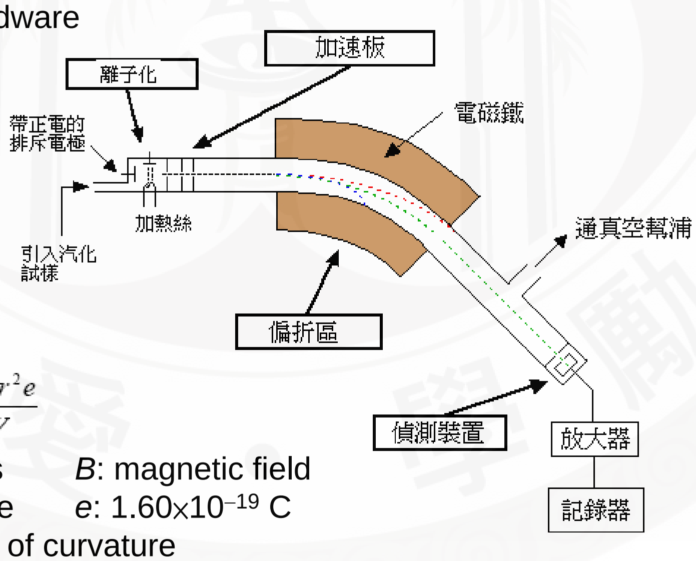
3 Stoichiometry (計量化學)

※ Atomic masses

1961 ^{12}C is used as standard
Assigned 12 atomic mass unit (amu)

1913 Thomson
Mass spectrometer
later refined by Aston (1877 -1945; 1922 Nobel prize)

The hardware



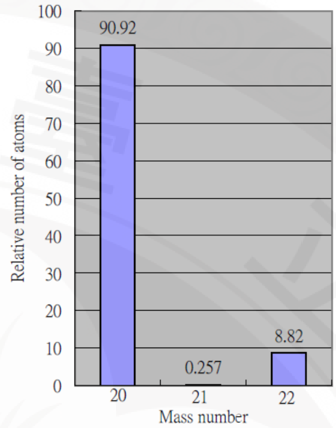
$$\frac{m}{z} = \frac{B^2 r^2 e}{2V}$$

m: mass　　*B*: magnetic field
z: charge　　*e*: 1.60×10^{-19} C
r: radius of curvature
V: voltage

Mass spectrometer

The most accurate method for mass determination

1919 Mass spec. of Ne
20 and 22 (isotopes)
plus minute amt. of ^{21}Ne



Some common elements

^{16}O 15.9949 ^{17}O 16.9991

^{18}O 17.9992

Ratio = 100 : 0.04 : 0.20

^{35}Cl 100 ^{37}Cl 32.5

^{79}Br 100 ^{81}Br 98.0

^{1}H 100 ^{2}H 0.016

Ex. $M_{^{13}C} / M_{^{12}C} = 1.0836129$

$AW_{^{13}C} = (1.0836129)(12\ amu) = 13.003355\ amu$

The atomic mass used for weight measurement is an average weight

Ex. ^{12}C natural abundance: 98.89%
^{13}C 1.11%
^{14}C negligible

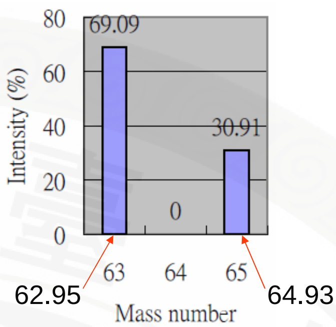
Average: $12.00 \times 98.89\% + 13.0034 \times 1.11\%$
$= 12.01$ amu

↑

Used in elementary analysis

Ex. Cu

Average AW
= 62.93(0.6909) + 64.93(0.3091)
= 63.55



※ The mole (莫耳)

Abbreviated as mol
A unit of measure for use in counting atoms
一種計量原子或分子數量的單位

1911 Rutherford and Boltwood
Count α-particle/sec of Ra

$$^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\text{He}$$

α-particle
Determine the volume

1971 Define mole as the number of atoms in 12 g of ^{12}C
1 mole = 6.022137×10^{23} units
↑ Avogadro's numbers

Mass of 1 mole ^{12}C = 12 g
⇨ Mass of 1 mole ^{13}C = 13 g

1 mole ^{12}C = 12 g = $(6.02 \times 10^{23}) \times 12$ amu
1 g = 6.02×10^{23} amu
1 amu = $1/(6.02 \times 10^{23})$ g

Molar mass
The mass in grams of 1 mole of the compound

Percent composition of compounds
The mass percent (weight percent) of each element
Determined by elementary analysis or mass spec.

