Ch.4 Reactions in Aqueous Solution

4-1: Solute Concentration：

1. Molarity (M)： 容積莫耳濃度
2. Normality (N)： 當量濃度

4-2: Precipitation Reaction

1. Net Ionic Equations fig 4.4
2. Stoichiometry

4-3: Acid-base Reactions

1. Strong and Weak Acids and Bases
2. Equations for Acid –Base Reactions
3. Acid –Base Titrations

4-4: Oxidation-reduction reactions

1. Oxidation number 氧化數
2. Balancing half equations (oxidation or reduction)
3. Balancing Redox Equations

§4-1 Solute Concentrations: Molarity (M)容積莫耳濃度

$$\text{M} = \frac{\textit{moles of}\ \text{solute}}{\textit{liters}\ \text{of solution}} = \frac{\text{溶質 mole 數}}{\text{溶液公升數}}$$

The symbol: [ ]

例： A solution containing 1.20 mol of substance A in 2.50 L of solution.

$$[\text{A}] = \frac{\textit{moles of}\ \text{solute}}{\textit{liters}\ \text{of solution}} = \frac{1.20\ \text{mol}}{2.50\ \text{L}} = 0.480\ \text{M (mol/L)}$$

Fig 4.1. Preparing one liter of 0.100 M potassium chromate (K_2CrO_4)鉻酸鉀, 需鉻酸鉀若干克?

Ans:

$$0.100 = \frac{m/MM}{1}$$

$$0.100 = \frac{m}{194.2}$$

$$m = 19.4\ g$$

$$\begin{aligned} MM &= 2\times(39.10)+1\times(52.00)+4\times(16.00) \\ &= 78.20 + 52.00 + 64.00 \\ &= 194.2g \end{aligned}$$

a) 取 1 個 1 L 之定量瓶 volumetric flask，置入 19.4 g K_2CrO_4
b) 加入少量水，完全溶解K_2CrO_4
c) 加足量水主頸線，搖晃均勻

Ex 4.1: Nitric acid, HNO_3, is extensively used in the manufacture of fertilizer, A bottle containing 75.0 mL of nitric acid solution is labeled 6.0 M HNO_3.

a) How many moles of HNO_3 are in the bottle?
b) A reaction needs 5.00 g of HNO_3. How many mL of solution are required?
c) Ten mL of water are added to the solution. What is the molarity of the resulting solution? (Assume volumes are additive.)

MM_{HNO_3} = 63.02 g/ mol

Ans:

a) $\text{n}_{HNO_3} = 75.0\ \text{mL} \times \frac{6.0\ \textit{mol}\ \text{HNO}_3}{1\ \text{L}} \times \frac{1\ \text{L}}{1000\ \text{mL}} = 0.45\ \text{mol}$

b) $\text{V} = \frac{5.00\ \text{g}}{63.02\ \text{g/mol}} \times \frac{1\ \text{L}}{6.0\ \textit{mol}\ \text{HNO}_3} \times \frac{1000\ \text{mL}}{1\ \text{L}} = 13\ \text{mL}$

c) $M = \frac{moles\ of\ solute}{liters\ of\ solution} = \frac{0.45}{(75.0 + 10.0)/\ 1000} = 5.3\ \text{mol/L}$

An ionic solid dissolves in water, the cations and anions separate from each other.

$$NaCl(s) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq)$$
$$MgCl_2(s) \xrightarrow{H_2O} Mg^{2+}(aq) + 2Cl^-(aq)$$

$$\textit{molarity } Mg^{2+} = \text{molarity } \mathrm{MgCl_2} \Rightarrow [\mathrm{Mg^{2+}}] = [\mathrm{MgCl_2}]$$
$$\textit{molarity } \mathrm{Cl^-} = 2 \times \text{molarity } \mathrm{MgCl_2} \Rightarrow [\mathrm{Cl^-}] = 2\,[\mathrm{MgCl_2}]$$

例：

$$(NH_4)_3PO_4(s) \xrightarrow{H_2O} 3NH_4^+(aq) + PO_4^{3-}(aq)$$
$$\textit{molarity } NH_4^+ = 3 \times \text{molarity } (NH_4)_3PO_4$$
$$\textit{molarity } \mathrm{PO_4^-} = 1 \times \text{molarity } (NH_4)_3PO_4$$

$$Cr_2(SO_4)_3(s) \xrightarrow{H_2O} 2Cr^{3+}(aq) + 3SO_4^{2-}(aq)$$
$$\textit{molarity } Cr^{3+} = 2 \times \text{molarity } Cr_2(SO_4)_3$$
$$\textit{molarity } \mathrm{SO_4^{2-}} = 3 \times \text{molarity } Cr_2(SO_4)_3$$

Ex 4-2: Potassium dichromate, $K_2Cr_2O_7$, is used in the tanning of leather. A flask containing 125 mL of solution is labeled 0.145 M $K_2Cr_2O_7$.

a) What is the molarity of each ion in solution?

b) A sample containing 0.200 moles of K^+ is added to the solution. Assuming no volume change, what is the molarity of the new solution?

