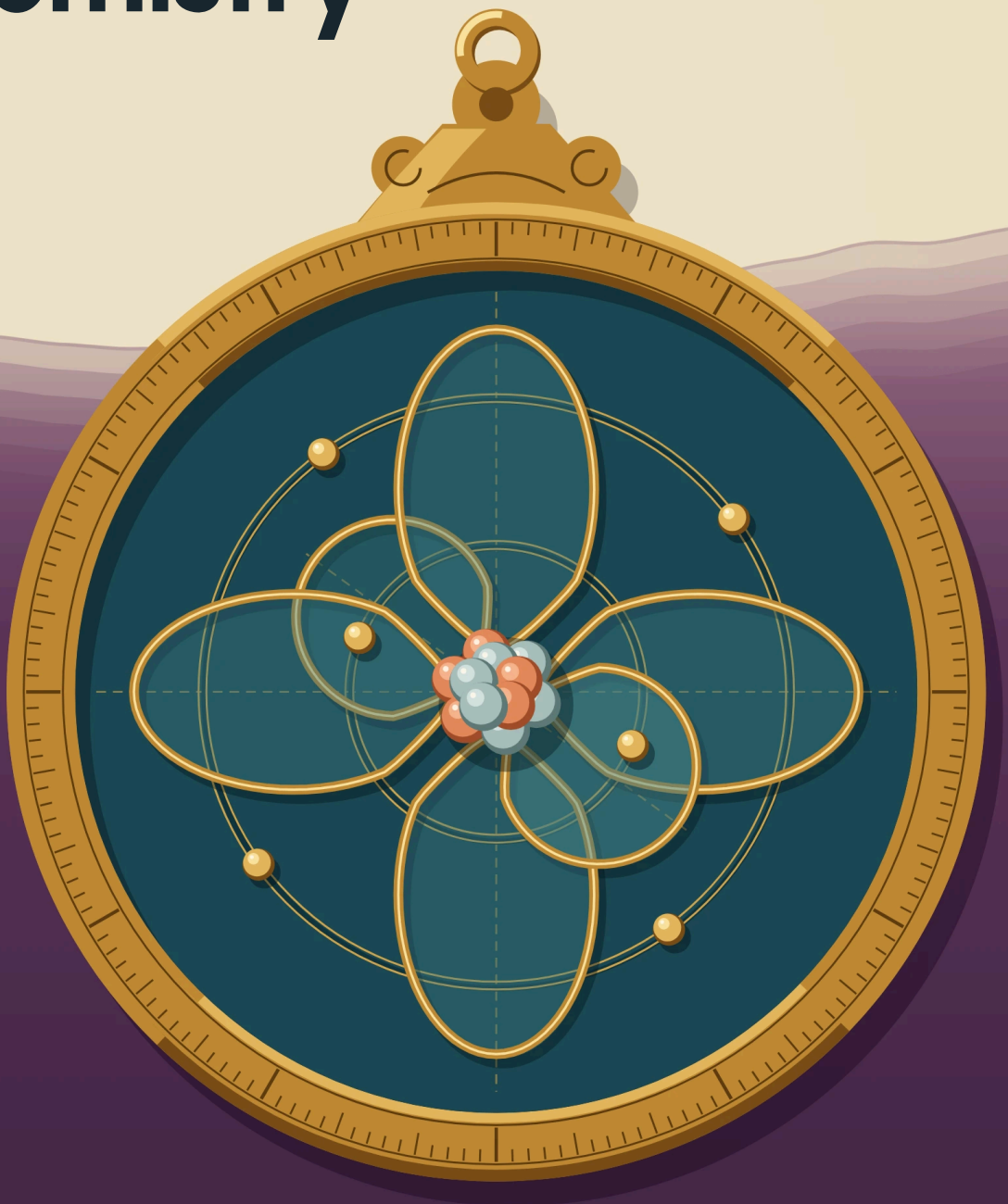
LEARNERS' ALLEY
Designed by Khow Willard

JC1

H2 Chemistry

Book 1

For the 9476 syllabus



NAME _____

9476 Scheme of Assessment

H2 Chemistry (Syllabus 9476, first examined in 2026). All candidates are required to enter for Papers 1, 2, 3 and 4.

Paper 1
Multiple Choice

DURATION	MARKS	WEIGHTING	TIME PER MARK
1 h	30	15%	2 min

- 30 compulsory multiple choice questions, each with 4 options.
- 5 to 8 of them are multiple completion questions.

Paper 2
Structured Questions

DURATION	MARKS	WEIGHTING	TIME PER MARK
2 h	75	30%	1.6 min

- A variable number of structured questions, all compulsory. Answers are written on the question paper.
- Includes data-based question(s) worth 20 to 25 marks in total.

Paper 3
Structured Questions

DURATION	MARKS	WEIGHTING	TIME PER MARK
2 h	75	35%	1.6 min

- **Section A** (55 marks): 3 to 4 compulsory structured questions of 15 to 25 marks each.
- **Section B** (20 marks): two 20-mark questions, answer **one**.

Paper 4
Practical

DURATION	MARKS	WEIGHTING	TIME PER MARK
2 h 30 min	50	20%	3 min

- **Planning**: 4% of the total.
- **Manipulation, measurement and observation**, **presentation of data and observations**, and **analysis, conclusions and evaluation**: 16% of the total.
- No books or laboratory notebooks may be used.

How to use these notes

Fill in the blanks

Write the missing key word on each line, e.g. electrons are added to the _____. The answers are the phrases examiners look for.

Labels

NOTE marks a special case, an exception or a point that is easy to miss. EXAM TIP marks advice on how to phrase an answer or set out working. ANSWER STRUCTURE shows how to set out the answer to a type of question you will meet again and again.

Explanations and examples

Numbered points in an explanation are separate mark points: write every one. Each WORKED EXAMPLE starts from a real exam question.

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01 Atomic Structure

1 Sub-atomic Particles

1.1 Protons, neutrons and electrons

Particle	Relative charge	Relative mass
proton	+1	1
neutron		1
electron	−1	

- Protons and neutrons reside together in the **nucleus**, which holds almost all the mass and all the positive charge.
- Electrons are found in regions of space around the nucleus, and are **attracted electrostatically** by the protons.

1.2 Proton number and nucleon number

DEFINITION **Nucleon number**: total number of _____ in the nucleus of an atom.

DEFINITION **Proton number**: number of _____ in the nucleus of an atom. It determines the _____ of the element.

DEFINITION **Nuclide**: a specific combination of protons and neutrons in a nucleus.

$^{35}_{17}Cl$

35 nucleon number (mass number) = p + n
17 proton number (atomic number) = p

Atom	Cation	Anion
no. of p = no. of e^-	loses e^-: p > e^-	gains e^-: e^- > p

1.3 Isotopes

DEFINITION **Isotopes** are atoms of the same element with the same number of _____ but different numbers of _____.

^{35}Cl	**17 p, 18 n**
^{37}Cl	**17 p, 20 n**

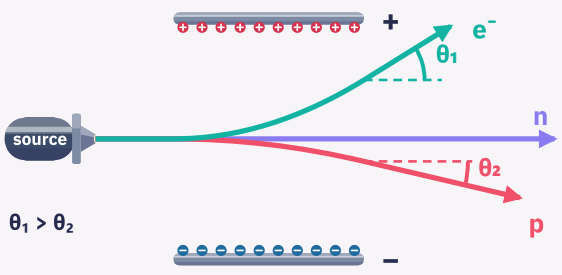
Same electronic configuration
Same _____

Different masses
Different _____

Name an isotope with its nucleon number, e.g. ^{2}H. In every stable isotope except ^{1}H and ^{3}He, neutrons ≥ protons.

1.4 Beams of p, n and e^- in an electric field

$$\text{angle of deflection} \propto \frac{\quad}{\quad}$$



- **Protons** are deflected towards the negatively charged plate.
- **Electrons** are deflected towards the positively charged plate. They are much lighter than protons, so are deflected to a **larger extent**.
- **Neutrons** have no charge and are undeflected.

WORKED EXAMPLE A beam of $^{241}Am^+$ ions is deflected by +2°. Under the same conditions, find the angle of deflection of $^{32}S^-$ ions.

$\theta = k \times \frac{\text{charge}}{\text{mass}}$ $\quad Am^+$: $+2 = k \times \frac{+1}{241} \rightarrow k = 482$ $\quad S^-$: $\theta = 482 \times \frac{-1}{32} = \mathbf{-15.1°}$

2 Relative Masses of Atoms

2.1 Relative isotopic mass

DEFINITION **Relative isotopic mass**: the mass of one mole of atoms of an _____ relative to 1/12 the mass of one mole of ^{12}C atoms.

2.2 Relative abundance

Relative abundance: the _____ of atoms of each isotope in a naturally occurring sample of the element.

e.g. chlorine: 75% ^{35}Cl, 25% ^{37}Cl

2.3 Relative atomic mass, A_r

DEFINITION **Relative atomic mass**: the _____ mass of one mole of atoms of an element relative to 1/12 the mass of one mole of ^{12}C atoms.

$$A_r = \frac{\Sigma \text{ (relative isotopic mass} \times \text{relative abundance)}}{\text{total abundance (100)}}$$

Cl: $\frac{(35 \times 75) + (37 \times 25)}{100} =$ _____

3 Shells, Subshells and Orbitals

3.1 Principal quantum shells, subshells and orbitals

DEFINITION **Orbital**: the region of space where there is a _____ _____ (95%) of finding an electron. Each orbital can accommodate _____ electrons.

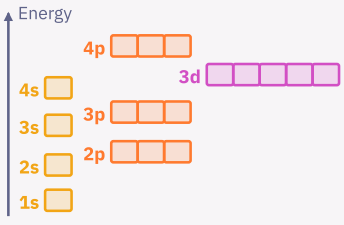
Atom → **principal quantum shells (n)** → **subshells (s, p, d, f)** → **orbitals** → **max. 2 e⁻ each**

A larger n gives a larger, more diffused orbital further from the nucleus, and hence a higher energy.

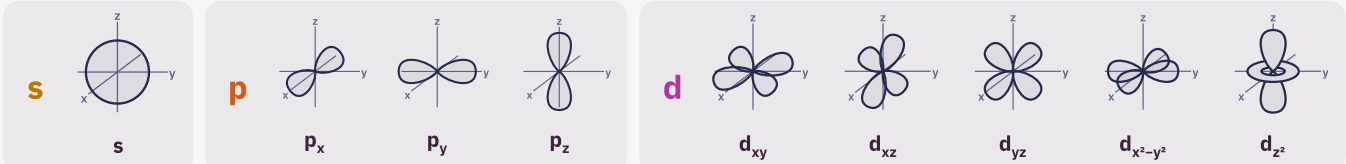
n	Subshell	No. of orbitals	Types of orbitals	Total (n^2)	Max e^- ($2n^2$)
1	1s	1	1s	1	2
2	2s	1	2s	4	8
	2p	3	$2p_x$, $2p_y$, $2p_z$		
3	3s	1	3s	9	18
	3p	3	$3p_x$, $3p_y$, $3p_z$		
	3d	5	$3d_{xy}$, $3d_{xz}$, $3d_{yz}$, $3d_{x^2-y^2}$, $3d_{z^2}$		
4	4s 4p 4d (4f)	1, 3, 5	4f not in syllabus	16	32

3.2 Relative energies of the orbitals

- Within a shell: **s < p < d < f**, as an s electron is more likely to be near the nucleus than a p, and a p than a d.
- Levels get closer as n increases. First overlap: _____ and _____ (4s fills first).



3.3 Shapes of orbitals



- **s** spherical, **p** dumb-bell. Orbitals within a subshell have the same energy: **degenerate**.
- $d_{x^2-y^2}$, d_{z^2}: along the axes. d_{xy}, d_{xz}, d_{yz}: between the axes.

4 Electronic Configuration

4.1 Rules for filling orbitals

1. Aufbau principle

Electrons fill the orbitals of _____ first. After 3p, **4s** is filled before 3d.

2. Pauli exclusion principle

An orbital holds a maximum of two electrons, of _____.

3. Hund's rule

Orbitals of a subshell are filled **singly** first, with parallel spins, before pairing. This gives less _____.

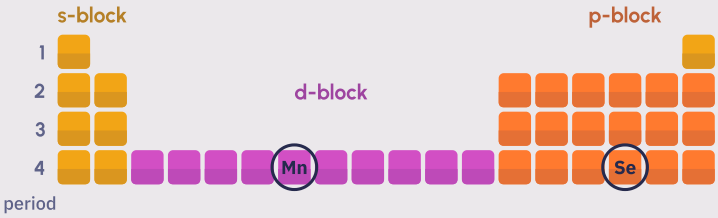


Electrons-in-boxes: label the boxes with the subshell only (2p, not $2p^6$). **Ground state**: all e^- in the lowest energy levels. **Excited state**: an e^- promoted, e.g. O: $1s^2\ 2s^2\ 2p^3\ 3s^1$.

4.2 Writing configurations of atoms

From the Periodic Table

1. **Period** = n of the valence shell. A new period starts when e^- enter a new principal quantum shell
2. **Block**: the subshell filled last. The d-block is one shell behind: 3d in Period 4
3. **Position in the block**: the number of e^- in that subshell



e.g. **Mn**: Period 4, 5th in the d-block → [Ar] $3d^5\ 4s^2$

e.g. **Se**: Period 4, 4th in the p-block → [Ar] $3d^{10}\ 4s^2\ 4p^4$

Elements in the same Group have similar valence shell configurations.

Noble gas configuration

Inner electrons shown as the previous noble gas: Li: [He] $2s^1$.

EXAM TIP Write the **full** configuration in order of increasing n: ...$3d^6\ 4s^2$.

Anomalies: Cr and Cu

Cr [Ar] $\mathbf{3d^5\ 4s^1}$ ~~$3d^4\ 4s^2$~~

Cu [Ar] $\mathbf{3d^{10}\ 4s^1}$ ~~$3d^9\ 4s^2$~~

A half-filled (d^5) or fully-filled (d^{10}) 3d subshell is more stable.

4.3 Configurations of ions

- Write the configuration of the atom first.
- **Cation**: electrons are removed from the outermost shell of the ground state configuration (_____ before 3d).
- **Anion**: electrons are added to the empty or partially-filled valence orbitals.

S^{2-}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
Na^+	$1s^2\ 2s^2\ 2p^6$
Fe^{2+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$

5 Ionisation Energy

DEFINITION **Ionisation energy**: the energy required to remove 1 mole of _____ from 1 mole of _____ atoms or ions.

DEFINITION **2nd IE**: the enthalpy change when 1 mole of electrons is removed from 1 mole of gaseous, singly charged cations.

$X(g) \rightarrow X^+(g) + e^-$	ΔH = 1st IE of X
$X^+(g) \rightarrow X^{2+}(g) + e^-$	ΔH = 2nd IE of X
$X^{(n-1)+}(g) \rightarrow X^{n+}(g) + e^-$	ΔH = n^{th} IE of X

All IEs are **endothermic**. Always show (g) in the equation.

