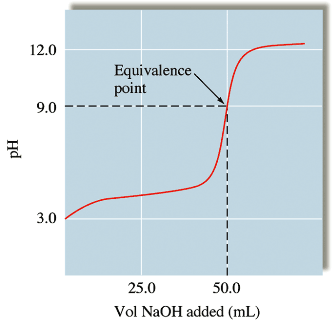
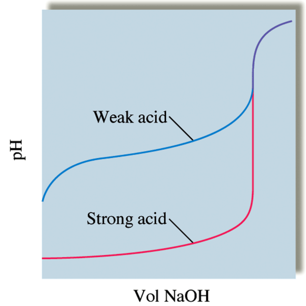


Fig. 15.3: The pH curve for the titration of 50.0 mL of 0.100 *M* $HC_2H_3O_2$ with 0.100 *M* NaOH.



Comparison of strong and weak acid titration curves.

強鹼滴定弱酸 ⇒ 當量點 pH > 7

Fig. 15.4: The pH curves for the titrations of 50.0-mL samples of 0.10 *M* acids with various K_a values with 0.10 *M* NaOH.

The strength of the acid has a significant effect on the shape of its pH curve.

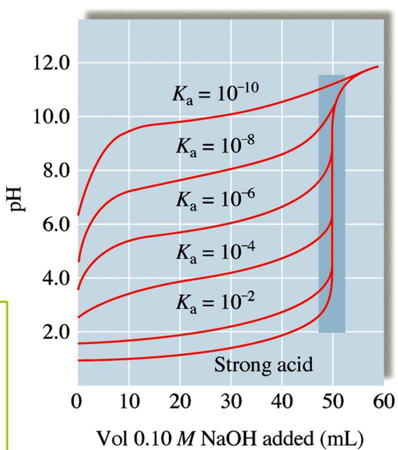
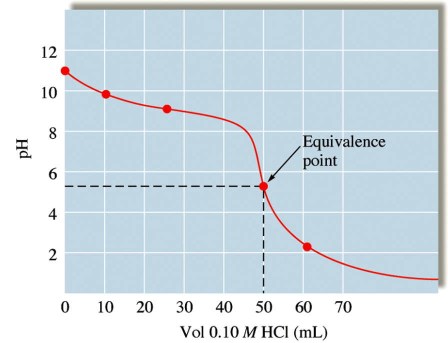


Fig. 15.5: The pH curve for the titration of 100.0 mL of 0.050 *M* NH_3 with 0.10 *M* HCl.



強酸滴定弱鹼 ⇒ 當量點 pH < 7

15.5 Acid-Base Indicators

Acid-Base Indicator

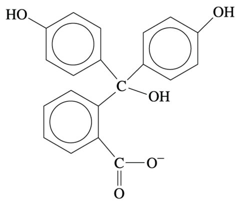
酸鹼指示劑

. . . marks the end point (終點) of a titration by changing color.

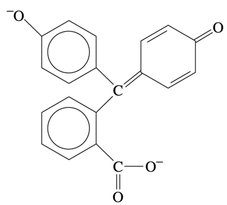
The equivalence point is not necessarily the same as the end point. 終點不一定是當量點

一般酸鹼指示劑本身為弱酸 (HIn)，其變色之pH範圍為: $pK_a \pm 1$

Fig. 15.6: The acid and base forms of the indicator phenolphthalein. In the acid form (HIn), the molecule is colorless. When a proton (plus H_2O) is removed to give the base form (In-), the color changes to pink.



(Colorless acid form, HIn)



(Pink base form, In^-)

酚?

於酸環境下: 無色

於鹼環境下: 粉紅色

Methyl orange indicator is yellow in basic solution and red in acidic solution.

甲基橙

鹼 酸

Fig. 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.

溴瑞香草藍

酸 酸 → 鹼 鹼

Fig. 15.8: The useful pH ranges for several common indicators. Note that most indicators have a useful range of about two pH units, as predicted by the expression $pK_a \pm 1$.