Ans:

a) $K_2Cr_2O_7(s) \xrightarrow{H_2O} 2K^+(aq) + Cr_2O_7^{2-}(aq)$

$[K^+] = 2 \times 0.145 = 0.290$ M

$[Cr_2O_7^{2-}] = 1 \times 0.145 = 0.145$ M

b) $n_{K^+_i} = 0.290 \times 125/1000 = 0.0363$ mol

$n_{K^+_f} = 0.0363 + 0.200 = 0.236$ mol

$$[\mathrm{K^+}] = \frac{0.236 \text{ mol}}{0.125 \text{ L}} = 1.89 \text{ M}$$

$$[\mathrm{K}_2Cr_2O_7] = \frac{1.89 \text{ mol } \mathrm{K^+}}{1 \text{ L}} \cdot \frac{1 \text{ mol } \mathrm{K}_2Cr_2O_7}{2 \text{ mol } \mathrm{K^+}} = 0.945 \text{ M}$$

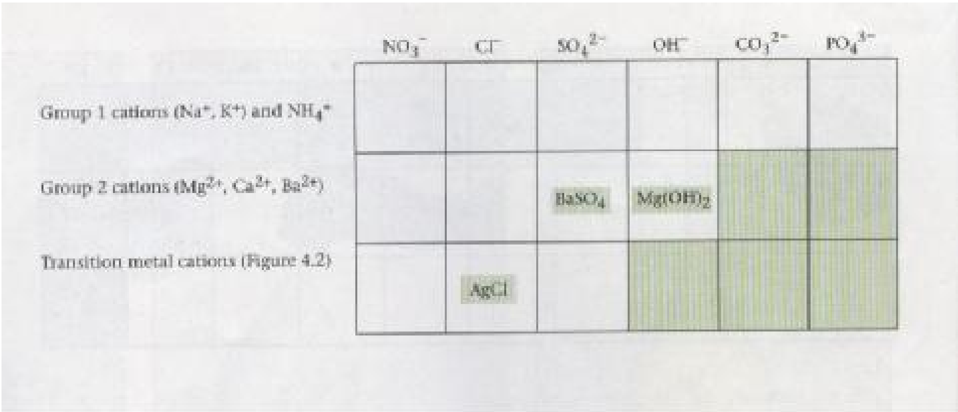
§ 4-2 Precipitation Reactions 沈澱反應

Sometimes when water solutions of two different ionic compounds are mixed , <u>an insoluble solid</u> separate out of solution.

└→ precipitate

Ksp: solubility product 溶解度積

Fig 4.3: 沉澱圖



	NO_3^-	Cl^-	SO_4^{2-}	OH^-	CO_3^{2-}	PO_4^{3-}
Group 1 cations (Na^+, K^+) and NH_4^+						
Group 2 cations (Mg^{2+}, Ca^{2+}, Ba^{2+})			$BaSO_4$	$Mg(OH)_2$		
Transition metal cations (Figure 4.2)		AgCl				

Ex 4-3: Using the precipitation diagram (Fig 4.3), predict what will happen when the following pairs of aqueous solutions are mixed.

a) $Cu(NO_3)_2$ and $(NH_4)_2SO_4$

b) $FeCl_3$ and $AgNO_3$

Ans:

a) $CuSO_4 \Rightarrow$ No precipitate.

$NH_4NO_3 \Rightarrow$ No precipitate.

$\therefore$ No precipitate.

b) $Fe(NO_3)_3 \Rightarrow$ No precipitate.

AgCl $\Rightarrow$ Yes.

$\therefore$ AgCl 沉澱.