5 Ionisation Energy (continued)

5.1 Trends in first IE Z_{eff} = Z – shielding constant

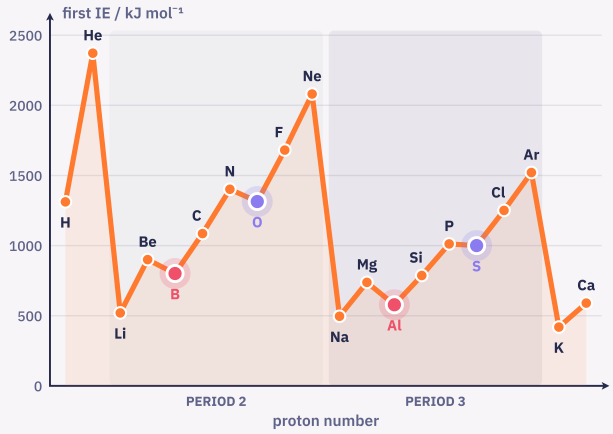
Across periods 2 and 3, 1st IE generally ↑

1. Nuclear charge ↑, while there is a _____ ↑ in inner shell _____, as e^- are added to the same shell
2. → effective nuclear charge _____, atomic radius _____
3. → valence e^- _____ by the nucleus → _____ required to remove them

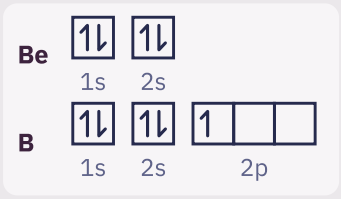
Down a group, 1st IE ↓

1. Atomic radius _____
2. No. of principal quantum shells ↑ → _____ _____ ↑, which _____ the ↑ in nuclear charge
3. → valence e^- _____ by the nucleus → _____ required to remove them

First IE of elements 1 to 20 / kJ mol⁻¹



Dip: Be → B also Mg → Al



The 2p e^- removed from B is _____ than the 2s e^- removed from Be → _____ required to remove it → 1st IE of B < Be

Dip: N → O also P → S



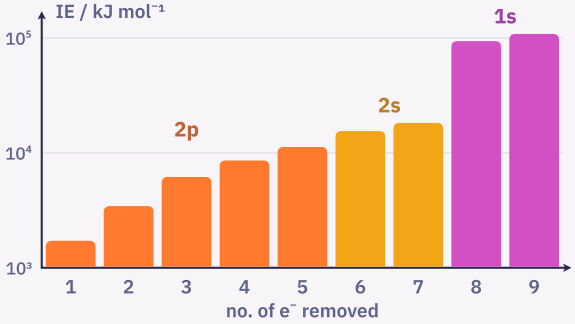
_____ between the _____ 2p e^- in O → easier to remove one of them than an unpaired 2p e^- from N → _____ required → 1st IE of O < N

5.2 Successive ionisation energies

ANSWER STRUCTURE **Reading a successive IE graph**

1. **General trend**: successive IEs ↑ as each e^- is removed from an ion of _____
2. **Gradual increase** (1st to 7th IE): removal of e^- from the _____
3. **Sharp increase** from 7th to 8th IE: 8th e^- removed from an _____, nearer to the nucleus, with less shielding

F: $1s^2\ 2s^2\ 2p^5$ · log IE



Note: the small jump from 5th to 6th IE is an e^- from a _____ (2s after 2p) of the same shell.

WORKED EXAMPLE The successive IEs of element X are shown below. Predict the Group of X.

IE / kJ mol⁻¹	870	1800	3000	3600	5800	7000	**13000**

1. Successive IEs ↑ as each e^- is removed from an ion of _____
2. 1st to 6th IE ↑ gradually: removal of the _____ e^- only
3. Sharp ↑ from 6th to 7th IE: 7th e^- removed from an _____, nearer to the nucleus, with _____
4. ∴ 6 e^- in the outermost shell ($ns^2\ np^4$) → X is in Group _____. Big jumps + 1 = occupied shells.

06 The Mole Concept and Stoichiometry



1 Relative Masses

Masses are compared with the **carbon-12** standard: one unit is $\frac{1}{12}$ of the mass of one mole of ^{12}C atoms. Relative masses have **no units**.

Term	DEFINITION
Relative isotopic mass	the mass of one mole of an _____ relative to $\frac{1}{12}$ the mass of one mole of ^{12}C atoms
Relative atomic mass, A_r	the _____ mass of one mole of atoms of an element relative to $\frac{1}{12}$ the mass of one mole of ^{12}C atoms
Relative molecular mass, M_r	the average mass of one mole of _____ relative to $\frac{1}{12}$ the mass of one mole of ^{12}C atoms
Relative formula mass, M_r	the average mass of one mole of _____ of a compound relative to $\frac{1}{12}$ the mass of one mole of ^{12}C atoms (ionic compounds)

$$A_r = \frac{\Sigma(\%\ \text{abundance} \times \text{relative isotopic mass})}{100}$$

A_r is rarely a whole number: it is a weighted average over the isotopes.

WORKED EXAMPLE Chlorine is 75.77% ^{35}Cl and 24.23% ^{37}Cl. Find $A_r(Cl)$.

$$A_r = \frac{75.77(35) + 24.23(37)}{100} = ____$$

WORKED EXAMPLE A copper wire has $A_r(Cu) = 63.54$. Find the percentage abundances of ^{63}Cu and ^{65}Cu.

Let ^{63}Cu be x%: $63.54 = \frac{63x + 65(100 - x)}{100}$ → x = _____, so ^{63}Cu = 73.0% and ^{65}Cu = _____

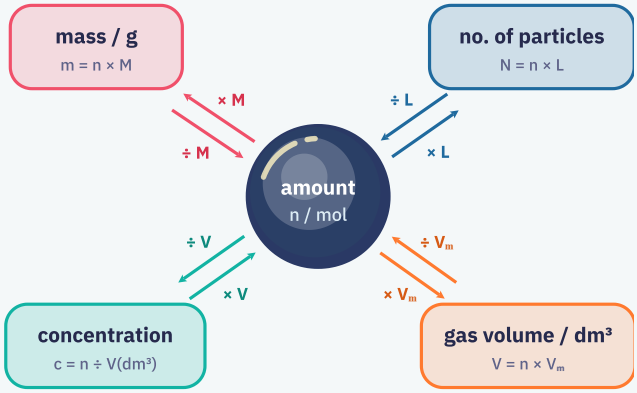
2 The Mole

DEFINITION **Mole**: the amount of substance that contains _____ (the Avogadro constant, L) elementary entities. The entity must be stated: atoms, molecules, ions or electrons.

DEFINITION **Molar mass, M**: the mass of one mole of the specified substance (g mol^{-1}), numerically equal to A_r or M_r.

DEFINITION **Molar gas volume, V_m**: the volume occupied by one mole of a gas under given conditions of temperature and pressure: _____ $dm^3\ mol^{-1}$ at r.t.p. (20 °C, 1 atm), _____ $dm^3\ mol^{-1}$ at s.t.p. (0 °C, 1 bar).

DEFINITION **Concentration**: the amount or mass of solute in a given volume of solution (mol dm^{-3} or g dm^{-3}).



Mole ratio: in 1 mol of A_mB_n there are m mol of A and n mol of B, e.g. 1 mol $CaCl_2$ has 2 mol Cl^-.

NOTE "1 mole of oxygen" is ambiguous: say 1 mol of O atoms or 1 mol of O_2 molecules. 1 dm^3 = 1000 cm^3.

2.1 Particles and gas volume

WORKED EXAMPLE A cylinder releases 16 dm^3 of NH_3 gas at s.t.p. How many NH_3 molecules is this?

$$n_{NH_3} = \frac{16}{22.7} = 0.7048 \text{ mol} \rightarrow N = 0.7048 \times 6.02 \times 10^{23} = _____$$

2.2 Preparing a solution

Weigh the solute, dissolve it in a little water, then make up to the mark in a volumetric flask and invert to mix.

WORKED EXAMPLE A technician makes 500 cm^3 of H_2SO_4 solution with $[H^+] = 2.00$ mol dm^{-3}. What mass of H_2SO_4 is needed?

$n_{H^+} = 2.00 \times 0.500 = 1.000$ mol. Each H_2SO_4 gives $2H^+$

$n_{H_2SO_4} = 0.5000$ mol → mass = $0.5000 \times 98.1 =$ _____

3 Empirical and Molecular Formulae

DEFINITION **Empirical formula**: the formula showing the _____ of the atoms of each element in the substance.

DEFINITION **Molecular formula**: the formula showing the _____ of atoms of the different elements in one molecule of the compound, a multiple of the empirical formula.

ANSWER STRUCTURE **Finding the formula: fill in the table**

	element 1	element 2	element 3
Mass / g (or %)	given	given	given
Amount / mol	mass ÷ A_r	mass ÷ A_r	mass ÷ A_r
Ratio (÷ smallest)	whole number	whole number	whole number

Ratio → empirical formula → molecular formula = empirical formula × $\frac{M_r}{\text{empirical formula mass}}$

3.1 From % by mass

WORKED EXAMPLE Compound X (M_r = 114) is 63.2% C, 12.2% H and 24.6% N by mass. Find its molecular formula.

	C	H	N
Mass / g	63.2	12.2	24.6
Amount / mol	5.267	12.20	1.757
Ratio (÷ 1.757)	____	____	____

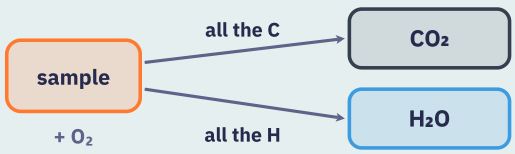
Take 100 g of X, so each percentage becomes a mass in grams.

Empirical C_3H_7N (M = 57.0),
114 ÷ 57.0 = 2 ∴ _____

3.2 From combustion data

WORKED EXAMPLE A sugar, mannose (C, H and O only, M_r 180), is burnt completely in oxygen. 2.36 g of it gives 3.46 g of CO_2 and 1.42 g of H_2O. Find its molecular formula.

1. All the C in the CO_2 came from the sample (12 g of C in every 44 g of CO_2): mass of C = $\frac{12}{44}$ × 3.46 = 0.9436 g
2. All the H in the H_2O came from the sample (2 g of H in every 18 g of H_2O): mass of H = $\frac{2}{18}$ × 1.42 = 0.1578 g
3. O cannot be found this way, as some O in CO_2 and H_2O came from the O_2 burnt:
   mass of O = 2.36 − 0.9436 − 0.1578 = 1.259 g



	C	H	O
Mass / g	0.9436	0.1578	1.259
Amount / mol	0.07863	0.1578	0.07869
Ratio (÷ 0.07863)	____	____	____

Empirical CH_2O (M = 30), 180 ÷ 30 = 6 ∴ _____

4 Stoichiometry, Limiting Reagent and Yield

- A balanced equation gives the _____ of reactants and products: $2H_2 + O_2 \rightarrow 2H_2O$ means 2 mol H_2 ≡ 1 mol O_2 ≡ 2 mol H_2O
- The **limiting reagent** is used up first, it fixes the maximum amount of product (the **theoretical yield**)

recipe	**2 bread**	+	**1 cheese**	→ **1 sandwich**
we have	10 bread		4 cheese	4 sandwiches
	2 left over: in **excess**		all used: **limiting**	the theoretical yield

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

Actual yield is lower: incomplete reaction, side reactions and losses during purification.

4.1 Limiting reagent and yield

WORKED EXAMPLE A student precipitates $PbCl_2$ by mixing 100 cm³ of 0.0600 mol dm⁻³ $Pb(NO_3)_2$ with 200 cm³ of 0.0500 mol dm⁻³ NaCl, and collects 1.1558 g of $PbCl_2$. Find the limiting reagent and the percentage yield.

1. $Pb(NO_3)_2 + 2NaCl \rightarrow PbCl_2 + 2NaNO_3$
2. $n(Pb(NO_3)_2) = 6.000 \times 10^{-3}$ mol, $n_{NaCl} = 1.000 \times 10^{-2}$ mol
3. 6.000×10^{-3} mol $Pb(NO_3)_2$ needs 1.200×10^{-2} mol NaCl → _____ is limiting
4. $n_{PbCl_2} = ½ \times 1.000 \times 10^{-2} = 5.000 \times 10^{-3}$ mol
5. maximum mass = $5.000 \times 10^{-3} \times 278.1$ = _____
6. % yield = $\frac{1.1558}{1.391} \times 100$ = _____

4.2 Reacting mass to gas volume

WORKED EXAMPLE A 0.230 g piece of sodium is dropped into excess water. Find the volume of H_2 produced at s.t.p.

1. $2Na + 2H_2O \rightarrow 2NaOH + H_2$. Water is in excess, so Na is limiting
2. $n_{Na} = 0.230 \div 23.0 = 1.000 \times 10^{-2}$ mol → $n_{H_2} = 5.000 \times 10^{-3}$ mol
3. $V(H_2) = 5.000 \times 10^{-3} \times 22.7$ = _____

EXAM TIP Give intermediate answers to 4 s.f. and final answers to 3 s.f. unless told otherwise, A_r and M_r to 1 d.p.

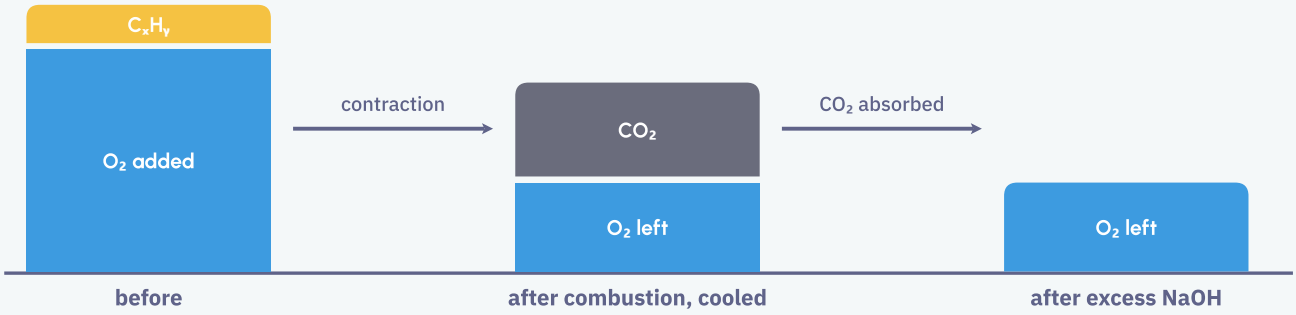
5 Gas Volumes and Combustion

5.1 Gas volumes

- **Avogadro's law**: at the same temperature and pressure, equal volumes of all gases contain the same number of particles → for gases, _____
- Only gases count: water at r.t.p. is a **liquid**, so its volume is ignored

5.2 Combustion of hydrocarbons

$$C_xH_y(g) + (x + \frac{y}{4})O_2(g) \rightarrow xCO_2(g) + \frac{y}{2}H_2O(l)$$



$NaOH(aq)$ absorbs CO_2: $CO_2(g) + 2NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O(l)$

WORKED EXAMPLE A chemist explodes 10 cm³ of a gaseous hydrocarbon C_xH_y with 110 cm³ of O_2 (excess). After cooling to r.t.p. the volume is 85 cm³, falling to 35 cm³ after passing through excess NaOH(aq). Find the formula of the hydrocarbon.

