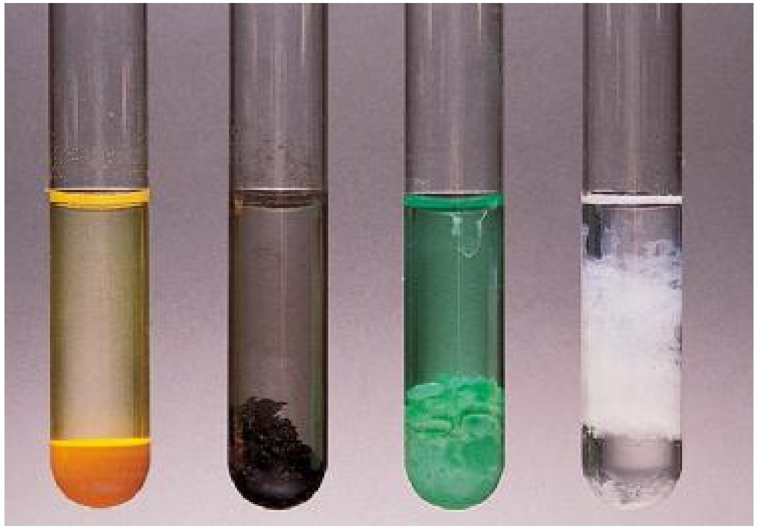
Chapter 4

Reactions in Aqueous Solution

The Important types of aqueous reaction



These include-

1.Precipiatation reactions

2.acid-base reactions

3.Oxidation-reduction reactions

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

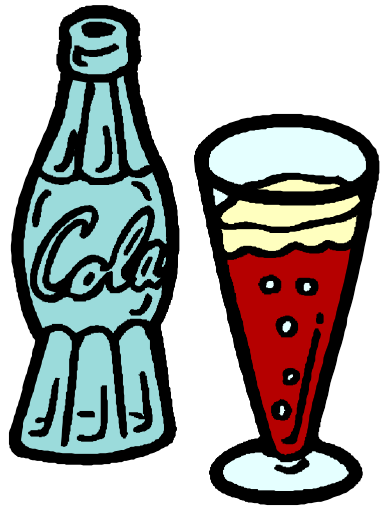
1. Oxidation number 氧化數
2. Balancing half-equations (oxidation or reduction)
3. Balancing Redox Equations

溶液(solution)－由二種或二種以上的純物質均勻混合形成一個單相(single phase)，其中含溶質與溶劑。

溶質(***solute)***－被溶解的物質，溶液中較少量的物質

溶劑(***solvent***)－溶解其他物質者，溶液中較大量的物質。

溶　液	溶　劑	溶　質
碳酸飲料 (*l*)	H_2O	糖, CO_2
空氣 (*g*)	N_2	O_2, Ar, CH_4
合金 (*s*)	Pb	Sn



溶質的濃度

- 定量的溶劑或溶液中，所含溶質之量的多寡，稱為該溶質的濃度。共有八種表示法

1. 重量百分率(weight percentage),%
2. 克式量濃度(formality)
3. 體積莫耳濃度(molarity), M
4. 重量莫耳濃度(molality), m
5. 當量濃度(normality),N
6. 莫耳分率(mole fraction),x_i
7. 百萬分數(parts per million),ppm
8. 十億萬分數(parts per billion),ppb

Cl^-

範例4.1 鹽酸的瓶子上標示著「濃鹽酸」， 表示1公升的這種溶液含有12.0mol的 HCl，亦即「HCl」= 12.0 M。

(a) 在25.0 mL的這種溶液中，含有多少moles的HCl?

$$n_{HCl} = 25.0\,\cancel{mL} \times \frac{1\,\cancel{L}}{1000\,\cancel{mL}} \times \frac{12.0\,mol\ \ HCl}{1\,\cancel{L}}$$

$$= 0.300 mol\ HCl$$

(b) 需多少體積的濃鹽酸才能含有 1.00 mol的HCl?

$$V_{HCl} = 1.00\cancel{mol\ HCl} \times \frac{\cancel{1L}}{12.0\cancel{mol\ HCl}} \times \frac{1000mL}{\cancel{1L}}$$

$$= 83.3 mL\ HCl$$

§4-1 Solute Concentrations: Molarity (M)

1.The concentration of a solute in solution can be expressed in terms of its **Molarity**

Molarity (M)= $\frac{moles.of.solute}{liters.of.solution}$

The symbol [ ] is commonly used to represent the molarity of a species in a solution. 表示在溶液中的莫耳濃度

