

2023 JC1 H2 CHEMISTRY (9729) CORE IDEA 3: TRANSFORMATION Topic 1: THE MOLE CONCEPT & STOICHIOMETRY

Name: _____

Civics Group: _____

The use of the Data Booklet is relevant for this topic. Please have a copy with you as you attend the lectures.

Please note that Sections 1, 2, 3, 4.1, 5.2 & 5.3 involve concepts which have been covered at the secondary school level. Please read through these areas on your own and refresh your concepts before the lectures. Another independent study segment, Section 6.7, will be covered in greater detail in your practicals or later topics.

[the term relative formula mass or M_r will be used for ionic compounds]

Students should be able to:

- (a) define the terms relative atomic, isotopic, molecular and formula mass
- (b) define the term *mole* in terms of the Avogadro constant
- (c) calculate the relative atomic mass of an element given the relative abundances of its isotopes
- (d) define the terms *empirical* and *molecular* formula
- (e) calculate empirical and molecular formulae using combustion data or composition by mass
- (f) write and/or construct balanced equations
- (g) perform calculations, including use of the mole concept, involving:
 - (i) reacting masses (from formulae and equations)
 - (ii) volumes of gases (e.g. in the burning of hydrocarbons)
 - (iii) volumes and concentrations of solutions

[when performing calculations, candidates' answers should reflect the number of significant figures given or asked for in the question]

(h) deduce stoichiometric relationships from calculations such as those in (g)

From the topics of Electrochemistry & Transition Elements Chemistry:

- (i) describe and explain redox processes in terms of electron transfer and/or of changes in oxidation number (oxidation state);
- (j) construct redox equations using the relevant half-equations
- (k) describe and explain the use of Fe³⁺/Fe²⁺, MnO_4^-/Mn^{2+} and $Cr_2O_7^{2-}/Cr^{3+}$ as examples of redox systems

REFERENCES

- 1. Chemistry (for CIE AS & A Level) by Peter Cann & Peter Hughes (540 CAN)
- 2. Chemistry: The Molecular Nature of Matter & Change by Martin S. Silberberg (540 SIL)
- 3. Calculations in A Level Chemistry (4th Edition) by E.N. Ramsden
- 4. Calculations for AS/A Level Chemistry by Jim Clark

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Relative Masses of Atoms and Molecules (INDEPENDENT STUDY) 1

LO (a) define the terms relative atomic, isotopic, molecular and formula mass

(c) calculate the relative atomic mass of an element given the relative abundances of its isotopes

Relative Atomic Mass Scale: Carbon-12 scale

- Atoms are too light to be weighed directly. Instead, chemists compare the masses of atoms with the masses of a standard atom: Carbon-12 atom (IUPAC Agreement 1960).
- On this relative atomic mass scale, a ¹²C atom is assigned a mass of 12 units and the relative masses of all other atoms are obtained by comparison with the mass of a ¹²C atom.

Hence, 1 unit of this mass scale is equivalent to $\frac{1}{12}$ of the mass of a ¹²C atom.

- 1.1 Relative Isotopic Mass (no unit)
- Isotopes are atoms of the same element whose nuclei have Uke Video on "What are Isotopes?" • the same number of protons but different number of neutrons.

https://www.youtube.com/wa

tch?v=EboWeWmh5Pg

e.g: ${}^{35}_{17}Cl$ and ${}^{37}_{17}Cl$, ${}^{79}_{35}Br$ and ${}^{81}_{35}Br$.

Relative isotopic mass is the **ratio** of the **mass of an atom of** isotope to $\frac{1}{12}$ of the **mass of a** ¹²C atom.

The **relative abundance** of the isotopes refers to the percentage by mass of the isotopes as they are found in the naturally occurring element.

Example:

isotope	relative isotopic mass	relative abundance (%)
¹² C	12.0000	98.90
¹³ C	13.0034	1.10
³⁵ Cl	34.9689	75.77
³⁷ C <i>l</i>	36.9659	24.23
¹ H	1.0078	99.985
² H	2.0140	0.015
¹⁶ O	15.9949	99.760
¹⁷ O	16.9991	0.040
¹⁸ O	17.9991	0.200

1.2 Relative Atomic Mass (symbol: Ar, no unit)

Relative atomic mass is the **ratio** of the <u>weighted average</u> mass of an atom of an element to $\frac{1}{12}$ of the mass of a ¹²C atom.

• The relative atomic mass of element can be determined by the expression:

$$\mathbf{A}_{r} = \sum_{r=1}^{\infty} \left(\text{relative isotopic mass} \times \frac{\text{relative abundance \%}}{100} \right)$$

Q: Why is the relative atomic mass (*A*_r) not necessarily close to a whole number?

A: The naturally occurring elements often consist of a mixture of isotopes and the relative atomic mass of an element accounts for the **different isotopes and their relative proportions**.

Worked Example 1A

1 Chlorine consists of two naturally–occurring isotopes, ³⁵C*l* and ³⁷C*l*, with the relative abundance of 75.77% and 24.23% respectively. Calculate the relative atomic mass of chlorine.

Apply the formula: $A_r = \sum \left(\text{relative isotopic mass} \times \frac{\text{relative abundance \%}}{100} \right)$

$$A_{\rm r}$$
 of chlorine = $\left(35 \times \frac{75.77}{100}\right) + \left(37 \times \frac{24.23}{100}\right) = \underline{35.5}$

2 Given the A_r of copper is 63.54, calculate the relative abundance of its two isotopes, ${}^{63}Cu$ and ${}^{65}Cu$.

Let the relative abundance of 63 Cu be x %. (*i.e.* relative abundance of 65 Cu is (100-x) %)

$$63.54 = \left(63 \times \frac{x}{100}\right) + \left(65 \times \frac{100 - x}{100}\right)$$
$$x = 73.0$$

The relative abundance of 63Cu is 73.0 % and that of 65Cu is 27.0 %.

Note:

For calculations, numerical answers <u>for intermediate steps are generally</u> given to 4 sig. fig. and <u>final steps to be expressed to 3 sig. fig.</u> unless otherwise specified.



Video on "Significant Figures & Rules?"

thttps://www.youtube.com/wa tch?v=TZIPNzc5yT0

1.3 Relative Molecular Mass (symbol: *M*_r, no unit)

Relative molecular mass is the ratio of the <u>weighted average</u> mass of a molecule to $\frac{1}{12}$ of	of the
mass of a ¹² C atom.	

• $M_r = \sum (A_r \text{ of all atoms present in one molecule})$ Example: $M_r \text{ of oxygen gas } (O_2) = 2(16.0) = \underline{32.0}$ $M_r \text{ of octane } (C_8H_{18}) = 8(12.0) + 18(1.0) = \underline{114.0}$ $M_r \text{ of octane } (C_8H_{18}) = 8(12.0) + 18(1.0) = \underline{114.0}$

1.4 Relative Formula Mass (symbol: *M*_r, no unit)

Relative formula mass is the ratio of the <u>weighted average</u> mass of a formula unit of an ionic compound to $\frac{1}{12}$ of the mass of a ¹²C atom.

- The term is used for relative masses of ionic compounds or ions.
- $M_r = \sum (A_r \text{ of all atoms present in one formula unit of ionic compound})$

Example:

 $M_{\rm r}$ of MgC l_2 = 24.3 + 2(35.5) = <u>95.3</u> $M_{\rm r}$ of FeSO₄·7H₂O = 55.8 + 32.1 + 4(16.0) + 7[2(1.0) + 16.0] = <u>277.9</u>

Self Check 1A

1	The relative atomic mass of rubidium, which consists of the isotopes ${}^{85}_{37}$ Rb and ${}^{87}_{37}$ Rb is 85.5. What is the percentage of ${}^{87}_{37}$ Rb atoms in the isotopic mixture?								
	Α	0.25%	В	0.75%	С	25%	D)	75%
2	Naturally occurring silicon is a mixture of three isotopes, ²⁸ Si, ²⁹ Si and ³⁰ Si. The relative atomic mass of silicon is 28.109.								
	What could be the relative abundance of each of the three isotopes?								
	Α	91.1% ²⁸ Si, 7.9% ²	²⁹ Si	and 1.0% ³⁰ Si					
	В	92.2% ²⁸ Si, 4.7% ²	²⁹ Si	and 3.1% ³⁰ Si					
	С	95.0% ²⁸ Si, 3.2% ²	²⁹ Si	and 1.8% ³⁰ Si					
	D	96.3% ²⁸ Si, 0.3% ²	²⁹ Si	and 3.4% ³⁰ Si					

Worked Example 1B

Most elements contain more than one isotope, atoms that have the same chemical 1. properties but different masses.

Which expression correctly defines the term relative atomic mass of an element?

- the mass of 1 atom of an element relative to the mass of 1 atom of ¹²C. Α
- the mass of 1 mole of atoms of an element divided by 6.02×10^{23} . В
- the mass of 1 mole of atoms of an element relative to the mass of 1 atom of ¹²C. С
- the mass of 1 mole of atoms of an element relative to the mass of 1 mole of ^{12}C atoms. D

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2 The Mole and Related Concepts (INDEPENDENT STUDY)

LO (b) define the term *mole* in terms of the Avogadro constant;

- (g) perform calculations, including use of the mole concept, involving:
 - (i) reacting masses (from formulae and equations);
 - (ii) volume of gases and;
 - (iii) volumes and concentrations of solutions

2.1 The Mole and Avogadro constant

2.1.1 Definition of the mole

- The mole is the SI unit for measuring the amount of substance. • Usual symbol: n: unit: mol
- The definition of the mole is as follows:

One mole of any substance is the amount of that substance which contains 6.02 × 10²³ (Avogadro constant) elementary entities (or particles).

Note: The term elementary entities must be specified and could refer to atoms, molecules, ions or electrons etc.

- The Avogadro constant, L, is the number of particles (N) in one mole of a substance. i.e. $L = 6.02 \times 10^{23} \text{ mol}^{-1}$
- Since 1 mole of particles = 6.02×10^{23} particles,

amount of particles (in mol) =



Hence, the relative masses (Section 1.1 to 1.4) can be defined in terms of "1 mole" instead of "1 atom/molecule/formula units". Refer to worked example 1B.