§ Net ionic equation

$$Na_2CO_3(aq) + CaCl_2(aq) \longrightarrow 2NaCl(aq) + CaCO_3(s)$$

$$\text{Reactants}: 2Na^+;\ CO_3^{2-};\ Ca^{2+};\ 2Cl^-$$

$$\text{Products}: 2Na^+;\ 2Cl^-;\ CaCO_3(s)$$

$$\Rightarrow \cancel{2Na^+} + CO_3^{2-} + Ca^{2+} + \cancel{2Cl^-} \longrightarrow \cancel{2Na^+} + \cancel{2Cl^-} + CaCO_3(s)$$

Net ionic equation:

$CO_3^{2-} + Ca^{2+} \longrightarrow CaCO_3(s)$ spectator (旁觀) ions: $2Na^+$; $2Cl^-$

Ex 4-4: Write a net ionic equation for any precipitation reaction that occurs when solutions of the followings ionic compounds are mixed.

a) $NaOH$ and $Cu(NO_3)_2$

b) $BaCl_2$ and Ag_2SO_4

c) $(NH_4)_3PO_4$ and K_2CO_3

Ans:

a) $NaNO_3 \Rightarrow$ No prepcipitate.

$Cu(OH)_2 \Rightarrow$ Yes.

$\therefore\ Cu^{2+}(aq) + 2OH^-(aq) \longrightarrow Cu(OH)_2(s)$

b) $BaSO_4 \Rightarrow$ Yes.

$\therefore\ Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$

AgCl $\Rightarrow$ Yes. ∴

$\therefore\ Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

$\therefore\ BaCl_2(aq) + AgSO_4(aq) \longrightarrow BaSO_4(s) + 2AgCl(s)$

c) $K_3PO_4 \Rightarrow$ No prepcipitate.

$(NH_4)_2CO_3 \Rightarrow$ No prepcipitate.

$\therefore$ No equation.

本章中，都使用 net ionic equation 表示之.

§ Stoichiometry 化學計量

Mole-mass calculation.

Ex 4.5: When aqueous solutions of sodium hydroxide and iron (III) nitrate are mixed, a red precipitate forms.

a) Write a net ionic equation for the reaction.

b) What volume of 0.136 M iron (III) nitrate is required to produce 0.886 g of precipitate?

c) How many grams of precipitate are formed when 50.00 mL of 0.200 M NaOH and 30.00 mL 0.125 M $Fe(NO_3)_3$ are mixed.

Ans:

a) $Fe^{3+}(aq) + 3OH^-(aq) \longrightarrow Fe(OH)_3(s)$

b) $n_{Fe(OH)_3} = \dfrac{m}{MM_{Fe(OH)_3}} = \dfrac{0.886}{55.85+3\times(1.008+16.00)} = 8.29\times 10^{-3}$ mol

$n_{Fe^{3+}} = 1 \times 8.29\times 10^{-3} = 8.29\times 10^{-3}$ mol

$n_{Fe^{3+}} = V \times M$

$8.29\times 10^{-3} = V \times 0.136$

$V = 0.0610$ L

c) $n_{Fe(NO_3)_3} = 0.125\times \dfrac{30.00}{1000} = 3.75\times 10^{-3}$ mol

$n_{OH^-} = 0.200\times\dfrac{50.00}{1000} = 0.0100\ mol$

$Fe^{3+}(aq) + 3OH^-(aq) \longrightarrow Fe(OH)_3(s)$

$n_{Fe(OH)_3} = 0.0100\ mol \times \dfrac{1\text{ mol } Fe(OH)_3}{3\text{ mol } OH^-} = 3.33 \times 10^{-3}$ mol (smaller)

∴ OH^- limiting reactant.

∴ $m_{Fe(OH)_3} = 3.33 \times 10^{-3} \times 106.87$ g/mol = 0.356 g

§ 4-3 Acid-base reactions

Acidic solution： 1. sour taste.
2. Litmus(石蕊) turns from blue to red.

Basic solution： 1. slippery feeling
2. Litmus turns from red to blue.

Svante Arrhenius： Acid-base definitions：

An acid is a species that produces H^+ ions in water solution.
A base is a species that produces OH^- ions in water solution.

J. Brj nsted - T.Lowry ： (Ch. 13)

酸：反應中提供 H^+ 者

鹼：反應中接受 H^+ 者

共軛酸鹼對

鹼 2 — 酸 2

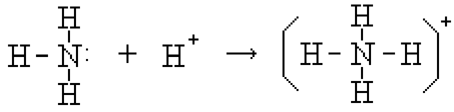
$HCl(aq) + H_2O(l) \longrightarrow Cl^-(aq) + H_3^+O(aq)$

酸 1 — 鹼 1

G.N.Lewis ：

酸：反應中接受共用電子對者

鹼：反應中提供共用電子對者



§ Strong and Weak Acids and Bases.

