8020 ENGLISH

Cambridge International AS & A Level Chemistry

Giáo trình luyện thi chuyên sâu

Song ngữ Anh–Việt

8020 ENGLISH

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Lời mở đầu · Foreword

Cuốn sách này thuộc bộ giáo trình luyện thi chương trình quốc tế của **8020 English (8020 Education)** — trung tâm luyện thi trọng điểm **IELTS · SAT · AP · IB · A-level · IGCSE** và săn học bổng du học. Toàn bộ nội dung được biên soạn bởi đội ngũ **Giáo sư · Tiến sĩ · Thạc sĩ** tốt nghiệp các trường top đầu thế giới, bám sát khung chương trình chính thức, trình bày đầy đủ lý thuyết, ví dụ mẫu, hình minh hoạ và hệ thống bài tập có lời giải chi tiết.

This book is part of the 8020 English international exam-prep series: complete English theory with Vietnamese explanations, worked examples, illustrations and fully-solved practice, aligned to the official framework.

Thành tích 8020 English

9.0 IELTS cao nhất	**1570** SAT cao nhất
5/5 AP — điểm tuyệt đối	**90/100** IB Diploma
100% GV $\geq$ 8.0 IELTS / 1500 SAT	**CMU** Tiến sĩ ĐH #1 Hoa Kỳ về CS

Đội ngũ tiêu biểu: Thầy Châu Cát Tường (Academic Head, ThS Western Sydney, top 1% IELTS 8.5) · TS Nguyễn Anh Huy (Carnegie Mellon, cựu kỹ sư Amazon) · TS Nguyễn Phước Trường (Toán, ĐH Klagenfurt) · cùng đội ngũ giảng viên SAT 1500–1600, IELTS 8.0–8.5.

Kết quả học viên — điểm thi thật: IELTS 8.0–9.0 · SAT 1550 / 1570 / 1590 · AP 5/5 (Calculus BC, Microeconomics) · IB 90/100 (Economics) · Duolingo 110 · PTE 90 · TOEFL 120. **Bảng vàng SAT:** Khánh Đăng 1510 · Thảo Nguyên 1520 · Tâm Anh 1530.

"Cuối cùng đã đậu vào trường top như mong muốn." — Phan Thị Thanh Hằng, IELTS Overall 8.5.

Cách dùng sách hiệu quả: mỗi Unit gồm (1) **Lý thuyết trọng tâm** tiếng Anh kèm **giải thích tiếng Việt**; (2) **Ví dụ mẫu** có lời giải; (3) **Hệ thống bài tập** kèm **lời giải chi tiết**. Hãy tự làm bài trước khi xem lời giải để đạt hiệu quả tối đa.

THÀNH TÍCH THỰC TẾ · 8020 ENGLISH

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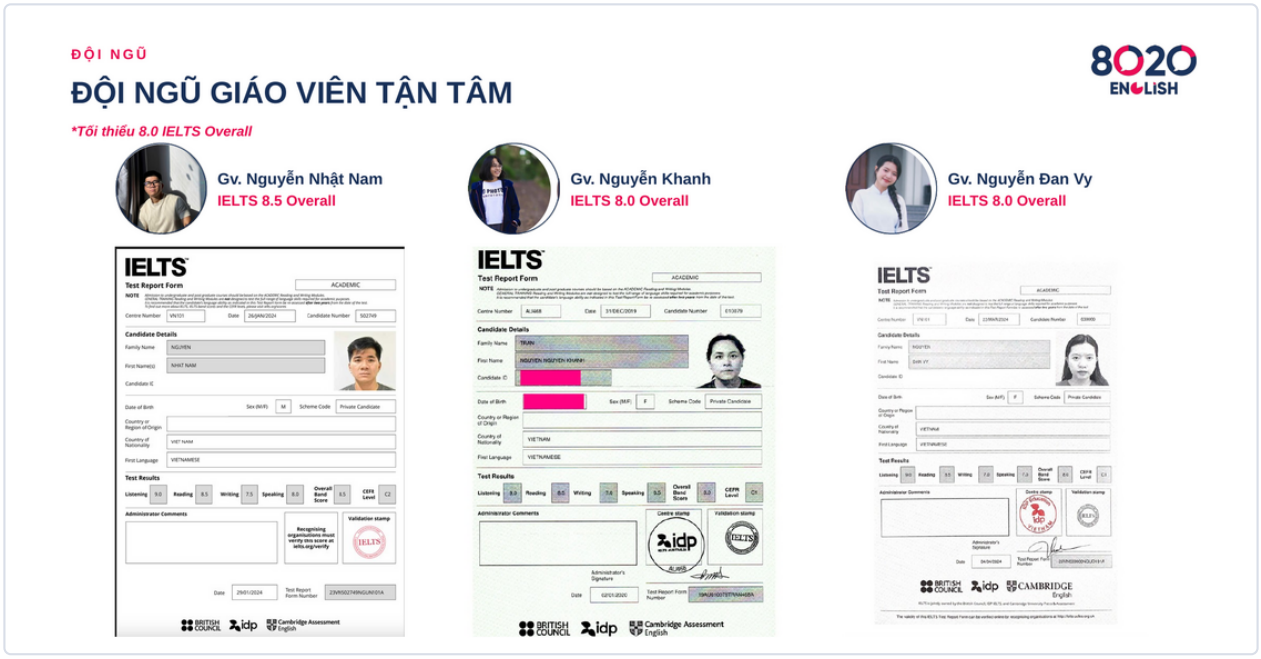
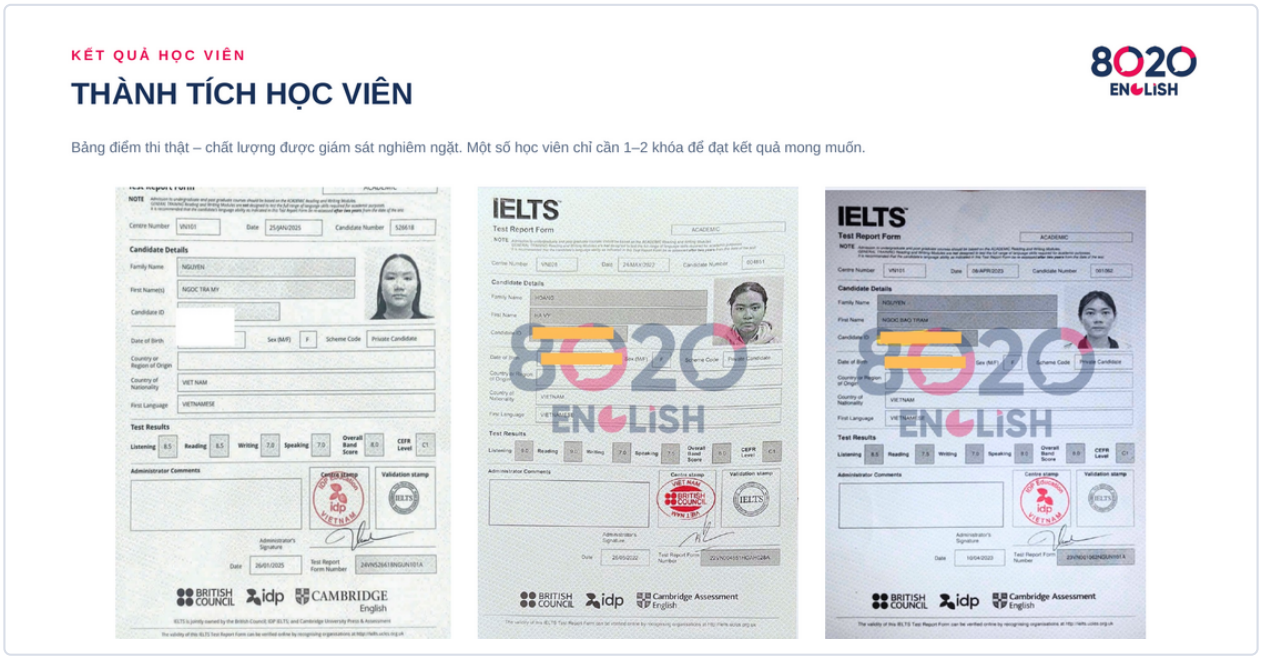


Giảng viên 8020 — IELTS 8.5 & 8.0 Overall (British Council · IDP · Cambridge)



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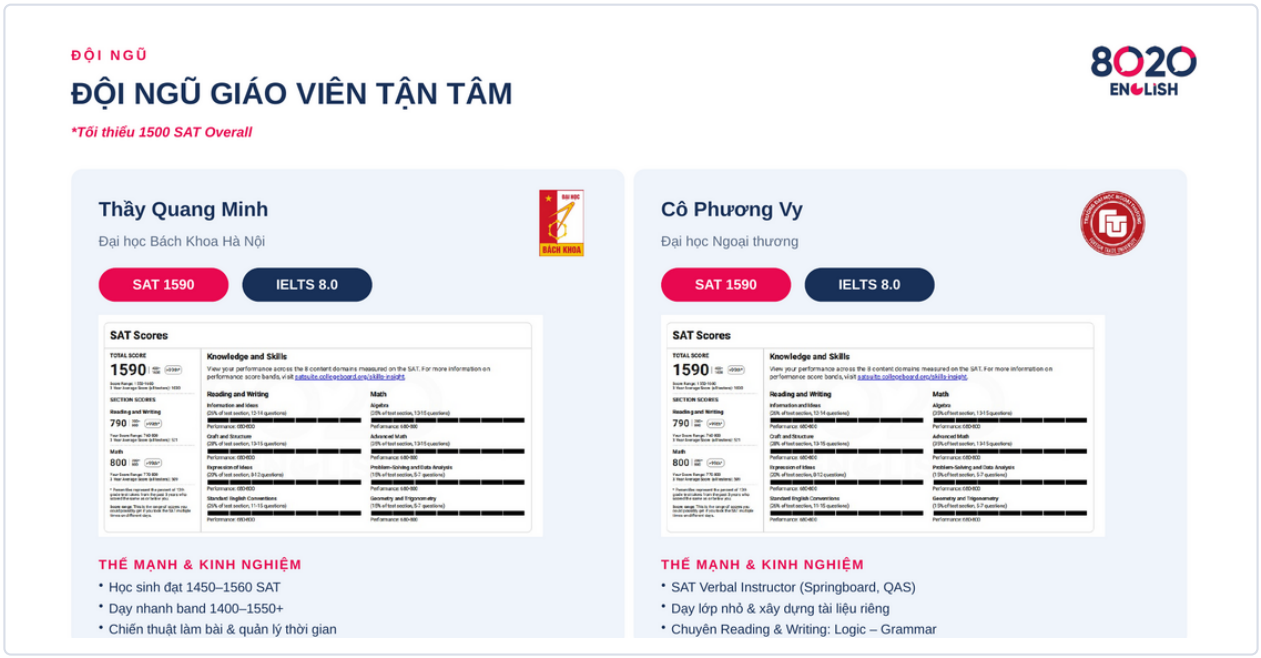

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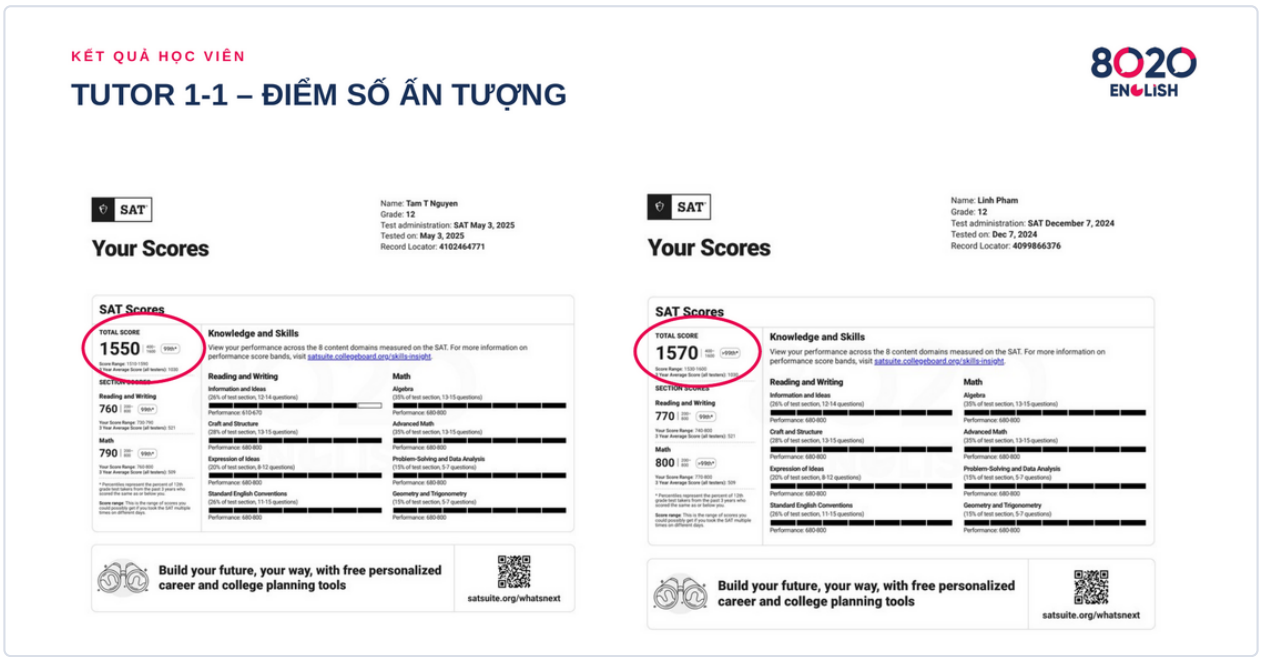

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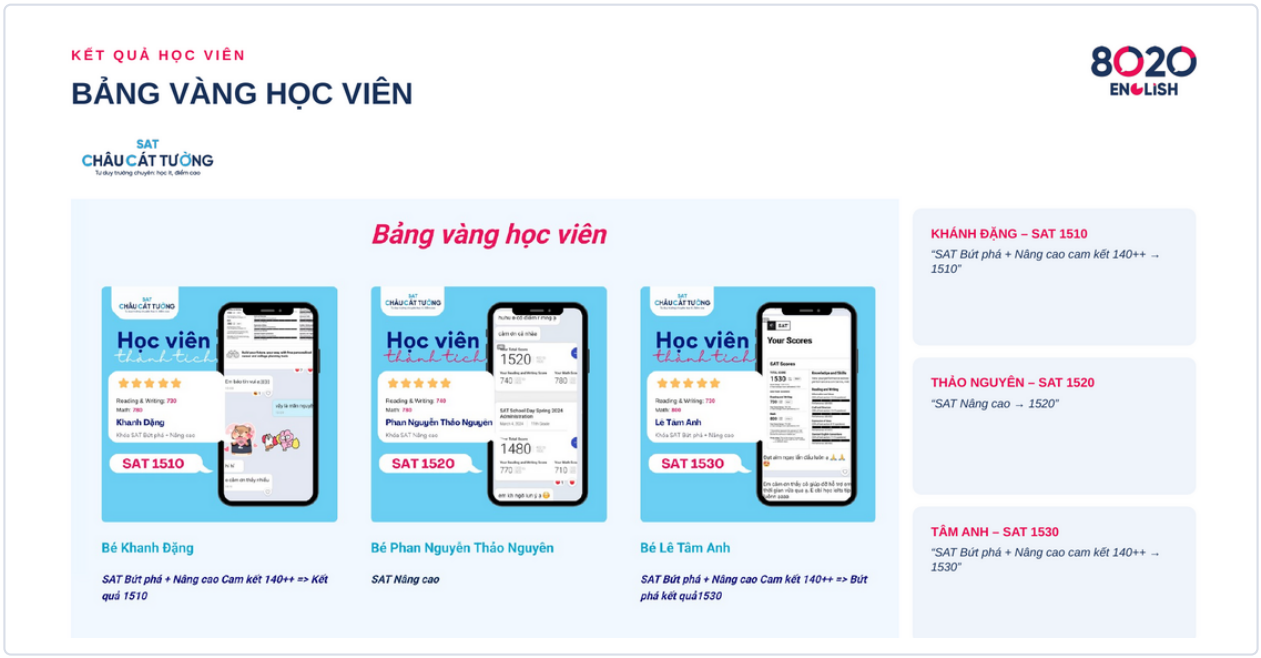
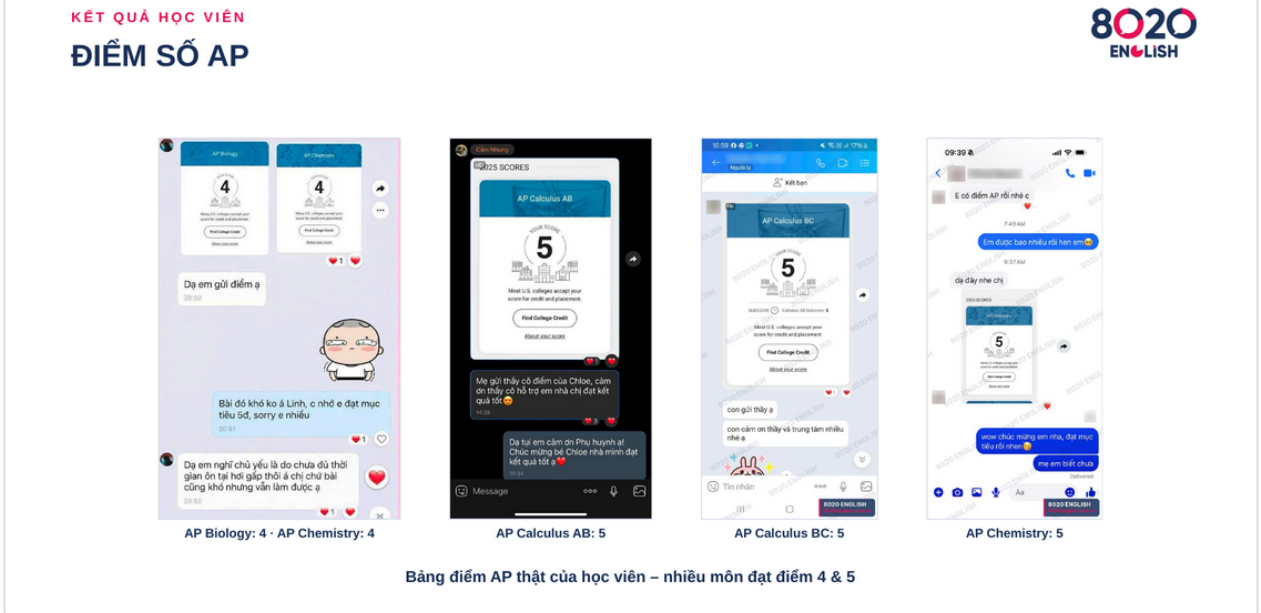


Bảng vàng SAT — Học viên đạt 1510 · 1520 · 1530



Điểm AP thật — Calculus AB/BC 5/5 · Biology & Chemistry 4–5 (College Board)

Mục lục • Contents

Atomic Structure

Mục tiêu Unit: Hạt hạ nguyên tử, đồng vị và khối phổ kế (mass spectrometer), cấu hình electron theo orbital s, p, d, hình dạng orbital, và xu hướng năng lượng ion hoá (ionisation energy) — nền tảng để hiểu toàn bộ chương trình 9701.

1.1 Sub-atomic particles and nuclide notation

An atom is built from three sub-atomic particles: **protons**, **neutrons** and **electrons**. Protons and neutrons occupy the tiny, dense, positively-charged **nucleus** at the centre of the atom; electrons occupy the much larger volume of space around the nucleus, arranged in shells, sub-shells and orbitals.

Particle	Relative mass	Actual mass (kg)	Relative charge (actual charge, C)
Proton	1	1.673×10^{-27}	$+1$ ($+1.60 \times 10^{-19}$)
Neutron	1	1.675×10^{-27}	0
Electron	$1/1836$ (≈ 0.00055)	9.11×10^{-31}	-1 (-1.60×10^{-19})

Table 1.1 — properties of the three fundamental sub-atomic particles.

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Ba hạt hạ nguyên tử: **proton** và **neutron** (khối lượng gần bằng nhau, nằm trong hạt nhân) và **electron** (khối lượng chỉ bằng khoảng $1/1836$ khối lượng proton, chuyển động quanh hạt nhân). Proton mang điện tích $+1$, electron mang điện tích -1, neutron trung hoà điện. Vì khối lượng electron quá nhỏ so với proton/neutron, khối lượng nguyên tử gần như tập trung hoàn toàn ở hạt nhân.

1.1.1 Nuclide notation, proton number and nucleon number

Every nuclide (a specific type of atom) is written as ${}^{A}_{Z}\mathrm{X}$, where X is the element symbol, Z is the **proton (atomic) number** — the number of protons in the nucleus, which defines the element and (in a neutral atom) equals the number of electrons — and A is the **nucleon (mass) number** — the total number of protons *and* neutrons in the nucleus. The number of neutrons is therefore always $A - Z$.

Đồng vị · Isotopes

Isotopes are atoms of the same element (identical proton number Z, so identical chemical behaviour) that have different numbers of neutrons, and therefore different nucleon numbers A and different masses. Because isotopes of an element have the same electron configuration, they show (almost) identical chemical properties, but their physical properties that depend on mass (e.g. density, rate of diffusion, radioactive stability) can differ.

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Đồng vị là các nguyên tử của **cùng một nguyên tố** (cùng số proton Z nên có tính chất hoá học gần như giống hệt nhau vì cấu hình electron giống nhau) nhưng khác nhau về số neutron, do

đó khác số khối A và khác khối lượng. Tính chất vật lý phụ thuộc khối lượng (khối lượng riêng, tốc độ khuếch tán,...) có thể khác nhau giữa các đồng vị.

Ví dụ mẫu · Counting particles in an ion

Determine the number of protons, neutrons and electrons in the ion $^{35}_{17}\text{Cl}^-$.
Proton number $Z = 17$, so there are **17 protons**. Nucleon number $A = 35$, so neutrons $= A - Z = 35 - 17 =$ **18 neutrons**. The atom is neutral with 17 electrons, but the $1-$ charge means one *extra* electron has been gained, giving $17 + 1 =$ **18 electrons**.

Relative isotopic mass is the mass of one atom of a specific isotope compared with $\frac{1}{12}$ of the mass of one atom of carbon-12. **Relative atomic mass,** A_r**,** is the *weighted mean* mass of one atom of an element (taking into account the relative abundance of all its naturally-occurring isotopes) compared with $\frac{1}{12}$ of the mass of one atom of carbon-12. Because A_r is a weighted average, it need not be a whole number (e.g. $A_r(\text{Cl}) = 35.5$), whereas relative isotopic mass is always very close to a whole number.

VN **GIẢI THÍCH TIẾNG VIỆT**

Khối lượng đồng vị tương đối là khối lượng của một nguyên tử của một đồng vị cụ thể so với $1/12$ khối lượng một nguyên tử carbon-12 — luôn gần một số nguyên. **Khối lượng nguyên tử tương đối** A_r là khối lượng **trung bình có trọng số** của một nguyên tử của nguyên tố đó (tính đến tỉ lệ phần trăm của tất cả đồng vị tự nhiên) — có thể không phải số nguyên (ví dụ $A_r(\text{Cl}) = 35.5$).

1.2 Mass spectrometry

A **mass spectrometer** measures the masses (strictly, the mass-to-charge ratios) of atoms, molecules or ions, and their relative abundances, producing a mass spectrum from which relative atomic and relative molecular masses can be calculated. A modern time-of-flight (TOF) mass spectrometer works in five stages.

Các giai đoạn trong khối phổ kế TOF

1. **Vaporisation:** the sample is turned into a gas (if it is not gaseous already) so that individual particles are free and separate.
2. **Ionisation:** the gaseous particles are converted into positive ions — for example, by *electron impact*, in which a high-energy electron beam from an electron gun knocks one electron out of each particle, $\text{X(g)} + \text{e}^- -> \text{X}^+\text{(g)} + 2\text{e}^-$; larger, less volatile molecules may instead be ionised by *electrospray ionisation*.
3. **Acceleration:** the positive ions are accelerated by an electric field (a set of charged plates) to a constant, known kinetic energy.
4. **Ion drift (time-of-flight):** the ions pass into a field-free flight tube (the drift region); ions with a smaller mass-to-charge ratio m/z travel faster and reach the detector first.
5. **Detection:** a detector at the far end of the tube records the arrival (and hence the relative abundance) of ions of each m/z value, producing the mass spectrum — a plot of relative abundance against m/z.

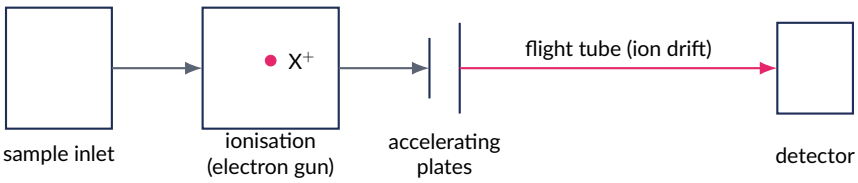

Figure 1.1 — schematic of a time-of-flight (TOF) mass spectrometer: vaporisation → ionisation → acceleration → ion drift → detection.

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Năm giai đoạn của khối phổ kế TOF: **hoá hơi** mẫu, **ion hoá** (thường bằng chùm electron bắn phá tạo ion dương X^+), **gia tốc** ion bằng điện trường đến cùng động năng, **bay tự do** trong ống bay (ion nhẹ hơn — m/z nhỏ hơn — bay nhanh hơn), và **phát hiện** tại đầu dò để vẽ phổ khối (độ phong phú tương đối theo m/z).

1.2.1 The physics of time-of-flight

During acceleration, every singly- or multiply-charged ion gains the *same* kinetic energy from the same accelerating voltage V: $E_k = zeV = \tfrac{1}{2}mv^2$, where z is the number of charges and e is the charge on an electron. Rearranging gives the ion's speed, $v = \sqrt{\dfrac{2zeV}{m}}$, and since the flight tube has a fixed length L, the time of flight is

$$t = \frac{L}{v} = L\sqrt{\frac{m}{2zeV}}.$$

For ions of the same charge z, $t \propto \sqrt{m}$ (equivalently $t \propto \sqrt{m/z}$ in general): **lighter ions (smaller m/z) arrive at the detector sooner.**

Ví dụ mẫu · Comparing times of flight

Two singly-charged ions have $m/z = 16$ and $m/z = 64$ respectively (a mass ratio of 4:1). The lighter ion takes $12.0\ \mu$s to reach the detector. Calculate the time taken by the heavier ion.

Since $t \propto \sqrt{m}$ for ions of equal charge,

$$\frac{t_{64}}{t_{16}} = \sqrt{\frac{64}{16}} = \sqrt{4} = 2.00 \implies t_{64} = 2.00 \times 12.0 = 24.0\ \mu\text{s}.$$

The heavier ion takes exactly twice as long, because its mass is four times greater and time of flight scales with $\sqrt{m}$, not m.

VN **GIẢI THÍCH TIẾNG VIỆT**

Vì mọi ion cùng điện tích được gia tốc đến **cùng động năng**, ion nào có khối lượng lớn hơn sẽ có tốc độ nhỏ hơn, nên thời gian bay t tỉ lệ với $\sqrt{m}$ (không phải tỉ lệ thuận với m). Ion nhẹ đến đầu dò trước, ion nặng đến sau.

Ví dụ mẫu · Ion velocity from an accelerating voltage

A singly-charged positive ion of mass 2.00×10^{-26} kg is accelerated through a potential difference of 5000 V. Calculate its velocity as it leaves the accelerating plates ($e = 1.60 \times 10^{-19}$ C).

$$E_k = zeV = (1)(1.60 \times 10^{-19})(5000) = 8.00 \times 10^{-16}\ \text{J}.$$

$$v = \sqrt{\frac{2E_k}{m}} = \sqrt{\frac{2 \times 8.00 \times 10^{-16}}{2.00 \times 10^{-26}}} = \sqrt{8.00 \times 10^{10}} = 2.83 \times 10^{5}\ \text{m s}^{-1}.$$

1.2.2 Calculating relative atomic mass from a mass spectrum

The mass spectrum of an element records the m/z value and relative abundance of every isotope present. Because each peak's height (or percentage) represents its abundance, the relative atomic mass is calculated as a **weighted mean**:

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

Ví dụ mẫu · A_r from a two-isotope spectrum

Chlorine has two naturally-occurring isotopes: ^{35}Cl (abundance 75.0%) and ^{37}Cl (abundance 25.0%). Calculate $A_r(\text{Cl})$.

$$A_r = \frac{(35 \times 75.0) + (37 \times 25.0)}{100} = \frac{2625 + 925}{100} = \frac{3550}{100} = 35.5.$$

Ví dụ mẫu · A_r from a three-isotope spectrum

Magnesium has three naturally-occurring isotopes: ^{24}Mg (79.0%), ^{25}Mg (10.0%) and ^{26}Mg (11.0%). Calculate $A_r(\text{Mg})$ to 3 significant figures.

$$A_r = \frac{(24 \times 79.0) + (25 \times 10.0) + (26 \times 11.0)}{100} = \frac{1896 + 250 + 286}{100} = \frac{2432}{100} = 24.32.$$

$A_r(\text{Mg}) = 24.3$ (3 s.f.) — consistent with the Periodic Table value of 24.3.

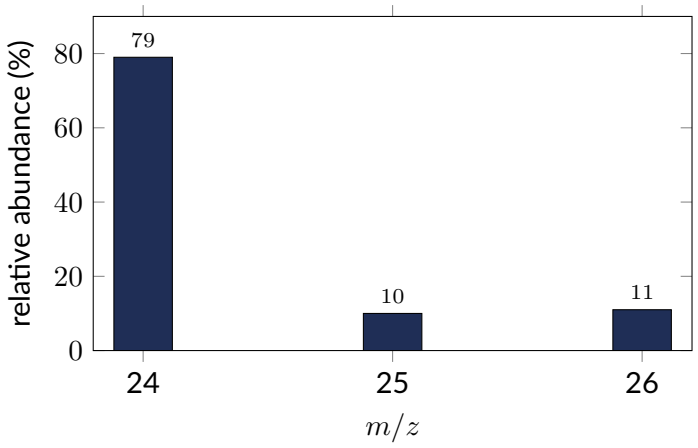

Figure 1.2 — mass spectrum of magnesium: three peaks at $m/z = 24, 25, 26$ with relative abundances $79.0\%, 10.0\%, 11.0\%$.

When calculating A_r from a spectrum, always *multiply each isotopic mass by its own abundance*, sum these products, then *divide by the total abundance* (100, or the sum of the relative peak heights if abundances are not already given as percentages). A common error is to simply average the isotopic masses without weighting by abundance.

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Công thức tính A_r là **trung bình có trọng số**: nhân khối lượng mỗi đồng vị với phần trăm (hoặc chiều cao pic) của nó, cộng lại rồi chia cho tổng (thường là 100). Lỗi thường gặp là lấy trung bình cộng đơn giản các khối lượng đồng vị mà không nhân với tỉ lệ phần trăm tương ứng.

1.3 Electron configuration and orbitals

Electrons occupy discrete **shells** (given by the principal quantum number $n = 1, 2, 3, \ldots$), which are divided into **sub-shells** (s, p, d, f), which are themselves divided into **orbitals** — regions of space where there is a high probability of finding an electron. Each orbital can hold a maximum of **two electrons**, which must have opposite spins.

Sub-shell	Number of orbitals	Max. electrons	Orbital shape
s	1	2	spherical
p	3	6	dumbbell (two lobes), three mutually perpendicular (p_x, p_y, p_z)
d	5	10	more complex (four have a four-lobed "cloverleaf" shape)
f	7	14	complex

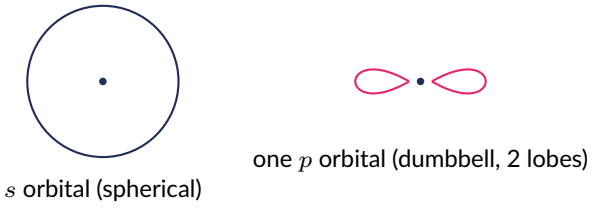

Figure 1.3 — an s orbital is a sphere centred on the nucleus; each p orbital has two lobes pointing in opposite directions along one axis (there are three perpendicular p orbitals per shell, from $n = 2$ onwards).

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Mỗi orbital chứa tối đa **2 electron** (spin ngược nhau). Orbital s có hình **cầu**; orbital p có hình **quả tạ** (2 thuỳ), có 3 orbital p vuông góc nhau (p_x, p_y, p_z) từ lớp $n = 2$ trở đi. Phân lớp d có 5 orbital (tối đa 10 electron), phân lớp f có 7 orbital (tối đa 14 electron).

Nguyên tắc điền electron

- **Aufbau principle:** orbitals are filled in order of increasing energy, from lowest to highest ($1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, \ldots$) — note that $4s$ is filled *before* $3d$, since $4s$ is (marginally) lower in energy in the build-up process.
- **Pauli exclusion principle:** no atomic orbital can hold more than two electrons, and if it holds two they must have opposite spins.
- **Hund's rule:** when filling a set of orbitals of equal energy (e.g. the three $2p$ orbitals), electrons occupy separate orbitals singly (with parallel spins) before any pairing occurs, since electrons in separate orbitals repel each other less than two electrons forced into the same orbital.

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Ba nguyên tắc điền electron: **Aufbau** (điền từ mức năng lượng thấp đến cao, lưu ý $4s$ điền trước $3d$); **Pauli** (mỗi orbital tối đa 2 electron, spin ngược chiều); **Hund** (điền mỗi electron riêng lẻ vào từng orbital cùng mức năng lượng trước khi ghép đôi, vì các electron ở orbital riêng đẩy

nhau ít hơn).

Ví dụ mẫu · Configuration of Fe and Fe^{3+}

Write the full electron configuration of an iron atom ($Z = 26$) and of the Fe^{3+} ion.
Filling orbitals in Aufbau order: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$ (26 electrons total) — usually written with the sub-shells grouped by shell: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$.
Forming Fe^{3+} removes three electrons. Electrons are always removed first from the *highest principal quantum number* sub-shell available — here the $4s$ sub-shell empties before any $3d$ electrons are removed (even though $4s$ filled before $3d$ during Aufbau build-up). So Fe loses both $4s$ electrons, then one $3d$ electron:

$$Fe^{3+}: \ 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 \quad (\text{i.e. } [Ar]3d^5).$$

The resulting $3d^5$ configuration is a half-filled sub-shell, which is relatively stable.

(!) Lỗi thường gặp: When removing electrons to form a transition-metal ion, always remove $4s$ electrons *before* $3d$ electrons, even though $4s$ was filled first when building up the neutral atom. Writing Fe^{3+} as $[Ar]3d^3 4s^2$ (removing $3d$ electrons instead) is one of the most common mistakes at this level.

Ví dụ mẫu · The Cr and Cu exceptions

Write the electron configurations of chromium ($Z = 24$) and copper ($Z = 29$), and explain why each differs from the pattern predicted by strict Aufbau filling.
Simple Aufbau filling predicts Cr : $[Ar]3d^4 4s^2$ and Cu : $[Ar]3d^9 4s^2$. The *actual* configurations are:

$$Cr: \ [Ar]3d^5 4s^1 \qquad Cu: \ [Ar]3d^{10} 4s^1.$$

In both cases, one electron is promoted from $4s$ into $3d$ so that the $3d$ sub-shell becomes exactly **half-filled** ($3d^5$, for Cr) or **completely filled** ($3d^{10}$, for Cu). A half-filled or fully-filled sub-shell has a more symmetrical, evenly-spread electron distribution, which minimises electron–electron repulsion and gives extra stabilisation (exchange energy) — the resulting configuration is lower in overall energy than the "expected" one, even though it leaves only one electron in the $4s$ sub-shell.

Ví dụ mẫu · Ions of the exceptional elements

Deduce the electron configurations of Cr^{3+}, Cu^{2+} and Zn^{2+}.
Cr^{3+}: Cr is $[Ar]3d^5 4s^1$; removing 3 electrons removes the single $4s$ electron first, then two $3d$ electrons: $Cr^{3+} = [Ar]3d^3$.
Cu^{2+}: Cu is $[Ar]3d^{10} 4s^1$; removing 2 electrons removes the $4s^1$ electron, then one $3d$ electron: $Cu^{2+} = [Ar]3d^9$ — note the stable $3d^{10}$ configuration of the atom is *not* preserved in the $2+$ ion.
Zn^{2+}: Zn is $[Ar]3d^{10} 4s^2$; removing both $4s$ electrons leaves $Zn^{2+} = [Ar]3d^{10}$, a fully-filled, stable configuration.

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Hai ngoại lệ kinh điển: Cr $=$ [Ar]3d^{5}4s^1 và Cu $=$ [Ar]3d^{10}4s^1 (thay vì $3d^4 4s^2$ và $3d^9 4s^2$ như dự đoán), vì cấu hình $3d$ bán bão hoà hoặc bão hoà hoàn toàn bền hơn. Khi tạo ion, electron $4s$ luôn bị mất trước $3d$ — vì vậy Cu^{2+} $=$ [Ar]3d^9 (không còn giữ được cấu hình $3d^{10}$ bền của nguyên tử Cu).

Ví dụ mẫu · Configuration practice across the s, p, d blocks

Write the full electron configurations of: (a) K ($Z = 19$); (b) S^{2-} ($Z = 16$); (c) Br ($Z = 35$); (d) Br$^-$.

(a) K : 1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^1, i.e. [Ar]4s^1.

(b) S^{2-} has $16 + 2 = 18$ electrons: 1s^{2}2s^{2}2p^{6}3s^{2}3p^6, i.e. [Ne]3s^{2}3p^6 — the same configuration as argon.

(c) Br has 35 electrons: 1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}3d^{10}4s^{2}4p^5, i.e. [Ar]3d^{10}4s^{2}4p^5.

(d) Br$^-$ gains one electron into the $4p$ sub-shell: [Ar]3d^{10}4s^{2}4p^6 — the same configuration as krypton.

VN **GIẢI THÍCH TIẾNG VIỆT**

Khi một ion có cấu hình electron giống hệt một khí hiếm (ví dụ S^{2-} và Br$^-$ ở trên), ion đó rất bền vì lớp vỏ ngoài cùng đã bão hoà hoàn toàn — đây là lý do các ion đơn giản của kim loại nhóm chính và phi kim thường có điện tích tương ứng với việc đạt cấu hình khí hiếm gần nhất.

1.4 Ionisation energy

The **first ionisation energy** (IE$_1$) of an element is the energy required to remove one electron from each atom in one mole of gaseous atoms, forming one mole of gaseous $1+$ ions:

$$\mathrm{M(g)} -> \mathrm{M^+(g)} + \mathrm{e^-} \qquad \mathrm{IE_1} > 0 \text{ (always endothermic)}.$$

The **second ionisation energy** (IE$_2$) removes a further mole of electrons from the resulting $1+$ ions: M$^+$(g) $->$ M^{2+}(g) + e$^-$, and so on for successive ionisation energies. Every successive ionisation energy is *larger* than the one before, because each electron is being removed from an ion of increasing positive charge — the remaining electrons are pulled in more strongly and are (on average) closer to the nucleus, so more energy is needed to remove the next one.

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Năng lượng ion hoá thứ nhất IE$_1$: năng lượng cần để tách 1 mol electron ra khỏi 1 mol nguyên tử khí, tạo ion $1+$. Luôn là quá trình **thu nhiệt**. Các năng lượng ion hoá liên tiếp luôn **tăng dần**, vì mỗi electron tiếp theo bị tách ra khỏi một ion có điện tích dương lớn hơn (lực hút hạt nhân mạnh hơn).

1.4.1 Successive ionisation energies reveal shell structure

Plotting the successive ionisation energies of an element (on a logarithmic scale, because the values span several orders of magnitude) reveals sudden, very large jumps. A large jump occurs whenever the *next* electron to be removed comes from a shell that is closer to the nucleus and no longer shielded by the shell(s) already removed. Counting how many electrons are removed *before* each large jump tells us how many electrons occupy each shell — direct experimental evidence for the shell structure of the atom.

Ví dụ mẫu · Successive ionisation energies of aluminium

The successive ionisation energies of aluminium ($Z = 13$, electron arrangement $2, 8, 3$) are (in kJ mol^{-1}): $577,\ 1817,\ 2745,\ 11577,\ 14842,\ 18379,\ 23326,\ 27465,\ 31853,\ 38473,\ 42647,\ 201266,\ 222316$. Identify where the two largest jumps occur and relate them to aluminium's electron arrangement.

The first large jump is between $\text{IE}_3 = 2745$ and $\text{IE}_4 = 11577$ (a factor of about 4.2): the first 3 electrons removed come from the outermost $n = 3$ shell (3 electrons: $3s^2 3p^1$); the 4th electron must come from the full, closer, less-shielded $n = 2$ shell. The second large jump is between $\text{IE}_{11} = 42647$ and $\text{IE}_{12} = 201266$ (a factor of about 4.7): electrons 4–11 (8 electrons) come from the $n = 2$ shell ($2s^2 2p^6$), and the 12th electron must come from the innermost $n = 1$ shell ($1s^2$). This $2, 8, 3$ pattern (3 electrons, then 8, then 2) exactly matches the electron arrangement of aluminium.

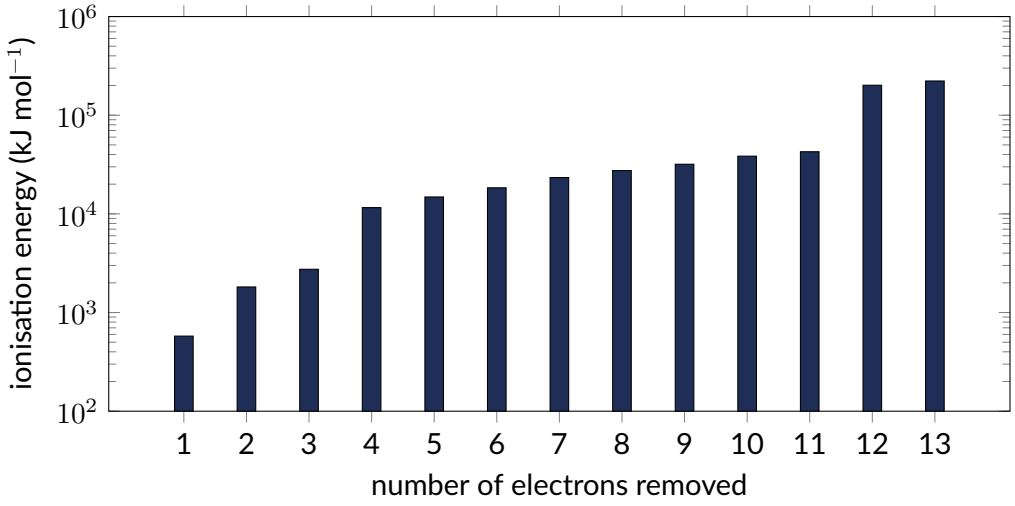

Figure 1.4 — the 13 successive ionisation energies of aluminium (log scale). The jumps after the 3rd and 11th electrons confirm the electron arrangement $2, 8, 3$.

VN **GIẢI THÍCH TIẾNG VIỆT**

Đồ thị năng lượng ion hoá liên tiếp (theo thang log) của nhôm cho thấy hai bước nhảy lớn: sau electron thứ 3 (chuyển từ lớp $n = 3$ sang lớp $n = 2$) và sau electron thứ 11 (chuyển từ lớp $n = 2$ sang lớp $n = 1$) — khớp đúng với cách sắp xếp electron $2, 8, 3$ của nhôm. Đây là bằng chứng thực nghiệm trực tiếp cho cấu trúc lớp vỏ electron.

Ví dụ mẫu · Successive ionisation energies of sodium

The successive ionisation energies of sodium ($Z = 11$, electron arrangement $2, 8, 1$) are (in kJ mol^{-1}): $496,\ 4560,\ 6910,\ 9540,\ 13400,\ 16600,\ 20120,\ 25490,\ 28930,\ 141360,\ 159080$. Explain the pattern of jumps.

There is already a substantial jump between $\text{IE}_1 = 496$ and $\text{IE}_2 = 4560$ (factor ≈ 9.2): sodium's single outer electron ($3s^1$) is removed first, and the second electron must come from the full $n = 2$ shell. Electrons 2–9 (8 electrons) are removed from the $n = 2$ shell, with a much larger jump between $\text{IE}_9 = 28930$ and $\text{IE}_{10} = 141360$ (factor ≈ 4.9) as the 10th electron is removed from the innermost, unshielded $n = 1$ shell. The pattern — 1 electron, then 8, then 2 — matches sodium's arrangement $2, 8, 1$.

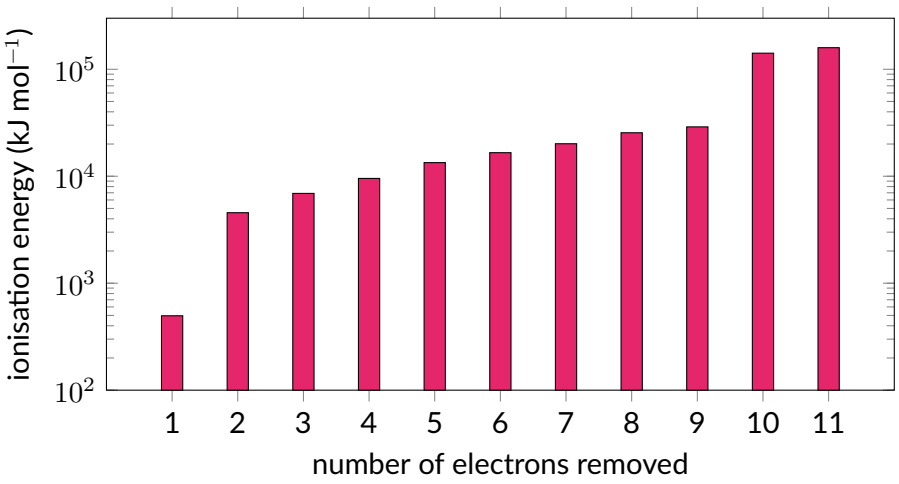

Figure 1.5 — the 11 successive ionisation energies of sodium. The dramatic jump after only 1 electron (Group 1 signature) and the second jump after 9 electrons confirm the arrangement $2, 8, 1$.

VN **GIẢI THÍCH TIẾNG VIỆT**

Natri có bước nhảy lớn ngay sau electron đầu tiên (vì chỉ có 1 electron lớp ngoài cùng $3s^1$ — đặc trưng của nhóm 1), rồi bước nhảy cực lớn sau electron thứ 9 (chuyển sang lớp $n = 1$ trong cùng). Số electron trước mỗi bước nhảy lớn = số electron trong mỗi lớp vỏ, xác nhận cách sắp xếp $2, 8, 1$.

Reading successive ionisation energy data: the number of electrons removed *before* a big jump equals the number of electrons in the *outermost occupied shell*, and — for a simple main-group element — this is also equal to the element's **group number** (using the 1–18 or 1–8 group convention as appropriate). This is one of the most important pieces of experimental evidence for electron shells.

1.4.2 Trends in first ionisation energy

Xu hướng năng lượng ion hoá thứ nhất

Across a period (left to right): IE_1 generally *increases*. Nuclear charge increases (more protons) while the outer electrons are added to the *same* shell, so shielding by inner shells stays roughly constant; the increasing nuclear charge pulls the outer electrons in more strongly and decreases atomic radius, so more energy is needed to remove an electron.

Down a group: IE_1 *decreases*. Each successive element has one more complete inner shell, so atomic radius increases substantially and shielding from inner-shell electrons increases; both effects outweigh the increased nuclear charge, so the outermost electron is held less strongly and is easier to remove.

VN **GIẢI THÍCH TIẾNG VIỆT**

Theo chu kỳ (trái sang phải): IE_1 **tăng dần** vì điện tích hạt nhân tăng trong khi electron vẫn ở cùng lớp vỏ (chắn electron gần như không đổi) → bán kính nguyên tử giảm, lực hút electron ngoài cùng mạnh hơn. Theo nhóm (trên xuống dưới): IE_1 **giảm dần** vì có thêm lớp vỏ trong đầy đủ → bán kính nguyên tử tăng và hiệu ứng chắn tăng, lấn át ảnh hưởng của điện tích hạt nhân tăng.

Ví dụ mẫu · The Group 13 dip: Mg vs Al

$IE_1(Mg) = 738\,kJ\,mol^{-1}$ but $IE_1(Al) = 577\,kJ\,mol^{-1}$ — lower, even though aluminium has one more proton. Explain this dip.

Magnesium's outermost electron is removed from a filled $3s^2$ sub-shell, whereas aluminium's outermost electron is removed from the single $3p^1$ electron. The $3p$ sub-shell is at slightly higher energy than $3s$, and the $3p$ electron is also (slightly) shielded by the inner $3s^2$ electrons, so it is easier to remove than one of the paired $3s^2$ electrons in magnesium — even though aluminium has one extra proton. This dip is direct evidence that the $n = 3$ shell is itself divided into $3s$ and $3p$ **sub-shells** of different energy.

