Stoichiometry

The story so far…

- The structure of an atom – protons, neutrons & electrons
- Electron structure & the Periodic Table
- Shapes of electron orbitals (Quantum Numbers)
- Essential and toxic elements – quantity & availability

The next topic: Stoichiometry & mole calculations

- Recap of the mole concept and balancing equations
- Calculations involving moles
- The ideal gas equation
- Partial pressures

1

Mole Concept

- One mole is the number of atoms in exactly 12.0 g of the pure isotope carbon-12
- Avogadro's number (N_A) is the number of atoms/ions/molecules in one mole (6.022×10^{23})

$$\text{No of moles} = \frac{\text{Mass (g)}}{\text{Molar mass (g mol}^{-1}\text{)}}$$

Significance:

- Easy to measure mass; but can not determine number of atoms/molecules directly.
- All reactions depend on *ratios* of reacting atoms/molecule.

2

Balancing Chemical Equations

An equation is a quick way to represent a reaction

- Correct formula of all reactants & products
- Correct ratio of reacting species
- Balance of type & number of each element
- Indication of state (solid, liquid, gas, aqueous)
- May indicate conditions over the arrow

e.g. metabolism of glucose

$$C_6H_{12}O_6\text{(aq)} + 6\,O_2\text{ (g)} \xrightarrow{\textit{in vivo}} 6\,CO_2\text{ (g)} + 6\,H_2O\text{ (l)}$$

+ energy

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Balance These Equations

1. Anaerobic fermentation of glucose ($C_6H_{12}O_6$) to form ethanol (C_2H_5OH) and carbon dioxide.

2. Combustion of butane (C_4H_{10}) to form carbon dioxide and water.

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Calculations involving moles

e.g. Converting mass to moles $n=m/M$

- How many moles of glucose are in 10.0g?

Molar mass of $C_6H_{12}O_6$ is (6x12.01)+(12x1.008)+(6x16.00)=180.16
Amount of glucose (10.0 g)/(180.16 g mol^{-1}) = 0.0555 mol

Question: What mass of $FeSO_4.7H_2O$ do you need to dose an anaemic cat with 50 mg of iron?

Molar mass of Fe = 55.85; Molar mass of $FeSO_4.7H_2O$ = 278.0

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Calculations involving moles

e.g. How much ethanol do I obtain from the fermentation of 1.0 kg of glucose? $n=m/M$

	$C_6H_{12}O_6$ (aq) $\longrightarrow$	$2C_2H_5OH$(aq) + $2CO_2$(g)
Mass/g	1000	510
Molar mass/gmol^{-1}	180.16	46.07
Amount/mol	5.55	11.10

Question: What mass of CO_2 is produced from the animal metabolism of 1.0 kg of glucose?

$C_6H_{12}O_6(aq) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$

Mass/g
Molar mass/gmol^{-1}
Amount/mol

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Gases

It may not be convenient to measure the *mass* of a gas

Properties of Gases:

- are compressible
- exert pressure
- expand to fill the entire volume of the container
- diffuse rapidly
- density (ρ) is << than liquids or solids.

A gas consists of very small, widely separated particles in rapid motion.

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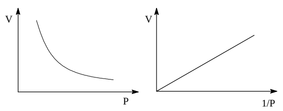
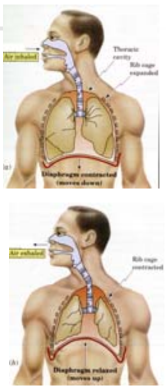
Gases

- Boyle noticed an inverse relationship between volume and pressure.

Pressure x volume = constant

PV = *a*



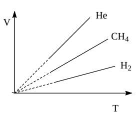


Gases

- Charles found the volume of a gas, at constant pressure, increased linearly with temperature.

Volume = constant x temperature

V = *b*T



Different gases extrapolated to zero volume at the same temperature. This is *absolute zero* at -273.15 °C = 0 K.

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Gases

- Avagadro proposed that equal volumes of gases at the same temperature and pressure contained the same number of “particles”.