6.02 × 10²³ (in mol⁻

Example:

Relative Atomic Mass is the ratio of the mass of <u>1 mole of atoms</u> of an element to $\frac{1}{12}$ of the

mass of <u>1 mole of ¹²C atoms</u>.

- 1 mole of carbon (C) consists of 6.02×10^{23} atoms of carbon. \geq
- 1 mole of water (H₂O) consists of 6.02×10^{23} molecules of H₂O. \triangleright
- 1 mole of calcium chloride (CaCl₂) consists of 6.02×10^{23} formula units of CaCl₂. \geq (*i.e.* 6.02×10^{23} **Ca²⁺ ions** and 12.04×10^{23} **Ct ions**).

Why is "1 mole of oxygen" ambiguous? It can refer to atoms or molecules.

2.1.2 Mole Ratio

• In 1 mole of $A_m B_n$, there is *m* mol of A and *n* mol of B (*i.e.* $A_m B_n \equiv m A \equiv n B$). amount of $\mathbf{A} = \mathbf{m} \times \text{amount of } A_m B_n$ amount of **B** = \mathbf{n} × amount of A_mB_n

Example: $NH_3\equiv N\equiv 3H$ amount of N atoms = $1 \times \text{amount of NH}_3$ amount of H atoms = $3 \times$ amount of NH₃

Worked Example 2A

Fill in the blanks by calculating the corresponding amount of particles and number of particles.

	amount of substance	number of particles
(a)	amount of N ₂ molecules = $\frac{1.23 \times 10^{22}}{6.02 \times 10^{23}} = 0.0204$ mol	1.23 × 10 ²² N ₂ molecules
(b)	0.050 mol CO ₂ molecules	Since $CO_2 \equiv C \equiv 2O$, $0.05 \times (6.02 \times 10^{23}) = 3.01 \times 10^{22}$ CO ₂ molecules $1 \times (3.01 \times 10^{22}) = 3.01 \times 10^{22}$ C atoms $2 \times (3.01 \times 10^{22}) = 6.02 \times 10^{22}$ O atoms
	·	

Video on "Converting between

2.2 Molar Mass

- Molar mass of a substance is the mass, in grams, of 1 mole of the substance. (units: g mol⁻¹)
- Molar mass of a substance is **numerically equal** to the A_r or M_r of the same substance.

Example:

substance	A _r or <i>M</i> _r (no units!)	molar mass
carbon (C)	12.0	12.0 g mol⁻¹
water (H ₂ O)	2(1.0) + 16.0 = 18.0	18.0 g mol⁻¹
carbonate ion (CO_3^{2-})	12 + 3(16.0) = 60.0	60.0 g mol⁻¹



[*Conversion*: 1 mg = 10^{-3} g ; 1 kg = 10^{3} g ; 1 tonne = 1000 kg = 10^{6} g]

2.3 Molar Volume of Gas

• Molar volume of a gas, V_m, is the volume, in dm³, occupied by 1 mole of the gas under a given set of temperature and pressure. (units: dm³ mol⁻¹)

Conditions	Volume of 1 mol of gas	V _m
room temperature & pressure (r.t.p) 20 °C [293 K], 1 atm [101325 Pa]	24.0 dm ³ [24000 cm ³]	24.0 dm ³ mol ⁻¹
standard temperature & pressure (s.t.p) 0 °C [273 K], 1 bar [10 ⁵ Pa]	22.7 dm ³ [22700 cm ³]	22.7 dm ³ mol ⁻¹

[*Conversion*: 1 dm = 0.1 m = 10 cm \Rightarrow 1 dm³ = 10⁻³ m³ = 1000 cm³ = 1000 mL = 1 L]

• The amount of a gas A can be determined from its volume and molar volume measured under the same conditions of temperature and pressure.

amount of gas A (in mol) =
$$\frac{\text{volume of gas A}(\text{in dm}^3)}{\text{molar volume (in dm}^3 \text{ mol}^{-1})}$$

For **GASEOUS** species **only**:

• The Avogadro's Law states that at the **same temperature and pressure**, the **same volume of all gases** contain the **same amount of gas particles**.

i.e. **MOLE RATIO = VOLUME RATIO**

The application of this law will be covered in Section 4.4.

Worked Example 2B

1 Calculate the number of NH_3 molecules in 16 dm³ of NH_3 at s.t.p.

Amount of $NH_3 = \frac{16}{22.7} = 0.7048$ mol

No. of NH₃ molecules = $0.7048 \times 6.02 \times 10^{23} = \frac{4.24 \times 10^{23}}{10^{23}}$

2 What is the volume of CO₂, in dm³, that contains 1.00×10^{23} molecules at r.t.p?

Amount of $CO_2 = \frac{1.00 \times 10^{23}}{6.02 \times 10^{23}} = 0.1661 \text{ mol}$

Volume of CO₂ at r.t.p = $0.1661 \times 24.0 = 3.99 \text{ dm}^3$

2.4 Molar concentration

- The *concentration* of a substance in solution is the **amount** of a solute dissolved in a solvent to make 1 dm³ of solution. Water is a commonly used solvent. When water is the solvent, it is known as an aqueous solution. (units: mol dm⁻³)
- For species in solution:
 amount of A (in mol) = conc. of A (in mol dm⁻³) × vol. of solution containing A (in dm³)



[Conversion: $1 \text{ dm}^3 = 10^{-3} \text{ m}^3 = 1000 \text{ cm}^3 = 1000 \text{ mL} = 1 \text{ L}$]

Worked Example 2C

Calculate the mass of H₂SO₄ needed to prepare each of the following: (a) 500 cm³ of 4 mol dm⁻³ of H₂SO₄(aq); (b) 500 cm³ of a solution containing 2 mol dm⁻³ of H⁺ ions. (a) Amount of H₂SO₄ = $4 \times \frac{500}{1000} = \frac{2.00 \text{ mol}}{1000}$ Mass of H₂SO₄ needed = $2.00 \times [2(1.0) + 32.1 + 4(16.0)] = 196 \text{ g}$

(b) Amount of H⁺ ions $= 2 \times \frac{500}{1000} = \underline{1.00 \text{ mol}}$ Since H₂SO₄ $\equiv 2$ H⁺, Amount of H₂SO₄ $= \underline{\frac{1}{2}} \times 1.00 = \underline{0.500 \text{ mol}}$ Mass of H₂SO₄ needed $= \underline{0.500} \times [2(1.0) + 32.1 + 4(16.0)] = 49.1 \text{ g}$



3 Empirical and Molecular Formulae (INDEPENDENT STUDY)

LO (d) define the terms *empirical* and *molecular formula* and; (e) calculate empirical and molecular formulae using composition by mass

3.1 Definitions

Empirical formula is the formula that shows the <u>simplest</u> whole number ratio of the number of atoms of each element present in the substance.

Molecular formula is the formula that shows the <u>actual</u> number of atoms of each element in one molecule of the compound. It is a multiple of the empirical formula.

• Example:

substance	empirical formula	<i>molecular</i> formula
methane	CH ₄	CH ₄
butane	C_2H_5	C_4H_{10}
glucose	CH₂O	$C_6H_{12}O_6$
sodium chloride	NaCl	_

• The formulae of *ionic* compounds are <u>usually</u> the same as their empirical formulae.

3.2 Calculations using percentage composition by mass

Worked Example 3A

The % by mass of elements in compound **X** (M_r = 114) are C: 63.2%, H: 12.2 % and N: 24.6 %. Find the empirical and molecular formulae of compound **X**.

<u>Step</u> ①: Construct MARS table to determine empirical formula. (Taking 100 g of the compound X, % by mass = mass (in g) per 100 g.)

	С	Н	Ν
Mass in 100 g of substance / g	63.2	12.2	24.6
Amount / mol	$\frac{63.2}{12.0}$ = 5.267	$\frac{12.2}{1.0}$ = 12.20	$\frac{24.6}{14.0}$ = 1.757
Simplest mole Ratio	$\frac{5.267}{1.757}\approx 3$	$\frac{12.20}{1.757}\approx7$	1.757 1.757 ≈ 1

Empirical formula of compound X is $\underline{C_3H_7N}$.

<u>Step @</u>: Using M_r of substance to determine molecular formula.

Let the molecular formula of **X** be $C_{3n}H_{7n}N_n$.

$$M_r$$
 of $\mathbf{X} = n [3(12.0) + 7(1.0) + 14.0] = 114$

∴ *n* = <u>2</u>

:. The molecular formula of X is $\underline{C_6H_{14}N_2}$.

Self Check 3A

The % by mass of elements in compound **Y** are Mn: 72.0% and O: 28.0 %.

Find the empirical formula of compound Y.

	Mn	0			
Mass in 100 g of substance / g	72.0	28.0			
A mount / mol					
Simplest mole Ratio					

Empirical formula of compound Y is _____

<u>Useful TIP</u>:

You need to recognise some common fractions and decimals so as to do conversions quickly.

Example:

$$1.25 = \frac{5}{4}$$
; $1.50 = \frac{3}{2}$

$$0.333 = \frac{1}{3}$$
; 0.667 = $\frac{2}{3}$

$$1.33 = \frac{4}{3}$$
; $1.67 = \frac{5}{3}$

<u>Important</u>! "nC₃H₇N" and "(C₃H₇N)_n" are **wrong** representations of the molecular formula!

3.3 Calculations using combustion data

Worked Example 3B

Mannose is a sugar that contains only carbon, hydrogen and oxygen and has a relative molecular mass of 180. When 2.36 g sample of mannose undergoes combustion, 3.46 g of CO_2 and 1.42 g of H_2O are formed.

Find the molecular formula of mannose.

$$C_xH_yO_z$$
 + excess $O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$ (*Note*: The equation is not balanced)

<u>Step ①</u>: Construct MARS table to determine empirical formula.