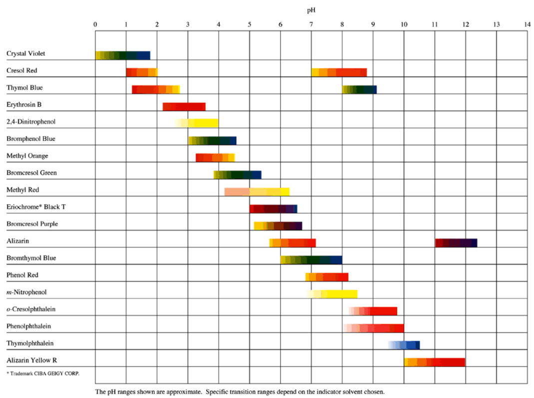


Fig. 15.10: The pH curve for the titration of 50 mL of 0.1 *M* $HC_2H_3O_2$ with 0.1 *M* NaOH.

對於弱酸或弱鹼的滴定，指示劑的選擇很重要，選取原則為指示劑變色範圍的中間點愈接近當量點的pH值愈適合。

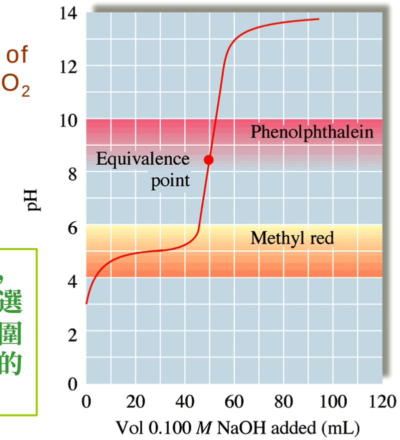


TABLE 15.3
Selected pH Values Near the Equivalence Point in the Titration of 100.0 mL of 0.10 *M* HCl with 0.10 *M* NaOH

NaOH Added (mL)	pH
99.99	5.3
100.00	7.0
100.01	8.7

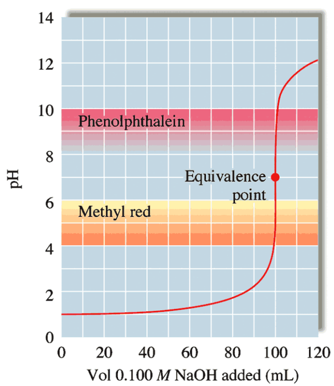


Fig. 15.9 The pH curve for the titration of 100.0 mL of 0.10 *M* HCl with 0.10 *M* NaOH.

Solubility Equlibria

15.6 Solubility Equilibria & the Solubility Product

Solubility Product

For solids dissolving to form aqueous solutions

例如

$$Bi_2S_3(s) \rightleftharpoons 2Bi^{3+}(aq) + 3S^{2-}(aq)$$

K_{sp} = solubility product constant

$$K_{sp} = [Bi^{3+}]^2[S^{2-}]^3$$

Solubility vs. Solubility Product

"Solubility"(溶解度) = s = concentration of Bi_2S_3 that dissolves, which in pure water equals $1/2[Bi^{3+}]$ or $1/3[S^{2-}]$.

K_{sp} is constant (at a given temperature)

s is variable (especially with a common ion present)