Ex a solution containing 1.20mol of substance A in 2.50L of solution

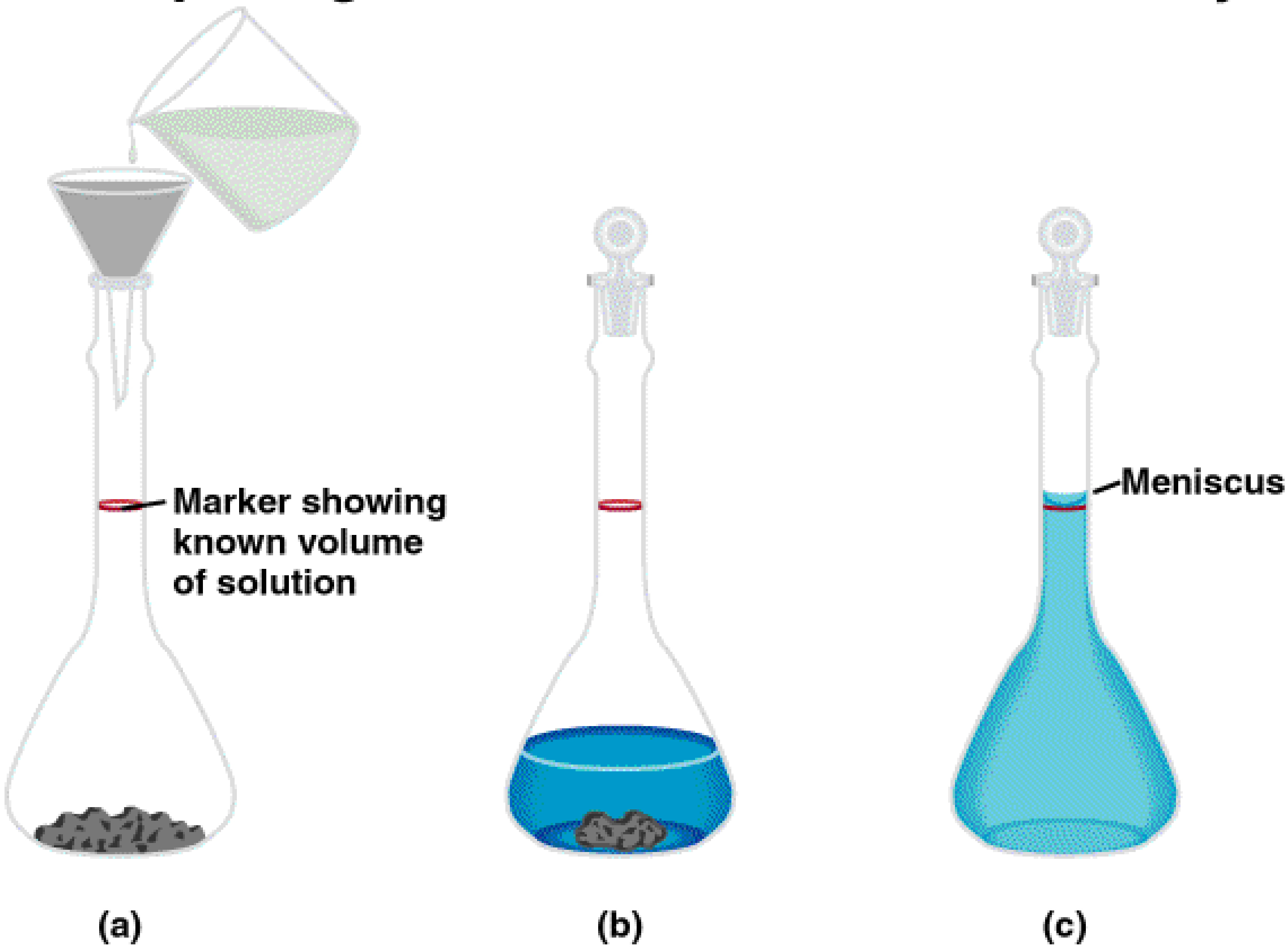
$$[A]=\frac{1.20mol}{2.50L}=0.480^{mol}/_{L}=0.480M$$

2.The molarity of a solution can be used to Calculate:

(1) The number of moles of solute in a given volume of solution.

(2) The volume of solution containing a given number of moles of solute.

Preparing a Solution of Known Molarity



Ex 4-1： The bottle labeled dilute nitric acid in the lab contains 6.0 mol of per liter of solution 6.0 M

a) How many moles of are in 75 ml of this solution?

b) What volume of dilute nitric acid must be taken to contain one mole of?

Sol：

a) $$n_{HNO_3} = 75mL \times \frac{1L}{1000mL} \times \frac{60mol}{1L} = 0.45 mole HNO_3$$

b)
$$V = 1.00 mol HNO_3 \times \frac{1L}{6.0 mol HNO_3} = 0.17L$$

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

- $NaCl_{(S)} \xrightarrow{H_2O} Na^{+}_{(aq)} + Cl^{-}_{(aq)}$
- $MgCl_{2(S)} \xrightarrow{H_2O} Mg^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$ Cl^{-}
- molarity = molarity $MgCl_2$ 【Mg^{2+}】 = 【$MgCl_2$】
- molarity = 2 molarity Cl^{-} 【Cl^{-}】 = 2 【$MgCl_2$】
- $(NH_4)_3PO_{4(S)} \longrightarrow 3NH^{+}_{4(aq)} + PO^{3-}_{4(aq)}$

molarity NH_4^{+} = 3 molarity $(NH_4)_3PO_4$

molarity PO_4^{3-} = 1 molarity $(NH_4)_3PO_4$

Ex 4-2： Give the concentration, in moles per liter, of each ion in

a) 0.08 M b) 0.40 M

- a) $K_2SO_{4(S)} \longrightarrow 2K^+_{(aq)} + SO_4^{2-}$
- 【K^+】 = 2 × 0.08 = 0.16 M
- 【SO_4^{2-}】 = 1 × 0.08 = 0.08 M
- b) $FeCl_{3(S)} \longrightarrow Fe^{3+}_{(aq)} + 3Cl^-_{(aq)}$
  【Fe^{3+}】 = 1× 0.40 = 0.40 M
- 【Cl^-】 = 3 × 0.40 = 1.2 M

§ 4-2 Precipitation Reactions 沈澱反應

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

- ⤷ precipitate
- Ksp solubility product 溶解度積
- 沈澱 – 由兩種不同溶液的陽離子與陰離子相互作，不可溶的固體將會被分離出來

Figure 4.3 The precipitation diagram

	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)		$AgCl$				

沈澱反應規則

- 所有鹼金屬(IA族)及銨(NH_4^+)化合物均具可溶性
- 所有含NO_3^-(硝酸根)、 ClO_3^-(氯酸根)、 ClO_4^-(過氯酸根)的化合物均可溶
- 除IA族之氫氧化物、$Ba(OH)_2$為可溶、$Ca(OH)_2$為微溶外，其餘之氫氧化物(OH^-)均不可溶
- 多數氯化物(Cl^-)、溴化物(Br^-)、碘化物(I^-)是可溶，但含Ag^+、Hg_2^{+2}、Pb^{+2}例外
- 所有碳酸根(CO_3^{-2})、磷酸根(PO_4^{-3})及硫化物(S^{-2})均為不溶性
- 大多數SO_4^{-2}(硫酸根)為可溶性，但$CaSO_4$(硫酸鈣)及Ag_2SO_4(硫酸銀)為微溶；$BaSO_4$(硫酸鋇)、$HgSO_4$(硫酸汞)及$PbSO_4$(硫酸鉛)為不溶性

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

(a) $CuSO_4$和$NaNO_3$

$$CuSO_{4(aq)} \rightleftharpoons Cu^{+2}{}_{(aq)} + SO_4{}^{-2}{}_{(aq)}$$

$$NaNO_{3(aq)} \rightleftharpoons Na^{+}{}_{(aq)} + NO_3{}^{-}{}_{(aq)}$$

Possible precipitates:Cu(NO)$_3$及Na_2SO_4，form figure , both of these compounds are soluble So no precipitate forms.