1. CO_2 is absorbed by NaOH: $V(CO_2) = 85 - 35 = 50\ cm^3 = 10x \rightarrow$ _____
2. Contraction on combustion = $(10 + 110) - 85 = 35\ cm^3$
3. Contraction = $V(C_xH_y) + V(O_2\ reacted) - V(CO_2) = 10 + 10(x + \frac{y}{4}) - 10x = 10 + \frac{10y}{4} = 35 \rightarrow$ _____
4. ∴ the hydrocarbon is _____

6 Volumetric Analysis

Term	DEFINITION
Standard solution	a solution whose concentration is _____
Titrant	the solution added from the burette
Analyte	the fixed volume of solution in the conical flask
Equivalence point	the point at which _____ of reactants have reacted, independent of the indicator used
End-point	the point when the indicator _____

6 Volumetric Analysis (continued)

6.1 Choosing an acid–base indicator

Titration	Indicator	Colour, acid → alkali
strong acid–strong base	methyl orange or phenolphthalein	either change below
strong acid–weak base	methyl orange (pH 3–5)	**red** → **yellow**, orange at the end-point
weak acid–strong base	phenolphthalein (pH 8–10)	colourless → **pale pink** at the end-point
weak acid–weak base	no suitable indicator	

A suitable indicator has a **distinct colour change** at the equivalence point.

6.2 Dilution

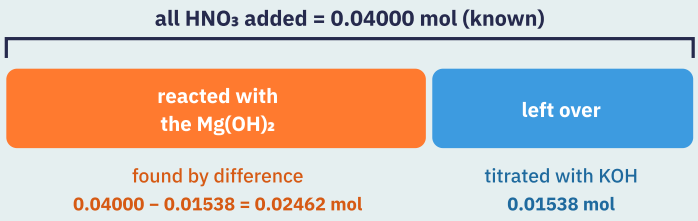
$c_1V_1 = c_2V_2$ Amount of solute withdrawn = amount in the diluted solution.

6.3 Back-titration

When A cannot be titrated directly (e.g. insoluble $CaCO_3$ or $Mg(OH)_2$)

1. Add a known **excess** of B, so all of A reacts
2. Titrate the **unreacted** B that is left over
3. $n_{B\ reacted\ with\ A} = n_{B\ added} - n_{B\ left\ over}$, then n_A from the equation

WORKED EXAMPLE An antacid tablet contains impure $Mg(OH)_2$, which is insoluble, so it cannot be titrated directly. 1.00 g of it is added to 100 cm³ of 0.400 mol dm⁻³ HNO_3 (excess). The leftover HNO_3 needs 20.50 cm³ of 0.750 mol dm⁻³ KOH. Find the percentage of $Mg(OH)_2$.



$$Mg(OH)_2 + 2HNO_3 \rightarrow Mg(NO_3)_2 + 2H_2O$$

1. $n_{HNO_3\ added} = 0.400 \times 0.100 = 0.04000$ mol
2. $n_{HNO_3\ left\ over} = n_{KOH} = 0.750 \times 0.02050 = 0.01538$ mol
3. $n(HNO_3$ reacted with $Mg(OH)_2) = 0.04000 - 0.01538 = 0.02462$ mol → $n(Mg(OH)_2) = ½ \times 0.02462 = 0.01231$ mol
4. mass = $0.01231 \times 58.3 = 0.7177$ g → _____ $Mg(OH)_2$

7 Redox Reactions

Oxidation	Reduction
gain of oxygen	loss of oxygen
loss of hydrogen	gain of hydrogen
_____	_____
increase in oxidation number	decrease in oxidation number



Zn
loses 2e⁻: **oxidised**, the **reducing agent**

Cu²⁺
gains 2e⁻: **reduced**, the **oxidising agent**

DEFINITION **Oxidising agent**: oxidises another species and is itself _____.

DEFINITION **Reducing agent**: reduces another species and is itself _____.

DEFINITION **Disproportionation**: a redox reaction in which one species is simultaneously oxidised and reduced, e.g. $Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O$, with the oxidation numbers of Cl under it: Cl_2 **0** → Cl in ClO^- **+1** (oxidised) and Cl^- **−1** (reduced).

7.1 Oxidation number rules, in order of priority

Apply them from the top: when two rules disagree, the higher one wins.

1. Element: **0** (Mg, O_2, P_4)
2. Sum of O.N. = overall _____ of the species (Al^{3+}: +3)
3. Group 1: +1, Group 2: +2, Al: +3
4. F: −1
5. H: +1 (so −1 in NaH, where Na comes first)
6. O: −2 (so −1 in H_2O_2 and +2 in OF_2)
7. Otherwise, the more electronegative atom takes the negative O.N.

WORKED EXAMPLE Find the oxidation number of Mn in MnO_4^-.

$x + 4(-2) = -1 \rightarrow x =$ _____

Charge is written "2+", oxidation number is written "+2".

7.2 Balancing redox equations: MnO_4^- + I^- in acid

AOHC Half-equation method

A	Balance **atoms** other than O and H	$MnO_4^- \rightarrow Mn^{2+}$ $2I^- \rightarrow I_2$
O	Balance **O** with H_2O	$MnO_4^- \rightarrow Mn^{2+} + 4H_2O$
H	Balance **H** with H^+	$MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$
C	Balance **charge** with e^-	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ $2I^- \rightarrow I_2 + 2e^-$
Add	Match the e^- (× 2 and × 5), add, cancel	_____

ACOH Oxidation number method

A	Balance **atoms** other than O and H	$MnO_4^- + 2I^- \rightarrow Mn^{2+} + I_2$
C	Balance the **change** in O.N.: Mn −5 each, I +1 each	$2MnO_4^- + 10I^- \rightarrow 2Mn^{2+} + 5I_2$
O	Balance **O** with H_2O	$2MnO_4^- + 10I^- \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$
H	Balance **H** with H^+	_____

NOTE In **alkaline** solution MnO_4^- is reduced to MnO_2. Balance with H^+ first, then add the same number of OH^- to both sides to turn H^+ into H_2O.

8 Redox Titrations

Titration	Half-equation of oxidising agent	Indicator	End-point colour
$KMnO_4$ (burette) with Fe^{2+} or H_2O_2	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	none (self-indicating)	colourless → _____
	↳ Acidify with **H_2SO_4**, not HCl (Cl^- is oxidised to Cl_2) or HNO_3 (itself an oxidising agent)		
$K_2Cr_2O_7$ with Fe^{2+}	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	N-phenylanthranilic acid	green → red-violet
$S_2O_3^{2-}$ (burette) with I_2	$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$	starch, near the end	dark blue → _____
	↳ **Iodometric titration**: the oxidising agent is added to _____, so it reacts completely and the I_2 stays dissolved as I_3^-. The I_2 released is then titrated with $S_2O_3^{2-}$: the titre gives the amount of I_2, and so the original amount of oxidising agent (e.g. IO_3^-)		
	↳ Add starch only near the end-point (pale yellow): at high $[I_2]$ the starch–iodine complex precipitates		

8.1 Iodometric titration

WORKED EXAMPLE To standardise a sodium thiosulfate solution, 0.875 g of KIO_3 is made up to 250 cm³. 25.0 cm³ of this is added to excess KI and acid, and the I_2 formed needs 22.70 cm³ of $Na_2S_2O_3$. Find $[S_2O_3^{2-}]$.

1. $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$, $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$
2. $n_{IO_3^-}$ in 25.0 cm³ $= \dfrac{0.875}{214.0} \times \dfrac{25.0}{250} = 4.089 \times 10^{-4}$ mol
3. $IO_3^- \equiv 3I_2 \equiv$ _____ $\rightarrow n_{S_2O_3^{2-}} = 2.453 \times 10^{-3}$ mol
4. $[S_2O_3^{2-}] = 2.453 \times 10^{-3} \div 0.02270 =$ _____

8.2 Finding a new oxidation number

electrons lost = electrons gained

30.0 cm³ of 0.0500 mol dm⁻³ Fe^{2+} reacts exactly with 15.0 cm³ of 0.0250 mol dm⁻³ MnO_4^-, and Fe ends as +3. Find the final oxidation number of Mn.

1. $n_{Fe^{2+}} = 1.500 \times 10^{-3}$ mol, each losing 1 e^- → 1.500×10^{-3} mol e^-
2. $n_{MnO_4^-} = 3.750 \times 10^{-4}$ mol → each gains $\dfrac{1.500 \times 10^{-3}}{3.750 \times 10^{-4}} =$ _____ e^-
3. Mn: +7 − 4 = _____

8.3 Common oxidising and reducing agents

Oxidising agent	Medium	Product
MnO_4^-	acidic	Mn^{2+}
MnO_4^-	neutral or alkaline	MnO_2
$Cr_2O_7^{2-}$	acidic	Cr^{3+}
I_2	neutral or acidic	I^-
IO_3^-	acidic	I_2
H_2O_2	acidic	H_2O

Reducing agent	Medium	Product
Fe^{2+}	acidic or neutral	Fe^{3+}
I^-	any	I_2
$S_2O_3^{2-}$	neutral	$S_4O_6^{2-}$ with I_2
$C_2O_4^{2-}$	acidic	CO_2
H_2O_2	acidic	O_2

H_2O_2 can act as an oxidising agent or as a reducing agent. With a stronger oxidising agent such as Cl_2, $S_2O_3^{2-}$ gives SO_4^{2-}.

02 Chemical Bonding

1 Types of Chemical Bonds

All bonds and intermolecular forces are _____ attractions between ...

Strong bonds	
metallic	positive metal cations and a sea of _____ valence electrons
ionic	oppositely charged _____
covalent	the nuclei of each atom and the _____ of electrons

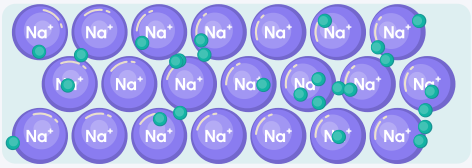
Weak intermolecular forces (IMFs)	
id–id	_____ molecules
pd–pd	_____ molecules
H bond	the _____ of one molecule and a lone pair on F, O or N of another

id–id: instantaneous dipole–induced dipole, pd–pd: permanent dipole–permanent dipole. Structures: giant metallic, giant ionic, giant molecular, simple molecular.

2 Metallic Bonding

2.1 Structure and bonding

Metals have a **giant metallic lattice** structure, with strong electrostatic forces of attraction between a sea of _____ and a lattice of positive metal cations.



2.2 Factors affecting strength

Strength of metallic bond ↑ when

1. Charge of cation ↑ and ionic radius ↓ → _____ of cation ↑
2. No. of valence e^- ↑ → more delocalised e^- in the sea
3. → stronger attraction → _____ required to overcome it → m.p. ↑

WORKED EXAMPLE Explain why the melting point of aluminium (660 °C) is higher than that of sodium (98 °C).

1. Both Al and Na have a _____ structure
2. Al delocalises _____ valence e^- per atom, Na only 1. Al^{3+} has a higher charge and _____ than Na^+
3. → more energy is needed to overcome the stronger electrostatic forces of attraction between Al^{3+} cations and the sea of delocalised e^- than between _____ and its sea of delocalised e^-

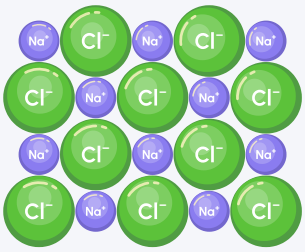
2.3 Physical properties

- **Conduct electricity in all states**: delocalised valence e^- become mobile and migrate freely when a potential difference is applied. More delocalised e^- → higher conductivity.
- **Good thermal conductors**: delocalised e^- throughout the structure transfer kinetic energy quickly from one end to the other.
- **Malleable and ductile**: metallic bonds are _____, so layers of cations slide over one another without overcoming the attraction between cations and the sea of e^-.

3 Ionic Bonding

3.1 Structure and bonding

Ionic compounds have a **giant ionic lattice** structure with strong electrostatic forces of attraction between _____ and _____.



DEFINITION **Coordination number**: the number of oppositely charged ions surrounding an ion in a crystal lattice (6 for both Na^+ and Cl^- in NaCl).

Dot-and-cross diagram of MgO

- Show valence e^- only, as dots and crosses
- **Square** brackets with the charge outside
- No. of each ion as a coefficient, e.g. Ca^{2+} $2[F]^-$



3.2 Factors affecting strength

$$\text{Lattice energy} \propto \frac{q_+ \times q_-}{r_+ + r_-}$$

Greater charge and smaller ionic radii → greater magnitude of lattice energy → _____ required to overcome the attraction.

WORKED EXAMPLE Explain why the melting point of MgO (2852 °C) is higher than that of Na_2O (1132 °C).

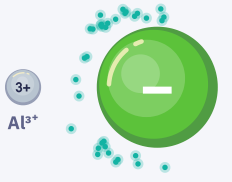
1. Both have a _____ structure
2. Mg^{2+} has a _____ and smaller ionic radius than Na^+ → greater magnitude of lattice energy
3. → more energy is needed to overcome the stronger electrostatic forces of attraction between Mg^{2+} and O^{2-} ions than between _____ ions

3.3 Physical properties

- **Conducts when molten or aqueous**: ions are _____ and migrate to the electrodes when a p.d. is applied. In the solid, ions are held in fixed positions.
- **Hard**: large amount of energy needed to overcome the strong attraction. **Brittle**: under force, layers slide, ions of _____ come together and repel → lattice shatters.
- **Soluble in polar solvents**: energy released forming _____ interactions compensates for overcoming the ionic attraction and the solvent–solvent forces. Insoluble in non-polar solvents.

3.4 Ionic bonds with covalent character

- A small, highly charged cation such as **Al^{3+} polarises** (distorts) the electron cloud of an anion such as **Cl^-** → electron density drawn between the nuclei → partial _____ of e^- → covalent character
- **Polarising power** of cation ↑ with _____ $\propto q_+ / r_+$
- **Polarisability** of anion ↑ with anion size



Cl^-, its electrons drawn towards Al^{3+}

WORKED EXAMPLE Are Al_2O_3 and $AlBr_3$ largely ionic or covalent? Compare with $AlCl_3$.