TABLE 15.4 K_{sp} Values at 25°C for Common Ionic Solids

Ionic Solid	K_{sp} (at 25°C)
Fluorides	
BaF_2	2.4×10^{-5}
MgF_2	6.4×10^{-9}
PbF_2	4×10^{-8}
SrF_2	7.9×10^{-10}
CaF_2	4.0×10^{-11}
Chlorides	
$PbCl_2$	1.6×10^{-5}
AgCl	1.6×10^{-10}
Hg_2Cl_2*	1.1×10^{-18}
Bromides	
$PbBr_2$	4.6×10^{-6}
AgBr	5.0×10^{-13}
Hg_2Br_2*	1.3×10^{-22}
Iodides	
PbI_2	1.4×10^{-8}
AgI	1.5×10^{-16}
Hg_2I_2*	4.5×10^{-29}
Sulfates	
$CaSO_4$	6.1×10^{-5}
Ag_2SO_4	1.2×10^{-5}
$SrSO_4$	3.2×10^{-7}
$PbSO_4$	1.3×10^{-8}
$BaSO_4$	1.5×10^{-9}
Chromates	
$SrCrO_4$	3.6×10^{-5}
Hg_2CrO_4*	2×10^{-9}
$BaCrO_4$	8.5×10^{-11}
Ag_2CrO_4	9.0×10^{-12}
$PbCrO_4$	2×10^{-16}
Carbonates	
$NiCO_3$	1.4×10^{-7}
$CaCO_3$	8.7×10^{-9}
$BaCO_3$	1.6×10^{-9}
$SrCO_3$	7×10^{-10}
$CuCO_3$	2.5×10^{-10}
$ZnCO_3$	2×10^{-10}
$MnCO_3$	8.8×10^{-11}
$FeCO_3$	2.1×10^{-11}
Ag_2CO_3	8.1×10^{-12}
$CdCO_3$	5.2×10^{-12}
$PbCO_3$	1.5×10^{-15}
$MgCO_3$	6.8×10^{-6}
Hg_2CO_3*	9.0×10^{-15}
Hydroxides	
$Ba(OH)_2$	5.0×10^{-3}
$Sr(OH)_2$	3.2×10^{-4}
$Ca(OH)_2$	1.3×10^{-6}
AgOH	2.0×10^{-8}
$Mg(OH)_2$	8.9×10^{-12}
$Mn(OH)_2$	2×10^{-13}
$Cd(OH)_2$	5.9×10^{-15}
$Pb(OH)_2$	1.2×10^{-15}
$Fe(OH)_2$	1.8×10^{-15}
$Co(OH)_2$	2.5×10^{-16}
$Ni(OH)_2$	1.6×10^{-16}
$Zn(OH)_2$	4.5×10^{-17}
$Cu(OH)_2$	1.6×10^{-19}
$Hg(OH)_2$	3×10^{-26}
$Sn(OH)_2$	3×10^{-27}
$Cr(OH)_3$	6.7×10^{-31}
$Al(OH)_3$	2×10^{-32}
$Fe(OH)_3$	4×10^{-38}
$Co(OH)_3$	2.5×10^{-43}
Sulfides	
MnS	2.3×10^{-13}
FeS	3.7×10^{-19}
NiS	3×10^{-21}
CoS	5×10^{-22}
ZnS	2.5×10^{-22}
SnS	1×10^{-26}
CdS	1.0×10^{-28}
PbS	7×10^{-29}
CuS	8.5×10^{-45}
Ag_2S	1.6×10^{-49}
HgS	1.6×10^{-54}
Phosphates	
Ag_3PO_4	1.8×10^{-18}
$Sr_3(PO_4)_2$	1×10^{-31}
$Ca_3(PO_4)_2$	1.3×10^{-32}
$Ba_3(PO_4)_2$	6×10^{-39}
$Pb_3(PO_4)_2$	1×10^{-54}

TABLE 15.5 Calculated Solubilities for CuS, Ag_2S, and Bi_2S_3 at 25°C

Salt	K_{sp}	Calculated Solubility (mol/L)
CuS	8.5×10^{-45}	9.2×10^{-23}
Ag_2S	1.6×10^{-49}	3.4×10^{-17}
Bi_2S_3	1.1×10^{-73}	1.0×10^{-15}

Precipitation of bismuth sulfide (Bi_2S_3).

15.7 Precipitation and Qualitative Analysis

Flame test for potassium (K).

Flame test for sodium (Na).

Fig. 15.11: The separation of Cu^{2+} and Hg^{2+} from Ni^{2+} and Mn^{2+} using H_2S.

