2 Atoms, Molecules, and Ions

※ A historical background of chemistry

(ref. *The History of Chemistry* by John Hudson, 1992)

Early chemistry: Development of technologies (Experiments)

◎ Neolithic revolution

stone age → bronze age → iron age

Important tool of technology: fire

✓ Extraction of metal:

Au, Ag, Cu, Fe ← from meteorite

Through chemical reactions

Ex. Malachite ($CuCO_3$) $\xrightarrow{\text{charcoal}}$ Cu

✓ Pottery and glass ← as early as 4000 BC

✓ Pigments and dyes ← Ex. indigo

↑ as early as 30,000 yrs

red: iron oxide

yellow: iron carbonate

black: manganese dioxide

◎ Early speculation

The first principle

◎ The ionian: materialistic explanation

Thales (~585 BC)

Water

Anaximander (~555 BC)

Boundless

Anaximenes (~535 BC)

Mist

Heraclitus (~500 BC)

Fire

◎ Western Greek philosopher

Pythagoras (~560 BC)

Mathematical approach

Parmenides (~500 BC)

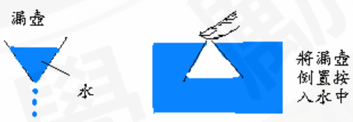
Truth should be sought by reason alone

Empedocles (~450 BC)

Observation is important

ex. Clepsydra experiment

→ air is a material substance



Idea

four roots: earth, air, fire, and water

two forces: attraction, and repulsion

◎ Greek mainland

Anaxagoras (500 – 428 BC)

Every material always retains a portion of every other material

Leucippus (478 BC)
Democritus (420 BC) } Proposed atoms (indivisible)

Socrates (470 – 399 BC)

Socrates method

Focused on moral and ethical issues

Plato (427 – 347 BC)

Primary roots: five regular polyhedra

Aristotle (384 – 322 BC)

Four element theory (from Empedocles)

Against atomic theory

Perform little experiment

◎ The era of alchemy (煉金)

Primary goal: base metal → gold

632 AC Islam expansion

Baghdad became center of learning

The idea of alchemy imported from China

12th century

Influenced European scholars

Ex. Wine distillation, water cooled condenser

13th century

Discovery of sulfuric acid, nitric acid

◎ From alchemy to chemistry

Three traditions
- The Aristotelian
- The Magical
- The Mechanical

17th century – modern science began to emerge
- Up rise of mechanical philosophy
- Influence of Archimedes (287 – 212 BC)

Bacon (1561 – 1626)
- Experiments should be planned.
- Results should be repeated and verified.

Experimental science emerged → New ideas

✓ Robert Boyl (1627 – 1691)

A strong believer in mechanistic interpretation of chemical phenomenon

Critical to Aristotle’s concept of four elements

Studied combustion

Exp. red hot iron plate in a vessel → evacuate
→ drop combustible materials on it
→ catch no fire
→ release air in
→ catch fire

Exp.

$$\text{metal} \xrightarrow{\Delta} \text{calx (oxide)}$$

gain weight

Conclusion: metal + phlogiston → calx

Exp. Fe + H^+ → H_2 ← inflammable

✓ Robert Hooke (1635 – 1703)

Constructed a coherent theory of combustion

Air: Absorbs phlogiston
When saturated – ceased burning
In vacuum – no combustion because vac. can not absorb phlogiston

Problem: Burning of metal
→ gives off phlogiston
But calx gains weight?

✓ Black (1728 – 1799)

1756 $MgCO_3$ —heat→ MgO + CO_2

$MgCO_3$: magnesia alba; MgO: magnesia; CO_2: Fixed air

$MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$

$MgSO_4 + K_2CO_3 \rightarrow MgCO_3 + K_2SO_4$

(K_2CO_3: mild alkali)

Similarly for quick-lime ($CaCO_3$)

✓ Priestley (1733 – 1804)

1774 HgO $\xrightarrow[\text{from light}]{\text{heat}}$ Hg + O_2

↑ Strongly absorbs phlogiston

1778 Aquatic plants → give off O_2

✓ Scheele (1742 – 1786)

Exp. K_2S absorbs O_2 in the air

→ residual gas is lighter than ordinary air

→ termed foul air (N_2)