(b) Na_2CO_3和 $CaCl_2$

$$Na_2CO_{3(aq)} \rightleftharpoons 2Na^{+}{}_{(aq)} + CO_3{}^{-2}{}_{(aq)}$$

$$CaCl_{2(aq)} \rightleftharpoons Ca^{+2}{}_{(aq)} + 2Cl^{-}{}_{(aq)}$$

Possible precipitates: NaCl and$CaCO_3$，form figure NaCl is soluble，$CaCO_3$ is not. So $CaCO_3$ precipitates.

Precipitation Reactions

PbI_2

沈澱 ↓

$Pb(NO_3)_2\ (aq) + 2NaI\ (aq) \longrightarrow PbI_2\ (s) + 2NaNO_3\ (aq)$

Molecule reaction equation 分子反應方程式

$Pb^{2+} + \cancel{2NO_3^-} + \cancel{2Na^+} + 2I^- \longrightarrow PbI_2\ (s) + \cancel{2Na^+} + \cancel{2NO_3^-}$

Ionic reaction equation 離子反應方程式

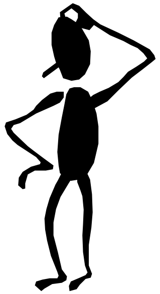
$Pb^{2+} + 2I^- \longrightarrow PbI_2\ (s)$

Net ionic equation 淨離子反應方程式

Na^+ and NO_3^- is ***旁觀（no part in the reaction）ion***

§1.Net ionic equation

1. 寫出平衡之分子反應方程式
2. 寫出其全部之離子反應方程式
3. 刪除反應式兩邊之「旁觀」離子



Write the net ionic equation for the reaction of silver nitrate with sodium chloride.

$$AgNO_3\ (aq) + NaCl\ (aq) \longrightarrow AgCl\ (s) + NaNO_3\ (aq)$$

$$Ag^+ + \cancel{NO_3^-} + \cancel{Na^+} + Cl^- \longrightarrow AgCl\ (s) + \cancel{Na^+} + \cancel{NO_3^-}$$

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

Net ionic equation must show

- atom balance
  - There must be the same number of atoms of each element on both sides.方程式兩邊原子數相同。
- charge balance
  - There must be the same total charge on both sides.方程式兩邊總電荷必須相等。

In particular all of the chemical equations written throughout this chapter are net ionic equations.

Ex 4-4： Write a net ionic equation of the followings：

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

Ions present：Na^+, OH^-, Cu^{+2}, NO_3^-

Possible precipitates：$NaNO_3$,$Cu(OH)_2$， $NaNO_3$ is soluble， $Cu(OH)_2$is not

$$Cu^{+2}{}_{(aq)} + 2OH^-{}_{(aq)} \rightleftharpoons Cu(OH)_{2(s)}$$

(b) $BaCl_2$和Ag_2SO_4

Ions present：Ba^{+2}, Cl^-, Ag^+, SO_4^{-2}

Possible precipitates：$BaSO_4$,AgCl，Both compounds are insoluble.

$$Ba^{+2}{}_{(aq)} + SO_4^{-2}{}_{(aq)} \rightleftharpoons BaSO_{4(s)}$$

$$Ag^+{}_{(aq)} + Cl^-{}_{(aq)} \rightleftharpoons AgCl_{(s)}$$

(c) $(NH_4)_3PO_4$和K_2CO_3

Ions present：NH_4^+, PO_4^{-3}, K^+, CO_3^{-2} there is no precipitation reaction.

2.Stoichiometry 化學計量

- Calculate mole-mass relations in reactions is readily applied to solution reaction represented by net ionic equations.
- 計算反應中莫耳－質量的關係.以淨離子反應方程式來表達溶液的反應
- 以一般的方法來解決限量反應物在淨離子反應方程式中的變化

Ex 4-5： When aqueous solutions of sodium hydroxide and iron nitrate are mixed, a red precipitate forms.
(a) Write a net ionic equation for the reaction.
(b) Determine the mass of precipitate formed when 30.0mL of 0.125M $Fe(NO_3)_3$ reacts.

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

  (b) $n_{Fe^{3+}} = \dfrac{30}{1000} \times 0.125\text{mol/L}$

  $= 3.75 \times 10^{-3} mol$

-
- $m_{Fe(OH)_3} = n \times MM = 3.75 \times 10^{-3} \times (55.85 + 3 \times (1.008 + 16.00))$
-
- $= 3.75 \times 10^{-3} \times 106.88 = 0.401 g$

Exam4.5 (c) Whe aqueous solutions of sodium (NaOH) and iron (III) nitrate $Fe(NO_3)_3$ are mixed，a red precipitate forms. Calculate the mass of precipitate formed when50.00mL，0.200M NaOH and 30.00mL，0.125M$Fe(NO_3)_3$?

$$Fe^{+3}{}_{(aq)} + 3OH^{-}{}_{(aq)} \rightleftharpoons Fe(OH)_{3(s)}$$

$$n_{Fe^{+3}} = 0.03000LFe(NO_3)_3 \times \frac{0.125molFe(NO_3)_3}{1LFe(NO_3)_3} \times \frac{1molFe^{+3}}{1molFe(NO_3)_3} = 3.75 \times 10^{-3} molFe^{+3}$$

$$n_{OH^-} = 50.0mL \times \frac{1L}{1000mL} \times 0.0200\frac{mol}{L} NaOH = 0.0100molOH^-$$

If $Fe^{+3}$is limiting reactant:

$$W_{Fe(OH)_3} = 3.75 \times 10^{-3} molFe^{+3} \times \frac{1molFe(NO_3)_3}{1molFe^{+3}} \times \frac{106.87gFe(OH)_3}{1molFe(NO_3)_3} = 0.401gFe(OH)_3$$

If $OH^-$is limiting reactant

$$W_{Fe(OH)_3} = 1.00 \times 10^{-3}\ mol\ OH^- \times \frac{1\ mol\ Fe(NO_3)_3}{3\ mol\ OH^-} \times \frac{106.87\ g\ Fe(NO_3)_3}{1mol\ Fe(NO_3)_3} = 0.356\ g\ Fe(OH)_3$$

範例4.5 考慮範例4.4的淨離子反應方程式，需要多少體積的0.106M $Cu(NO_3)_2$溶液，用以形成6.52g的$Cu(OH)_2$?