Ex.	$^{12}C^{16}O$	27.9949
	$^{14}N_2$	28.0062
	$^{12}C_2{}^{1}H_4$	28.0312

Determining the formula
percent composition → empirical formula
molar mass → molecular formula

Ex. A compound composed of C, H, N

Burning 0.1156 g of sample → 0.1638 g CO_2, 0.1676 g H_2O

$$0.1638 \times \frac{12.011 \text{ g C}}{44.009 \text{ g } CO_2} = 0.04470 \text{ g C}$$

$$0.1676 \times \frac{2.016 \text{ g H}}{18.015 \text{ g } H_2O} = 0.01876 \text{ g H}$$

$$\text{C: } \frac{0.04470}{0.1156} = 38.67\% \qquad \text{H: } \frac{0.01876}{0.1156} = 16.23\%$$

N: 100.00% − 38.67% − 16.23% = 45.10%

Mole ratio

$$C : H : N = \frac{38.67}{12.011} : \frac{16.23}{1.008} : \frac{45.10}{14.007}$$

$$= 1:5:1$$

The smallest whole-number ratio

Empirical formula (最簡式) = CH_5N

Molecular formula – obtained from molecular mass

Knowing the molar mass as 31.06 g/mol

→ CH_5N is the molecular formula

※ Stoichiometric calculations

處理化學反應物間數量的關係

✓ Balancing chemical equations

Ex.

$$C_2H_5OH(l) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$$

↳ Start with the most complicated structure

$$1C_2H_5OH(l) + 3O_2(g) \rightarrow 2\,CO_2(g) + 3\,H_2O(g)$$

✓ Limiting reactant

If mixed in stoichiometric quantities

No limiting reagent

When one is in excess,
the other one is limiting reagent

Ex. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

5.0 mol 9.0 mol

↳ limiting reagent

⇨ theoretically will obtain 6.0 mole of NH_3

⇨ theoretical yield = $17 \times 6.0 = 102$ g or 1.0×10^2 g

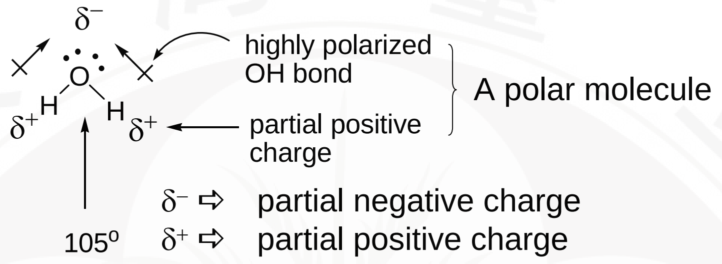
$$\frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100\% = \text{percent yield}$$

4 Solution Stoichiometry

※ Aqueous solution (水溶液)

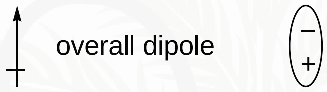
Water as solvent (溶劑)

◎ Structure of water



δ⁻ ⇨ partial negative charge

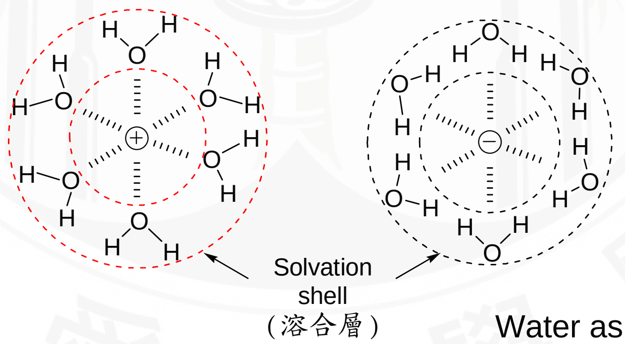
δ+ ⇨ partial positive charge



有時會以這種圖像表示之

◎ Hydration

When ionic compound dissolves in water:



The ions are solvated

Water as solvent: hydration (水合)

Ex. $NH_4NO_3(s) \xrightarrow{H_2O(l)} NH_4^+(aq) + NO_3^-(aq)$

Does not dissolve nonpolar substances

Dissolves polar substances

※ The nature of aqueous solution

◎ Electric conductivity

1884 Arrhenius (1859 – 1927; 1903 Nobel prize)
Studied the conductivity of solutions of acids, bases and salts

Proposed : electric conductivity was due to the presence of ions

Electrolytes
Dissolves, ionized, and the solution conducts electricity

- Strong electrolyte (強電解質)
- Weak electrolyte (弱電解質)
- Nonelectrolyte (非電解質)

✓ Strong electrolytes
soluble salts: NaCl, ……
strong acids: HCl, ……
strong bases: NaOH, …..