Ví dụ mẫu · The Group 16 dip: P vs S

$IE_1(P) = 1012\,kJ\,mol^{-1}$ but $IE_1(S) = 1000\,kJ\,mol^{-1}$ — again lower, despite sulfur having one more proton. Explain.

Phosphorus has the configuration $3s^2 3p^3$ — the three $3p$ electrons occupy three separate p orbitals singly (Hund's rule), so there is no electron-pairing repulsion. Sulfur has $3s^2 3p^4$: the fourth $3p$ electron must pair up with one of the three already present, in the same orbital. The extra repulsion between two paired electrons sharing one orbital makes that electron easier to remove than a lone, unpaired electron would be — so IE_1 dips slightly, despite the increased nuclear charge.

Evidence for sub-shells from ionisation energy trends: the small dips in IE_1 at Group 13 (e.g. Mg → Al, or Be → B) and at Group 16 (e.g. P → S, or N → O) — superimposed on the overall increasing trend across a period — are experimental evidence that each shell (from $n = 2$ onward) is itself split into s and p sub-shells of different energy, and that electrons occupying the same orbital in a sub-shell repel each other more than electrons in separate orbitals.

VN **GIẢI THÍCH TIẾNG VIỆT**

Hai "vết lõm" nhỏ trong xu hướng tăng dần của IE_1 theo chu kỳ — tại nhóm 13 (do electron ngoài cùng ở phân lớp p năng lượng cao hơn, ít bị hút hơn phân lớp s đầy) và tại nhóm 16 (do electron thứ tư ở phân lớp p phải ghép đôi, chịu lực đẩy electron–electron) — là bằng chứng thực nghiệm cho sự tồn tại của **phân lớp con** (s, p) trong mỗi lớp vỏ.

(!) Lỗi thường gặp: Do not confuse the Group 13/16 dips (which occur when comparing *different elements* across a period, in the trend of IE_1) with the large jumps seen in a *successive* ionisation energy graph of a single element (which occur when moving between different principal shells, n). Both are genuine features of ionisation energy data, but they arise from different causes and appear on different types of graph.

1.5 Exam-style practice

Bài tập luyện tập

Which of the following correctly describes an isotope?

(A) An atom with a different number of protons from another atom of the same element

(B) An atom of the same element with a different number of neutrons

(C) An atom with a different number of electrons but the same number of protons

(D) A charged particle formed by loss or gain of electrons

Lời giải chi tiết

Isotopes have the *same* proton number (same element) but a *different* number of neutrons. **(B).**

Bài tập luyện tập

Determine the number of protons, neutrons and electrons present in the ion $^{24}_{12}\text{Mg}^{2+}$.

Lời giải chi tiết

Protons $= Z = 12$. Neutrons $= A - Z = 24 - 12 = 12$. A neutral Mg atom has 12 electrons; the $2+$ charge means 2 electrons have been *lost*, leaving $12 - 2 = 10$ electrons. **12 protons, 12 neutrons, 10 electrons.**

Bài tập luyện tập

Bromine has two naturally-occurring isotopes, ^{79}Br and ^{81}Br, present in equal abundance (50.0% each). Calculate $A_r(\text{Br})$.

Lời giải chi tiết

$$A_r = \frac{(79 \times 50.0) + (81 \times 50.0)}{100} = \frac{3950 + 4050}{100} = \frac{8000}{100} = \mathbf{80.0}.$$

Bài tập luyện tập

Silicon has three isotopes: ^{28}Si (92.2%), ^{29}Si (4.7%) and ^{30}Si (3.1%). Calculate $A_r(\text{Si})$ to 3 significant figures.

Lời giải chi tiết

$$A_r = \frac{(28 \times 92.2) + (29 \times 4.7) + (30 \times 3.1)}{100} = \frac{2581.6 + 136.3 + 93.0}{100} = \frac{2810.9}{100} = 28.109.$$

$A_r(\text{Si}) = \mathbf{28.1}$ (3 s.f.).

Bài tập luyện tập

Neon's mass spectrum shows peaks at $m/z = 20$ (abundance 90.5%), $m/z = 21$ (abundance 0.3%) and $m/z = 22$ (abundance 9.2%). Calculate $A_r(\text{Ne})$ to 3 significant figures.

Lời giải chi tiết

$$A_r = \frac{(20 \times 90.5) + (21 \times 0.3) + (22 \times 9.2)}{100} = \frac{1810.0 + 6.3 + 202.4}{100} = \frac{2018.7}{100} = 20.187.$$

$A_r(\text{Ne}) = \mathbf{20.2}$ (3 s.f.).

Bài tập luyện tập

In a TOF mass spectrometer, two singly-charged ions have $m/z = 25$ and $m/z = 100$. If the lighter ion takes $8.00\ \mu$s to reach the detector, calculate the time taken by the heavier ion.

Lời giải chi tiết

$t \propto \sqrt{m}$ for equal charge: $\frac{t_{100}}{t_{25}} = \sqrt{\frac{100}{25}} = \sqrt{4} = 2.00$. $t_{100} = 2.00 \times 8.00 =$ **16.0** μs.

Bài tập luyện tập

The successive ionisation energies (kJ mol^{-1}) of an unknown element are: $738,\ 1451,\ 7733,\ 10540,\ 13630,\ 18020,\ 21711$. Deduce the group of the Periodic Table to which this element belongs, giving your reasoning.

Lời giải chi tiết

There is a large jump between the 2nd ionisation energy (1451) and the 3rd (7733, a factor of ≈ 5.3), showing that only **2** electrons are removed from the outer shell before the next electron comes from a much closer, less-shielded inner shell. Two outer-shell electrons corresponds to **Group 2** (these are, in fact, the real successive ionisation energies of magnesium).

Bài tập luyện tập

Write the full electron configuration of a calcium atom ($Z = 20$) and of the Ca^{2+} ion.

Lời giải chi tiết

Ca: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$, i.e. $[Ar]4s^2$. Removing the two $4s$ electrons to form Ca^{2+} gives $[Ar]$ — the same (stable) configuration as argon.

Bài tập luyện tập

Deduce the electron configuration of Cr^{3+}, explaining which electrons are removed first.

Lời giải chi tiết

Chromium is $[Ar]3d^5 4s^1$ (an exception to simple Aufbau filling). To form Cr^{3+}, the single $4s^1$ electron is removed first, then two of the five $3d$ electrons: $Cr^{3+} = [Ar]3d^3$.

Bài tập luyện tập

Deduce the electron configuration of Cu^{2+}, and explain why it is *not* the same as the stable $3d^{10}$ arrangement found in atomic copper.

Lời giải chi tiết

Copper is $[Ar]3d^{10}4s^1$. Forming Cu^{2+} removes the $4s^1$ electron first, then one electron from the (previously full) $3d$ sub-shell: $Cu^{2+} = [Ar]3d^9$. The fully-filled $3d^{10}$ arrangement that stabilises the neutral atom is broken once a second electron must be removed, since only one electron

remained outside the $3d$ sub-shell.

Bài tập luyện tập

Deduce the electron configuration of the sulfide ion, S^{2-} ($Z = 16$), and name the noble gas whose configuration it matches.

Lời giải chi tiết

S^{2-} has $16 + 2 = 18$ electrons: $1s^2 2s^2 2p^6 3s^2 3p^6$, i.e. $[Ne]3s^2 3p^6$ — the same configuration as **argon**.

Bài tập luyện tập

State the maximum number of electrons that can occupy (a) a single d orbital, (b) the entire $3d$ sub-shell, and (c) the whole $n = 3$ shell.

Lời giải chi tiết

(a) A single orbital holds a maximum of **2** electrons (Pauli exclusion). (b) The $3d$ sub-shell has 5 orbitals, so it holds a maximum of $5 \times 2 = \mathbf{10}$ electrons. (c) The $n = 3$ shell comprises $3s$ (2), $3p$ (6) and $3d$ (10), giving a maximum of $2 + 6 + 10 = \mathbf{18}$ electrons.

Bài tập luyện tập

Which shape correctly describes an s orbital and a p orbital respectively?

(A) Spherical; dumbbell (two lobes)
(B) Dumbbell; spherical
(C) Both spherical
(D) Both dumbbell-shaped

Lời giải chi tiết

An s orbital is spherical (symmetric in all directions about the nucleus); a p orbital has two lobes pointing in opposite directions along one axis. **(A)**.

Bài tập luyện tập

Write a balanced equation, including state symbols, defining the first ionisation energy of magnesium.

Lời giải chi tiết

$Mg(g) -> Mg^+(g) + e^-$. This equation must show one mole of *gaseous* atoms forming one mole of gaseous $1+$ ions plus one mole of electrons.

Bài tập luyện tập

Explain, in terms of nuclear charge and electron shielding, why the second ionisation energy of any element is always greater than its first ionisation energy.

Lời giải chi tiết

Removing the first electron leaves a $1+$ ion with one fewer electron but the same number of protons, so the remaining electrons experience a greater effective nuclear charge (less electron–electron repulsion to offset the nuclear attraction) and are pulled in closer to the nucleus. Consequently, more energy is required to remove the next electron, so $\mathrm{IE}_2 > \mathrm{IE}_1$ for every element.

Bài tập luyện tập

Explain why the first ionisation energy of potassium is lower than that of sodium.

Lời giải chi tiết

Potassium's outermost electron is in the $n = 4$ shell, one shell further from the nucleus than sodium's outermost ($n = 3$) electron, and is shielded by an additional complete inner shell of electrons. Both the larger atomic radius and the increased shielding outweigh potassium's larger nuclear charge, so its outermost electron is held less strongly and is removed more easily: $\mathrm{IE}_1(\mathrm{K}) < \mathrm{IE}_1(\mathrm{Na})$.

Bài tập luyện tập

Explain why the first ionisation energy generally increases from sodium to argon across Period 3.

Lời giải chi tiết

Across Period 3, each successive element has one more proton (increasing nuclear charge) while electrons are added to the *same* outer shell ($n = 3$), so shielding by inner-shell electrons stays roughly constant. The increasing nuclear charge, largely unshielded by additional inner electrons, pulls the outer electrons in more strongly and reduces atomic radius, so progressively more energy is required to remove the outermost electron.

Bài tập luyện tập

The first ionisation energy of beryllium ($899\,\mathrm{kJ\,mol^{-1}}$) is higher than that of boron ($801\,\mathrm{kJ\,mol^{-1}}$), even though boron has one more proton. Explain this observation.

Lời giải chi tiết

Beryllium's outermost electron is removed from the filled $2s^2$ sub-shell, while boron's outermost electron is the single $2p^1$ electron. The $2p$ sub-shell is at higher energy than $2s$ and is slightly shielded by the inner $2s^2$ electrons, so boron's $2p^1$ electron is easier to remove than one of beryllium's paired $2s^2$ electrons — despite boron's greater nuclear charge. This Group 13 dip is evidence for the existence of s and p sub-shells.

Bài tập luyện tập

The first ionisation energy of nitrogen ($1402\,\mathrm{kJ\,mol^{-1}}$) is higher than that of oxygen ($1314\,\mathrm{kJ\,mol^{-1}}$), even though oxygen has one more proton. Explain this observation.

Lời giải chi tiết

Nitrogen has the configuration $2s^2 2p^3$, with each of the three $2p$ orbitals occupied singly (Hund's rule) — no electron pairing, so no extra repulsion. Oxygen has $2s^2 2p^4$: the fourth $2p$ electron must pair up in an orbital that already contains one electron. The additional electron–electron repulsion between this paired electron makes it easier to remove than a singly-occupied electron, so $\text{IE}_1(\text{O})$ dips below $\text{IE}_1(\text{N})$ despite oxygen's larger nuclear charge. This Group 16 dip is further evidence for sub-shell structure.

Bài tập luyện tập

Which particle has a mass that is negligible compared with the mass of a proton or neutron?

(A) Proton
(B) Neutron
(C) Electron
(D) Positron

Lời giải chi tiết

The electron has a relative mass of only about $1/1836$ that of a proton, so it is considered to have negligible mass compared with protons and neutrons. **(C)**.

Bài tập luyện tập

Explain the difference between relative isotopic mass and relative atomic mass, and state which of the two is essentially always a whole number.

Lời giải chi tiết

Relative isotopic mass is the mass of one atom of one specific isotope compared with $1/12$ of the mass of a carbon-12 atom — since it refers to a single isotope, it is always very close to a whole number. **Relative atomic mass,** A_r, is the weighted mean mass of an atom of the element, averaged over all its naturally-occurring isotopes according to their abundances — because it is a weighted average, it is often not a whole number (e.g. $A_r(\text{Cl}) = 35.5$). **Relative isotopic mass** is (essentially) always a whole number.

Bài tập luyện tập

State the number of electrons present in the ion Fe^{2+} ($Z = 26$), and write its electron configuration.

Lời giải chi tiết

Neutral Fe has 26 electrons; Fe^{2+} has lost 2 electrons, leaving $26 - 2 =$ **24** electrons. Fe is $[\text{Ar}]3d^6 4s^2$; removing the two $4s$ electrons (always removed before $3d$) gives $Fe^{2+} = [\text{Ar}]3d^6$.

Bài tập luyện tập

In the ionisation of gaseous fluorine atoms, would you expect $\text{IE}_1(\text{F})$ to be higher or lower than $\text{IE}_1(\text{O})$? Justify your answer using nuclear charge and shielding.

Lời giải chi tiết

$\mathrm{IE}_1(\mathrm{F})$ is **higher** than $\mathrm{IE}_1(\mathrm{O})$. Fluorine has one more proton than oxygen, and its outermost electron is removed from the same $n = 2$ shell (same shielding from inner electrons), so the extra nuclear charge is felt directly by the outer electrons, pulling them in more strongly and raising the ionisation energy. (This continues the general period trend; fluorine's $2p^5$ configuration, with two paired and one unpaired orbital, does not introduce a further dip.)

Bài tập luyện tập

A student accelerates two ions, X^+ (mass m) and X^{2+} (mass m, same ion but doubly ionised), through the same potential difference V in a TOF mass spectrometer. Which ion reaches the detector first, and why?

Lời giải chi tiết

Kinetic energy gained is $E_k = zeV$, so the doubly-charged ion X^{2+} ($z = 2$) gains *twice* the kinetic energy of X^+ ($z = 1$) for the same accelerating voltage. Since both ions have the same mass m, the ion with greater kinetic energy has the greater speed ($v = \sqrt{2E_k/m}$), so X^{2+} travels faster and reaches the detector **first**.

Atoms, Molecules & Stoichiometry

Mục tiêu Unit: Khái niệm mol, khối lượng mol, công thức đơn giản nhất/phân tử, nồng độ dung dịch và chuẩn độ, phương trình khí lý tưởng, thể tích mol ở r.t.p., hiệu suất phản ứng và kinh tế nguyên tử — bộ công cụ tính toán dùng xuyên suốt cả chương trình.

2.1 The mole, molar mass and relative masses

The **mole (mol)** is the SI unit for amount of substance: one mole of any particle (atoms, molecules, ions, electrons, ...) contains exactly the same number of particles as there are atoms in exactly $12\,\text{g}$ of carbon-12. This number is the **Avogadro constant**, $N_A = 6.02 \times 10^{23}\ \text{mol}^{-1}$.

$$n = \frac{m}{M} \qquad \text{and} \qquad n = \frac{N}{N_A},$$

where n is the amount in moles, m is the mass (g), M is the molar mass (g mol^{-1}, numerically equal to A_r or M_r), and N is the number of particles.

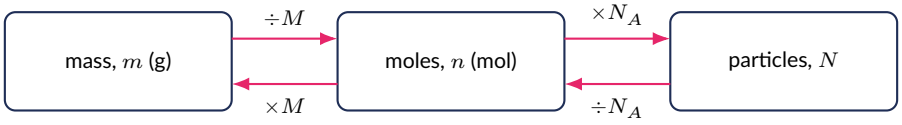

Figure 2.1 — the "mole bridge": moles connect a measurable mass to a countable number of particles.

VN **GIẢI THÍCH TIẾNG VIỆT**

Mol là "cầu nối" giữa **khối lượng** (đo được bằng cân) và **số hạt** (đếm được về mặt lý thuyết): $n = m/M$ và $n = N/N_A$ với $N_A = 6.02 \times 10^{23}\ \text{mol}^{-1}$. Khối lượng mol M có cùng giá trị số với A_r (nguyên tử) hoặc M_r (phân tử/công thức), chỉ khác đơn vị (g mol^{-1} thay vì không đơn vị).

Relative molecular mass, M_r (for simple molecules) or **relative formula mass** (for ionic/giant compounds) is the sum of the relative atomic masses of all the atoms shown in the molecular or empirical formula. For example, $M_r(\text{H}_2\text{SO}_4) = 2(1.0) + 32.1 + 4(16.0) = 98.1$.

Ví dụ mẫu · Basic mole–particle conversions

Calculate the number of molecules present in $8.80\,\text{g}$ of carbon dioxide, CO_2 ($M_r = 44.0$).

$$n(\text{CO}_2) = \frac{m}{M} = \frac{8.80}{44.0} = 0.200\,\text{mol}.$$

$$N = n \times N_A = 0.200 \times 6.02 \times 10^{23} = 1.20 \times 10^{23}\ \text{molecules (3 s.f.)}.$$

2.2 Empirical and molecular formulae

The **empirical formula** of a compound shows the simplest whole-number ratio of atoms of each element present. The **molecular formula** shows the actual number of atoms of each element in one molecule, and is always a whole-number multiple of the empirical formula: molecular formula $=$ $(\text{empirical formula})_x$, where $x = M_r(\text{molecular})/M_r(\text{empirical})$.

Ví dụ mẫu · Empirical/molecular formula from combustion data

A sample of a gaseous hydrocarbon of mass $0.210\,\text{g}$ is burned completely in excess oxygen, producing $0.660\,\text{g}$ of CO_2 and $0.270\,\text{g}$ of H_2O. Given that $M_r(\text{hydrocarbon}) = 42.0$, find its molecular formula.

Moles of C (from CO_2, $M_r = 44.0$): $n(CO_2) = 0.660/44.0 = 0.0150\,\text{mol} \Rightarrow n(C) = 0.0150\,\text{mol}$.
Moles of H (from H_2O, $M_r = 18.0$): $n(H_2O) = 0.270/18.0 = 0.0150\,\text{mol} \Rightarrow n(H) = 2\times0.0150 = 0.0300\,\text{mol}$.
Check: mass of C + mass of H $= (0.0150 \times 12.0) + (0.0300 \times 1.00) = 0.180 + 0.030 = 0.210\,\text{g}$, exactly equal to the original sample mass — confirming the compound contains *only* C and H (no oxygen).
Ratio C:H $= 0.0150 : 0.0300 = 1 : 2$, so the empirical formula is CH_2 ($M_r = 14.0$). Since $42.0/14.0 = 3$, the molecular formula is C_3H_6 (propene).

VN **GIẢI THÍCH TIẾNG VIỆT**
Phương pháp đốt cháy: tính số mol C từ khối lượng CO_2 sinh ra, số mol H từ khối lượng H_2O sinh ra (nhân đôi vì mỗi phân tử H_2O có 2 nguyên tử H). Nếu tổng khối lượng C và H tính được bằng đúng khối lượng mẫu ban đầu, hợp chất chỉ chứa C và H (hydrocarbon thuần tuý). Công thức phân tử $=$ (công thức đơn giản nhất)$_x$ với $x = M_r(\text{phân tử})/M_r(\text{đơn giản nhất})$.

Ví dụ mẫu · Empirical/molecular formula from % composition (3 elements)

A compound is found by analysis to contain 40.9% carbon, 4.55% hydrogen, with the remainder oxygen. Its $M_r = 176$. Determine its molecular formula.
$\%O = 100 - 40.9 - 4.55 = 54.55\% \approx 54.5\%$ (oxygen found "by difference").
Assume $100\,\text{g}$ of compound, so the percentages are also masses in grams:

$$n(C) = \frac{40.9}{12.0} = 3.408, \qquad n(H) = \frac{4.55}{1.00} = 4.55, \qquad n(O) = \frac{54.5}{16.0} = 3.406.$$

Divide by the smallest value (3.406): $C : 1.000,\ H : 1.336,\ O : 1.000$. Multiplying by 3 to clear the fraction gives the whole-number ratio $C : H : O = 3 : 4 : 3$, so the empirical formula is $C_3H_4O_3$ ($M_r = 3(12.0) + 4(1.00) + 3(16.0) = 88.0$).
Since $176/88.0 = 2$, the molecular formula is $C_6H_8O_6$ — ascorbic acid (vitamin C).

When a ratio does not come out to whole numbers directly, look for a simple fraction close to the decimal obtained (e.g. $x.33 \approx x\frac{1}{3}$, $x.5 = x\frac{1}{2}$, $x.25 = x\frac{1}{4}$) and multiply every ratio by the appropriate small whole number (3, 2, or 4 respectively) to clear it.

VN **GIẢI THÍCH TIẾNG VIỆT**
Khi tỉ lệ mol không ra số nguyên ngay (ví dụ $1.336 \approx 1\frac{1}{3}$), hãy nhân toàn bộ tỉ lệ với mẫu số phù hợp (ở đây nhân 3) để được tỉ lệ số nguyên tối giản. Nguyên tố "còn lại" (thường là oxy) được tính **bằng hiệu số** (100% trừ tổng các nguyên tố đã cho).

(!) Lỗi thường gặp: A very common error is forgetting to divide the mass of hydrogen obtained from combustion data by its own atomic mass of 1.00 (since $M_r(\mathrm{H}) = 1.00$, moles of H equal the mass of H directly) — or forgetting to double the moles of water to get moles of H. Always write out $n(\mathrm{H}) = 2 \times n(\mathrm{H_2O})$ explicitly to avoid this slip.

2.3 Solution concentration and volumetric titrations

The concentration of a solution is usually expressed in mol dm^{-3} (molarity):

$$c = \frac{n}{V} \qquad (V \text{ in dm}^3;\ 1\ \text{dm}^3 = 1000\ \text{cm}^3).$$

In a titration, at the equivalence point the moles of acid and base reacted are related by the stoichiometric ratio of the balanced equation.

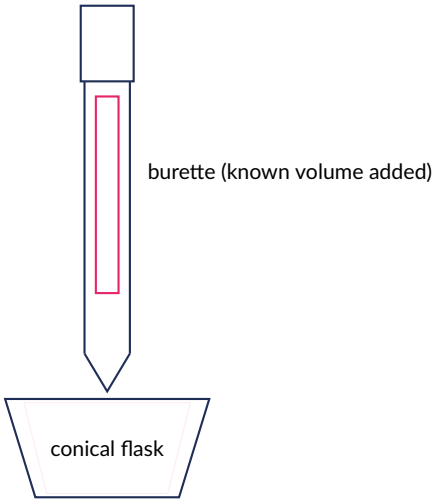

Figure 2.2 — titration apparatus: a solution of accurately known concentration is added from a burette to a measured volume of the other solution in a conical flask, until the indicator shows the equivalence point.

Ví dụ mẫu · Titration: sodium carbonate against hydrochloric acid

$25.0\ \text{cm}^3$ of $0.0500\ \text{mol dm}^{-3}$ $\mathrm{Na_2CO_3}$ solution requires $23.60\ \text{cm}^3$ of dilute hydrochloric acid for complete neutralisation:

$$\mathrm{Na_2CO_3 + 2HCl -> 2NaCl + H_2O + CO_2}.$$

Calculate the concentration of the hydrochloric acid.

$$n(\mathrm{Na_2CO_3}) = 0.0250\ \text{dm}^3 \times 0.0500\ \text{mol dm}^{-3} = 1.25 \times 10^{-3}\ \text{mol}.$$

From the equation, $n(\mathrm{HCl}) = 2 \times n(\mathrm{Na_2CO_3}) = 2.50 \times 10^{-3}$ mol.

$$c(\mathrm{HCl}) = \frac{n}{V} = \frac{2.50 \times 10^{-3}}{0.02360} = 0.1059 \approx \mathbf{0.106}\ \text{mol dm}^{-3}\ (3\ \text{s.f.}).$$

VN GIẢI THÍCH TIẾNG VIỆT

Chuẩn độ: dùng phương trình cân bằng để tìm tỉ lệ mol giữa hai chất phản ứng tại điểm tương đương. Luôn đổi thể tích sang dm^3 ($\div 1000$ từ cm^3) trước khi dùng $c = n/V$.

Ví dụ mẫu · Back-titration: analysing an antacid tablet

A 0.500 g antacid tablet (assume it contains only $CaCO_3$ and inert impurities) is crushed and added to 50.0 cm^3 of 0.200 mol dm^{-3} HCl — a known *excess*:

$$CaCO_3 + 2HCl -> CaCl_2 + H_2O + CO_2.$$

The excess (unreacted) acid requires 15.0 cm^3 of 0.100 mol dm^{-3} NaOH for neutralisation ($HCl + NaOH -> NaCl + H_2O$). Calculate the percentage of $CaCO_3$ in the tablet ($M_r(CaCO_3) = 100.1$).

Total HCl added: $n = 0.0500 \times 0.200 = 1.00 \times 10^{-2}$ mol.

Excess HCl (equal to moles of NaOH used, 1:1 ratio): $n = 0.0150 \times 0.100 = 1.50 \times 10^{-3}$ mol.

HCl that reacted with $CaCO_3$: $1.00 \times 10^{-2} - 1.50 \times 10^{-3} = 8.50 \times 10^{-3}$ mol.

$n(CaCO_3) = \dfrac{8.50 \times 10^{-3}}{2} = 4.25 \times 10^{-3}$ mol (2 mol HCl per mol $CaCO_3$).

$m(CaCO_3) = 4.25 \times 10^{-3} \times 100.1 = 0.4254$ g.

$$\%CaCO_3 = \frac{0.4254}{0.500} \times 100 = \textbf{85.1\%}\ (3\text{ s.f.}).$$

Chuẩn độ ngược · Back-titration

A **back-titration** is used when a substance cannot be titrated directly (for example, an insoluble solid, or a reaction that is too slow or has no sharp indicator colour change). A known *excess* of one reagent is added to react completely with the sample; the amount of that reagent left over (*unreacted*) is then found by titrating it against a second, standard solution. Subtracting the "leftover" moles from the total moles originally added gives the moles that reacted with the sample.

VN **GIẢI THÍCH TIẾNG VIỆT**

Chuẩn độ ngược dùng khi không thể chuẩn độ trực tiếp (chất rắn không tan, phản ứng chậm, không có điểm dừng rõ). Thêm **dư** một thuốc thử đã biết chính xác lượng, để nó phản ứng hết với mẫu; sau đó chuẩn độ lượng thuốc thử **còn dư** bằng một dung dịch chuẩn thứ hai. Lượng đã phản ứng với mẫu = tổng lượng ban đầu − lượng dư đo được.

Ví dụ mẫu · Serial dilution

A stock solution of $CuSO_4$ has concentration 2.00 mol dm^{-3}. A student takes 10.0 cm^3 of this stock and dilutes it to 100 cm^3 (dilution A). She then takes 10.0 cm^3 of dilution A and dilutes it to 250 cm^3 (dilution B). Calculate the concentration of dilution B.

Using $c_1V_1 = c_2V_2$ (moles are conserved on dilution):

Dilution A: $2.00 \times 10.0 = c_A \times 100 \Rightarrow c_A = \dfrac{20.0}{100} = 0.200$ mol dm^{-3}.

Dilution B: $0.200 \times 10.0 = c_B \times 250 \Rightarrow c_B = \dfrac{2.00}{250} = \textbf{8.00} \times \textbf{10}^{-3}$ mol dm^{-3}.

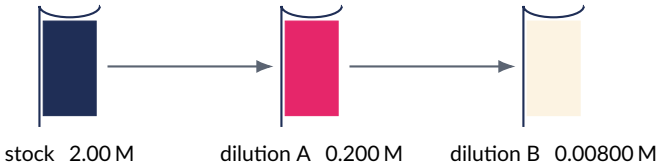

Figure 2.3 — serial dilution: each successive dilution uses $c_1V_1 = c_2V_2$, so concentration falls sharply after each step.

For any dilution (with no reaction occurring), the number of moles of solute is unchanged, so $c_1V_1 = c_2V_2$ (as long as V_1 and V_2 are expressed in the same units). Repeated (serial) dilutions simply apply this formula step by step.

VN **GIẢI THÍCH TIẾNG VIỆT**

Pha loãng bậc thang (serial dilution): số mol chất tan không đổi qua mỗi lần pha loãng, áp dụng $c_1V_1 = c_2V_2$ liên tiếp cho từng bước. Nồng độ giảm rất nhanh qua vài bước pha loãng liên tiếp.

2.4 The ideal gas equation and molar gas volume

For an ideal gas, pressure p, volume V, amount n and absolute (kelvin) temperature T are related by:

$$pV = nRT, \qquad R = 8.31\ \text{J K}^{-1}\ \text{mol}^{-1}.$$

Consistent SI units must be used: p in Pa, V in m^3, T in K ($T(\text{K}) = \theta(^\circ\text{C}) + 273$).

(!) **Lỗi thường gặp:** Temperature must always be in **kelvin** in $pV = nRT$ — never Celsius. Volumes in cm^3 must be converted to m^3 ($\div 10^6$), and pressures in kPa must be converted to Pa ($\times 1000$), before substituting into the equation.

At **room temperature and pressure (rtp)** — taken as $25\,^\circ$C and 100 kPa — one mole of any gas occupies a **molar gas volume** of $24.0\ \text{dm}^3$ ($24\,000\ \text{cm}^3$). This is a direct consequence of Avogadro's Law (below) and provides a quick shortcut: $n = V/24.0$ (with V in dm^3), avoiding the need for $pV = nRT$ when conditions are exactly rtp.

VN **GIẢI THÍCH TIẾNG VIỆT**

Phương trình khí lý tưởng $pV = nRT$ với $R = 8.31\ \text{J K}^{-1}\text{mol}^{-1}$, luôn dùng đơn vị chuẩn SI (Pa, m^3, K). Ở điều kiện phòng r.t.p. ($25\,^\circ$C, 100 kPa), 1 mol khí bất kỳ chiếm thể tích $24.0\ \text{dm}^3$ — công thức tắt $n = V/24.0$ chỉ áp dụng đúng ở điều kiện r.t.p.

Ví dụ mẫu · Volume of gas from thermal decomposition

2.00 g of calcium carbonate ($M_r = 100$) is heated strongly until it fully decomposes: $\text{CaCO}_3 -> \text{CaO} + \text{CO}_2$. Calculate the volume of CO_2 produced, measured at rtp.

$$n(\text{CaCO}_3) = \frac{2.00}{100} = 0.0200\ \text{mol} \implies n(\text{CO}_2) = 0.0200\ \text{mol (1:1 ratio)}.$$

$$V(\text{CO}_2) = 0.0200 \times 24.0 = 0.480\ \text{dm}^3 = \mathbf{480}\ \text{cm}^3.$$

Ví dụ mẫu · Finding M_r of a volatile liquid

0.500 g of a volatile liquid is completely vaporised at $100\,^\circ$C (373 K) and a pressure of 100 kPa, producing $215\ \text{cm}^3$ of vapour. Calculate the relative molecular mass of the liquid.
Convert to SI units: $V = 215 \times 10^{-6}\ \text{m}^3 = 2.15 \times 10^{-4}\ \text{m}^3$; $p = 1.00 \times 10^5$ Pa; $T = 373$ K.

$$n = \frac{pV}{RT} = \frac{(1.00 \times 10^5)(2.15 \times 10^{-4})}{8.31 \times 373} = \frac{21.5}{3099.6} = 6.937 \times 10^{-3}\ \text{mol}.$$

$$M_r = \frac{m}{n} = \frac{0.500}{6.937 \times 10^{-3}} = \textbf{72.1}\ \text{g mol}^{-1}\ (\text{consistent with butanone, } CH_3COC_2H_5,\ M_r = 72.1).$$

Ví dụ mẫu · Molar mass of a gas from its density

The density of a gas Y at rtp is $1.833\ \text{g dm}^{-3}$. Calculate the relative molecular mass of Y.
At rtp, 1 mol occupies $24.0\ \text{dm}^3$, so the mass of 1 mole (i.e. M_r in grams) is:

$$M_r = \text{density} \times V_m = 1.833 \times 24.0 = \textbf{44.0}\ \text{g mol}^{-1}\ (\text{consistent with } CO_2).$$

VN **GIẢI THÍCH TIẾNG VIỆT**
Với chất khí, khối lượng riêng (density) nhân với thể tích mol ($24.0\ \text{dm}^3$ ở r.t.p.) cho ngay M_r — vì khối lượng riêng chính là khối lượng của một đơn vị thể tích, và thể tích mol là thể tích của đúng 1 mol khí.

2.4.1 Avogadro's Law and reacting gas volumes

Định luật Avogadro

Avogadro's Law: equal volumes of any gases, measured at the same temperature and pressure, contain equal numbers of molecules (and therefore equal numbers of moles). Consequently, for a reaction involving only gases (at constant T, p), the coefficients in the balanced equation give directly the *ratio of reacting volumes* — there is no need to convert to moles first.

VN **GIẢI THÍCH TIẾNG VIỆT**
Định luật Avogadro: các thể tích khí bằng nhau, ở cùng nhiệt độ và áp suất, chứa **số mol bằng nhau**. Vì vậy, với phản ứng chỉ có chất khí, tỉ lệ hệ số cân bằng chính là tỉ lệ **thể tích** phản ứng — không cần đổi qua số mol.

Ví dụ mẫu · Reacting gas volumes: the Haber process

In the Haber process, $N_2 + 3H_2 -> 2NH_3$. If $40.0\ \text{cm}^3$ of N_2 reacts completely with excess H_2 at constant temperature and pressure, calculate the volume of H_2 that reacts and the volume of NH_3 produced.
By Avogadro's Law, volume ratio = mole ratio = $N_2 : H_2 : NH_3 = 1 : 3 : 2$.

$$V(H_2) = 3 \times 40.0 = \textbf{120}\ \text{cm}^3, \qquad V(NH_3) = 2 \times 40.0 = \textbf{80.0}\ \text{cm}^3.$$

2.5 Limiting reagents

When two reactants are mixed in amounts that do *not* match the exact stoichiometric ratio of the balanced equation, one reactant runs out first: this is the **limiting reagent**, and it determines the maximum possible amount of product. The other reactant, present in more than the amount needed, is said to be **in excess**.

Method: calculate the moles of *each* reactant available; using the balanced equation, calculate how many moles of one reactant would be needed to react exactly with all of the other. Whichever reactant would run out first (i.e. there is not enough of it) is the limiting reagent, and all product calculations must be based on *its* number of moles.

VN **GIẢI THÍCH TIẾNG VIỆT**

Thuốc thử **giới hạn (limiting reagent)** là chất hết trước, quyết định lượng sản phẩm tối đa tạo thành; chất còn lại là chất **dư (excess)**. Phương pháp: tính số mol mỗi chất, so sánh với tỉ lệ trong phương trình cân bằng để xác định chất nào hết trước, rồi tính sản phẩm dựa trên số mol của chất giới hạn.

Ví dụ mẫu · Limiting reagent: magnesium and hydrochloric acid

$2.00\,\text{g}$ of magnesium ribbon ($A_r = 24.3$) is added to $80.0\,\text{cm}^3$ of $1.00\,\text{mol dm}^{-3}$ hydrochloric acid: $\text{Mg} + 2\text{HCl} -> \text{MgCl}_2 + \text{H}_2$. Determine the limiting reagent and calculate the volume of H_2 produced at rtp.

$$n(\text{Mg}) = \frac{2.00}{24.3} = 0.0823\,\text{mol}; \qquad n(\text{HCl}) = 0.0800 \times 1.00 = 0.0800\,\text{mol}.$$

HCl needed to react with *all* the Mg: $2 \times 0.0823 = 0.1646$ mol — but only 0.0800 mol is available, so HCl **is the limiting reagent** (and Mg is in excess).

$$n(\text{H}_2) = \frac{n(\text{HCl})}{2} = \frac{0.0800}{2} = 0.0400\,\text{mol}.$$

$$V(\text{H}_2)\text{ at rtp} = 0.0400 \times 24.0 = \mathbf{0.960}\,\text{dm}^3 = 960\,\text{cm}^3.$$

Ví dụ mẫu · Limiting reagent: a precipitation reaction

$50.0\,\text{cm}^3$ of $0.200\,\text{mol dm}^{-3}$ BaCl_2 is mixed with $50.0\,\text{cm}^3$ of $0.150\,\text{mol dm}^{-3}$ Na_2SO_4: $\text{BaCl}_2 + \text{Na}_2\text{SO}_4 -> \text{BaSO}_4 + 2\text{NaCl}$. Calculate the mass of BaSO_4 precipitate formed ($M_r(\text{BaSO}_4) = 233.4$).

$$n(\text{BaCl}_2) = 0.0500 \times 0.200 = 1.00 \times 10^{-2}\,\text{mol}; \qquad n(\text{Na}_2\text{SO}_4) = 0.0500 \times 0.150 = 7.50 \times 10^{-3}\,\text{mol}.$$

The equation shows a 1:1 ratio, and Na_2SO_4 (7.50×10^{-3} mol) is present in a smaller amount than BaCl_2 (1.00×10^{-2} mol), so Na_2SO_4 **is the limiting reagent**.

$$n(\text{BaSO}_4) = n(\text{Na}_2\text{SO}_4) = 7.50 \times 10^{-3}\,\text{mol}.$$

$$m(\text{BaSO}_4) = 7.50 \times 10^{-3} \times 233.4 = \mathbf{1.75\,g}\ (3\text{ s.f.}).$$

(!) Lỗi thường gặp: Never assume the reactant present in the smaller *mass* or smaller *volume* is automatically the limiting reagent — the comparison must always be made in **moles**, scaled by the stoichiometric ratio from the balanced equation, not in raw grams or cm^3.

2.6 Water of crystallisation

Many ionic solids crystallise from aqueous solution with a fixed number of water molecules incorporated into their crystal lattice — this is **water of crystallisation**, and the compound is described as

hydrated, written e.g. $CuSO_4 \cdot 5H_2O$. Heating a hydrated salt drives off the water of crystallisation, leaving the **anhydrous** salt.

Ví dụ mẫu · Determining x in $CuSO_4 \cdot xH_2O$

5.002 g of hydrated copper(II) sulfate, $CuSO_4 \cdot xH_2O$, is heated to constant mass, leaving 3.202 g of anhydrous $CuSO_4$ ($M_r = 160.1$). Determine x.

Mass of water lost $= 5.002 - 3.202 = 1.800$ g $\Rightarrow$ $n(H_2O) = \dfrac{1.800}{18.0} = 0.1000$ mol.

$n(CuSO_4) = \dfrac{3.202}{160.1} = 0.02000$ mol.

$$x = \frac{n(H_2O)}{n(CuSO_4)} = \frac{0.1000}{0.02000} = \mathbf{5} \implies CuSO_4 \cdot 5H_2O.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Muối ngậm nước (hydrated salt) chứa số nguyên tử nước kết tinh cố định trong tinh thể. Đun nóng đến khối lượng không đổi để loại hết nước, tính số mol nước mất đi và số mol muối khan còn lại, rồi lấy tỉ lệ $x = n(H_2O)/n(\text{muối khan})$.

The heating must continue **to constant mass** (repeated heating and reweighing until the mass no longer changes) to ensure *all* the water of crystallisation has been driven off, without decomposing the anhydrous salt itself.

2.7 Percentage purity of an impure sample

Real samples of a solid are rarely 100% pure; a mixture of the desired compound with inert (unreactive) impurities is common. Percentage purity can be found by reacting the sample completely and measuring a suitable quantity of product (mass, gas volume, or titre).

Ví dụ mẫu · Percentage purity from a gas volume

A 2.50 g impure sample of calcium carbonate (containing only $CaCO_3$ and inert impurities) is reacted with excess dilute HCl: $CaCO_3 + 2HCl -> CaCl_2 + H_2O + CO_2$. The CO_2 produced is collected and its volume measured as 528 cm^3 at rtp. Calculate the percentage purity of the sample ($M_r(CaCO_3) = 100$).

$$n(CO_2) = \frac{528}{24000} = 0.0220 \text{ mol} \implies n(CaCO_3) = 0.0220 \text{ mol (1:1 ratio)}.$$

$$m(CaCO_3) = 0.0220 \times 100 = 2.20 \text{ g}.$$

$$\%\text{purity} = \frac{2.20}{2.50} \times 100 = \mathbf{88.0\%}.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Độ tinh khiết % $= \dfrac{\text{khối lượng chất tinh khiết thực sự có}}{\text{khối lượng mẫu (không tinh khiết)}} \times 100$. Khối lượng chất tinh khiết được suy ra gián tiếp từ lượng sản phẩm đo được (thể tích khí, khối lượng kết tủa, hoặc kết quả chuẩn độ).

2.8 Percentage yield and atom economy

$$\%\text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100, \qquad \%\text{ atom economy} = \frac{M_r(\text{desired product})}{\sum M_r(\text{all products})} \times 100.$$

Percentage yield compares the *actual* mass of product obtained with the maximum (*theoretical*) mass calculated from stoichiometry — it accounts for practical losses (incomplete reaction, side reactions, losses during purification). Atom economy is a purely theoretical measure of how much of the total mass of reactants ends up in the *desired* product, assuming the reaction goes to completion.

VN **GIẢI THÍCH TIẾNG VIỆT**

Hiệu suất phản ứng (% yield) so sánh lượng sản phẩm **thực tế** thu được với lượng **lý thuyết** tính từ phương trình — phản ánh tổn thất trong thực nghiệm. **Kinh tế nguyên tử (atom economy)** chỉ là một con số lý thuyết, đo tỉ lệ khối lượng nguyên liệu chuyển hoá thành sản phẩm **mong muốn**, giả định phản ứng xảy ra hoàn toàn.

Ví dụ mẫu · Percentage yield: hydration of ethene

Ethene is hydrated industrially using a phosphoric acid catalyst: $C_2H_4 + H_2O -> C_2H_5OH$. $280\,\text{g}$ of ethene ($M_r = 28.0$) is used, and the actual mass of ethanol ($M_r = 46.0$) obtained is $322\,\text{g}$. Calculate the percentage yield, and state the atom economy of this reaction.

$$n(C_2H_4) = \frac{280}{28.0} = 10.0\,\text{mol} \implies n(C_2H_5OH)_{\text{theoretical}} = 10.0\,\text{mol (1:1 ratio)}.$$

$$m(C_2H_5OH)_{\text{theoretical}} = 10.0 \times 46.0 = 460\,\text{g}.$$

$$\%\text{yield} = \frac{322}{460} \times 100 = \textbf{70.0\%}.$$

Since ethanol is the *only* product of this addition reaction, the atom economy is $\frac{46.0}{46.0} \times 100 =$ **100%**.

Ví dụ mẫu · Atom economy across a multi-step industrial process

Zinc metal is extracted from zinc sulfide ore in two stages: roasting, $2ZnS + 3O_2 -> 2ZnO + 2SO_2$, followed by reduction with carbon, $ZnO + C -> Zn + CO$. Calculate the overall atom economy of converting ZnS into Zn across both steps, and compare it with the 100% atom economy of the ethene hydration route to ethanol above.

Consider the reactants needed to make exactly $1\,\text{mol}$ of Zn. From step 2, $1\,\text{mol}$ ZnO and $1\,\text{mol}$ C are needed. From step 1, $1\,\text{mol}$ ZnO requires $1\,\text{mol}$ ZnS ($M_r = 97.5$) and $1.5\,\text{mol}$ O_2 ($M_r = 32.0$).

$$\text{total reactant mass} = m(ZnS) + m(O_2) + m(C) = 97.5 + (1.5 \times 32.0) + 12.0 = 97.5 + 48.0 + 12.0 = 157.5\,\text{g}.$$

$$\%\text{atom economy} = \frac{M_r(Zn)}{\text{total reactant mass}} \times 100 = \frac{65.4}{157.5} \times 100 = \textbf{41.5\%}.$$

This is far lower than the 100% atom economy of the single-step ethene hydration reaction, illustrating why addition reactions (with a single product) are inherently more atom-efficient than multi-step processes that release by-products (SO_2 and CO) which are not the desired output.

Addition reactions (all reactant atoms end up in a single product) always have 100% atom economy. Reactions that produce more than one product — substitution, elimination, or multi-step industrial processes with by-products — have atom economy below 100%, since some reactant mass is "wasted" in the by-products.

Reaction type	Example	Typical atom economy
Addition (single product)	$C_2H_4 + H_2O -> C_2H_5OH$	100%
Substitution (2 products)	$C_2H_6 + Br_2 -> C_2H_5Br + HBr$	well below 100%
Multi-step process	roasting + reduction of ZnS to Zn	well below 100%

Figure 2.4 — reaction type strongly affects atom economy: addition reactions with one product are the most atom-efficient.

(!) Lỗi thường gặp: Do not confuse percentage yield with atom economy: a reaction can have a very high atom economy (100% for a simple addition) but still give a low percentage *yield* in practice (due to side reactions, an incomplete reaction, or losses on purification) — the two quantities measure completely different things and are calculated by completely different methods.

2.9 Exam-style practice

Bài tập luyện tập

A compound is analysed and found to contain 40.0% carbon, 6.7% hydrogen and 53.3% oxygen by mass. Determine its empirical formula.

Lời giải chi tiết

Assume 100 g: $n(\text{C}) = 40.0/12.0 = 3.33$; $n(\text{H}) = 6.7/1.00 = 6.7$; $n(\text{O}) = 53.3/16.0 = 3.33$. Divide by smallest ($3.33$): $\text{C} : 1,\ \text{H} : 2,\ \text{O} : 1$. Empirical formula $= CH_2O$.

Bài tập luyện tập

The empirical formula CH_2O (from the previous question) corresponds to a compound of $M_r = 60.0$. Determine its molecular formula.

Lời giải chi tiết

$M_r(CH_2O) = 12.0 + 2.0 + 16.0 = 30.0$. Multiplier $= 60.0/30.0 = 2$. Molecular formula $= C_2H_4O_2$ (acetic acid).

Bài tập luyện tập

$25.0\,\text{cm}^3$ of a monoprotic acid HA of unknown concentration requires $20.0\,\text{cm}^3$ of $0.156\,\text{mol dm}^{-3}$ NaOH for neutralisation. Calculate [HA].

Lời giải chi tiết

$n(\text{NaOH}) = 0.0200 \times 0.156 = 3.12 \times 10^{-3}$ mol $= n(\text{HA})$ (1:1 ratio).
$[\text{HA}] = \dfrac{3.12 \times 10^{-3}}{0.0250} =$ **0.125** mol dm^{-3}.

Bài tập luyện tập

A 1.00 g sample of impure Na_2CO_3 is dissolved and reacted with 50.0 cm^3 of 0.400 mol dm^{-3} HCl (a known excess). The excess acid requires 12.5 cm^3 of 0.200 mol dm^{-3} NaOH to neutralise it. Given $Na_2CO_3 + 2HCl -> 2NaCl + H_2O + CO_2$ and $M_r(Na_2CO_3) = 106$, calculate the % purity of the sample.

Lời giải chi tiết

Total HCl: $n = 0.0500 \times 0.400 = 2.00 \times 10^{-2}$ mol.
Excess HCl $= n(\text{NaOH}) = 0.0125 \times 0.200 = 2.50 \times 10^{-3}$ mol.
HCl reacted with Na_2CO_3: $2.00 \times 10^{-2} - 2.50 \times 10^{-3} = 1.75 \times 10^{-2}$ mol.
$n(Na_2CO_3) = 1.75 \times 10^{-2}/2 = 8.75 \times 10^{-3}$ mol; $m = 8.75 \times 10^{-3} \times 106 = 0.9275$ g.
$\%\text{purity} = 0.9275/1.00 \times 100 =$ **92.8%** (3 s.f.).

Bài tập luyện tập

A stock solution of NaCl is 0.500 mol dm^{-3}. 20.0 cm^3 is diluted to 200 cm^3 (dilution 1), then 25.0 cm^3 of dilution 1 is diluted to 500 cm^3 (dilution 2). Find the concentration of dilution 2.

Lời giải chi tiết

Dilution 1: $0.500 \times 20.0 = c_1 \times 200 \Rightarrow c_1 = 10.0/200 = 0.0500$ mol dm^{-3}.
Dilution 2: $0.0500 \times 25.0 = c_2 \times 500 \Rightarrow c_2 = 1.25/500 =$ **2.50** $\times$ **10**$^{-3}$ mol dm^{-3}.

Bài tập luyện tập

8.40 g of sodium hydrogencarbonate ($M_r = 84.0$) is heated fully: $2NaHCO_3 -> Na_2CO_3 + H_2O + CO_2$. Calculate the volume of CO_2 produced at rtp.

Lời giải chi tiết

$n(NaHCO_3) = 8.40/84.0 = 0.100$ mol $\Rightarrow n(CO_2) = 0.0500$ mol (ratio 2:1).
$V(CO_2) = 0.0500 \times 24.0 =$ **1.20** dm^3 $= 1200$ cm^3.