↑ Does not absorb phlogiston

✓ Cavendish (1731 – 1810)

$2H_2 + O_2 \rightarrow H_2O$

Theory:

(H_2O + phlogiston) + (H_2O – phlogiston) → H_2O

◎ New era

Lavoisier (1743 – 1794)

Exp. Boiling of H_2O in a closed vessel

→ discredit phlogiston

Exp. Heating Sn in a sealed apparatus

→ SnO_2

Exp. HgO $\xrightarrow{\text{heating}}$ Hg $\xrightarrow{O_2}$ HgO

} Oxygen theory

➡ Air is composed of two parts

✓ The question of H_2

Known: metal + acid → H_2

Theory based on phlogiston:

phlogiston ≡ H_2

(calx + phlogiston) + acid → (calx + acid) + phlogiston

(calx + phlogiston) = metal; phlogiston → H_2

Q: For Lavoisier:
If H_2 is not phlogiston, then what is H_2?

Hint from Cavendish's exp.

$$2H_2 + O_2 \rightarrow 2H_2O$$

Exp. H_2O + red hot Fe → calx + H_2

Theory: metal + H_2O → metal oxide + H_2

H_2O → (H & O); metal oxide → calx

※ Fundamental chemical laws

Lavoisier – Law of conservation of mass
(quantitative analysis)

Proust (1754 – 1826)
Law of definite proportion
(by 1808 generally accepted)

Dalton (1766 – 1844)
Law of constant composition:
Compound is composed of atoms
with the same combination

Ex. Two ways to combine C & O

Compound I	1 g C	1.33 g O
Compound II	1 g C	2.66 g O

➡ Law of multiple proportions
(Berzelius, 1779 – 1848, determined 200 inorganic compound in 10 years)

Problem

could not determine absolute formula

CO C_2O_2 ---------

CO_2 C_2O_4 ---------

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※ Dalton's atomic theory (1808)

1. Element – composed of atoms
2. Different element – different atoms
3. Compound – atoms combined in a definite ratio
4. Chemical reaction – reorganize atoms

Atomic weights (1805)

1 g H, 8 g O → water

If AW(O) = 8 × AW(H) → water = OH ✓ Principle of simplicity

If AW(O) = 16 × AW(H) → water = OH_2

etc.

(by 1826, Berzelius's table contained 49 elements)

1809 Gay-Lussac (1778 – 1850)

Studied reactions of gases

existence of simple whole number

Ex. $2\ H_2 + 1\ O_2 \rightarrow 2\ H_2O$

$1\ H_2 + 1\ Cl_2 \rightarrow 2\ HCl$

$1\ N_2 + 1\ O_2 \rightarrow 2\ NO$

1811 Avogadro (1776 – 1856)

Avogadro hypothesis

Same T, P

equal volumes of different gases

contain the same number of particles

Proposed

diatomic molecules (accepted in 1860)

⇨ Water = H_2O

Problem: the idea of diatomic molecule was not accepted

※ The new era

(Cannizarro's interpretation)

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1860 First International Chemical Congress at Karlsruhe

(Organizer: Kekule (1829 – 1896))

Cannizarro (1826 – 1910)

1. Compounds contain whole number of atoms
2. Adopt Avogadro's hypothesis

AW(H) = 1 → MW(H_2) = 2

$$\frac{W_{1L\ O_2}}{W_{1L\ H_2}} = \frac{16}{1} = \frac{32}{2}$$ ⇨ AW(O) = 16

Carbon dioxide: relative mass = 44
(compared with hydrogen)
with 27% of C ($44 \times 0.27 = 12$)

44 g CO_2: 12 g C 32 g O

If AW(C) = 12 → CO_2
6 → CO

How can we determine the AW of C?