	С	Н	0
M ass in 2.36 g of mannose / g	$\frac{12.0}{44.0} \times 3.46 = 0.9436$	$\frac{2(1.0)}{18.0} \times 1.42$ = 0.1578	2.36 – 0.9437 – 0.1578 = <u>1.259</u>
Amount / mol	0.07864	0.1578	$\frac{1.259}{16.0} = 0.07866$
Simplest mole Ratio	$\frac{0.07864}{0.07864} \approx 1$	$\frac{0.1578}{0.07864} \approx 2$	$\frac{0.07866}{0.07864} \approx 1$

Empirical formula of mannose is <u>CH₂O</u>.

Why is the mass of O in mannose NOT equal to the total mass of O in CO₂ and O in H₂O? The O atoms in CO₂ & H₂O comes from BOTH O₂ gas & O in mannose.

Find the molecular formula of mannose.

<u>Step @</u>: Using M_r of substance to determine molecular formula. Let the molecular formula of mannose be $C_nH_{2n}O_n$.

 $M_{\rm r}$ of mannose = n [12.0 + 2(1.0) + 16.0] = 180

∴ *n* = <u>6</u>

 \therefore The molecular formula of mannose is <u>C₆H₁₂O₆</u>.

4 Stoichiometry

LO (f) write and/or construct balanced equations;

- (g) perform calculations, including use of the mole concept (and ratio), involving:
 - (i) reacting masses (from formulae and equations) and;
 - (ii) volume of gases (e.g. in the burning of hydrocarbons)
- Stoichiometry refers to the relationship between the amounts of substances that react together in a particular chemical reaction, and the amounts of products that are formed.
- The amounts of substances undergoing reaction as shown in a balanced equation are known as stoichiometric amounts.

4.1 Quantitative Information from a Balanced Equation

• A balanced equation indicates the mole proportion in which reactants MUST react to give fixed mole proportion of products (i.e. stoichiometric ratio between reactants and products). *Example:*

	2 H ₂ (g)	+ O ₂ (g)	\rightarrow 2 H ₂ O(<i>l</i>)		
stoichiometric ratio:	2 mol	1 mo	l 2 mol		
which can be represented as $2H_2 \equiv O_2 \equiv 2H_2O$.					

A balanced equation is useful as other quantities can be deduced from the stoichiometric ratio:

- masses of reactants and products
 - 4 g of H_2 reacts with 32 g of O_2 to produce 36 g of H_2O .
- > volumes of gases at r.t.p. and s.t.p.
 - (2 × 24.0) dm³ of H₂ reacts with 24.0 dm³ of O₂ at r.t.p.
 - (2×22.7) dm³ of H₂ reacts with 22.7 dm³ of O₂ at s.t.p.
- volumes of gases at the same temperature and pressure
 20 cm³ of H₂ reacts with 10 cm³ of O₂
 NOTE: The reactant/product must exist as a gas under the specified temperature and conditions for its volume to be determined from stoichiometric ratios.
- The equation does **NOT** indicate the **actual amount** in which the reactants are present in the mixture. This is where the concept of limiting reagent comes in.

4.2 Limiting Reagent

- Often in carrying out the chemical reactions, the **reactants are not added in stoichiometric proportions** (*i.e.* one or more of the reactants may be used in excess) and the **reaction stops once the limiting reagent is completely used up**.
- The **maximum amount of product formed** and **amount of reactants reacted** is determined by the starting **amount** of **LIMITING REAGENT**.

4.3 Percentage Yield

- The <u>maximum</u> amount of product that will be formed if all of the limiting reagent reacts is called the **theoretical yield**.
- Many reactions however, **do not go to completion** or have **undesired side reactions**, and there may also be a **loss of product** in practice, for example, through purification.
- Hence, the **actual yield** is usually <u>less</u> than 100% of the theoretical yield that is calculated based on the limiting reagents.
- The percentage yield relates the actual yield to the theoretical yield and is expressed as:

percentage yield = $\frac{\text{actual mass (or amount) of product formed}}{\text{theoretical mass (or amount) of product}} \times 100\%$

Worked Example 4A

In an experiment, 100 cm³ of 0.0600 mol dm⁻³ lead(II) nitrate solution was mixed with 200 cm³ of 0.0500 mol dm⁻³ sodium chloride solution. The precipitate of lead(II) chloride formed was dried and weighed. A mass of 1.1558 g was recorded.

(a) Calculate the maximum mass of lead(II) chloride that can be precipitated.

<u>Step ①:</u> Construct **balanced equation** for the reaction.

 $Pb(NO_3)_2(aq) + 2 NaCl(aq) \rightarrow PbCl_2(s) + 2 NaNO_3(aq)$

- <u>Step (2)</u>: **Calculate amount** of reagents used for the reaction. amount of $Pb(NO_3)_2 = 0.0600 \times \frac{100}{1000} = \underline{0.006000 \text{ mol}}$ amount of $NaCl = 0.0500 \times \frac{200}{1000} = \underline{0.01000 \text{ mol}}$
- <u>Step ③</u>: Determine the limiting reagent. Since $Pb(NO_3)_2 = 2NaCl_1$, <u>NaCl_</u> is the limiting reagent.
- Step ④: Solve using mole ratio between limiting reagent and species concerned. Since $2\text{NaC}l = \text{PbC}l_2$, amount of $\text{PbC}l_2 = \frac{1}{2} \times 0.0100 = \frac{5.000 \times 10^{-3} \text{ mol}}{10^{-3} \text{ mol}}$ maximum mass of $\text{PbC}l_2$ produced = $(5.000 \times 10^{-3}) \times [207.2 + 2(35.5)] = 1.39 \text{ g}$



Self Check 4A

- 1 25.0 g of zinc and 8.00 g of oxygen are heated until reaction is complete (zinc oxide is formed).
 - (a) Identify the limiting reagent.
 - (b) What is the mass of each of the substances present in the mixture at the end of the reaction? [31.1 g of ZnO, 1.88 g of O₂]

2 Hydrogen sulfide burns in oxygen as follows: $2H_2S(g) + 3O_2(g) \rightarrow 2SO_2(g) + 2H_2O(l)$

If 4.0 dm ³ of hydrogen sulfide is sparked with 10.0 dm ³	³ of oxygen, find the final volume of
the reaction mixture at r.t.p.	[8.0 dm ³]

4.4 Calculations on Combustion Reactions

• General Equation (for *complete* combustion of hydrocarbons, C_xH_y):

 $C_xH_y(g) + (x + \frac{y}{4})O_2(g) \longrightarrow xCO_2(g) + \frac{y}{2}H_2O(l)$ at r.t.p. ------ reaction 1 Note:

(a) CO₂ and H₂O are the only products formed upon complete combustion. (*i.e.* combustion was performed in excess of oxygen).

(b) H₂O formed immediately after combustion exists as a gas (*i.e.* steam).

However, when the mixture is cooled to room temperature, H_2O will condense and exist as a liquid which occupies negligible volume compared to the other gaseous substances. Thus, volume of $H_2O(l)$ is ignored.

- (c) Usually after complete combustion, there will be a *contraction* (*i.e.* decrease) in volume based on reaction 1.
- (d) If the resulting gaseous mixture is passed through a base (e.g. NaOH(aq) or KOH(aq)), there will be a *further contraction* in volume because the acidic CO₂ in the mixture will react with the base.

```
CO_2(g) + 2NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O(l) ------ reaction 2
```

Illustration



Suppose $z \text{ cm}^3$ of C_xH_y was burnt in excess oxygen:

	$(1)C_xH_y(g)$	+ $\left(x+\frac{y}{4}\right)O_2(g) \rightarrow$	<i>x</i> CO ₂ (g) +	$\frac{y}{2}H_2O(l)$	<u>Recall</u> : For gases at same <i>T</i> and
vol of gas reacted / cm ³	z (1)	$z\left(x+\frac{y}{4}\right)$	0	-	mole ratio = volume ratio
vol of gas formed / cm ³	0	0	z (x)	_	

$= \left(V_{C_{x}H_{y}} + \boxed{V_{O_{2} \text{ added}}}\right) - \left(V_{CO_{2}} + V_{O_{2} \text{ unreacted}}\right)$ $= \left(V_{C_{x}H_{y}} + \boxed{V_{O_{2} \text{ reacted}} + V_{O_{2} \text{ unreacted}}}\right) - \left(V_{CO_{2}} + V_{O_{2} \text{ unreacted}}\right)$ $= V_{C_{x}H_{y}} + V_{O_{2} \text{ reacted}} - V_{CO_{2}}$ $= \mathbf{z} + \mathbf{z} \left(\mathbf{x} + \frac{\mathbf{y}}{\mathbf{z}}\right) - \mathbf{z}\mathbf{x}$	Decrease in volume after combustion	Decrease in volume after reaction with base
$= \mathbf{z} + \frac{\mathbf{z}\mathbf{y}}{4} \leftarrow \text{ solve for } \mathbf{y}!$	$= \left(V_{C_{x}H_{y}} + \boxed{V_{O_{2} \text{ added}}}\right) - \left(V_{CO_{2}} + V_{O_{2} \text{ unreacted}}\right)$ $= \left(V_{C_{x}H_{y}} + \boxed{V_{O_{2} \text{ reacted}} + V_{O_{2} \text{ unreacted}}}\right) - \left(V_{CO_{2}} + V_{O_{2} \text{ unreacted}}\right)$ $= V_{C_{x}H_{y}} + V_{O_{2} \text{ reacted}} - V_{CO_{2}}$ $= \mathbf{Z} + \mathbf{Z}\left(\mathbf{X} + \frac{\mathbf{y}}{4}\right) - \mathbf{Z}\mathbf{X}$ $= \mathbf{Z} + \frac{\mathbf{Z}\mathbf{y}}{4} \leftarrow \text{ solve for } \mathbf{y}!$	$= (V_{CO_2} + V_{O_2 \text{ unreacted}}) - V_{O_2 \text{ unreacted}}$ $= V_{CO_2}$ $= \mathbf{z} \mathbf{x} \leftarrow \text{ solve for } \mathbf{x}!$

Note: $V_{O_2 \text{ added}} = V_{O_2 \text{ reacted}} + V_{O_2 \text{ unreacted}}$

Worked Example 4C

10 cm³ of a hydrocarbon, C_xH_y , was exploded with 110 cm³ of oxygen. The total volume after the explosion was 85 cm³, which decreased to 35 cm³ on shaking with excess sodium hydroxide. All volumes were measured at r.t.p.