Bài tập luyện tập

A 3.00 dm^3 flask contains a gas at 100 kPa and $27\,^\circ$C. Use $pV = nRT$ to calculate the number of moles of gas present.

Lời giải chi tiết

$T = 27 + 273 = 300$ K; $p = 1.00 \times 10^5$ Pa; $V = 3.00 \times 10^{-3}$ m^3.
$n = \dfrac{pV}{RT} = \dfrac{(1.00 \times 10^5)(3.00 \times 10^{-3})}{8.31 \times 300} = \dfrac{300}{2493} =$ **0.120** mol (3 s.f.).

Bài tập luyện tập

0.320 g of a volatile liquid produces 100 cm^3 of vapour at $127\,^\circ$C and 100 kPa. Calculate its M_r.

Lời giải chi tiết

$T = 127 + 273 = 400$ K; $V = 100 \times 10^{-6} = 1.00 \times 10^{-4}$ m^3; $p = 1.00 \times 10^5$ Pa.
$n = \dfrac{pV}{RT} = \dfrac{(1.00 \times 10^5)(1.00 \times 10^{-4})}{8.31 \times 400} = \dfrac{10.0}{3324} = 3.009 \times 10^{-3}$ mol.
$M_r = \dfrac{0.320}{3.009 \times 10^{-3}} =$ **106** g mol^{-1} (3 s.f.).

Bài tập luyện tập

A gas Y has density 1.964 g dm^{-3} at rtp. Calculate its relative molecular mass.

Lời giải chi tiết

$M_r =$ density $\times\, 24.0 = 1.964 \times 24.0 =$ **47.1** g mol^{-1} (3 s.f.).

Bài tập luyện tập

Methane burns completely in oxygen: $CH_4 + 2O_2 -> CO_2 + 2H_2O(g)$ (all species gaseous). 30.0 cm^3 of CH_4 is burned completely at constant temperature and pressure. Calculate the volume of O_2 required and the volume of CO_2 formed.

Lời giải chi tiết

By Avogadro's Law, volume ratio = mole ratio $= 1 : 2 : 1 : 2$.
$V(O_2) = 2 \times 30.0 =$ **60.0** cm^3; $V(CO_2) = 1 \times 30.0 =$ **30.0** cm^3.

Bài tập luyện tập

3.25 g of zinc ($A_r = 65.4$) is added to 60.0 cm^3 of 2.00 mol dm^{-3} HCl: $Zn + 2HCl -> ZnCl_2 + H_2$. Determine the limiting reagent and calculate the volume of H_2 produced at rtp.

Lời giải chi tiết

$n(Zn) = 3.25/65.4 = 0.0497$ mol; $n(HCl) = 0.0600 \times 2.00 = 0.1200$ mol.
HCl needed for all Zn: $2 \times 0.0497 = 0.0994$ mol < 0.1200 mol available, so **Zn is the limiting reagent**.
$n(H_2) = n(Zn) = 0.0497$ mol $\Rightarrow$ $V(H_2) = 0.0497 \times 24.0 =$ **1.19** dm^3 (3 s.f.).

Bài tập luyện tập

10.0 cm^3 of propane, C_3H_8, is mixed with 40.0 cm^3 of O_2 and sparked to complete combustion: $C_3H_8 + 5O_2 -> 3CO_2 + 4H_2O$ (all volumes measured at the same temperature and pressure, with water as vapour). Determine which gas is in excess, and by what volume.

Lời giải chi tiết

O_2 needed for all the propane: $5 \times 10.0 = 50.0\,\text{cm}^3 > 40.0\,\text{cm}^3$ available, so O_2 **is the limiting reagent**.
Propane that reacts with $40.0\,\text{cm}^3$ O_2: $40.0/5 = 8.0\,\text{cm}^3$.
Propane left unreacted (in excess) $= 10.0 - 8.0 =$ **2.0** cm^3.

Bài tập luyện tập

$4.51\,\text{g}$ of hydrated magnesium sulfate, $MgSO_4 \cdot xH_2O$, is heated to constant mass, leaving $2.20\,\text{g}$ of anhydrous $MgSO_4$ ($M_r = 120.4$). Determine x.

Lời giải chi tiết

Water lost $= 4.51 - 2.20 = 2.31\,\text{g} \Rightarrow n(H_2O) = 2.31/18.0 = 0.1283\,\text{mol}$.
$n(MgSO_4) = 2.20/120.4 = 0.01827\,\text{mol}$.
$x = 0.1283/0.01827 = 7.02 \approx$ **7** $\Rightarrow$ $MgSO_4 \cdot 7H_2O$ (Epsom salt).

Bài tập luyện tập

A $5.00\,\text{g}$ sample of impure NaCl is dissolved and treated with excess $AgNO_3$: $NaCl + AgNO_3 -> AgCl + NaNO_3$. The AgCl precipitate formed has mass $11.48\,\text{g}$ ($M_r(AgCl) = 143.5$). Calculate the % purity of the sample ($M_r(NaCl) = 58.5$).

Lời giải chi tiết

$n(AgCl) = 11.48/143.5 = 0.0800\,\text{mol} = n(NaCl)$ (1:1 ratio).
$m(NaCl) = 0.0800 \times 58.5 = 4.68\,\text{g}$.
$\%\text{purity} = 4.68/5.00 \times 100 =$ **93.6%**.

Bài tập luyện tập

Aspirin is prepared from salicylic acid: $C_7H_6O_3 + C_4H_6O_3 -> C_9H_8O_4 + C_2H_4O_2$. $4.00\,\text{g}$ of salicylic acid ($M_r = 138$) reacts with excess acetic anhydride, giving an actual yield of $4.20\,\text{g}$ of aspirin ($M_r = 180$). Calculate the percentage yield.

Lời giải chi tiết

$n(\text{salicylic acid}) = 4.00/138 = 0.02899\,\text{mol} \Rightarrow n(\text{aspirin})_{\text{theoretical}} = 0.02899\,\text{mol}$ (1:1 ratio).
$m_{\text{theoretical}} = 0.02899 \times 180 = 5.217\,\text{g}$.
$\%\text{yield} = 4.20/5.217 \times 100 =$ **80.5%** (3 s.f.).

Bài tập luyện tập

Compare the atom economy of (a) the addition reaction $C_2H_4 + Br_2 -> C_2H_4Br_2$ and (b) the substitution reaction $C_2H_6 + Br_2 -> C_2H_5Br + HBr$ (M_r: $C_2H_6 = 30.1$, $Br_2 = 159.8$, $C_2H_5Br = 108.9$).

Lời giải chi tiết

(a) The addition reaction has only one product, so atom economy $=$ **100%**.

(b) %atom economy $= \dfrac{M_r(\text{C}_2\text{H}_5\text{Br})}{M_r(\text{C}_2\text{H}_6) + M_r(\text{Br}_2)} \times 100 = \dfrac{108.9}{30.1 + 159.8} \times 100 = \dfrac{108.9}{189.9} \times 100 =$ **57.3%**.
The addition reaction is far more atom-efficient, because it produces no by-product.

Bài tập luyện tập

Calculate the number of molecules in 8.80 g of CO_2 ($M_r = 44.0$), using $N_A = 6.02 \times 10^{23}$ mol^{-1}.

Lời giải chi tiết

$n = 8.80/44.0 = 0.200$ mol. $N = 0.200 \times 6.02 \times 10^{23} =$ **1.20 × 10^{23}** molecules (3 s.f.).

Bài tập luyện tập

0.0500 mol of a compound has a mass of 5.85 g. Calculate its relative molecular mass.

Lời giải chi tiết

$M_r = m/n = 5.85/0.0500 =$ **117** g mol^{-1}.

Bài tập luyện tập

Calculate the concentration (in mol dm^{-3}) of a solution made by dissolving 4.00 g of NaOH ($M_r = 40.0$) in water to make 250 cm^3 of solution.

Lời giải chi tiết

$n = 4.00/40.0 = 0.100$ mol. $c = n/V = 0.100/0.250 =$ **0.400** mol dm^{-3}.

Bài tập luyện tập

25.0 cm^3 of 2.00 mol dm^{-3} HCl is diluted to 500 cm^3. Calculate the new concentration.

Lời giải chi tiết

$c_2 = \dfrac{c_1 V_1}{V_2} = \dfrac{2.00 \times 25.0}{500} =$ **0.100** mol dm^{-3}.

Bài tập luyện tập

Calculate the mass of CaO ($M_r = 56.0$) produced when 5.00 g of CaCO_3 ($M_r = 100$) is fully decomposed: $\text{CaCO}_3 -> \text{CaO} + \text{CO}_2$.

Lời giải chi tiết

$n(\text{CaCO}_3) = 5.00/100 = 0.0500$ mol $\Rightarrow$ $n(\text{CaO}) = 0.0500$ mol.
$m(\text{CaO}) = 0.0500 \times 56.0 =$ **2.80 g**.

Bài tập luyện tập

Calculate the percentage by mass of oxygen in calcium carbonate, $CaCO_3$ (A_r: Ca $= 40.1$, C $= 12.0$, O $= 16.0$).

Lời giải chi tiết

$M_r(CaCO_3) = 40.1 + 12.0 + 3(16.0) = 100.1$. Mass of O $= 48.0$.
$\%O = 48.0/100.1 \times 100 =$ **48.0%** (3 s.f.).

Bài tập luyện tập

0.290 g of a gaseous hydrocarbon burns completely to give 0.880 g CO_2 and 0.450 g H_2O. Given $M_r = 58.0$, find its molecular formula.

Lời giải chi tiết

$n(CO_2) = 0.880/44.0 = 0.0200$ mol $= n(C)$; mass C $= 0.0200 \times 12.0 = 0.240$ g.
$n(H_2O) = 0.450/18.0 = 0.0250$ mol $\Rightarrow$ $n(H) = 0.0500$ mol; mass H $= 0.0500$ g.
Check: $0.240 + 0.050 = 0.290$ g = original mass, confirming a pure hydrocarbon.
Ratio C : H $= 0.0200 : 0.0500 = 2 : 5$ $\Rightarrow$ empirical C_2H_5 ($M_r = 29.0$). Since $58.0/29.0 = 2$, molecular formula $= C_4H_{10}$ (butane).

Bài tập luyện tập

Equal volumes of any two gases, measured at the same temperature and pressure, contain:

(A) Equal masses
(B) Equal numbers of molecules
(C) Equal numbers of atoms
(D) Equal densities

Lời giải chi tiết

This is a direct statement of Avogadro's Law. **(B)**.

Bài tập luyện tập

Which quantity is defined as the amount of substance containing as many particles as there are atoms in exactly 12 g of carbon-12?

(A) Molar mass
(B) The mole
(C) Avogadro constant
(D) Relative atomic mass

Lời giải chi tiết

This is the definition of **the mole**. **(B)**.

Bài tập luyện tập

Calculate the volume of oxygen (at rtp) required to completely combust 5.00 dm^3 of propane gas, $C_3H_8 + 5O_2 -> 3CO_2 + 4H_2O$, at the same temperature and pressure.

Lời giải chi tiết

By Avogadro's Law, volume ratio = mole ratio $= 1 : 5$.
$V(\mathrm{O_2}) = 5 \times 5.00 =$ **25.0** $\mathrm{dm^3}$.

Chemical Bonding

Mục tiêu Unit: Bản chất của liên kết ion (chuyển electron, cấu trúc mạng tinh thể khổng lồ NaCl), liên kết cộng hoá trị (cặp electron dùng chung, liên kết đơn/đôi/ba, độ dài và năng lượng liên kết, liên kết sigma và pi), liên kết cho–nhận (dative/coordinate) và liên kết kim loại (biển electron linh động); áp dụng đầy đủ thuyết đẩy cặp electron vỏ hoá trị (VSEPR) để dự đoán hình dạng phân tử, kể cả các dạng nâng cao như chữ T và vuông phẳng; độ âm điện theo thang Pauling và xu hướng biến đổi; phân biệt độ phân cực liên kết với độ phân cực phân tử; và xếp hạng đầy đủ các lực liên phân tử (lực phân tán London, lực lưỡng cực–lưỡng cực, liên kết hydro) để giải thích và so sánh nhiệt độ sôi/nóng chảy của các chất.

3.1 Ionic, covalent, dative and metallic bonding

3.1.1 Ionic bonding and the giant ionic lattice

Khái niệm cốt lõi

Ionic bonding is the strong electrostatic force of attraction between oppositely charged ions, formed by the complete **transfer of one or more electrons** from a metal atom to a non-metal atom. Both atoms achieve a full outer (usually noble-gas) electron shell.

- The metal atom **loses** electrons to form a positively charged **cation**.
- The non-metal atom **gains** those electrons to form a negatively charged **anion**.
- The cation and anion then attract each other electrostatically in all directions, building up a **giant ionic lattice** — not a single discrete molecule.

Electron transfer in ionic bond formation (electron arrangement shown by shell):

Atom	Electron arrangement	Ion formed	Electron arrangement of ion
Na	$2, 8, 1$	Na$+$ (loses $1e^-$)	$2, 8$ (neon arrangement)
Mg	$2, 8, 2$	Mg^{2+} (loses $2e^-$)	$2, 8$ (neon arrangement)
Cl	$2, 8, 7$	Cl$-$ (gains $1e^-$)	$2, 8, 8$ (argon arrangement)
O	$2, 6$	O^{2-} (gains $2e^-$)	$2, 8$ (neon arrangement)

Ví dụ mẫu · Forming the ionic bonds in NaCl and MgO

Sodium chloride: a sodium atom $(2, 8, 1)$ transfers its single outer electron directly to a chlorine atom $(2, 8, 7)$. Sodium becomes Na$+$ $(2, 8$, a stable neon arrangement); chlorine becomes Cl$-$ $(2, 8, 8$, a stable argon arrangement). The overall change is Na $+$ Cl$- >$ Na $+ +$Cl$-$, and the two oppositely charged ions are then held together by electrostatic attraction.

Magnesium oxide: a magnesium atom $(2, 8, 2)$ transfers *both* outer electrons to an oxygen atom $(2, 6)$. Magnesium becomes Mg^{2+} $(2, 8)$; oxygen becomes O^{2-} $(2, 8)$ — both now have the neon arrangement. Because the ions carry twice the charge of Na$+$/Cl$-$ and are smaller, the electrostatic attraction in MgO is far stronger than in NaCl, giving MgO a much higher

melting point (2852°C) than NaCl (801°C).

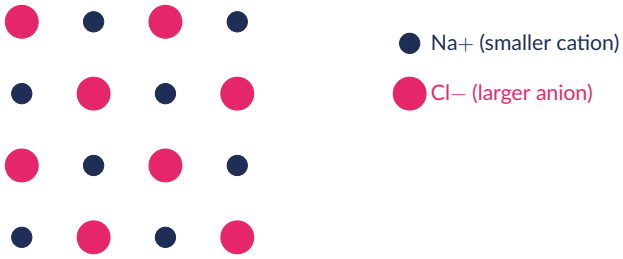

Figure 1. A cross-section through the giant ionic lattice of NaCl: each Na+ is surrounded by 6 nearest-neighbour Cl− ions and vice versa (6:6 coordination), repeated regularly in three dimensions.

Consequences of the giant ionic lattice — typical physical properties:

- **High melting and boiling points:** very strong electrostatic forces act in *all* directions throughout the lattice, so a large amount of energy is needed to separate the ions.
- **Conduct electricity only when molten or dissolved in water:** in the solid, ions are fixed in position and cannot move to carry charge; once molten or in solution, ions are free to move.
- **Hard but brittle:** a sharp blow can shift one layer of ions relative to the next, bringing ions of *like* charge next to each other; the resulting repulsion splits the crystal apart.

VN **GIẢI THÍCH TIẾNG VIỆT**

Liên kết ion hình thành khi nguyên tử kim loại **nhường hẳn** electron cho nguyên tử phi kim, tạo ra cation và anion hút nhau bằng lực tĩnh điện theo mọi hướng, xếp thành **mạng tinh thể khổng lồ** chứ không phải một phân tử riêng lẻ. Ví dụ Na $(2, 8, 1)$ nhường 1 electron cho Cl $(2, 8, 7)$ tạo Na+ và Cl−, mỗi ion đạt cấu hình khí hiếm bền. Vì lực hút mạnh và tác dụng theo mọi phía nên hợp chất ion có nhiệt độ nóng chảy/sôi cao, chỉ dẫn điện khi nóng chảy hoặc hoà tan (lúc đó ion mới di chuyển tự do), và cứng nhưng giòn (khi bị va đập, các lớp ion trượt khiến ion cùng dấu kề nhau, đẩy nhau làm tinh thể vỡ).

3.1.2 Covalent bonding: single, double and triple bonds

Khái niệm cốt lõi

A **covalent bond** is a strong electrostatic attraction between two positive nuclei and a **shared pair of electrons** between them (one electron contributed by each atom, typically). Atoms can share more than one pair:

- **Single bond** (e.g. H — H, C — C): one shared pair.
- **Double bond** (e.g. O = O, C = C): two shared pairs.
- **Triple bond** (e.g. N ≡ N, C ≡ C): three shared pairs.

More shared pairs pull the two nuclei closer together and hold them more tightly: bond length **decreases** and bond energy (strength) **increases** from single to double to triple.

Bond length and bond energy trend between two carbon atoms:

Bond	Bond length / pm	Bond energy / kJ mol^{-1}	Number of shared pairs
C – C	154	347	1
C = C	134	612	2
C ≡ C	120	838	3

Shorter bond ⇒ stronger bond: going single → double → triple, length falls while the energy needed to break the bond rises.

Ví dụ mẫu · Using bond energies: hydrogenation of ethyne to ethene

Estimate ΔH for C2H2 + H2 −> C2H4 (ethyne → ethene), using $E(\text{C} \equiv \text{C}) = 838$, $E(\text{C} = \text{C}) = 612$, $E(\text{C} - \text{H}) = 413$ and $E(\text{H} - \text{H}) = 436$ kJ mol^{-1}.

Bonds broken (reactants): one C ≡ C and one H – H (the two C – H bonds already present in ethyne are unchanged).
Σ(broken)$= 838 + 436 = 1274$ kJ mol^{-1}.

Bonds formed (products): the triple bond becomes a double bond, and two *new* C – H bonds are made as the two H atoms add across it.
Σ(formed)$= 612 + 2(413) = 612 + 826 = 1438$ kJ mol^{-1}.

$\Delta H = \Sigma$(broken)$-\Sigma$(formed)$= 1274 - 1438 = -164$ kJ mol^{-1}.
The reaction is exothermic, consistent with hydrogenation reactions generally releasing energy.

VN **GIẢI THÍCH TIẾNG VIỆT**
Liên kết cộng hoá trị là lực hút giữa hai hạt nhân và (các) cặp electron dùng chung. Càng nhiều cặp electron dùng chung (đơn → đôi → ba) thì độ dài liên kết càng **ngắn** và năng lượng liên kết càng **lớn** — ví dụ C – C (154 pm, 347 kJ/mol) → C = C (134 pm, 612 kJ/mol) → C ≡ C (120 pm, 838 kJ/mol). Dùng năng lượng liên kết có thể ước tính ΔH phản ứng bằng công thức: năng lượng liên kết bị phá vỡ trừ năng lượng liên kết được tạo thành.

3.1.3 Sigma (σ) and pi (π) bonds

Khái niệm cốt lõi

Every single covalent bond is a σ **(sigma) bond**, formed by the **head-on (end-on) overlap** of two atomic orbitals directly along the line joining the two nuclei. A σ bond allows free rotation of the two bonded atoms about the bond axis, because the orbital overlap is symmetric around that axis.
A **double bond** consists of one σ bond *plus* one π **(pi) bond**: the π bond forms from the **sideways (parallel) overlap** of two unhybridised p-orbitals, one above and one below the internuclear axis. A **triple bond** consists of one σ bond plus *two* mutually perpendicular π bonds.

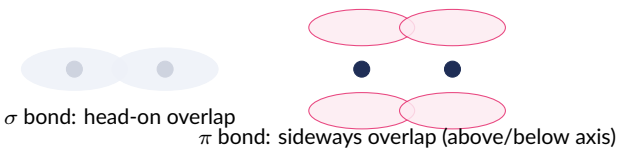

Figure 2. σ bonds form by head-on orbital overlap along the bond axis; π bonds form by sideways overlap of p-orbitals above and below that axis.

Because a π bond depends on the two p-orbital lobes staying aligned above and below the axis, rotating one end of a C = C double bond relative to the other would break the sideways overlap — so **rotation about a C=C double bond is restricted**. This restricted rotation is the physical basis for *E/Z* (geometric) isomerism, met later in organic chemistry: the two groups on each carbon of a C = C bond are effectively locked in place relative to one another.

VN **GIẢI THÍCH TIẾNG VIỆT**

Liên kết đơn luôn là liên kết **sigma (σ)** — hai orbital chồng lấp trực diện dọc theo trục nối hai hạt nhân, cho phép quay tự do quanh trục đó. Liên kết đôi gồm 1 liên kết σ và 1 liên kết **pi (π)** — orbital p chồng lấp song song ở trên và dưới trục liên kết. Vì liên kết π cần hai thuỳ orbital p thẳng hàng, việc quay một đầu liên kết đôi C = C sẽ phá vỡ sự chồng lấp này — do đó liên kết đôi **không quay tự do được**, đây chính là cơ sở của đồng phân hình học E/Z sẽ học ở phần hoá hữu cơ.

3.1.4 Dative (coordinate) covalent bonding

Khái niệm cốt lõi

A **dative (coordinate) bond** is a covalent bond in which *both* shared electrons come from the **same** atom (the donor), rather than one from each atom. Once formed, a dative bond is identical in every way to an ordinary covalent bond — equal length, equal strength — the only difference is in how it was formed.

VN **GIẢI THÍCH TIẾNG VIỆT**

Liên kết cho–nhận (dative/coordinate) là liên kết cộng hoá trị mà **cả hai** electron dùng chung đều do **một** nguyên tử cung cấp (nguyên tử cho, có cặp electron chưa liên kết), còn nguyên tử kia chỉ nhận (thường là ion H+ không có electron nào). Ví dụ kinh điển: phân tử NH3 có một cặp electron chưa liên kết trên N; khi gặp ion H+ (hoàn toàn không có electron), cặp electron này được N "cho" dùng chung để tạo liên kết cho–nhận N→H, hình thành ion NH4+: NH3 + H + − > NH4+. Sau khi hình thành, liên kết cho–nhận N–H thứ tư hoàn toàn giống 3 liên kết N–H thường về độ dài và độ bền — không có cách nào phân biệt được chúng trong phân tử sản phẩm.

Requirements for a dative bond: the donor atom must have at least one **lone pair** of electrons available (e.g. N in NH3, O in H2O, Cl in a bridging chloride ion); the acceptor must have an empty orbital that can receive that pair (e.g. H+, or a metal/boron/aluminium atom with an incomplete outer shell such as BF3 or AlCl3).

3.1.5 Metallic bonding

Khái niệm cốt lõi

Metallic bonding is the strong electrostatic attraction between a lattice of positively charged metal ions (cations) and a "sea" of **delocalised electrons** (the outer-shell electrons of every metal atom, free to move throughout the whole structure rather than belonging to any one ion).

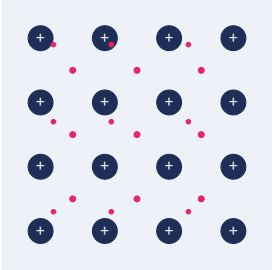

Figure 3. Metallic bonding: a fixed lattice of cations (labelled +) immersed in a mobile "sea" of delocalised electrons (small pink dots).

Properties explained by metallic bonding:

- **Good electrical conductor, solid or molten:** delocalised electrons are free to flow and carry charge in both states (unlike ionic solids, which conduct only when molten/aqueous).
- **Good thermal conductor:** the mobile electrons transfer kinetic energy rapidly through the structure.
- **Malleable and ductile:** when a layer of cations is forced to slide over another, the electron sea simply flows to re-envelop them — the bonding is not broken and the metal deforms smoothly, rather than shattering like an ionic lattice.
- **Melting point depends on the strength of metallic bonding:** more delocalised electrons per atom and smaller, more highly charged cations increase the attraction. For example magnesium (Mg^{2+}, 2 delocalised electrons per atom, melting point 650°C) has a much stronger metallic bond — and a much higher melting point — than sodium ($Na+$, 1 delocalised electron per atom, melting point 98°C).

Ví dụ mẫu · Comparing the melting points of sodium and magnesium

Sodium melts at 98°C; magnesium melts at 650°C. Explain the difference in terms of metallic bonding.

Reasoning: Mg contributes *two* delocalised electrons per atom to the "sea" (forming Mg^{2+}), compared with only *one* from Na (forming $Na+$). Mg^{2+} also has a smaller ionic radius and a greater positive charge than $Na+$. Both effects increase the electrostatic attraction between the cations and the electron sea, so more energy is required to separate the ions in magnesium — giving magnesium the much higher melting point.

VN **GIẢI THÍCH TIẾNG VIỆT**

Liên kết kim loại là lực hút tĩnh điện giữa mạng cation kim loại và "biển" electron hoá trị bị **giải toả (delocalised)**, di chuyển tự do khắp cấu trúc chứ không thuộc về nguyên tử nào. Nhờ electron di động, kim loại dẫn điện tốt ở cả thể rắn và lỏng, dẫn nhiệt tốt, và dẻo/dễ dát mỏng vì khi các lớp cation trượt lên nhau, biển electron vẫn bao bọc chúng nên liên kết không bị đứt (khác hẳn tinh thể ion dễ vỡ). Liên kết kim loại càng mạnh (nhiều electron giải toả hơn, ion nhỏ và điện tích lớn hơn) thì nhiệt độ nóng chảy càng cao — ví dụ Mg (2 electron/nguyên tử) nóng chảy ở 650°C, cao hơn nhiều so với Na (1 electron/nguyên tử) chỉ 98°C.

3.2 Shapes of molecules: VSEPR theory

Khái niệm cốt lõi

The **Valence Shell Electron Pair Repulsion (VSEPR)** theory predicts molecular shape using a simple method:

1. Draw the structure and identify the **central atom**.
2. Count the number of **electron domains** (regions of electron density) around that central atom. A single, double or triple bond each counts as **one** domain; a lone pair also counts as **one** domain.
3. These domains arrange themselves as far apart as possible in three dimensions, to minimise repulsion — this gives the **electron-domain geometry** (2 domains: linear; 3: trigonal planar; 4: tetrahedral; 5: trigonal bipyramidal; 6: octahedral).
4. The **molecular shape** is named from the positions of the *atoms only* — lone pairs are invisible in the name, even though they still occupy space and still push the bonded atoms around.
5. Bond angles are refined using the repulsion hierarchy:

   lone pair–lone pair $>$ **lone pair–bond pair** $>$ **bond pair–bond pair**.

   A lone pair is held closer to the central nucleus (it is not shared, so it occupies a broader, more diffuse region) and so repels neighbouring pairs more strongly than a bonding pair does.
6. For 5 domains (trigonal bipyramidal base), lone pairs occupy **equatorial** positions in preference to axial ones, since an equatorial position has only two close ($90°$) neighbours compared with three for an axial position — minimising the strongest repulsions.

Molecular shapes from VSEPR theory:

Domains	Shape	Bond pairs / lone pairs	Example	Bond angle(s)
2	Linear	2 / 0	CO2, BeCl2	$180°$
3	Trigonal planar	3 / 0	BF3	$120°$
4	Tetrahedral	4 / 0	CH4	$109.5°$
4	Trigonal pyramidal	3 / 1	NH3	$107°$
4	Bent (V-shaped)	2 / 2	H2O	$104.5°$
5	Trigonal bipyramidal	5 / 0	PCl5	$90°/120°$
5	T-shaped	3 / 2	ClF3	$\approx 87.5°$
6	Octahedral	6 / 0	SF6	$90°$
6	Square planar	4 / 2	XeF4	$90°$

Ví dụ mẫu · Deriving the shape of NH3

Nitrogen contributes 5 valence electrons; each of the 3 N–H bonds uses one of them, leaving one lone pair. Total electron domains $= 3$ bond pairs $+1$ lone pair $= 4 \Rightarrow$ tetrahedral electron-domain geometry. Since the shape is named from atom positions only, and one domain is a lone pair (invisible in the name), the **molecular shape** is **trigonal pyramidal**. Because lone pair–

bond pair repulsion exceeds bond pair–bond pair repulsion, the H–N–H angle is compressed from the ideal tetrahedral 109.5° down to 107°.

Ví dụ mẫu · Deriving the shape of ClF3

Chlorine contributes 7 valence electrons; 3 are used to bond to the 3 F atoms, leaving 2 lone pairs. Total domains $= 3 + 2 = 5 \Rightarrow$ trigonal bipyramidal electron-domain geometry. Both lone pairs occupy **equatorial** positions (each avoiding a 90° neighbour that an axial position would have), leaving one F atom equatorial and two F atoms axial. The atoms alone trace out a **T-shape**; the F–Cl–F bond angle is compressed slightly below 90° (to about 87.5°) by the strong lone pair repulsion.

Ví dụ mẫu · Deriving the shape of XeF4

Xenon (Group 18) contributes 8 valence electrons; 4 are used to bond to the 4 F atoms, leaving 2 lone pairs. Total domains $= 4 + 2 = 6 \Rightarrow$ octahedral electron-domain geometry. The two lone pairs move as far apart from each other as possible, occupying positions directly **opposite (trans)** each other (180° apart) — the arrangement that minimises the strongest (lone pair–lone pair) repulsion. This leaves the 4 F atoms arranged in a single plane around Xe: the molecular shape is **square planar**, with F–Xe–F angles of 90°.

VN **GIẢI THÍCH TIẾNG VIỆT**

Phương pháp VSEPR: (1) đếm số **miền electron** quanh nguyên tử trung tâm — mỗi liên kết (dù đơn/đôi/ba) tính là 1 miền, mỗi cặp electron chưa liên kết cũng tính là 1 miền; (2) các miền xếp xa nhau nhất có thể → cho **hình học miền electron** (2 miền: thẳng; 3: tam giác phẳng; 4: tứ diện; 5: lưỡng chóp tam giác; 6: bát diện); (3) **hình dạng phân tử** chỉ gọi tên theo vị trí các nguyên tử, bỏ qua cặp electron riêng dù nó vẫn chiếm chỗ và vẫn đẩy các nguyên tử khác; (4) mức độ đẩy giảm dần: cặp riêng–cặp riêng > cặp riêng–cặp liên kết > cặp liên kết–cặp liên kết. Ví dụ ClF3 (5 miền: 3 liên kết + 2 cặp riêng) có hình chữ T vì 2 cặp riêng chiếm vị trí xích đạo; XeF4 (6 miền: 4 liên kết + 2 cặp riêng) có hình vuông phẳng vì 2 cặp riêng nằm đối diện nhau.

(!) Lỗi thường gặp: The name of a shape (e.g. "trigonal pyramidal", "T-shaped", "square planar") never mentions lone pairs, but this does **not** mean lone pairs can be ignored when predicting bond angles or overall geometry. A common mistake is assuming a molecule with 4 electron domains is always "tetrahedral 109.5°": it is only *shaped* tetrahedrally if all 4 domains are bonding pairs (CH4); with 1 or 2 lone pairs among those 4 domains, the electron-domain arrangement is still (roughly) tetrahedral, but the *molecular shape* and bond angle change (trigonal pyramidal 107° for NH3; bent 104.5° for H2O).

3.3 Electronegativity, bond polarity and molecular polarity

Khái niệm cốt lõi

Electronegativity is a measure of the ability of an atom (in a covalent bond) to attract the shared pair of electrons towards itself. It is usually quoted on the **Pauling scale**, a dimensionless number.

Pauling electronegativity values:

Period 2	Li	Be	B	C	N	O	F
Value	1.0	1.5	2.0	2.5	3.0	3.5	4.0

Group 17	F	Cl	Br	I
Value	4.0	3.0	2.8	2.5

Across a period (Li $\rightarrow$ F), electronegativity **increases**: nuclear charge increases while the outer electrons remain in the same principal shell (shielding stays roughly constant), so the nucleus attracts the bonding pair more strongly. **Down a group** (F $\rightarrow$ I), electronegativity **decreases**: atomic radius and the number of inner shielding shells increase faster than nuclear charge, so despite a larger nuclear charge the outer/bonding electrons are held less tightly.

Ví dụ mẫu · Bond polarity vs. molecular polarity: CO2, CCl4 and CHCl3

CO2**:** each C $=$ O bond is polar (ΔEN $= 3.5 - 2.5 = 1.0$), with the dipole pointing towards O. Carbon has 2 electron domains (each C $=$ O double bond counts as one) and no lone pairs $\Rightarrow$ linear, O $=$ C $=$ O. The two *equal and opposite* bond dipoles cancel exactly by symmetry $\Rightarrow$ CO2 **is a non-polar molecule** despite having polar bonds.

CCl4**:** each C $-$ Cl bond is polar (ΔEN $= 3.0 - 2.5 = 0.5$). Carbon has 4 identical bonding domains, no lone pairs $\Rightarrow$ perfectly symmetric tetrahedral shape. The four equal bond dipoles cancel by symmetry $\Rightarrow$ CCl4 **is non-polar**.

CHCl3 **(chloroform):** still tetrahedral (4 bonding domains, no lone pairs on C), but the substituents are *not* all identical (1 H $+$ 3 Cl). The bond dipoles no longer point in a symmetric, cancelling arrangement $\Rightarrow$ CHCl3 **has a net molecular dipole and is polar**.

Conclusion: a molecule with polar bonds is only non-polar overall if its shape and substituents are symmetric enough for the individual bond dipoles to cancel exactly.

(!) Lỗi thường gặp: Do not assume that "the bonds are polar" automatically means "the molecule is polar" (or vice versa). Bond polarity depends only on the electronegativity difference between the two bonded atoms; *molecular* polarity also depends on the molecular shape and on whether the individual bond dipoles cancel by symmetry.

VN **GIẢI THÍCH TIẾNG VIỆT**

Độ âm điện là khả năng một nguyên tử hút cặp electron dùng chung về phía mình, theo thang Pauling. Độ âm điện **tăng** khi đi từ trái sang phải trong một chu kỳ (điện tích hạt nhân tăng, số lớp không đổi) và **giảm** khi đi từ trên xuống trong một nhóm (bán kính nguyên tử và số lớp chắn tăng nhanh hơn điện tích hạt nhân). Một liên kết có thể phân cực (do chênh lệch độ âm điện) nhưng **cả phân tử** chỉ phân cực nếu các mô-men lưỡng cực của từng liên kết **không triệt tiêu nhau** — ví dụ CO2 và CCl4 có liên kết phân cực nhưng phân tử đối xứng nên không phân cực, trong khi CHCl3 không đối xứng (1 H và 3 Cl khác nhau) nên phân tử phân cực.

3.4 Intermolecular forces

Khái niệm cốt lõi

Intermolecular forces (IMFs) act *between* separate molecules and are always much weaker than the covalent bonds *within* a molecule. There are three types, in order of increasing strength:

1. **London (induced-dipole–induced-dipole) dispersion forces:** present in *every* molecule (polar or non-polar), caused by random, momentary fluctuations in electron distribution that create a temporary dipole, inducing a matching dipole in a neighbouring molecule. Strength **increases with the number of electrons** (larger molecules/atoms) and with **surface area / molecular shape** — more elongated molecules have more contact area and stronger dispersion forces than compact, branched isomers of the same molar mass.
2. **Permanent dipole–dipole forces:** act between molecules that have a permanent bond dipole that is *not* cancelled by symmetry (polar molecules); the $\delta+$ end of one molecule attracts the $\delta-$ end of a neighbour.
3. **Hydrogen bonding:** an especially strong type of permanent dipole–dipole attraction. It requires (a) a hydrogen atom covalently bonded **directly** to **N, O or F** (small, highly electronegative atoms that leave the H atom strongly $\delta+$), and (b) a lone pair on an N, O or F atom of a *neighbouring* molecule to accept that hydrogen.

Summary of intermolecular forces:

Type	Cause	Typical strength	Example
London dispersion	temporary induced dipoles from electron fluctuation	0.05–40 kJ mol^{-1}	all molecules; e.g. I2
Permanent dipole–dipole	attraction between permanent bond dipoles	5–20 kJ mol^{-1}	CH3Cl
Hydrogen bonding	H bonded to N/O/F, attracted to a lone pair on N/O/F of a neighbour	10–40 kJ mol^{-1}	H2O, NH3, HF

Ví dụ mẫu · Why does H2O boil at a much higher temperature than H2S?

H2O boils at 100°C; H2S (molar mass 34, heavier than H2O's 18) boils at only -60°C. Despite H2S having more electrons (stronger dispersion forces), it boils far lower, because **only** H2O **can hydrogen bond**: O is small and highly electronegative (3.5) with lone pairs, so O — H bonds are strongly polarised and O readily accepts a neighbouring hydrogen bond. Sulfur is larger and less electronegative (2.5), so H2S molecules experience only weaker permanent dipole–dipole and dispersion forces — far less energy is needed to separate them.

Ví dụ mẫu · Branching and boiling point: n-pentane vs. neopentane

n-Pentane (CH3(CH2)3CH3) and neopentane (2,2-dimethylpropane) are both C5H12 — same molecular formula, same molar mass, same total number of electrons. Yet n-pentane boils at 36°C, while the more highly branched, compact neopentane boils at only 9.5°C.

Reasoning: n-pentane's long, thin chain shape allows extensive surface contact between neighbouring molecules, maximising London dispersion forces. Neopentane's branching makes

the molecule more spherical/compact, drastically **reducing its surface area** of contact with neighbours and weakening the dispersion forces — hence the lower boiling point, even though both molecules have identical numbers of electrons.

Ví dụ mẫu · Anomalous boiling point of HF compared with HCl

Down Group 17, boiling points of the hydrogen halides would be expected to **increase** with molar mass (more electrons ⇒ stronger dispersion forces): this is true for HCl (-85°C), HBr (-67°C) and HI (-35°C). But HF, despite being the *lightest* and having the *fewest* electrons, boils at 19.5°C — far higher than HCl. This is because F is the most electronegative element and bears lone pairs, so HF molecules hydrogen bond strongly to one another; HCl cannot, since Cl (electronegativity 3.0) does not polarise the H — Cl bond enough, and the atom is too large, for effective hydrogen bonding. The extra energy needed to break these hydrogen bonds outweighs HF's weaker dispersion forces.

(!) Lỗi thường gặp: It is easy to say that boiling water "breaks the hydrogen bonds" and wrongly conclude that the covalent O — H bonds inside each molecule are broken. In fact, boiling only overcomes the (much weaker) *intermolecular* hydrogen bonds *between* separate H2O molecules; the covalent O — H bonds *within* each molecule remain fully intact — steam is still made of complete H2O molecules, not free H and O atoms.

VN **GIẢI THÍCH TIẾNG VIỆT**

Lực liên phân tử luôn yếu hơn nhiều so với liên kết cộng hoá trị bên trong phân tử. Có 3 loại, mạnh dần: (1) **lực phân tán London** — có ở mọi phân tử, do dao động ngẫu nhiên của electron tạo lưỡng cực tạm thời, mạnh hơn khi phân tử có nhiều electron hơn và diện tích tiếp xúc lớn hơn (mạch thẳng mạnh hơn mạch nhánh cùng khối lượng); (2) **lực lưỡng cực–lưỡng cực thường trực**, ở phân tử phân cực; (3) **liên kết hydro** — mạnh nhất, chỉ xảy ra khi H liên kết trực tiếp với N, O hoặc F, và hút vào cặp electron riêng trên N/O/F của phân tử bên cạnh. Ví dụ: H2O sôi ở 100°C cao hơn hẳn H2S (-60°C) nhờ liên kết hydro; HF sôi cao bất thường so với HCl cùng lý do; còn neopentan phân nhánh sôi thấp hơn n-pentan mạch thẳng dù cùng công thức phân tử, vì diện tích tiếp xúc nhỏ hơn làm lực phân tán yếu hơn.

3.5 Practice

Bài tập luyện tập

What is the shape of the SF4 molecule?

(A) Tetrahedral
(B) Trigonal pyramidal
(C) Seesaw
(D) Square planar

Lời giải chi tiết

S has 6 valence electrons: 4 used for bonding (to 4 F) $+1$ lone pair $= 5$ domains ⇒ trigonal bipyramidal electron-domain geometry, with the lone pair equatorial. The atoms alone trace out a **seesaw** shape. **(C)**.

Bài tập luyện tập

Explain why CO2 is a non-polar molecule even though each C = O bond is polar.

Lời giải chi tiết

CO2 is linear (O = C = O, 180°) because carbon has 2 electron domains and no lone pairs. The two C = O bond dipoles are equal in size and point in exactly opposite directions, so they cancel each other out by symmetry — giving zero overall molecular dipole moment, i.e. a non-polar molecule.

Bài tập luyện tập

Explain the boiling point order CH4 (-162°C) < CH3Cl (-24°C) < CH3OH (65°C).

Lời giải chi tiết

CH4 is non-polar, so only weak London dispersion forces act between molecules — the weakest of the three. CH3Cl is polar (C–Cl bond dipole not cancelled), adding permanent dipole–dipole forces on top of dispersion, so more energy is needed to separate its molecules. CH3OH has an O − H bond, so its molecules can hydrogen bond to each other — the strongest of the three types of intermolecular force — giving it by far the highest boiling point.

Bài tập luyện tập

In dimeric Al2Cl6, two AlCl3 units join together using dative bonds. Explain which atoms act as the dative bond donors, and why.

Lời giải chi tiết

Each Al in AlCl3 has only 6 electrons around it (electron-deficient), while each terminal Cl atom carries lone pairs. Two of the four Cl atoms become "bridging" chlorines: each bridging Cl keeps one normal covalent bond to its own Al atom and additionally donates one of its lone pairs to form a **dative bond** to the *other* Al atom, completing that Al's octet. So the chlorine atoms are the dative-bond donors (they supply the lone pair), and the aluminium atoms are the acceptors (they have the empty orbital).

Bài tập luyện tập

Explain why MgO has a much higher melting point (2852°C) than NaCl (801°C).

Lời giải chi tiết

Mg^{2+} and O^{2-} each carry twice the charge of $Na+$ and $Cl-$, and are also smaller ions. By Coulomb's law, electrostatic attraction increases with the product of the charges and decreases with distance, so the ionic bonds in MgO are far stronger than in NaCl — requiring much more energy (a much higher temperature) to break down the lattice.

Bài tập luyện tập

Which type of bonding holds atoms together in solid magnesium?

(A) Ionic bonding
(B) Covalent bonding
(C) Metallic bonding
(D) Hydrogen bonding

Lời giải chi tiết

Magnesium is a metal: its atoms are held together by the electrostatic attraction between Mg^{2+} cations and a sea of delocalised electrons. **(C)**.

Bài tập luyện tập

How many electron domains surround the central P atom in PCl5, and what is the resulting shape?

(A) 4; tetrahedral
(B) 5; trigonal bipyramidal
(C) 5; square pyramidal
(D) 6; octahedral

Lời giải chi tiết

P has 5 bonding domains (to 5 Cl atoms) and no lone pairs: 5 domains $\Rightarrow$ trigonal bipyramidal, with bond angles of 90° (axial–equatorial) and 120° (equatorial–equatorial). **(B)**.

Bài tập luyện tập

Predict the shape of BeCl2, given that Be does not obey the octet rule here.

(A) Bent
(B) Linear
(C) Trigonal planar
(D) Tetrahedral

Lời giải chi tiết

Be contributes only 2 valence electrons, used for 2 Be $-$ Cl bonds, with no lone pairs remaining: 2 electron domains $\Rightarrow$ **linear**, Cl $-$ Be $-$ Cl at 180°. **(B)**.

Bài tập luyện tập

Predict the shape and approximate bond angle of SO2.

Lời giải chi tiết

S has 6 valence electrons: one S $=$ O double bond and one S $-$ O single bond each count as 1 domain, plus 1 lone pair remains: $2 + 1 = 3$ domains $\Rightarrow$ trigonal planar electron-domain geometry. With the atoms alone, the shape is **bent (V-shaped)**, with an O–S–O angle slightly less than 120° (about 119°) due to lone pair–bond pair repulsion.

Bài tập luyện tập

Rank C $-$ C, C $=$ C and C $\equiv$ C in order of **increasing** bond length.

(A) C $-$ C $<$ C $=$ C $<$ C $\equiv$ C
(B) C $\equiv$ C $<$ C $=$ C $<$ C $-$ C
(C) C $=$ C $<$ C $-$ C $<$ C $\equiv$ C
(D) All three are equal

Lời giải chi tiết

More shared electron pairs pull the nuclei closer together, so bond length decreases from single to triple: C ≡ C (120 pm) < C = C (134 pm) < C − C (154 pm). **(B).**

Bài tập luyện tập

Rank C − C, C = C and C ≡ C in order of **increasing** bond energy (strength).

(A) C − C < C = C < C ≡ C
(B) C ≡ C < C = C < C − C
(C) C = C < C − C < C ≡ C
(D) All three are equal

Lời giải chi tiết

More shared pairs means a stronger bond: C − C (347) < C = C (612) < C ≡ C (838 kJ mol^{-1}). **(A).**

Bài tập luyện tập

Explain, in terms of orbital overlap, why rotation about a C = C double bond is restricted, and why this matters for organic chemistry.

Lời giải chi tiết

A C = C double bond consists of one σ bond (head-on overlap) and one π bond (sideways overlap of p-orbitals above and below the bond axis). Rotating one carbon relative to the other would twist the p-orbital lobes out of alignment, breaking the sideways overlap that makes up the π bond. Because this rotation cannot happen without breaking a bond, the groups attached to each carbon of a C = C are held in fixed relative positions — this restricted rotation is the structural basis for *E/Z* (geometric) isomerism.

Bài tập luyện tập

Distinguish between how a σ bond and a π bond are formed.

Lời giải chi tiết

A σ bond forms by the **head-on (end-on)** overlap of two orbitals directly along the line joining the two nuclei; it permits free rotation about the bond axis. A π bond forms by the **sideways (parallel)** overlap of two unhybridised p-orbitals, one lobe above and one below the internuclear axis; because the lobes must stay aligned, a π bond restricts rotation about that axis.

Bài tập luyện tập

Which of the following molecules can form hydrogen bonds with other molecules of itself?

(A) HF
(B) HCl
(C) CH4
(D) PH3

Lời giải chi tiết

Hydrogen bonding requires H bonded directly to N, O or F. Only HF satisfies this: F is small, highly electronegative, and carries lone pairs. HCl's H is bonded to Cl (not N/O/F); CH4's H atoms are bonded to C; PH3's H atoms are bonded to P. **(A)**.

Bài tập luyện tập

NH3 boils at -33°C, while PH3 (heavier, more electrons) boils at -87°C. Explain this anomaly.

Lời giải chi tiết

NH3's N–H bonds allow hydrogen bonding between molecules (N is small, highly electronegative, with a lone pair), which is a much stronger intermolecular force than the dispersion forces that dominate in PH3 (P is larger and far less electronegative, so P–H bonds cannot hydrogen bond effectively). Even though PH3 has more electrons and therefore stronger dispersion forces, this is outweighed by the loss of hydrogen bonding, so NH3 boils at a substantially higher temperature.

Bài tập luyện tập

Explain why the boiling points of the halogens increase down Group 17: F2 (-188°C) $<$ Cl2 (-34°C) $<$ Br2 (59°C) $<$ I2 (184°C).

Lời giải chi tiết

All halogen molecules are non-polar diatomics, so the only intermolecular force present is London dispersion. Down the group, each molecule has progressively more electrons, so the temporary induced dipoles are larger and more polarisable — dispersion forces strengthen steadily down the group, requiring more energy (a higher temperature) to separate the molecules and so boiling point rises from F2 (gas at room temperature) to I2 (solid at room temperature).

Bài tập luyện tập

Which of n-pentane and neopentane (2,2-dimethylpropane) has the higher boiling point, and why?

(A) n-Pentane, because it has more surface contact area between molecules

(B) Neopentane, because it is more compact and packs more efficiently

(C) They are identical, since both are C5H12

(D) Neopentane, because it has more electrons

Lời giải chi tiết

Both isomers have identical molecular formula (C5H12) and the same number of electrons, so dispersion-force strength depends on shape. n-Pentane's elongated chain allows much greater surface contact between neighbouring molecules than neopentane's compact, near-spherical shape, giving n-pentane the stronger dispersion forces and hence the higher boiling point. **(A)**.

Bài tập luyện tập

Explain how electronegativity changes across Period 3 (Na to Cl) and why.

(A) Increases, because nuclear charge increases while shielding stays roughly constant

(B) Decreases, because atomic radius increases

(C) Stays constant across a period

(D) Increases, because the number of shells increases

Lời giải chi tiết

Across a period, protons are added to the nucleus while electrons are added to the *same* outer shell, so shielding barely changes; the increasing nuclear charge attracts the bonding pair of electrons more strongly, so electronegativity rises from Na (0.9) to Cl (3.0). **(A)**.