Strong acids

$$HCl \xrightarrow{H_2O} H^+(aq) + Cl^-(aq)$$

$$HNO_3 \xrightarrow{H_2O} H^+(aq) + NO_3^-(aq)$$

$$H_2SO_4 \xrightarrow{H_2O} H^+(aq) + HSO_4^-(aq)$$

↑ They all generate $H^+(aq)$

Arrhenius definition of acids
Any substance that produces H^+ ion when it is dissolved in water

✓ Weak electrolytes

When dissolved in water dissociates weakly

$$CH_3COOH(aq) \xrightarrow{H_2O} CH_3COO^-(aq) + H^+(aq)$$

~1% ionized
(for a 1 *M* solution)

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※ The composition of solutions

Glossaries

solute	溶質
solvent	溶劑
solution	溶液
dilute	稀釋

◎ Concentration

Molarity (體積莫耳濃度)

Moles of solute per liter of solution

$$M = \text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

※ Types of chemical reactions

◎ Precipitation reactions

A solid forms and separates from the solution

$K_2CrO_4(aq)$ + $Ba(NO_3)_2(aq)$ → yellow precipitate (ppt)

⇨ $2K^+(aq)$ + $CrO_4^{2-}(aq)$ + $Ba^{2+}(aq)$ + $2NO_3^-(aq)$

⇨ possible combinations: K_2CrO_4，KNO_3，$BaCrO_4$，$Ba(NO_3)_2$

soluble (KNO_3)　precipitate ($BaCrO_4$)

$K_2CrO_4(aq)$ + $Ba(NO_3)_2(aq)$ → $BaCrO_4(s)$ + $2\ KNO_3(aq)$

reactants　　products　　soluble

✓ Knowledge of solubility is useful

Some rules

1. NO_3^- salts → soluble
2. Na^+, K^+, NH_4^+ salts → soluble
3. Cl^- salts → soluble
   except AgCl, $PbCl_2$, Hg_2Cl_2
   ($PbCl_2$: Dissolves in hot water)
4. SO_4^{2-} salts → soluble
   except $BaSO_4$, $PbSO_4$, $CaSO_4$
5. OH^- salts → slightly soluble
   except NaOH, KOH, $Ca(OH)_2$ (marginal)
6. S^{2-}, CO_3^{2-}, PO_4^{2-} salts → slightly soluble

✓ Selective precipitation

Q: Can we separate Ag^+, Ba^{2+}, Fe^{3+} (NO_3^-)

A:

Ag^+, Ba^{2+}, Fe^{3+}

$AgCl(s)$ ← ↓ $NaCl(aq)$

Ba^{2+}, Fe^{3+}

$BaSO_4(s)$ ← ↓ $Na_2SO_4(aq)$

Fe^{3+} (yellow color)

↓ $NaOH(aq)$

$Fe(OH)_3(s)$ (reddish brown)

The whole process is called qualitative analysis

Measurement of the ppt to determine the amt of certain ion – Gravimetric analysis

◎ Acid-base reactions

1923 Brønsted and Lowry

acid → proton donor

base → proton acceptor

Works also in non-aqueous system

Ex.

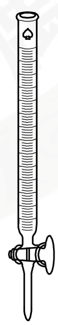
$$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$$

Acid-base titration

Requires standard acid or base (the titrant)

Use a buret (滴定管)

Indicator to differentiate equivalence point



◎ Oxidation-reduction reactions

Electron transfer involved

- Losing electrons：
  - Oxidation
  - Oxidation state increases
  - Used as reducing agent
- Accept electrons：
  - Reduction
  - Oxidation state decreases
  - Used as oxidizing agent

✓ Rules of assigning oxidation state

1. An atom in an element: zero

   Ex. Na(*s*), $O_2(g)$, $O_3(g)$

2. Monoatomic ion: equals the charge

   Ex. Na^+: +1

3. Hydrogen: covalent bond with nonmetal ⇨ +1

   with metal ⇨ –1 (Ex. NaH)

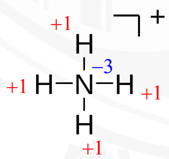
4. Oxygen: –2

   but O_2^{2-}: –1

5. A–B

   +1 –1 (more electronegative)

6. Overall charge must be balanced

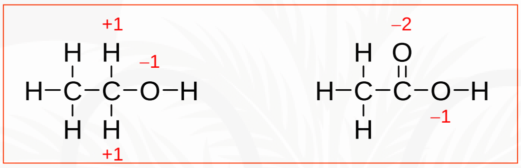


$4(+1) + (-3) = +1$

◎ Balancing oxidation-reduction equations

✓ The half-reaction method

1. Balance the elements first (except O, H)
   $1\ CH_3CH_2OH \rightarrow 1\ CH_3COOH$
2. Use H_2O to balance missing O
   $1\ CH_3CH_2OH + 1\ H_2O \rightarrow 1\ CH_3COOH$
3. Use H^+ to balance missing H
   $1\ CH_3CH_2OH + 1\ H_2O \rightarrow 1\ CH_3COOH + 4\ H^+$
4. Use electron to balance charges
   $1\ CH_3CH_2OH + 1\ H_2O \rightarrow 1\ CH_3COOH + 4\ H^+ + 4\ e^-$