Write a balanced equation for the combustion of C_xH_y . Deduce the molecular formula of the hydrocarbon.





Self Check 4B

20 cm³ of a gaseous hydrocarbon was exploded with 150 cm³ of oxygen. The resulting gaseous mixture had a total volume of 130 cm³. When this mixture was passed through aqueous NaOH, the final volume of the mixture decreased to 90 cm³. Volumes of all gases were measured at r.t.p.

Deduce the molecular formula of the hydrocarbon.

 $[C_2H_4]$

Checkpoint for Section 1–4:

Section 1

- To remember the definitions for *relative atomic*, *isotopic*, *molecular* and *formula mass* and apply them accordingly.
- To know how to use relative abundances of isotopes to calculate relative atomic mass of an element, vice versa.

Section 2

- To know the definition of the mole.
- To make use of the important formulae (on page 10) to perform calculations involving moles, masses, volume of gases and concentrations of solutions.

Section 3

- To know the definitions of empirical and molecular formulae and know how to determine them from composition by mass information.

Section 4

- To know how to write and balance chemical equations and make use of the mole ratio to perform calculations.
- To be able to identify the limiting reagents in reactions.
- To calculate percentage yield.
- To make use of the relationship where mole ratio = volume ratio (for gases at same *T* and *p*) to determine the formulae of hydrocarbons from volumes of gases.

5 Volumetric Analysis (VA)

- LO (f) write and/or construct balanced equations;
 - (g) perform calculations, including use of the mole concept (and ratio), involving:(iii) volumes and concentrations of solutions and;
 - (h) deduce stoichiometric relationship from calculations such as those in (g)
- VA is a method of quantitative analysis which depends on the accurate measurement of the volumes of two solutions which react *completely*.
- Concentration of one solution (standard solution) is accurately known and it is used to determine the concentration of another solution.
- This is done through a titration process where one solution (from a burette) is gradually added to a fixed volume of another solution (usually in a conical flask) until stoichiometric amounts of the two reactants have reacted.
- The equivalence point is then said to have been reached and it marks the completion of the titration.



5.1 Acid-Base Titrations (will be covered in detail in Acid-base equilibria)

- Acid-base titrations are carried out to determine the stoichiometric amounts of acid and base required to neutralise each other.
- There are four main types of acid-base titrations; strong acid-strong base titration, strong acidweak base titration, weak acid-strong base titration and weak acid-weak base titration.



Weak bases: NH₃(aq), organic bases (e.g. CH₃NH₂) aq soln

- (b) Equivalence Point and End-Point
- Equivalence Point of a titration is reached when the reactants have just reacted with each other according to the stoichiometric ratio given by the balanced equation of the reaction.
- The completion of the titration is detected by some physical change, usually by the addition of an auxiliary reagent, known as an indicator; alternatively some other physical measurement such as pH may be used. After the reaction between the substance and the standard solution is practically complete, the indicator should give a clear visual change in the liquid being titrated.
- End-Point of a titration is reached when the indicator in the titration just changed its colour. At the end-point, the indicator shows a colour that is midway between its extreme colours.
- In the ideal titration, the visible end-point will coincide with the equivalence point. In practice, however, a very small difference usually occurs; this represents the **titration error**. The indicator and the experimental conditions should be selected so the difference between the visible end-point and the equivalence point is as small as possible.

- (c) Titration Curves and Equivalence Point
- A titration curve is a graph of pH against volume of an acid or base. It shows how the pH of an acid (or base) solution in a conical flask changes with the addition of a base (or acid) from a burette.



- (d) Common Acid–Base titration Indicators
- A *suitable* indicator is one which has a <u>working pH range that coincide with the sharp</u> <u>change in pH near the equivalence point of the titration</u>.



5.2 Calculations on Acid-Base Reactions (INDEPENDENT STUDY)

Worked Example 5A

25.0 cm³ of aqueous sodium hydroxide is neutralised by 15.00 cm³ of a solution of hydrochloric acid of concentration 0.250 mol dm⁻³. Determine the concentration of sodium hydroxide in the aqueous solution.

<u>Step ①</u>: Construct **balanced equation** for the reaction. NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H₂O(l) Step ②: **Calculate amount** of reagents used for the reaction.

amount of HCl reacted = $0.250 \times \frac{15.00}{1000} = \frac{3.750 \times 10^{-3} \text{ mol}}{1000}$

Step 3: Complete calculations required using mole ratio between the species concerned.

Since NaOH = HCl,

amount of NaOH in 25.0 cm³ of solution = $1 \times (3.750 \times 10^{-3}) = 3.750 \times 10^{-3}$ mol

concentration of NaOH = $(3.750 \times 10^{-3}) \div \frac{25.0}{1000} = 0.150 \text{ mol dm}^{-3}$

Worked Example 5B

A solution is made by dissolving 5.00 g of an impure sample of sodium hydroxide in water and making it up to 1.00 dm³ of solution. 25.0 cm³ of this solution is neutralised by 15.15 cm³ of sulfuric acid, of concentration 0.102 mol dm⁻³. Calculate the percentage purity of the sample of sodium hydroxide. Neutralised by 15.15 cm³ of Make up to 1 dm³ 0.102 mol dm⁻³ H₂SO₄ NaOH solution (in volumetric flask) Withdraw 25.0 cm³ Dissolve 5.00 g impure NaOH 25 cm³ of NaOH solution <u>Step</u> ①: **2**NaOH(aq) + H₂SO₄(aq) \rightarrow Na₂SO₄(aq) + 2H₂O(l) <u>Step (2)</u>: amount of H_2SO_4 reacted = $0.102 \times \frac{15.15}{1000} = \frac{1.545 \times 10^{-3}}{1000}$ Step ③: Since $2NaOH \equiv H_2SO_4$, amount of NaOH in 25.0 cm³ of solution = $2 \times (1.545 \times 10^{-3}) = 3.091 \times 10^{-3}$ mol amount of NaOH in 1 dm³ of solution = $(3.091 \times 10^{-3}) \times \frac{1000}{25.0} = 0.1236$ mol

 $\frac{25.0}{25.0}$ mass of NaOH in 1dm³ of solution = 0.1236 × (23.0 + 16.0 + 1.0) = 4.945 g % purity of NaOH = $\frac{\text{mass of NaOH in sample}}{\text{mass of sample}} \times 100\% = \frac{4.945}{5.00} \times 100\% = \frac{98.9\%}{5.00}$

Worked Example 5C



5.3 Dilution of Solutions (INDEPENDENT STUDY)

Suppose V_1 cm³ of c_1 mol dm⁻³ of solution A is withdrawn and then diluted to V_2 cm³ (by adding deionised water).

What is the concentration of A in the diluted solution?

amount of A in V_1 cm³ of ORIGINAL solution = amount of A in V_2 cm³ of DILUTED solution

$$\boldsymbol{c}_1 \boldsymbol{V}_1 = \boldsymbol{c}_2 \boldsymbol{V}_2$$

where c_1 is the conc. of **original** solution; V_1 is the volume of **original solution** <u>withdrawn</u>;

 c_2 is the conc. of **diluted** solution; V_2 is the **total** volume of **diluted solution**.

$$c(\text{diluted}) = c(\text{original}) \times \frac{V_{\text{withdrawn}}}{V_{\text{total diluted soln}}}$$

Worked Example 5D

0.500 g of KMnO₄ crystals is dissolved in 100 cm³ of water. 10.0 cm³ of this solution is withdrawn and diluted to 250 cm³. What is the concentration of KMnO₄ in the diluted solution? Withdraw 10 cm³ Dissolve 0.500 g 10 cm³ original 250 cm³ diluted KMnO₄ in 100 cm³ KMnO₄ solution KMnO₄ solution (original solution) amount of KMnO₄ in **100 cm³** of **ORIGINAL** solution = $\frac{0.500}{39.1 + 54.9 + 4(16.0)} = \frac{3.165 \times 10^{-3} \text{ mol}}{39.1 + 54.9 + 4(16.0)}$ Using amt of A in V_1 cm³ of **ORIGINAL** solution = amt of A in V_2 cm³ of **DILUTED** solution, amount of KMnO₄ in **10 cm³** of **ORIGINAL** solution = $(3.165 \times 10^{-3}) \times \frac{10.0}{100} = \frac{3.165 \times 10^{-4}}{100}$ mol concentration of KMnO₄ in **DILUTED** solution = $(3.165 \times 10^{-4}) \div \frac{250}{1000} = 1.27 \times 10^{-3} \text{ mol dm}^{-3}$ OR QR amount of KMnO₄ in **100 cm³** of **ORIGINAL** solution = $\frac{0.500}{39.1 + 54.9 + 4(16.0)} = \frac{3.165 \times 10^{-3} \text{ mol}}{39.1 + 54.9 + 4(16.0)}$ concentration of KMnO₄ in **ORIGINAL** solution = $(3.165 \times 10^{-3}) \div \frac{100}{1000} = 0.03165 \text{ mol dm}^{-3}$ Using $c_1V_1 = c_2V_2$, concentration of KMnO₄ in **DILUTED** solution, $c_2 = 0.03165 \times \frac{10.0}{250} = 1.27 \times 10^{-3}$ mol dm⁻³

5.4 Back-Titrations

- Back titrations are used when the determination of the amount of a substance cannot be done using the direct titration method. e.g. some substances such as CaCO₃ are insoluble in water and would be **difficult to titrate directly** against an acid in an acid–carbonate reaction.
- To overcome this difficulty, the following procedure is carried out:
 - Step^①: A **known amount** of **excess** reagent (*i.e.* **B**) is first added to the impure or insoluble substance to be analysed (*i.e.* **A**), so that **A is completely reacted**.
 - Step²: The amount of **B that remained unreacted** (with **A**) is then **determined by titration** with another **standard solution**, one in which the concentration is accurately known (*i.e.* **C**). This is known as **back titration**.