Bài tập luyện tập

Explain how electronegativity changes down Group 17 (F to I) and why.

(A) Increases, because nuclear charge increases

(B) Decreases, because atomic radius and shielding increase faster than nuclear charge

(C) Stays constant down a group

(D) Decreases because atoms become more metallic

Lời giải chi tiết

Down a group, extra full inner shells are added, increasing both atomic radius and shielding of the nuclear charge from the bonding electrons. Although nuclear charge also increases, the shielding/radius effect dominates, so the outer bonding electrons are attracted less strongly and electronegativity falls: F (4.0) $>$ Cl (3.0) $>$ Br (2.8) $>$ I (2.5). **(B)**.

Bài tập luyện tập

The electronegativity difference between K and Br is large (K ≈ 0.8, Br $= 2.8$, ΔEN $= 2.0$). What type of bonding is expected in KBr?

Lời giải chi tiết

Such a large electronegativity difference means the more electronegative atom (Br) essentially removes the electron entirely from the less electronegative atom (K), rather than merely sharing it unevenly. This corresponds to **ionic bonding**: K forms K$+$ and Br forms Br$-$, held together by electrostatic attraction in a giant ionic lattice, rather than covalent bonding with a shared electron pair.

Bài tập luyện tập

Explain, using their structures, why ionic compounds are typically brittle while metals are malleable.

Lời giải chi tiết

In an ionic lattice, a sharp force can shift one layer of ions relative to its neighbour, bringing ions of the *same* charge into contact; the strong repulsion between like charges then splits the crystal — so ionic solids are brittle. In a metal, the delocalised electron sea is not tied to any particular ion: when one layer of cations slides over another, the electron sea simply redistributes to keep surrounding every cation, so the metallic bonding is maintained and the metal deforms smoothly (malleable/ductile) rather than fracturing.

Bài tập luyện tập

A molecule has a T-shaped structure. How many lone pairs are on its central atom?

(A) 0
(B) 1
(C) 2
(D) 3

Lời giải chi tiết

A T-shape arises from a trigonal bipyramidal electron-domain arrangement (5 domains total) in which 3 domains are bonding pairs and the shape is named from the atoms only. So $5 - 3 = 2$ domains must be lone pairs, both occupying equatorial positions (as in ClF3). **(C)**.

Bài tập luyện tập

XeF4 and CH4 both have 4 atoms bonded to the central atom, yet XeF4 is square planar while CH4 is tetrahedral. Explain why.

Lời giải chi tiết

CH4's central C atom has exactly 4 electron domains, all bonding pairs and no lone pairs, so both the electron-domain geometry and the molecular shape are tetrahedral (109.5°). XeF4's central Xe atom has *6* electron domains in total (4 bonding pairs $+2$ lone pairs), giving an octahedral electron-domain geometry; the two lone pairs occupy positions directly opposite each other (minimising lone pair–lone pair repulsion), leaving the 4 F atoms arranged in a single plane — a square planar *molecular* shape, even though 4 atoms are bonded in both molecules.

Bài tập luyện tập

Which type of intermolecular force is present in *every* covalent molecule, whether polar or non-polar?

(A) Hydrogen bonding
(B) Permanent dipole–dipole forces
(C) London (induced-dipole–induced-dipole) dispersion forces
(D) Ionic bonding

Lời giải chi tiết

Every molecule, however non-polar, has electrons whose distribution fluctuates momentarily, creating temporary induced dipoles — this gives rise to London dispersion forces in all molecules. Permanent dipole–dipole forces and hydrogen bonding only occur in molecules that are polar (and, for hydrogen bonding, that have H bonded to N/O/F). **(C)**.

Bài luyện nâng cao (A2)

A student claims that because ClF3 and PCl5 both have a central atom from a similar part of the Periodic Table bonded to halogens, they should have the same shape. Explain why this reasoning is flawed, referring to electron domain counts.

Lời giải chi tiết

Shape depends on the *total number of electron domains* (bonding pairs *and* lone pairs) around the central atom, not simply on which elements are present. In PCl5, P has 5 valence electrons, all used in bonding to 5 Cl atoms, giving 5 domains and *no* lone pairs $\Rightarrow$ trigonal bipyramidal. In ClF3, Cl has 7 valence electrons, only 3 used in bonding to F, leaving 2 lone pairs $\Rightarrow$ also 5 domains in total, but with 2 of them being lone pairs, giving a *different* molecular shape (T-shaped, not trigonal bipyramidal). Two central atoms with the same total domain count can therefore have very different molecular shapes if their split between bonding pairs and lone pairs differs.

Bài tập luyện tập

A molecule XY2 has a bond angle of exactly 180°. Which of the following best describes its central atom X?

(A) 2 bonding domains, 0 lone pairs
(B) 2 bonding domains, 1 lone pair
(C) 3 bonding domains, 0 lone pairs
(D) 4 bonding domains, 2 lone pairs

Lời giải chi tiết

A 180° bond angle with only 2 atoms bonded to the central atom requires exactly 2 electron domains in total, with no lone pairs present to compress the angle: 2 bonding domains and 0 lone pairs $\Rightarrow$ linear, as in CO2 or BeCl2. **(A)**.

States of Matter

Mục tiêu Unit: Thuyết động học phân tử chất khí và phương trình khí lý tưởng $pV = nRT$; các định luật riêng — Boyle (áp suất–thể tích ở nhiệt độ không đổi), Charles (thể tích–nhiệt độ ở áp suất không đổi), và Avogadro (thể tích bằng nhau chứa số mol bằng nhau ở cùng điều kiện); khí thực và nguyên nhân lệch khỏi ứng xử lý tưởng, phương trình van der Waals (mức A2) cùng ý nghĩa các số hạng hiệu chỉnh áp suất và thể tích; cấu trúc bốn loại chất rắn (ion khổng lồ, cộng hoá trị khổng lồ, phân tử đơn giản, kim loại khổng lồ), so sánh sâu kim cương–than chì–fullerene và silic–silic đioxit; sự chuyển thể, đường cong đun nóng và nhiệt ẩn; áp suất hơi và mối liên hệ với nhiệt độ sôi.

4.1 The gaseous state: kinetic theory

Khái niệm cốt lõi

The **kinetic theory of gases** makes several simplifying assumptions about an **ideal gas**:

- Gas particles are in continuous, random motion, colliding with each other and with the container walls.
- Collisions are perfectly **elastic**: no kinetic energy is lost overall in a collision.
- The volume of the gas particles themselves is **negligible** compared with the volume of the container.
- There are **no intermolecular forces** of attraction or repulsion between particles, except during the instant of collision.
- The **average kinetic energy** of the particles is directly proportional to the **absolute (Kelvin) temperature**.

The ideal gas equation:

$$pV = nRT$$

where p is pressure (Pa), V is volume (m^3), n is amount of gas (mol), T is absolute temperature (K), and $R = 8.31$ J K^{-1}mol^{-1} is the molar gas constant. At room temperature and pressure (r.t.p., 25°C and 100 kPa), one mole of any gas occupies 24.0 dm^3.

Ví dụ mẫu · Finding the amount of gas from $pV = nRT$

A flask of volume 500 cm^3 contains a gas at a pressure of 150 kPa and a temperature of 27°C. Calculate the amount, in mol, of gas present.

Convert units to SI: $p = 150\,000$ Pa; $V = 500$ cm^3 $= 5.00 \times 10^{-4}$ m^3; $T = 27 + 273 = 300$ K.

$$n = \frac{pV}{RT} = \frac{150\,000 \times 5.00 \times 10^{-4}}{8.31 \times 300} = \frac{75.0}{2493} = 0.0301 \text{ mol (3 s.f.)}$$

GIẢI THÍCH TIẾNG VIỆT

VN

Thuyết động học phân tử coi khí lý tưởng có: chuyển động hỗn loạn liên tục, va chạm hoàn toàn đàn hồi (không mất động năng), thể tích phân tử không đáng kể so với thể tích bình chứa, không có lực hút/đẩy giữa các phân tử (trừ lúc va chạm), và động năng trung bình tỉ lệ thuận với nhiệt độ tuyệt đối (Kelvin). Từ đó suy ra phương trình trạng thái khí lý tưởng $pV = nRT$ với $R = 8.31$ J K^{-1}mol^{-1}; ở điều kiện phòng (r.t.p., 25°C, 100 kPa), 1 mol khí bất kỳ chiếm thể tích 24.0 dm^3.

4.1.1 Boyle's Law

Khái niệm cốt lõi

Boyle's Law: at constant temperature and constant amount of gas, the pressure of a fixed mass of gas is **inversely proportional** to its volume:

$$pV = \text{constant}, \qquad \text{i.e.} \qquad p_1V_1 = p_2V_2.$$

This follows directly from $pV = nRT$: if n and T are both fixed, then pV must also stay fixed.

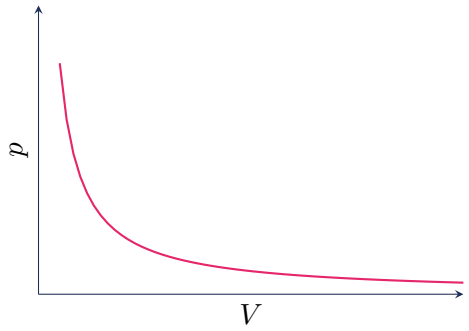

Figure 1. Boyle's Law: at constant T and n, pressure and volume trace out a hyperbola ($p \propto 1/V$).

Ví dụ mẫu · Applying Boyle's Law

A gas occupies 240 cm^3 at a pressure of 100 kPa. At constant temperature, it is compressed to 80 cm^3. Find the new pressure.

$$p_1V_1 = p_2V_2 \;\Rightarrow\; p_2 = \frac{p_1V_1}{V_2} = \frac{100 \times 240}{80} = 300 \text{ kPa}.$$

4.1.2 Charles's Law

Khái niệm cốt lõi

Charles's Law: at constant pressure and constant amount of gas, the volume of a fixed mass of gas is **directly proportional** to its absolute temperature:

$$\frac{V}{T} = \text{constant}, \qquad \text{i.e.} \qquad \frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (T \text{ in kelvin}).$$

Extrapolating a graph of V against temperature in $^{\circ}$C back to $V = 0$ gives -273°C — this is why the Kelvin scale is defined with its zero at -273°C (absolute zero).

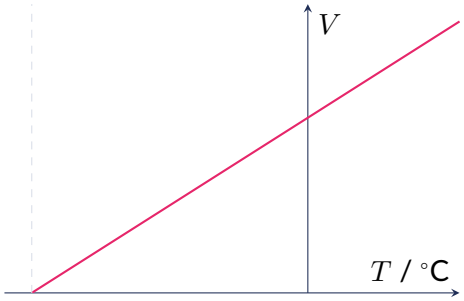

Figure 2. Charles's Law: at constant p and n, V is directly proportional to absolute temperature; extrapolating to $V = 0$ gives -273°C, the absolute zero of temperature.

Ví dụ mẫu · Applying Charles's Law

A gas occupies 200 cm^3 at 20°C and constant pressure. Find its volume at 100°C, same pressure. Convert to kelvin: $T_1 = 293$ K, $T_2 = 373$ K.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \;\Rightarrow\; V_2 = \frac{V_1 T_2}{T_1} = \frac{200 \times 373}{293} = 255 \text{ cm}^3 \text{ (3 s.f.)}$$

4.1.3 Avogadro's Law

Khái niệm cốt lõi

Avogadro's Law: equal volumes of any gases, measured at the same temperature and pressure, contain **equal numbers of moles** (and hence equal numbers of molecules). Consequently, for a gas-phase reaction, the ratio of **volumes** of reactants and products (at the same T and p) is identical to the ratio of **moles** given by the balanced equation.

Ví dụ mẫu · Reacting gas volumes

In the reaction $\mathrm{N2(g) + 3H2(g) -> 2NH3(g)}$, 40 cm^3 of N2 reacts completely with excess H2 at constant temperature and pressure. What volume of H2 is used, and what volume of NH3 is formed?

By Avogadro's Law, volume ratio = mole ratio = N2 : H2 : NH3 $= 1 : 3 : 2$.
Volume of H2 used $= 3 \times 40 = 120$ cm^3. Volume of NH3 formed $= 2 \times 40 = 80$ cm^3.

VN **GIẢI THÍCH TIẾNG VIỆT**

Định luật Boyle: ở nhiệt độ và số mol không đổi, $pV =$ hằng số (áp suất tỉ lệ nghịch thể tích). Định luật Charles: ở áp suất và số mol không đổi, $V/T =$ hằng số (thể tích tỉ lệ thuận nhiệt độ tuyệt đối) — ngoại suy đồ thị V theo $T(^{\circ}\mathrm{C})$ về $V = 0$ cho ra -273°C, chính là gốc của thang Kelvin. Định luật Avogadro: các thể tích khí bằng nhau ở cùng nhiệt độ, áp suất chứa số mol bằng nhau — nên trong phản ứng có chất khí, tỉ lệ **thể tích** bằng đúng tỉ lệ **số mol** trong phương trình cân bằng.

4.2 Real gases and deviations from ideal behaviour

Khái niệm cốt lõi

A **real gas** deviates from ideal behaviour because two of the kinetic theory's assumptions break down:

- real gas particles **do** have a finite volume, which is no longer negligible compared with the container volume at **high pressure** (particles are squeezed close together);
- real gas particles **do** experience intermolecular forces of attraction, which become significant at **low temperature** (particles move slowly enough for attractions to pull them together) and at high pressure (particles are close enough for attractions to act).

The **compressibility factor** $Z = \dfrac{pV}{nRT}$ equals exactly 1 for an ideal gas at all conditions; deviations of Z from 1 measure how non-ideal a real gas is.

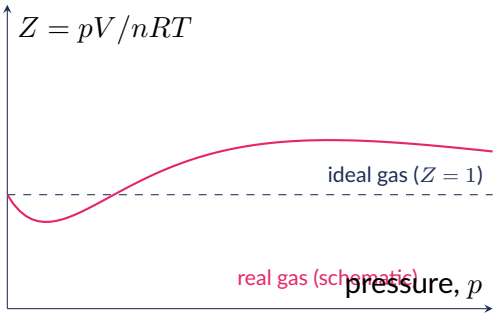

Figure 3. Schematic variation of compressibility factor Z with pressure for a real gas: $Z < 1$ at moderate pressure (attractive forces dominate, real volume is smaller than ideal), rising above 1 at high pressure (the finite volume of the molecules themselves dominates).

A real gas behaves most ideally at low pressure and high temperature:

- **Low pressure:** particles are far apart on average, so their own volume is negligible next to the (large) container volume, and they are too far apart for intermolecular attractions to have much effect — the **mean free path** (average distance travelled between collisions) is large.
- **High temperature:** the average kinetic energy of the particles is large compared with the (roughly constant) attractive potential energy between them, so intermolecular attractions barely slow the particles down or pull them together — collisions still behave close to elastic and independent.

Conversely, at **high pressure** the mean free path shrinks (particles are forced close together, so their own volume is no longer negligible), and at **low temperature** the average kinetic energy falls until it becomes comparable with the attractive potential energy, allowing attractions to noticeably pull particles together — both effects push Z away from 1.

Ví dụ mẫu · Explaining non-ideal behaviour

Explain, using kinetic theory, why real gases deviate most strongly from ideal behaviour at high pressure and low temperature.

High pressure: particles are forced much closer together, so the volume actually occupied by the gas particles becomes a significant fraction of the total volume (no longer negligible, contrary to kinetic theory's assumption); the reduced mean free path also means intermolecular

forces act over a larger fraction of the particles' motion.
Low temperature: particles move more slowly, so their average kinetic energy falls; once it becomes comparable to the attractive potential energy between particles, those attractions are no longer negligible and start to pull particles together and towards the container walls less forcefully than an ideal gas would predict, lowering the measured pressure/volume relative to the ideal prediction.

4.2.1 The van der Waals equation (A2)

Khái niệm cốt lõi

The **van der Waals equation** adjusts the ideal gas equation with two correction terms:

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

- The term $\frac{an^2}{V^2}$ **corrects the pressure**: intermolecular attractions pull particles away from the container walls, so the pressure a real gas actually exerts is *lower* than an ideal gas would exert — this term adds back the "missing" pressure. The constant a is larger for molecules with stronger intermolecular attractions (more electrons/larger, more polarisable molecules, or permanent dipoles/hydrogen bonding).
- The term nb **corrects the volume**: the molecules themselves take up real space, so the volume actually *available* for the particles to move in is less than the container volume V. The constant b is larger for physically bigger molecules.

Typical van der Waals constants (illustrative):

Gas	a / atm dm^{6}mol^{-2}	b / dm^{3}mol^{-1}	Notes
He	0.034	0.0237	few electrons, very small atom
N2	1.39	0.0391	more electrons, larger molecule
CO2	3.59	0.0427	many electrons, polarisable, larger

Ví dụ mẫu · Ranking the size of real-gas corrections

Explain why the van der Waals constants a and b are both much larger for CO2 than for He.

The b term (volume correction): a CO2 molecule is physically much larger than a helium atom (more atoms, more electrons, bigger electron cloud), so it excludes far more volume from the container than a tiny He atom does — $b(\text{CO2}) \gg b(\text{He})$.
The a term (attraction correction): CO2 has many more electrons than He, giving it much stronger London dispersion forces (more polarisable electron cloud); helium, with only 2 electrons held very tightly to its nucleus, has almost negligible intermolecular attraction. Hence $a(\text{CO2}) \gg a(\text{He})$, and CO2 deviates far more strongly from ideal behaviour than He does under the same conditions.

VN **GIẢI THÍCH TIẾNG VIỆT**
Khí thực lệch khỏi khí lý tưởng vì (1) phân tử khí thực có thể tích riêng đáng kể ở áp suất cao (khi bị nén gần nhau), và (2) có lực hút liên phân tử đáng kể ở nhiệt độ thấp (khi động năng trung

bình không còn vượt trội hẳn thế năng hút). Khí thực gần lý tưởng nhất ở áp suất thấp, nhiệt độ cao (quãng đường tự do trung bình lớn, động năng lớn hơn nhiều thế năng hút). Phương trình van der Waals $(p + an^2/V^2)(V - nb) = nRT$ thêm 2 số hạng hiệu chỉnh: an^2/V^2 bù lại áp suất bị "mất" do lực hút kéo phân tử vào trong; nb trừ đi thể tích thực sự bị các phân tử chiếm chỗ. Hằng số a, b càng lớn với phân tử càng to, càng nhiều electron (ví dụ CO2 lớn hơn nhiều so với He).

4.3 Structures of solids

Four types of crystal structure:

Structure type	Melting point	Electrical conductivity	Example
Giant ionic	high	only molten/aqueous	NaCl, MgO
Giant covalent	very high	usually none (graphite is the exception)	diamond, SiO2, graphite
Simple molecular	low	none (no free ions/electrons)	CO2, I2, ice
Giant metallic	high (usually)	good, solid and molten	Na, Mg, Fe

Diamond and graphite are both giant covalent forms of pure carbon, but their properties differ sharply because of how the carbon atoms are arranged and bonded. In **diamond**, every carbon atom forms 4 strong covalent σ bonds to 4 neighbours in a rigid 3-dimensional tetrahedral network — all electrons are localised in these bonds, so diamond does not conduct electricity, and is extremely hard because a force applied in any direction must break many strong covalent bonds. In **graphite**, each carbon atom forms only 3 σ bonds within a flat hexagonal layer, leaving one electron per atom in a delocalised π system spread over the whole layer; these delocalised electrons make graphite a good conductor *along* the layers (but a poor conductor perpendicular to them). The layers themselves are held together only by weak London dispersion forces, letting them slide over each other — this is why graphite is soft and slippery, and is used as a lubricant and in pencils.

Ví dụ mẫu · Comparing the melting points of SiO2 and CO2

SiO2 (silicon dioxide, quartz) melts at approximately 1710°C; CO2 sublimes at -78°C at atmospheric pressure. Both have the formula XO2 — why such a huge difference?

SiO2 is a **giant covalent** structure: every Si atom is covalently bonded to 4 O atoms (and every O to 2 Si), building an infinite 3-D network. Melting requires breaking a huge number of strong covalent bonds throughout the entire structure, needing enormous energy.
CO2 is a **simple molecular** structure: small, discrete O = C = O molecules held together only by weak London dispersion forces. Only these weak intermolecular forces need to be overcome to separate the molecules — the strong C = O covalent bonds within each molecule are never broken — so only a small amount of energy is required, giving CO2 a very low sublimation temperature.

4.3.1 Fullerene (C60)

Khái niệm cốt lõi

Fullerene (C60, "buckminsterfullerene") is a third form of pure carbon: a **discrete molecule** of 60 carbon atoms arranged as a hollow, roughly spherical cage of fused hexagons and pentagons (like a football). Each carbon atom is covalently bonded to 3 neighbours (as in graphite), with the remaining electrons delocalised over the cage surface — but, unlike diamond and graphite, C60 forms individual **molecules**, not an infinite giant covalent lattice.

Ví dụ mẫu · Fullerene compared with diamond and graphite

Explain why solid C60 has a much lower melting point than diamond or graphite, and why it dissolves in some non-polar organic solvents while diamond and graphite do not.

Diamond and graphite are each a *single*, *continuous*, *giant covalent* network of covalent bonds — melting or dissolving either would require breaking huge numbers of strong covalent bonds throughout the whole structure. C60, in contrast, consists of **discrete individual molecules**: the covalent bonds *within* each C60 cage are strong, but separate C60 molecules are held to each other only by **weak London dispersion forces**. Melting solid C60, or dissolving it in a non-polar solvent, only needs to overcome these weak intermolecular forces between whole molecules (leaving each cage intact) — requiring far less energy, and allowing C60 to dissolve like other non-polar molecular substances.

VN **GIẢI THÍCH TIẾNG VIỆT**

Fullerene (C60) là một dạng thù hình khác của carbon nguyên chất: một **phân tử rời rạc** gồm 60 nguyên tử C ghép thành khối cầu rỗng dạng lục giác/ngũ giác (như quả bóng đá), mỗi C liên kết cộng hoá trị với 3 nguyên tử láng giềng. Khác với kim cương và than chì (mạng cộng hoá trị khổng lồ liên tục), C60 là các phân tử riêng biệt chỉ liên kết với nhau bằng lực phân tán London yếu, nên nóng chảy ở nhiệt độ thấp hơn nhiều và có thể hoà tan trong một số dung môi hữu cơ không phân cực — điều kim cương và than chì không làm được.

4.3.2 Silicon and silicon dioxide

Elemental **silicon** adopts the same giant covalent, diamond-like structure as carbon (each Si atom bonded to 4 neighbours), melting at about 1414°C. Unlike diamond, however, silicon is a **semiconductor**: its band gap (about 1.1 eV) is small enough that a small fraction of electrons can be thermally promoted into a conducting state at room temperature, and conductivity *increases* with temperature as more electrons are promoted (the opposite trend to metals, whose conductivity falls as temperature rises). **Silicon dioxide**, SiO2, keeps the same overall giant covalent network idea (each Si bonded to 4 O, each O bridging 2 Si), but the polar Si — O bonds localise the bonding electrons strongly on oxygen, giving SiO2 a much larger band gap — so it behaves as an electrical **insulator**, not a semiconductor, despite melting at a similarly enormous temperature (about 1710°C).

Ví dụ mẫu · Silicon vs. silicon dioxide

Both silicon and SiO2 are giant covalent solids with very high melting points. State one key electrical difference between them, and explain it.

Difference: silicon is a semiconductor (poor conductor at room temperature, improving as temperature rises); SiO2 is an electrical insulator at all normal temperatures.
Explanation: in pure silicon, all bonding electrons are shared fairly equally in non-polar Si–Si bonds, and a small energy gap (band gap) separates the filled bonding states from empty,

higher-energy conducting states — enough electrons are thermally excited across this gap at room temperature to allow weak conduction. In SiO2, the Si — O bonds are much more polar (O is far more electronegative than Si), so the bonding electrons are held tightly and asymmetrically on oxygen; this produces a far larger band gap that thermal energy at ordinary temperatures cannot bridge, so essentially no electrons become mobile and SiO2 does not conduct.

VN **GIẢI THÍCH TIẾNG VIỆT**

Silic nguyên chất có cấu trúc cộng hoá trị khổng lồ giống kim cương (mỗi Si liên kết với 4 nguyên tử), nóng chảy ở khoảng 1414°C, nhưng là **chất bán dẫn**: vùng cấm hẹp (≈ 1.1 eV) cho phép một số electron được kích thích nhiệt để dẫn điện, và độ dẫn điện **tăng** theo nhiệt độ (ngược với kim loại). SiO2 cũng là mạng cộng hoá trị khổng lồ tương tự nhưng liên kết Si–O phân cực mạnh khiến electron liên kết bị giữ chặt trên O, tạo vùng cấm rất rộng — nên SiO2 là chất **cách điện**, dù nhiệt độ nóng chảy cũng rất cao ($\approx 1710^{\circ}$C).

4.3.3 Density and packing: diamond vs. graphite

Density comparison of carbon allotropes:

Allotrope	Density / g cm^{-3}	Structure detail
Diamond	3.51	compact 3-D tetrahedral network, all atoms strongly bonded
Graphite	2.25	flat hexagonal layers, large gap (≈ 0.335 nm) between layers
Fullerene (C60) solid	≈ 1.65	discrete spherical molecules with empty space between/inside cag

Ví dụ mẫu · Why is graphite less dense than diamond?

Explain, in terms of structure, why graphite (2.25 g cm^{-3}) is noticeably less dense than diamond (3.51 g cm^{-3}), even though both are pure carbon.

In diamond, every carbon atom is packed into a compact, continuous 3-dimensional network, with strong covalent bonds in *all* directions holding atoms close together throughout the structure. In graphite, atoms are tightly packed only *within* each hexagonal layer; the layers themselves are separated by a comparatively large gap (≈ 0.335 nm, much longer than a covalent bond) and held together only by weak London dispersion forces. This extra, mostly empty space between the layers means graphite packs the same carbon atoms into a larger overall volume, giving it a lower density than diamond.

4.4 Phase changes, vapour pressure and boiling

Khái niệm cốt lõi

When a pure substance is heated steadily at constant pressure, its temperature rises smoothly *except* at the melting point and boiling point, where the temperature stays constant for a time even though heating continues. At these plateaus, the energy supplied is used entirely to overcome intermolecular forces (**latent heat**) — increasing the potential energy of the particles as they rearrange into a less-ordered state — rather than increasing their kinetic energy (temperature).

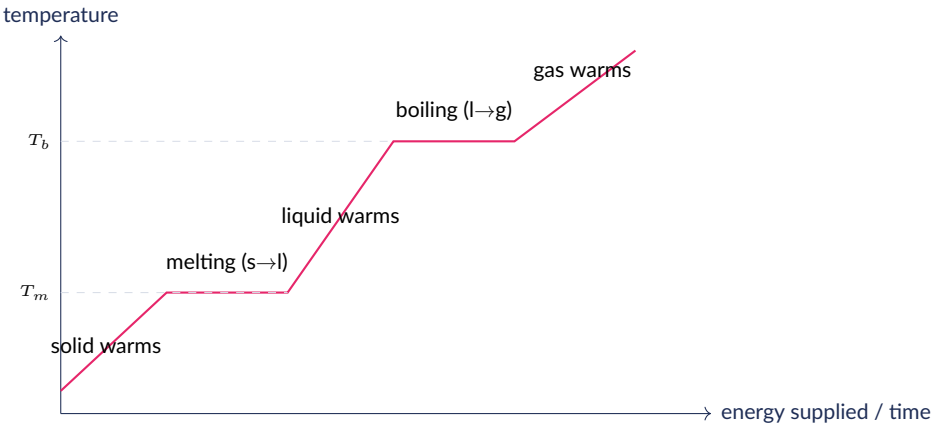

Figure 4. A heating curve: temperature rises steadily within each phase, but plateaus at the melting point T_m and boiling point T_b while latent heat is absorbed.

VN **GIẢI THÍCH TIẾNG VIỆT**

Khi đun một chất tinh khiết ở áp suất không đổi, nhiệt độ tăng đều trừ tại điểm nóng chảy và điểm sôi — ở đó nhiệt độ **giữ nguyên** một thời gian dù vẫn cấp nhiệt liên tục. Lý do: toàn bộ năng lượng cấp vào lúc này dùng để **phá vỡ lực liên phân tử** (nhiệt ẩn), làm tăng thế năng khi các hạt sắp xếp lại thành trạng thái kém trật tự hơn (rắn→lỏng, lỏng→khí), chứ không làm tăng động năng trung bình (nên nhiệt độ không đổi) cho đến khi toàn bộ chất đã chuyển thể xong.

4.4.1 Vapour pressure and boiling

Khái niệm cốt lõi

In a closed container, molecules continually evaporate from the surface of a liquid and condense back into it; when these two rates become equal, a dynamic equilibrium is reached and the pressure exerted by the vapour above the liquid is called the **(saturated) vapour pressure**. Vapour pressure **increases with temperature**, since more molecules gain enough kinetic energy to escape the liquid. A liquid **boils** when its vapour pressure becomes equal to the external (atmospheric) pressure — at that point, bubbles of vapour can form throughout the liquid, not just evaporate from the surface.

Ví dụ mẫu · Why does water boil at a lower temperature on a mountain?

Explain why water boils at a lower temperature at high altitude than at sea level.

Atmospheric pressure is lower at high altitude (there is less air pressing down from above). Since boiling occurs when the liquid's vapour pressure rises to *match* the external pressure, a lower external pressure means the liquid needs to reach only a *lower* vapour pressure — and therefore a *lower* temperature — before it boils. This is also why food cooked in boiling water takes longer at high altitude: the water boils at a lower temperature, so less thermal energy is being delivered to the food per unit time even while it is "boiling".

VN **GIẢI THÍCH TIẾNG VIỆT**

Áp suất hơi là áp suất do hơi chất lỏng gây ra khi đạt cân bằng động (tốc độ bay hơi = tốc độ ngưng tụ) trong bình kín; áp suất hơi **tăng** theo nhiệt độ. Chất lỏng **sôi** khi áp suất hơi của nó bằng đúng áp suất khí quyển bên ngoài. Ở vùng núi cao, áp suất khí quyển thấp hơn nên nước chỉ cần đạt áp suất hơi thấp hơn (tức nhiệt độ thấp hơn) đã sôi — đây là lý do nấu ăn ở vùng cao lâu chín hơn dù nước "đã sôi".

4.5 Practice

Bài tập luyện tập

Under which conditions does a real gas deviate **most** strongly from ideal gas behaviour?

(A) Low pressure, high temperature
(B) High pressure, low temperature
(C) High pressure, high temperature
(D) Low pressure, low temperature

Lời giải chi tiết

High pressure squeezes molecules close together, so their own volume is no longer negligible; low temperature reduces average kinetic energy until it becomes comparable with intermolecular attractive forces, which then significantly affect motion. Both push the gas furthest from ideal behaviour. **(B)**.

Bài tập luyện tập

A flask of fixed volume 2.00 dm^3 contains 0.0800 mol of a gas at 27°C. Calculate the pressure inside the flask.

Lời giải chi tiết

Using $pV = nRT$ with $V = 2.00 \times 10^{-3}$ m^3, $T = 300$ K:

$$p = \frac{nRT}{V} = \frac{0.0800 \times 8.31 \times 300}{2.00 \times 10^{-3}} = \frac{199.4}{2.00 \times 10^{-3}} = 99\,700 \text{ Pa} \approx 99.7 \text{ kPa}.$$

Bài tập luyện tập

Explain why graphite conducts electricity well **within** a layer but very poorly **between** layers (perpendicular to the layers).

Lời giải chi tiết

Within each layer, every carbon atom contributes one electron to a delocalised π system spread across the whole hexagonal sheet; these mobile electrons can flow freely along the layer when a potential difference is applied along it, giving good in-plane conductivity. Between layers, there is no covalent bonding and no delocalised electron system — only weak London dispersion forces hold the layers together — so there is no equivalent pathway for charge to move perpendicular to the layers, and conductivity in that direction is very poor.

Bài tập luyện tập

Br2 (melting point -7°C) and I2 (melting point 114°C) are both simple molecular solids/liquids held together only by London dispersion forces. Explain why I2 has the higher melting point.

Lời giải chi tiết

I2 molecules have more electrons than Br2 molecules (iodine atoms are larger, with more electron shells), giving I2 stronger, more polarisable electron clouds and hence stronger London dispersion forces between molecules. More energy is needed to overcome these stronger dispersion forces, so I2 has the higher melting point (and is a solid at room temperature, unlike

liquid Br2).

Bài tập luyện tập

A gas occupies 600 cm^3 at a pressure of 120 kPa and constant temperature. What is its new volume if the pressure is increased to 200 kPa?

(A) 360 cm^3
(B) 400 cm^3
(C) 1000 cm^3
(D) 720 cm^3

Lời giải chi tiết

Boyle's Law: $p_1V_1 = p_2V_2 \Rightarrow V_2 = \dfrac{120 \times 600}{200} = 360$ cm^3. **(A)**.

Bài tập luyện tập

A gas occupies 150 cm^3 at 17°C and constant pressure. What volume does it occupy at 87°C?

(A) 150 cm^3
(B) 186 cm^3
(C) 190 cm^3
(D) 300 cm^3

Lời giải chi tiết

Convert to kelvin: $T_1 = 290$ K, $T_2 = 360$ K. Charles's Law: $V_2 = \dfrac{V_1T_2}{T_1} = \dfrac{150 \times 360}{290} = 186$ cm^3 (3 s.f.). **(B)**.

Bài tập luyện tập

30 cm^3 of methane, CH4, is burned completely in excess oxygen at constant temperature and pressure: CH4(g) + 2O2(g)− > CO2(g) + 2H2O(g). What volume of CO2 is formed?

(A) 15 cm^3
(B) 30 cm^3
(C) 60 cm^3
(D) 90 cm^3

Lời giải chi tiết

By Avogadro's Law, volume ratio = mole ratio. From the equation, CH4 : CO2 $= 1 : 1$, so 30 cm^3 of CH4 produces 30 cm^3 of CO2. **(B)**.

Bài tập luyện tập

In the van der Waals equation, what does the term an^2/V^2 physically represent?

(A) The volume excluded by the gas molecules themselves
(B) A correction added to the observed pressure to account for intermolecular attractions lowering it
(C) The number of moles of gas present
(D) The kinetic energy of the gas molecules

Lời giải chi tiết

Intermolecular attractions pull molecules away from the container walls just before they collide, so a real gas exerts a slightly lower pressure than an ideal gas would; an^2/V^2 is added back to correct for this "missing" pressure. **(B)**.

Bài tập luyện tập

In the van der Waals equation, what does the term nb physically represent?

(A) The pressure correction due to intermolecular attraction

(B) The total kinetic energy of the gas

(C) The volume actually occupied/excluded by the gas molecules themselves

(D) The amount of gas present, in moles

Lời giải chi tiết

Real gas molecules have a finite size, so the volume genuinely available for particles to move within is less than the container's measured volume V; nb is subtracted to correct for this excluded volume. **(C)**.

Bài tập luyện tập

Which gas would you expect to deviate least from ideal behaviour at a given temperature and pressure: helium or carbon dioxide?

(A) Helium, because it has few electrons and very weak intermolecular attractions

(B) Carbon dioxide, because it is heavier

(C) They deviate identically, since both are gases

(D) Carbon dioxide, because it has more atoms

Lời giải chi tiết

Helium atoms are very small (small van der Waals b) and have only 2 electrons, giving extremely weak London dispersion forces (small van der Waals a); both corrections in the van der Waals equation are therefore small for He, so it behaves closest to an ideal gas. Carbon dioxide, with many more electrons and larger molecules, has much larger a and b values and deviates more. **(A)**.

Bài tập luyện tập

Explain, in terms of mean free path, why increasing the pressure on a gas makes it deviate more from ideal behaviour.

Lời giải chi tiết

Increasing pressure (at constant temperature and amount) forces the gas into a smaller volume, so the molecules are, on average, much closer together and the mean free path (average distance travelled between collisions) becomes much shorter. This means the finite volume actually occupied by the molecules is no longer negligible compared with the total volume, and molecules spend proportionally more time close enough for intermolecular attractive forces to act — both assumptions of the ideal gas model are violated, so behaviour deviates from ideal.

Bài tập luyện tập

Which of the following best describes the structure of diamond?

(A) Simple molecular, weak forces between molecules

(B) Giant ionic lattice of $C+$ and C^{4-} ions

(C) Giant covalent lattice, each C bonded to 4 others

(D) Giant metallic lattice with delocalised electrons

Lời giải chi tiết

Diamond is a giant covalent structure: every carbon atom forms 4 strong covalent bonds to 4 neighbouring carbon atoms in a continuous 3-D network. **(C)**.

Bài tập luyện tập

Match each substance to its structure type: (i) NaCl, (ii) graphite, (iii) solid CO2 (dry ice), (iv) magnesium metal.

Lời giải chi tiết

(i) NaCl — giant ionic lattice. (ii) Graphite — giant covalent (layered, with delocalised π electrons within each layer). (iii) Solid CO2 — simple molecular lattice held by London dispersion forces. (iv) Magnesium — giant metallic lattice (Mg^{2+} cations in a sea of delocalised electrons).

Bài tập luyện tập

Explain why diamond does not conduct electricity, while graphite conducts well along its layers.

Lời giải chi tiết

In diamond, every one of carbon's 4 outer electrons is used in a localised σ bond to a neighbouring atom, so there are no mobile charge carriers anywhere in the structure. In graphite, each carbon uses only 3 outer electrons for σ bonds within its layer, leaving one electron per atom delocalised over a π system spanning the whole layer; these delocalised electrons are free to move along the layer when a voltage is applied, carrying an electric current.

Bài tập luyện tập

Fullerene, C60, is best described as which type of structure?

(A) Giant covalent lattice, like diamond

(B) Simple molecular — discrete C60 cage molecules held by dispersion forces

(C) Giant ionic lattice

(D) Giant metallic lattice

Lời giải chi tiết

C60 forms discrete, individual cage-shaped molecules (60 carbon atoms each), not an infinite covalent network; separate C60 molecules are held to each other only by weak London dispersion forces, so it behaves as a simple molecular substance. **(B)**.

Bài tập luyện tập

Explain why C60 has a much lower melting point than diamond, even though both are pure carbon with strong covalent bonds present.

Lời giải chi tiết

In diamond, the strong covalent bonds extend throughout the *entire* giant structure, so melting means breaking huge numbers of covalent bonds. In C60, the strong covalent bonds only hold together each individual 60-atom cage; separate cages interact with each other only via weak London dispersion forces. Melting C60 only requires overcoming these weak forces *between* molecules (the strong covalent bonds within each cage stay intact), needing far less energy — hence its much lower melting point.

Bài tập luyện tập

Which property distinguishes silicon from silicon dioxide, even though both are giant covalent solids?

(A) Silicon is a semiconductor; SiO2 is an electrical insulator

(B) Silicon has a lower melting point by several thousand degrees

(C) SiO2 conducts electricity when solid; silicon does not

(D) They have identical electrical properties

Lời giải chi tiết

Silicon's non-polar Si–Si bonds and comparatively small band gap allow a small fraction of electrons to be thermally promoted to conduct at room temperature (a semiconductor); SiO2's more polar Si–O bonds localise electrons strongly on oxygen, giving a much larger band gap, so it does not conduct (an insulator). **(A)**.

Bài tập luyện tập

Explain why SiO2 has an extremely high melting point, similar in magnitude to that of diamond.

Lời giải chi tiết

SiO2, like diamond, is a giant covalent structure: every silicon atom is covalently bonded to 4 oxygen atoms, and every oxygen atom bridges 2 silicon atoms, extending as a continuous 3-D network throughout the whole crystal. Melting requires breaking enormous numbers of strong covalent bonds spread across the entire structure, which needs a very large amount of energy — just as in diamond — giving both substances very high melting points, unlike simple molecular solids.

Bài tập luyện tập

Which has the higher density, diamond or graphite, and why?

(A) Diamond, because its 3-D network packs atoms more compactly than graphite's widely spaced layers

(B) Graphite, because delocalised electrons add extra mass

(C) They have identical densities, since both are pure carbon

(D) Graphite, because its layers are closer together than diamond's bonds

Lời giải chi tiết

Diamond's rigid 3-D tetrahedral network packs carbon atoms closely together in all directions. Graphite's carbon atoms are closely packed only within each layer; the layers themselves are separated by a comparatively large gap held only by weak dispersion forces, adding a lot of "empty" volume between layers. Packing the same carbon atoms into a larger overall volume gives graphite (2.25 g cm^{-3}) a lower density than diamond (3.51 g cm^{-3}). **(A)**.

Bài tập luyện tập

On a heating curve for a pure solid heated at a constant rate, why does the temperature remain constant while the solid is melting?

Lời giải chi tiết

While melting occurs, all the energy being supplied is used to overcome the intermolecular/interionic/interatomic forces holding the solid's particles in their fixed lattice positions, converting the ordered solid into a more disordered liquid (increasing potential energy). None of the supplied energy is going into increasing the particles' average kinetic energy during this process, so the temperature (which depends only on average kinetic energy) stays constant until melting is complete.

Bài tập luyện tập

Explain why boiling a liquid generally requires more energy (a larger latent heat) than melting the same mass of the solid form.

Lời giải chi tiết

Melting only needs to loosen the fixed, ordered arrangement of particles in a solid into the more disordered but still closely-packed arrangement of a liquid — many intermolecular attractions remain intact (particles stay in contact). Boiling requires separating particles completely from one another, moving them far enough apart that essentially *all* of the intermolecular forces between them are overcome, to form widely-spaced, independent gas particles — this requires overcoming far more attractive interactions in total, so the latent heat of vaporisation is normally much greater than the latent heat of fusion.

Bài tập luyện tập

What does it mean, in terms of vapour pressure, for a liquid to be "boiling" at a particular temperature?

(A) The liquid's vapour pressure is zero

(B) The liquid's vapour pressure equals the external (atmospheric) pressure

(C) The liquid's vapour pressure exceeds its critical pressure

(D) The liquid's vapour pressure is less than atmospheric pressure

Lời giải chi tiết

Boiling begins when the saturated vapour pressure of the liquid rises to equal the pressure of the surrounding atmosphere, allowing vapour bubbles to form and grow throughout the bulk of the liquid, not just evaporate from its surface. **(B)**.

Bài tập luyện tập

Explain why water boils at a lower temperature at the top of a high mountain than at sea level.

Lời giải chi tiết

Atmospheric pressure is lower at high altitude. Since a liquid boils once its vapour pressure equals the surrounding (external) pressure, a lower external pressure means the water only needs to reach a lower vapour pressure to boil — and vapour pressure of a given liquid is a function only of its temperature, so a lower required vapour pressure corresponds to a lower boiling temperature.

Bài tập luyện tập

Rank the noble gases He, Ne, Ar, Kr in order of **increasing** strength of London dispersion forces between their atoms.

(A) He $<$ Ne $<$ Ar $<$ Kr

(B) Kr $<$ Ar $<$ Ne $<$ He

(C) All equal, since they are all noble gases

(D) Ar $<$ He $<$ Kr $<$ Ne

Lời giải chi tiết

London dispersion forces strengthen with increasing number of electrons (more polarisable electron clouds). Down Group 18, atomic number and electron count increase: He (2 electrons) $<$ Ne (10) $<$ Ar (18) $<$ Kr (36), so dispersion forces strengthen in that order. **(A)**.

Bài luyện nâng cao (A2)

Explain why heavier noble gases (e.g. Xe) deviate more strongly from ideal gas behaviour than lighter ones (e.g. He) at the same temperature and pressure, linking your answer to the van der Waals constants a and b.

Lời giải chi tiết

Heavier noble gas atoms (e.g. Xe) have many more electrons than lighter ones (e.g. He), giving larger, more polarisable electron clouds and hence much stronger London dispersion forces — a larger van der Waals constant a. Heavier noble gas atoms are also physically larger, excluding more volume from the container — a larger constant b. Both corrections in the van der Waals equation are therefore more significant for Xe than for He under the same conditions, so Xe deviates more strongly from ideal gas behaviour.

Bài tập luyện tập

A sample of gas has volume V_1 at pressure p_1 and temperature T_1 (in kelvin). It is compressed and heated to a new pressure p_2 and temperature T_2. Write the combined gas law relating p_1, V_1, T_1 to p_2, V_2, T_2 for a fixed amount of gas, and use it to explain how Boyle's and Charles's Laws are special cases of it.

Lời giải chi tiết

Since $pV = nRT$ and n is fixed, $\frac{pV}{T} = nR =$ constant, so $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$ (the combined gas law). Setting $T_1 = T_2$ (constant temperature) reduces this to $p_1V_1 = p_2V_2$ — Boyle's Law. Setting $p_1 = p_2$ (constant pressure) reduces it to $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ — Charles's Law. Both laws are therefore special cases of the general ideal gas equation with one variable held fixed.

Chemical Energetics

Mục tiêu Unit: Nắm vững khái niệm enthalpy và các loại enthalpy chuẩn (tạo thành, đốt cháy, trung hoà, hoà tan, hydrat hoá, mạng lưới) cùng phương trình định nghĩa chính xác; tính toán bằng phương pháp nhiệt lượng kế ($q = mc\Delta T$) và phân tích sai số do thất thoát nhiệt; áp dụng thành thạo Định luật Hess qua nhiều chu trình khác nhau (dữ liệu đốt cháy và dữ liệu tạo thành); ước lượng ΔH bằng năng lượng liên kết trung bình và hiểu giới hạn của phương pháp này; dựng và giải chu trình Born–Haber để tính năng lượng mạng lưới cho muối 1:1 và 2:1 (A2); dự đoán dấu của entropy và tính ΔG để đánh giá tính khả thi nhiệt động của phản ứng (A2).

5.1 Enthalpy changes, standard conditions and calorimetry

Chemical reactions are almost always accompanied by a transfer of energy between the **system** (the reacting chemicals) and the **surroundings**. At constant pressure — the condition under which almost all school and laboratory chemistry is carried out, including reactions in open beakers or flasks — this energy transfer is called the **enthalpy change**, given the symbol ΔH, measured in kJ mol^{-1}.

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}.$$

A reaction that releases energy to the surroundings (usually observed as a rise in temperature) is **exothermic**: the products have lower enthalpy than the reactants, so ΔH is **negative**. A reaction that absorbs energy from the surroundings (a fall in temperature) is **endothermic**: the products have higher enthalpy than the reactants, so ΔH is **positive**.

Khái niệm cốt lõi

Sign convention: exothermic $\Rightarrow \Delta H < 0$ (energy leaves the system); endothermic $\Rightarrow \Delta H > 0$ (energy enters the system). This is the opposite of what many students initially expect — a negative sign describes heat being *given out*, not energy being lost from existence.

VN **GIẢI THÍCH TIẾNG VIỆT**

Enthalpy (ΔH) là nhiệt lượng trao đổi ở áp suất không đổi. Phản ứng **toả nhiệt** (exothermic) giải phóng năng lượng ra môi trường xung quanh $\Rightarrow \Delta H < 0$ (âm); phản ứng **thu nhiệt** (endothermic) hấp thụ năng lượng từ môi trường $\Rightarrow \Delta H > 0$ (dương). Dấu âm/dương mô tả *chiều* trao đổi nhiệt, không phải độ lớn năng lượng.

5.1.1 Standard conditions and standard enthalpy changes

Because the enthalpy change of a reaction depends on temperature, pressure and the physical states of the substances involved, enthalpy changes are quoted under **standard conditions** so that values can be compared meaningfully: a temperature of 298 K ($25\,^{\circ}$C), a pressure of 100 kPa, and all solutions at a concentration of 1 mol dm^{-3}; every substance must be in its normal physical state under these conditions (its **standard state**). A standard enthalpy change is written with the symbol ΔH° (or a subscript to show the type of change, e.g. ΔH°_{f}).

Standard enthalpy change	Symbol	Defining equation / definition
Enthalpy change of formation	ΔH_f°	the enthalpy change when **1 mole** of a compound is formed from its **elements** in their standard states, under standard conditions. e.g. $\mathrm{C(s) + O_2(g) \rightarrow CO_2(g)}$, $\Delta H_f^\circ = -393.5$ kJ mol^{-1}. By definition, ΔH_f° of any element in its standard state is **zero**.
Enthalpy change of combustion	ΔH_c°	the enthalpy change when **1 mole** of a substance is completely burned in excess oxygen, under standard conditions, all reactants and products in their standard states. e.g. $\mathrm{CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)}$.
Enthalpy change of neutralisation	ΔH_{neut}°	the enthalpy change when an acid and an alkali react, under standard conditions, to form **1 mole of water**. e.g. $\mathrm{HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)}$.
Enthalpy change of atomisation	ΔH_{at}°	the enthalpy change when **1 mole of gaseous atoms** is formed from an element in its standard state. e.g. $\mathrm{\frac{1}{2}Cl_2(g) \rightarrow Cl(g)}$.
Enthalpy change of solution	ΔH_{sol}°	the enthalpy change when **1 mole** of an ionic solid dissolves completely in a large excess of water (so that further dilution causes no further enthalpy change).
Enthalpy change of hydration	ΔH_{hyd}°	the enthalpy change when **1 mole of gaseous ions** is dissolved in a large excess of water, always exothermic.