1. Al^{3+} has a high charge density → high polarising power
2. O^{2-} is smaller and less polarisable than Cl^- → electron density unshared with Al^{3+} → Al_2O_3 largely _____
3. Br^- is larger and more polarisable than Cl^- → electron density largely shared → $AlBr_3$ largely _____

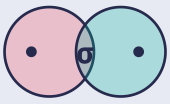
4 Covalent Bonding

4.1 Structure and bonding

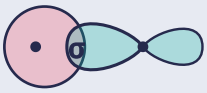
DEFINITION **Covalent bond**: the strong electrostatic forces of attraction between the _____ of each atom and the _____.

DEFINITION **σ bond**: a covalent bond formed by _____ overlap of orbitals. Electron density is concentrated between the nuclei.

DEFINITION **π bond**: a covalent bond formed by _____ overlap of p orbitals, giving two regions of overlap above and below the inter-nuclear axis.



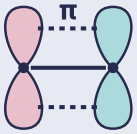
σ: s + s
H_2



σ: s + p
HCl



σ: p + p head-on
Cl_2



π: p + p sideways
after the σ bond

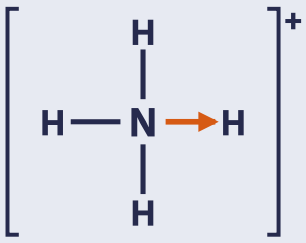
1. π overlap lies above and below the inter-nuclear axis → _____ overlap → π bond weaker than σ
2. A π bond only forms after a σ bond: the σ overlap brings the atoms close enough for the p orbitals to overlap sideways

Bond	σ	π
single	1	0
double	1	1
triple	1	_____

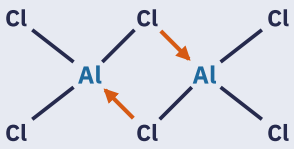
Co-ordinate (dative) bonds

DEFINITION **Dative bond**: a covalent bond formed when an atom donates a _____ of electrons into an _____ of an electron-deficient atom for sharing.

- Shown as an arrow from donor to acceptor, or as 2 e^- of the same type in a dot-and-cross diagram
- Once formed, identical to a normal covalent bond
- **Lewis acid**: electron pair _____. **Lewis base**: electron pair _____. E.g. BF_3 (acid) + NH_3 (base) → $H_3N{\rightarrow}BF_3$



NH_4^+: H^+ accepts the lone pair on N



Al_2Cl_6: 2 dative bonds, each Al gets an octet

4 Covalent Bonding (continued)

4.2 Dot-and-cross diagrams and the octet rule

Drawing steps

1. Central atom: forms the most bonds, or is the least electronegative (not H)
2. Anion: add e^- to the more electronegative atom(s). Cation: remove e^- from the less electronegative atom(s).
   Square brackets, charge outside
3. Give each atom an octet with single, double or triple bonds
4. Period 2 atoms: _____ valence e^-

Exceptions to the octet rule

Type	Examples (e^- around central atom)
Expanded octet	PCl_5 (10), SF_6 (12), XeF_4 (12)
Electron-deficient	$BeCl_2$ (4), BF_3 (6), $AlCl_3$ (6)
Odd no. of e^- (radicals)	NO, NO_2, ClO_2 (11, 17, 19 valence e^- in all)

KEY IDEA Period 3 and higher atoms have _____ _____, so they can **expand the octet**.
Period 2 atoms have no valence d orbitals, so NCl_5 does not exist.



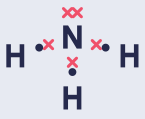
N_2 a triple bond



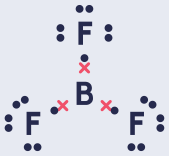
CO_2 two double bonds



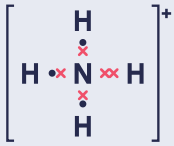
C_2H_4 a C=C double bond



NH_3 one lone pair on N



BF_3 only 6 e^- around B



NH_4^+ dative pair from N

× and • are electrons from different atoms.

4.3 Electronegativity: covalent bonds with ionic character

DEFINITION **Electronegativity**: the measure of an atom's ability to _____ in a bond.

- Across a period ↑: nuclear charge ↑, shielding about constant → bonding e^- more strongly attracted
- Down a group ↓: more shells → bonding e^- further away and more _____
- Different electronegativities → bonding e^- drawn to the more electronegative atom → permanent **dipole**: a _____ bond

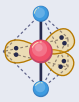
4 Covalent Bonding (continued)

4.4 Shapes of molecules (VSEPR)

VSEPR theory

1. Electron pairs around the central atom are arranged as _____ as possible to minimise repulsion
2. Repulsion: lone pair–lone pair > lone pair–bond pair > _____

- A lone pair repels more strongly: it is non-bonding, so its electron density is **closer to the nucleus**
- A double or triple bond counts as **one** region of electron density

2 e^- pairs	 **linear** **180°** CO_2 (2 bp, 0 lp)		
3 e^- pairs	 **trigonal planar** **120°** BF_3 (3 bp, 0 lp)	 **bent** **<120°** SO_2 (2 bp, 1 lp)	
4 e^- pairs	 **tetrahedral** **109.5°** CH_4 (4 bp, 0 lp)	 **trigonal pyramidal** **107°** NH_3 (3 bp, 1 lp)	 **bent** **104.5°** H_2O (2 bp, 2 lp)
5 e^- pairs lone pairs equatorial	 **trigonal bipyramidal** **120°, 90°** PCl_5 (5 bp, 0 lp)	 **see-saw** **<120°, <90°** SF_4 (4 bp, 1 lp)	 **T-shaped** **<90°** ClF_3 (3 bp, 2 lp)  **linear** **180°** XeF_2 (2 bp, 3 lp)
6 e^- pairs lone pairs axial	 **octahedral** **90°** SF_6 (6 bp, 0 lp)	 **square pyramidal** **<90°** BrF_5 (5 bp, 1 lp)	 **square planar** **90°** XeF_4 (4 bp, 2 lp)

ANSWER STRUCTURE **Shape of NH_3**

1. There are _____ bond pairs and _____ lone pair around N
2. To minimise repulsion, the _____ electron pairs are arranged as far apart as possible
3. → NH_3 is _____, bond angle _____

Electronegativity and bond angle

1. **NF_3 102° < NH_3 107°**: F more electronegative → bonding e^- closer to F → _____ around N → less repulsion → smaller angle
2. **H_2O 104.5° > H_2S 92°**: O more electronegative → bonding e^- drawn towards O → more crowding → _____ _____ → larger angle

4 Covalent Bonding (continued)

4.5 Finding the shape of an ion or an unfamiliar molecule

Counting the electron pairs

1. Valence e^- of the central atom + one e^- per surrounding atom bonded to it
2. Add 1 for each negative charge, subtract 1 for each positive charge
3. Divide by 2 for the number of electron pairs. Surrounding atoms give the bond pairs, the rest are lone pairs

ICl_4^-: 7 + 4 + 1 = 12, so 6 pairs: 4 bp, 2 lp, square planar. **PH_4^+**: 5 + 4 − 1 = 8, so 4 pairs: 4 bp, tetrahedral.

Oxygen and substitution

- Try **=O** first (CO_2, SO_2). In an oxoanion the charge gives the number of **$-O^-$** (CO_3^{2-}, SO_4^{2-}). Use **→O** when the central atom cannot take =O (NO_2). O joining two atoms has 2 single bonds (H_2O_2)
- Swap an unfamiliar atom for one with the same **covalency** (number of bonds): $CHCl_3$ as CH_4, F_2O as H_2O, BH_4^- as CH_4, CH_3^+ as BCl_3

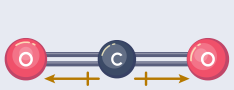
4.6 Polarity of molecules

Steps

1. Identify any **polar bonds** (bond dipoles)
2. Determine the **shape** of the molecule
3. Resolve the dipoles: net dipole → polar

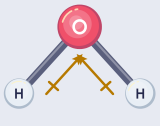
ANSWER STRUCTURE

X is a **polar / non-polar** molecule as the dipoles _____ each other out. Hence there _____ an overall dipole moment.



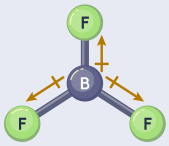
dipoles cancel

CO_2 non-polar



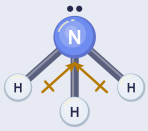
net dipole

H_2O polar



dipoles cancel

BF_3 non-polar



net dipole

NH_3 polar

4.7 Factors affecting strength

DEFINITION **Bond dissociation energy**: the enthalpy change when one mole of a particular covalent bond between atoms in a _____ molecule is broken. **$Cl_2(g) \rightarrow 2Cl(g)$ +244 kJ mol^{-1}**

DEFINITION **Bond length**: the distance between the _____ of the atoms in a covalent bond. Shorter bond = stronger bond.

Factors affecting covalent bond strength

1. **Orbital overlap**: larger bonding atoms → larger, more _____ valence orbitals → less effective overlap → weaker bond. Cl–Cl 244 > Br–Br 193 > I–I 151 kJ mol^{-1}
2. **Polarity**: the more electronegative atom has a larger share of the electron density → dipole, ionic character, may ↑ or ↓ strength (deduce from data). N–H 390 < O–H 460 < F–H 562
3. **Multiplicity**: triple > double > single. C–C 350, C=C 610, C≡C 840. BE(C=C) < 2 × BE(C–C) as the π bond is _____ than σ

Bond strength and reactivity

- A weaker, longer bond breaks more easily → more _____. N≡N 944 kJ mol^{-1}: N_2 is unreactive.
- C–I 240 < C–Br 280 < C–Cl 340 < C–F 485 → R–I hydrolyses fastest: bond strength outweighs polarity.
- A polar bond has a δ+ atom for nucleophiles to attack, e.g. C in C–Cl. Non-polar C–H has none, so alkanes are unreactive.

5 Intermolecular Forces

5.1 Instantaneous dipole–induced dipole (id–id)

DEFINITION **id–id**: weak electrostatic forces of attraction between _____ molecules (present between all molecules).

How id–id forms

1. Continuous movement of e^- → at an instant, one region has slightly _____
2. This instantaneous dipole _____ a dipole in a nearby molecule
3. The two molecules attract by weak electrostatic forces between opposite partial charges

Factors: strength and extent of id–id

- **No. of electrons ↑** (larger M_r) → electron cloud more _____ → stronger id–id. F_2 −188, Cl_2 −34, Br_2 59 °C
- **Surface area ↑** → more extensive id–id. pentane 36 °C > 2,2-dimethylpropane 10 °C

5.2 Permanent dipole–permanent dipole (pd–pd)

DEFINITION **pd–pd**: weak electrostatic forces of attraction between _____ molecules, in addition to id–id.

Strength of pd–pd: the larger the magnitude of the overall _____, the stronger the pd–pd interactions.

Similar vs very different M_r

Compound	M_r	Polarity	b.p. / °C
propene	**42**	non-polar	**−48**
ethanal	**44**	polar	**20**
CH_3Cl	**50.5**	more polar	**−24**
CH_3Br	**94.9**	less polar	**4**

- Similar M_r: polar ethanal has pd–pd as well as id–id → higher b.p.
- Very different M_r: CH_3Br has many more e^- → stronger id–id _____ the pd–pd of CH_3Cl

5 Intermolecular Forces (continued)

5.3 Hydrogen bonding (H bond)

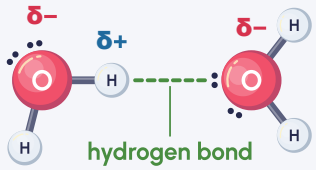
DEFINITION **Hydrogen bond**: weak electrostatic forces of attraction between the _____ of one molecule and a _____ on a highly electronegative atom of another molecule.

Conditions for hydrogen bonding

1. At least one H atom directly bonded to _____
2. The neighbouring molecule has at least one _____ on F, O or N

Why only F, O or N?

They are highly electronegative, so H carries a large δ+, and their lone pair sits in a small 2p orbital with high electron density.



Draw: the lone pair, both δ+ / δ− pairs, and label the hydrogen bond.

Strength of a hydrogen bond

The more _____ the H–X bond, the _____ the hydrogen bond.
Electronegativity F > O > N → H–F is the most polar → strength of one H bond: _____

Extent of hydrogen bonding

Molecule	H on F, O, N	Lone pairs	H bonds / molecule
H_2O	2	2	_____
HF	1	3	1
NH_3	3	1	1

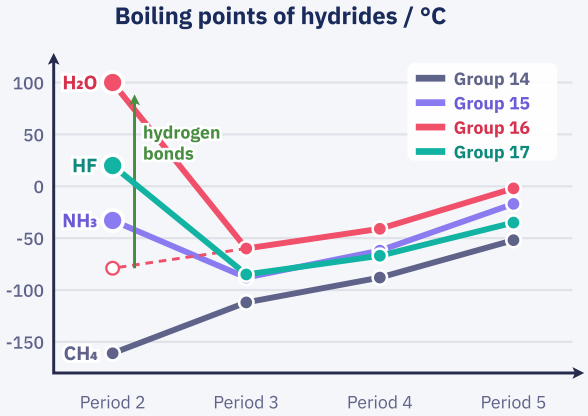
H bonds per molecule = the smaller number (HF: 1 H, NH_3: 1 lone pair).

6 Physical Properties of Covalent Substances

6.1 Simple molecular substances: boiling points

Low m.p. and b.p.: only the **weak IMF** between the discrete molecules are overcome, not the covalent bonds within them.

H_2O, HF and NH_3 boil far higher than the trend in id–id predicts, because of hydrogen bonding.



WORKED EXAMPLE Explain why the boiling points are H_2O (100 °C) > HF (20 °C) > NH_3 (−33 °C), using both the strength and the extent of hydrogen bonding.

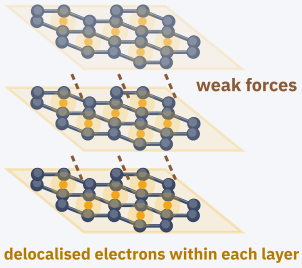
1. All three have hydrogen bonds between molecules, b.p. depends on both their _____ and their _____
2. **Strength**: H–F is the most polar bond, so one H bond between HF molecules is the strongest, then H_2O, then NH_3
3. **Extent**: each H_2O can form _____ H bonds (2 H atoms, 2 lone pairs), but HF and NH_3 form only _____ on average
4. H_2O: more energy is required to overcome the more _____ H bonds between H_2O molecules, which outweighs their slightly lower strength → highest b.p.
5. HF vs NH_3: same extent, but the H bonds between HF molecules are _____ → b.p. HF > NH_3

6.2 Giant molecular structures

Diamond



Graphite



Property	Diamond	Graphite
Bonding	Each C covalently bonded to _____ others, tetrahedrally	Each C bonded to _____ others in hexagonal layers. The 4th valence e^- is _____ within each layer
m.p.	Very high: a large amount of energy is needed to overcome the strong and extensive _____	
Hardness	**Hard**: atoms are held rigidly and do not slide	**Soft**: weak _____ between layers let them slide
Electrical conductivity	**Non-conductor**: all 4 valence e^- are used in covalent bonding → no _____	**Conducts** parallel to the layers: delocalised e^- move when a p.d. is applied
Solubility	Insoluble in all solvents: energy released forming solute–solvent interactions cannot overcome the strong covalent bonds	

NOTE **m.p. diamond (3350 °C) > Si (1410 °C)**: C uses smaller, less diffused $2sp^3$ orbitals than Si ($3sp^3$) → more effective overlap → stronger C–C bonds. Other giant molecular examples: Si, SiO_2, BN.