 $\underbrace{amount \text{ of } \textbf{B} \text{ reacted with } \textbf{A}}_{step 1} = total amount \text{ of } \textbf{B} \text{ added} - \underbrace{amount \text{ of } \textbf{B} \text{ unreacted}}_{step 2}$

Thus the amount of analysed substance, A, can be determined.





Worked Example 5F

0.738 g of a Group 2 metal carbonate, MCO_3 , is reacted with 25.0 cm³ of 1.00 mol dm⁻³ HC*l*(aq). The resultant solution is transferred to a volumetric flask and made up to 250 cm³.

25.0 cm³ of this solution is titrated against 0.0500 mol dm⁻³ NaOH(aq). The titration requires 20.55 cm³ of NaOH(aq) for complete neutralisation.



Checkpoint for Section 5:

- To know the difference between equivalence point and end-point for a titration.
- To appreciate that indicators for various titrations are selected as their working pH range falls within the sharp change in pH near the equivalence point.
- Remember the indicators that are suitable for a particular type of titration.
- To know how to perform calculations involving:
 - Acid-base titrations
 - o Dilutions
 - o Back-titrations

6 Redox Reactions

- LO (i) describe and explain redox processes in terms of electron transfer and/or of changes in oxidation number (oxidation state) and;
 - (j) construct redox equation using the relevant half-equations
- Other than acid–base reactions, another class of reactions that occur frequently around us are reduction–oxidation (redox) reactions.

6.1 Definitions of oxidation and reduction

• A redox reaction is one in which oxidation and reduction take place at the same time.

	Oxidation involves a:	Reduction involves a:
(a)	gain of oxygen or;	loss of oxygen or;
(b)	loss of hydrogen or;	gain of hydrogen or;
(c)	loss of electrons ⇒ results in an <u>increase in oxidation no.</u>	gain of electrons ⇒ results in a <u>decrease in oxidation no.</u>
	Example: $\uparrow \text{ in 0.N}$ $\downarrow (0) (+2)$ $Zn \rightarrow Zn^{2+} + 2e^{-}$	Example: $\downarrow \text{ in 0.N}$ (+2) $Cu^{2+} + 2e^- \rightarrow Cu$
	loss of e⁻	gain of e⁻

• Oxidising agent (oxidant) oxidises others while itself is reduced in a redox reaction. Reducing agent (reductant) reduces others while itself is oxidised in a redox reaction.

: Redox = simultaneous Reduction and Oxidation

Example:

$$[\mathbf{R}]: \text{ gain of } 2e^{-} (\downarrow \text{ in O.N})$$

$$(+2) (0) (0) (+2) (0) (2e^{-}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq))$$

$$[\mathbf{O}]: \text{ loss of } 2e^{-} (\uparrow \text{ in O.N})$$

$$(\mathbf{C}u^{2+}(aq) + Zn(s) (2e^{-}(f) + Zn^{2+}(aq))$$

Oxidising agent: Cu²⁺ Reducing agent: Zn

The overall equation for a redox reaction is the sum of the two half-equations:

[O]: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ half-equations

$$[R]: \qquad Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$$

Overall: $Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$

total no. of e^{-1} lost by reducing agent = total no. of e^{-1} gained by oxidising agent

6.2 Common Oxidising and Reducing Agents

common oxidising agents	medium	product	common reducing agents		medium	product
MnO₄ [−]	acidic	Mn²⁺ manganese(II) ion		Fe²⁺ iron(II) ion	acidic /neutral	Fe³⁺ iron(III) ion
ion	neutral /alkaline	MnO₂ manganese(IV) oxide) I - iodide ion		acidic /neutral /alkaline	I2 iodine
Cr₂O 7 ^{2−} dichromate(VI) ion	acidic	Cr³⁺ chromium(III) ion		S₂O₃²- thiosulfate ion	neutral	S₄O 6 ^{2−} tetrathionate ion (*when reacted with I ₂)
I2 iodine	neutral /acidic	I - iodide ion	C₂O₄²- ethanedioate ion		acidic	CO2
IO 3 ⁻ iodate(V) ion	acidic	I2 iodine				
H ₂ O ₂ hydrogen peroxide	acidic	H₂O		H ₂ O ₂ hydrogen peroxide	acidic	O ₂

* H_2O_2 can act as an oxidising or a reducing agent.

<u>Note</u>: For the moment, you need to know the Table above. This topic is linked to Electrochemistry which involves the study of redox reactions. It depends on E_{cell}^{\ominus} value (and Kinetics) to determine whether the reaction occurs or not. If it occurs, then the species may act as oxidising agent or reducing agent depending on the E_{cell}^{\ominus} . Redox reactions involve the transfer of electrons which would be linked to the concepts covered in the second topic, Atomic Structure.

*SO₄²⁻ sulfate ion will be formed when $S_2O_3^{2-}$ reacts with stronger oxidising agents (for example, Cl_2).

6.3 Oxidation Numbers

- The oxidation number (oxidation state) is a measure of the degree of oxidation of an atom in a substance.
- To keep track of the number of electrons transferred in redox reactions, it is useful to assign oxidation numbers to the elements in the reactants and products.

Oxidation number, *x*, is written as "+*x*" or "-*x*".

Oxidation number = 0

Sign is positive \Rightarrow the atom lost *x* electrons as compared to the atom in its elemental form Sign is negative \Rightarrow the atom gained *x* electrons as compared to the atom in its elemental form

Note: Charges are written as "x+" or "x-" (e.g. Mg²⁺, O²⁻). Oxidation number are written as "+x" or "-x".

Rules for assigning oxidation numbers:

(a) The oxidation number of an atom in its elemental form is zero.

<u>e.g</u>: $\underline{0}$ in Mg $\underline{0}$ in O₂ $\underline{0}$ in P₄ (phosphorus)

(b) The oxidation number of the atom in a monoatomic ion is equal to the charge of the ion.

<u>e.g</u>: NaC*l*: <u>+1</u> in Na⁺ and <u>-1</u> in C*t*

Al₂O₃: <u>+3</u> in Al³⁺ and <u>-2</u> in O²⁻

- (c) Some atoms *nearly always* have the same oxidation number in their compounds.
 - (i) All Group 1 metals+1(ii) All Group 2 metals+2(iii) Al+3(iv) H+1, (except in metal hydrides, e.g. NaH, O.N = -1)(v) O-2, (except in peroxides, e.g. H₂O₂, O.N = -1; and OF_2 , O.N = +2)(vi) F-1(vii) Cl-1 (except in compounds with F and O)
- (d) The sum of oxidation no. of all atoms in a species equals the overall charge of that species.

For neutral compounds:	For charged ions:
$e.g. Al_2O_3: 2(+3) + 3(-2) = 0$	e.g. NH_4^+ : (-3) + 4(+1) = +1
$H_2O: 2(+1) + (-2) = 0$	SO_4^{2-} : (+6) + 4(-2) = -2

What is the oxidation number of Cl in $HClO_4$? Let the oxidation number of Cl be x. (+1) + x + 4(-2) = 0 $\Rightarrow x = +7$ What is the oxidation number of Mn in MnO_4^- ? Let the oxidation number of Mn be *x*.

$$x + 4(-2) = -1$$
$$\Rightarrow x = +7$$

- (e) In a covalent bond containing 2 atoms, the more electronegative atom will be assigned the negative oxidation number.
 - *e.g.* In HF, O.N of F = -1 and O.N of H = +1 since F is more electronegative than H.

In BrF_3 , O.N of F = -1 and O.N of Br = +3 since F is more electronegative than Br.

Recall:

- *Electronegativity* is the the ability of an atom to attract the shared pair(s) of electrons in a covalent bond.
- The more electronegative an atom, the greater is its tendency to attract electrons to itself.
- Electronegativity *increases across the Period* from left to right and *decreases down a Group.* F is the most electronegative atom. (This will be explained in the topic Atomic Structure)
- (f) In more complicated molecules or ions, it is helpful to deduce the oxidation states of the atoms from their structural formula.

e.g. Assign oxidation numbers to all the atoms present in an ethanal molecule, C_2H_4O . If we were to use **steps (a-e)** to deduce the oxidation number, we will end up with the following:



However, after examining the structural formula of ethanal, the two C atoms in the molecule are **bonded to different atoms**. This calculated value of –1 actually represents the **average O.N** of the 2 C atoms present in this molecule.

Given the structural formula, oxidation numbers of atoms can be assigned by:

- 1. Picking a bond between 2 atoms.
- 2. The more electronegative atom will "gain" both the shared electrons in the bond, while the less electronegative atom "loses" its shared electron.

For the two atoms, X and Y, in a bond, where X is more electronegative than Y, for

- a single bond, assign an O.N of -1 to X and assign an O.N of +1 to Y
- a double bond, assign an O.N –2 to X and assign an O.N of +2 to Y
- a triple bond, assign an O.N –3 to X and assign an O.N of +3 to Y
- 3. If the 2 atoms are identical, each atom will be assigned 0.
- 4. The sum of the assigned O.N will be the actual oxidation number of the atom.
- 5. If the particle carries a charge, the overall charge must be considered in the calculation of O.N.



C is more electronegative than H while O is more electronegative than C and H.

6.4 Disproportionation

• *Disproportionation* is a redox reaction in which <u>one</u> species is simultaneously oxidised <u>and</u> reduced.

Examples:

(a) $\mathbf{Cl}_2 + 2\mathbf{OH}^- \rightarrow \mathbf{Cl}\mathbf{O}^- + \mathbf{Cl}^+ + \mathbf{H}_2\mathbf{O}$

Oxidation state of C*l* increases from 0 in C l_2 to +1 in C $lO^$ and decreases from 0 in C l_2 to -1 in C l^- simultaneously.