⇨ C: $-1 \rightarrow +3$
oxidation

Q: $CrO_4^{2-} \rightarrow Cr^{3+}$

Soln:

⇨ $CrO_4^{2-} \rightarrow Cr^{3+} + 4H_2O$

⇨ $CrO_4^{2-} + 8H^+ \rightarrow Cr^{3+} + 4H_2O$

⇨ $CrO_4^{2-} + 8H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O$

(Cr: $+6 \rightarrow +3$ ⇨ reduction)

Combine the two

$(CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e^-) \times 3$

$(CrO_4^{2-} + 8H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O) \times 4$

$3CH_3CH_2OH + 4CrO_4^{2-} + 20H^+ \rightarrow 3CH_3COOH + 4Cr^{3+} + 13H_2O$

Ex. $Ag(s) + CN^-(aq) + O_2(g) \rightarrow Ag(CN)_2^-(aq)$

Soln: $Ag(s) \rightarrow Ag(CN)_2^-(aq)$

⇨ $Ag(s) + 2CN^-(aq) \rightarrow Ag(CN)_2^-(aq)$

⇨ $Ag(s) + 2CN^-(aq) \rightarrow Ag(CN)_2^-(aq) + e^-$

$O_2(g) \rightarrow$

⇨ $O_2(g) \rightarrow 2H_2O(l)$

⇨ $O_2(g) + 4H^+(aq) \rightarrow 2H_2O(l)$

⇨ $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

$4Ag(s) + 8CN^-(aq) \rightarrow 4Ag(CN)_2^-(aq) + 4e^-$

$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

$4Ag(s) + 8CN^-(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Ag(CN)_2^-(aq) + 2H_2O(l)$

$4Ag(s) + 8CN^-(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Ag(CN)_2^-(aq) + 2H_2O(l)$

In basic condition:

$4Ag(s) + 8CN^-(aq) + O_2(g) + 4H^+(aq) + 4OH^-(aq)$

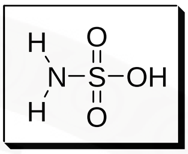
$\rightarrow 4Ag(CN)_2^-(aq) + 2H_2O(l) + 4OH^-(aq)$

⇨ $4Ag(s) + 8CN^-(aq) + O_2(g) + 2H_2O(l)$

$\rightarrow 4Ag(CN)_2^-(aq) + 4OH^-(aq)$

Ex. $NaNO_2 + H_2NSO_3H \rightarrow N_2$

+3 −3 0



$NO_2^- \rightarrow N_2$

⇨ $2NO_2^- \rightarrow N_2$

⇨ $2NO_2^- \rightarrow N_2 + 4H_2O$

⇨ $2NO_2^- + 8H^+ \rightarrow N_2 + 4H_2O$

⇨ $2NO_2^- + 8H^+ + 6e^- \rightarrow N_2 + 4H_2O$

$H_2NSO_3H \rightarrow N_2$

⇨ $2H_2NSO_3H \rightarrow N_2$

⇨ $2H_2NSO_3H \rightarrow N_2 + 2SO_4^{2-}$

⇨ $2H_2NSO_3H + 2H_2O \rightarrow N_2 + 2SO_4^{2-}$

⇨ $2H_2NSO_3H + 2H_2O \rightarrow N_2 + 2SO_4^{2-} + 10H^+$

⇨ $2H_2NSO_3H + 2H_2O \rightarrow N_2 + 2SO_4^{2-} + 10H^+ + 6e^-$

Overall

$NO_2^- + H_2NSO_3H \rightarrow N_2 + H_2O + SO_4^{2-} + H^+$

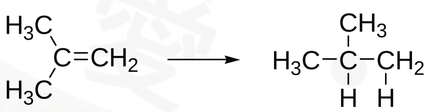
◎ A quick way to judge oxidation or reduction in organic molecules

Oxidation if the number of O ↑
the number of H ↓

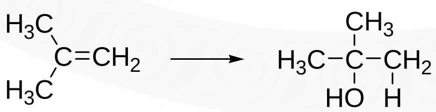
Ex. $CH_3CH_2OH \rightarrow CH_3COOH$ Oxidation

Reduction if the number of O ↓
the number of H ↑

Ex. $CH_3COOH \rightarrow CH_3CH_2OH$ Reduction



Reduction



H ↑
O ↑ } No net change