6 Physical Properties of Covalent Substances (continued)

6.3 Special effects of hydrogen bonding

Ice is less dense than water

1. Ice adopts an _____, crystalline structure with hexagonal holes
2. Each H_2O forms H bonds with _____ other H_2O molecules
3. Each O is surrounded tetrahedrally by 4 H atoms: 2 covalent bonds, 2 H bonds
4. The regular arrangement spaces molecules more widely than in the liquid
5. → water expands on freezing → ice is _____ than water

Intramolecular H bonds lower the boiling point

2-nitrophenol (b.p. 216 °C) < 4-nitrophenol (279 °C)

1. The –OH and $–NO_2$ groups are in close proximity and correctly oriented for an _____ H bond
2. → the H atom of –OH is less available for _____ H bonds
3. Boiling overcomes intermolecular H bonds → less energy needed → lower b.p.

Ethanol, NH_3, HF and ethanoic acid are miscible with water: they form H bonds with water molecules. Ethanoic acid in benzene forms H-bonded **dimers** (apparent M_r 120, not 60).

7 Structure and Physical Properties

Structure	m.p. / b.p.	Electrical conductivity	Solubility	Hardness
Giant metallic **e.g. Cu**	high: strong metallic bonds	good in all states: delocalised e^-	insoluble (some react with water)	malleable, ductile
Giant ionic **e.g. NaCl, MgO**	high: strong ionic bonds	only molten / aqueous: mobile ions	soluble in polar solvents (ion–dipole)	hard, brittle
Giant molecular **e.g. diamond, graphite**	very high: strong, extensive covalent bonds	non-conductor (graphite: along layers)	insoluble in all solvents	diamond hard, graphite soft
Simple molecular **e.g. I_2**	low: _____ between molecules	non-conductor: discrete, uncharged molecules	like dissolves like: polar in polar, non-polar in non-polar	soft: weak IMF easily overcome

ANSWER STRUCTURE **Melting point**

State each structure → more energy is needed to overcome the stronger _____ _____ between the _____ of ZZ than the weaker ... of YY.

Same structure? Explain the _____ that makes one attraction stronger, e.g. charge and ionic radius (ionic), no. of valence e^- and cation size (metallic), no. of e^- or surface area (id–id), extent of H bonding.

ANSWER STRUCTURE **Solubility**

Energy released forming _____ interactions is / is not able to compensate for the energy needed to overcome the solute–solute and solvent–solvent interactions → soluble / insoluble.

03 The Gaseous State



1 Gases and their Units

1.1 Properties of gases

- Much **lower density** than solids and liquids
- Take the **volume and shape** of the container
- Highly **compressible**, exert pressure equally in all directions

Pressure: the force exerted by gas particles colliding with a surface, _____. p ↑ with n ↑, T ↑ and V ↓.

1.2 S.I. units and conversions

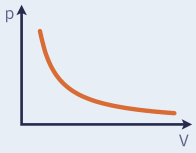
Quantity	S.I. unit	Conversions
pressure, p	**Pa** ($N\ m^{-2}$)	1 atm = 101 325 Pa = 760 mm Hg, 1 bar = 10^5 Pa
volume, V	**m^3**	1 dm^3 = 1 L = 10^{-3} m^3, 1 cm^3 = 1 mL = _____ m^3
temperature, T	**K**	T / K = T / °C + _____
amount, n	**mol**	n = mass / M_r

2 The Gas Laws

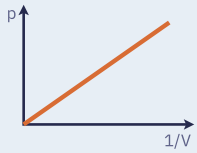
Boyle's law (fixed n, T)

At constant temperature, the volume of a fixed mass of gas is _____ to its pressure.

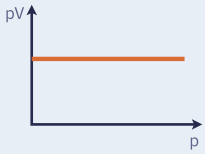
$pV = k \quad p_1V_1 = p_2V_2$



p against V



p against 1/V



pV against p

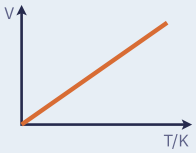
WORKED EXAMPLE: BOYLE A balloon holds 600 cm^3 of gas. Its pressure falls to one-third at constant temperature. Find its new volume.

$p(600) = (p/3)V_2 \rightarrow V_2 =$ _____

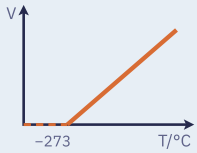
Charles's law (fixed n, p)

The volume of a fixed mass of gas at constant pressure is _____ to its temperature in _____.

$V / T = k \quad V_1/T_1 = V_2/T_2$



V against T / K



V against T / °C

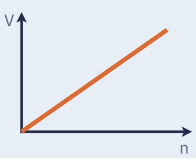
WORKED EXAMPLE: CHARLES 32.0 cm^3 of CO_2 is collected at 0 °C and 1 atm. Find its volume at r.t.p. (20 °C, 1 atm).

$V_2 = 32.0 \times \frac{293}{273} =$ _____ (use kelvin, never °C)

Avogadro's law (fixed p, T)

Under the same temperature and pressure, equal volumes of all gases contain _____ of molecules.

$V / n = k \quad V_1/n_1 = V_2/n_2$



V against n

2 The Gas Laws (continued)

2.1 Explaining the gas laws with kinetic theory

- **Boyle**: V ↓ → particles travel a **shorter distance** between collisions with the walls → less time between collisions → _____ collisions with the walls → p ↑
- **Charles**: T ↑ → particles have higher KE and move faster → hit the walls more often and with _____ → walls move out (V ↑) until p is restored
- **Avogadro / Dalton**: p depends on the no. of collisions per second, which is proportional to the _____

3 The Ideal Gas Equation

$$pV = nRT$$

R = 8.31 J K^{-1} mol^{-1}, all quantities in _____

n, T constant	$p \propto 1/V$	Boyle
n, p constant	$V \propto T$	Charles
p, T constant	$V \propto n$	Avogadro
n, V constant	$p \propto T$	

An **ideal gas** obeys pV = nRT exactly at all pressures and temperatures.

NOTE Two special forms of pV = nRT, derived by substitution

$M_r = \frac{mRT}{pV}$ substitute $n = \frac{m}{M_r}$ into pV = nRT

$\rho = \frac{pM_r}{RT}$ then use density, $\rho = \frac{m}{V}$

WORKED EXAMPLE: M_R OF A GAS 0.10 g of a gas occupies 83.1 cm^3 at 1.0 × 10^5 Pa and 27 °C. Find its M_r.

$M_r = \frac{mRT}{pV} = \frac{0.10 \times 8.31 \times \square}{1.0 \times 10^5 \times \square}$

= _____

WORKED EXAMPLE: MOLAR VOLUME AT S.T.P. Find the volume of 1 mol of an ideal gas at s.t.p. (0 °C, 1 bar).

$V = \frac{nRT}{p} = \frac{1 \times 8.31 \times 273}{10^5} = 2.27 \times 10^{-2}$

m^3 = _____

WORKED EXAMPLE: DENSITY Find the density of H_2S (M_r 34.1) at 20 °C and 2.00 atm.

$\rho = \frac{pM_r}{RT} = \frac{2.00 \times 101\,325 \times 34.1}{8.31 \times 293}$

= 2840 g m^{-3} = _____

WORKED EXAMPLE: CHANGE OF CONDITIONS A gas at 25 °C is heated until both its pressure and volume double (n constant). Find the final temperature.

$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$ → $T_2 = 4 \times 298$ = _____

4 Dalton's Law of Partial Pressures

In a mixture of gases that do not react, each gas behaves as if it were _____ present. The total pressure is the _____ of the partial pressures.

$p_{total} = p_A + p_B + \ldots$ Total pressure = sum of the partial pressures. **Partial pressure** p_A: the pressure gas A would exert if it _____.

$x_A = n_A / n_{total}$ **Mole fraction** x_A: the fraction of all the gas particles that are A.

$p_A = x_A \times p_{total}$ A's share of the pressure = A's share of the particles.

WORKED EXAMPLE: PARTIAL PRESSURES A cylinder holds 0.5 mol He, 2.0 mol Ne and 2.5 mol Ar at a total pressure of 100 kPa. Find each partial pressure.

1. $n_{total} = 0.5 + 2.0 + 2.5 = 5.0$ mol
2. $x_{He} = 0.5 \div 5.0 = 0.1$
   $x_{Ne} = 2.0 \div 5.0 = 0.4$
   $x_{Ar} = 2.5 \div 5.0 = 0.5$
3. $p_{He} = 0.1 \times 100 =$ _____
   $p_{Ne} = 0.4 \times 100 = 40$ kPa
   $p_{Ar} = 0.5 \times 100 =$ _____

WORKED EXAMPLE: CONNECTING FLASKS A 1 dm^3 flask of He at 2 kPa is connected to a 2 dm^3 flask of Ne at 1 kPa at constant temperature. Find the final pressure.

1. Each gas spreads through all 3 dm^3 as if alone, so $p_1V_1 = p_2V_2$ for each
2. He: $2 \times 1 = p_{He} \times 3$, so $p_{He} = 0.667$ kPa
   Ne: $1 \times 2 = p_{Ne} \times 3$, so $p_{Ne} = 0.667$ kPa
3. $p_{total} = p_{He} + p_{Ne} = 0.667 + 0.667$
   = _____

5 Kinetic Theory of Gases

5.1 Assumptions for an ideal gas

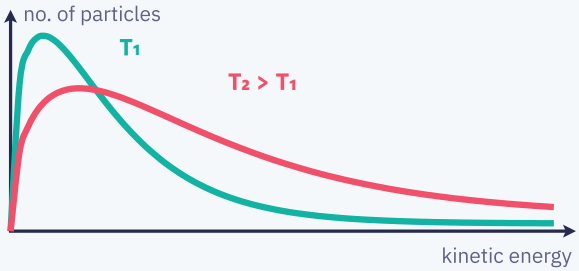
1. Gas particles have _____ compared to the volume of the container (point masses)
2. Gas particles exert _____ on one another
3. Collisions between particles are perfectly _____ → no loss of kinetic energy
4. Particles are in constant, _____ motion

Average kinetic energy of the particles ∝ T (in kelvin). The first two are the **2 main features** of an ideal gas.

5.2 Maxwell–Boltzmann distribution

When temperature increases

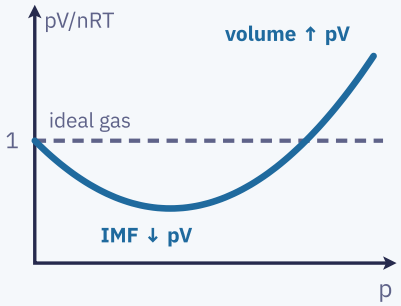
1. The peak shifts to the _____: the most probable speed or energy increases
2. The curve _____: a larger spread of speeds, more particles at high speeds
3. The area under the curve stays _____: the total no. of particles is unchanged



6 Real Gases

6.1 Deviation from ideality

For an ideal gas pV / nRT = 1 at all p. Real gases deviate most at **high p** and **low T**, because of (1) **IMF** between particles and (2) the **volume of the particles**.



↓ Dip: IMF significant

1. A particle about to hit the wall is _____ by the particles around it
2. → hits the wall with less force → p lower than ideal → pV ↓

↑ Rise at high p: particle volume significant

1. Volume of the gas particles is no longer negligible compared to the _____
2. → volume of real gas > ideal gas → pV ↑

WORKED EXAMPLE Rank CH_4, HCl and HF in order of decreasing ideality at the same conditions.

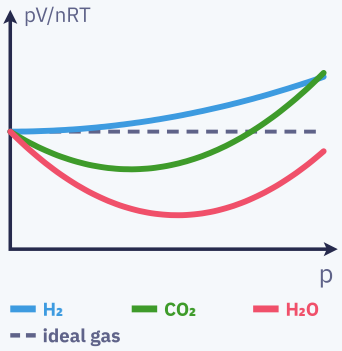
1. CH_4 has only weak id–id, HCl has _____, HF has strong _____
2. Stronger IMF → greater deviation → ideality: CH_4 > HCl > HF

6.2 Conditions for ideal behaviour

1. **Low pressure**: the gas occupies a large volume, so the volume of the particles is _____ compared to the container. Particles are far apart, so IMF are negligible
2. **High temperature**: particles have high _____, enough to overcome the IMF

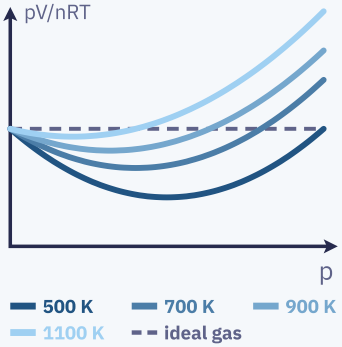
6.3 Effect of IMF

- Stronger IMF → greater deviation. H_2O (H bonds) > CO_2 > H_2 (weak id–id). H_2's id–id are so weak that its pV never dips below the ideal value
- **Polar** molecules: pd–pd or H bonds are stronger than id–id of non-polar molecules of similar M_r
- **Large electron cloud**: stronger, more extensive IMF, and larger particle volume



6.4 Effect of temperature

T ↑ → particles have higher KE and move faster → IMF become _____ → pV approaches the ideal value → less deviation. At very low T the particles move slowly, so IMF dominate and the gas condenses to a liquid, far from ideal.



07 Chemical Energetics I

1 Enthalpy Changes

DEFINITION **Enthalpy, H:** the measure of the energy content of a substance. A substance with lower enthalpy has greater _____.

Bond breaking _____ energy, bond forming _____ energy. ΔH is the heat change at constant pressure (kJ mol^{-1}).

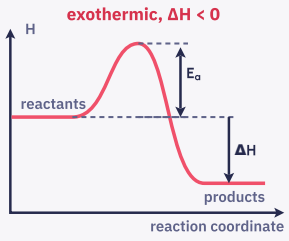
	Exothermic	Endothermic
ΔH	negative	positive
Heat	released to surroundings	absorbed from surroundings
Surroundings	temperature ↑	temperature ↓
Products	more stable	less stable

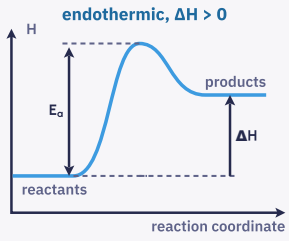
1.1 Energy profile diagrams

DEFINITION **Activation energy, E_a:** the minimum amount of energy reacting particles must possess for an _____ to take place.