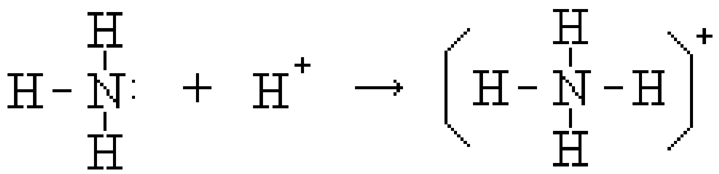
$$Cu^{+2}{}_{(aq)} + 2OH^{-}{}_{(aq)} \rightleftharpoons Cu(OH)_{2(s)}$$

$$V_{Cu(OH)_2} = 6.52g\,Cu(OH)_2 \times \frac{1mol\,Cu(OH)_2}{97.57g\,Cu(OH)_2} \times \frac{1mol\,Cu^{+2}}{1mol\,Cu(OH)_2} \times \frac{1mol\,Cu(NO_3)_2}{1mol\,Cu^{+2}} \times \frac{1L\,Cu(NO_3)_2}{0.106mol\,Cu(NO_3)_2} = 0.630L\,Cu(NO_3)_2$$

§ 4-3 Acid-base reactions

Acid
Acidic solution：
1. sour taste
2. Litmus(石蕊) turns from blue to red.
3.It is a species that produces H^+ ion in water solution.

Base
Basic solution：
1. slippery feeling
2. Litmus turns from red to blue
3.It is a species that produces OH^- ion in water solution.



NH_3

OH^-

$$2HCl\ (aq) + Mg\ (s) \longrightarrow MgCl_2\ (aq) + H_2\ (g)$$

$$2HCl\ (aq) + CaCO_3\ (s) \longrightarrow CaCl_2\ (aq) + CO_2\ (g) + H_2O\ (l)$$

1. Strong and Weak Acids and Bases.

- There are two types of acids, strong and weak,

Strong acid：ionize completely, forming H+ ions and anions. Table 4.1

- Ex $$HCl_{(aq)} \rightarrow H^{+}{}_{(aq)} + Cl^{-}{}_{(aq)}$$

Start 0.10 mol — —

balance 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.

$$HB_{(aq)} \Leftrightarrow H^{+}{}_{(aq))} + B^{-}{}_{(aq)}$$

- 開始 0.10 mol — —
- 平衡 0.09 mol 0.01 mol 0.01 mol partially ionized

Table4.1 Common Strong Acids and Bases

Acid	Name of Acid	Base	Name of Base
HCl	Hydrochloric acid 氫氯酸	LiOH	Lithium hydroxide氫氧化鋰
HBr	Hydrobromic acid 氫溴酸	NaOH	Sodium hydroxide氫氧化鈉
HI	Hydriodic acid氫碘酸	KOH	Potassium hydroxide氫氧化鉀
HNO_3	Nitric acid 硝酸	$Ca(OH)_2$	Calcium hydroxide 氫氧化鈣
$HClO_4$	Perchloric acid過氯酸	$Sr(OH)_2$	Strontium hydroxide 氫氧化鍶
H_2SO_4	Sulfuric acid 硫酸	$Ba(OH)_2$	Barium htdroxide 氫氧化鋇

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

Ex.

$$NaOH_{(s)} \rightarrow Na^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$Ca(OH)_{2(S)} \longrightarrow Ca^{2+}{}_{(aq)} + 2OH^-{}_{(aq)}$$

Weak base：

They react with 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.

2. Equations for Acid-Base reactions
Table 4.2 Types of Acid-Base Reactions

- 1. Strong acid-Strong base
  - 中和(neutralization)
  - $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$ net ionic Equation

2. Weak acid-Strong base
  - $HB_{(aq)} \rightleftharpoons H^+_{(aq)} + B^-_{(aq)}$
  - $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$
  - $HB_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} + B^-_{(aq)}$ net ionic Equation

3. Strong acid-Weak base
  - $NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$
  - $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$
  - $H^+_{(aq)} + NH_{3(aq)} \rightarrow NH_4^+{}_{(l)}$ 總反應
  - $H^+_{(aq)} + B_{(aq)} \rightarrow BH_{(aq)}^+$ net ionic Equation

Neutralization Reaction(中和反應)

acid + base $\longrightarrow$ salt + water

$HCl\ (aq) + NaOH\ (aq) \longrightarrow NaCl\ (aq) + H_2O$

$H^+ + \cancel{Cl^-} + \cancel{Na^+} + OH^- \longrightarrow \cancel{Na^+} + \cancel{Cl^-} + H_2O$

$H^+ + OH^- \longrightarrow H_2O$

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

a) Hyopchlorous acid次氯酸 and calcium hydroxide

b) Ammonia with perchloric acid 過氯酸

c) Hydriodic acid () with sodium hydroxide

- Ans：
- a) HClO weak acid strong base
- $HClO_{(aq)} + OH^-_{(aq)} \longrightarrow ClO^-_{(aq)} + H_2O$
- b) weak base strong acid
- $NH_{3\ (aq)} + H^+_{(aq)} \longrightarrow NH^+_{4\ (aq)}$
- c) strong acid strong base
- $H^+_{(aq)} + OH^-_{(aq)}$(l) $\longrightarrow H_2O$

Write a net ionic equation for each of the following reactions in dilute water solution

(a) 亞硝酸(HNO_2)與氫氧化鈉(NaOH)的反應

$$HNO_{2(aq)} \rightleftharpoons H^+_{(aq)} + NO_2{}^-{}_{(aq)}$$

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

$$HNO_{2(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} + NO_2{}^-{}_{(aq)}$$ 總反應

(b) 乙胺($CH_3CH_2NH_2$)與過氯酸($HClO_4$)的反應

$$C_2H_5NH_{2(aq)} + H_2O_{(l)} \rightleftharpoons C_2H_5NH_3{}^+{}_{(aq)} + OH^-_{(aq)}$$

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

$$C_2H_5NH_{2(aq)} + H^+_{(aq)} \rightarrow C_2H_5NH_3{}^+{}_{(l)}$$ 總反應

(c) 溴酸(HBr)與氫氧化鉀(KOH)的反應

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

3.Acid-Base Titration

titration滴定

- Measuring the volume of a standard solution (a solution of known concentration) required to react with a measured amount of sample.
  - 用已知濃度之標準溶液，滴定未知溶液，而測定出其樣品的含量。

equivalence point當量點

- The number of equivalent mole of base equal to the number of equivalent mole of acid .
  - 酸的莫耳數等於鹼的莫耳數

Neutralization point中和點

  - 酸鹼滴定後，其滴定終點恰為pH7。強酸強鹼。

End point滴定終點

- The point of the indicator change color
  - 酸鹼滴定，指示劑變色點。

Ex4.7 In titration, it is found that 25.0mL of 0.500M NaOH is required to react with

(a) a 15.00mL sample of HCl. What is the molarity of HCl?