	Rel. mass	% C	Rel. mass	
Methane	16	75	12	← 16×0.75
Ethane	30	80	24	
Propane	44	82	36	
Butane	58	83	48	
CO_2	44	27	12	

⇨ Conclusion: AW(C) = 12

Mendeleev

"我清楚的記得他的演講帶給我的印象，可說是在闡述確實的真理而無懈可擊，而這些真理是基於亞佛加厥，蓋哈特(Gerhardt)以及雷諾(Regnault)等在當時幾乎完全不被認同的觀念。雖然真正的共識在當時尚未能達成，但是這個會議的目的卻達到了，因為在數年之後，卡氏的想法證實為唯一能通過檢驗的理論，也代表原子為分子或化合物組成的最小部分。唯有如此真實的原子量，而非過去的各種數值，才能成為一切理論的基礎。"

Meyer (1830 – 1895)
“The Modern Theory of Chemistry” 1864

“當這些數值鑽入我眼中時，所有的疑問都已消失，
取代而之的是一種最為平和的確實感”
-- a feeling of the most peaceful assurance --

1869
The first periodic table

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※ Characterization of atom

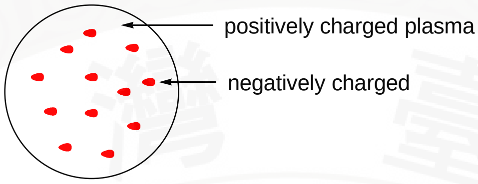
1856-1940 J. J. Thomson

Study of cathode ray tubes
→ cathode ray
→ different metals, same result

Thomson’s postulation
negatively charged particles
(electrons)

$$\frac{e}{m} = -1.76 \times 10^{8}\ \text{C/g}$$

Thomson's plum pudding model (1904)



1909 Millikan (1868 – 1953)

determined the charge of electron

→ the mass of e^- = 9.11×10^{-31} kg

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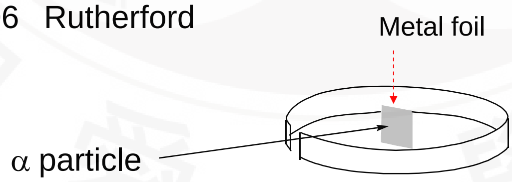
※ Nuclear atom

Early 20th century: radioactivity

α particle: +2 charge

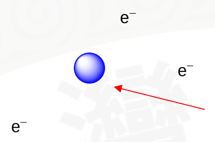
mass = 7300 M_{e^-}

1906 Rutherford



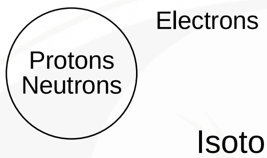
Most of the particles passed through
but some particles were deflected at large angles

1911 Rutherford's model



Tiny heavy nucleus
with positive charge

Modern views



Representation:

mass number → 23
atomic number → 11

$^{23}_{11}Na$

Isotopes: same # of protons but different # of neutrons

Molecules: Atoms combined through chemical bonds

Ions: Cations (ex. Na^+)
Anions (ex. Cl^-)

※ Periodic table

1869 Medeleev The 1st periodic table

1A	2A											3A	4A	5A	6A	7A	8A
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Unt	Fl	Uup	Lv	Uus	Uuo

A relationship between AW and properties
Eight statements were made

1. Periodicity of properties
2. Some elements with similar properties have similar AW (Pt, Ir, Os), or increase regularly (K, Rb, Cs)
3. The order of AW corresponds with element's valencies
4. Most widely distributed elements in nature have small AW
5. AW determines the character of an element
6. New elements may be expected

   Ex. AW of 65 similar to Al(27.4) → Ga(69.7) in 1875
   AW of 75 similar to Si(28) → Ge(73) in 1886
7. Some AWs may need correction

   Ex. Te(128) should be 123~126 → 127.6
8. The table reveals new analogies between elements

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※ Naming simple compounds

(nomenclature)

1782 De Morveau
A substance should have one fixed name, which should reflect its composition

1787 Lavoisier
"Methods of Chemical Nomenclature"

統一命名法則： IUPAC systematic nomenclature
↑國際化學與化工學會
International Union of Pure and Applied Chemistry

◎ Type I：binary ionic compounds 離子化合物

$M^+ A^-$

M^+ ： metal cation 金屬陽離子(only one charge type)

A^- ： anion 陰離子

Rules：

1. cation first
2. Cation takes the name of the atom
   Ex. NaCl sodium chloride
3. anion with -ide suffix
   Ex. chlorine ⇨ chloride