Volume = constant x No of moles

$V = c\,n$

$$\left.\begin{array}{l} PV = a \\ V = bT \\ V = c\,n \end{array}\right\} \quad \mathbf{PV = nRT}$$

R = universal gas constant

= 8.3145 J mol^{-1} K^{-1}

= 0.082 L atm K^{-1} mol^{-1}

1 mole of any gas at standard temp & pressure (0 ^{o}C & 1 atm) occupies 22.4 L (or 24.4 L at 25 ^{o}C & 1 atm)

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Gases

n = 1 mol	n = 1 mol	n = 1 mol
P = 1 atm (760 torr)	P = 1 atm (760 torr)	P = 1 atm (760 torr)
T = 0°C (273 K)	T = 0°C (273 K)	T = 0°C (273 K)
V = 22.4 L	V = 22.4 L	V = 22.4 L
Number of gas particles = 6.022×10^{23}	Number of gas particles = 6.022×10^{23}	Number of gas particles = 6.022×10^{23}
Mass = 4.003 g	Mass = 28.02 g	Mass = 32.00 g
d = 0.179 g/L	d = 1.25 g/L	d = 1.43 g/L

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Example

The mass of 1.00 L of a gas at 2.00 atm and 25 °C is 2.76 g. What is the molecular weight of the gas?

PV = nRT and n = m/M

(2.00 atm)(1.00 L) = n (0.082 L atm K^{-1} mol^{-1})(273 + 25 K)

∴ n = (2.00 / 24.436) mol = 0. 0 818 mol

M = 2.76 g / 0.0818 mol = 33.7 g mol^{-1} (H_2S)

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Question

What volume does 1500 g of CO_2 occupy at 1.0 atm and 38 ^{0}C?

$PV = nRT$ and $n = m/M$

Use data from slide 6 and R = 0.082 L atm K^{-1} mol^{-1}

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Question – Air bags

1996 – Textbook: $2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$!
$6NaN_3(s) + Fe_2O_3(s) \rightarrow 3Na_2O(s) + 2Fe(s) + 9N_2(g)$

How many grams of NaN_3 would be required to provide 75.0 L of nitrogen at 25° C and 0.984 atm?

$PV = nRT$ and $n = m/M$ and R = 0.082 L atm K^{-1} mol^{-1}

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Partial pressures

In a mixture of gases, the total pressure exerted is the sum of the *partial pressures* that each gas would exert if it were alone.

$$P_{TOTAL} = p_A + p_B + p_C + \ldots.$$

The partial pressure is related to the number of moles present, expressed as a mole fraction, x

Mole fraction of A = x_A = (No of moles of A) / (Total No of moles present)

Thus $p_A = x_A P_{TOTAL}$ and $p_B = x_B P_{TOTAL}$

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Partial pressures - example

Air consists of approximately 20 % oxygen and 80 % nitrogen. What are the partial pressures of these gases at 1 atm and 10 atm ?

Mole fraction of O_2 = x_{O2} = (20 %) / (20 % + 80 %) = 0.20
Mole fraction of N_2 = x_{N2} = (80 %) / (80 % + 20 %) = 0.80
(check: Σ mole fractions = 1)

At 1 atmosphere: p_{O2} = 0.20 x 1 atm = 0.2 atm
p_{N2} = 0.80 x 1 atm = 0.8 atm
(check: Σ partial pressure = total pressure)

At 10 atmosphere: p_{O2} = 0.20 x 10 atm = 2 atm
p_{N2} = 0.80 x 10 atm = 8 atm
(check: Σ partial pressure = total pressure)

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Significance $p = x P_{TOTAL}$

During a surgical procedure an animal may be ventilated to ensure a regular supply of oxygen to the brain. If the absorption of oxygen by the lungs is impaired it is desirable to increase the partial pressure of oxygen in the lungs.

This may be achieved by

- Increasing the total pressure
- Increase the mole fraction of O_2

Convenient to do surgery at atmospheric pressure

Breathing pure oxygen increases p_{O2} in the lungs by five times

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Chemical Bonding

The story so far…

- Atomic structure & the Periodic Table
- The mole concept
- Balancing equations
- Stoichiometry – mole calculations and gases

This topic: Types of chemical bond

- Ionic, metallic, covalent bonds
- Lewis structures, multiple bonds & resonance

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Overview

Elements…

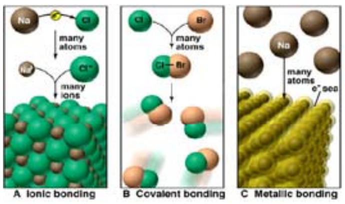
- Currently 120 elements known, 90 possess stable isotopes
- Understand the Periodic Table in terms of orbitals (s, p, d, f) and electron shells (n = 1, 2, 3…)
- Use the relative masses of the atoms to do calculations
- Gases conveniently treated in terms of P, V & T

The questions remain:

- Why are there 15,000,000 known compounds but only 110 elements?
- Can we rationalise bonding in terms of electronic structure?
- Can we use our knowledge of atomic orbitals to predict the shape of molecules?