VN **GIẢI THÍCH TIẾNG VIỆT**

Các **enthalpy chuẩn** luôn được đo ở 298 K, 100 kPa, dung dịch 1 mol dm^{-3}: ΔH_f° (tạo thành 1 mol hợp chất từ nguyên tố, ở trạng thái chuẩn; nguyên tố ở trạng thái chuẩn có $\Delta H_f^\circ = 0$), ΔH_c° (đốt cháy hoàn toàn 1 mol chất trong oxi dư), ΔH_{neut}° (tạo thành 1 mol nước từ phản ứng acid–base), ΔH_{at}° (tạo 1 mol nguyên tử khí từ nguyên tố), ΔH_{sol}° (hoà tan 1 mol chất rắn ion trong lượng nước dư), ΔH_{hyd}° (hydrat hoá 1 mol ion khí, luôn toả nhiệt).

5.1.2 Measuring enthalpy changes: calorimetry

Most enthalpy changes are measured experimentally using **calorimetry**: the reaction is carried out in an insulated container and the temperature change of a known mass of surroundings (usually water) is recorded. The heat energy transferred is calculated from

$$q = mc\Delta T,$$

where q is the heat energy in joules, m is the mass (in g) of the substance being heated or cooled (usually the water), c is its specific heat capacity ($c_{\text{water}} = 4.18$ J g^{-1}K^{-1}), and ΔT is the temperature change (in K or °C — the size of one kelvin equals the size of one degree Celsius, so ΔT is the same numerical value in either unit). Once q is known, the enthalpy change **per mole** of the limiting reactant is found by dividing by the number of moles reacted, and a minus sign is inserted for an exothermic reaction (since q calculated from $mc\Delta T$ is a positive quantity of heat released, while ΔH of an exothermic reaction is negative):

$$\Delta H = -\frac{q}{n} \quad \text{(exothermic reaction, temperature of the surroundings rises)}.$$

Ví dụ mẫu · Worked example — enthalpy of neutralisation

In a polystyrene cup, 50.0 cm^3 of 1.0 mol dm^{-3} hydrochloric acid was mixed with 50.0 cm^3 of 1.0 mol dm^{-3} sodium hydroxide solution. The temperature rose by 6.8 °C. Taking the density

of the mixture as 1.00 g cm^{-3} and $c = 4.18$ J g^{-1}K^{-1}, calculate the standard enthalpy change of neutralisation.

Total mass of solution: $m = 50.0 + 50.0 = 100.0$ g.

$$q = mc\Delta T = 100.0 \times 4.18 \times 6.8 = 2842 \text{ J} = 2.84 \text{ kJ}.$$

Moles of water formed: $n(\text{HCl}) = n(\text{NaOH}) = \dfrac{1.0 \times 50.0}{1000} = 0.050$ mol, and since the acid and base react in a 1:1 ratio to form 1 mol of water per mole of acid, $n(\text{H}_2\text{O}) = 0.050$ mol.

$$\Delta H^\circ_{neut} = -\frac{2.84}{0.050} = -56.8 \text{ kJ mol}^{-1}.$$

This is close to the accepted value for the neutralisation of any strong acid by any strong alkali (≈ -57.3 kJ mol^{-1}), because in every such reaction the overall change is essentially the same: $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$.

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Ví dụ trên minh hoạ cách dùng $q = mc\Delta T$ để tính ΔH°_{neut}: tính nhiệt lượng toả ra q, tính số mol nước tạo thành, rồi chia và đổi dấu (vì phản ứng toả nhiệt). Giá trị -56.8 kJ mol^{-1} gần với giá trị chuẩn cho mọi phản ứng acid mạnh–base mạnh, vì bản chất phản ứng luôn là $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$.

5.1.3 Reaction pathway (energy profile) diagrams

An **energy profile diagram** plots the enthalpy of the reacting system against the progress of the reaction. Every reaction must pass through a high-energy, unstable arrangement called the **transition state**, at the top of the energy barrier; the minimum extra energy needed to reach it, measured from the reactants, is the **activation energy**, E_a. The vertical distance between the reactants' enthalpy level and the products' enthalpy level is ΔH.

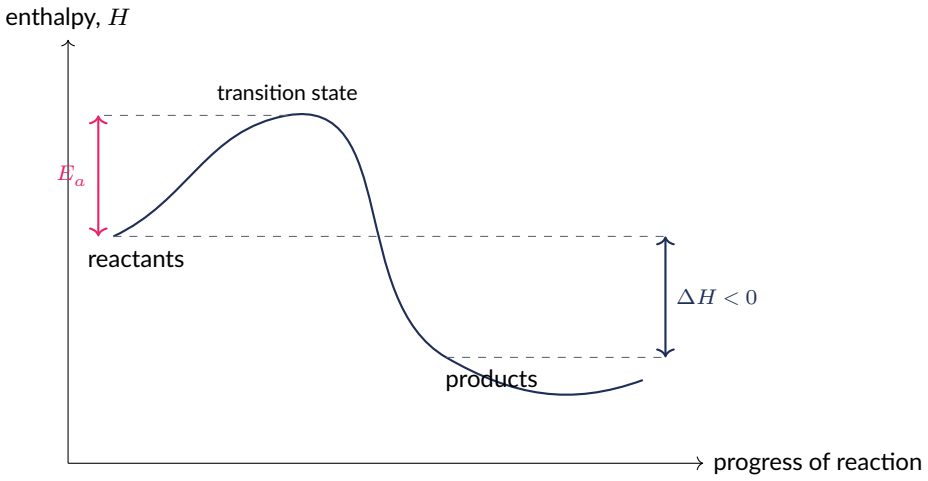


Figure 5.1 — Energy profile for an **exothermic** reaction: products lie *below* reactants ($\Delta H < 0$); E_a is measured from reactants up to the peak.

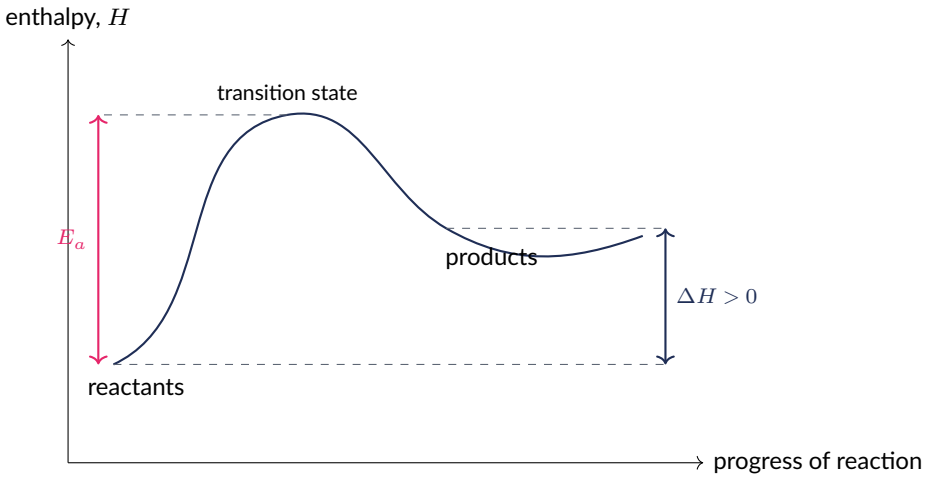


Figure 5.2 — Energy profile for an **endothermic** reaction: products lie *above* reactants ($\Delta H > 0$).

(!) Lỗi thường gặp: E_a is *always* measured from the reactants up to the transition state, never from the products — even in an endothermic reaction. The activation energy for the *reverse* reaction is measured from the products up to the same transition state, and is a different quantity from the forward E_a.

VN GIẢI THÍCH TIẾNG VIỆT

Giản đồ năng lượng phản ứng biểu diễn enthalpy theo tiến trình phản ứng. Mọi phản ứng đều đi qua **trạng thái chuyển tiếp** (đỉnh năng lượng); năng lượng hoạt hoá E_a luôn được đo từ chất phản ứng lên đỉnh, kể cả với phản ứng thu nhiệt. ΔH là khoảng cách (theo chiều dọc) giữa mức năng lượng chất phản ứng và sản phẩm.

5.1.4 A full calorimetry experiment: enthalpy of combustion of ethanol

The enthalpy change of combustion of a liquid fuel can be measured by burning it beneath a metal container of water and recording the temperature rise, exactly as in the neutralisation experiment above, but here the mass of *fuel* burnt (not the mass of solution) is used to find n.

Ví dụ mẫu · Worked example — enthalpy of combustion of ethanol

A spirit burner containing ethanol, C_2H_5OH ($M_r = 46.0$), was weighed, used to heat 100.0 g of water in a metal can from $20.0\,^\circ$C to $51.2\,^\circ$C, then reweighed. The mass of ethanol burnt was 0.50 g. Calculate the experimental enthalpy change of combustion, and compare it with the data-book (literature) value of -1367 kJ mol^{-1}.

Heat absorbed by the water:

$$\Delta T = 51.2 - 20.0 = 31.2\,^\circ\text{C}, \qquad q = mc\Delta T = 100.0 \times 4.18 \times 31.2 = 13\,042\ \text{J} = 13.04\ \text{kJ}.$$

Moles of ethanol burnt:

$$n = \frac{0.50}{46.0} = 0.01087\ \text{mol}.$$

Experimental enthalpy of combustion:

$$\Delta H_c(\text{exp}) = -\frac{13.04}{0.01087} = -1200\ \text{kJ mol}^{-1}\ (\text{to 3 s.f.}).$$

The experimental value (-1200 kJ mol^{-1}) is smaller in magnitude than the literature value (-1367 kJ mol^{-1}) — the experiment captures only about $\dfrac{1200}{1367} \times 100\% \approx 88\%$ of the energy

released.

(!) Lỗi thường gặp: The experimental value from a simple spirit-burner calorimetry experiment is almost always **smaller in magnitude** than the literature value, because:

- much of the heat released escapes to the surrounding air rather than heating the water (**heat loss** — the single largest source of error, since the flame and can are open to the room);
- some heat is used to warm the metal can and the thermometer itself, not just the water;
- combustion may be **incomplete** (some carbon escapes as smoke/soot rather than fully forming CO_2), releasing less energy than complete combustion would;
- some ethanol may **evaporate** before burning, without releasing its full combustion energy into the water.

A draught excluder, a lid on the can, and a copper (rather than heat-insulating) container all reduce — but never eliminate — this heat loss, so experimental ΔH_c values determined this way *always* underestimate the true magnitude.

VN **GIẢI THÍCH TIẾNG VIỆT**

Thí nghiệm đốt ethanol để đun nước đo được $\Delta H_c(\text{thực nghiệm}) \approx -1200$ kJ mol^{-1}, nhỏ hơn nhiều so với giá trị chuẩn -1367 kJ mol^{-1}. Nguyên nhân chính là **thất thoát nhiệt** ra môi trường xung quanh (ngọn lửa hở), một phần nhiệt dùng để làm nóng bình chứa, đốt cháy không hoàn toàn (tạo muội than), và một phần ethanol bay hơi trước khi cháy. Các thí nghiệm nhiệt lượng kế đơn giản luôn cho giá trị $|\Delta H_c|$ **nhỏ hơn** giá trị thực.

5.2 Hess's Law and enthalpy cycles

Hess's Law states that the total enthalpy change for a reaction is **independent of the route taken**, provided the initial and final conditions are the same. This is a direct consequence of the conservation of energy: if two different routes between the same reactants and products gave different total enthalpy changes, energy could be created or destroyed by cycling around the two routes, which is impossible.

Khái niệm cốt lõi

Hess's Law lets us calculate an enthalpy change that cannot easily be measured directly, by combining other enthalpy changes that *can* be measured, using an **enthalpy cycle**: a diagram showing two (or more) alternative routes between the same starting and finishing point, with arrows for each known ΔH, so that the unknown ΔH can be found by equating the two routes.

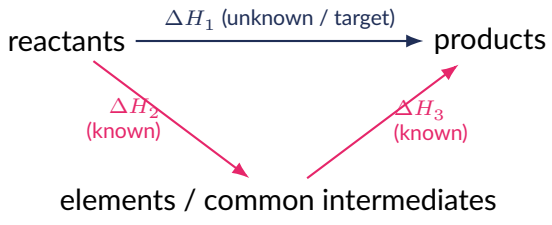


Figure 5.3 — General Hess cycle: since both routes start and end at the same points, $\Delta H_1 = \Delta H_2 + \Delta H_3$.

GIẢI THÍCH TIẾNG VIỆT

VN Định luật Hess: ΔH của một phản ứng không phụ thuộc vào đường đi, chỉ phụ thuộc trạng thái đầu và cuối — hệ quả trực tiếp của định luật bảo toàn năng lượng. Ta dùng chu trình (hai đường đi khác nhau giữa cùng điểm đầu/cuối) để tính một ΔH chưa biết từ các ΔH đã biết.

5.2.1 Cycles built from enthalpies of combustion

When the target enthalpy change is a formation enthalpy that cannot be measured directly (because the elements will not simply combine cleanly to form the compound), it can often be found from combustion data, since burning the compound and burning its elements both lead to the same final products (CO_2 and H_2O, for a hydrocarbon).

Ví dụ mẫu · Worked example — ΔH_f° of propane from combustion data

Given $\Delta H_c^\circ[C(s)] = -393.5$ kJ mol^{-1}, $\Delta H_c^\circ[H_2(g)] = -285.8$ kJ mol^{-1}, and $\Delta H_c^\circ[C_3H_8(g)] = -2220.0$ kJ mol^{-1}, calculate ΔH_f° of propane, $C_3H_8(g)$.

Target: $3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$, $\Delta H_f^\circ = ?$

Route A (direct): $3C + 4H_2 \xrightarrow{\Delta H_f^\circ} C_3H_8$, then combust: $C_3H_8 + 5O_2 \xrightarrow{\Delta H_c^\circ(C_3H_8)} 3CO_2 + 4H_2O$.
Route B (indirect): burn the elements directly: $3C + 3O_2 \rightarrow 3CO_2$ (using $3 \times \Delta H_c^\circ[C]$) and $4H_2 + 2O_2 \rightarrow 4H_2O$ (using $4 \times \Delta H_c^\circ[H_2]$), reaching the *same* products, $3CO_2 + 4H_2O$.
Equating the two routes (both begin at $3C + 4H_2$ and end at $3CO_2 + 4H_2O$):

$$\Delta H_f^\circ(C_3H_8) + \Delta H_c^\circ(C_3H_8) = 3\Delta H_c^\circ(C) + 4\Delta H_c^\circ(H_2).$$

$\Delta H_f^\circ(C_3H_8) = 3(-393.5) + 4(-285.8) - (-2220.0) = -1180.5 - 1143.2 + 2220.0 = -103.7$ kJ mol^{-1}.

So $\Delta H_f^\circ(C_3H_8) \approx -104$ kJ mol^{-1}.

Ví dụ mẫu · Worked example — ΔH_f° of carbon monoxide from combustion data

Carbon monoxide cannot be formed cleanly from its elements (burning carbon in a limited supply of oxygen gives a mixture of CO and CO_2), so $\Delta H_f^\circ(CO)$ cannot be measured directly. Given $\Delta H_c^\circ[C(s)] = -393.5$ kJ mol^{-1} (i.e. $C(s) + O_2(g) \rightarrow CO_2(g)$) and $\Delta H_c^\circ[CO(g)] = -283.0$ kJ mol^{-1} (i.e. $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$), calculate $\Delta H_f^\circ(CO)$.

Target: $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$, $\Delta H_f^\circ = ?$
Route A (direct): form CO (ΔH_f°), then burn it to CO_2 ($\Delta H_c^\circ[CO] = -283.0$).
Route B (indirect): burn carbon directly to CO_2 ($\Delta H_c^\circ[C] = -393.5$) — the *same* final product, CO_2.
Equating the two routes:

$$\Delta H_f^\circ(CO) + \Delta H_c^\circ(CO) = \Delta H_c^\circ(C).$$

$$\Delta H_f^\circ(CO) = \Delta H_c^\circ(C) - \Delta H_c^\circ(CO) = -393.5 - (-283.0) = \textbf{-110.5 kJ mol}^{-1}.$$

5.2.2 Cycles built directly from enthalpies of formation

More generally, for *any* reaction whose reactants and products all have known standard enthalpies of formation, Hess's Law gives directly

$$\Delta H^\circ_{rxn} = \sum \Delta H^\circ_f(\text{products}) - \sum \Delta H^\circ_f(\text{reactants}),$$

because both the reactants and the products can be imagined as having been built up from the same set of elements (a cycle with the elements at the bottom, reactants on one side, products on the other).

Ví dụ mẫu · Worked example — ΔH°_c of methane from enthalpies of formation

Given $\Delta H^\circ_f(\text{CH}_4, \text{g}) = -74.8$ kJ mol^{-1}, $\Delta H^\circ_f(\text{CO}_2, \text{g}) = -393.5$ kJ mol^{-1}, $\Delta H^\circ_f(\text{H}_2\text{O}, \text{l}) = -285.8$ kJ mol^{-1}, calculate ΔH°_c of methane: $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$.

$$\Delta H^\circ_{rxn} = [\Delta H^\circ_f(\text{CO}_2) + 2\Delta H^\circ_f(\text{H}_2\text{O})] - [\Delta H^\circ_f(\text{CH}_4) + 2\Delta H^\circ_f(\text{O}_2)].$$

Since O_2 is an element in its standard state, $\Delta H^\circ_f(\text{O}_2) = 0$:

$$\Delta H^\circ_{rxn} = [(-393.5) + 2(-285.8)] - [(-74.8) + 0] = (-965.1) - (-74.8) = -890.3 \text{ kJ mol}^{-1}.$$

This value, -890 kJ mol^{-1}, is the accepted experimental enthalpy of combustion of methane — it will be compared with an *estimate* from mean bond energies in the next section.

VN **GIẢI THÍCH TIẾNG VIỆT**

Có hai cách dựng chu trình Hess phổ biến: (1) dùng **dữ liệu đốt cháy** khi các nguyên tố/hợp chất đều cháy về cùng sản phẩm (CO_2, H_2O) — ví dụ tính ΔH_f của propane; (2) dùng trực tiếp **công thức tổng quát** $\Delta H^\circ_{rxn} = \sum \Delta H^\circ_f(\text{sản phẩm}) - \sum \Delta H^\circ_f(\text{chất phản ứng})$ khi đã biết ΔH°_f của mọi chất — ví dụ tính ΔH_c của methane, cho kết quả -890 kJ mol^{-1}, sẽ được so sánh với ước lượng bằng năng lượng liên kết ở phần sau.

5.3 Bond energies

An alternative way to **estimate** an enthalpy change is to consider bonds broken and bonds formed. Breaking a covalent bond always requires an input of energy (endothermic, $+$), and forming a covalent bond always releases energy (exothermic, $-$). Using **mean bond energies** — average values taken across many different compounds containing that type of bond, since the exact bond strength varies slightly depending on the rest of the molecule —

$$\Delta H \approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed}).$$

Ví dụ mẫu · Worked example — estimating ΔH_c of methane from bond energies

Using mean bond energies $E(\text{C}-\text{H}) = 410$, $E(\text{O}=\text{O}) = 496$, $E(\text{C}=\text{O}, \text{in } \text{CO}_2) = 805$, $E(\text{O}-\text{H}) = 460$ kJ mol^{-1}, estimate ΔH_c for $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$.

Bonds broken: $4 \times \text{C}-\text{H}$ (in CH_4) and $2 \times \text{O}=\text{O}$ (in 2O_2):

$$4(410) + 2(496) = 1640 + 992 = 2632 \text{ kJ mol}^{-1}.$$

Bonds formed: $2 \times \text{C}=\text{O}$ (in CO_2) and $4 \times \text{O}-\text{H}$ (in $2\text{H}_2\text{O}$):

$$2(805) + 4(460) = 1610 + 1840 = 3450 \text{ kJ mol}^{-1}.$$

$$\Delta H \approx 2632 - 3450 = -818 \text{ kJ mol}^{-1}.$$

(!) Lỗi thường gặp: The bond-energy estimate for methane's combustion (≈ -818 kJ mol^{-1}) does **not** exactly match the accepted experimental value found from enthalpies of formation (-890 kJ mol^{-1}, Section 5.2). This is because **mean bond energies are averages** taken over many different molecules — the actual C – H bonds in methane, or the actual O – H bonds in water, are not exactly equal to the tabulated mean value. Bond-energy calculations are therefore always only **estimates**; enthalpy cycles based on measured ΔH_f° or ΔH_c° values give the true (more accurate) result. A further limitation: mean bond energies also assume all species are **gaseous**, so they cannot be applied directly to a reactant or product that is a liquid or solid without an extra allowance for the enthalpy change of vaporisation/fusion.

VN **GIẢI THÍCH TIẾNG VIỆT**

Năng lượng liên kết trung bình chỉ cho kết quả **ước lượng**, không chính xác tuyệt đối, vì đây là giá trị trung bình lấy từ nhiều phân tử khác nhau — liên kết thực tế trong một phân tử cụ thể có thể khác giá trị trung bình. Do đó ΔH tính từ năng lượng liên kết (-818 kJ mol^{-1} với methane) thường lệch so với giá trị thực nghiệm chính xác hơn (-890 kJ mol^{-1}, tính từ ΔH_f°). Phương pháp năng lượng liên kết cũng giả định mọi chất đều ở thể khí.

Ví dụ mẫu · Worked example — hydrogenation of ethene

Using $E(\text{C}=\text{C}) = 610$, $E(\text{H}-\text{H}) = 436$, $E(\text{C}-\text{C}) = 350$, $E(\text{C}-\text{H}) = 410$ kJ mol^{-1}, estimate ΔH for $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$.

Only the C = C (in ethene) and H – H bonds are broken; a new C – C bond and **two** new C – H bonds are formed (the two H atoms from H_2 each bond to a carbon):

$$\text{broken} = 610 + 436 = 1046 \text{ kJ mol}^{-1}, \qquad \text{formed} = 350 + 2(410) = 1170 \text{ kJ mol}^{-1}.$$

$$\Delta H \approx 1046 - 1170 = -124 \text{ kJ mol}^{-1}.$$

The reaction is exothermic, consistent with hydrogenation reactions generally releasing energy.

5.4 Enthalpy of solution and enthalpy of hydration

When an ionic solid dissolves in water, two separate processes are involved. First, the ionic lattice must be broken apart into free gaseous ions — the reverse of the **lattice energy** of formation (lattice energy, ΔH_L°, is defined as the enthalpy change when 1 mole of a solid ionic compound forms from its constituent gaseous ions, and is always strongly **exothermic**; it is examined further, and calculated via Born–Haber cycles, in Section 5.5). Second, the free gaseous ions become surrounded by, and strongly attracted to, polar water molecules — this releases the **enthalpy of hydration**, ΔH_{hyd}°, always exothermic since new ion–dipole attractions are formed.

$$\text{MX(s)} \rightarrow \text{M}^+(\text{g}) + \text{X}^-(\text{g}) \qquad (-\Delta H_L^\circ, \text{ endothermic, since it reverses lattice formation})$$

$$\text{M}^+(\text{g}) + \text{X}^-(\text{g}) \rightarrow \text{M}^+(\text{aq}) + \text{X}^-(\text{aq}) \qquad (\Delta H_{hyd}^\circ(M^+) + \Delta H_{hyd}^\circ(X^-), \text{ exothermic})$$

so that, by Hess's Law,

$$\Delta H_{sol}^\circ(\text{MX}) = -\Delta H_L^\circ(\text{MX}) + \Delta H_{hyd}^\circ(M^+) + \Delta H_{hyd}^\circ(X^-).$$

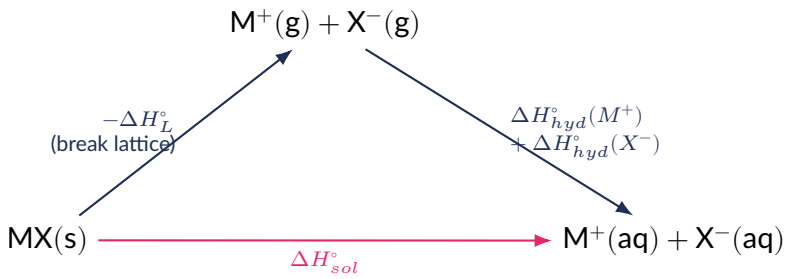


Figure 5.4 — Enthalpy cycle relating lattice energy, hydration enthalpies and enthalpy of solution.

VN **GIẢI THÍCH TIẾNG VIỆT**

Khi một chất rắn ion hoà tan, hai bước xảy ra: (1) phá vỡ mạng lưới ion thành các ion khí tự do — đây là quá trình **ngược** với sự hình thành mạng lưới (thu nhiệt, $= -\Delta H^\circ_L$); (2) các ion khí được **hydrat hoá** bởi phân tử nước phân cực (toả nhiệt, ΔH°_{hyd}). Tổng hai bước, theo định luật Hess, cho ΔH°_{sol}.

Ví dụ mẫu · Worked example — enthalpy of solution of sodium chloride

Given $\Delta H^\circ_L(\text{NaCl}) = -787$ kJ mol^{-1}, $\Delta H^\circ_{hyd}(\text{Na}^+) = -406$ kJ mol^{-1}, $\Delta H^\circ_{hyd}(\text{Cl}^-) = -364$ kJ mol^{-1}, calculate $\Delta H^\circ_{sol}(\text{NaCl})$.

$$\Delta H^\circ_{sol} = -(-787) + (-406) + (-364) = 787 - 770 = +17 \text{ kJ mol}^{-1}.$$

The small **positive** value shows that dissolving NaCl is slightly endothermic overall — consistent with the small cooling felt when NaCl dissolves in water. NaCl nonetheless dissolves readily, because the dissolving process is also accompanied by a large **increase in entropy** (Section 5.6), which makes the overall process thermodynamically favourable even though it is (slightly) endothermic.

Hydration enthalpies become **much more exothermic** as ionic charge increases and ionic radius decreases, exactly as for lattice energies (Section 5.5) — both are governed by the same electrostatic attraction between an ion and its surroundings. For example, $\Delta H^\circ_{hyd}(\text{Na}^+) \approx -406$ kJ mol^{-1}, but $\Delta H^\circ_{hyd}(\text{Mg}^{2+}) \approx -1920$ kJ mol^{-1} — far more exothermic, since Mg^{2+} carries twice the charge and has a substantially smaller ionic radius than Na^+.

VN **GIẢI THÍCH TIẾNG VIỆT**

Enthalpy hydrat hoá càng **âm (toả nhiệt mạnh)** khi điện tích ion càng lớn và bán kính ion càng nhỏ — cùng quy luật với năng lượng mạng lưới. Ví dụ Mg^{2+} (điện tích $2+$, bán kính nhỏ) có ΔH°_{hyd} âm hơn nhiều so với Na^+ (điện tích $1+$, bán kính lớn hơn).

5.5 Born--Haber cycles and lattice energy (A2)

The **lattice energy** of an ionic compound, ΔH°_L, is defined as the enthalpy change when **1 mole** of the solid ionic compound is formed from its constituent ions **in the gaseous state**, under standard conditions:

$$\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NaCl(s)}, \qquad \Delta H^\circ_L(\text{NaCl}).$$

Lattice energy is always strongly **exothermic** (bringing oppositely-charged gaseous ions together to form a solid releases a very large amount of electrostatic energy), but it **cannot be measured directly**

— gaseous ions cannot simply be mixed together in a test tube. Instead, lattice energy is **calculated** using an enthalpy cycle called a **Born–Haber cycle**, which relates the (measurable) standard enthalpy of formation of the compound to a sequence of other, individually measurable, enthalpy changes.

Steps needed to build up an ionic solid from its elements, one atom/ion at a time (all except lattice energy are endothermic, except electron affinities which are typically exothermic for the first electron added):

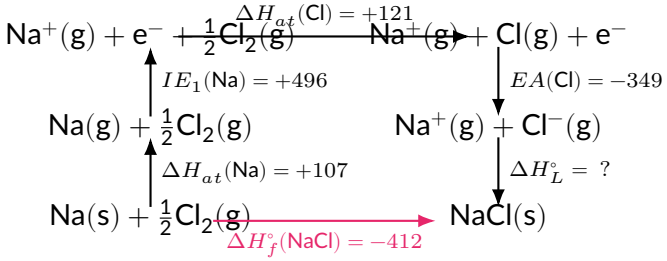
- **Atomisation** of the metal: $\mathrm{M(s)} \rightarrow \mathrm{M(g)}$ — endothermic (breaks metallic bonding).
- **Ionisation energy/energies** of the metal: $\mathrm{M(g)} \rightarrow \mathrm{M^+(g)} + \mathrm{e^-}$ (and a second ionisation energy if a $2+$ ion is required) — always endothermic (energy needed to remove an electron against nuclear attraction).
- **Atomisation** of the non-metal: $\frac{1}{2}\mathrm{X_2(g)} \rightarrow \mathrm{X(g)}$ — endothermic (breaks a covalent bond).
- **(First) electron affinity** of the non-metal: $\mathrm{X(g)} + \mathrm{e^-} \rightarrow \mathrm{X^-(g)}$ — exothermic (the atom attracts an extra electron). A **second** electron affinity, $\mathrm{X^-(g)} + \mathrm{e^-} \rightarrow \mathrm{X^{2-}(g)}$ (needed for oxide/sulfide ions), is always strongly **endothermic**, since an incoming electron is now repelled by the negative ion.
- **Lattice energy**: $\mathrm{M^{n+}(g)} + \mathrm{X^{n-}(g)} \rightarrow \mathrm{MX(s)}$ — strongly exothermic.

By Hess's Law, the sum of all these steps must equal ΔH_f° of the compound, since both routes start at the elements and end at the solid compound.

VN **GIẢI THÍCH TIẾNG VIỆT**

Năng lượng mạng lưới (ΔH_L°) là enthalpy khi 1 mol chất rắn ion hình thành từ các ion **ở thể khí**; luôn **toả nhiệt mạnh** nhưng không thể đo trực tiếp. Chu trình **Born–Haber** tính ΔH_L° gián tiếp bằng cách cộng các bước: nguyên tử hoá kim loại, (các) năng lượng ion hoá, nguyên tử hoá phi kim, (các) ái lực electron, rồi năng lượng mạng lưới — tổng tất cả bằng ΔH_f° của hợp chất (định luật Hess).

5.5.1 Worked Born–Haber cycle: sodium chloride (1:1 salt)



$$\Delta H_f^\circ = -412$$

Figure 5.5 — Born–Haber cycle for NaCl (values in kJ $\mathrm{mol^{-1}}$). All energies shown are relative changes for each labelled step.

Ví dụ mẫu · Worked example — lattice energy of NaCl

Given $\Delta H_f^\circ(\mathrm{NaCl}) = -412$, $\Delta H_{at}^\circ(\mathrm{Na}) = +107$, $IE_1(\mathrm{Na}) = +496$, $\Delta H_{at}^\circ(\mathrm{Cl}) = +121$, $EA(\mathrm{Cl}) = -349$ kJ $\mathrm{mol^{-1}}$, calculate $\Delta H_L^\circ(\mathrm{NaCl})$.

By Hess's Law, going round the cycle:

$$\Delta H_f^\circ = \Delta H_{at}^\circ(\mathrm{Na}) + IE_1(\mathrm{Na}) + \Delta H_{at}^\circ(\mathrm{Cl}) + EA(\mathrm{Cl}) + \Delta H_L^\circ.$$

$$-412 = 107 + 496 + 121 - 349 + \Delta H_L^\circ = 375 + \Delta H_L^\circ.$$

$$\Delta H_L^\circ(\text{NaCl}) = -412 - 375 = -787 \text{ kJ mol}^{-1}.$$

(This is the lattice energy value used, as given data, in the enthalpy-of-solution example of Section 5.4.)

5.5.2 Worked Born–Haber cycle: magnesium oxide (2:2 salt)

For a $2+/2-$ salt such as MgO, the cycle needs **two** ionisation energies for the metal (removing two electrons from Mg) and **two** electron affinities for the non-metal (adding two electrons to O, of which the second is strongly endothermic).

Ví dụ mẫu · Worked example — lattice energy of magnesium oxide

Given the following data (all in kJ mol^{-1}): $\Delta H_f^\circ(\text{MgO}) = -601.7$; $\Delta H_{at}^\circ(\text{Mg}) = +148$; $IE_1(\text{Mg}) = +738$; $IE_2(\text{Mg}) = +1451$; $\Delta H_{at}^\circ(\text{O}) = +249$; $EA_1(\text{O}) = -141$; $EA_2(\text{O}) = +798$. Calculate the lattice energy of MgO.

The Born–Haber cycle for MgO requires two extra steps compared with NaCl: a *second* ionisation energy of magnesium (to form Mg^{2+}) and a *second* electron affinity of oxygen (to form O^{2-}):

$$\Delta H_f^\circ = \Delta H_{at}^\circ(\text{Mg}) + IE_1(\text{Mg}) + IE_2(\text{Mg}) + \Delta H_{at}^\circ(\text{O}) + EA_1(\text{O}) + EA_2(\text{O}) + \Delta H_L^\circ.$$

$$-601.7 = 148 + 738 + 1451 + 249 - 141 + 798 + \Delta H_L^\circ = 3243 + \Delta H_L^\circ.$$

$$\Delta H_L^\circ(\text{MgO}) = -601.7 - 3243 = -3844.7 \approx -3845 \text{ kJ mol}^{-1}.$$

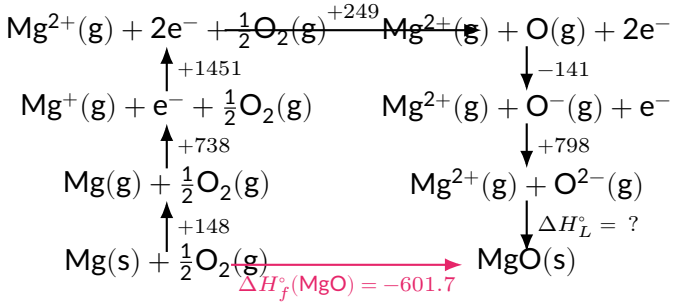


Figure 5.6 — Born–Haber cycle for MgO (values in kJ mol^{-1}), showing the extra second-ionisation and second-electron-affinity steps needed for a $2+/2-$ salt.

VN **GIẢI THÍCH TIẾNG VIỆT**

Với muối $2+/2-$ như MgO, chu trình Born–Haber cần **thêm** năng lượng ion hoá thứ hai của kim loại và ái lực electron thứ hai của phi kim (luôn thu nhiệt mạnh, vì electron đi vào ion đã mang điện âm). Kết quả: $\Delta H_L^\circ(\text{MgO}) \approx -3845$ kJ mol^{-1} — âm hơn **rất nhiều** so với NaCl (-787 kJ mol^{-1}).

5.5.3 Trends in lattice energy: charge and ionic radius

Comparing $\Delta H_L^\circ(\text{NaCl}) = -787$ kJ mol^{-1} with $\Delta H_L^\circ(\text{MgO}) = -3845$ kJ mol^{-1} shows a striking difference in magnitude — nearly five times larger for MgO. Two factors, both governed by Coulomb's Law for electrostatic attraction, act together:

- **Ionic charge:** the electrostatic attraction between ions is proportional to the *product* of their charges, $q_+ \times q_-$. NaCl involves $(+1) \times (-1) = 1$; MgO involves $(+2) \times (-2) = 4$ — four times greater attraction from charge alone.
- **Ionic radius:** electrostatic attraction is also inversely proportional to the distance between ion centres. Mg^{2+} (radius ≈ 0.072 nm) and O^{2-} (radius ≈ 0.140 nm) are both considerably **smaller** than Na^+ (≈ 0.102 nm) and Cl^- (≈ 0.181 nm), so the ions in MgO pack closer together, further increasing the attraction.

Both effects reinforce one another, which is why lattice energies become dramatically more exothermic for small, highly-charged ions.

VN **GIẢI THÍCH TIẾNG VIỆT**

Năng lượng mạng lưới càng **âm (toả nhiệt mạnh)** khi (1) điện tích ion càng lớn (lực hút tỉ lệ với $q_+ \times q_-$) và (2) bán kính ion càng nhỏ (ion càng gần nhau, lực hút càng mạnh). MgO ($2+/2-$, bán kính nhỏ) có năng lượng mạng lưới âm hơn nhiều so với NaCl ($1+/1-$, bán kính lớn hơn) — cả hai yếu tố cùng chiều, cộng hưởng làm tăng độ lớn năng lượng mạng lưới.

5.6 Entropy and Gibbs free energy (A2)

Entropy, S, is a measure of the number of ways in which the particles and their energy can be arranged — informally, a measure of **disorder**. A system tends to move towards states of higher entropy. The **entropy change** of a reaction, ΔS°, can often be predicted qualitatively from the change in the number of moles of gas, since gases have vastly higher entropy than liquids or solids (particles in a gas can move and spread out far more freely).

Khái niệm cốt lõi

Qualitative rules for the sign of ΔS°:

- An **increase** in the number of moles of gas $\Rightarrow \Delta S^\circ > 0$ (more disorder) — e.g. thermal decomposition of a solid or liquid to give a gas.
- A **decrease** in the number of moles of gas $\Rightarrow \Delta S^\circ < 0$ (less disorder) — e.g. the Haber process, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, 4 mol gas → 2 mol gas.
- Dissolving a solid in water usually gives a small **positive** ΔS° (the rigid lattice is replaced by freely-moving hydrated ions), even though hydration itself imposes some order on the surrounding water molecules.
- If the number of moles of gas is unchanged, ΔS° is usually small in magnitude (either sign).

Ví dụ mẫu · Worked example — predicting the sign of ΔS°

Predict the sign of ΔS° for each reaction, with a reason.
(a) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
(b) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
(c) $NaCl(s) \xrightarrow{\text{water}} Na^+(aq) + Cl^-(aq)$

(a) 0 mol gas → 1 mol gas: ΔS° is strongly **positive** (a gas is produced from a solid).
(b) 3 mol gas → 0 mol gas (all liquid): ΔS° is strongly **negative** (a large decrease in disorder — gas molecules are far more disordered than the same particles in a liquid).
(c) a rigid ionic lattice becomes freely-moving hydrated ions in solution: ΔS° is (mildly) **positive**.

VN **GIẢI THÍCH TIẾNG VIỆT**

Entropy (S) đo mức độ hỗn loạn/số cách sắp xếp hạt và năng lượng. Quy tắc dự đoán dấu ΔS°: số mol khí **tăng** $\Rightarrow \Delta S^\circ > 0$; số mol khí **giảm** $\Rightarrow \Delta S^\circ < 0$; hoà tan chất rắn thường cho ΔS° dương nhẹ.

5.6.1 Gibbs free energy and feasibility

Whether a reaction is thermodynamically **feasible** (spontaneous) depends on *both* the enthalpy change and the entropy change, combined in the **Gibbs free energy** equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ,$$

where T is the absolute temperature in kelvin (so ΔS°, normally quoted in J K^{-1}mol^{-1}, must be converted to kJ K^{-1}mol^{-1} — divide by 1000 — to keep units consistent with ΔH° in kJ mol^{-1}). A reaction is feasible (thermodynamically favourable) at a given temperature if

$$\Delta G^\circ < 0.$$

(!) Lỗi thường gặp: A negative ΔG° shows only that a reaction is thermodynamically **feasible** — it says *nothing* about the **rate** of the reaction, exactly as with E° values in electrochemistry (Chapter 6). The Haber process ($\Delta G^\circ < 0$ at 298 K, Example below) still requires a catalyst and elevated temperature to proceed at a useful rate; a thermodynamically feasible reaction can still be kinetically extremely slow.

Ví dụ mẫu · Worked example — feasibility of thermal decomposition of calcium carbonate

For $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$, $\Delta H^\circ = +178$ kJ mol^{-1} and $\Delta S^\circ = +161$ J K^{-1}mol^{-1}. Find the minimum temperature at which the decomposition becomes feasible.

The reaction becomes just feasible when $\Delta G^\circ = 0$, i.e. $\Delta H^\circ = T\Delta S^\circ$:

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{178\,000 \text{ J mol}^{-1}}{161 \text{ J K}^{-1}\text{mol}^{-1}} = 1105.6 \text{ K} \approx 1106 \text{ K}.$$

Below this temperature $\Delta G^\circ > 0$ (not feasible); above it $\Delta G^\circ < 0$ (feasible) — consistent with limestone requiring a very hot kiln (> 1100 K, about $830\,^\circ$C) to decompose.

Ví dụ mẫu · Worked example — ΔG° of the Haber process at 298 K

For $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, $\Delta H^\circ = -92.2$ kJ mol^{-1} and $\Delta S^\circ = -198.7$ J K^{-1}mol^{-1} (the large negative ΔS° reflects 4 mol of gas becoming 2 mol of gas). Calculate ΔG° at 298 K and interpret the sign.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -92\,200 - 298 \times (-198.7) = -92\,200 + 59\,214.6 = -32\,985.4 \text{ J mol}^{-1}.$$

$$\Delta G^\circ \approx -33.0 \text{ kJ mol}^{-1} \quad (\text{at } 298 \text{ K}).$$

Since $\Delta G^\circ < 0$, the Haber process **is** thermodynamically feasible at room temperature, despite the large negative ΔS° — the very negative ΔH° dominates at this comparatively low temperature. (Industrially, the process is nonetheless run at a much higher temperature, around $450\,^\circ$C, purely to achieve a commercially useful **rate**, using an iron catalyst — a kinetic, not thermodynamic, decision; raising T actually makes ΔG° *less* negative here, since $\Delta S^\circ < 0$.)

VN **GIẢI THÍCH TIẾNG VIỆT**

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$; phản ứng khả thi nhiệt động khi $\Delta G^\circ < 0$. Với sự phân huỷ $CaCO_3$ (thu nhiệt, $\Delta S^\circ > 0$), có một **nhiệt độ tối thiểu** để khả thi ($T = \Delta H^\circ/\Delta S^\circ \approx 1106$ K). Với quá trình Haber (toả nhiệt, $\Delta S^\circ < 0$), phản ứng **đã khả thi** ở 298 K ($\Delta G^\circ \approx -33.0$ kJ mol^{-1}), nhưng vẫn cần nhiệt độ cao và xúc tác vì lý do **tốc độ**, không phải vì lý do nhiệt động học.

5.7 Practice

Bài tập luyện tập

Which statement correctly defines the standard enthalpy change of formation of a compound?

(A) The enthalpy change when 1 mole of a compound is completely burned in oxygen

(B) The enthalpy change when 1 mole of a compound is formed from its elements in their standard states, under standard conditions

(C) The enthalpy change when 1 mole of bonds is broken in the gas phase

(D) The enthalpy change when 1 mole of solid dissolves in excess water

Lời giải chi tiết

Option (B) is the definition of ΔH_f°; (A) describes ΔH_c°, (C) describes bond dissociation energy, (D) describes ΔH_{sol}°. **(B).**

Bài tập luyện tập

In a displacement reaction, 25.0 cm^3 of 0.500 mol dm^{-3} $CuSO_4(aq)$ was reacted with excess zinc powder in an insulated cup; the temperature rose by $10.5\,^\circ$C. Taking the density of the solution as 1.00 g cm^{-3} and $c = 4.18$ J g^{-1}K^{-1}, calculate the enthalpy change of reaction per mole of $CuSO_4$.

Lời giải chi tiết

$$q = mc\Delta T = 25.0 \times 4.18 \times 10.5 = 1097.3 \text{ J} = 1.097 \text{ kJ}.$$

$$n(\text{CuSO}_4) = 0.500 \times \frac{25.0}{1000} = 0.0125 \text{ mol}.$$

$$\Delta H = -\frac{1.097}{0.0125} = \textbf{-87.8 kJ mol}^{-1} \text{ (exothermic; zinc displaces copper)}.$$

Bài tập luyện tập

Dissolving solid ammonium nitrate in water causes the temperature of the solution to **fall**. What does this indicate about ΔH_{sol}° and the process overall?

(A) ΔH_{sol}° is negative; the process is exothermic

(B) ΔH_{sol}° is positive; the process is endothermic

(C) No enthalpy change occurs since no reaction takes place

(D) The entropy change must be negative

Lời giải chi tiết

A fall in temperature means the surroundings lose heat to the system — the process absorbs energy, so it is **endothermic** and $\Delta H^{\circ}_{sol} > 0$. **(B)**.

Bài tập luyện tập

An enthalpy cycle has two known steps: Step 1 (reactant → intermediate), $\Delta H_1 = +150$ kJ mol^{-1}; Step 2 (intermediate → product), $\Delta H_2 = -84$ kJ mol^{-1}. Use Hess's Law to find the overall enthalpy change for reactant → product.

Lời giải chi tiết

By Hess's Law, the overall change equals the sum of the steps on the indirect route:

$$\Delta H_{overall} = \Delta H_1 + \Delta H_2 = 150 + (-84) = \textbf{+66 kJ mol}^{-1}.$$

Bài tập luyện tập

Which statement is the correct form of Hess's Law?

(A) The enthalpy change of a reaction is always negative if the reaction occurs spontaneously

(B) The total enthalpy change for a reaction depends only on the initial and final states, not on the route taken

(C) The enthalpy change of combustion is always greater than the enthalpy change of formation

(D) Enthalpy changes can only be measured, never calculated

Lời giải chi tiết

Hess's Law states that ΔH is independent of the route taken, depending only on the initial and final states — a direct consequence of conservation of energy. **(B)**.

Bài tập luyện tập

Estimate ΔH for the complete combustion of ethane, $C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$, using $E(C-H) = 410$, $E(C-C) = 350$, $E(O=O) = 496$, $E(C=O) = 805$, $E(O-H) = 460$ kJ mol^{-1}.

Lời giải chi tiết

Bonds broken (in C_2H_6: 6 $C-H$, 1 $C-C$; in $\frac{7}{2}O_2$: 3.5 $O=O$):

$$6(410) + 350 + 3.5(496) = 2460 + 350 + 1736 = 4546 \text{ kJ mol}^{-1}.$$

Bonds formed (in $2CO_2$: 4 $C=O$; in $3H_2O$: 6 $O-H$):

$$4(805) + 6(460) = 3220 + 2760 = 5980 \text{ kJ mol}^{-1}.$$

$$\Delta H \approx 4546 - 5980 = \textbf{-1434 kJ mol}^{-1}.$$

Bài tập luyện tập

Mean bond energies are best described as:

(A) Exact values measured for every individual molecule

(B) Average values taken across many different compounds containing that bond type

(C) Values that apply only to ionic compounds

(D) Always identical to enthalpy of formation values

Lời giải chi tiết

Mean bond energies are averaged over many different molecules, so they only give an *estimate* of ΔH for any specific reaction. **(B)**.

Bài tập luyện tập

Which quantity is defined as "the enthalpy change when 1 mole of gaseous ions dissolves in a large excess of water"?

(A) Lattice energy

(B) Enthalpy of formation

(C) Enthalpy of hydration

(D) Enthalpy of atomisation

Lời giải chi tiết

This is the definition of **enthalpy of hydration**, ΔH°_{hyd}, always exothermic. **(C)**.

Bài tập luyện tập

Given $\Delta H^\circ_L(\text{KCl}) = -711$ kJ mol^{-1}, $\Delta H^\circ_{hyd}(\text{K}^+) = -322$ kJ mol^{-1}, $\Delta H^\circ_{hyd}(\text{Cl}^-) = -364$ kJ mol^{-1}, calculate $\Delta H^\circ_{sol}(\text{KCl})$.

Lời giải chi tiết

$\Delta H^\circ_{sol} = -\Delta H^\circ_L + \Delta H^\circ_{hyd}(\text{K}^+) + \Delta H^\circ_{hyd}(\text{Cl}^-) = -(-711) + (-322) + (-364) = 711 - 686 =$ **+25 kJ mol^{-1}**.

Small and positive — consistent with KCl dissolving being slightly endothermic (the solution feels cool), while still dissolving readily due to the favourable entropy increase.

Bài luyện nâng cao (A2)

For potassium chloride, $\Delta H^\circ_f(\text{KCl}) = -436$ kJ mol^{-1}; $\Delta H^\circ_{at}(\text{K}) = +89$; $\Delta H^\circ_{at}(\text{Cl}) = +121$; $EA(\text{Cl}) = -349$; $\Delta H^\circ_L(\text{KCl}) = -711$ kJ mol^{-1} (all in kJ mol^{-1}). Use a Born–Haber cycle to calculate $IE_1(\text{K})$.