Some common cations and anions

H^+	hydrogen	H^-	hydride
Li^+	lithium	OH^-	hydroxide
Na^+	sodium	F^-	fluoride
K^+	potassium	Cl^-	chloride
Mg^{2+}	magnesium	Br^-	bromide
Ca^{2+}	calcium	I^-	iodide
Ba^{2+}	barium	O^{2-}	oxide
Al^{3+}	aluminum	S^{2-}	sulfide
		N^{3-}	nitride
		N_3^-	azide

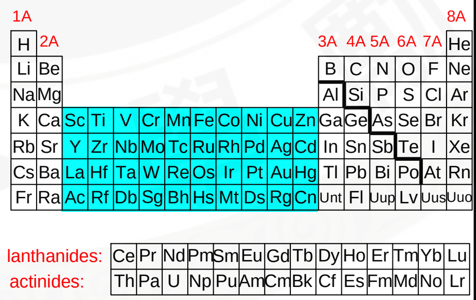
Li_3N	lithium nitride	(氮：nitrogen)
NaN_3	sodium azide	
MgO	magnesium oxide	(氧：oxygen)

◎ Type II：binary ionic compounds
cation with more than one type of charge

Ex. $Fe(II)Cl_2$, $Fe(III)Cl_3$

$FeCl_2$ IUPAC: iron(II) chloride Common: ferrous chloride
$FeCl_3$ IUPAC: iron(III) chloride Common: ferric chloride
Common names: -ous (lower charge), -ic (higher charge)

△ Some common type I cations
IA, IIA cations
IIIA: Al^{3+} (aluminum)
Transition metals:
Zn^{2+}, Ag^+
(Zn: zinc; Ag: silver)



△ Some common type II cations

Cu^{+}： cuprous　　　Cu^{2+}： cupric
Sn^{2+}： stannous　　　Sn^{4+}： stannic
Hg_2^{2+}： mercurous　　　Hg^{2+}： mercuric

Ex. Al_2O_3 aluminum oxide
only one type of charge

$CoBr_2$ cobalt(II) bromide

△ Polyatomic anions

SO_4^{2-}： sulfate (硫酸根)
SO_3^{2-}： sulfite (亞硫酸根)

Rules: -ate (with more O)，-ite (with fewer O)

ClO^-： hypochlorite (次氯酸根)
ClO_2^-： chlorite (亞氯酸根)
ClO_3^-： chlorate (氯酸根)
ClO_4^-： perchlorate (過氯酸根)
Rules：hypo (with fewer O)，per (with more O)

NO_3^-： nitrate (硝酸根)
NO_2^-： nitrite (亞硝酸根)

PO_4^{3-}： phosphate (磷酸根)
HPO_4^{2-}： hydrogen phosphate
$H_2PO_4^-$： dihydrogen phosphate

CO_3^{2-}： carbonate (碳酸根)
HCO_3^-： hydrogen carbonate (also called bicarbonate)

O_2^{2-}： peroxide (過氧根)

△ Polyatomic cation

NH_4^+ ammonium ion
Ex. NH_4Cl ammonium chloride

△ Prefix (to indicate number)

mono-	1
di-	2
tri-	3
tetra-	4
penta-	5
hexa-	6
hepta-	7
octa-	8

◎ Type III：binary covalent compounds
contain two nonmetals

Very similar to ionic compounds

N_2O dinitrogen monoxide (common: nitrous oxide)
NO nitrogen monoxide (or oxide) (common: nitric oxide)
NO_2 nitrogen dioxide
N_2O_3 dinitrogen trioxide
N_2O_4 dinitrogen tetraoxide
N_2O_5 dinitrogen pentaoxide

Note:
monooxide but not monoxide (N_2O and NO are exception)
pentaoxide but not pentoxide
mono never used for the first element

◎ Acids (酸)

△ Without oxygen

HCl	hydrochloric acid	(hydrogen chloride)
H_2S	hydrosulfuric acid	(hydrogen sulfide)
HCN	hydrocyanic acid	(hydrogen cyanide)

△ With oxygen

SO_4^{2-} : sulfate　　H_2SO_4 : sulfuric acid

SO_3^{2-} : sulfite　　H_2SO_3 : sulfurous acid

HNO_3 : nitric acid

HNO_2 : nitrous acid

HClO : hypochlorous acid (次氯酸)

$HClO_2$: chlorous acid (亞氯酸)

$HClO_3$: chloric acid (氯酸)

$HClO_4$: perchloric acid (過氯酸)