- **Standard conditions**: _____, 1 bar (10^5 Pa), 1 mol dm^{-3} for solutions. $\Delta H^{\ominus}$(element in standard state) = 0
- Thermochemical equations need **state symbols**, ΔH scales with the amounts: doubling the equation doubles ΔH

NOTE Standard conditions (298 K, 1 bar) are **not** s.t.p. (273 K, 1 bar).





2 Standard Enthalpy Changes

Term	DEFINITION	Example equation	Sign
Reaction, $\Delta H_r^{\ominus}$	the enthalpy change when molar quantities of reactants, as specified by the balanced equation, react to form products under _____	$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$	exo / endo
Formation, $\Delta H_f^{\ominus}$	the enthalpy change when one mole of the substance is formed from its _____ in their standard states under standard conditions ↳ $\Delta H_f^{\ominus}$ measures stability relative to the elements: negative → compound _____ than its elements	$2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH(l)$	exo / endo
Combustion, $\Delta H_c^{\ominus}$	the enthalpy change when one mole of the substance is _____ in oxygen under standard conditions	$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$	exo
Neutralisation, $\Delta H_{neut}^{\ominus}$	the enthalpy change when one mole of _____ is formed from the reaction of an acid and an alkali under standard conditions ↳ Strong acid + strong base: always −57.0 kJ mol^{-1}, as both fully dissociate → the reaction is just $H^+ + OH^- \rightarrow H_2O$. **Weak acid or base**: ΔH_{neut} is less exothermic than −57.0 (e.g. CH_3CO_2H, −55.2): (1) weak acid is only _____, (2) energy is absorbed to dissociate the undissociated acid → less energy released overall	$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$	exo

2 Standard Enthalpy Changes (continued)

Term	DEFINITION	Example equation	Sign
Bond energy, BE	the _____ enthalpy change when one mole of covalent bonds between atoms in gaseous molecules is broken	$Cl–Cl(g) \rightarrow 2Cl(g)$	endo
Atomisation, $\Delta H_{at}^{\ominus}$	the enthalpy change when one mole of _____ is formed from the element in its standard state under standard conditions	$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ (= ½BE)	endo
1st / 2nd IE	the enthalpy change when one mole of electrons is removed from one mole of gaseous atoms / _____	$Mg(g) \rightarrow Mg^+(g) + e^-$	endo
1st / 2nd EA	the enthalpy change when one mole of gaseous atoms / singly charged anions _____ one mole of electrons ↳ **Why is 1st EA negative but 2nd EA positive?** (1) 1st EA: energy is given off when electrostatic _____ forms between the positive nucleus and the electron added. (2) 2nd EA: energy is needed to overcome the _____ between the electron added and the singly charged anion, both negatively charged	$O(g) + e^- \rightarrow O^-(g)$	1st exo, 2nd endo
Lattice energy, LE	the energy released when one mole of the solid ionic compound is formed from its constituent _____ under standard conditions	$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$	exo
Hydration, $\Delta H_{hyd}^{\ominus}$	the enthalpy change when one mole of _____ is hydrated under standard conditions ↳ Hydration is always exothermic: _____ interactions form between the ions and water molecules	$Na^+(g) + aq \rightarrow Na^+(aq)$	exo
Solution, $\Delta H_{sol}^{\ominus}$	the enthalpy change when one mole of the substance is completely dissolved to give an _____ solution under standard conditions, so that no further enthalpy change takes place on adding more solvent	$NaCl(s) + aq \rightarrow Na^+(aq) + Cl^-(aq)$	exo / endo

IE, EA and LE values are per mole: e.g. IE(Mg) +736, $EA_1(O)$ −141, $EA_2(O)$ +844, LE(NaCl) −776 kJ mol^{-1}.

EXAM TIP **Read the definition off the term itself.** The term names what there is **one mole** of: **formation** → per mole of compound formed, **combustion** → per mole of substance burnt, **neutralisation** → per mole of water formed, **atomisation** → per mole of gaseous atoms formed, **hydration** → per mole of gaseous ions hydrated.

ANSWER STRUCTURE The enthalpy change when _____ of *(what the term names)* is *(formed / burnt / hydrated …)* under _____.

Equation: give that species a coefficient of 1, then balance the rest, using fractions if needed, e.g. formation: $2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow \mathbf{1}\ C_2H_5OH(l)$.

3 Calorimetry

$q = -mc\Delta T$

m	mass of **solution** / g
c	specific heat capacity, 4.18 J g^{-1} K^{-1}
ΔT	$T_{final} - T_{initial}$

$\Delta H = q / n$

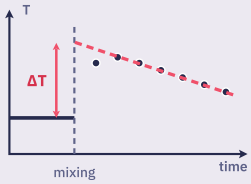
n	amount of **limiting** reagent (or the specified substance) / mol

Assumptions

- Negligible heat loss to the _____
- Negligible heat absorbed by the calorimeter
- Density of solution = _____, c of solution = c of water

Temperature correction

For slow reactions, plot T against time and **extrapolate** back to the time of mixing to account for heat loss.



WORKED EXAMPLE: NEUTRALISATION A student mixes 40.0 cm^3 of 2.0 mol dm^{-3} HCl at 22.3 °C with 50.0 cm^3 of 2.0 mol dm^{-3} NaOH at 22.5 °C. The highest temperature reached is 34.6 °C. Find ΔH_{neut}.

1. Initial T = $\frac{40.0(22.3) + 50.0(22.5)}{90.0}$
   = 22.41 °C (weighted average)
2. $q = -(90.0)(4.18)(34.6 - 22.41)$
   = _____
3. n_{HCl} = 0.08000 mol (limiting) = n_{H_2O} formed
4. ΔH_{neut} =
   −4586 ÷ 0.08000 = _____

WORKED EXAMPLE: COMBUSTION Burning 0.530 g of ethanol in a spirit burner heats 250 g of water by 10.4 °C. Find ΔH_c of ethanol.

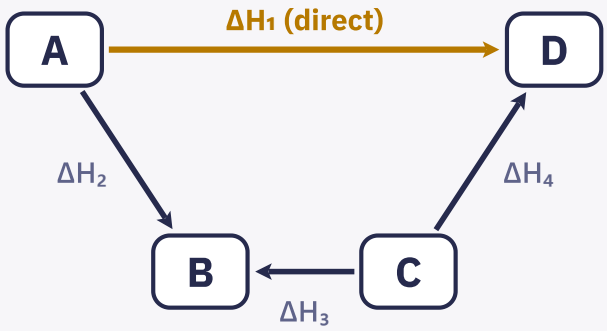
1. q = −250 × 4.18 × 10.4 = −10 870 J
   = −10.87 kJ
2. $n_{ethanol}$ = 0.530 ÷ 46.0 = 0.01152 mol
3. ΔH_c = −10.87 ÷ 0.01152 = _____

Less exothermic than the data value (−1368) because of heat loss to surroundings, heat absorbed by the calorimeter, or _____ _____. Efficiency: q′ = (x / 100) q.

4 Hess' Law

DEFINITION **Hess' Law**: the enthalpy change of a chemical reaction depends only on the _____ of the system and is independent of the _____ taken.

From ΔH_c	$\Delta H_r = \Sigma\Delta H_c$(reactants) − $\Sigma\Delta H_c$(products)
From ΔH_f	$\Delta H_r = \Sigma\Delta H_f$(products) − $\Sigma\Delta H_f$(reactants)
From BE	$\Delta H_r = \Sigma$BE(bonds broken) − ΣBE(bonds formed)



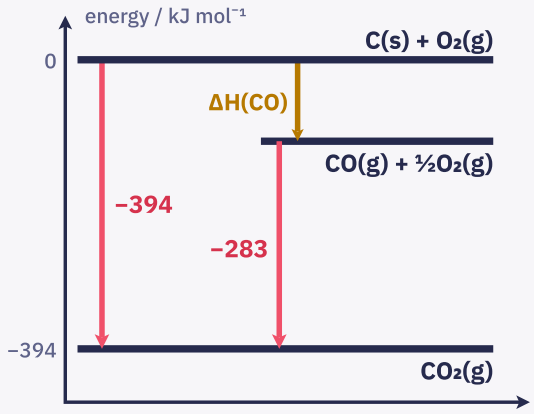
$\Delta H_1 = \Delta H_2 - \Delta H_3 + \Delta H_4$: going against an arrow changes its sign

4.1 Energy level diagram: ΔH_f(CO)

$C(s) + O_2(g) \rightarrow CO_2(g)$	$\Delta H_c(C) = -394$
$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$	$\Delta H_c(CO) = -283$

$\Delta H_f(CO) = -394 - (-283) =$ _____

Check: arrows down for exothermic, elements at 0, state symbols.



4.2 Using combustion and bond energies

WORKED EXAMPLE: FROM ΔH_c Propane cannot be made directly from its elements. Find $\Delta H_f(C_3H_8)$ given ΔH_c / kJ mol⁻¹: C −394, H_2 −286, C_3H_8 −2220.

$3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$

$\Delta H_f = 3(-394) + 4(-286) - (-2220)$

= _____

WORKED EXAMPLE: FROM BE Estimate ΔH for the Haber process, $N_2 + 3H_2 \rightarrow 2NH_3$, given BE / kJ mol⁻¹: N≡N 944, H–H 436, N–H 390.

$\Delta H = [944 + 3(436)] - [6(390)]$

= _____

BE values are **averages** over many molecules, so ΔH from bond energies differs from values found by other methods.

5 Lattice Energy and the Born–Haber Cycle

5.1 Factors affecting lattice energy

$$LE \propto \frac{q_+ \times q_-}{r_+ + r_-}$$

Compound	LE / kJ mol^{-1}
NaCl	**−776**
NaBr	**−742**
$MgCl_2$	**−2375**

- Br^- has the same charge but a _____ than Cl^- → LE(NaBr) less exothermic than LE(NaCl)
- Mg^{2+}: higher charge, smaller radius than Na^+ → LE($MgCl_2$) _____

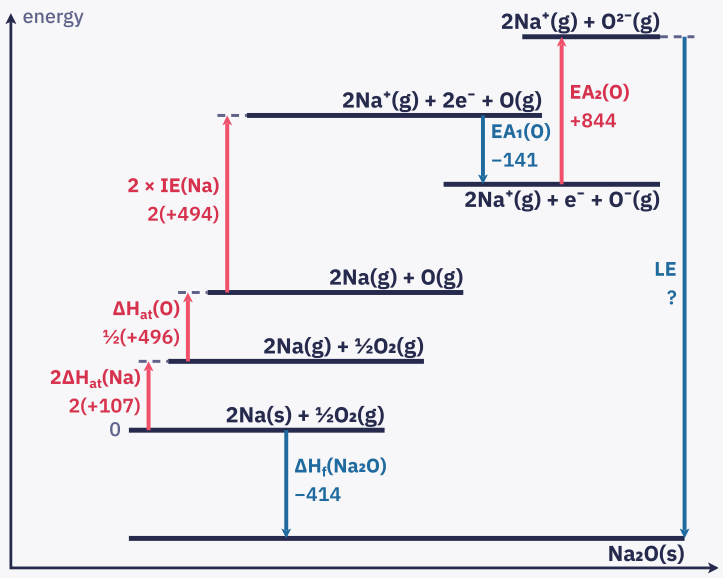
EXAM TIP Compare lattice energies as "more / less exothermic", never "larger / smaller".

NOTE Experimental LE more exothermic than theoretical (e.g. AgI, $MgCl_2$) → _____ from polarisation of the anion.

5.2 Born–Haber cycle for Na_2O

How to build a Born–Haber cycle (not to scale)

1. Draw the **elements** in their standard states at 0
2. **Atomise** each element (up): ΔH_{at}, times the number of atoms
3. **Ionise** the metal atoms (up): sum of IEs
4. **Add electrons** to the non-metal: EA_1 down, EA_2 up
5. Gaseous ions → solid: **LE** (down), ΔH_f joins elements to solid



Calculating LE:
ΔH_f = sum of the other steps

$-414 = 2(107) + ½(496) + 2(494) - 141 + 844 + LE$

LE = _____

6 Hydration and Solution

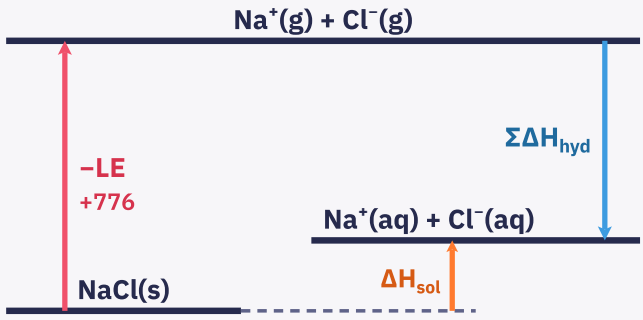
6.1 Using hydration and lattice energies

$\Delta H_{hyd} \propto q / r$

Small, highly charged ions attract water molecules more strongly → more exothermic hydration.

$\Delta H_{sol} = -LE + \Sigma\Delta H_{hyd}$

Dissolving happens in two steps: **(1)** break the lattice into gaseous ions, which **takes in** energy (−LE), then **(2)** surround the gaseous ions with water, which **gives out** energy ($\Sigma\Delta H_{hyd}$).



not to scale

WORKED EXAMPLE The enthalpy change of solution of NaCl is +5 kJ mol^{-1}. The lattice energy of NaCl is −776 kJ mol^{-1} and the enthalpy change of hydration of Na^+ is −390 kJ mol^{-1}.
(a) Calculate the enthalpy change of hydration of Cl^-.
(b) $\Delta H_{hyd}(I^-)$ is −308 kJ mol^{-1}. Explain why it is less exothermic than $\Delta H_{hyd}(Cl^-)$.

(a)

1. $\Delta H_{sol} = -LE + \Delta H_{hyd}(Na^+) + \Delta H_{hyd}(Cl^-)$
2. $+5 = -(-776) + (-390) + \Delta H_{hyd}(Cl^-)$
3. $\Delta H_{hyd}(Cl^-) = 5 - 776 + 390 =$ _____

(b)

1. I^- has the same charge but a _____ _____ than Cl^-
2. → lower charge density
3. → _____ ion–dipole interactions with water molecules → less energy released

07 Chemical Energetics II



7 Spontaneity and Entropy

Spontaneous reaction: a reaction that is energetically feasible, i.e. _____. Once started, it proceeds on its own _____ of energy from the surroundings.

NOTE Spontaneous says nothing about **rate**: a spontaneous reaction can be very slow.

7.1 Entropy

DEFINITION **Entropy, S**: a measure of the _____ in a system. The more disordered a system, the greater the number of ways for particles and energy to be _____, therefore the larger is the entropy.

$\Delta S = S_{final} - S_{initial}$

units: $J\ mol^{-1}\ K^{-1}$

8 Factors Affecting Entropy

Temperature ↑

$\Delta S > 0$: particles have more average _____ and there are more ways to distribute the larger number of quanta of energy.