(b) A 15.0mL sample of a weak acid , H_2A.What is the molarity of H_2A, assuming the reaction to be

©An aspirin tablet weighing 2.50g. What is the percentage of acetylsalicylic acid, , in the aspirin tablet?

$$HC_9H_7O_{4(aq)} + OH^-_{(aq)} \rightarrow C_9H_7O_4^-{}_{(aq)} + H_2O_{(l)}$$

Sol:

$$\text{(a)}\quad n_{HCl} = n_{NaOH} = (25.0 \times 10^{-3}\ L)(0.500 mol/L)$$

$$= 1.25 \times 10^{-2}\ mol$$

$$[HCl] = \frac{1.25 \times 10^{-2}\ mol}{15.0L \times 10^{-3}} = 0.833M$$

$$(b).nH_2A = n_{OH^-} = \frac{0.0125mol}{2} = 0.01mol$$

$$M_{H_2A} = \frac{0.01}{0.0150L} = 0.417 mol/L$$

$$H_2A + 2OH^- \rightarrow 2H_2O + A^{2-}$$

$$(c)nHC_9H_7O_4 = nOH^- = 0.0125mol$$

$$massnHC_9H_7O_4 = 0.0125mol \times 180.15 g/mol = 2.25g$$

$$nHC_9H_7O_4 = \frac{2.25g}{2.50g} \times 100 = 90.0$$

§ 4-4 Oxidation-Reduction Reactions

Common type of reaction in aqueous solution involves a transfer of electrons between two species . Such r reaction is called an oxidation-reduction or **redox reaction**. ()

$$Zn_{(s)} + 2H^{+}_{(g)} \longrightarrow Zn^{+2}_{(aq)} + H_{2(g)}$$

$Zn \longrightarrow Zn^{2+} + 2e^{-}$ ***Oxidation*** half-reaction (lose e^{-})

$2H^{+} + 2e^{-} \longrightarrow H_2$ ***Reduction*** half-reaction (gain e^{-})

$$Zn + 2H^{+} + \cancel{2e^{-}} \longrightarrow Zn^{2+} + H_2 + \cancel{2e^{-}}$$

$$Zn_{(s)} + 2H^{+}_{(g)} \longrightarrow Zn^{+2}_{(aq)} + H_{2(g)}$$

§ 4-4 Oxidation-reduction Reactions
Redox reactions

The type of reaction in aqueous solution involves a transfer of electron between two species .the reactions is called an oxidation-reduction

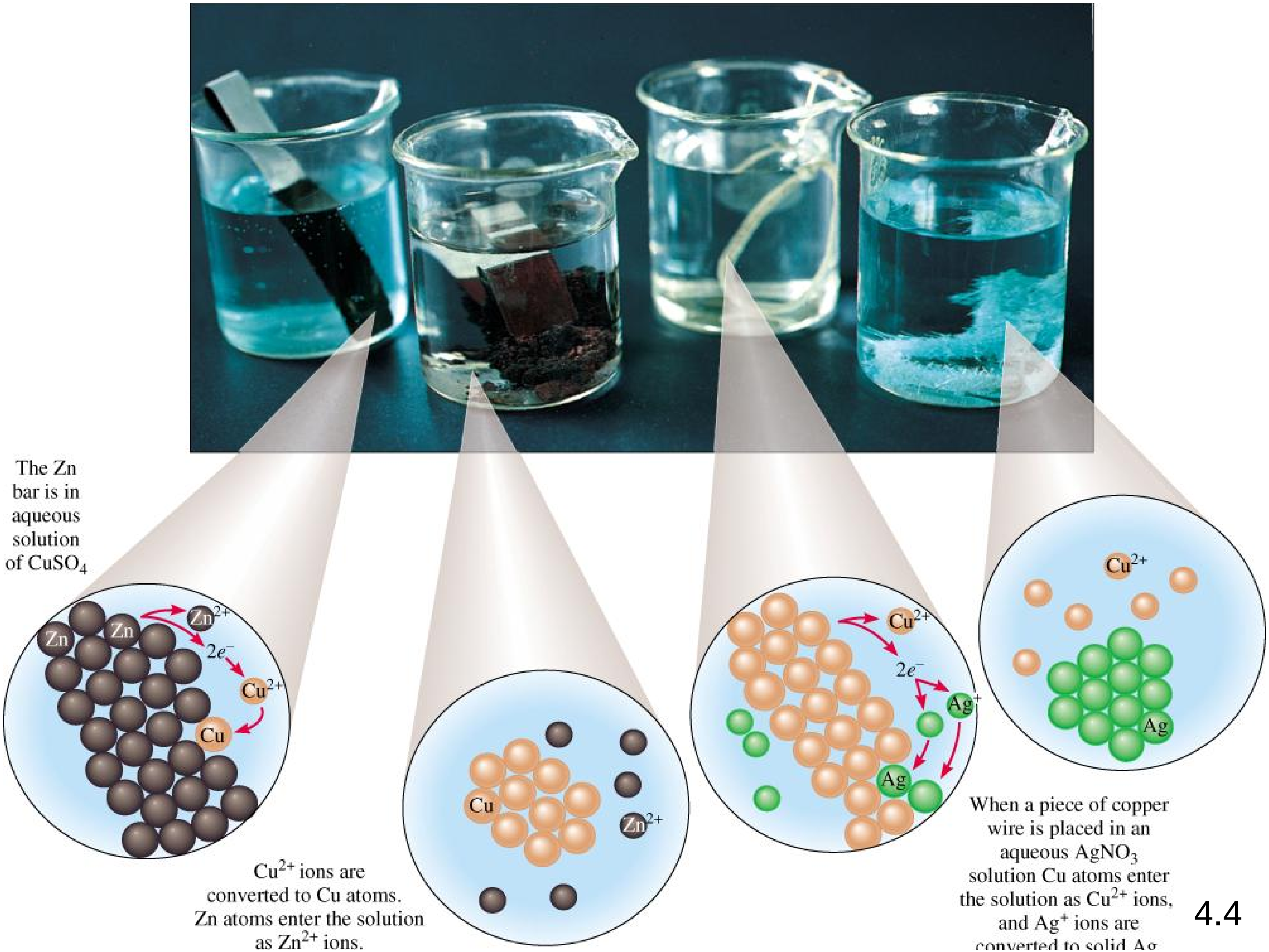
- Loses electron
- Donates electron
- Increase in oxidation numbers
- Is oxidized 被氧化
- Reducing agent