Major types of bonding

A. Ionic bonding
B. Covalent bonding
C. Metallic bonding

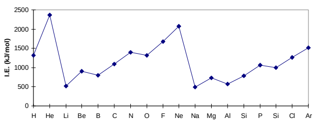


Of the elements only Group 18 (Noble Gases) always occur as uncombined atoms – suggests that a filled electron shell is particular stable.

e.g. Ar: $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$

A few definitions

- *Core Electrons* are the other electrons of an element and generally play no part in the reactivity and bonding of the element.
- *Valence Electrons* are those in the outer most shell of an element and are responsible for the bonding characteristics of that element.
- *Electron Affinity* is the energy associated with X (g) + e- → X- (g).
- The *First Ionisation Energy* increases across a period and decreases down a group. The trend reflects the effective nuclear charge experienced by the electron being removed.



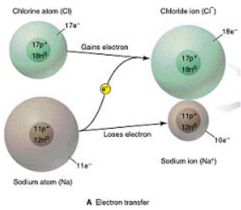
Formation of ions

Metals form *cations;* non-metals form *anions*

- Driving force being the formation of a filled outer electron shell.
- Gain/loss of electrons does not occur in isolation.

Cl [Ne] $3s^2 3p^5 \rightarrow$ Cl^- [Ne] $3s^2 3p^6$

Na [He]$2s^2 2p^6 3s^1 \rightarrow$ Na^+ [He] $2s^2 2p^6$

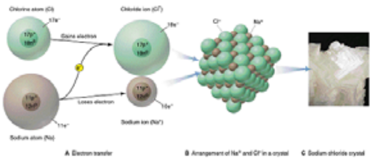


Ionic Bonding

An ionic bond is a chemical bond formed by the electrostatic attraction between positive and negative ions.

An ionic compound is a compound composed of cations and anions.

Ionic compounds form when elements with low ionisation energies (eg. metals) react with elements with high electron affinities (eg. non-metals).



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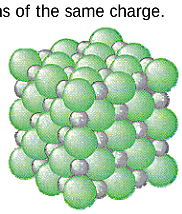
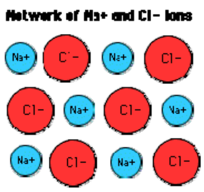
Ionic Compounds

Anions and cations are arranged in lattices to maximize attractions between oppositely charged ions and to minimize repulsion between ions of the same charge.





Bonding is non-directional and forms an extensive 3-D lattice.

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Examples

All Group 1 elements combine with chlorine to form compounds of the type MCl (Group 2 elements form MCl_2).

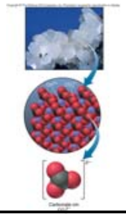
Analogous M_2O and MO compounds form with oxygen.

All such compounds involve the transfer of one or two electrons from the metal atom to the non-metal atom to form positively charged ions (cations) and negatively charged ions (anions).

NaCl, LiF

$MgCl_2$, $CaBr_2$

K_2O, CaO



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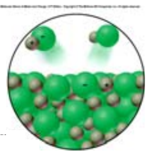
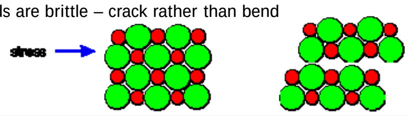
Properties of ionic compounds

Electrostatic attraction between ions

- To make the crystal lattice collapse (melt) requires high temperatures
- Gaseous ion pairs exist when the compound vaporises – this requires very high temperatures



- Solutions of ionic compounds (but not solids) conduct electricity (because ions split up on dissolution)
- Ionic solids are brittle – crack rather than bend



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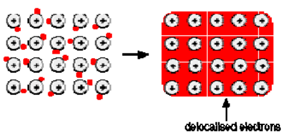
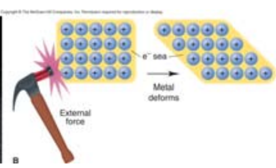
Metallic Bonding

Metallic bonding involves positively charged atomic cores surrounded by delocalised electrons. It occurs in metallic solids.