(b) $2H_2O_2 \rightarrow 2H_2O + O_2$

Oxidation state of O increases from -1 in H_2O_2 to 0 in O_2 and decreases from -1 in H_2O_2 to -2 in H_2O simultaneously.

(c) $Cu_2O + H_2SO_4 \rightarrow CuSO_4 + Cu + H_2O$

Oxidation state of Cu **increases from +1** in Cu₂O **to +2** in CuSO₄ and **decreases from +1** in Cu₂O **to 0** in Cu simultaneously.

6.5 Balancing Half- Equations for Redox Reactions

All balanced equations MUST satisfy two criteria:
 (i) Conservation of <u>number of ATOMS</u>
 (ii) Conservation of <u>CHARGE</u>

Rules for balancing half-equations:

Example:

 $\mathsf{MnO}_4^- + \mathrm{I}^- \xrightarrow{acidic} \rightarrow$

1	<i>Identify species</i> oxidised/reduced in the reaction, using change in oxidation no. (O.N)	$[\mathbf{R}]: \underbrace{\mathbf{Mn}}_{(+7)} O_4^- \to \underbrace{\mathbf{Mn}}_{(+2)}^{2+}$ $[\mathbf{O}]: \underbrace{\mathbf{I}}_{(-1)}^- \to \underbrace{\mathbf{I}}_2_{(0)}$
2	Balance all atoms other than O and H.	[R]: $\underline{Mn}O_4^- \rightarrow \underline{Mn}^{2+}$ [O]: $2\underline{I}^- \rightarrow \underline{I}_2$
3	Add H ₂ O to appropriate side of equation to balance the number of O atoms	[R]: $MnO_4^- \rightarrow Mn^{2+} + 4H_2O$ [O]: $2\underline{I}^- \rightarrow \underline{I}_2$
4	Add H ⁺ to appropriate side of equation to balance the number of H atoms	[R]: $MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$ [O]: $2\underline{I}^- \rightarrow \underline{I}_2$
5	Add electrons to appropriate side of equation to balance the total charge	$[\mathbf{R}]: \underbrace{MnO_{4}^{-} + 8H^{+}}_{(1-) + 8(1+) = 7_{+}} + 5e^{-} \rightarrow \underbrace{Mn^{2+} + 4H_{2}O}_{1(2+) + 4(0) = 2_{+}}$ $[\mathbf{O}]: \underbrace{2\underline{I}^{-}}_{2(1-) = 2^{-}} \rightarrow \underbrace{I_{2}}_{0} + 2e^{-}$
6	<i>Multiply</i> each half–equation by appropriate factor to equate the number of electrons.	 [R]: MnO₄⁻ + 8H⁺ + 5e⁻ → Mn²⁺ + 4H₂O (×2) [O]: 2I⁻ → I₂ + 2e⁻ (×5) For each half-equation, <u>check</u> that the number of electrons are: on the correct side of equation (<i>i.e.</i> must correspond to [R] or [O]) total number of electrons transferred = total change in oxidation number
Ø	Add the two half-eqns and eliminate any common species (e.g. e^- , H_2O , H^+ and OH^-).	$[R]: 2MnO_{4}^{-} + 16H^{+} + 10e^{-} \rightarrow 2Mn^{2+} + 8H_{2}O$ $[O]: 10I^{-} \rightarrow 5I_{2} + 10e^{-}$ $Overall: 2MnO_{4}^{-} + 10I^{-} + 16H^{+} \rightarrow 2Mn^{2+} + 5I_{2} + 8H_{2}O$

 \Rightarrow Check your equation by ensuring BOTH ATOMS AND CHARGES are fully balanced! \Rightarrow There should be no electrons present in the overall equation. When balancing redox reactions, it is important to take note of the medium that the redox reaction is carried out in. The products formed in the redox can vary depending on the medium. If the same reaction above was carried out in an alkaline medium, the product formed from the reduction of MnO₄⁻ will be different.

Ex	ample:	$InO_4^- + I^- \xrightarrow{alkaline}$
0	<i>Identify species</i> oxidised/reduced in the reaction, using change in oxidation no . (O.N)	[R]: $\underline{Mn}_{(+7)}O_4^- \rightarrow \underline{MnO_2}_{(+2)}$ Under alkaline condition, MnO_4^- is reduced to MnO_2 instead of Mn^{2+} . [O]: $\underline{I}^- \rightarrow \underline{I}_2$ (-1) (0) Under alkaline condition, I ⁻ is similarly oxidised to I ₂ . As such, the
2	Balance all atoms other than O and H.	[R]: $\underline{\text{Mn}}\text{O}_4^- \rightarrow \underline{\text{Mn}}\text{O}_2$
3	Add H ₂ O to appropriate side of equation to balance the number of O atoms	[R]: $MnO_4^- \rightarrow MnO_2 + 2H_2O$
4	Add H ⁺ to appropriate side of equation to balance the number of H atoms	[R]: $MnO_4^- + 4H^+ \rightarrow MnO_2 + 2H_2O$
5	Addelectronstoappropriatesideofequationtobalancethetotalcharge	$[\mathbf{R}]: \underbrace{MnO_4^- + 4H^+}_{(1-) + 4(1+) = 3+} + 3e^- \rightarrow \underbrace{MnO_2 + 2H_2O}_{O}$
6	Multiply each half–equation by appropriate factor to equate the number of electrons.	[R]: MnO ₄ ⁻ + 4H ⁺ + 3e ⁻ → MnO ₂ + 2H ₂ O (×2) [O]: $2I_{-}^{-} \rightarrow I_{2} + 2e^{-}$ (×3) For each half-equation, <u>check</u> that the number of electrons are: - on the correct side of equation (<i>i.e.</i> must correspond to [R] or [O]) - total number of electrons transferred = total change in oxidation number
Ø	Add the two half-eqns and eliminate any common species (e.g. e^- , H_2O , H^+ and OH^-).	$[R]: 2MnO_4^- + 8H^+ + 6e^- \rightarrow 2MnO_2 + 4H_2O$ $[O]: 6I^- \rightarrow 3I_2 + 6e^-$ $2MnO_4^- + 6I^- + 8H^+ \rightarrow 2MnO_2 + 3I_2 + 4H_2O$
8	For redox reaction carried out in alkaline medium , add the same number of OH ⁻ as there are H ⁺ to BOTH sides of equation (<i>i.e.</i> to convert H ⁺ to H ₂ O) then simplify the equation by cancelling off any extra H ₂ O.	$2MnO_{4}^{-} + 6I^{-} + \underline{8H^{+}} + \underline{8OH^{-}} \rightarrow 2MnO_{2} + 3I_{2} + 4H_{2}O + \underline{8OH^{-}}$ reacts to give water $2MnO_{4}^{-} + 6I^{-} + \underline{8H_{2}O} \rightarrow 2MnO_{2} + 3I_{2} + 4H_{2}O + 8OH^{-}$ $\underline{2MnO_{4}^{-} + 6I^{-} + 4H_{2}O \rightarrow 2MnO_{2} + 3I_{2} + 8OH^{-}}$

• For <u>neutral</u> conditions, either H^+ or OH^- can be used to balance the equation.

W	orked Example 6B	
Bala (a)	anced the following equations under the specified cond $Cr_2O_7^{2-} + I^- \rightarrow$ (acidic)	ditions. <u><i>Hint</i></u> : Determine the products formed using Section
	[R]:	6.2 & follow the steps stated in Section 6.5.
	[O]:	
(b)	$S_2O_3^{2-}$ + $I_2 \rightarrow$	
	[R]:	
	[O]:	
(c)	$IO_3^- + I^- \rightarrow$ (acidic)	
	[R]:	
	[O]:	
(d)	$Cr_2O_7^{2-}$ + $Fe^{2+} \rightarrow$ (acidic)	
	[R]:	
	[O]:	
(e)	$Cl_2 \rightarrow Cl^- + ClO^-$ (alkaline)	
	[R]:	
	[O]:	

Self-Check 6A

Write balanced equations for each of the following reactions under acidic conditions.

(a) $H_2O_2 + S^{2-} \rightarrow SO_4^{2-} + H_2O$

(b) $HNO_3 + H_2S \rightarrow NO + S$

6.6 Determination of oxidation numbers using half-equation

- In a redox reaction which involves transfer of electrons, the number of electrons transferred can be deduced from the change in oxidation number of the atom being oxidised or reduced.
- Remember, for redox reactions:

total amount of e^- released = total amount of e^- gained

Worked Example 6C

50.0 cm³ of 0.0500 mol dm⁻³ KC $lO_4(aq)$ requires 50.0 cm³ of 0.200 mol dm⁻³ TiC $l_3(aq)$ to reach end-point. Given that ClO_4^- is reduced to Cl^{3+} in this reaction, what is the oxidation state of the oxidised product of the Ti³⁺ ion?

 $[\mathsf{R}]: \mathsf{C}l\mathsf{O}_4^- \to \mathsf{C}l^{3+}$

 $[O]: Ti^{3+} \rightarrow Ti^{m+} + \underline{?}e^{-}$

<u>Step ①</u>: **Identify BOTH** oxidised and reduced **species** and **determine** the **mole ratio** of the species.

	C <i>I</i> O ₄ -	Ti ³⁺		
Amount / mol	$0.0500 \times \frac{50.0}{1000} = \underline{2.500 \times 10^{-3} \text{ mol}}$:	$0.200 \times \frac{50.0}{1000}$ = <u>0.01000 mol</u>	
Mole Ratio :				
∴C/O₄ ⁻ ≡Ti ³⁺				

Worked Example 6C ContinuedStep @:Using the given/known product (i.e. Cl^{3+}), complete one corresponding half-equation. (Equation may sometimes be provided in the question/Data Booklet.)[R]: $ClO_4^- + 8H^+ + 4e^- \rightarrow Cl^{3+} + 4H_2O$ $_e^- = _ClO_4^-$ and use it to determine the mole ratio of species reacted and e^- transferred. $_e^- = _ClO_4^- = _Ti^{3+}$ Step @:Using the established mole ratio to solve question!Since $_e^- = _Ti^{3+}$ (i.e. [O]: each Ti^{3+} _____e^-) O.N of Ti __ by ___.Final oxidation number of Ti species, m = ____.