Lời giải chi tiết

$$\Delta H^\circ_f = \Delta H^\circ_{at}(\text{K}) + IE_1(\text{K}) + \Delta H^\circ_{at}(\text{Cl}) + EA(\text{Cl}) + \Delta H^\circ_L.$$

$$-436 = 89 + IE_1 + 121 - 349 - 711 = IE_1 - 850.$$

$$IE_1(\text{K}) = -436 + 850 = \textbf{+414 kJ mol}^{-1}.$$

Bài luyện nâng cao (A2)

For magnesium chloride, $\Delta H_f^\circ(\text{MgCl}_2) = -641.3$ kJ mol^{-1}; $\Delta H_{at}^\circ(\text{Mg}) = +148$; $IE_1(\text{Mg}) = +738$; $IE_2(\text{Mg}) = +1451$; $\Delta H_{at}^\circ(\text{Cl}) = +121$; $EA(\text{Cl}) = -349$ kJ mol^{-1}. Note that **two** moles of chlorine atoms and **two** electron affinities are needed. Calculate $\Delta H_L^\circ(\text{MgCl}_2)$.

Lời giải chi tiết

$$\Delta H_f^\circ = \Delta H_{at}^\circ(\text{Mg}) + IE_1 + IE_2 + 2\Delta H_{at}^\circ(\text{Cl}) + 2EA(\text{Cl}) + \Delta H_L^\circ.$$

$$-641.3 = 148+738+1451+2(121)+2(-349)+\Delta H_L^\circ = 148+738+1451+242-698+\Delta H_L^\circ = 1881+\Delta H_L^\circ.$$

$$\Delta H_L^\circ(\text{MgCl}_2) = -641.3 - 1881 = \textbf{-2522 kJ mol}^{-1}.$$

Bài tập luyện tập

Which of the following ionic compounds would be expected to have the *most exothermic* lattice energy?

(A) NaCl (radii: Na^+ 0.102 nm, Cl^- 0.181 nm)

(B) KBr (radii: K^+ 0.138 nm, Br^- 0.196 nm)

(C) MgO (radii: Mg^{2+} 0.072 nm, O^{2-} 0.140 nm)

(D) CsI (radii: Cs^+ 0.170 nm, I^- 0.220 nm)

Lời giải chi tiết

MgO has both the highest ionic charges ($2+/2-$) and the smallest ionic radii of the options — both factors independently increase the magnitude of lattice energy, and they reinforce each other here. **(C)**.

Bài tập luyện tập

Rank the following in order of *increasing* magnitude of lattice energy, with a brief reason: NaF, NaCl, MgO.

Lời giải chi tiết

Order of increasing magnitude: NaCl $<$ NaF $<$ MgO. NaF has a smaller lattice energy magnitude than... *(reasoning)*: Cl^- is larger than F^-, so NaCl has the ions furthest apart and the weakest attraction of the two 1:1 sodium halides, giving it the smallest magnitude; NaF, with the smaller F^- ion, has ions closer together and a larger magnitude than NaCl; MgO has both doubled ionic charges (attraction $\propto q_+q_-$, four times greater) and much smaller ionic radii than either sodium halide, giving by far the largest magnitude of the three.

Bài tập luyện tập

Which reaction would be expected to have the most *positive* ΔS°?

(A) $2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$

(B) $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$

(C) $2\text{H}_2\text{O}_2(\text{l}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$

(D) $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$

Lời giải chi tiết

(A): 2 mol gas → 4 mol gas, ΔS° strongly positive (moles of gas double). (B) has no change in moles of gas. (C) has 0 mol gas → 1 mol gas (positive, but a smaller increase than doubling gas moles from 2 to 4). (D) has 3 mol gas → 2 mol gas (negative). The largest *increase* in gas moles is in (A). **(A)**.

Bài luyện nâng cao (A2)

Predict the sign of ΔS° for $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ and use it, together with $\Delta H^\circ = -572$ kJ mol^{-1}, to comment on whether the reaction is feasible at 298 K (without a full calculation).

Lời giải chi tiết

3 mol of gas form 2 mol of liquid, so ΔS° is **strongly negative** (large decrease in disorder). Since ΔH° is very strongly negative and $T\Delta S^\circ$ (at 298 K, with ΔS° of only a few hundred J K^{-1}mol^{-1} in magnitude) is much smaller in magnitude than ΔH°, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ remains **negative** overall: the reaction is thermodynamically **feasible** at 298 K (though, as with the Haber process, it is kinetically very slow without a spark or catalyst to initiate it).

Bài luyện nâng cao (A2)

For the decomposition $CuCO_3(s) \rightarrow CuO(s) + CO_2(g)$, $\Delta H^\circ = +87$ kJ mol^{-1} and $\Delta S^\circ = +175$ J K^{-1}mol^{-1}. Calculate the minimum temperature at which decomposition becomes thermodynamically feasible.

Lời giải chi tiết

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{87\,000}{175} = \textbf{497 K}\ (\text{to 3 s.f.}).$$

Bài luyện nâng cao (A2)

For $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$, $\Delta H^\circ = -197$ kJ mol^{-1} and $\Delta S^\circ = -188$ J K^{-1}mol^{-1}. Calculate ΔG° at 298 K and comment on the feasibility of the reaction at this temperature.

Lời giải chi tiết

$\Delta G^\circ = -197\,000 - 298 \times (-188) = -197\,000 + 56\,024 = -140\,976$ J mol^{-1} $\approx$ **-141.0 kJ mol^{-1}**.

$\Delta G^\circ < 0$, so the reaction is thermodynamically feasible at 298 K (industrially it is carried out at a much higher temperature, around $450\,^\circ$C, purely for reasons of rate and equilibrium yield, not because it is thermodynamically unfeasible at room temperature).

Bài tập luyện tập

Which rearrangement of $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ correctly gives ΔS° in terms of the other quantities?

(A) $\Delta S^\circ = \dfrac{\Delta H^\circ - \Delta G^\circ}{T}$

(B) $\Delta S^\circ = \Delta H^\circ \times T - \Delta G^\circ$

(C) $\Delta S^\circ = \dfrac{\Delta G^\circ - \Delta H^\circ}{T}$

(D) $\Delta S^\circ = T(\Delta H^\circ - \Delta G^\circ)$

Lời giải chi tiết

Rearranging $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ gives $T\Delta S^\circ = \Delta H^\circ - \Delta G^\circ$, so $\Delta S^\circ = \dfrac{\Delta H^\circ - \Delta G^\circ}{T}$. **(A)**.

Bài tập luyện tập

Standard conditions for thermodynamic quantities in this chapter are:

(A) 298 K and 100 kPa, solutions at 1 mol dm^{-3}

(B) 273 K and 101 kPa only

(C) Any convenient temperature and pressure, as long as they are stated

(D) 298 K and 1 kPa

Lời giải chi tiết

Standard conditions are 298 K ($25\,^\circ$C) and 100 kPa, with solutions at 1 mol dm^{-3}. **(A)**.

Bài tập luyện tập

A student burns 0.23 g of ethanol ($M_r = 46.0$) to heat 100 g of water and records a temperature rise of $30.0\,^\circ$C. Using $\Delta H_c^\circ(\text{ethanol}) = -1367$ kJ mol^{-1} from a data book, calculate the heat that *should theoretically* have been released by this mass of ethanol if combustion were complete and no heat were lost, compare it with the heat actually absorbed by the water, and comment on the result.

Lời giải chi tiết

Heat theoretically available:

$$n(\text{ethanol}) = \frac{0.23}{46.0} = 0.005 \text{ mol}, \qquad q_{\text{theoretical}} = 0.005 \times 1367 = 6.835 \text{ kJ}.$$

Heat actually absorbed by the water:

$$q_{\text{observed}} = mc\Delta T = 100 \times 4.18 \times 30.0 = 12\,540 \text{ J} = 12.54 \text{ kJ}.$$

The observed heat absorbed by the water (12.54 kJ) is **greater** than the maximum heat that this small mass of ethanol could theoretically release (6.835 kJ) — an efficiency of $\dfrac{12.54}{6.835} \times 100\% \approx 183\%$, which is **physically impossible** (a calorimetry experiment can never capture more energy than the fuel releases; heat is always lost, never gained, so efficiency must be $\leq 100\%$). This shows that at least one measurement in the experiment must be in error — for example, more ethanol than recorded may actually have been burnt, the mass or temperature rise of the water may have been misread, or an arithmetic slip has occurred; the result as stated cannot be correct.

Bài tập luyện tập

Which of the following processes is *always* exothermic?

(A) Breaking a covalent bond
(B) Ionisation of a gaseous atom
(C) Formation of a lattice from gaseous ions
(D) Sublimation of a solid metal

Lời giải chi tiết

Forming an ionic lattice from free gaseous ions always releases a large amount of electrostatic energy — it is always exothermic (this is lattice energy). Breaking bonds, removing electrons (ionisation), and converting solid to gas (sublimation) are all endothermic. **(C)**.

Bài tập luyện tập

An enthalpy diagram shows three steps of an indirect route from A to D: A $\rightarrow$ B, $\Delta H_1 = +220$ kJ mol^{-1}; B $\rightarrow$ C, $\Delta H_2 = -95$ kJ mol^{-1}; C $\rightarrow$ D, $\Delta H_3 = -40$ kJ mol^{-1}. A direct route A $\rightarrow$ D also exists. Use Hess's Law to find ΔH for the direct route.

Lời giải chi tiết

Since both routes start at A and finish at D, by Hess's Law:

$$\Delta H(\text{A} \rightarrow \text{D}) = \Delta H_1 + \Delta H_2 + \Delta H_3 = 220 - 95 - 40 = \textbf{+85 kJ mol}^{-1}.$$

Bài luyện nâng cao (A2)

Given (all kJ mol^{-1}): $\Delta H_f^\circ(\text{NaF}) = -573.6$; $\Delta H_{at}^\circ(\text{Na}) = +107$; $IE_1(\text{Na}) = +496$; $\Delta H_{at}^\circ(\text{F}) = +79$; $\Delta H_L^\circ(\text{NaF}) = -918$. Use a Born–Haber cycle to calculate the electron affinity of fluorine, $EA(\text{F})$.

Lời giải chi tiết

$$\Delta H_f^\circ = \Delta H_{at}^\circ(\text{Na}) + IE_1(\text{Na}) + \Delta H_{at}^\circ(\text{F}) + EA(\text{F}) + \Delta H_L^\circ.$$

$$-573.6 = 107 + 496 + 79 + EA(\text{F}) - 918 = -236 + EA(\text{F}).$$

$$EA(\text{F}) = -573.6 + 236 = \textbf{-337.6 kJ mol}^{-1} \approx -338 \text{ kJ mol}^{-1}.$$

Bài tập luyện tập

Which is the most significant single source of error in a simple spirit-burner calorimetry experiment to find ΔH_c of a fuel?

(A) The precision of the balance used to weigh the fuel
(B) Heat lost to the surroundings rather than heating the water
(C) Rounding errors in the value of the specific heat capacity of water
(D) The volume of water used

Lời giải chi tiết

Because the flame is open to the air, most of the heat released escapes to the surroundings without heating the water — by far the largest source of error, causing the experimental $|\Delta H_c|$ to be much smaller than the true value. **(B)**.

Bài tập luyện tập

Explain, using ionic charge and radius, why the enthalpy of hydration of Mg^{2+} is very much more exothermic than that of Na^{+}.

Lời giải chi tiết

Mg^{2+} carries twice the ionic charge of Na^{+} and has a considerably smaller ionic radius. Both factors increase the electrostatic attraction between the ion and the surrounding polar water molecules (attraction increases with charge and decreases with ionic radius), so far more energy is released when Mg^{2+} is hydrated than when Na^{+} is hydrated.

Bài tập luyện tập

Estimate ΔH for the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ using mean bond energies $E(N \equiv N) = 945$, $E(H - H) = 436$, $E(N - H) = 391$ kJ mol^{-1}.

Lời giải chi tiết

Bonds broken: 1 $N \equiv N$ and 3 $H - H$:

$$945 + 3(436) = 945 + 1308 = 2253 \text{ kJ mol}^{-1}.$$

Bonds formed: 2 NH_3, each with 3 $N - H$ bonds, so 6 $N - H$ bonds total:

$$6(391) = 2346 \text{ kJ mol}^{-1}.$$

$\Delta H \approx 2253 - 2346 =$ **-93 kJ mol^{-1}** (close to the accepted value of -92.2 kJ mol^{-1}).

Bài tập luyện tập

A reaction has $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$. As temperature increases, ΔG°:

(A) Becomes more negative (more feasible)

(B) Becomes less negative, and may eventually become positive (less feasible)

(C) Stays exactly the same at all temperatures

(D) Cannot be calculated without knowing ΔH_f° of every species

Lời giải chi tiết

Since $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and $\Delta S^\circ < 0$, the term $-T\Delta S^\circ$ becomes more *positive* as T increases, making ΔG° less negative (and, at a high enough T, eventually positive). **(B)**.

Bài tập luyện tập

Combine the following to find $\Delta H_f^\circ(\mathrm{C_2H_5OH, l})$ (ethanol): $\Delta H_c^\circ(\mathrm{C, graphite}) = -393.5$; $\Delta H_c^\circ(\mathrm{H_2, g}) = -285.8$; $\Delta H_c^\circ(\mathrm{C_2H_5OH, l}) = -1367.0$ kJ mol^{-1} (ethanol contains 2 C atoms and 6 H atoms per molecule; combustion also involves $\mathrm{O_2}$, which is already an element in its standard state).

Lời giải chi tiết

Target: $2\mathrm{C(s)} + 3\mathrm{H_2(g)} + \frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{C_2H_5OH(l)}$.
Both the direct route (form ethanol, then combust it) and the indirect route (combust the elements directly) reach the same final products ($2\mathrm{CO_2} + 3\mathrm{H_2O}$):

$$\Delta H_f^\circ(\mathrm{C_2H_5OH}) + \Delta H_c^\circ(\mathrm{C_2H_5OH}) = 2\Delta H_c^\circ(\mathrm{C}) + 3\Delta H_c^\circ(\mathrm{H_2}).$$

$\Delta H_f^\circ(\mathrm{C_2H_5OH}) = 2(-393.5)+3(-285.8)-(-1367.0) = -787.0-857.4+1367.0 =$ **-277.4 kJ mol^{-1}**.

Electrochemistry

Mục tiêu Unit: Cân bằng thành thạo các bán phản ứng oxi hoá–khử trong môi trường acid và ghép chúng thành phương trình ion tổng quát (bao gồm tính toán chuẩn độ oxi hoá–khử); hiểu và sử dụng dãy điện hoá (electrochemical series) với các giá trị E° để dự đoán chiều và tính khả thi của phản ứng; viết đúng quy ước sơ đồ pin (cell notation); tính E°_{cell} và áp dụng phương trình Nernst cho nồng độ không chuẩn (A2); phân biệt pin sơ cấp, pin thứ cấp (sạc lại được) và pin nhiên liệu; áp dụng định luật Faraday để tính khối lượng/thể tích sản phẩm điện phân, dự đoán sản phẩm điện phân dung dịch nước và nóng chảy dựa trên tính ưu tiên phóng điện, và hiểu quy trình công nghiệp Hall–Héroult sản xuất nhôm.

6.1 Redox reactions and oxidation numbers

A **redox** reaction is one in which oxidation and reduction occur simultaneously — electrons are transferred from one species to another. The mnemonic **OIL RIG** summarises the electron-transfer definitions:

Oxidation **I**s **L**oss (of electrons) **R**eduction **I**s **G**ain (of electrons).

The species that is oxidised (loses electrons) is the **reducing agent**; the species that is reduced (gains electrons) is the **oxidising agent**.

Khái niệm cốt lõi

Oxidation number rules (most useful, in order of priority): (1) an uncombined element $= 0$; (2) a simple monatomic ion = its charge; (3) H $= +1$ (except metal hydrides, -1); (4) O $= -2$ (except peroxides, -1, and OF_2, $+2$); (5) the sum of oxidation numbers in a neutral compound $= 0$, and in an ion $=$ the ion's charge. Oxidation = an **increase** in oxidation number; reduction = a **decrease**.

VN **GIẢI THÍCH TIẾNG VIỆT**

OIL RIG: Oxi hoá là mất electron (Oxidation Is Loss), Khử là nhận electron (Reduction Is Gain). Chất bị oxi hoá (mất electron) đóng vai trò **chất khử**; chất bị khử (nhận electron) đóng vai trò **chất oxi hoá**. Số oxi hoá tăng ⇒ bị oxi hoá; số oxi hoá giảm ⇒ bị khử.

6.1.1 Balancing half-equations in acidic solution

Many redox half-equations, especially those of oxidising agents containing oxygen, are balanced systematically: balance the atom being reduced/oxidised first, then balance oxygen using H_2O, then balance hydrogen using H^+ (since these reactions occur in acidic solution), and finally balance charge using electrons.

Ví dụ mẫu · Worked example — half-equation for dichromate reduction

Construct the half-equation for the reduction of dichromate(VI) ions, $Cr_2O_7^{2-}$, to chromium(III) ions, Cr^{3+}, in acidic solution.

Step 1 (balance Cr): $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$.
Step 2 (balance O with H_2O): $Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$.
Step 3 (balance H with H^+): $Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$.
Step 4 (balance charge with e^-): left-hand charge $= -2 + 14 = +12$; right-hand charge $= 2(+3) = +6$; add $6e^-$ to the left:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O.$$

Check: charge — left $= -2 + 14 - 6 = +6$, right $= +6$ ✓; atoms — Cr: 2=2, O: 7=7, H: 14=14 ✓.

Ví dụ mẫu · Worked example — half-equation for manganate(VII) reduction

Construct the half-equation for the reduction of manganate(VII) ions, MnO_4^-, to manganese(II) ions, Mn^{2+}, in acidic solution.

Following the same procedure: $MnO_4^- \rightarrow Mn^{2+}$ (Mn balanced) → add $4H_2O$ to balance O → add $8H^+$ to balance H:

$$MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O.$$

Charge: left $= -1 + 8 = +7$; right $= +2$; add $5e^-$ to the left:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O.$$

Check: charge — left $= -1 + 8 - 5 = +2$, right $= +2$ ✓; atoms — Mn:1=1, O:4=4, H:8=8 ✓.

VN **GIẢI THÍCH TIẾNG VIỆT**

Quy trình cân bằng bán phản ứng trong môi trường acid: (1) cân bằng nguyên tử trung tâm bị oxi hoá/khử; (2) cân bằng O bằng H_2O; (3) cân bằng H bằng H^+; (4) cân bằng điện tích bằng electron. Luôn kiểm tra lại cả nguyên tử **và** điện tích ở bước cuối.

6.1.2 Combining half-equations: redox titrations

To obtain the overall ionic equation for a redox reaction, the two half-equations are scaled so that the number of electrons lost equals the number of electrons gained, then added together, cancelling the electrons (and any species that appear unchanged on both sides).

Ví dụ mẫu · Worked example — combining half-equations: the manganate(VII)–iron(II) titration

Combine the reduction half-equation for MnO_4^- (above, 5 electrons gained) with the oxidation of iron(II): $Fe^{2+} \rightarrow Fe^{3+} + e^-$ (1 electron lost), to give the overall equation for the classic titration of iron(II) with potassium manganate(VII).

Since 5 electrons are gained per MnO_4^- but only 1 electron is lost per Fe^{2+}, the iron half-equation must be multiplied by 5 before adding:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

$$5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-$$

Adding and cancelling the $5e^-$ on each side:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}.$$

Check: charge — left $= -1 + 8 + 5(2) = 17$, right $= 2 + 0 + 5(3) = 17$ ✓; atoms — Mn:1, O:4, H:8, Fe:5, all balanced ✓. This reaction is the basis of a redox titration: the deep purple MnO_4^- acts as its own indicator, decolourising as it is reduced, so the end-point is the first permanent faint pink/purple tinge.

Ví dụ mẫu · Worked example — concentration from a redox titration

25.0 cm^3 of an acidified $FeSO_4$ solution required 22.50 cm^3 of 0.0200 mol dm^{-3} $KMnO_4$ for complete reaction (equation above). Calculate the concentration of the Fe^{2+} solution.

$$n(MnO_4^-) = 0.0200 \times \frac{22.50}{1000} = 4.50 \times 10^{-4} \text{ mol}.$$

From the 5:1 mole ratio (Fe^{2+} : MnO_4^-):

$$n(Fe^{2+}) = 5 \times 4.50 \times 10^{-4} = 2.25 \times 10^{-3} \text{ mol}.$$

$$c(Fe^{2+}) = \frac{2.25 \times 10^{-3}}{25.0/1000} = \textbf{0.0900 mol dm}^{-3}.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Để ghép hai bán phản ứng thành phương trình tổng: nhân mỗi bán phản ứng sao cho số electron cho = số electron nhận, cộng lại, rồi triệt tiêu electron (và các chất giống nhau ở hai vế). Đây là cơ sở của **chuẩn độ oxi hoá–khử** (ví dụ MnO_4^- chuẩn độ Fe^{2+}), dùng tỉ lệ mol để tính nồng độ.

6.2 Electrochemical cells and standard electrode potentials

When two different half-cells (each consisting of a metal in contact with a solution of its own ions, or an inert electrode in contact with a solution containing both oxidised and reduced forms of a species) are connected by a wire and a **salt bridge**, electrons flow through the wire and a voltage can be measured — an **electrochemical cell**. A **standard electrode potential**, E°, is the voltage of a half-cell measured against the **standard hydrogen electrode** (defined as $E^\circ = 0.00$ V, using H_2 gas at 100 kPa bubbled over a platinum electrode in 1 mol dm^{-3} $H^+(aq)$, at 298 K), under standard conditions.

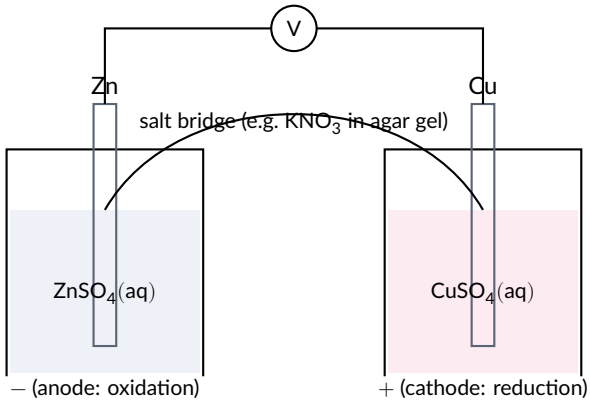


Figure 6.1 — The Daniell cell: zinc/copper half-cells joined by a salt bridge and an external wire through a voltmeter.

For a complete cell, the overall standard cell potential is

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = E^\circ_{\text{(reduced at)}} - E^\circ_{\text{(oxidised at)}},$$

where both E° values are quoted as standard **reduction** potentials (the convention used throughout this chapter and in all data books) — the electrode with the more positive E° is the **cathode** (reduction occurs there; electrons flow to it through the external circuit), and the electrode with the more negative (or less positive) E° is the **anode** (oxidation occurs there).

Ví dụ mẫu · Worked example — the Daniell cell

Given $E^\circ(\text{Cu}^{2+}/\text{Cu}) = +0.34$ V and $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76$ V, calculate E°_{cell} for the Daniell cell, and identify the cathode and anode.

Copper has the more positive E°, so it is the cathode (reduction, $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$); zinc is the anode (oxidation, $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$):

$$E^\circ_{cell} = E^\circ(\text{Cu}^{2+}/\text{Cu}) - E^\circ(\text{Zn}^{2+}/\text{Zn}) = 0.34 - (-0.76) = \textbf{+1.10 V}.$$

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

VN **GIẢI THÍCH TIẾNG VIỆT**

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$, dùng thế khử chuẩn của cả hai điện cực. Điện cực có E° **dương hơn** là cathode (xảy ra khử); điện cực có E° **âm hơn** là anode (xảy ra oxi hoá). Pin Daniell (Zn/Cu) có $E^\circ_{cell} = +1.10$ V.

6.3 The electrochemical series

Arranging half-cells in order of E° produces the **electrochemical series**. A species higher in the table (more negative E°) is a **stronger reducing agent** in its reduced form (it more readily loses electrons); a species lower in the table (more positive E°) is a **stronger oxidising agent** in its oxidised form (it more readily gains electrons).

Half-equation (reduction)	E° (V)
$\text{Li}^+ + \text{e}^- \rightleftharpoons \text{Li}$	-3.03
$\text{K}^+ + \text{e}^- \rightleftharpoons \text{K}$	-2.92
$\text{Mg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mg}$	-2.37
$\text{Al}^{3+} + 3\text{e}^- \rightleftharpoons \text{Al}$	-1.66
$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}$	-0.76
$\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe}$	-0.44
$\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb}$	-0.13
$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$	0.00
$\text{Sn}^{4+} + 2\text{e}^- \rightleftharpoons \text{Sn}^{2+}$	$+0.15$
$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}$	$+0.34$
$\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-$	$+0.54$
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	$+0.77$
$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$	$+0.80$
$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{NO} + 2\text{H}_2\text{O}$	$+0.96$
$\text{Br}_2 + 2\text{e}^- \rightleftharpoons 2\text{Br}^-$	$+1.07$
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	$+1.33$
$\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	$+1.36$
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	$+1.51$

Table 6.1 — Selected standard electrode potentials (298 K, 100 kPa, 1 mol dm^{-3}).

Ví dụ mẫu · Worked example — predicting feasibility with the electrochemical series (I)

Use Table 6.1 to predict whether copper metal will displace silver ions from solution, and calculate E°_{cell}.

Proposed reaction: $Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$. Silver has the more positive E° ($+0.80$ V vs. $+0.34$ V for copper), so Ag^+ is reduced (cathode reaction) and Cu is oxidised (anode reaction):

$$E^\circ_{cell} = E^\circ(Ag^+/Ag) - E^\circ(Cu^{2+}/Cu) = 0.80 - 0.34 = \textbf{+0.46 V}.$$

Since $E^\circ_{cell} > 0$, the reaction is thermodynamically feasible: copper does displace silver from solution.

Ví dụ mẫu · Worked example — predicting feasibility with the electrochemical series (II)

Use Table 6.1 to predict whether chlorine gas can oxidise bromide ions to bromine.

Proposed reaction: $Cl_2(g) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$.

$$E^\circ_{cell} = E^\circ(Cl_2/Cl^-) - E^\circ(Br_2/Br^-) = 1.36 - 1.07 = \textbf{+0.29 V}.$$

$E^\circ_{cell} > 0$: the reaction is feasible — chlorine is a strong enough oxidising agent to displace bromine from bromide solution, exactly as observed experimentally.

VN **GIẢI THÍCH TIẾNG VIỆT**

Dãy điện hoá sắp xếp các bán phản ứng theo E° tăng dần. Chất ở **trên** (thế âm hơn), dạng khử là **chất khử mạnh**; chất ở **dưới** (thế dương hơn), dạng oxi hoá là **chất oxi hoá mạnh**. Một phản ứng khả thi khi $E^\circ_{cell} = E^\circ(\text{chất oxi hoá}) - E^\circ(\text{chất khử}) > 0$.

6.4 Cell notation and conventions

A standard shorthand, **cell notation**, records a cell without needing to draw it. By convention: a single vertical line, |, marks a **phase boundary** (e.g. solid electrode / solution); a double vertical line, ‖, marks the **salt bridge**; the **anode** (oxidation, negative terminal in a cell providing current) is written on the **left**, the **cathode** (reduction, positive terminal) on the **right**; species within one half-cell are separated by commas if they are in the same phase.

Khái niệm cốt lõi

Daniell cell in full notation:

$$Zn(s)|Zn^{2+}(aq)\|Cu^{2+}(aq)|Cu(s), \qquad E^\circ_{cell} = +1.10 \text{ V}.$$

Reading left to right follows the direction electrons flow through the external circuit: oxidation at the left-hand electrode, reduction at the right-hand electrode. Where neither half-cell involves a solid metal electrode (e.g. a redox couple such as Fe^{3+}/Fe^{2+}), an inert electrode — usually platinum, Pt — is included and written at the outer edge of that half-cell.

Ví dụ mẫu · Worked example — cell notation with an inert electrode

Write the cell notation, and calculate E°_{cell}, for a cell combining the standard hydrogen electrode with an Fe^{3+}/Fe^{2+} half-cell ($E^\circ = +0.77$ V).

The hydrogen electrode ($E^\circ = 0.00$ V) has the more negative potential, so it is the anode (left);

the Fe^{3+}/Fe^{2+} half-cell, using an inert Pt electrode (since neither species is a solid metal), is the cathode (right):

$$Pt(s)|H_2(g)|H^+(aq)||Fe^{3+}(aq), Fe^{2+}(aq)|Pt(s).$$

$$E^\circ_{cell} = E^\circ(Fe^{3+}/Fe^{2+}) - E^\circ(H^+/H_2) = 0.77 - 0.00 = \textbf{+0.77 V}.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Quy ước sơ đồ pin: một vạch đứng (|) = ranh giới pha; hai vạch đứng (‖) = cầu muối; **anode** (oxi hoá) viết bên **trái**, **cathode** (khử) viết bên **phải**. Nếu không có kim loại rắn tham gia (ví dụ cặp Fe^{3+}/Fe^{2+}), dùng điện cực trơ Pt.

6.5 Using E° values to predict feasibility

Ví dụ mẫu · Worked example — can manganate(VII) oxidise chloride to chlorine?

Use $E^\circ(MnO_4^-/Mn^{2+}) = +1.51$ V and $E^\circ(Cl_2/Cl^-) = +1.36$ V to decide whether acidified potassium manganate(VII) can oxidise chloride ions to chlorine gas.

$$E^\circ_{cell} = E^\circ(MnO_4^-/Mn^{2+}) - E^\circ(Cl_2/Cl^-) = 1.51 - 1.36 = \textbf{+0.15 V}.$$

$E^\circ_{cell} > 0$: the reaction *is* thermodynamically feasible. (This is in fact why hydrochloric acid, rather than dilute sulfuric acid, cannot be used to acidify $KMnO_4$ in titrations — the chloride ion would be oxidised, introducing an unwanted side reaction.)

(!) Lỗi thường gặp: A positive E°_{cell} shows only that a reaction is **thermodynamically feasible** — exactly as with ΔG° (Chapter 5) — it says *nothing* about the **rate** of the reaction. Some reactions with a large positive E°_{cell} proceed extremely slowly at room temperature due to a high activation energy; E° values must never be used to predict how fast a reaction will occur.

VN **GIẢI THÍCH TIẾNG VIỆT**

$E^\circ_{cell} > 0$ chỉ cho biết phản ứng **khả thi về mặt nhiệt động**, không cho biết **tốc độ** phản ứng — giống hệt nguyên tắc với ΔG°. Một phản ứng có E°_{cell} dương lớn vẫn có thể xảy ra rất chậm nếu năng lượng hoạt hoá cao.

6.6 The Nernst equation (A2)

Standard electrode potentials apply only under standard conditions (1 mol dm^{-3}, 298 K, 100 kPa). For **non-standard** concentrations, the actual electrode potential is given by the **Nernst equation**, which at 298 K takes the simplified form

$$E = E^\circ - \frac{0.0592}{n} \log Q,$$

where n is the number of electrons transferred in the half-equation (or overall equation) and Q is the reaction quotient (ratio of product-side ion concentrations to reactant-side ion concentrations, each raised to its stoichiometric power). Decreasing the concentration of the oxidised species (the species being reduced, on the left of the half-equation) makes E **more negative** (less favourable for reduction); decreasing the concentration of the reduced species makes E **more positive**.

Ví dụ mẫu · Worked example — Nernst equation for a single half-cell

Calculate E for the Fe^{3+}/Fe^{2+} half-cell ($E^\circ = +0.77$ V, $n = 1$) when $[Fe^{3+}] = 0.10$ mol dm^{-3} and $[Fe^{2+}] = 1.0$ mol dm^{-3}.

$$E = E^\circ - \frac{0.0592}{1}\log\frac{[Fe^{2+}]}{[Fe^{3+}]} = 0.77 - 0.0592\log\frac{1.0}{0.10} = 0.77 - 0.0592(1) = \textbf{+0.71 V}.$$

Lowering $[Fe^{3+}]$ (the oxidised species) has made E less positive, as expected.

Ví dụ mẫu · Worked example — Nernst equation applied to the Daniell cell

The standard Daniell cell has $E^\circ_{cell} = +1.10$ V ($n = 2$ electrons transferred in $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$). Calculate E_{cell} if $[Zn^{2+}]$ is reduced to 0.01 mol dm^{-3} while $[Cu^{2+}]$ remains at 1.0 mol dm^{-3}.

For the overall cell reaction, $Q = \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$ (products over reactants):

$$E_{cell} = E^\circ_{cell} - \frac{0.0592}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]} = 1.10 - 0.0296\log\frac{0.01}{1.0} = 1.10 - 0.0296(-2) = 1.10 + 0.0592.$$

$$E_{cell} \approx \textbf{+1.16 V}.$$

Diluting the product-side ion, Zn^{2+}, pulls the equilibrium of the half-cell further towards oxidation, making the cell potential slightly **larger** than the standard value.

VN **GIẢI THÍCH TIẾNG VIỆT**

Phương trình Nernst $E = E^\circ - \dfrac{0.0592}{n}\log Q$ điều chỉnh E° khi nồng độ không chuẩn (298 K). Giảm nồng độ ion sản phẩm (bên phải, ví dụ Zn^{2+} khi pha loãng) làm E_{cell} **tăng** so với E°_{cell}; giảm nồng độ ion chất phản ứng làm E_{cell} **giảm**.

6.7 Primary cells, secondary cells and fuel cells

Practical batteries and cells are classified by whether — and how — the chemicals that produce electrical energy can be replenished.

Type	Description	Example
Primary cell	Chemicals are consumed as the cell discharges; the reaction cannot be reversed, so the cell is discarded (or recycled) once flat	Zinc–carbon and alkaline dry cells
Secondary (rechargeable) cell	The cell reaction can be **reversed** by passing a current through the cell from an external supply, regenerating the original reactants	Lead–acid car battery, lithium-ion battery
Fuel cell	Fuel and oxidant are supplied **continuously** from outside the cell and react to generate electrical energy directly, without combustion	Hydrogen–oxygen fuel cell

Table 6.2 — Primary cells, secondary cells and fuel cells compared.

Ví dụ mẫu · Worked example — the hydrogen–oxygen fuel cell

Write the electrode half-equations and overall equation for a hydrogen–oxygen fuel cell operating in **alkaline** conditions.

Anode (oxidation): $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$.
Cathode (reduction): $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$.
Adding and cancelling the $4e^-$, and the $4OH^-$, and $2H_2O$ common to both sides:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l).$$

Hydrogen–oxygen fuel cells offer two key advantages over combustion engines burning hydrocarbon fuels: (1) the only product is **water** — there is no CO_2 emission at the point of use; (2) fuel cells convert chemical energy **directly** into electrical energy through an electrochemical reaction, avoiding the intermediate step of generating heat and mechanical work, and so can achieve a higher overall energy-conversion efficiency than a combustion engine (which is fundamentally limited by the thermodynamics of heat engines). Fuel cells are used in some vehicles and in spacecraft.

VN **GIẢI THÍCH TIẾNG VIỆT**

Pin nhiên liệu hydro–oxy cung cấp nhiên liệu và chất oxi hoá **liên tục** từ bên ngoài, phản ứng trực tiếp tạo điện năng (không đốt cháy). Sản phẩm duy nhất là **nước**, không phát thải CO_2; hiệu suất chuyển hoá năng lượng cũng cao hơn động cơ đốt trong vì chuyển hoá năng lượng hoá học trực tiếp thành điện năng, không qua bước nhiệt năng trung gian.

6.8 Electrolysis and Faraday's Laws

Electrolysis is the decomposition of an ionic compound (molten or in solution) by passing an electric current through it. Positive ions (cations) migrate to the **cathode** (negative electrode) and are reduced (gain electrons); negative ions (anions) migrate to the **anode** (positive electrode) and are oxidised (lose electrons) — note that in electrolysis, unlike in a cell producing current, the cathode is the negative electrode.

The quantity of charge passed is

$$Q = It,$$

where Q is charge in coulombs (C), I is current in amperes (A), and t is time in seconds (s). The **Faraday constant**, $F = 96\,500$ C mol^{-1}, is the charge carried by one mole of electrons, so the number of moles of electrons passed is

$$n(e^-) = \frac{Q}{F} = \frac{It}{F}.$$

The amount of a product formed is then found from $n(e^-)$ using the electrode half-equation.

Ví dụ mẫu · Worked example — mass of copper deposited

A current of 0.500 A is passed through aqueous copper(II) sulfate for 1 hour, depositing copper at the cathode: $Cu^{2+} + 2e^- \rightarrow Cu$. Calculate the mass of copper deposited ($A_r(Cu) = 63.5$).

$$Q = It = 0.500 \times 3600 = 1800 \text{ C}.$$

$$n(e^-) = \frac{1800}{96\,500} = 0.01865 \text{ mol}, \qquad n(Cu) = \frac{0.01865}{2} = 0.009327 \text{ mol}.$$

$$\text{mass} = 0.009327 \times 63.5 = \mathbf{0.592\ g}.$$

Ví dụ mẫu · Worked example — mass of silver deposited

A current of 2.00 A is passed through aqueous silver nitrate for 30.0 minutes, depositing silver: $Ag^+ + e^- \rightarrow Ag$. Calculate the mass of silver deposited ($A_r(Ag) = 108$).

$$Q = It = 2.00 \times (30.0 \times 60) = 3600 \text{ C}, \qquad n(e^-) = \frac{3600}{96\,500} = 0.03731 \text{ mol}.$$

Since 1 mol e^- deposits 1 mol Ag:

$$\text{mass} = 0.03731 \times 108 = \mathbf{4.03\ g}.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Điện phân: cation di chuyển đến **cathode** (điện cực âm, bị khử); anion di chuyển đến **anode** (điện cực dương, bị oxi hoá). Định luật Faraday: $Q = It$, số mol electron $n(e^-) = Q/F$ với $F = 96\,500$ C mol^{-1}; từ đó dùng bán phản ứng để tính khối lượng/thể tích sản phẩm.

6.9 Electrolysis of aqueous and molten solutions

When an **aqueous** solution is electrolysed using inert electrodes, water itself can be discharged instead of the dissolved ions, since H_2O molecules are always present. Which species is actually discharged is decided by **discharge preference**:

- **At the cathode:** the *less reactive* species is discharged preferentially. If the metal is more reactive than hydrogen (any metal above hydrogen in the electrochemical series, e.g. Na^+, Mg^{2+}, Al^{3+}), H_2 is produced instead of the metal, from $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$. Only if the metal is *less* reactive than hydrogen (e.g. Cu^{2+}, Ag^+) is the metal itself deposited.
- **At the anode:** a halide ion present at reasonably high (e.g. molar) concentration is discharged preferentially over water, $2X^- \rightarrow X_2 + 2e^-$. If the halide is very dilute, or absent (e.g. a sulfate or nitrate solution), water is instead discharged: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$.

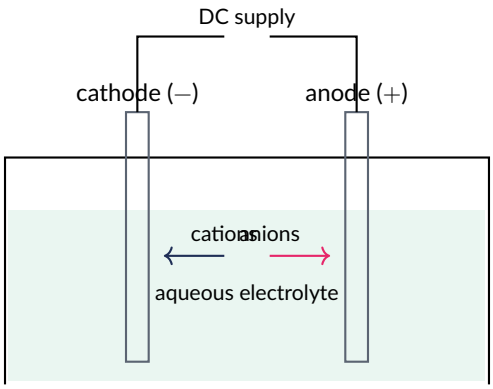


Figure 6.2 — General electrolytic cell: cations migrate to the cathode, anions to the anode.

Ví dụ mẫu · Worked example — electrolysis of aqueous sodium chloride: the chlor-alkali process

State and explain the products formed at each electrode when **concentrated** aqueous sodium chloride (brine) is electrolysed using inert electrodes, and contrast this with electrolysing (a) very **dilute** aqueous NaCl, and (b) **molten** NaCl.

Concentrated aqueous NaCl **(the industrial chlor-alkali process):** Na^+ is far more reactive than hydrogen, so at the cathode water is discharged instead: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$. Chlo-

ride ions are present at high concentration, so at the anode chloride (not water) is discharged: $2Cl^- \rightarrow Cl_2 + 2e^-$. Three valuable products result: $H_2(g)$ and $Cl_2(g)$, and $NaOH(aq)$ left behind in solution (since Na^+ and the newly-formed OH^- remain in solution).

(a) Very dilute aqueous NaCl: the cathode product is unchanged (H_2), but with Cl^- now too dilute to be discharged preferentially, the anode instead discharges water: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$, giving O_2 rather than Cl_2.

(b) Molten NaCl **(no water present):** there is no water to compete, so the ions of the salt itself are discharged directly — cathode: $Na^+ + e^- \rightarrow Na$; anode: $2Cl^- \rightarrow Cl_2 + 2e^-$; overall $2NaCl(l) \rightarrow 2Na(l) + Cl_2(g)$. This is how sodium metal is manufactured industrially (the Downs process).

(!) Lỗi thường gặp: A very common error is to assume the electrolysis of *any* aqueous halide solution always gives the halogen at the anode. This is only true when the halide ion is present at a reasonably high concentration; in dilute solution, water is discharged preferentially at the anode, giving O_2 instead. Similarly, at the cathode, any metal *more* reactive than hydrogen is never deposited from aqueous solution — H_2 is produced instead, regardless of how concentrated the metal ion is.

VN **GIẢI THÍCH TIẾNG VIỆT**

Điện phân dung dịch nước: tại **cathode**, ion kim loại hoạt động mạnh hơn hydro (như Na^+) **không** bị khử — nước bị khử thay, tạo H_2; chỉ kim loại kém hoạt động hơn hydro mới được giải phóng. Tại **anode**, halide nồng độ cao ưu tiên bị oxi hoá tạo halogen; nếu loãng, nước bị oxi hoá tạo O_2 thay thế. Điện phân NaCl nóng chảy (không có nước) cho trực tiếp Na và Cl_2 (quy trình Downs).

Ví dụ mẫu · Worked example — volume of gas from electrolysis of dilute sulfuric acid

A current of 0.500 A is passed through dilute sulfuric acid using inert (platinum) electrodes for 1000 s. Calculate the volume of hydrogen gas produced at the cathode, measured at r.t.p. (molar gas volume $= 24.0$ dm^{3}mol^{-1}).

Cathode: $2H^+ + 2e^- \rightarrow H_2$.

$$Q = It = 0.500 \times 1000 = 500\ \text{C}, \qquad n(e^-) = \frac{500}{96\,500} = 5.181 \times 10^{-3}\ \text{mol}.$$

$$n(H_2) = \frac{5.181 \times 10^{-3}}{2} = 2.591 \times 10^{-3}\ \text{mol}.$$

$$V(H_2) = 2.591 \times 10^{-3} \times 24.0 = 0.0622\ \text{dm}^3 = \mathbf{62.2\ cm^3}.$$

6.9.1 Industrial extraction of aluminium: the Hall–Héroult process

Aluminium is too reactive to be extracted by reduction with carbon (Section on discharge preference above shows why it cannot be deposited from aqueous solution either), so it is extracted by **electrolysis of molten aluminium oxide**. Since pure Al_2O_3 melts only above $2000\,^\circ$C — impractically expensive to maintain — the oxide is dissolved in molten **cryolite** (Na_3AlF_6), which lowers the operating temperature to around $950\,^\circ$C.

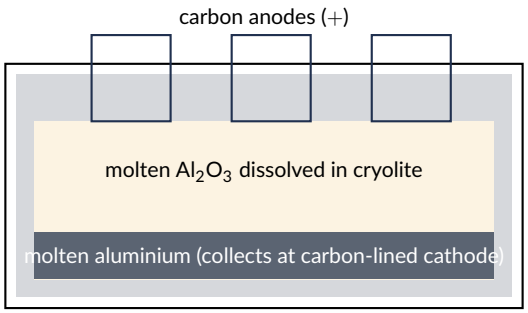


Figure 6.3 — Simplified Hall–Héroult cell: carbon anodes dip into molten cryolite/alumina; the carbon lining of the steel shell acts as the cathode, and molten aluminium collects at the bottom.

At the (carbon-lined) cathode, Al^{3+} ions are reduced: $Al^{3+} + 3e^- \rightarrow Al(l)$, and molten aluminium (denser than the molten cryolite mixture) collects at the bottom and is periodically tapped off. At the carbon anodes, oxide ions are oxidised: $2O^{2-} \rightarrow O_2 + 4e^-$; the hot oxygen produced reacts with the carbon anodes themselves ($C + O_2 \rightarrow CO_2$), so the anodes are gradually consumed and must be replaced regularly. The overall simplified cell reaction is

$$2Al_2O_3 \rightarrow 4Al + 3O_2.$$

Ví dụ mẫu · Worked example — mass of aluminium produced

A Hall–Héroult cell operates at a current of $200\,000$ A for 24 hours. Calculate the mass of aluminium produced ($A_r(Al) = 27.0$).

$$Q = It = 200\,000 \times (24 \times 3600) = 200\,000 \times 86\,400 = 1.728 \times 10^{10} \text{ C}.$$

$$n(e^-) = \frac{1.728 \times 10^{10}}{96\,500} = 1.7907 \times 10^5 \text{ mol}.$$

Since $Al^{3+} + 3e^- \rightarrow Al$, 3 mol e^- are needed per mole of Al:

$$n(Al) = \frac{1.7907 \times 10^5}{3} = 5.969 \times 10^4 \text{ mol}.$$

$$\text{mass} = 5.969 \times 10^4 \times 27.0 = 1.611 \times 10^6 \text{ g} \approx \textbf{1610 kg}\ (1.61 \text{ tonnes}).$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Nhôm được sản xuất bằng điện phân Al_2O_3 nóng chảy hoà tan trong **cryolite** (hạ nhiệt độ nóng chảy từ $> 2000\,^\circ$C xuống $\approx 950\,^\circ$C) — quy trình **Hall–Héroult**. Cathode (than chì lót đáy bể): $Al^{3+} + 3e^- \rightarrow Al$; anode (than chì): $2O^{2-} \rightarrow O_2 + 4e^-$, oxi sinh ra ăn mòn dần điện cực than nên phải thay thế định kỳ.

6.10 Practice

Bài tập luyện tập

What is the oxidation number of manganese in MnO_4^-?

(A) $+2$
(B) $+4$
(C) $+6$
(D) $+7$

Lời giải chi tiết

Oxygen is -2 (4 oxygens $= -8$); the ion charge is -1, so Mn $+ (-8) = -1 \Rightarrow$ Mn $= +7$. **(D).**

Bài tập luyện tập

Construct the half-equation for the reduction of nitrate ions, NO_3^-, to nitrogen monoxide, NO, in acidic solution.

Lời giải chi tiết

Balance N (already 1:1), then O with H_2O, then H with H^+, then charge with e^-:

$$NO_3^- \rightarrow NO + 2H_2O \;\Rightarrow\; NO_3^- + 4H^+ \rightarrow NO + 2H_2O.$$

Charge: left $= -1 + 4 = +3$, right $= 0$; add $3e^-$:

$$\boxed{NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O}$$

Check: charge $-1 + 4 - 3 = 0 = 0$ ✓; atoms N:1=1, O:3=1+2=3, H:4=4 ✓.

Bài tập luyện tập

Combine the half-equations $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ and $Fe^{2+} \rightarrow Fe^{3+} + e^-$ to give the overall ionic equation for the reaction between acidified dichromate and iron(II) ions.

Lời giải chi tiết

Multiply the iron half-equation by 6 (to match the 6 electrons gained by dichromate), then add and cancel the $6e^-$:

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}.$$

Check: charge — left $= -2 + 14 + 12 = 24$, right $= 2(3) + 0 + 6(3) = 6 + 18 = 24$ ✓; atoms — Cr:2, O:7 (in $7H_2O$), H:14, Fe:6, all balanced ✓.

Bài tập luyện tập

In the equation $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$, which species is the oxidising agent?

(A) Fe^{3+} **(C)** Fe^{2+}

(B) I^- **(D)** I_2

Lời giải chi tiết

Fe^{3+} is reduced to Fe^{2+} (gains an electron), so it is the species that oxidises iodide — the **oxidising agent**. **(A)**.

Bài tập luyện tập

Using $E^\circ(Ag^+/Ag) = +0.80$ V and $E^\circ(Mg^{2+}/Mg) = -2.37$ V, calculate E°_{cell} for a cell combining these two half-cells.

Lời giải chi tiết

Silver has the more positive E° (cathode); magnesium is the anode:

$$E^\circ_{cell} = 0.80 - (-2.37) = \textbf{+3.17 V}.$$

Bài tập luyện tập

Using $E^\circ(\text{Pb}^{2+}/\text{Pb}) = -0.13$ V and $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76$ V, will zinc metal displace lead from lead(II) ions in solution?

(A) Yes, $E^\circ_{cell} = +0.63$ V, feasible

(B) No, $E^\circ_{cell} = -0.63$ V, not feasible

(C) Yes, but only above 373 K

(D) No reaction is possible between two solid metals

Lời giải chi tiết

$E^\circ_{cell} = E^\circ(\text{Pb}^{2+}/\text{Pb}) - E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.13 - (-0.76) = +0.63 \text{ V} > 0$: feasible. **(A)**.