- Gains electron
- Accept(Receives) electrons
- Decrease in oxidation numbers
- Is reduced
- Oxidizing agent

1.Oxidation and reduction occur together ,

2.There is no net change in the number of electrons in a redox reaction.

$$Zn_{(s)} + 2H^{+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)}$$


The Zn bar is in aqueous solution of $CuSO_4$
Zn
Zn
Zn^{2+}
$2e^-$
Cu^{2+}
Cu
Cu
Zn^{2+}
Cu^{2+}
$2e^-$
Ag^+
Ag
Cu^{2+}
Ag
Cu^{2+} ions are converted to Cu atoms. Zn atoms enter the solution as Zn^{2+} ions.
When a piece of copper wire is placed in an aqueous $AgNO_3$ solution Cu atoms enter the solution as Cu^{2+} ions, and Ag^+ ions are converted to solid Ag

1.Oxidation number

在氧化還原反應中其原子的淨電荷數，陰電性較大的原子傾向於獲得電子而得到負的氧化數。

1. The oxidation number of an element in an elementary substance is O元素(未化合狀態)其氧化數為0

   Na, Be, K, Pb, H_2, O_2, P_4 = 0

2. The oxidation number of an element in a monatomic ion is equal to the charge of that ion.單原子離子其氧化數恰為其電荷數

   Li^+, Li = +1; Fe^{3+}, Fe = +3; O^{2-}, O = -2

3.Certain elements have the same oxidation number in all or almost all their compounds.

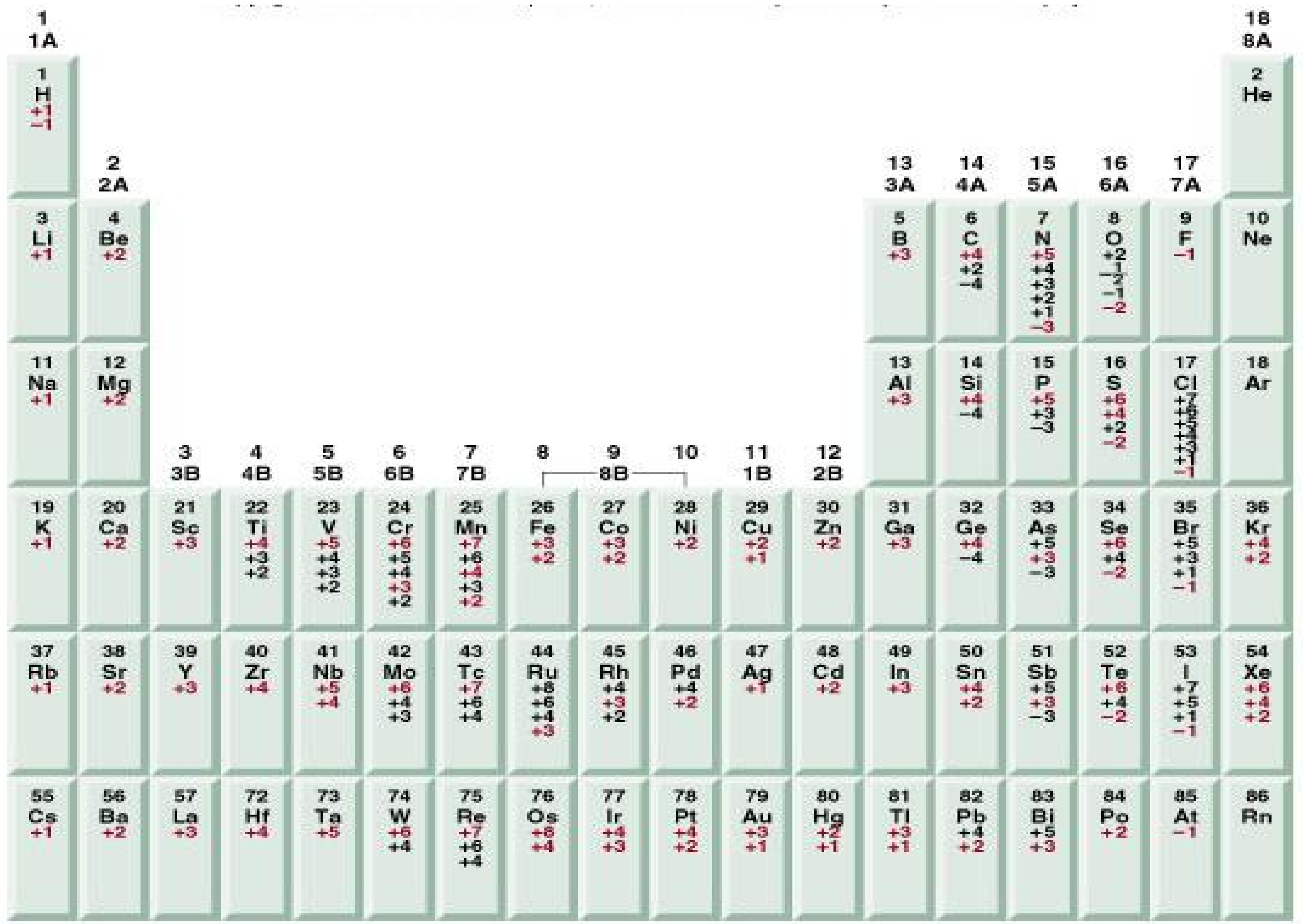
(1) **group metals1 as +1 ; group metals 2 as +2**

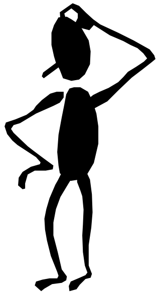
(2) O is an oxidation number of –2. But is H_2O_2 及O_2^{2-} is –1. –1/2

(3) Hydrogen is an Oxidation number of +1，*the in metal hydrides , Where hydrogen is present the H is* –1. H_2O , H = +1; LiH, H = -1

4.he sum of the oxidation numbers in a neutral species is 0 ;in a polyatomic ion ，it is equal to the charge of that ion.