Metallic solids have good electrical conductivity since the valence electrons are delocalised and easily moved by an electric field.



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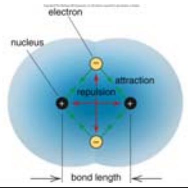
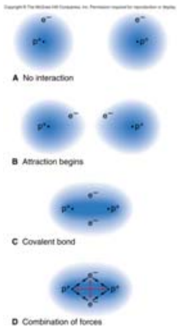
Covalent Bonding

A **covalent bond** is a chemical bond formed by the sharing of a pair of electrons between atoms.

In a covalent bond the electron density is found in the region between the two atoms. Reactions between non-metals give covalent bonds.





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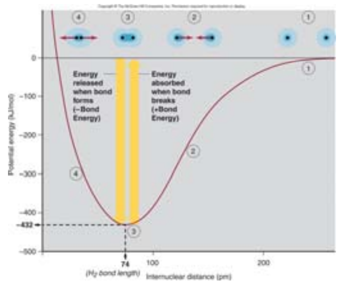
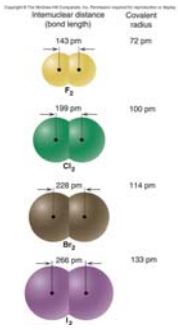
Covalent Bonding

For a covalent bond between two atoms of the same type (for example H_2 or F_2) each has an equal share of the electrons in the bond.





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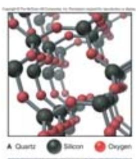
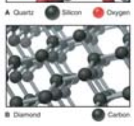
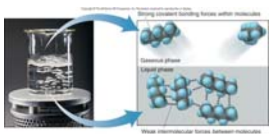
Properties of covalent compounds

Sharing of electrons – directional bonds

- Defined shapes
- Low melting points (except network solids)
- Non-conducting either as solids or solutions
- Covalent compounds are generally soft







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What compound is this?

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	57-71	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	***Pb***	Bi	Po	At	Rn
Fr	Ra	89-105															

Using only the elements highlighted, deduce the correct formula of this compound: mp = -94 ; bp = 76

- CsF
- PCl_3
- SiO_2
- Sn-Pb alloy

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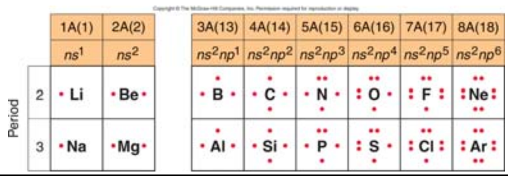
Lewis Structures

Lewis structures are a means of determining stable electron arrangements in molecules.

It considers the valence electrons of an atom only. A stable arrangement is one in which each atom has achieved a Noble gas electron configuration by distribution of the electrons as bond pairs or lone pairs (non-bonded pairs).

A Noble gas electron configuration is 2 for hydrogen and 8 for C, N, O and F. This is sometimes called *The Octet Rule*.



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Lewis Structures

To draw a *Lewis Structure* you need to know which atoms are bonded to which. Then:

- Add up the total number of valence electrons present, add or subtract electrons to account for any charge.
- Join the appropriate atoms using an electron pair for each bond.
- Distribute the remaining electrons to result in an octet of electrons on each atom (except hydrogen that always has two electrons associated with it).
- If there are too few electrons to give every atom an octet, move non-bonded pairs between atoms to give multiple bonds.
- If there are electrons left over after forming octets, place them on the central atom.
- Indicate the overall charge.

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Examples and question

- Examples: CH_4, CF_4, NH_3, CO_2, H_3O^+
- Draw Lewis Structures of: H_2O, HCN, NH_4^+

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Exceptions to the "Octet Rule"

- Compounds of Be and B may have less than 8 electrons surrounding those atoms.
- Compounds of Cl, Br, I, P, S may have more than 8 electrons surrounding those atoms.
- Examples: $BeCl_2$, PCl_5, ClF_3
- Question: Draw Lewis Structures of BF_3, SF_6, IF_5

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Resonance

- Where equivalent Lewis Structures may be drawn, resonance occurs – the electrons are delocalised and the actual structure a combination of the Lewis representations.
- Example: NO_3^-
- Question: Draw Lewis Structures of CO_3^{2-}

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