Change in phase

S: solid < liquid ≪ gas. Melting: particles no longer in _____ → more ways to arrange particles and distribute energy. Boiling: particles move randomly, large ↑ in volume.

More gas particles

$\Delta S > 0$: disorder increases as the number of moles of _____ increases, e.g. $2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$. No change in moles of gas → $\Delta S \approx 0$.

Predict ΔS	Sign	Reason
$2N_2O(g) + O_2(g) \rightarrow 4NO(g)$	+	moles of gas ↑ (3 → 4) → more ways to distribute particles and energy
$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$	_____	a gas forms from liquids
$3O_2(g) \rightarrow 2O_3(g)$	_____	moles of gas ↓ (3 → 2)
$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$	–	moles of gas ↓ (3 → 2) → fewer ways to distribute

NOTE **Dissolving an ionic solid**: two opposing effects: ions become free to move (S ↑), but water molecules become more _____ around the ions (S ↓). Usually the first wins, e.g. $NaCl(s) + aq \rightarrow Na^+(aq) + Cl^-(aq)$, $\Delta S > 0$.

9 Gibbs Free Energy

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

T in kelvin, convert ΔS to _____ before use

DEFINITION The **standard Gibbs free energy, $\Delta G^{\ominus}$**, is used to predict the _____ of a reaction.

$\Delta G < 0$	$\Delta G = 0$	$\Delta G > 0$
spontaneous, K > 1, products favoured	at equilibrium (e.g. at m.p. or b.p.)	non-spontaneous, spontaneous in reverse

$$\Delta G_r = \Sigma \Delta G_f(\text{products}) - \Sigma \Delta G_f(\text{reactants})$$

WORKED EXAMPLE: RUSTING Iron rusts in air:

$$2Fe(s) + \frac{3}{2} O_2(g) \rightarrow Fe_2O_3(s)$$

$\Delta H = -825$ kJ mol^{-1} and $\Delta S = -272$ J mol^{-1} K^{-1}. Is rusting spontaneous at 298 K?

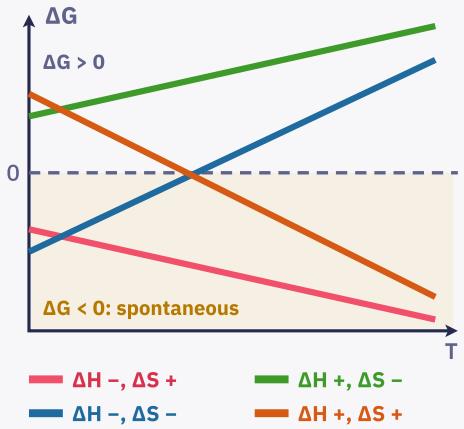
1. Convert ΔS to kJ: −272 J mol^{-1} K^{-1} = _____ kJ mol^{-1} K^{-1}
2. $\Delta G = \Delta H - T\Delta S = -825 - 298 \times (-0.272)$
3. ΔG = _____
4. $\Delta G < 0$ → spontaneous at 298 K

WORKED EXAMPLE: MELTING ICE Ice melts at 273 K. The enthalpy change of fusion is +6.0 kJ mol^{-1}. Find ΔS for melting.

1. At the m.p., ice and water are at equilibrium → $\Delta G = 0$
2. $0 = \Delta H - T\Delta S \rightarrow \Delta S = \Delta H \div T$
3. $\Delta S = 6000 \div 273$ = _____

10 Effect of Temperature on Spontaneity

ΔH	ΔS	Spontaneity
–	+	Since ΔS > 0, –TΔS < 0 → ΔG negative at _____: always spontaneous
+	–	Since ΔS < 0, –TΔS > 0 → ΔG positive at all temperatures: _____ spontaneous
–	–	Since ΔS < 0, –TΔS > 0. As T ↑, –TΔS becomes more positive → ΔG positive eventually: spontaneous only at _____
+	+	Since ΔS > 0, –TΔS < 0. As T ↑, –TΔS becomes more negative → ΔG negative eventually: spontaneous at _____



Case	Examples
ΔH –, ΔS +	combustion of octane, decomposition of nitroglycerine
ΔH +, ΔS –	photosynthesis: must be driven by a continuous energy input (sunlight)
ΔH –, ΔS –	precipitation of AgCl, condensation, freezing (enthalpy driven)
ΔH +, ΔS +	melting, boiling, decomposition of Group 2 carbonates (entropy driven)

WORKED EXAMPLE: MINIMUM TEMPERATURE

In a blast furnace:
$C(s) + CO_2(g) \rightarrow 2CO(g)$
ΔH = +172.5 kJ mol^{-1} and ΔS = +176.2 J mol^{-1} K^{-1}. Find the minimum temperature for the reaction to be spontaneous.

1. At 298 K: ΔG = 172.5 – 298 × 0.1762 = +120 kJ mol^{-1} > 0 → not spontaneous
2. Spontaneous when ΔG < 0: ΔH – TΔS < 0 → T > ΔH ÷ ΔS
3. T > 172.5 ÷ 0.1762 = _____

WORKED EXAMPLE Baking powder releases CO_2 on heating:
$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$
ΔH = +130 kJ mol^{-1} and ΔS = +335 J mol^{-1} K^{-1}. Above what temperature is this spontaneous?

1. At 298 K: ΔG = 130 – 298 × 0.335 = +30.2 kJ mol^{-1} > 0 → not spontaneous
2. Spontaneous when ΔG < 0 → T > ΔH ÷ ΔS
3. T > 130 ÷ 0.335 = _____

Likewise $MgCO_3$ decomposes above 576 K but $BaCO_3$ only above 1566 K: ΔH($MgCO_3$) is _____ _____, ΔS similar.

11 Limitations of $\Delta G^{\ominus}$

11.1 Standard states

$\Delta G^{\ominus}$ is worked out for _____ only (1 bar, 1 mol dm^{-3}). Real conditions are often different, so $\Delta G^{\ominus}$ can give the wrong prediction.

e.g. $H_2O(l) \rightarrow H_2O(g)$ at 298 K: $\Delta G^{\ominus} = 44.0 - 298 \times 0.118 = +8.84$ kJ mol^{-1}, so water should not boil. Yet at a low enough pressure, water does boil at 298 K.

11.2 Temperature

Using $\Delta G = \Delta H - T\Delta S$ at a new temperature assumes ΔH and ΔS stay _____ as T changes. This is not true if a substance _____ in between, as ΔH and ΔS then change a lot.

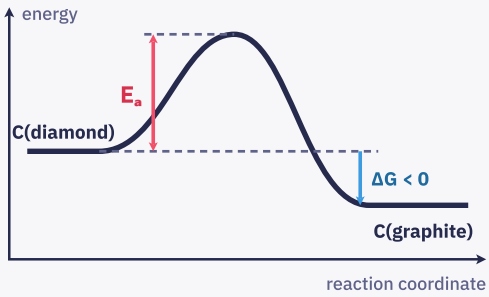
e.g. $H_2 + I_2 \rightarrow 2HI$: $\Delta G = +3.5$ kJ mol^{-1} at 298 K (I_2 solid) but -20.0 kJ mol^{-1} at 500 K (I_2 gas), so 298 K data cannot predict ΔG at 500 K.

11.3 Kinetics

ΔG only tells us whether a reaction is energetically feasible, **not how fast** it goes.

C(diamond) → C(graphite) has $\Delta G < 0$, so it is spontaneous. But its _____ is very high, so almost no particles have enough energy to react at room temperature, and the change is far too slow to observe.

→ Diamond is energetically unstable but _____ _____ relative to graphite.



08 Reaction Kinetics



1 Collision Theory

For a reaction to occur, particles must collide with

1. sufficient kinetic energy, greater than or equal to the _____ (E_a)
2. the correct _____ (orientation)

Such a collision is an **effective collision**. The greater the frequency of effective collisions, the faster the rate. Usually at most **two** particles collide in one step.

DEFINITION **Activation energy**: the minimum amount of energy reacting particles must possess for an effective collision to take place for reaction to occur.

Collision	Energy ≥ E_a?	Right orientation?	Result
effective	✓	✓	bonds break and form: products
ineffective	✗	✓	bounce apart
ineffective	✓	✗	bounce apart

✓ right orientation



C meets the B end: B–C forms

✗ wrong orientation



C meets the A end: they bounce apart

2 Factors Affecting Rate

2.1 Concentration, pressure and surface area

Concentration or pressure ↑

1. No. of reactant particles per _____ ↑
2. → frequency of collisions ↑, and hence frequency of _____ ↑ → rate ↑

Particle size of solid ↓

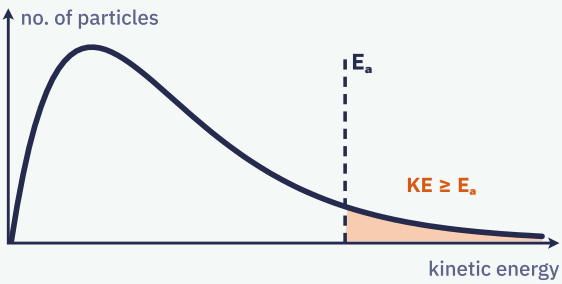
1. Larger _____ of contact between reactant particles
2. → frequency of effective collisions ↑ → rate ↑

Rate is fastest at the start, when reactant concentrations are highest.

2.2 The Boltzmann distribution curve

Features of the curve

- Starts at the **origin** and never touches the energy axis
- Area under the curve = total no. of particles
- Shaded area = particles with energy **≥ E_a**



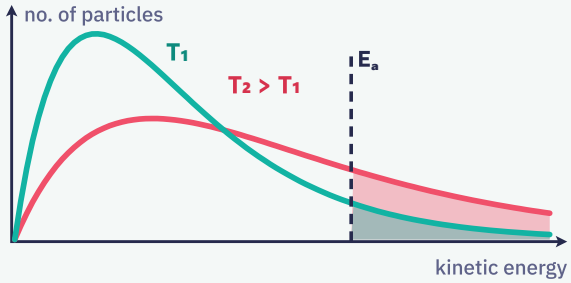
How the curve changes when T increases

- The peak shifts to the _____, as the most probable energy increases
- The curve _____ out: a larger spread of energies, with more particles at higher energies and fewer at lower energies
- The area under the curve stays _____, as the total number of particles is constant

2 Factors Affecting Rate (continued)

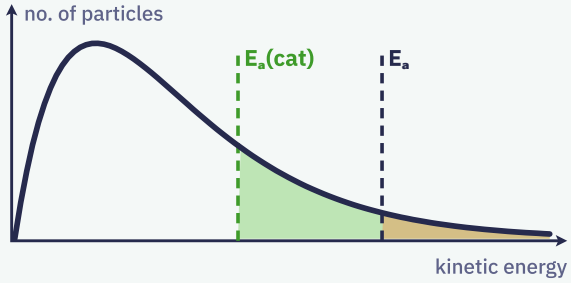
2.3 Effect of temperature on rate

1. As the temperature increases, the average _____ of the particles increases
2. → a larger number of reactant particles have energy _____ (larger shaded area)
3. → frequency of effective collisions ↑ → rate ↑ (k ↑). Rate roughly doubles for every 10 °C rise.



2.4 Effect of a catalyst on rate

1. Provides an _____ with a lower E_a
2. → more reactant particles possess energy ≥ E_a (larger shaded area)
3. → frequency of effective collisions ↑ → rate ↑ (k ↑)



3 Rate of Reaction

DEFINITION **Rate of reaction**: the change in concentration of a reactant or product per _____.

Measuring rate

$$\text{rate} = \frac{\text{change in [reactant] or [product]}}{\text{time taken}}$$

Rate is always positive: [reactant] falls with time and [product] rises. Units: mol dm^{-3} s^{-1}.

Rates of different species are related by the mole ratio

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

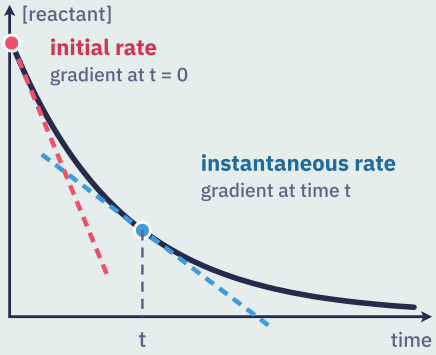
- Br^- is used up _____ as fast as BrO_3^-
- Br_2 is formed _____ as fast as BrO_3^- is used up

So "the rate" must say which species it refers to.

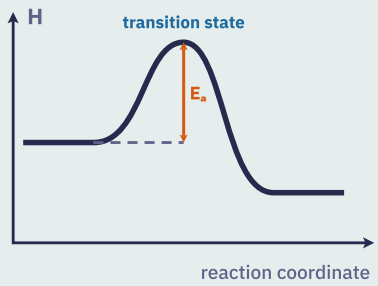
Instantaneous and initial rate

DEFINITION **Instantaneous rate**: gradient of the _____ to the concentration–time graph at time t.

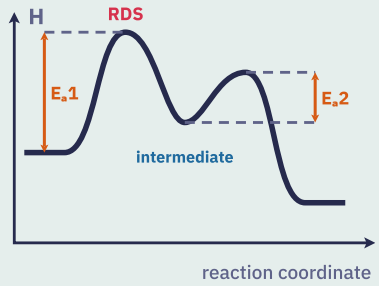
Initial rate: gradient of the tangent at _____, the highest rate, as [reactant] is at its maximum.



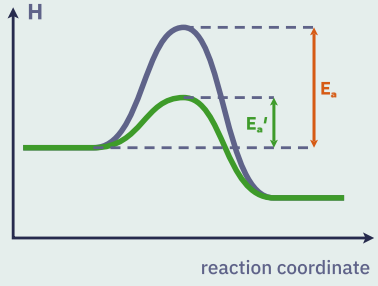
4 Energy Profile Diagrams



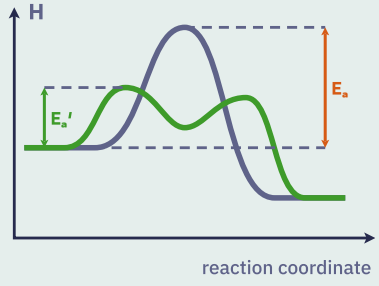
One step
one transition state



Two steps
intermediate in the dip, step 1 is the RDS



Heterogeneous catalyst
one lower hump



Homogeneous catalyst
two lower humps

- **Transition state**: the unstable arrangement at the energy maximum, equally likely to form reactants or products
- **Intermediate**: short-lived species formed in one step and used up in a later step
- The **rate-determining step** (slow step) has the _____
- Higher E_a → slower reaction. Very high E_a: reactant is _____

5 Catalysis

DEFINITION **Catalyst**: a substance that increases the rate of a chemical reaction by providing an _____ _____ with lower activation energy but remains _____ at the end of the reaction.