中性分子中，所有原子之氧化數總和為零。在多原子離子中所有元素的氧化數總和必定與其電荷數相同。





Oxidation numbers of all the elements in the following ?

IF_7

F = -1

7x(-1) + ? = 0

I = +7

$NaIO_3$

Na = +1 O = -2

3x(-2) + 1 + ? = 0

I = +5

$K_2Cr_2O_7$

O = -2 K = +1

7x(-2) + 2x(+1) + 2x(?) = 0

Cr = +6

Ex 4-8 ：What is the oxidation number o f phosphorus in sodium phosphate, Na_3PO_4 ?

In the dihydrogen phosphate ion $H_2PO_4^-$?

Sol：

Na_3PO_4

$(+1)\times 3 + x + (-2)\times 4 = 0$

$x = +5$

$H_2PO_4^-$

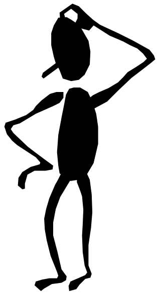
$(+1)\times 2 + x + (-2)\times 4 = -1$

$x = +5$

$$Zn\ (s) + CuSO_4\ (aq) \longrightarrow ZnSO_4\ (aq) + Cu\ (s)$$

$Zn \longrightarrow Zn^{2+} + 2e^-$ Zn is oxidized Zn is reducing agent

$Cu^{2+} + 2e^- \longrightarrow Cu$ Cu^{2+} is reduced Cu^{2+} is oxidizing agent



銅與硝酸銀反應生成硝酸銀與銀?在本反應中何者為氧化劑?

$$Cu\ (s) + 2AgNO_3\ (aq) \longrightarrow Cu(NO_3)_2\ (aq) + 2Ag\ (s)$$

$Cu \longrightarrow Cu^{2+} + 2e^-$

$Ag^+ + 1e^- \longrightarrow Ag$ Ag^+ is reduced Ag^+ is oxidizing agent

Types of Oxidation-Reduction Reactions

<u>Combination Reaction</u>

$$A + B \longrightarrow C$$

$$\overset{0}{S} + \overset{0}{O_2} \longrightarrow \overset{+4}{S}\overset{-2}{O_2}$$

<u>Decomposition Reaction</u>

$$C \longrightarrow A + B$$

$$2\overset{+1}{K}\overset{+5}{Cl}\overset{-2}{O_3} \longrightarrow 2\overset{+1}{K}\overset{-1}{Cl} + 3\overset{0}{O_2}$$

Types of Oxidation-Reduction Reactions

Displacement Reaction

$$A + BC \longrightarrow AC + B$$

$$\overset{0}{Sr} + 2\overset{+1}{H}_2O \longrightarrow \overset{+2}{Sr}(OH)_2 + \overset{0}{H}_2$$ Hydrogen Displacement

$$\overset{+4}{Ti}Cl_4 + 2\overset{0}{Mg} \longrightarrow \overset{0}{Ti} + 2\overset{+2}{Mg}Cl_2$$ Metal Displacement

$$\overset{0}{Cl}_2 + 2K\overset{-1}{Br} \longrightarrow 2K\overset{-1}{Cl} + \overset{0}{Br}_2$$ Halogen Displacement

2. Balancing half-equation (Oxidation or Reduction)

To balance half equation ：

1.Balance the atoms of the element being oxidized or reduced.

2.Balance the oxidation number by adding electrons.

- 平衡氧化數: 氧化數多的一邊加電子

3.Balance charge by adding ions in acidic solution, ions in basic solution.

- 平衡電荷數: 酸溶液加(電荷數較少之一邊)，鹼溶液加 (電荷數較多之一邊)

4. Balance hydrogen by adding molecules. 平衡H:

5. Balance Oxygen number. 平衡O

Balancing half-equation

- Oxidation reaction氧化反應
  - $Fe^{+2}(aq) \rightarrow Fe^{+3}(aq)$ (鐵的氧化數: +2 →+3)
  - $Fe^{+2}(aq) \rightarrow Fe^{+3}(aq) + e^{-}$
- Reduction reaction 還原反應
  - $Cl_2(aq) \rightarrow 2Cl^{-}(aq)$ (氯的氧化數: 0 →-1)
  - $Cl_2(aq) + 2e^{-} \rightarrow 2Cl^{-}(aq)$

Ex 4-9： Balance the following half-equations

A) $MnO_4^-{}_{(aq)} \rightarrow Mn^{+2}{}_{(aq)}$ (acidic solution)

B) $Cr(OH)_{3(s)} \rightarrow CrO_4^{-2}{}_{(aq)}$ (basic solution)

(A) $MnO_4^-{}_{(aq)} \rightarrow Mn^{+2}{}_{(aq)}$ (acid solution)

(a) There is one atom of Mn on both sides,Mn $MnO_4^-{}_{(aq)} \rightarrow Mn^{+2}{}_{(aq)}$

(b) Mn an oxidation number of +7 → +2，is reduced reaction

$$MnO_4^-{}_{(aq)} + 5e^- \rightarrow Mn^{+2}{}_{(aq)}$$

(c) The total charge of balance，left -6，right +2，酸性溶液中，以H^+平衡電荷

$$MnO_4^-{}_{(aq)} + 5e^- + 8H^+{}_{(aq)} \rightarrow Mn^{+2}{}_{(aq)}$$

(d) Balance the eight H ions on the left ,add four 4 H_2O to the right

$$MnO_4^-{}_{(aq)} + 5e^- + 8H^+{}_{(aq)} \rightarrow Mn^{+2}{}_{(aq)} + 4H_2O_{(l)}$$