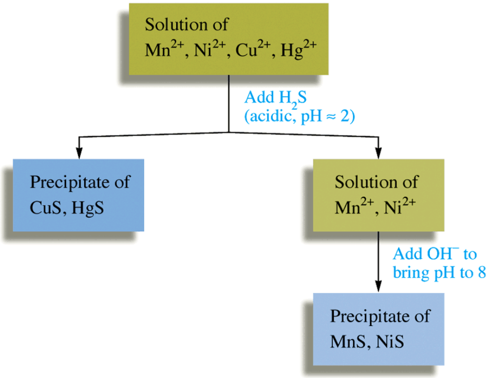
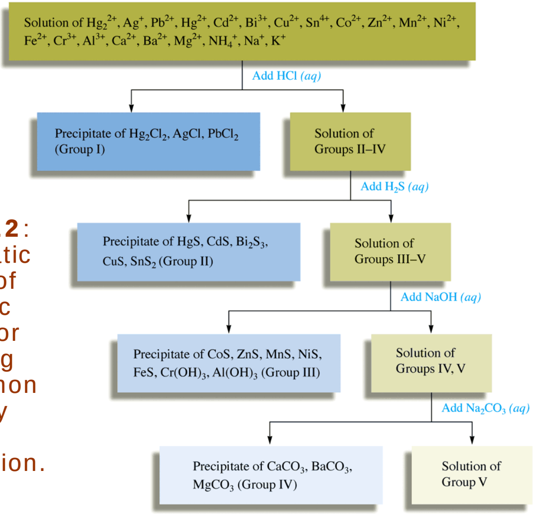
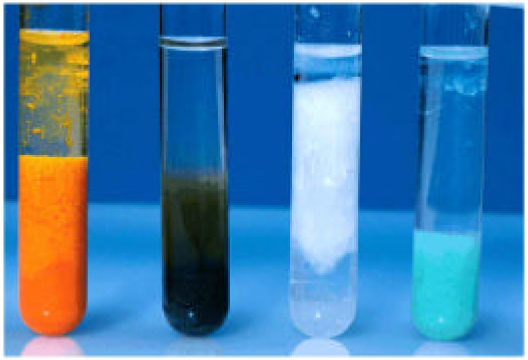


Fig. 15.12: A schematic diagram of the classic method for separating the common cations by selective precipitation.



From left to right, cadmium sulfide, chromium(III) hydroxide, aluminum hydroxide, and nickel(II) hydroxide.



Complex Ion Equlibria

15.8 Equilibria Involving Complex Ions

Complex Ions

- **Complex Ion (錯合離子)**: A charged species consisting of a metal ion surrounded by ligands (Lewis bases).
- **Coordination Number (配位數):** Number of ligands attached to a metal ion. (Most common are 6, 4, and 2.)
- **Formation (Stability) Constants:** The equilibrium constants characterizing the stepwise addition of ligands to metal ions.

(left) Aqueous ammonia is added to silver chloride (white). (right) Silver chloride, insoluble in water, dissolves to form $Ag(NH_3)_2^+$(*aq*) and Cl^-(*aq*).

$$AgCl_{(s)} + 2\ NH_{3(aq)} \rightleftharpoons Ag(NH_3)_2^+{}_{(aq)} + Cl^-{}_{(aq)}$$

$$2H^+{}_{(aq)} + Ag(NH_3)_2^+{}_{(aq)} + Cl^-{}_{(aq)} \rightarrow 2NH_4^+{}_{(aq)} + AgCl_{(s)}$$

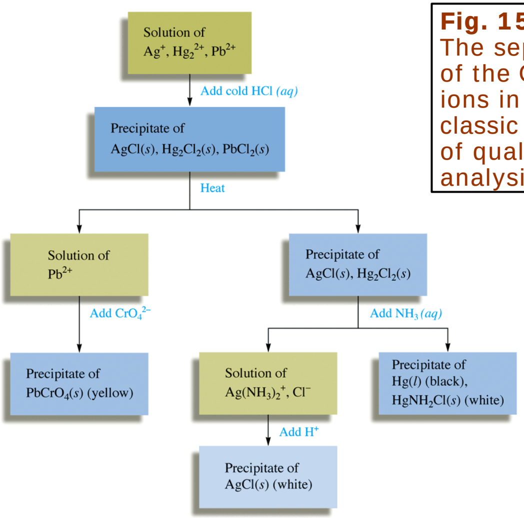


Fig. 15.13: The separation of the Group I ions in the classic scheme of qualitative analysis.