1. It is _____
2. It is regenerated at the end of the reaction
3. It does not affect the overall stoichiometry
4. It does not affect the position of equilibrium or ____

DEFINITION **Homogeneous** catalysis: catalyst and reactants in the _____.

DEFINITION **Heterogeneous** catalysis: catalyst and reactants in _____.

5.1 Heterogeneous: adsorption theory

1. **Adsorption**: reactant particles form weak bonds to _____ on the catalyst surface, weakening the bonds within them
2. **Reaction**: reactants are held close together in the _____
3. **Desorption**: weak bonds to the products break, products diffuse away and the active sites are freed



Process	Catalyst
Haber: $N_2 + 3H_2 \rightleftharpoons 2NH_3$	_____
Contact: $2SO_2 + O_2 \rightleftharpoons 2SO_3$	_____
Hydrogenation of alkenes	Ni
Catalytic converter: $2CO + 2NO \rightarrow 2CO_2 + N_2$	Pt, Pd, Rh

5 Catalysis (continued)

5.2 Homogeneous: Fe^{2+} in the I^- / $S_2O_8^{2-}$ reaction

Iodide ions are oxidised by peroxodisulfate ions. Without a catalyst this is very slow, adding a little Fe^{2+} speeds it up. $2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$

Why is the reaction slow, and how does Fe^{2+} help?

1. Without a catalyst, the reaction is slow: it has a high E_a, as a large amount of energy is needed to overcome the _____ between the two negatively charged reactant ions
2. Step 1: $2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$
3. Step 2: $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$ (Fe^{2+} regenerated)
4. Each step is between _____ ions → lower E_a for each step

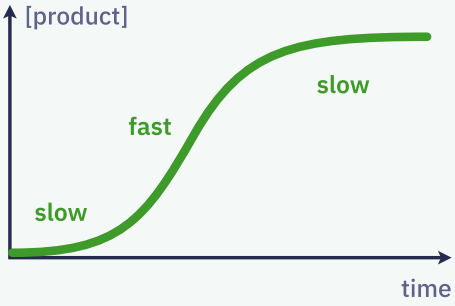
Oxides of nitrogen in the oxidation of atmospheric SO_2

- $NO_2 + SO_2 \rightarrow SO_3 + NO$
- $NO + \frac{1}{2}O_2 \rightarrow NO_2$ (NO_2 regenerated)
- $SO_3 + H_2O \rightarrow H_2SO_4$, forming _____

5.3 Autocatalysis

DEFINITION **Autocatalysis**: catalysis in which one of the _____ of the reaction catalyses the reaction.

1. Slow at first: very little catalyst (product) present
2. Fast as more product, the catalyst, forms
3. Slow again as the reactants are used up



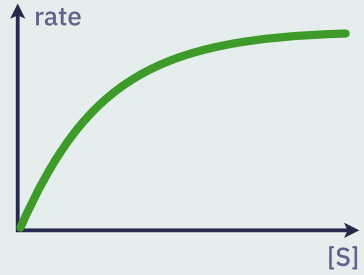
Example: MnO_4^- with ethanedioate ions

$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

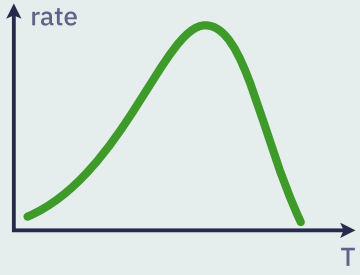
The product **Mn^{2+}** catalyses the reaction, so the purple colour fades slowly at first, then quickly.

5.4 Enzymes

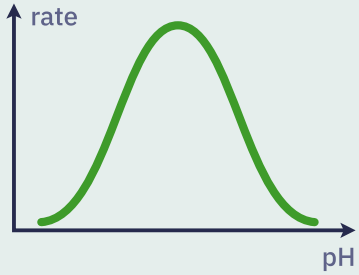
- Protein catalysts, highly _____ (lock-and-key)
- Low [S]: first order. High [S]: zero order, as all _____ are saturated
- [S] in excess: rate ∝ [E]
- pH or T beyond optimum changes the 3D structure and active site → _____



rate vs [S]
levels off: sites saturated



rate vs T
optimum 20–50 °C



rate vs pH
optimum pH 5–8

6 The Rate Equation

DEFINITION **Rate equation**: the _____ determined relationship between rate and the concentrations of reactants.

$$\text{rate} = k[A]^x[B]^y$$

DEFINITION **Order of reaction** w.r.t. a reactant: the _____ of its concentration term in the experimentally determined rate equation.

Overall order = _____

DEFINITION **Rate constant, k**: the proportionality constant in the rate equation.

6.1 Meaning of order

Order	Rate	[A] × 2: rate
0	independent of [A]	_____
1	rate ∝ [A]	_____
2	rate ∝ $[A]^2$	_____

6.2 What changes k?

Change	Rate	k
[reactant] ↑	↑ (if order ≠ 0)	_____
temperature ↑	↑	_____
add a catalyst	↑	_____

6.3 Units of k units of rate ÷ $(\text{mol dm}^{-3})^{\text{overall order}}$

Overall order	0	1	2	3
Rate equation	rate = k	rate = k[A]	rate = $k[A]^2$	rate = $k[A]^2[B]$
Units of k	_____	_____	_____	_____

7 Mechanisms and the Rate Equation

Rules for a reaction mechanism

- Each elementary step involves at most _____ reacting particles
- Steps add up to the overall equation
- The rate equation contains the reactants in the _____ (slow step), with orders = their coefficients in that step
- **Intermediates** do not appear in the overall equation or the rate equation

7.1 Proposing a mechanism

WORKED EXAMPLE $2NO(g) + F_2(g) \rightarrow 2ONF(g)$ has rate = $k[NO][F_2]$. It takes place in two steps, and one step forms ONF and the radical F• in equimolar amounts. Suggest a mechanism.

1. Slow step contains _____, from the rate equation

2. Rate equation ≠ overall equation → not a single step, one more NO still to react

Step 1 (slow) _____ **Step 2 (fast)** _____

7 Mechanisms and the Rate Equation (continued)

7.2 Testing a mechanism

WORKED EXAMPLE For $2A + B \rightarrow A_2B$, the rate equation is found to be rate = $k[A]^2$. Which mechanism is consistent with it?

Mechanism 1	Mechanism 2
$A + A \rightarrow A_2$ (slow)	$A + B \rightarrow AB$ (slow)
$A_2 + B \rightarrow A_2B$ (fast)	$AB + A \rightarrow A_2B$ (fast)

1. Mechanism 1: the slow step involves _____ → predicted rate = $k[A]^2$, which matches the experimental rate equation
2. Mechanism 2: the slow step involves one A and _____ → predicted rate = $k[A][B]$, which does not match
3. ∴ only _____ is consistent

8 Collecting Rate Data

	Continuous method	Initial rate method
Experiments	_____: [reactant] followed over time	_____: one concentration changed at a time
Data	concentration at intervals	time taken for a fixed change
Analysis	concentration–time graph, half-life	rate–concentration graph or the ratio method

8.1 Physical measurements: a property that changes as the reaction goes

gas volume
Mg + 2HCl, H_2 given off

mass loss
$CaCO_3$ + 2HCl, CO_2 escapes

pH
$CH_3Br + OH^-$, pH falls

conductivity
no. of ions changes

colorimetry
brown I_2 used up

pressure at fixed V
$N_2O_4 \rightarrow 2NO_2$

8.2 Titrimetric method

Withdraw portions at intervals, **quench**, then titrate. Quenching slows the reaction abruptly so the concentration at that time can be found:

- rapid cooling in _____
- removing the _____ (e.g. neutralising H^+ with $NaHCO_3$)
- adding a large volume of cold water to _____

8.3 Clock reactions

Time taken, t, for a sudden visible change.

- **Sulfur**: $S_2O_3^{2-} + 2H^+ \rightarrow S + SO_2 + H_2O$, time for the X to be hidden
- **Iodine clock**: fixed, small amount of $S_2O_3^{2-}$ removes I_2 as it forms, blue-black with starch appears once all $S_2O_3^{2-}$ is used up

A **fixed amount** of product forms in every run → rate $\propto \frac{1}{t}$

Disappearance of colour: the amount of coloured reactant varies between runs, so rate = $\frac{[\text{coloured reactant}]}{t}$, it _____ be simplified to 1/t.

9 Initial Rates Method

9.1 Initial rates

WORKED EXAMPLE The initial rates of $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ were measured at different concentrations. Find the rate equation and the rate constant.

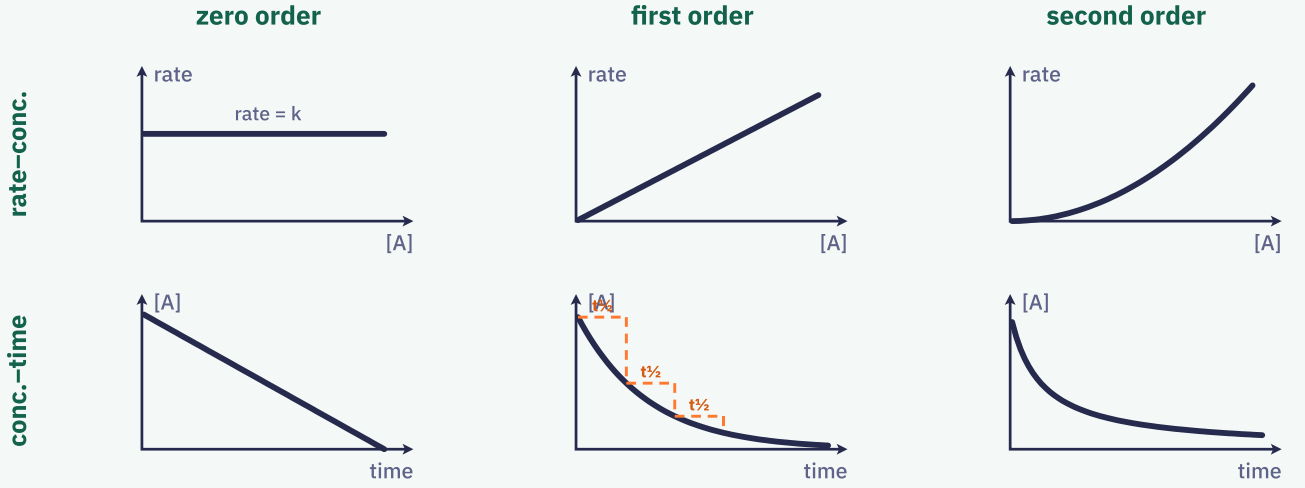
Expt	[NO] / mol dm⁻³	[O₂] / mol dm⁻³	rate / mol dm⁻³ h⁻¹
1	0.001	0.001	7×10^{-6}
2	0.001	0.002	14×10^{-6}
3	0.001	0.003	21×10^{-6}
4	0.002	0.003	84×10^{-6}

1. Let rate = $k[NO]^x[O_2]^y$. Choose two experiments where only one concentration changes.
2. Expts 1 and 2: $\frac{\text{rate 2}}{\text{rate 1}} = \frac{k(0.001)^x(0.002)^y}{k(0.001)^x(0.001)^y} \rightarrow \frac{14}{7} = 2^y \rightarrow y =$ ____
3. Expts 3 and 4: $\frac{\text{rate 4}}{\text{rate 3}} = \frac{k(0.002)^x(0.003)^y}{k(0.001)^x(0.003)^y} \rightarrow \frac{84}{21} = 2^x \rightarrow x =$ ____
4. rate = _____
5. Expt 1: $7 \times 10^{-6} = k(0.001)^2(0.001) \rightarrow k =$ _____

EXAM TIP Always deduce orders with the **ratio method** above, choosing two experiments where only one concentration changes. Describing it in words ("when $[O_2]$ doubles, rate doubles") is easy to phrase wrongly, and fails when more than one concentration changes.

Volumes instead of concentrations: water is added to keep the _____, so [reactant] in the mixture ∝ volume of reactant used. Relative rate = 1/t.

10 Graphical Methods



- From a concentration–time graph: **linear** → zero order, **curve** → check the half-lives
- Rate–conc. for second order: plot rate against $[A]^2$ to get a straight line through the origin

10 Graphical Methods (continued)

10.1 Half-life

DEFINITION **Half-life, t½**: the time taken for the concentration of a reactant to fall to _____ of its initial value.

$$\text{First order: } t_{½} = \frac{\ln 2}{k}$$

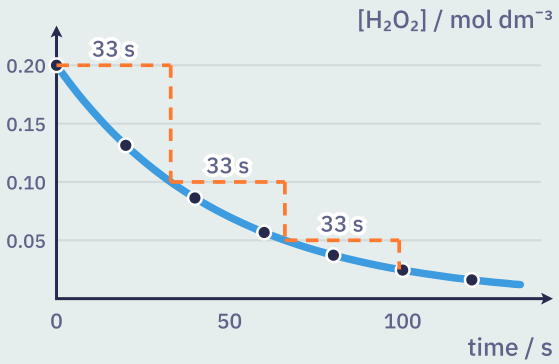
- Any point may be taken as the "initial" concentration, half-lives need not be consecutive
- Half-lives must be read from a _____ _____, not from the data table

time	[reactant]	[product]
0	100%	0%
1 t½	50%	_____
2 t½	25%	_____
3 t½	12.5%	_____

WORKED EXAMPLE The decomposition of hydrogen peroxide, $2H_2O_2 \rightarrow 2H_2O + O_2$, was followed over time. Use the graph to find the order with respect to H_2O_2 and the rate constant.

Rate decreases with a _____ _____ ∴ first order w.r.t. H_2O_2

rate = k[H_2O_2], $k = \frac{\ln 2}{33}$ = _____



11 Pseudo Order

B in large excess (≥ 10 × [A]): why is rate independent of [B]?

1. B is in large excess
2. → only a _____ of B is used up
3. → [B] remains approximately _____
4. → rate appears independent of [B]

rate = $k'[A]^{m}$, where k' = _____

Also applies to a solvent (e.g. H_2O in hydrolysis) or a catalyst: its order cannot be found.

WORKED EXAMPLE $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$ is run with CH_3Br in large excess (1.5 mol dm⁻³) and [OH^-] = 0.01 mol dm⁻³. The initial rate is 8.33×10^{-5} mol dm⁻³ min⁻¹. The [OH^-]–time graph has a constant half-life, and repeating with [CH_3Br] × 1.5 makes the initial rate 1.5 times faster. Find the rate equation and k.

1. **Continuous**: [OH^-]–time graph has a constant t½ → _____ order w.r.t. OH^-
2. **Initial rates**: $\frac{\text{rate 2}}{\text{rate 1}} = \frac{k(1.5 \times 1.5)^m}{k(1.5)^m}$ → $1.5 = 1.5^m$ → m = 1: first order w.r.t. CH_3Br
3. rate = k[CH_3Br][OH^-], so $8.33 \times 10^{-5} = k(1.5)(0.01)$
4. k = _____