(e) 方程式左右各有4個O，為己平衡之還原半反應

$MnO_4^-{}_{(aq)} + 5e^- + 8H^+(aq) \rightarrow Mn^{+2(}aq) + 4H_2O(l$

(B) $Cr(OH)_{3(s)} \rightarrow CrO_4^{-2}{}_{(aq)}$ basic solution

(a) 兩邊均含一個Cr，所以不必平衡Cr　$Cr(OH)_{3(aq)} \rightarrow CrO_4^{-2}{}_{(aq)}$

(b) Cr的氧化數+3 → +6，為氧化半反應

$Cr(OH)_{3(aq)} \rightarrow CrI_4^{-2}{}_{(aq)} + 3e^-$

(c) 平衡總電荷，左邊 0，右邊 -5，鹼性溶液中，以OH⁻平衡電荷

$Cr(OH)_{3(aq)} + 5OH^-{}_{(aq)} \rightarrow Mn^{+2}{}_{(aq)} + 3e^-$

(d) 平衡H，左邊 8個H，所以右邊加入4 H_2O

$Cr(OH)_{3(aq)} + 5OH^- \rightarrow CrO_4^{-2}{}_{(aq)} + 3e^- + 4H_2O_{(l)}$

(e) 方程式左右各有8個O，為已平衡之還原半反應

$Cr(OH)_{3(aq)} + 5OH^- \rightarrow CrO_4^{-2}{}_{(aq)} + 3e^- + 4H_2O_{(l)}$

3. Balancing Redox equation

1. Split the equation into tow half-equations, one for reduction, the other for oxidation.

- 將反應方程式分別以兩個半反應方程式表示，一個氧化，一個還原。

2. Balance one of the half-equations with respect to both atoms and charge as described above

- 平衡其中一個半反應方程式中的原子數及電荷數

3. Balance the other half-equation

平衡另一個半反應方程式中的原子數及電荷數

4. Combine the two half-equations in such a way as to eliminate electrons(2 + 3) 消去電子

- 藉著消去方程式兩邊的電子數，將兩個半反應方程式結合起來。

Ex 4-10：Balance the following redox equations

(a) $Fe^{+2}{}_{(aq)} + MnO_4^{-}{}_{(aq)} \rightarrow Fe^{+3}{}_{(aq)} + Mn^{+2}$ acid solution

(1) 氧化：$Fe^{+2}{}_{(aq)} \rightarrow Fe^{+3}{}_{(aq)}$ $\quad Fe^{+2}{}_{(aq)} \rightarrow Fe^{+3}{}_{(aq)} + e^{-}$

還原：$MnO_4^{-}{}_{(aq)} \rightarrow Mn^{+2}{}_{(aq)}$

$MnO_4^{-}{}_{(aq)} + 5e^{-} + 8H^{+}{}_{(aq)} \rightarrow Mn^{+2}{}_{(aq)} + 4H_2O_{(l)}$

為使電子可消去，故在氧化反應方程式乘以5

$5Fe^{+2}{}_{(aq)} \rightarrow 5Fe^{+3}{}_{(aq)} + \cancel{5e^{-}}$

$MnO_4^{-}{}_{(aq)} + \cancel{5e^{-}} + 8H^{+}{}_{(aq)} \rightarrow Mn^{+2}{}_{(aq)} + 4H_2O_{(l)}$

$MnO_4^{-}{}_{(aq)} + 5Fe^{+2} + 8H^{+}{}_{(aq)} \rightarrow Mn^{+2}{}_{(aq)} + 5Fe^{+3}{}_{(aq)} + 4H_2O_{(l)}$

(b) $Cl_{2(aq)} + Cr(OH)_{3(aq)} \rightarrow Cl^{-}{}_{(aq)} + CrO_4{}^{-2}{}_{(aq)}$ 鹼性溶液

(1) 氧化：$Cr(OH)_{3(aq)} \rightarrow CrO_4{}^{-2}{}_{(aq)}$

$$Cr(OH)_{3(s)} + 5OH^{-}{}_{(aq)} \rightarrow CrO_4{}^{-2}{}_{(aq)} + 3e^{-} + 4H_2O_{(l)}$$

還原：$Cl_{2(aq)} \rightarrow 2Cl^{-}{}_{(aq)}$ $\quad Cl_{2(aq)} + 2e^{-} \rightarrow 2Cl^{-}{}_{(aq)}$

為使電子可消去，故還原反應方程式×3

為使電子可消去，故在氧化反應方程式× 2

$$3Cl_{2(aq)} + \cancel{6e^{-}} \rightarrow 6Cl^{-}{}_{(aq)}$$

$$2Cr(OH)_{3(s)} + 10OH^{-}{}_{(aq)} \rightarrow 2CrO_4{}^{-2}{}_{(aq)} + \cancel{6e^{-}} + 8H_2O_{(l)}$$

$$3Cl_{2(aq)} + 2Cr(OH)_{3(s)} + 10OH^{-}{}_{(aq)} \rightarrow 2CrO_4{}^{-2}{}_{(aq)} + 6Cl^{-}{}_{(aq)} + 8H_2O_{(l)}$$

Ex 4-11：As you found in Example 4.10, the balanced equation for the reaction between and in acidic solution is What volume of 0.684 M KMnO4 solution is required to react completely with 27.5 ml 0.250 M Fe（NO3）$_2$？

$$MnO_4^-{}_{(aq)} + 5Fe^{+2} + 8H^+{}_{(aq)} \rightarrow Mn^{+2}{}_{(aq)} + 5Fe^{+3}{}_{(aq)} + 4H_2O_{(l)}$$

$$n_{Fe^{+2}} \rightarrow n_{KMnO_4} \rightarrow V_{KMnO_4} = \frac{n_{KMnO_4}}{M_{KMnO_4}}$$

$$n_{Fe^{+2}} = 0.02750L \times \frac{0.250 molFe(NO_3)_2}{1L} \times \frac{1 molFe^{+2}}{1 molFe(NO_3)_2} = 6.88 \times 10^{-3} mol\ Fe^{+2}$$

$$n_{MnO_4^-} = 6.88 \times 10^{-3} mol \times \frac{1 molMnO_4^-}{5 molFe^{+2}} = 1.38 \times 10^{-3} mol\ MnO_4^-$$

$$V_{MnO_4^-} = 1.38 \times 10^{-3} mol\ MnO_4^- \times \frac{1 mol\ KMnO_4}{1 mol\ MnO_4^-} \times \frac{1L}{0.684 mol\ KMnO_4}$$

$$= 2.02 \times 10^{-3} L$$