Worked Example 6D

The compound NH₂OH is oxidised by Mn³⁺, which itself is reduced to Mn²⁺. In an experiment, 25.0 cm³ of 0.100 mol dm⁻³ NH₂OH required 25.0 cm³ of 0.200 mol dm⁻³ Mn³⁺ for complete reaction. What change in oxidation number does the nitrogen in NH₂OH undergo?

<u>Step ①</u>: Identify BOTH oxidised and reduced species and determine the mole ratio of the species.

	Mn ³⁺	:	NH₂OH
Amount / mol	$0.200 \times \frac{25.0}{1000} = 5.000 \times 10^{-3} \text{ mol}$		$0.100 \times \frac{25.0}{1000} = \underline{2.500 \times 10^{-3} \text{ mol}}$
Mole Ratio	Mole Ratio :		
∴Mn ³⁺ ≡NH₂OH			

<u>Step</u> 2: Using the given/known product (i.e. Mn^{2+}), **complete one corresponding half**– equation. (Equation may sometimes be provided in the question/Data Booklet.)

[R]: $Mn^{3+} + e^- \rightarrow Mn^{2+}$

__e⁻ ≡ ___Mn³+

and use it to determine the mole ratio of species reacted and e^- transferred. ___e⁻ = ___Mn³⁺ = ___NH₂OH

=____.

<u>Step ③</u>: Using the established mole ratio to **solve question!**

Since $\underline{\mathbf{N}}\mathbf{H}_{2}\mathbf{O}\mathbf{H} \equiv \underline{\mathbf{e}}^{-}$ (*i.e.* **[O]: each N** $\underline{\mathbf{e}}^{-}$) O.N of N $\underline{\mathbf{b}}$ by $\underline{\mathbf{c}}$.

Final oxidation number of N =

... Oxidation number of N changes from ______.

Worked Example 6E

30.0 cm³ of 0.0500 mol dm⁻³ aqueous iron(II) sulfate is titrated against 0.0250 mol dm⁻³ acidified potassium manganate(VII) under certain conditions. It is determined that exactly 15.0 cm³ of the manganate(VII) solution is required to reach end-point.

If the final oxidation state of iron is +3, what would be the final oxidation state of manganese?

<u>Step ①</u>: Identify BOTH oxidised and reduced species and determine the mole ratio of the species.

_		Fe ²⁺	:	MnO₄ [−]	
	Amount / mol	$\frac{30.0}{1000} \times 0.0500$ = 1.500 × 10 ⁻³ mol	:	$\frac{15.0}{1000} \times 0.0250$ = 3.750 × 10 ⁻⁴ mol	
-	Mole Ratio		:		
		∴Fe²+ ≡	Mr	1O ₄ -	
Step 2	: Using the giver	n/known product (i.e. Fe	e ³⁺), cc	omplete one corresponding half–eqn.	
	[O]: $Fe^{2+} \rightarrow Fe$	[O]: $Fe^{2+} \rightarrow Fe^{3+} + e^{-}$			
	e ⁻ ≡Fe ²⁺				
	and use it to determine the mole ratio of species reacted and e ⁻ transferred.				
	e ⁻ ≡Fe ²⁺	≡MnO₄⁻			
Step 3	: Using the estat	blished mole ratio to so	lve qu	estion!	
	Since <u>Mn</u> O₄ [−] ≡	e⁻ (<i>i.e.</i> [R]: each Mı	n	e⁻) O.N of Mn by	
	Final oxidation	number of Mn =	=		



• On closer observation of the workings, the relationship given above can be further refined to:

amount of atoms oxidised \times change in O.N =	amount of atoms reduced × change in O.N
total amount of electrons released	total amount of electrons gained

Note:

- change in O.N = higher O.N lower O.N
- The change in oxidation number is an indication of the number of electrons that was transferred in the redox reaction.
- For reduction, the final oxidation number will be smaller than the initial oxidation number. Hence, to obtain a positive absolute value for the number of electrons that was transferred, the larger oxidation number value is subtracted by the smaller oxidation number value.

*** While this relationship provides a quick way to solve questions involving redox reactions (and comes in especially useful when solving MCQs), it is more important that you understand the concept of electron transfer for redox reactions.

Solving Worked Example 6E: (Alternative Method) [O]: $Fe^{2+} \rightarrow Fe^{3+} + e^{-}$ [R]: $MnO_{4^-} \rightarrow ?$ Let the final oxidation state of Mn be represented by x. amt of Fe atoms oxidised x change in O.N = amt of Mn atoms reduced x change in O.N $\frac{30.0}{1000} \times 0.0500 \times (3-2) = \frac{15.0}{1000} \times 0.0250 \times (+7-x)$ $1.500 \times 10^{-3} \text{ mol } \times 1 = 3.750 \times 10^{-4} \text{ mol } x (+7-x)$ $\frac{1.500 \times 10^{-3}}{3.750 \times 10^{-4}} = +7-x$ 4 = +7-x $x = \pm 3$

6.7 **Redox Titrations and Calculations**

LO (k) describe and explain the use of Fe³⁺/Fe²⁺, MnO₄⁻/Mn²⁺ and Cr₂O₇²⁻/Cr³⁺ as examples of redox systems

- In redox titrations, the reaction involves transfer of electrons from a reducing agent (electron donor) to an oxidising agent (electron acceptor).
- Commonly used oxidising / reducing agents in redox titrations include:

oxidising agent	reducing agent	indicator	Reagent in burette	Reagent in conical flask	colour change at end-point
acidified	C ₂ O ₄ ^{2–} , H ₂ O ₂ (<i>colourless</i>)	not required	KMnO₄	$C_2O_4^{2-}$ or H_2O_2	colourless to pale pink
KMnO₄ (purple)	Fe ²⁺ (green)	not required	KMnO ₄	Fe ²⁺	yellow* to orange (*due to the formation of Fe ³⁺)
acidified K ₂ Cr ₂ O ₇ (<i>orange</i>)	Fe ²⁺ (green)	<i>N</i> -phenylanthranilic acid	K ₂ Cr ₂ O ₇	Fe ²⁺	green to reddish- violet
I ₂ (brown) (liberated from	S-O-2-	starch	S ₂ O ₃ ²⁻	I ₂	dark blue to colourless
reaction between I⁻ and an O.A)	(colourless)	no indicator	S ₂ O ₃ ²⁻	I ₂	pale yellow to colourless

Common Redox Titrations

•

Three types of redox titrations are commonly done in the laboratory. They are:

- manganate(VII) titrations
 - kacidic medium dichromate(VI) titrations
- iodine-thiosulfate titrations

(a) manganate(VII) titrations

- > Manganate(VII) ion, MnO_4^- , is a powerful oxidising agent and can be used with a wide range of reducing agents (e.g. Fe²⁺, H₂O₂, etc)
- > In acidic medium, MnO_4^- , is reduced to manganese(II) ion, Mn^{2+} :

 $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ pale pink purple (but appears colourless in dilute soln)

- \rightarrow H₂SO₄(aq) is used to provide the acidic medium for manganate(VII) titrations. **HNO₃(aq) and HC**l(aq) are not used, as HNO₃ is an oxidising agent, and Cl in HCl can be
 - oxidised by MnO_4^- to Cl_2 .
- Since KMnO₄ is purple in colour and its reduced product, Mn²⁺, is pale pink (appears) colourless in dilute solutions), **no indicator** is necessary for manganate(VII) titrations.
- > The end-point (if the other reducing agent and its product are also colourless) occurs when one excess drop of purple KMnO₄(aq) turns the solution in the conical flask from colourless to permanent pale pink.
- > In the titration of Fe²⁺(aq) with acidified KMnO₄(aq) in the burette, the colour change in the conical flask will be yellow to orange.



(b) dichromate(VI) titrations

- Dichromate(VI) ion, Cr₂O₇²⁻, is a weaker oxidising agent than MnO₄⁻. Hence it can only be used to titrate against a limited variety of reducing agents.
- > In acidic medium, $Cr_2O_7^{2-}$ is reduced to chromium(III) ion, Cr^{3+} :

$$\begin{array}{cccc} Cr_2O_7{}^{2-} + & 14H^+ + & 6e^- \rightarrow & 2Cr^{3+} & + 7H_2O\\ orange & & green \end{array}$$

- Unlike in manganate(VII) titrations, both H₂SO₄ and HC*l* can be used to provide the acidic medium for dichromate(VII) titrations. Being a weaker oxidising agent than MnO₄⁻, Cr₂O₇²⁻ is not able to oxidise C*t*⁻ to C*l*₂ (under standard conditions).
- Although Cr₂O₇²⁻ (orange) and the product Cr³⁺ (green) are different in colour, it is difficult to judge the end-point as the green colour would dominate long before the end-point is reached. An indicator, such as *N*-phenylanthranilic acid, is usually required.



- (c) iodine-thiosulfate titrations
 - > Thiosulfate ions, $S_2O_3^{2-}$, is a common reducing agent for titration with iodine:

$$\begin{array}{ccc} I_2 + 2S_2O_3^{2-} & \rightarrow \underbrace{2I^- + S_4O_6^{2-}}_{colourless} \end{array}$$

- > Iodine-thiosulfate titrations can be used to determine the amount of
 - (i) iodine directly or
 - (ii) **oxidising agent that will liberate iodine with potassium iodide**. In this case, the iodometric titration (where we titrate the iodine that is formed) usually involves two steps:
 - 1. The oxidising agent is added to \underline{excess} KI(aq) to liberate I₂(aq).
 - 2. The liberated $I_2(aq)$ is then titrated against standard $S_2O_3^{2-}$ solution.

Why is **excess** KI needed in step 1 of the iodometric titration on point **(c)**(ii)? It is to ensure that the oxidising agent is completely reacted. In addition, I₂ is not very soluble in water and would dissolve in water by reacting with excess I⁻ to form soluble I₃⁻ (*i.e.* I₂(aq)).