Bài tập luyện tập

Write full cell notation for a cell combining Fe^{2+}/Fe ($E^\circ = -0.44$ V) and Ag^{+}/Ag ($E^\circ = +0.80$ V), and state E°_{cell}.

Lời giải chi tiết

Iron is the anode (more negative E°); silver is the cathode:

$$\text{Fe(s)}|\text{Fe}^{2+}\text{(aq)}\|\text{Ag}^{+}\text{(aq)}|\text{Ag(s)}.$$

$$E^\circ_{cell} = 0.80 - (-0.44) = \textbf{+1.24 V}.$$

Bài tập luyện tập

What is the role of the salt bridge in an electrochemical cell?

(A) To provide extra electrons to the circuit

(B) To complete the circuit by allowing ion flow, maintaining electrical neutrality in each half-cell

(C) To increase the voltage of the cell

(D) To act as a catalyst, speeding up the electrode reactions

Lời giải chi tiết

As electrons flow through the external wire, the salt bridge allows ions to migrate between the half-cells so that neither solution builds up an unbalanced charge — it completes the circuit without directly reacting with either solution. **(B)**.

Bài luyện nâng cao (A2)

Calculate E for the Cu^{2+}/Cu half-cell ($E^\circ = +0.34$ V, $n = 2$) when $[\text{Cu}^{2+}] = 0.0100$ mol dm^{-3} (compared with the standard 1.00 mol dm^{-3}).

Lời giải chi tiết

$$E = E^\circ - \frac{0.0592}{2}\log\frac{1}{[\text{Cu}^{2+}]} = 0.34 - 0.0296\log\frac{1}{0.0100} = 0.34 - 0.0296(2) = 0.34 - 0.0592.$$

$$E \approx \textbf{+0.28 V}.$$

Bài luyện nâng cao (A2)

For the Daniell cell ($E^\circ_{cell} = +1.10$ V, $n = 2$), calculate E_{cell} if instead $[\text{Cu}^{2+}]$ is reduced to 0.01 mol dm^{-3} while $[\text{Zn}^{2+}]$ remains at 1.0 mol dm^{-3}.

Lời giải chi tiết

$$E_{cell} = E^\circ_{cell} - \frac{0.0592}{2}\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 1.10 - 0.0296\log\frac{1.0}{0.01} = 1.10 - 0.0296(2) = 1.10 - 0.0592.$$

$$E_{cell} \approx \textbf{+1.04 V}.$$

Diluting the reactant-side ion, Cu^{2+}, this time makes the cell potential **smaller** than the standard value — the opposite effect to diluting Zn^{2+}.

Bài tập luyện tập

A current of 2.00 A is passed through molten lead(II) bromide for a time such that 9650 C of charge is passed. Identify the products at each electrode and calculate the mass of lead deposited ($A_r(\text{Pb}) = 207$).

Lời giải chi tiết

Cathode: $\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$; anode: $2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$.

$$n(e^-) = \frac{9650}{96\,500} = 0.100 \text{ mol}, \qquad n(\text{Pb}) = \frac{0.100}{2} = 0.0500 \text{ mol}.$$

$$\text{mass}(\text{Pb}) = 0.0500 \times 207 = \textbf{10.35 g}.$$

Bài tập luyện tập

What is the product at the **cathode** when electrolysing aqueous sodium chloride, regardless of concentration?

(A) Sodium metal
(B) Hydrogen gas
(C) Chlorine gas
(D) Oxygen gas

Lời giải chi tiết

Sodium is far more reactive than hydrogen, so it is never discharged from aqueous solution at the cathode; water is reduced instead, giving H_2. **(B)**.

Bài tập luyện tập

Aqueous copper(II) sulfate is electrolysed using inert (platinum) electrodes. Identify the products at each electrode and write the half-equations.

Lời giải chi tiết

Cu^{2+} is less reactive than hydrogen, so it *is* discharged at the cathode: $Cu^{2+} + 2e^- \rightarrow Cu$. SO_4^{2-} is not discharged in preference to water at the anode, so water is oxidised instead: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$. Products: copper deposited at the cathode, oxygen gas at the anode (and the solution becomes more acidic as H^+ accumulates).

Bài tập luyện tập

Using the same charge as the lead bromide question above (9650 C) passed through aqueous copper(II) sulfate with inert electrodes, calculate the volume of oxygen gas produced at the anode at r.t.p. (molar volume $= 24.0$ dm^{3}mol^{-1}).

Lời giải chi tiết

Anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$.

$$n(e^-) = \frac{9650}{96\,500} = 0.100 \text{ mol}, \qquad n(O_2) = \frac{0.100}{4} = 0.0250 \text{ mol}.$$

$$V(O_2) = 0.0250 \times 24.0 = \textbf{0.600 dm}^3 \ (600 \text{ cm}^3).$$

Bài tập luyện tập

In electrolysis, the **cathode** is the electrode at which:

(A) Oxidation occurs, and it is the positive electrode

(B) Reduction occurs, and it is the negative electrode

(C) Oxidation occurs, and it is the negative electrode

(D) Reduction occurs, and it is the positive electrode

Lời giải chi tiết

In electrolysis, the cathode is connected to the negative terminal of the external supply and is where cations are reduced (gain electrons). **(B)**.

Bài tập luyện tập

A Hall–Héroult cell produces aluminium at a current of $50\,000$ A. Calculate the time (in minutes) required to produce 5.40 kg of aluminium ($A_r(Al) = 27.0$).

Lời giải chi tiết

$$n(Al) = \frac{5400}{27.0} = 200.0 \text{ mol}, \qquad n(e^-) = 3 \times 200.0 = 600 \text{ mol} \ (Al^{3+} + 3e^- \rightarrow Al).$$

$$Q = n(e^-) \times F = 600 \times 96\,500 = 5.79 \times 10^7 \text{ C}.$$

$$t = \frac{Q}{I} = \frac{5.79 \times 10^7}{50\,000} = 1158 \text{ s} = \textbf{19.3 minutes}.$$

Bài tập luyện tập

Which type of cell can be recharged by passing a current through it from an external supply, reversing the cell reaction?

(A) Primary cell
(B) Secondary (rechargeable) cell
(C) Fuel cell
(D) None of these can be recharged

Lời giải chi tiết

A secondary cell's reaction is reversible by supplying an external current (e.g. lead–acid or lithium-ion batteries); a primary cell's reaction cannot be reversed, and a fuel cell requires continuous external fuel supply rather than recharging in this sense. **(B)**.

Bài tập luyện tập

Write the anode and cathode half-equations, and the overall equation, for a hydrogen–oxygen fuel cell operating in **acidic** conditions.

Lời giải chi tiết

Anode (oxidation): $H_2(g) \rightarrow 2H^+(aq) + 2e^-$.
Cathode (reduction): $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$.
Multiplying the anode equation by 2 to balance electrons (4 total) and adding:

$$\boxed{2H_2(g) + O_2(g) \rightarrow 2H_2O(l)}$$

the same overall equation as in alkaline conditions.

Bài tập luyện tập

State two advantages of hydrogen–oxygen fuel cells over internal combustion engines burning hydrocarbon fuel.

Lời giải chi tiết

(1) The only product is water — no CO_2 is released at the point of use, unlike burning a hydrocarbon fuel. (2) Chemical energy is converted **directly** into electrical energy by the electrochemical reaction, rather than via an intermediate heat/mechanical-work step, so fuel cells can achieve a higher overall energy-conversion efficiency than combustion engines.

Bài tập luyện tập

When aqueous sodium chloride is electrolysed, which ion is discharged at the cathode in preference to Na^+?

(A) Cl^-
(B) OH^-
(C) Water molecules (H_2O, giving H_2)
(D) No ion is discharged in preference; Na metal always forms

Lời giải chi tiết

Because Na^+ is far more reactive (higher up the electrochemical series) than hydrogen, water is reduced instead of Na^+ at the cathode, producing H_2 and leaving OH^- in solution. **(C).**

Bài tập luyện tập

Compare and explain the products formed at each electrode when (a) molten magnesium chloride and (b) aqueous magnesium chloride are electrolysed using inert electrodes.

Lời giải chi tiết

(a) Molten $MgCl_2$ (no water present): cathode $Mg^{2+} + 2e^- \rightarrow Mg$; anode $2Cl^- \rightarrow Cl_2 + 2e^-$; overall $MgCl_2(l) \rightarrow Mg(l) + Cl_2(g)$.
(b) Aqueous $MgCl_2$: Mg^{2+} is more reactive than hydrogen, so at the cathode water is reduced instead: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (no magnesium metal is formed). Chloride is present at reasonably high concentration, so the anode still discharges Cl^-: $2Cl^- \rightarrow Cl_2 + 2e^-$ (unchanged from the molten case).

Bài tập luyện tập

Using $E^\circ(Cr_2O_7^{2-}/Cr^{3+}) = +1.33$ V and $E^\circ(Sn^{4+}/Sn^{2+}) = +0.15$ V, write the overall balanced ionic equation for the reaction between acidified dichromate ions and tin(II) ions, and calculate E°_{cell} to show the reaction is feasible.

Lời giải chi tiết

Half-equations: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ (6 electrons gained) and $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$ (2 electrons lost, so multiply by 3):

$$Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 3Sn^{4+}.$$

Check: charge — left $= -2 + 14 + 3(2) = 18$, right $= 2(3) + 0 + 3(4) = 6 + 12 = 18$ ✓; atoms — Cr:2, O:7, H:14, Sn:3, all balanced ✓.

$$E^\circ_{cell} = E^\circ(Cr_2O_7^{2-}/Cr^{3+}) - E^\circ(Sn^{4+}/Sn^{2+}) = 1.33 - 0.15 = \textbf{+1.18 V} > 0 \text{ (feasible)}.$$

Bài tập luyện tập

As the temperature of a half-cell reaction is increased, what happens to the *rate* at which a thermodynamically feasible ($E^\circ_{cell} > 0$) redox reaction proceeds, and does this change the value of E°_{cell} itself?

Lời giải chi tiết

Increasing temperature increases the *rate* of the reaction (more particles have energy $\geq E_a$, as in Chapter 5's discussion of reaction rates), but E° values are defined at a fixed standard temperature (298 K); changing the actual operating temperature does not change whether the reaction is thermodynamically feasible as judged by the standard E°_{cell} value, but it can noticeably change the rate at which the (already feasible) reaction reaches equilibrium.

Bài tập luyện tập

A student calculates E°_{cell} for a reaction as -0.20 V and concludes the reverse reaction is feasible instead. Explain whether this reasoning is correct.

Lời giải chi tiết

The reasoning is correct: if a proposed reaction has $E^\circ_{cell} < 0$, it is not feasible as written, but the **reverse** reaction has $E^\circ_{cell} = +0.20$ V > 0 and *is* thermodynamically feasible. Swapping the direction of a redox reaction reverses the sign of E°_{cell} (cathode and anode roles swap).

Bài tập luyện tập

Using Table 6.1, predict whether iron(III) ions can oxidise iodide ions to iodine, and calculate E°_{cell}.

Lời giải chi tiết

Proposed reaction: $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$.

$$E^\circ_{cell} = E^\circ(Fe^{3+}/Fe^{2+}) - E^\circ(I_2/I^-) = 0.77 - 0.54 = \textbf{+0.23 V} > 0 \text{ (feasible)}.$$

Chemical Equilibria

Mục tiêu Unit: Cân bằng động và nguyên lý Le Chatelier; tính K_c và K_p từ bảng ICE (kể cả trường hợp phải giải phương trình bậc hai); mối liên hệ $K_p = K_c(RT)^{\Delta n}$; phân số mol và áp suất riêng phần; quá trình Haber như một ví dụ công nghiệp về sự thoả hiệp giữa hiệu suất và tốc độ; pH của axit/bazơ mạnh và yếu, dung dịch đệm, và tích số tan K_{sp} (A2).

7.1 Dynamic equilibrium and Le Chatelier's principle

A **reversible reaction** is one that can proceed in both the forward and the reverse direction, written with the symbol $\rightleftharpoons$, e.g. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$. If a reversible reaction is allowed to proceed in a **closed system** (no reactants or products can enter or leave), it eventually reaches **dynamic equilibrium**.

Dynamic equilibrium — precise definition

At dynamic equilibrium: (1) the reaction is occurring in a **closed system**; (2) the **forward and reverse reactions are still both occurring**, at the molecular level, continuously; (3) the **rate of the forward reaction equals the rate of the reverse reaction**; and consequently (4) the **macroscopic (measurable) concentrations of all species remain constant** over time, even though individual molecules are constantly being converted back and forth. Equilibrium is "dynamic", not static — it is a balance of opposing rates, not a cessation of reaction.

VN **GIẢI THÍCH TIẾNG VIỆT**

Cân bằng động cần **hệ kín** (không có chất ra vào), và **cả hai chiều phản ứng vẫn diễn ra liên tục** ở cấp độ phân tử, nhưng vì **tốc độ thuận = tốc độ nghịch**, nồng độ các chất đo được ở cấp độ vĩ mô **không đổi theo thời gian**. Đây là lý do gọi là cân bằng "động" — không phải phản ứng đã dừng, mà là hai tốc độ triệt tiêu lẫn nhau.

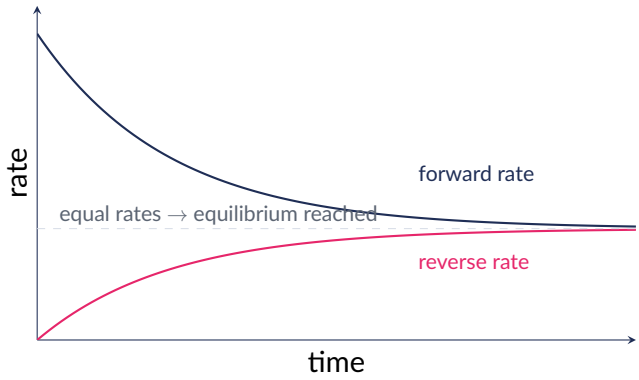


Figure 1. As a reversible reaction proceeds in a closed system, the forward rate falls (reactants are used up) while the reverse rate rises (products build up), until the two rates become equal — dynamic equilibrium.

7.1.1 Le Chatelier's principle

Le Chatelier's principle

If a system at equilibrium is subjected to a change in concentration, pressure, or temperature, the position of equilibrium shifts so as to **partially oppose** that change, until a new equilibrium is established.

VN **GIẢI THÍCH TIẾNG VIỆT**

Nguyên lý Le Chatelier: khi một hệ đang ở cân bằng bị tác động bởi sự thay đổi nồng độ, áp suất, hay nhiệt độ, vị trí cân bằng sẽ dịch chuyển theo hướng **chống lại một phần** sự thay đổi đó, cho đến khi đạt được cân bằng mới.

Change	Direction of shift (Le Chatelier)	Effect on the value of K_c / K_p
Increase [reactant]	shifts toward products, consuming some of the added reactant	unchanged (constant T)
Increase [product]	shifts toward reactants	unchanged (constant T)
Increase total pressure (gas system, unequal moles)	shifts toward the side with *fewer* gas moles	unchanged (constant T)
Decrease total pressure	shifts toward the side with *more* gas moles	unchanged (constant T)
Increase temperature	shifts toward the *endothermic* direction	changes: increases if forward reaction is endothermic, decreases if forward reaction is exothermic
Decrease temperature	shifts toward the *exothermic* direction	changes in the opposite sense to above
Add a catalyst	no shift in position; equilibrium reached *faster*	unchanged

Table 1. Summary of how changing conditions affects the position of equilibrium and the equilibrium constant.

(!) Lỗi thường gặp: A catalyst **never** shifts the position of equilibrium and **never** changes the value of K_c or K_p — it speeds up the forward and reverse reactions by *exactly the same factor*, so equilibrium is simply reached sooner, with the same final equilibrium concentrations (and hence the same % yield) as without the catalyst.

VN **GIẢI THÍCH TIẾNG VIỆT**

Chất xúc tác **không bao giờ** làm dịch chuyển vị trí cân bằng và **không bao giờ** thay đổi giá trị K_c/K_p — nó chỉ làm tăng tốc độ phản ứng thuận và nghịch theo **cùng một hệ số**, nên cân bằng đạt được nhanh hơn nhưng hiệu suất (% chuyển hoá) cuối cùng không đổi.

7.2 Calculating K_c and K_p

For a general homogeneous equilibrium $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$, the equilibrium constant in terms of concentration is

$$K_c = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$$

using *equilibrium* concentrations only (never initial concentrations). K_c depends only on temperature.

Ví dụ 1 · ICE table with equal (1:1:2) stoichiometry

1.00 mol each of $H_2(g)$ and $I_2(g)$ are placed in a sealed 1.00 dm^3 vessel at 698 K, where $K_c = 54.0$ for $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$. Calculate the equilibrium concentration of each species.

ICE table (concentrations in mol dm^{-3}, letting x = concentration of H_2 that reacts):

	H_2	I_2	HI
Initial	1.00	1.00	0
Change	$-x$	$-x$	$+2x$
Equilibrium	$1.00 - x$	$1.00 - x$	$2x$

$$K_c = \frac{(2x)^2}{(1.00-x)^2} = 54.0 \implies \frac{2x}{1.00-x} = \sqrt{54.0} = 7.348$$

$$2x = 7.348(1.00 - x) = 7.348 - 7.348x \implies 9.348x = 7.348 \implies x = 0.786.$$

Equilibrium concentrations: $[H_2] = [I_2] = 1.00 - 0.786 = 0.214$ mol dm^{-3}; $[HI] = 2(0.786) = 1.572 \approx 1.57$ mol dm^{-3}.
Check: $K_c = 1.572^2/0.214^2 = 54.0$ ✓. Because H_2 and I_2 start with equal concentrations and react in a 1:1 ratio, the square root can be taken directly — this shortcut is *only* valid when the two reactants start equal.

VN **GIẢI THÍCH TIẾNG VIỆT**

Với hệ số tỉ lượng 1:1:2 và nồng độ đầu của hai chất phản ứng bằng nhau, ta có thể khai căn hai vế trực tiếp (như trên) — đây là một lối tắt chỉ áp dụng được khi hai chất phản ứng có nồng độ đầu bằng nhau. Nếu không, phải giải phương trình bậc hai đầy đủ như ví dụ tiếp theo.

Ví dụ 2 · ICE table requiring the quadratic formula — unequal (1:1:1) stoichiometry from pure PCl_5

0.500 mol dm^{-3} of pure $PCl_5(g)$ is sealed in a vessel at 500 K, where $K_c = 0.0410$ mol dm^{-3} for $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. Calculate the equilibrium concentration of each species.

	PCl_5	PCl_3	Cl_2
Initial	0.500	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.500 - x$	x	x

$$K_c = \frac{x^2}{0.500 - x} = 0.0410 \implies x^2 = 0.0410(0.500 - x) = 0.0205 - 0.0410x$$

$$x^2 + 0.0410x - 0.0205 = 0.$$

This does *not* simplify by square-rooting (unequal products), so the quadratic formula is required:

$$x = \frac{-0.0410 + \sqrt{0.0410^2 + 4(0.0205)}}{2} = \frac{-0.0410 + \sqrt{0.08368}}{2} = \frac{-0.0410 + 0.2893}{2} = 0.124 \text{ mol dm}^{-3}.$$

(The negative root is rejected as physically meaningless.) **Equilibrium concentrations:** $[PCl_5] = 0.500 - 0.124 = 0.376$ mol dm^{-3}; $[PCl_3] = [Cl_2] = 0.124$ mol dm^{-3}.
Check: $K_c = 0.124^2/0.376 = 0.0409 \approx 0.0410$ ✓.

(!) Lỗi thường gặp: A common error is to assume x is negligible compared with the initial concentration (a valid shortcut when K_c is very small). Here $x = 0.124$ is about 25% of 0.500 — far too large to approximate $0.500 - x \approx 0.500$. Always check the size of x relative to the initial concentration before deciding whether an approximation is valid; when in doubt, solve the full quadratic.

VN **GIẢI THÍCH TIẾNG VIỆT**
Với phản ứng $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ bắt đầu từ PCl_5 tinh khiết, hệ số các chất là 1:1:1 nhưng số mol khí tăng ($\Delta n = +1$), nên không thể khai căn đơn giản — phải giải phương trình bậc hai đầy đủ. Luôn kiểm tra xem x có thực sự nhỏ so với nồng độ đầu hay không trước khi dùng phép gần đúng.

7.2.1 K_p, mole fraction and partial pressure

For gas-phase equilibria, it is often more convenient to work with **partial pressures** instead of concentrations, giving the equilibrium constant K_p.

The **mole fraction** of gas i is $x_i = \dfrac{n_i}{n_{\text{total}}}$, and its **partial pressure** is

$$p_i = x_i \, P_{\text{total}}.$$

For $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$,

$$K_p = \frac{p_C^c \, p_D^d}{p_A^a \, p_B^b}.$$

VN **GIẢI THÍCH TIẾNG VIỆT**
Phân số mol x_i = số mol khí i chia cho tổng số mol khí; áp suất riêng phần $p_i = x_i \times P_{\text{tổng}}$. K_p được tính từ áp suất riêng phần tại cân bằng, hoàn toàn tương tự cách K_c được tính từ nồng độ.

Ví dụ 3 · Partial pressures from mole fractions, then K_p — the Haber process

At equilibrium, a gas mixture in the Haber process contains 1.00 mol N_2, 3.00 mol H_2 and 4.00 mol NH_3, at a total pressure of 200 atm. Calculate the partial pressure of each gas and hence K_p for $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$.

Total moles $= 1.00 + 3.00 + 4.00 = 8.00$ mol.

$$x(\mathrm{N_2}) = \tfrac{1.00}{8.00} = 0.125, \quad x(\mathrm{H_2}) = \tfrac{3.00}{8.00} = 0.375, \quad x(\mathrm{NH_3}) = \tfrac{4.00}{8.00} = 0.500.$$

$$p(\mathrm{N_2}) = 0.125\times200 = 25.0\,\text{atm}, \quad p(\mathrm{H_2}) = 0.375\times200 = 75.0\,\text{atm}, \quad p(\mathrm{NH_3}) = 0.500\times200 = 100\,\text{atm}.$$

$$K_p = \frac{p(\mathrm{NH_3})^2}{p(\mathrm{N_2})\,p(\mathrm{H_2})^3} = \frac{100^2}{25.0\times75.0^3} = \frac{10\,000}{25.0\times421\,875} = 9.48\times10^{-4}\ \text{atm}^{-2}.$$

7.2.2 Relating K_p and K_c

$$K_p = K_c(RT)^{\Delta n}, \qquad \Delta n = (\text{moles of gaseous products}) - (\text{moles of gaseous reactants}).$$

Use $R = 0.0821$ dm^3 atm K^{-1} mol^{-1} when K_p is required in atmospheres. If $\Delta n = 0$, $K_p = K_c$ (both dimensionless / equal numerically).

VN **GIẢI THÍCH TIẾNG VIỆT**

Công thức $K_p = K_c(RT)^{\Delta n}$ chuyển đổi giữa K_c (theo nồng độ) và K_p (theo áp suất riêng phần), với Δn là hiệu số mol khí sản phẩm trừ mol khí chất phản ứng. Nếu $\Delta n = 0$ (số mol khí hai vế bằng nhau), $K_p = K_c$ về mặt số học.

Ví dụ 4 · Converting K_c to K_p

For $\mathrm{PCl_5(g)} \rightleftharpoons \mathrm{PCl_3(g)} + \mathrm{Cl_2(g)}$ at 500 K, $K_c = 0.0410$ mol dm^{-3} (Ví dụ 2). Calculate K_p.

$\Delta n = (1+1) - 1 = +1$.

$$RT = 0.0821 \times 500 = 41.1\ \text{dm}^3\ \text{atm mol}^{-1}.$$

$$K_p = K_c(RT)^1 = 0.0410 \times 41.1 = 1.68\ \text{atm}.$$

Ví dụ 5 · Calculating K_p directly from equilibrium partial pressures

At a certain temperature, the equilibrium partial pressures for $\mathrm{2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)}$ are $p(\mathrm{SO_2}) = 0.200$ atm, $p(\mathrm{O_2}) = 1.20$ atm, $p(\mathrm{SO_3}) = 1.00$ atm. Calculate K_p, including units.

$$K_p = \frac{p(\mathrm{SO_3})^2}{p(\mathrm{SO_2})^2\,p(\mathrm{O_2})} = \frac{1.00^2}{0.200^2\times1.20} = \frac{1.00}{0.0480} = 20.8\ \text{atm}^{-1}.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Ví dụ trên minh hoạ trực tiếp cách tính K_p khi đã biết áp suất riêng phần tại cân bằng — hoàn toàn giống cách tính K_c từ nồng độ, chỉ khác đơn vị (atm thay vì mol dm^{-3}). Luôn kiểm tra đơn vị của K_p/K_c dựa vào Δn của phản ứng.

7.3 The Haber process — an industrial compromise equilibrium

The synthesis of ammonia, $\mathrm{N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)}$, $\Delta H = -92$ kJ mol^{-1} (exothermic), is the classic real-world illustration of Le Chatelier's principle applied to industrial design. By Le Chatelier's

principle alone, the *highest possible* % yield of NH_3 would come from **low temperature** (favours the exothermic forward direction) and **very high pressure** (favours the side with fewer gas moles, $\Delta n = -2$). In practice, the conditions used are a deliberate **compromise**.

Compromise conditions in the Haber process

- **Temperature $\approx 450^\circ$C (moderate, not low):** a low temperature would give a higher equilibrium % yield, but the *rate* of reaching that equilibrium would be uneconomically slow. 450°C sacrifices some yield in exchange for a much faster, commercially viable rate.
- **Pressure ≈ 200 atm (high, not extremely high):** higher pressure would push the % yield still higher (fewer gas moles favoured), but building and maintaining vessels and pipework for much higher pressures is disproportionately expensive and hazardous. 200 atm balances improved yield against engineering and running costs.
- **Iron catalyst (with K_2O/Al_2O_3 promoters):** the catalyst does *not* shift the equilibrium position and does *not* change K_p or the % yield at all; it simply provides a lower-activation-energy pathway so that equilibrium is reached fast enough at the moderate 450°C chosen above, without needing an even higher (yield-reducing) temperature.

Unreacted N_2 and H_2 are recycled (rather than discarded) to improve the overall efficiency of the process, since single-pass % conversion is modest under these compromise conditions.

Condition	Value used	Effect of pushing it further toward "ideal" yield	Why a compromise is chosen instead
Temperature	$\sim 450^\circ$C	lower $T \rightarrow$ higher % yield (exothermic forward reaction)	lower $T \rightarrow$ far too slow a rate to be economical
Pressure	~ 200 atm	higher $P \rightarrow$ higher % yield (fewer gas moles favoured)	higher $P \rightarrow$ very costly, thick-walled reinforced vessels; safety risk
Catalyst	Fe (promoted)	— (does not affect % yield or K_p at all)	used only to speed up attainment of equilibrium at the moderate T chosen

Table 2. The Haber process: compromise conditions balancing equilibrium yield against economically viable rate.

VN **GIẢI THÍCH TIẾNG VIỆT**

Quá trình Haber là ví dụ kinh điển về sự **thoả hiệp** giữa hiệu suất cân bằng và tốc độ phản ứng. Nhiệt độ thấp cho hiệu suất cao hơn (phản ứng thuận toả nhiệt) nhưng tốc độ quá chậm; áp suất cao cho hiệu suất cao hơn (giảm số mol khí) nhưng chi phí thiết bị quá lớn. Vì vậy chọn 450°C và 200 atm làm điểm cân bằng kinh tế. Chất xúc tác Fe **không** làm thay đổi hiệu suất hay K_p — chỉ giúp đạt cân bằng nhanh hơn ở nhiệt độ vừa phải đã chọn.

7.4 Acid–base equilibria and solubility

7.4.1 Acids, bases, pH and K_w (A2)

Brønsted–Lowry definitions

A **Brønsted–Lowry acid** is a proton (H^+) donor; a **Brønsted–Lowry base** is a proton acceptor. A **strong** acid/base dissociates (ionises) *completely* in water; a **weak** acid/base dissociates only *partially*, establishing an equilibrium.

$$K_w = [H^+][OH^-] = 1.00 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6} \text{ at } 298\ \text{K}, \qquad \text{pH} = -\log_{10}[H^+].$$

VN GIẢI THÍCH TIẾNG VIỆT

Axit Brønsted–Lowry cho proton, bazơ Brønsted–Lowry nhận proton. Axit/bazơ **mạnh** phân li **hoàn toàn**; axit/bazơ **yếu** chỉ phân li **một phần**, tạo thành cân bằng. $K_w = [\text{H}^+][\text{OH}^-] = 1.00 \times 10^{-14}$ ở 298 K là hằng số dùng để chuyển đổi giữa nồng độ H^+ và OH^-.

Ví dụ 6 · pH of a strong acid

Calculate the pH of 0.100 mol dm^{-3} HCl(aq).

HCl is a strong acid — complete dissociation: $\text{HCl(aq)} \rightarrow \text{H}^+\text{(aq)} + \text{Cl}^-\text{(aq)}$, so $[\text{H}^+] = 0.100$ mol dm^{-3}.

$$\text{pH} = -\log_{10}(0.100) = \mathbf{1.00}.$$

Ví dụ 7 · pH of a weak acid

$K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$ mol dm^{-3}. Calculate the pH of 0.0500 mol dm^{-3} $\text{CH}_3\text{COOH(aq)}$.

CH_3COOH dissociates only slightly, so $[\text{CH}_3\text{COOH}]_{\text{eqm}} \approx 0.0500$ mol dm^{-3} and $[\text{H}^+] \approx [\text{CH}_3\text{COO}^-]$:

$$K_a = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]} \implies [\text{H}^+] = \sqrt{K_a \times C} = \sqrt{1.8 \times 10^{-5} \times 0.0500} = \sqrt{9.0 \times 10^{-7}} = 9.49 \times 10^{-4} \text{ mol dm}^{-3}.$$

$$\text{pH} = -\log_{10}(9.49 \times 10^{-4}) = \mathbf{3.02}.$$

Ví dụ 8 · pH of a strong base via pOH

Calculate the pH of 0.0200 mol dm^{-3} NaOH(aq).

NaOH is a strong base — complete dissociation, so $[\text{OH}^-] = 0.0200$ mol dm^{-3}.

$$\text{pOH} = -\log_{10}(0.0200) = 1.70.$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.70 = \mathbf{12.30}.$$

VN GIẢI THÍCH TIẾNG VIỆT

Với bazơ mạnh, tính $[\text{OH}^-]$ trực tiếp (phân li hoàn toàn), suy ra pOH, rồi dùng $\text{pH} + \text{pOH} = 14.00$ (ở 298 K) để tìm pH — không cần qua K_w tường minh vì đã biết quan hệ này.

7.4.2 Titration curves and choice of indicator (A2)

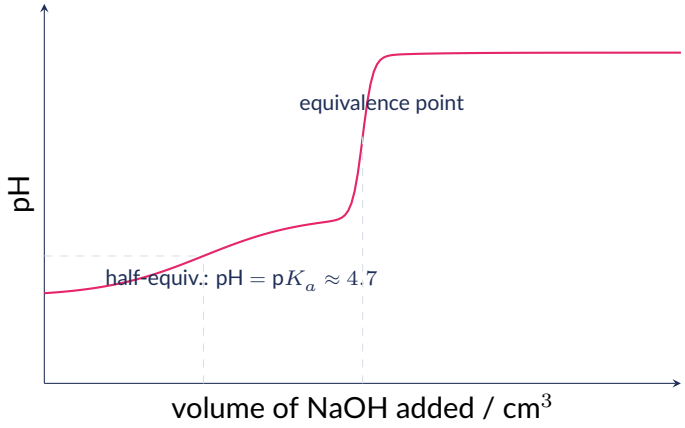


Figure 2. Titration curve for a weak acid (CH_3COOH) titrated with a strong base (NaOH): a shallow buffering region (pH $=$ pK_a at half-equivalence volume) leads into a steep rise through the equivalence point, at which pH > 7 (basic) because the salt formed hydrolyses.

Choosing an indicator: the four classic titration shapes

An indicator is suitable *only if* its colour-change range falls within the near-vertical (steep) portion of the titration curve, so that a single drop of titrant produces the colour change essentially at the true equivalence point. Methyl orange changes colour over pH 3.1–4.4; phenolphthalein changes colour over pH 8.2–10.0.

Combination	Equivalence pH	Suitable indicator	Steep-region size
Strong acid + strong base	≈ 7.0	phenolphthalein *or* methyl orange	very large, sharp jump
Weak acid + strong base	> 7 (basic, ~ 8–9)	phenolphthalein	large jump, entirely on the basic side
Strong acid + weak base	< 7 (acidic, ~ 5–6)	methyl orange	large jump, entirely on the acidic side
Weak acid + weak base	≈ 7 but *no* sharp jump	neither (use a pH meter)	very shallow, gradual slope

Table 3. The four classic titration-curve shapes, typical equivalence pH, and indicator choice.

(!) Lỗi thường gặp: For a **weak acid–weak base** titration, the curve has *no* sharp vertical region at all — the pH changes only gradually near equivalence. Neither phenolphthalein nor methyl orange gives a reliable, sudden colour change here; a pH meter (or pH probe/data-logger) must be used instead to locate the equivalence point.

VN **GIẢI THÍCH TIẾNG VIỆT**

Chỉ thị phù hợp phải đổi màu **trong đoạn dốc đứng** của đường chuẩn độ. Axit mạnh + bazơ mạnh: pH tương đương ≈ 7, dùng chỉ thị nào cũng được. Axit yếu + bazơ mạnh: pH tương đương > 7, dùng phenolphtalein. Axit mạnh + bazơ yếu: pH tương đương < 7, dùng metyl da cam. Axit yếu + bazơ yếu: không có đoạn dốc rõ rệt, phải dùng máy đo pH thay vì chỉ thị màu.

7.4.3 Buffer solutions (A2)

Buffers and the Henderson–Hasselbalch equation

A **buffer solution** resists changes in pH when small amounts of acid or base are added, by containing both a weak acid and its conjugate base (e.g. CH_3COOH/CH_3COO^-) in comparable amounts.

$$\text{pH} = \text{p}K_a + \log_{10}\left(\frac{[\text{conjugate base}]}{[\text{weak acid}]}\right).$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Dung dịch đệm chứa cả axit yếu và bazơ liên hợp của nó với lượng đáng kể, giúp giữ pH gần như không đổi khi thêm một lượng nhỏ axit/bazơ. Công thức Henderson–Hasselbalch cho phép tính pH từ tỉ lệ nồng độ bazơ liên hợp trên axit yếu.

Ví dụ 9 · Calculating buffer pH

A buffer contains 0.150 mol dm^{-3} CH_3COONa and 0.100 mol dm^{-3} CH_3COOH. $K_a(CH_3COOH) = 1.8 \times 10^{-5}$, so $\text{p}K_a = -\log_{10}(1.8 \times 10^{-5}) = 4.74$. Calculate the pH.

$$\text{pH} = \text{p}K_a + \log_{10}\left(\frac{0.150}{0.100}\right) = 4.74 + \log_{10}(1.50) = 4.74 + 0.18 = \mathbf{4.92}.$$

Ví dụ 10 · Rearranging Henderson–Hasselbalch to find the required ratio and volumes

Using CH_3COOH ($\text{p}K_a = 4.74$) and CH_3COONa, a buffer of exactly pH $= 5.00$ is required. (a) Calculate the ratio $[CH_3COO^-]/[CH_3COOH]$ needed. (b) Hence calculate the volumes of 0.200 mol dm^{-3} CH_3COOH and 0.200 mol dm^{-3} CH_3COONa needed to prepare 500 cm^3 of this buffer.

(a) Rearranging Henderson–Hasselbalch:

$$\log_{10}\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right) = \text{pH} - \text{p}K_a = 5.00 - 4.74 = 0.26 \implies \frac{[CH_3COO^-]}{[CH_3COOH]} = 10^{0.26} = 1.82.$$

(b) Since both stock solutions have the same concentration (0.200 mol dm^{-3}), the required volume ratio equals the required mole (concentration) ratio: $V_{\text{salt}}/V_{\text{acid}} = 1.82$. With $V_{\text{acid}} + V_{\text{salt}} = 500$ cm^3:

$$V_{\text{acid}} = \frac{500}{1 + 1.82} = 179 \text{ cm}^3, \qquad V_{\text{salt}} = 500 - 179 = 321 \text{ cm}^3.$$

Mix 179 cm^3 of 0.200 mol dm^{-3} CH_3COOH with 321 cm^3 of 0.200 mol dm^{-3} CH_3COONa.

VN **GIẢI THÍCH TIẾNG VIỆT**

Khi cần một pH đệm cụ thể, có thể đảo ngược phương trình Henderson–Hasselbalch để tìm tỉ lệ nồng độ bazơ liên hợp/axit yếu cần thiết, rồi từ đó suy ra thể tích cần pha trộn (nếu hai dung dịch gốc có cùng nồng độ, tỉ lệ thể tích bằng đúng tỉ lệ nồng độ cần tìm).

7.4.4 Solubility product K_{sp} (A2)

Solubility product

For a sparingly soluble salt, e.g. $\mathrm{AgCl(s)} \rightleftharpoons \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)}$, the **solubility product** is

$$K_{sp} = [\mathrm{Ag^+}][\mathrm{Cl^-}]$$

(equilibrium concentrations only; the solid itself does not appear). If the **ionic product**, Q_{sp}, calculated from the actual concentrations present exceeds K_{sp}, a precipitate forms; if $Q_{sp} < K_{sp}$, no precipitate forms (the solution is unsaturated).

VN **GIẢI THÍCH TIẾNG VIỆT**

K_{sp} là tích nồng độ các ion (theo hệ số tỉ lượng) của một muối ít tan ở trạng thái bão hoà. Nếu tích ion thực tế $Q_{sp} > K_{sp}$, kết tủa sẽ hình thành; nếu $Q_{sp} < K_{sp}$, dung dịch chưa bão hoà và không có kết tủa.

Ví dụ 11 · Common-ion effect on solubility

$K_{sp}(\mathrm{AgCl}) = 1.8 \times 10^{-10}$ mol^2 dm^{-6}. Calculate the molar solubility of AgCl (a) in pure water, and (b) in 0.100 mol dm^{-3} NaCl(aq).

(a) In water, $[\mathrm{Ag^+}] = [\mathrm{Cl^-}] = s$:

$$K_{sp} = s^2 \implies s = \sqrt{1.8 \times 10^{-10}} = 1.34 \times 10^{-5} \text{ mol dm}^{-3}.$$

(b) In 0.100 mol dm^{-3} NaCl, the $\mathrm{Cl^-}$ already present (the "common ion") means $[\mathrm{Cl^-}] \approx 0.100$ mol dm^{-3} (since $s \ll 0.100$):

$$K_{sp} = s \times 0.100 \implies s = \frac{1.8 \times 10^{-10}}{0.100} = 1.8 \times 10^{-9} \text{ mol dm}^{-3}.$$

The solubility of AgCl falls by a factor of about 7400 in the presence of the common ion $\mathrm{Cl^-}$ — a direct consequence of Le Chatelier's principle applied to the solubility equilibrium.

Ví dụ 12 · Will a precipitate form? Comparing Q_{sp} with K_{sp} (accounting for dilution)

50.0 cm^3 of 0.0100 mol dm^{-3} $\mathrm{AgNO_3(aq)}$ is mixed with 50.0 cm^3 of 0.0100 mol dm^{-3} NaCl(aq). Given $K_{sp}(\mathrm{AgCl}) = 1.8 \times 10^{-10}$ mol^2 dm^{-6}, determine whether a precipitate forms.

Total volume after mixing $= 50.0 + 50.0 = 100.0$ cm^3, so *each* solute is diluted by a factor of $\frac{50.0}{100.0} = 0.500$ before any reaction:

$$[\mathrm{Ag^+}] = 0.0100 \times 0.500 = 5.00 \times 10^{-3} \text{ mol dm}^{-3}, \qquad [\mathrm{Cl^-}] = 0.0100 \times 0.500 = 5.00 \times 10^{-3} \text{ mol dm}^{-3}.$$

$$Q_{sp} = [\mathrm{Ag^+}][\mathrm{Cl^-}] = (5.00 \times 10^{-3})^2 = 2.50 \times 10^{-5}.$$

Since $Q_{sp}(2.50 \times 10^{-5}) \gg K_{sp}(1.8 \times 10^{-10})$, **a precipitate of** AgCl **forms.**

(!) Lỗi thường gặp: When two solutions are mixed, always halve (or otherwise dilute) *each* concentration according to the new total volume *before* substituting into Q_{sp} — a very common error is to use the original, undiluted concentrations directly.

VN **GIẢI THÍCH TIẾNG VIỆT**

Khi trộn hai dung dịch, luôn phải tính lại nồng độ mới (bị pha loãng theo tổng thể tích) trước khi tính Q_{sp} — lỗi thường gặp là dùng thẳng nồng độ ban đầu. So sánh Q_{sp} với K_{sp}: nếu $Q_{sp} > K_{sp}$ thì kết tủa xuất hiện.

Ôn tập nhanh

Ôn tập nhanh: (1) Cân bằng động cần hệ kín, tốc độ thuận = tốc độ nghịch, nồng độ vĩ mô không đổi. (2) Le Chatelier: nồng độ/áp suất dịch chuyển vị trí cân bằng nhưng không đổi K; chỉ nhiệt độ mới đổi K; xúc tác không đổi cả vị trí lẫn K. (3) $K_c = [\text{sp}]/[\text{cđ}]$ từ bảng ICE — cẩn thận khi hệ số không đối xứng, có thể cần phương trình bậc hai. (4) $K_p = K_c(RT)^{\Delta n}$; $p_i = x_i P_{\text{tổng}}$. (5) Haber: 450°C/200 atm/Fe là thoả hiệp giữa hiệu suất và tốc độ, xúc tác không đổi hiệu suất. (6) pH axit/bazơ mạnh: tính trực tiếp từ nồng độ; axit yếu: $[\text{H}^+] = \sqrt{K_a C}$; đệm: Henderson–Hasselbalch. (7) Bốn dạng đường chuẩn độ và cách chọn chỉ thị (dựa vào đoạn dốc đứng). (8) K_{sp}: hiệu ứng ion chung làm giảm độ tan; so Q_{sp} với K_{sp} để dự đoán kết tủa (nhớ tính lại nồng độ sau khi pha trộn/pha loãng).

Practice

Bài tập luyện tập

Which of the following, if changed, alters the numerical value of K_c for a given reaction?

(A) Concentration of a reactant
(B) Total pressure
(C) Temperature
(D) Presence of a catalyst

Lời giải chi tiết

K_c (and K_p) depend only on temperature; concentration and pressure changes shift the position of equilibrium but leave K_c unchanged, and a catalyst affects neither the position nor K_c. **(C)**.

Bài tập luyện tập

For the exothermic reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$, predict the effect of *increasing temperature* on (i) the position of equilibrium, (ii) the rate of attaining equilibrium, (iii) K_c.

Lời giải chi tiết

(i) Shifts left (backward), favouring the endothermic reverse reaction, so % yield of NH_3 decreases. (ii) Increases — both forward and reverse rates increase with temperature, so equilibrium is reached faster. (iii) K_c decreases, since the exothermic forward reaction is disfavoured at higher T.

Bài tập luyện tập

For the exothermic reaction $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$, which combination of conditions gives the *highest* % yield of SO_3 at equilibrium?

(A) High temperature, low pressure
(B) Low temperature, high pressure
(C) High temperature, high pressure
(D) Low temperature, low pressure

Lời giải chi tiết

Low temperature favours the exothermic forward reaction; high pressure favours the side with fewer gas moles (forward, 3 mol → 2 mol). **(B).**

Bài tập luyện tập

0.500 mol dm^{-3} each of $H_2(g)$ and $I_2(g)$ are sealed in a vessel at 698 K, where $K_c = 54.0$ for $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$. Calculate the equilibrium concentration of HI.

Lời giải chi tiết

Let x = concentration of H_2 reacted. $K_c = \dfrac{(2x)^2}{(0.500-x)^2} = 54.0 \Rightarrow \dfrac{2x}{0.500-x} = \sqrt{54.0} = 7.348.$

$$2x = 3.674 - 7.348x \Rightarrow 9.348x = 3.674 \Rightarrow x = 0.393.$$

$[HI] = 2(0.393) =$ **0.786** mol dm^{-3} (note: the fraction reacted, 0.786, is identical to Ví dụ 1 because the reaction ratio and starting-concentration ratio are unchanged — only the absolute scale has halved).

Bài tập luyện tập

For $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, $K_c = 0.0410$ mol dm^{-3} at 600 K. Calculate K_p at this temperature ($R = 0.0821$ dm^3 atm K^{-1} mol^{-1}).

Lời giải chi tiết

$\Delta n = (1+1) - 1 = +1.$

$RT = 0.0821 \times 600 = 49.3$ dm^3 atm mol^{-1}, $\quad K_p = K_c(RT) = 0.0410 \times 49.3 =$ **2.02** atm.

Bài tập luyện tập

A gas mixture at a total pressure of 10.0 atm contains N_2, H_2 and NH_3 in the mole ratio $20\% : 30\% : 50\%$. Calculate the partial pressure of each gas.

Lời giải chi tiết

$p(N_2) = 0.20 \times 10.0 = 2.00$ atm; $p(H_2) = 0.30 \times 10.0 = 3.00$ atm; $p(NH_3) = 0.50 \times 10.0 =$ **5.00** atm.

Bài tập luyện tập

Why is an iron catalyst used in the Haber process, given that it does not change the % yield of ammonia?

Lời giải chi tiết

A catalyst provides an alternative reaction pathway of lower activation energy, so equilibrium is reached much faster. This allows the moderate temperature (450°C) to be used — which is more favourable for yield than an even higher temperature would be — while still achieving an

economically acceptable rate of production.

Bài tập luyện tập

Using Le Chatelier's principle, explain why the Haber process operates at about 200 atm rather than 1 atm.

Lời giải chi tiết

The forward reaction reduces the number of moles of gas (4 mol $\rightarrow$ 2 mol). By Le Chatelier's principle, increasing the pressure shifts the equilibrium toward the side with fewer gas moles — the product (NH_3) side — increasing the % yield at equilibrium. 200 atm is chosen because it gives a substantially improved yield without the excessive engineering cost and safety risk of even higher pressures.

Bài tập luyện tập

Explain why 450°C (rather than, say, 100°C) is used in the Haber process, even though the forward reaction is exothermic.

Lời giải chi tiết

A lower temperature such as 100°C would give a higher equilibrium % yield (favouring the exothermic forward reaction), but the rate of reaching that equilibrium would be far too slow to be commercially viable. 450°C is a compromise: some yield is sacrificed in exchange for a much faster, economically acceptable rate of ammonia production.

Bài tập luyện tập

Calculate the pH of 0.0500 mol dm^{-3} HCl(aq).

(A) 1.00 **(C)** 1.70

(B) 1.30 **(D)** 2.00

Lời giải chi tiết

HCl is a strong acid: $[H^+] = 0.0500$ mol dm^{-3}; pH $= -\log_{10}(0.0500) = 1.30$. **(B)**.

Bài tập luyện tập

$K_a(\text{HCOOH}) = 1.6 \times 10^{-4}$ mol dm^{-3}. Calculate the pH of 0.100 mol dm^{-3} HCOOH(aq). (A2)

Lời giải chi tiết

$$[H^+] = \sqrt{K_a C} = \sqrt{1.6 \times 10^{-4} \times 0.100} = \sqrt{1.6 \times 10^{-5}} = 4.0 \times 10^{-3} \text{ mol dm}^{-3}.$$

pH $= -\log_{10}(4.0 \times 10^{-3}) =$ **2.40**.

Bài tập luyện tập

Calculate the pH of 0.00500 mol dm^{-3} NaOH(aq). (A2)

Lời giải chi tiết

NaOH is a strong base: $[\text{OH}^-] = 0.00500$ mol dm^{-3}; $\text{pOH} = -\log_{10}(0.00500) = 2.30$.

$$\text{pH} = 14.00 - 2.30 = \mathbf{11.70}.$$

Bài tập luyện tập

Which indicator is most suitable for titrating a weak acid with a strong base? (A2)

(A) Methyl orange
(B) Phenolphthalein
(C) Either indicator works equally well
(D) Neither indicator is suitable

Lời giải chi tiết

The equivalence point for weak acid–strong base lies above pH 7 (basic), within phenolphthalein's colour-change range (8.2–10.0); methyl orange would change colour too early. **(B).**

Bài tập luyện tập

For a strong acid–weak base titration, state the approximate equivalence pH and the correct indicator, with a reason. (A2)

Lời giải chi tiết

Equivalence pH is below 7 (acidic, typically $\sim$ 5–6), because the conjugate acid of the weak base (e.g. NH_4^+) hydrolyses slightly, releasing H^+. Methyl orange (range 3.1–4.4) is used, since its colour-change range falls within the steep part of this titration curve; phenolphthalein would change colour too late (well after the true equivalence point).