There are two types of acids, strong and weak.

Strong acid：ionize completely, forming H^+ ions and anions.

Ex： $HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$

開始:	0.10 mol	-	-	
平衡:	0.00 mol	0.10 mol	0.10 mol	ionize completely.

Weak acid：Only partially ionized to H^+ ions in water . Double arrow implies that this reaction does not go to completion.

Ex: $HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$

開始:	0.10 mol	-	-	
平衡:	0.09 mol	0.01 mol	0.01 mol	partially ionized.

Strong base：In water solution is completely ionized to OH^- ions and cations.

Ex： $NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)$

$Ca(OH)_2(s) \longrightarrow Ca^{2+}(aq) + 2OH^-(aq)$ *ionize* completely.

Weak base：They react with H_2O molecules, acquiring H^+ ions and leaving OH^- ions behind.

Ex: $NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

開始:	0.10 mol	-	-	
平衡:	0.099 mol	0.001 mol	0.001 mol	partially ionized.

Table 4-1 Common Strong acids and bases.

Acid	Name of Acid	Base	Name of base
HCl (aq)	Hydrochloric acid	$LiOH$	Lithium hydroxide
HBr (aq)	Hydrobromic acid	$NaOH$	Sodium hydroxide
HI (aq)	Hydriodic acid	KOH	Potassium hydroxide
HNO_3	Nitric acid	$Ca(OH)_2$	Calcium hydroxide
$HClO_4$ 過氯酸	Perchloric acid	$Sr(OH)_2$	Strontium hydroxide
H_2SO_4	Sulfuric acid	$Ba(OH)_2$	Barium Hydroxide

Amine 弱鹼

$$CH_3NH_2(aq) + H_2O \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

Strong electrolytes 強電解質 $\Rightarrow$ completely ionized.

Weak electrolytes $\Rightarrow$ partially ionized.

§ Equations for Acid-Base reactions.

1. Strong acid-Strong base

$$HNO_3(aq) + NaOH \rightleftharpoons Na^+ NO_3^-(aq) + H_2O(l)$$

$$\Downarrow$$

neutralization： $H^+(aq) + OH^-(aq) \longrightarrow H_2O(\mathbf{l})$

$\Downarrow$ Na^+, NO_3^-: spectator ions

適合所有強酸－強鹼反應

2. Weak acid-Strong base

HB $NaOH$

$$HB \rightleftharpoons H^+(aq) + B^-(aq)$$

$$+)\ H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

net reaction： $HB + OH^-$ (aq) $\longrightarrow$ B^- (aq) + H_2O (**l**)

Ex： $NaOH \; + HF(aq)$ 弱酸

$$HF(aq) + OH^-(aq) \longrightarrow F^-(aq) + H_2O(l)$$

3. Strong acid-Weak base

HCl NH_3

$$NH_{3(aq)} + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$+)\quad H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

$$NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$$

通式: H^+ (aq) + B (aq) $\longrightarrow$ BH$^+$ (aq)

Ex： $HNO_3(aq) + CH_3NH_2(aq)$:

$$CH_3NH_2(aq) + H^+(aq) \longrightarrow CH_3NH_3^+(aq)$$

Table 4.2： Types of acid-base reactions.

Reactants	Reacting Species	Net ionic reaction
S acid – S base	H^+, OH^-	$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$
W acid – S base	HB, OH^-	$HB + OH^-(aq) \rightarrow B^-(aq) + H_2O$ (l)
S acid – W base	H^+, B	$H^+(aq)$ + B (aq) $\rightarrow$ BH$^+$ (aq)

Ex 4-6: Write a net ionic equation for each of the following reactions in dilute water solution.

a) Hypochlorous acid ($HClO$) 次氯酸 and calcium hydroxide

b) Ammonia with perchloric acid ($HClO_4$) 過氯酸

c) Hydriodic acid (HI) with sodium hydroxide

Ans：

a) HClO weak acid $Ca(OH)_2$ strong base

$$\therefore \quad HClO(aq) + OH^-(aq) \longrightarrow ClO^-(aq) + H_2O(l)$$

b) NH_3 weak base $HClO_4$ strong acid

$\therefore \quad NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$

c) HI strong acid $NaOH$ strong base

$\therefore \quad H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$

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