Why should iodine solution be titrated as soon as possible once it is prepared? I_2 is volatile. If not titrated as soon as possible, the amount of I_2 will decrease over time.

- In the absence of starch, the colour change at the end-point is pale yellow to colourless. When starch is used as an indicator, it is usually added near the end-point of the titration (when the solution is pale yellow). The unreacted I₂ forms a dark blue complex with starch, and the solution will turn colourless when all the iodine has been used up (*i.e.* end-point is reached).
- Why is the starch indicator added only near the end-point of the titration?

Starch solution cannot be added at the beginning of titration as starch–iodine complex can precipitate out at high concentration of I₂. Therefore, the starch solution should be added near the end-point to **avoid precipitation of starch–iodine complex**.

After complete titration, I⁻ formed may be slowly oxidised by O₂ in air to give I₂. Hence, a slow reappearance of blue coloration is observed. There is no need to re-titrate/continue with the titration.



Checkpoint for Section 6:

- To be able to assign oxidation states to atoms and determine the oxidising agent and reducing agent in a reaction.
- To write balanced half equations and determine the mole ratio of species reacted and electrons transferred.
- To perform calculations using the mole ratio.

APPENDIX

Appendix 1 – Double Indicator Titrations

Acid–carbonate and Acid–hydrogencarbonate Titrations

Hydrogencarbonate ions (HCO ₃ [−]) react with acid according to the following equation:		Carbonate ions (CO ₃ ^{2–}) react with excess acid according to the following overall equation:		
HCO₃⁻(aq)	+ $H^{+}(aq) \rightarrow CO_{2}(g) + H_{2}O(l)$	$\text{CO}_3^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(l)$		
\therefore <u>1</u> mol of H ⁺ reacts with 1 mol of HCO ₃ ⁻ (<i>i.e.</i> H ⁺ = HCO ₃ ⁻).		$\therefore \underline{2} \text{ mol of } \mathbf{H}^+ \text{ react with 1 mol of } \mathbf{CO}_3^{2-}$ $(i.e. \ 2\mathbf{H}^+ \equiv \mathbf{CO}_3^{2-}).$		
The reaction of C	CO ₃ ²⁻ with acids occurs in 2 step	S:		
Step 1:	CO₃²⁻(aq) + H⁺(aq) → HCO₃⁻	(aq)		
Step 2:	HCO₃⁻(aq) + H⁺(aq) → CO₂(g) + H ₂ O(<i>l</i>)		
Overall:	$CO_3^{2-}(aq) + 2H^+(aq) \rightarrow CO_2(q)$			

If the pH is monitored during an acid–carbonate titration, **2 sharp changes in pH** (*i.e.* 2 equivalence points) will be observed when *reaction (1)* and (2) are completed respectively.

For titration of solution containing ONLY CO₃²⁻:



With reference to the above pH graph,

When \boldsymbol{x} cm ³ of acid is added	When another x cm ³ of acid is added (<i>i.e.</i> total of 2x cm ³)
Reaction (1) is completed (<i>i.e.</i> all CO_3^{2-} has been converted to HCO_3^{-}).	Reaction (2) is completed.
Phenolphthalein can be used to detect this first end-point since the working pH range of phenolphthalein (<i>i.e.</i> pH 8–10) coincides with the sharp pH change of the equivalence point of reaction (1).	Methyl orange can be used to detect this second end-point since the working pH range of methyl orange (<i>i.e.</i> pH 3–5) coincides with the sharp pH change of the equivalence point of reaction (2).
If phenolphthalein is used, colour changes from pink to colourless. If thymol blue is used, colour changes from blue to green.	Colour changes from yellow to orange.



For titration of solution containing CO₃²⁻ AND HCO₃⁻:

CO₃²⁻ is a stronger base than HCO₃⁻. Hence the acid must react with all CO₃²⁻ first to form HCO₃⁻ before any HCO₃⁻ reacts with the acid.



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Worked Example B



Appendix 2 – Relevance of Redox Reactions in our daily lives

Redox reactions are among the most common and most important chemical reactions in everyday life. Combustion is an example of a redox reaction that occurs so rapidly that noticeable heat and light are produced. Corrosion, decay, and various biological processes are examples of oxidation that occurs so slowly that noticeable heat and light are *not* produced.

Combustion

Combustion means burning. Any time a material burns, an oxidation-reduction reaction occurs. The two equations below show what happens when coal (which is nearly pure carbon) and gasoline (C_8H_{18}) burn. You can see that the fuel is oxidised in each case:

 $\begin{array}{l} C+O_2 \rightarrow CO_2 \\ 2C_8H_{18}+25O_2 \rightarrow 16CO_2+18H_2O \end{array}$

In reactions such as these, oxidation occurs very rapidly and energy is released. That energy is put to use to heat homes and buildings; to drive automobiles, trucks, ships, airplanes, and trains; to operate industrial processes; and for numerous other purposes.

Spoiling and Aging

Oxidation-reduction reactions are responsible for the spoiling of food, the culprit here being the oxidation portion of the reaction. To prevent spoilage, manufacturers of food items often add preservatives, which act as reducing agents.

Oxidation may also be linked with the effects of aging in humans, as well as with other conditions such as cancer, hardening of the arteries, and rheumatoid arthritis. It appears that oxygen molecules and other oxidising agents, always hungry for electrons, extract these from the membranes in human cells. Over time, this can cause a gradual breakdown in the body's immune system.

To forestall the effects of oxidation, some doctors and scientists recommend antioxidants—natural reducing agents such as vitamin C and vitamin E. The vitamin C in lemon juice can be used to prevent oxidising on the cut surface of an apple, to keep it from turning brown.

Rusting

Most metals react with oxygen to form compounds known as oxides. Rust is the name given to the oxide of iron and, sometimes, the oxides of other metals. The process by which rusting occurs is also known as corrosion. Corrosion is very much like combustion, except that it occurs much more slowly, such as the rusting of iron.

 $4 \text{ Fe} + 3 \text{ O}_2 \rightarrow 2 \text{ Fe}_2 \text{O}_3$

Decaying

The compounds that make up living organisms, such as plants and animals, are very complex. They consist primarily of carbon, oxygen, and hydrogen. A simple way to represent such compounds is to use the letters x, y, and z to show that many atoms of carbon, hydrogen, and oxygen are present in the compounds.

When a plant or animal dies, the organic compounds of which it is composed begin to react with oxygen. The process is known as decay, and it is another example of a common oxidation-reduction reaction. The equation below represents the decay (oxidation) of a compound that might be found in a dead plant:

$$C_xH_yO_z + (x + \frac{y}{4} - \frac{z}{2}) O_2 \rightarrow x CO_2 + \frac{y}{2} H_2O$$

Self Check Answers

1 C; 2 B **1A**

3 V

	Mn	0
Mass in 100 g /g	72.0	28.0
Amount /mol	$\frac{72.0}{54.9}$ = 1.311	$\frac{28.0}{16.0}$ = 1.750
s implest mole R atio	$\frac{1.311}{1.311} \approx 1$ 1 x 3 = 3	$\frac{1.750}{1.311} \approx 1.33 \approx \frac{4}{3}$ $\frac{4}{3} \times 3 = 4$

Empirical formula of compound Y is Mn₃O₄.

4A (a) $2 \operatorname{Zn}(s) + O_2(g) \rightarrow 2 \operatorname{ZnO}(s)$ 1

> amount of Zn used = $\frac{25.0}{65.4} = \frac{0.382 \text{ mol}}{0.382 \text{ mol}}$ amount of O_2 used = $\frac{8.00}{2(16.0)} =$ **<u>0.250 mol</u>**

Since $2 Zn \equiv O_2$, <u>Zn</u> is the limiting reagent.

(b) Since Zn is the limiting reagent, ZnO formed and unreacted O₂ will remain at the end of reaction.

Since $2 ZnO \equiv 2 Zn$, amount of ZnO formed = $1 \times 0.382 = 0.382$ mol mass of ZnO formed = $0.382 \times [65.4 + 16.0] = 31.1g$

Since $O_2 \equiv 2 Zn$, Amount of O₂ reacted = $\frac{1}{2} \times 0.382 = 0.191$ mol amount of unreacted O_2 = amount of O_2 added – amount of O_2 reacted = 0.250 - 0.191 = **0.0589 mol**

mass of **unreacted** $O_2 = 0.0589 \times 2(16.0) = 1.88 g$

Since $2H_2S \equiv 3O_2$, <u> H_2S </u> is the limiting reagent. 2

	2H ₂ S(g) +	$3O_2(g) \rightarrow 2SO_2(g) +$	2H ₂ O(<i>l</i>)
<i>initial</i> vol. of gas /cm ³	4.0 -4.0	10.0 $2_{-3(4.0)}$ - $2_{+4.0}$	-
final vol. of gas /cm ³	0 📕	<u>4.0</u> 2 4.0	-

H₂O exists as a liquid at r.t.p. It has negligible volume, as compared to gases.

Final volume of reaction mixture = $4.0 + 4.0 = 8.0 \text{ dm}^3$



4B.



6A

(a) [R]: $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ (×4)

[O]: $\underline{S}^{2-} + 4H_2O \rightarrow \underline{S}O_4^{2-} + 8H^+ + 8e^-$ (×1) $4H_2O_2 + 8H^+ + S^{2-} + 4H_2O \rightarrow 8H_2O + SO_4^{2-} + 8H^+$

Overall: $4H_2O_2 + S^{2-} \rightarrow 4H_2O + SO_4^{2-}$

(b) [R]:
$$H\underline{N}O_3 + 3H^+ + 3e^- \rightarrow \underline{N}O + 2H_2O$$
 (x2)

[O]: $H_2\underline{S} \rightarrow \underline{S} + 2H^+ + 2e^-$ (×3) 2HNO₃ + 6H⁺ + 3H₂S \rightarrow 2NO + 4H₂O + 3S + 6H⁺

Overall: $2HNO_3 + 3H_2S \rightarrow 2NO + 4H_2O + 3S$