Bài tập luyện tập

Explain why indicators are unreliable for a weak acid–weak base titration. (A2)

Lời giải chi tiết

The titration curve for weak acid–weak base has no sharp, near-vertical region near equivalence — the pH changes only gradually over a wide range of added titrant. Since no indicator changes colour precisely and suddenly at the equivalence point, the endpoint cannot be located reliably by eye; a pH meter must be used instead.

Bài tập luyện tập

A buffer contains 0.200 mol dm^{-3} CH_3COOH and 0.0800 mol dm^{-3} CH_3COONa ($\text{p}K_a = 4.74$). Calculate the pH. (A2)

Lời giải chi tiết

$$\text{pH} = \text{p}K_a + \log_{10}\left(\frac{0.0800}{0.200}\right) = 4.74 + \log_{10}(0.400) = 4.74 + (-0.40) = \mathbf{4.34}.$$

Bài tập luyện tập

What ratio $[CH_3COO^-] : [CH_3COOH]$ is needed to prepare a buffer of pH $= 4.44$, given $pK_a(CH_3COOH) = 4.74$? (A2)

Lời giải chi tiết

$$\log_{10}(\text{ratio}) = 4.44 - 4.74 = -0.30 \implies \text{ratio} = 10^{-0.30} = \mathbf{0.50}\ (\text{i.e. } 1:2 \text{ salt : acid}).$$

Bài tập luyện tập

$K_{sp}(CaF_2) = 3.9 \times 10^{-11}$ mol^3 dm^{-9}. Which expression correctly gives the molar solubility s of CaF_2 in water? (A2)

(A) $s = K_{sp}$

(B) $s = (K_{sp}/4)^{1/3}$

(C) $s = (K_{sp})^{1/3}$

(D) $s = (4K_{sp})^{1/3}$

Lời giải chi tiết

$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$: if solubility is s, then $[Ca^{2+}] = s$ and $[F^-] = 2s$, so $K_{sp} = s(2s)^2 = 4s^3$, giving $s = (K_{sp}/4)^{1/3}$. **(B).**

Bài tập luyện tập

Using $K_{sp}(CaF_2) = 3.9 \times 10^{-11}$ mol^3 dm^{-9}, calculate the molar solubility of CaF_2 in pure water. (A2)

Lời giải chi tiết

$$s = \left(\frac{K_{sp}}{4}\right)^{1/3} = \left(\frac{3.9 \times 10^{-11}}{4}\right)^{1/3} = (9.75 \times 10^{-12})^{1/3} = \mathbf{2.14 \times 10^{-4}}\ \text{mol dm}^{-3}.$$

Bài tập luyện tập

100 cm^3 of 0.0100 mol dm^{-3} $CaCl_2(aq)$ is mixed with 100 cm^3 of 0.0200 mol dm^{-3} $NaF(aq)$. Given $K_{sp}(CaF_2) = 3.9 \times 10^{-11}$ mol^3 dm^{-9}, determine whether a precipitate of CaF_2 forms. (A2)

Lời giải chi tiết

Total volume $= 200$ cm^3, so each concentration is halved:

$$[Ca^{2+}] = 0.0100 \times \tfrac{100}{200} = 5.00 \times 10^{-3}\ \text{mol dm}^{-3}, \qquad [F^-] = 0.0200 \times \tfrac{100}{200} = 1.00 \times 10^{-2}\ \text{mol dm}^{-3}.$$

$$Q_{sp} = [Ca^{2+}][F^-]^2 = (5.00 \times 10^{-3})(1.00 \times 10^{-2})^2 = 5.00 \times 10^{-7}.$$

Since $Q_{sp}(5.00 \times 10^{-7}) \gg K_{sp}(3.9 \times 10^{-11})$, **a precipitate of CaF_2 forms.**

Bài tập luyện tập

Adding solid NaCl to a saturated solution of AgCl will:

(A) Increase the solubility of AgCl
(B) Decrease the solubility of AgCl
(C) Have no effect on the solubility of AgCl
(D) Dissolve the existing solid AgCl

Lời giải chi tiết

This is the common-ion effect: the added Cl^- shifts the dissolution equilibrium $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ to the left (Le Chatelier), reducing the solubility of AgCl. **(B)**.

Bài tập luyện tập

State two conditions that must both be satisfied for a system to be at dynamic equilibrium.

Lời giải chi tiết

(1) The reaction must occur in a **closed system** (no substance can enter or leave). (2) The rate of the forward reaction must equal the rate of the reverse reaction, so that the macroscopic concentrations of all species remain constant, even though both reactions continue at the molecular level.

Bài tập luyện tập

At dynamic equilibrium:

(A) The forward and reverse reactions have both stopped
(B) The forward and reverse rates are equal and the reaction continues
(C) Only the forward reaction occurs
(D) The concentration of reactants is zero

Lời giải chi tiết

(B). Equilibrium is dynamic, not static — both reactions continue at equal rates.

Bài tập luyện tập

Explain why increasing the concentration of a reactant does not change the numerical value of K_c, even though it does shift the position of equilibrium.

Lời giải chi tiết

K_c depends only on temperature. Increasing [reactant] momentarily makes the reaction quotient $Q_c < K_c$, so the system responds by shifting forward, converting some reactant into product until $Q_c = K_c$ is restored. The absolute equilibrium concentrations change, but their particular combination (raised to the stoichiometric powers) returns to the same K_c value, since T is unchanged.

Bài tập luyện tập

At equilibrium for $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, $K_p = 20.8$ atm^{-1}, $p(SO_2) = 0.400$ atm, $p(O_2) = 0.600$ atm. Calculate $p(SO_3)$.

Lời giải chi tiết

$$p(SO_3)^2 = K_p \times p(SO_2)^2 \times p(O_2) = 20.8 \times 0.400^2 \times 0.600 = 20.8 \times 0.0960 = 1.997.$$

$$p(SO_3) = \sqrt{1.997} = \mathbf{1.41}\text{ atm}.$$

Bài tập luyện tập

A gas mixture at total pressure 5.00 atm contains 2.00 mol N_2, 1.00 mol O_2 and 1.00 mol CO_2. What is the partial pressure of O_2?

(A) 1.00 atm
(B) 1.25 atm
(C) 2.00 atm
(D) 0.500 atm

Lời giải chi tiết

Total moles $= 4.00$; $x(O_2) = 1.00/4.00 = 0.25$; $p(O_2) = 0.25 \times 5.00 = \mathbf{1.25}$ atm. **(B)**.

Bài tập luyện tập

For $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $K_c = 0.105$ mol^{-2} dm^6 at 700 K. Calculate K_p ($R = 0.0821$ dm^3 atm K^{-1} mol^{-1}).

Lời giải chi tiết

$\Delta n = 2 - 4 = -2$.

$RT = 0.0821 \times 700 = 57.5$ dm^3 atm mol^{-1}, $\quad K_p = K_c(RT)^{-2} = \dfrac{0.105}{57.5^2} = \dfrac{0.105}{3306} = \mathbf{3.18 \times 10^{-5}}$ atm^{-2}.

Bài tập luyện tập

Adding a catalyst to a reaction already at equilibrium:

(A) Shifts the equilibrium toward products
(B) Shifts the equilibrium toward reactants
(C) Does not shift the position of equilibrium, but equilibrium is reached faster
(D) Increases K_c

Lời giải chi tiết

A catalyst speeds up the forward and reverse reactions equally, so the position of equilibrium (and K_c) is unchanged; only the *time* taken to reach equilibrium decreases. **(C)**.

Bài tập luyện tập

Explain, using the reactivity of ions, why Q_{sp} must be recalculated using diluted concentrations when two solutions are mixed, rather than using the original stock concentrations. (A2)

Lời giải chi tiết

As soon as the two solutions are combined, the total volume increases, so each ion's concentration in the new, larger volume is lower than in the original stock solution (moles are conserved but are now spread through more solvent). Using the original, undiluted concentrations would overstate Q_{sp} and could wrongly predict precipitation (or wrongly predict no precipitation, if the dilution is large); the ionic product must always be calculated from the concentrations that actually exist immediately after mixing.

Reaction Kinetics

Mục tiêu Unit: Thuyết va chạm và phân bố Maxwell–Boltzmann; các yếu tố ảnh hưởng tốc độ phản ứng; xúc tác đồng thể và dị thể với cơ chế cụ thể; phương trình tốc độ, bậc phản ứng và hằng số tốc độ từ phương pháp tốc độ đầu (A2); chu kỳ bán rã phản ứng bậc một (A2); phương trình Arrhenius theo cả hai chiều tính toán (A2); cơ chế phản ứng và bước quyết định tốc độ, kể cả trường hợp có cân bằng nhanh trước bước chậm (A2).

8.1 Collision theory and factors affecting reaction rate

Collision theory

For a reaction to occur between two particles, they must (1) **collide**, (2) with a combined kinetic energy *at least equal to* the **activation energy**, E_a (the minimum energy needed to break/weaken the bonds that must break for the reaction to start), and (3) with the **correct orientation**. A collision satisfying all three conditions is a **successful (effective) collision**.

VN **GIẢI THÍCH TIẾNG VIỆT**

Theo thuyết va chạm, phản ứng chỉ xảy ra khi các hạt **va chạm**, có **tổng động năng** $\geq$ **năng lượng hoạt hoá** E_a, và va chạm đúng **định hướng**. Va chạm thoả cả ba điều kiện gọi là va chạm hiệu quả.

Factor	Effect (via collision theory)	Everyday/industrial example
Concentration	more particles per unit volume → more frequent collisions → faster rate	diluting acid slows a reaction with a metal
Pressure (gases)	compresses gas into a smaller volume → effectively increases concentration → more frequent collisions	higher P speeds up gas-phase industrial reactions
Surface area / particle size	greater exposed surface area per unit mass → more frequent collisions at the solid's surface	powdered vs. lump reactant (see worked example below)
Temperature	raises average kinetic energy *and* shifts the Maxwell–Boltzmann distribution so a much larger fraction of particles have $E \geq E_a$ → far more frequent *successful* collisions	food spoils faster at room temperature than in a fridge
Catalyst	provides an alternative pathway with lower E_a, so a larger fraction of collisions become successful, *without* being used up	Fe in the Haber process; Pt/Pd in catalytic converters

Table 1. Factors affecting reaction rate, explained by collision theory.

Ví dụ 1 · Surface area — lump vs. powdered $CaCO_3$

2.00 g of calcium carbonate ($M_r = 100$) is reacted with excess dilute HCl(aq) in two separate experiments: (a) as a single marble lump, (b) as a fine powder, both at the same temperature. Predict and explain the shape of the volume-of-CO_2-against-time graph for each, and calculate the total volume of gas expected (at r.t.p., $24\,000$ cm^3 mol^{-1}).

$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$. Moles of $CaCO_3$: $n = \dfrac{2.00}{100} = 0.0200$ mol, so moles of $CO_2 = 0.0200$ mol, giving a total volume of $0.0200 \times 24\,000 =$ **480** cm^3 in *both* experiments (same mass of $CaCO_3$ reacts completely either way, since HCl is in excess).

Powdered $CaCO_3$ exposes a far greater total surface area per gram to the acid than a single lump does, so H^+ ions collide with $CaCO_3$ particles far more frequently — the *initial rate* is much faster (steeper initial gradient), and 480 cm^3 is reached sooner. The **lump** reacts more slowly (shallower gradient) but eventually produces the *same* final volume, 480 cm^3, once all the $CaCO_3$ has dissolved.

VN **GIẢI THÍCH TIẾNG VIỆT**

Cùng khối lượng $CaCO_3$ phản ứng hết với axit dư sẽ tạo ra **cùng một thể tích khí cuối cùng**, bất kể dạng cục hay bột. Tuy nhiên bột có diện tích bề mặt tiếp xúc lớn hơn nhiều → tần suất va chạm hiệu quả cao hơn → tốc độ ban đầu nhanh hơn (đường cong dốc hơn lúc đầu), dù điểm kết thúc là như nhau.

8.2 The Maxwell–Boltzmann distribution

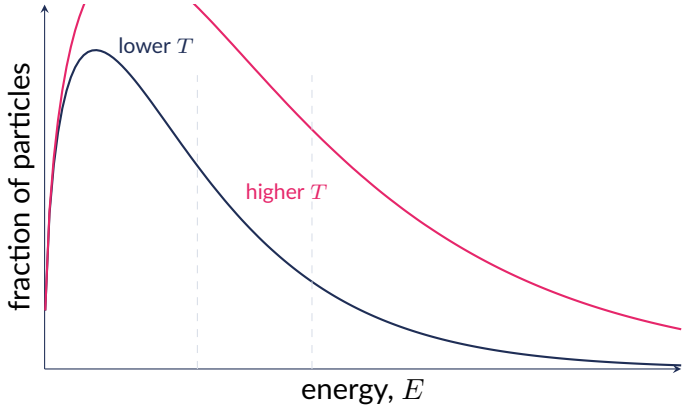


Figure 1. The Maxwell–Boltzmann distribution of molecular energies at two temperatures. Both curves enclose the *same total area* (same total number of particles). At the higher temperature the peak shifts right and the curve flattens/broadens, so the shaded area beyond E_a (fraction with enough energy to react) is much larger. A catalyst does not change the distribution — it lowers E_a itself, so a still-larger fraction of the *same* distribution now qualifies as "successful".

A catalyst provides an alternative reaction pathway with a **lower activation energy**, increasing the fraction of collisions that are successful and hence the rate — but it does **not** change ΔH of the reaction, and it does **not** change the equilibrium constant (K_c/K_p), since it speeds up the forward and reverse reactions by an identical factor.

VN **GIẢI THÍCH TIẾNG VIỆT**

Phân bố Maxwell–Boltzmann mô tả sự phân bố động năng của các phân tử khí; diện tích dưới đường cong (tổng số hạt) không đổi khi tăng nhiệt độ, nhưng đường cong dịch phải và bẹt ra,

làm tăng mạnh phần diện tích ứng với $E \geq E_a$. Xúc tác không làm dịch chuyển đường cong mà làm giảm E_a cần thiết — cả hai cơ chế đều làm tăng tỉ lệ va chạm hiệu quả. Xúc tác **không đổi** ΔH và **không đổi** K.

(!) Lỗi thường gặp: A very common misconception is that raising the temperature increases the *total number* of particles or the area under the Maxwell–Boltzmann curve. In fact the *total* area (total number of particles) is fixed; only the *shape* of the distribution changes (it flattens and shifts to higher energy), redistributing particles toward higher energies.

8.3 Catalysis: homogeneous and heterogeneous

Homogeneous vs. heterogeneous catalysis

A **homogeneous catalyst** is in the *same phase* as the reactants (e.g. a gas catalysing a gas-phase reaction, or an aqueous ion catalysing a reaction in solution) and typically acts by forming a reactive intermediate. A **heterogeneous catalyst** is in a *different phase* (almost always a solid catalysing gas- or solution-phase reactants) and acts via surface adsorption.

VN **GIẢI THÍCH TIẾNG VIỆT**
Xúc tác **đồng thể** cùng pha với chất phản ứng (thường tạo chất trung gian phản ứng); xúc tác **dị thể** khác pha (thường là chất rắn, hoạt động qua cơ chế hấp phụ bề mặt).

8.3.1 Homogeneous catalysis — NO-catalysed depletion of ozone

Ví dụ 2 · A homogeneous catalytic cycle

Nitrogen monoxide, NO, present in the upper atmosphere, catalyses the breakdown of ozone by O atoms via two propagation steps. Write both steps, the overall equation, and explain why NO is a catalyst (not a reactant).

Step 1: $\mathrm{NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)}$
Step 2: $\mathrm{NO_2(g) + O(g) \rightarrow NO(g) + O_2(g)}$
Overall (adding the steps, cancelling NO and $\mathrm{NO_2}$, which appear on both sides):

$$\mathrm{O_3(g) + O(g) \rightarrow 2O_2(g)}$$

NO is *consumed* in step 1 but exactly *regenerated* in step 2, so its concentration is unchanged overall and it does not appear in the overall equation — the defining behaviour of a catalyst. NO speeds up the otherwise slow direct reaction between $\mathrm{O_3}$ and O by providing a lower-activation-energy, two-step pathway, and it is a **homogeneous** catalyst because NO, $\mathrm{O_3}$ and O are all gases.

VN **GIẢI THÍCH TIẾNG VIỆT**
NO đóng vai trò xúc tác đồng thể trong sự phân huỷ ozon: bị tiêu thụ ở bước 1 nhưng được tái tạo hoàn toàn ở bước 2, nên không xuất hiện trong phương trình tổng, và nồng độ của nó không đổi sau chu trình — đây là dấu hiệu đặc trưng của một chất xúc tác thực sự.

Another well-known example of homogeneous catalysis is **autocatalysis**: in the reaction of acidified MnO_4^- with $C_2O_4^{2-}$ (oxalate), $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$, the reaction starts *slowly* (both reactant ions are negatively charged, hindering their approach), but the Mn^{2+} *product itself* acts as a catalyst for further reaction, so the rate *increases* as Mn^{2+} accumulates, before eventually slowing again as the reactants are used up.

8.3.2 Heterogeneous catalysis — adsorption mechanism

Ví dụ 3 · Heterogeneous catalysis: Fe in the Haber process and Pt/Pd in catalytic converters

Outline, in three stages, how a solid catalyst speeds up a gas-phase reaction, using (a) iron in the Haber process and (b) platinum/palladium in a catalytic converter as examples.

(1) Adsorption: gas molecules bond to **active sites** on the solid catalyst's surface — N_2 and H_2 onto Fe; CO, NO and unburned hydrocarbons onto Pt/Pd (coated on a ceramic honeycomb to maximise surface area).
(2) Bond weakening and surface reaction: adsorption weakens (and can break) the strong bonds within the adsorbed molecules (e.g. the $N \equiv N$ triple bond and the $H-H$ bond on Fe), lowering the activation energy needed for them to react together while held on the surface — atoms combine stepwise to form NH_3 on Fe; $2CO + O_2 \rightarrow 2CO_2$ and $2NO + 2CO \rightarrow N_2 + 2CO_2$ on Pt/Pd.
(3) Desorption: the product molecules (NH_3; CO_2, N_2) leave the surface, freeing the active sites for further reactant molecules to adsorb.

VN **GIẢI THÍCH TIẾNG VIỆT**

Xúc tác dị thể (chất rắn) hoạt động qua ba giai đoạn: **hấp phụ** chất khí lên bề mặt (tại các tâm hoạt động), **làm yếu liên kết** trong phân tử hấp phụ giúp phản ứng trên bề mặt dễ xảy ra hơn, và **giải hấp phụ** sản phẩm để giải phóng tâm hoạt động. Ví dụ: Fe trong quá trình Haber; Pt/Pd trong bộ chuyển đổi xúc tác ô tô.

8.4 Concentration–time and rate–time graphs (A2)

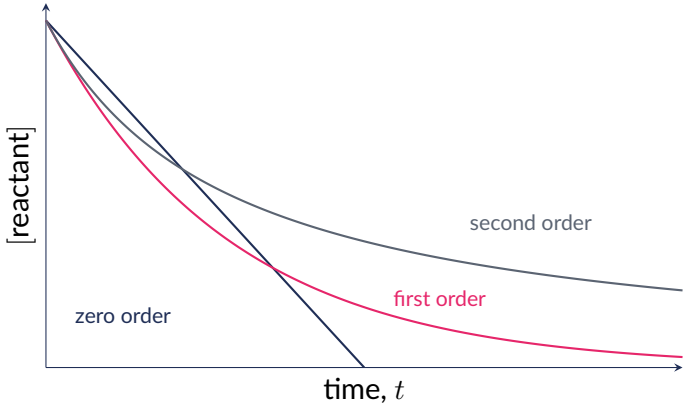


Figure 2. Schematic concentration–time curves. Zero order: constant negative gradient, straight line down to zero. First order: exponential-style decay with a *constant* half-life. Second order: decays more steeply at first but with a half-life that *lengthens* as the reaction proceeds (a longer "tail").

Reading order of reaction from a concentration–time graph: the constant half-life test

Measure the time taken for the concentration to fall to half its value, starting from *several different* points along the curve. If this half-life is **constant** regardless of starting concentration, the reaction is **first order** in that reactant. If successive half-lives get progressively **longer**, the reaction is **second order** (or higher) in that reactant. If the graph is a straight line to zero, the reaction is **zero order**.

VN **GIẢI THÍCH TIẾNG VIỆT**

Phép thử chu kỳ bán rã không đổi: đo thời gian để nồng độ giảm còn một nửa tại nhiều điểm khác nhau trên đồ thị. Nếu chu kỳ bán rã **không đổi** → bậc 1. Nếu chu kỳ bán rã **tăng dần** theo thời gian → bậc 2 (hoặc cao hơn). Nếu đồ thị là đường thẳng đi xuống 0 → bậc 0.

Ví dụ 4 · Applying the constant half-life test

Concentration–time data for reactant A: $t = 0$ s, $[\text{A}] = 1.00$; $t = 10$ s, $[\text{A}] = 0.50$; $t = 20$ s, $[\text{A}] = 0.25$; $t = 30$ s, $[\text{A}] = 0.125$ mol dm^{-3}. Determine the order with respect to A, and calculate the rate constant.

The concentration halves every 10 s regardless of the starting point ($1.00 \to 0.50$, $0.50 \to 0.25$, $0.25 \to 0.125$) — a **constant half-life**, so the reaction is **first order** in A.

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{10.0} = \mathbf{0.0693\ s^{-1}}.$$

(!) Lỗi thường gặp: Do not confuse the *shapes* of zero- and second-order decay: both curve downward, but only the zero-order graph is a **straight line**. A second-order graph curves throughout, and — unlike first order — its half-life visibly **lengthens** at later points along the curve; this lengthening (not just "curving") is the key diagnostic that distinguishes second order from first order.

VN **GIẢI THÍCH TIẾNG VIỆT**

Đừng nhầm bậc 0 (đường thẳng) với bậc 2 (đường cong) chỉ vì cả hai đều giảm dần. Dấu hiệu phân biệt bậc 1 và bậc 2 là chu kỳ bán rã: bậc 1 không đổi, bậc 2 **tăng dần** theo thời gian.

8.5 Rate equations, order of reaction and the rate constant (A2)

Rate equation and order

For a reaction with reactants A, B, the experimentally determined **rate equation** has the form

$$\text{rate} = k[\text{A}]^m[\text{B}]^n$$

where m is the **order with respect to A**, n is the **order with respect to B**, $m + n$ is the **overall order**, and k is the **rate constant** (constant at fixed temperature; changes only with temperature — see the Arrhenius equation below). Orders **cannot** be deduced from the balanced equation; they must be found **experimentally**, typically by the **method of initial rates**.

VN **GIẢI THÍCH TIẾNG VIỆT**

Phương trình tốc độ rate $= k[\text{A}]^m[\text{B}]^n$ có bậc m, n phải xác định bằng **thực nghiệm** (thường

bằng phương pháp tốc độ đầu), **không** thể suy ra từ hệ số cân bằng phương trình hoá học. k chỉ đổi theo nhiệt độ.

Ví dụ 5 · Method of initial rates — two reactants

Initial rate data for A + B → products:

Expt	[A]/mol dm^{-3}	[B]/mol dm^{-3}	Initial rate/mol dm^{-3} s^{-1}
1	0.100	0.100	2.0×10^{-3}
2	0.200	0.100	4.0×10^{-3}
3	0.100	0.200	8.0×10^{-3}

Order in A: experiments 1→2, [A] doubles at constant [B], rate doubles ($\times 2$) ⇒ order $= 1$.
Order in B: experiments 1→3, [B] doubles at constant [A], rate quadruples ($\times 4 = 2^2$) ⇒ order $= 2$.

$$\text{rate} = k[\text{A}][\text{B}]^2 \qquad (\text{overall order} = 1 + 2 = 3).$$

Using experiment 1: $k = \dfrac{2.0 \times 10^{-3}}{(0.100)(0.100)^2} = \dfrac{2.0 \times 10^{-3}}{1.00 \times 10^{-3}} =$ **2.0 mol^{-2} dm^{6} s^{-1}.**

Ví dụ 6 · Method of initial rates — three reactants, including a zero-order species

Initial rate data for A + B + C → products:

Expt	[A]	[B]	[C]	Initial rate/mol dm^{-3} s^{-1}
1	0.10	0.10	0.20	3.0×10^{-3}
2	0.20	0.10	0.20	1.2×10^{-2}
3	0.10	0.20	0.20	6.0×10^{-3}
4	0.10	0.10	0.40	3.0×10^{-3}

Order in A (1→2, [A] doubles): rate $\times 4$ ⇒ order $= 2$.
Order in B (1→3, [B] doubles): rate $\times 2$ ⇒ order $= 1$.
Order in C (1→4, [C] doubles): rate *unchanged* ⇒ order $= 0$ (C does not affect the rate at all).

$$\text{rate} = k[\text{A}]^2[\text{B}] \qquad (\text{overall order} = 2 + 1 + 0 = 3).$$

Using experiment 1: $k = \dfrac{3.0 \times 10^{-3}}{(0.10)^2(0.10)} = \dfrac{3.0 \times 10^{-3}}{1.0 \times 10^{-3}} =$ **3.0 mol^{-2} dm^{6} s^{-1}.**

(!) Lỗi thường gặp: A reactant with **zero order** still appears in the balanced equation and may even appear to be "used up", but changing its concentration has **no effect** on the rate — this is only revealed by experiment (as in experiments 1 and 4 above), never by inspecting the equation.

VN **GIẢI THÍCH TIẾNG VIỆT**
Chất có bậc phản ứng bằng 0 vẫn xuất hiện trong phương trình hoá học và vẫn bị tiêu thụ, nhưng thay đổi nồng độ của nó **không ảnh hưởng** đến tốc độ phản ứng — chỉ phát hiện được điều này qua thực nghiệm (so sánh thí nghiệm 1 và 4), không thể đoán từ phương trình.

8.6 Half-life of a first-order reaction (A2)

For a first-order reaction, the **half-life**, $t_{1/2}$, is **independent of concentration**:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Với phản ứng bậc 1, chu kỳ bán rã $t_{1/2} = \ln 2/k$ **không phụ thuộc** nồng độ ban đầu — đây là đặc điểm riêng của bậc 1 (khác hẳn bậc 0 và bậc 2).

Ví dụ 7 · Half-life from the rate constant

A first-order reaction has $k = 2.31 \times 10^{-2}$ s^{-1}. Calculate its half-life.

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{2.31 \times 10^{-2}} = \mathbf{30.0}\ \text{s}.$$

Ví dụ 8 · Fraction remaining after several half-lives

A first-order reaction has $t_{1/2} = 25$ s. Calculate the fraction of the original concentration of reactant remaining after 100 s.

Number of half-lives elapsed $= \dfrac{100}{25} = 4$.

$$\text{Fraction remaining} = \left(\frac{1}{2}\right)^4 = \frac{1}{16} = \mathbf{6.25}\%.$$

Second-order half-life: a qualitative contrast

For a second-order reaction, the half-life is **not** constant: as the reaction proceeds and the concentration of reactant falls, the rate ($\propto [\text{A}]^2$) falls off much more sharply than for first order, so **each successive half-life takes longer than the one before**. (By contrast, for a zero-order reaction, the half-life — the time for whatever concentration remains *at that point* to halve — actually gets **shorter** as the reaction proceeds, since the rate stays constant while less reactant remains.) The 9701 syllabus does not require an integrated rate law for second order; recognising this *lengthening half-life* behaviour from a graph or data table is sufficient.

VN **GIẢI THÍCH TIẾNG VIỆT**

Phản ứng bậc 2 **không có** chu kỳ bán rã cố định — mỗi chu kỳ bán rã sau **dài hơn** chu kỳ trước, vì tốc độ giảm rất nhanh khi nồng độ giảm (tỉ lệ với $[\text{A}]^2$). Ngược lại, ở bậc 0, do tốc độ không đổi, chu kỳ bán rã tại một thời điểm sẽ **ngắn dần** khi nồng độ còn lại giảm. Đây là điểm phân biệt quan trọng với bậc 1 (chu kỳ bán rã luôn không đổi).

8.7 The Arrhenius equation (A2)

$$k = Ae^{-E_a/RT}, \qquad \text{equivalently} \qquad \ln k = \ln A - \frac{E_a}{R}\cdot\frac{1}{T},$$

where A is the **pre-exponential (frequency) factor**, E_a is the activation energy, $R = 8.31$ J K^{-1} mol^{-1}, and T is the absolute temperature (kelvin). A graph of $\ln k$ against $1/T$ is a straight line of gradient $-E_a/R$ and intercept $\ln A$.

VN **GIẢI THÍCH TIẾNG VIỆT**

Phương trình Arrhenius $k = Ae^{-E_a/RT}$ liên hệ hằng số tốc độ k với nhiệt độ tuyệt đối T và năng lượng hoạt hoá E_a. Đồ thị $\ln k$ theo $1/T$ là đường thẳng có độ dốc $-E_a/R$, cho phép xác định E_a bằng thực nghiệm.

Ví dụ 9 · Finding k_2 at a new temperature, given E_a

A reaction has $E_a = 53.5$ kJ mol^{-1} and $k_1 = 1.50 \times 10^{-4}$ s^{-1} at $T_1 = 300$ K. Estimate k_2 at $T_2 = 310$ K.

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{53\,500}{8.31}\left(\frac{1}{300} - \frac{1}{310}\right) = 6438 \times (1.075 \times 10^{-4}) = 0.692.$$

$$\frac{k_2}{k_1} = e^{0.692} = 1.998 \approx 2.00 \implies k_2 = 1.50 \times 10^{-4} \times 2.00 = \mathbf{3.00 \times 10^{-4}\ s^{-1}}.$$

This illustrates the common "rule of thumb" that, for many reactions with $E_a \approx 50$–55 kJ mol^{-1}, the rate roughly **doubles for every** 10 K **rise** in temperature near room temperature.

Ví dụ 10 · Finding E_a from two (k, T) data pairs — the reverse calculation

A reaction has $k_1 = 3.00 \times 10^{-4}$ s^{-1} at $T_1 = 300$ K and $k_2 = 2.40 \times 10^{-3}$ s^{-1} at $T_2 = 320$ K. Calculate E_a.

Using the two-point form of the Arrhenius equation:

$$E_a = \frac{R\ln(k_2/k_1)}{\dfrac{1}{T_1} - \dfrac{1}{T_2}}.$$

$$\ln\left(\frac{k_2}{k_1}\right) = \ln\left(\frac{2.40 \times 10^{-3}}{3.00 \times 10^{-4}}\right) = \ln(8.00) = 2.079.$$

$$\frac{1}{T_1} - \frac{1}{T_2} = \frac{1}{300} - \frac{1}{320} = 2.083 \times 10^{-4}\ \text{K}^{-1}.$$

$$E_a = \frac{8.31 \times 2.079}{2.083 \times 10^{-4}} = \frac{17.28}{2.083 \times 10^{-4}} = 82\,900\ \text{J mol}^{-1} = \mathbf{82.9\ kJ\ mol^{-1}}.$$

(!) Lỗi thường gặp: Ví dụ 9 and Ví dụ 10 are the **two directions** of the same relationship — do not confuse them. Given E_a and one (k, T) pair, you solve for a *new* k at a *new* T (Ví dụ 9). Given *two* (k, T) pairs, you solve for E_a itself (Ví dụ 10). Always identify which quantity is unknown before rearranging.

VN **GIẢI THÍCH TIẾNG VIỆT**
Hai chiều tính toán của phương trình Arrhenius: (1) biết E_a và một cặp (k, T) → tìm k mới ở T mới (Ví dụ 9); (2) biết hai cặp (k, T) → tìm E_a (Ví dụ 10, dùng công thức hai điểm). Luôn xác định rõ đại lượng cần tìm trước khi biến đổi công thức.

8.8 Reaction mechanisms and the rate-determining step (A2)

Rate-determining step

Many reactions proceed through a **multi-step mechanism**. The **rate-determining step (RDS)** is the **slowest** step (equivalently, the step with the highest activation energy), and it alone determines the observed rate equation: only species involved *up to and including* the RDS can appear in the experimental rate equation.

VN **GIẢI THÍCH TIẾNG VIỆT**
Cơ chế phản ứng nhiều bước có một **bước quyết định tốc độ (RDS)** — bước **chậm nhất** (năng lượng hoạt hoá cao nhất). Chỉ các chất tham gia **đến và bao gồm** bước này mới xuất hiện trong phương trình tốc độ thực nghiệm.

Ví dụ 11 · Mechanism consistent with the observed second-order rate law

The reaction $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ is found experimentally to be second order in NO_2 and zero order in CO (rate $= k[NO_2]^2$). Suggest a two-step mechanism consistent with this rate law.

Step 1 (slow, rate-determining): $NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$
Step 2 (fast): $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$
Check overall: adding the steps and cancelling one NO_2 and the intermediate NO_3 gives $NO_2 + CO \rightarrow NO + CO_2$ ✓. Because the slow step involves two molecules of NO_2 and none of CO, the rate depends on $[NO_2]^2$ but not on $[CO]$ at all — consistent with the observed rate law. CO only reacts in the fast second step, after the rate has already been "set" by the slow first step.

Ví dụ 12 · Mechanism with a fast pre-equilibrium before a slow step

The reaction $2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$ is found experimentally to obey rate $= k[NO]^2[Br_2]$ (third order overall). A proposed mechanism involves the short-lived intermediate $NOBr_2$:

Step 1 (fast, reaches equilibrium): $NO(g) + Br_2(g) \rightleftharpoons NOBr_2(g)$
Step 2 (slow, rate-determining): $NOBr_2(g) + NO(g) \rightarrow 2NOBr(g)$

Check overall: adding the steps and cancelling the intermediate $NOBr_2$ gives $2NO + Br_2 \rightarrow 2NOBr$ ✓. Explain why this mechanism is consistent with the observed rate law.

Since step 2 is rate-determining, rate $= k_2[NOBr_2][NO]$. Because step 1 is a *fast, reversible* pre-equilibrium, $[NOBr_2]$ is not independent — it is fixed by the equilibrium of step 1, so $[NOBr_2] \propto [NO][Br_2]$. Substituting:

$$\text{rate} = k_2 \times (\text{constant} \times [NO][Br_2]) \times [NO] = k[NO]^2[Br_2],$$

exactly matching the experimentally observed third-order rate law. (This shows the mechanism is *consistent with* the data — kinetic evidence alone can never fully *prove* a mechanism, since a different mechanism might also fit.)

(!) Lỗi thường gặp: When an intermediate is formed in a **fast pre-equilibrium** before the slow step, its concentration is *not* independent of the reactants — it must be expressed in terms of the reactants using the fast step's equilibrium relationship before substituting into the rate expression for the slow step. Forgetting this step is a common error when checking whether a proposed mechanism is consistent with an observed rate law.

VN **GIẢI THÍCH TIẾNG VIỆT**

Khi chất trung gian hình thành qua một **cân bằng nhanh** trước bước chậm, nồng độ chất trung gian đó **không độc lập** — phải biểu diễn nó theo nồng độ chất phản ứng ban đầu (dựa vào biểu thức cân bằng của bước nhanh) rồi mới thay vào biểu thức tốc độ của bước chậm. Đây là bước hay bị bỏ sót khi kiểm tra một cơ chế đề xuất có phù hợp với phương trình tốc độ thực nghiệm hay không. Lưu ý: bằng chứng động học chỉ cho thấy cơ chế **phù hợp**, không chứng minh tuyệt đối đó là cơ chế đúng duy nhất.

Ôn tập nhanh

Ôn tập nhanh: (1) Va chạm hiệu quả cần đủ năng lượng $\geq E_a$ và đúng định hướng; nồng độ/áp suất/diện tích bề mặt/nhiệt độ/xúc tác đều tăng tốc độ theo thuyết va chạm, nhưng chỉ nhiệt độ và xúc tác thay đổi *tỉ lệ* va chạm hiệu quả (qua phân bố Maxwell–Boltzmann hoặc qua giảm E_a). (2) Xúc tác đồng thể (cùng pha, VD NO xúc tác phân huỷ ozon, tự xúc tác Mn^{2+}) khác xúc tác dị thể (khác pha, cơ chế hấp phụ–phản ứng–giải hấp, VD Fe/Haber, Pt-Pd/bộ chuyển đổi xúc tác) — cả hai đều không đổi ΔH hay K. (3) Đồ thị nồng độ–thời gian: bậc 0 là đường thẳng; bậc 1 có chu kỳ bán rã không đổi; bậc 2 có chu kỳ bán rã tăng dần. (4) Bậc phản ứng luôn xác định bằng thực nghiệm (phương pháp tốc độ đầu), không suy từ phương trình hoá học. (5) $t_{1/2} = \ln 2/k$ chỉ đúng cho bậc 1. (6) Arrhenius $k = Ae^{-E_a/RT}$: có thể tính k mới từ E_a đã biết, hoặc tính E_a từ hai cặp (k, T). (7) Cơ chế nhiều bước: bước chậm nhất quyết định tốc độ; nếu có cân bằng nhanh trước bước chậm, phải thay nồng độ chất trung gian theo biểu thức cân bằng đó.

Practice

Bài tập luyện tập

According to collision theory, increasing temperature increases the rate of reaction mainly because:

(A) Particles collide less often

(B) A much greater proportion of particles have energy $\geq E_a$

(C) The activation energy decreases

(D) The gas constant R decreases

Lời giải chi tiết

Raising T reshapes the Maxwell–Boltzmann distribution so a far larger fraction of particles possess energy at least equal to E_a, greatly increasing the frequency of successful collisions. **(B)**.

Bài tập luyện tập

Explain, using collision theory, why increasing the pressure of a gas-phase reaction increases its rate.

Lời giải chi tiết

Increasing pressure (at constant temperature and amount of gas) compresses the gas into a smaller volume, increasing the concentration (number of particles per unit volume) of the reacting gases. Particles are therefore closer together on average and collide more frequently per unit time, increasing the rate of reaction.

Bài tập luyện tập

A catalyst increases reaction rate mainly by:

(A) Increasing the frequency of all collisions

(B) Providing a reaction pathway of lower activation energy

(C) Raising the temperature of the reactants

(D) Shifting the equilibrium toward products

Lời giải chi tiết

A catalyst provides an alternative mechanism with a lower activation energy, so a larger fraction of collisions become successful. **(B)**.

Bài tập luyện tập

2.00 g of $CaCO_3$ ($M_r = 100$) reacts completely with excess dilute HCl. Calculate the total volume of CO_2 produced at r.t.p. ($24\,000$ cm^3 mol^{-1}), and state whether this volume differs between a powdered and a lump sample.

Lời giải chi tiết

$n(CaCO_3) = 2.00/100 = 0.0200$ mol $= n(CO_2)$. Volume $= 0.0200 \times 24\,000 =$ **480** cm^3. This final volume is the *same* for both powder and lump, since the same moles of $CaCO_3$ react completely either way (HCl in excess) — only the *time* taken to reach 480 cm^3 differs (faster for the powder, due to its greater surface area).

Bài tập luyện tập

Raising the temperature of a gas sample shifts the Maxwell–Boltzmann distribution so that:

(A) The peak moves to lower energy and the curve narrows

(B) The peak moves to higher energy, the curve broadens, and the area beyond E_a increases

(C) The total area under the curve increases

(D) The activation energy E_a decreases

Lời giải chi tiết

The total area (total number of particles) is fixed; raising T broadens and flattens the curve, shifting the peak to higher energy and increasing the fraction (area) with $E \geq E_a$. **(B)**.

Bài tập luyện tập

Explain, referring to the Maxwell–Boltzmann distribution, why a modest temperature rise (e.g. $10\,^{\circ}$C) can nearly double the rate of many reactions.

Lời giải chi tiết

The Maxwell–Boltzmann distribution has a long high-energy tail. A modest rise in T shifts the whole distribution only slightly, but because the number of particles with energy $\geq E_a$ lies in this sensitive tail region, even a small shift can substantially increase the *fraction* of particles exceeding E_a (often roughly doubling it), even though the average kinetic energy itself has increased only slightly. Since rate is proportional to the frequency of successful (energetic enough) collisions, the rate increases sharply.

Bài tập luyện tập

A reaction is zero order in reactant A. Which best describes the graph of [A] against time?

(A) Exponential decay with constant half-life

(B) A straight line of constant negative gradient, reaching zero

(C) A curve with an increasing half-life

(D) A horizontal line

Lời giải chi tiết

Zero order means rate is independent of [A], so [A] falls at a constant rate — a straight line down to zero. **(B)**.

Bài tập luyện tập

Concentration–time data for reactant A: $t = 0$ s, [A] $= 0.800$; $t = 20$ s, [A] $= 0.400$; $t = 40$ s, [A] $= 0.200$; $t = 60$ s, [A] $= 0.100$ mol dm^{-3}. Determine the order in A and calculate k. (A2)

Lời giải chi tiết

The concentration halves every 20 s regardless of starting point — a constant half-life, so the reaction is **first order** in A.

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{20.0} = \mathbf{3.47 \times 10^{-2}\ s^{-1}}.$$

Bài tập luyện tập

For a first-order reaction, doubling the initial concentration of the reactant will:

(A) Double the half-life

(B) Halve the half-life

(C) Leave the half-life unchanged

(D) Double the rate constant k

Lời giải chi tiết

$t_{1/2} = \ln 2/k$ for a first-order reaction is independent of concentration. **(C)**.

Bài tập luyện tập

Explain, without using an integrated rate law, why the half-life of a second-order reaction is not constant, in contrast to a first-order reaction. (A2)

Lời giải chi tiết

For a first-order reaction, rate $\propto [\text{A}]^1$, and this relationship gives a half-life that is independent of the starting concentration — a constant half-life. For a second-order reaction, rate $\propto [\text{A}]^2$, so as [A] falls the rate drops off much more steeply than for first order; the time required for the remaining concentration to halve becomes progressively **longer** as the reaction proceeds, because the reaction slows disproportionately more at lower concentrations.

Bài tập luyện tập

From initial-rate data for A + B → products: doubling [A] alone doubles the rate; doubling [B] alone quadruples the rate. What is the overall order of reaction? (A2)

(A) 1
(B) 2
(C) 3
(D) 4

Lời giải chi tiết

Order in A $= 1$; order in B $= 2$ (doubling → $\times 4 = 2^2$); overall order $= 1 + 2 = 3$. **(C)**.

Bài tập luyện tập

Initial rate data for P + Q → products: Expt 1, [P] $= 0.10$, [Q] $= 0.10$, rate $= 5.0 \times 10^{-3}$; Expt 2, [P] $= 0.20$, [Q] $= 0.10$, rate $= 1.0 \times 10^{-2}$; Expt 3, [P] $= 0.20$, [Q] $= 0.20$, rate $= 4.0 \times 10^{-2}$ mol dm^{-3} s^{-1}. Deduce the rate equation and calculate k with units. (A2)

Lời giải chi tiết

1→2: [P] doubles, rate doubles ⇒ order 1 in P. 2→3: [Q] doubles, rate quadruples ⇒ order 2 in Q.

$$\text{rate} = k[\text{P}][\text{Q}]^2. \qquad k = \frac{5.0 \times 10^{-3}}{(0.10)(0.10)^2} = \frac{5.0 \times 10^{-3}}{1.0 \times 10^{-3}} = \mathbf{5.0}\ \text{mol}^{-2}\ \text{dm}^{6}\ \text{s}^{-1}.$$

Bài tập luyện tập

What are the units of the rate constant k for an overall first-order reaction, rate $= k[\text{A}]$? (A2)

(A) s^{-1}
(B) mol dm^{-3} s^{-1}
(C) mol^{-1} dm^3 s^{-1}
(D) mol^{-2} dm^6 s^{-1}

Lời giải chi tiết

k = rate/[A]: units $=$ (mol dm^{-3} s^{-1})/(mol dm^{-3}) $=$ s^{-1}. **(A)**.

Bài tập luyện tập

What are the units of k for an overall third-order reaction, rate $= k[\text{A}]^2[\text{B}]$? (A2)

Lời giải chi tiết

$k = \text{rate}/([\text{A}]^2[\text{B}])$: units $= \dfrac{\text{mol dm}^{-3}\ \text{s}^{-1}}{\text{mol}^3\ \text{dm}^{-9}} = \text{mol}^{-2}\ \text{dm}^6\ \text{s}^{-1}$.

Bài tập luyện tập

A first-order reaction has $k = 0.0231\ \text{s}^{-1}$. What is its half-life? (A2)

(A) 15.0 s
(B) 30.0 s
(C) 45.0 s
(D) 60.0 s

Lời giải chi tiết

$t_{1/2} = \ln 2/k = 0.693/0.0231 = 30.0$ s. **(B)**.

Bài tập luyện tập

A first-order reaction has $t_{1/2} = 40.0$ s. Calculate the fraction of the original concentration remaining after 160 s. (A2)

Lời giải chi tiết

Number of half-lives $= 160/40 = 4$. Fraction remaining $= (1/2)^4 = 1/16 = \mathbf{6.25\%}$.

Bài tập luyện tập

According to the Arrhenius equation, increasing temperature increases k mainly because: (A2)

(A) A increases
(B) E_a decreases
(C) The exponential term $e^{-E_a/RT}$ increases
(D) R decreases

Lời giải chi tiết

Raising T makes $-E_a/RT$ less negative, so $e^{-E_a/RT}$ increases — A, E_a and R are unaffected by temperature. **(C)**.

Bài tập luyện tập

A reaction has $E_a = 53.5$ kJ mol^{-1} and $k = 2.00 \times 10^{-5}\ \text{s}^{-1}$ at 290 K. Estimate k at 300 K ($R = 8.31$ J K^{-1} mol^{-1}). (A2)

Lời giải chi tiết

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{290} - \frac{1}{300}\right) = \frac{53\,500}{8.31} \times (1.149 \times 10^{-4}) = 0.740.$$

$$\frac{k_2}{k_1} = e^{0.740} = 2.10 \implies k_2 = 2.00 \times 10^{-5} \times 2.10 = \mathbf{4.19 \times 10^{-5}}\ \text{s}^{-1}.$$

Bài tập luyện tập

A reaction has $k_1 = 4.00 \times 10^{-3}$ s^{-1} at 298 K and $k_2 = 1.60 \times 10^{-2}$ s^{-1} at 318 K. Calculate E_a ($R = 8.31$ J K^{-1} mol^{-1}). (A2)

Lời giải chi tiết

$$\ln\left(\frac{k_2}{k_1}\right) = \ln(4.00) = 1.386, \qquad \frac{1}{298} - \frac{1}{318} = 2.111 \times 10^{-4}\ \text{K}^{-1}.$$

$$E_a = \frac{8.31 \times 1.386}{2.111 \times 10^{-4}} = \frac{11.52}{2.111 \times 10^{-4}} = \mathbf{54.6 \times 10^3}\ \text{J mol}^{-1} = \mathbf{54.6}\ \text{kJ mol}^{-1}.$$

Bài tập luyện tập

A graph of $\ln k$ against $1/T$ has gradient -8490 K. Calculate E_a ($R = 8.31$ J K^{-1} mol^{-1}). (A2)

Lời giải chi tiết

Gradient $= -E_a/R$, so $E_a = -(\text{gradient}) \times R = 8490 \times 8.31 = 70\,552$ J mol^{-1} = **70.6** kJ mol^{-1}.

Bài tập luyện tập

In a multi-step mechanism, the rate-determining step is:

(A) Always the first step

(B) The step with the highest activation energy (the slowest step)

(C) Always the last step

(D) The step involving the catalyst

Lời giải chi tiết

The slowest step (highest E_a) limits the overall rate. **(B)**.

Bài tập luyện tập

The reaction $2\text{NO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO}_2\text{(g)}$ is second order in NO and first order in O_2. NO and O_2 are known to form a short-lived intermediate N_2O_2 in a fast pre-equilibrium. Suggest a two-step mechanism consistent with this rate law. (A2)

Lời giải chi tiết

Step 1 (fast, equilibrium): $2\text{NO(g)} \rightleftharpoons \text{N}_2\text{O}_2\text{(g)}$
Step 2 (slow, rate-determining): $\text{N}_2\text{O}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO}_2\text{(g)}$
Overall: adding the steps gives $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ ✓. Since step 2 is rate-determining, rate $= k_2[\text{N}_2\text{O}_2][\text{O}_2]$; because N_2O_2 is in a fast pre-equilibrium with NO, $[\text{N}_2\text{O}_2] \propto [\text{NO}]^2$, giving rate $\propto [\text{NO}]^2[\text{O}_2]$ — consistent with the observed third-order rate law.

Bài tập luyện tập

A catalyst that exists in the same phase as the reactants is called:

(A) Heterogeneous
(B) Homogeneous
(C) Autocatalytic
(D) An inhibitor

Lời giải chi tiết

(B). A homogeneous catalyst shares the same phase as the reactants.

Bài tập luyện tập

Using the NO-catalysed depletion of ozone, write the two propagation steps and the overall equation, and explain why NO is a catalyst.

Lời giải chi tiết

Step 1: $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$. Step 2: $NO_2(g) + O(g) \rightarrow NO(g) + O_2(g)$. Overall: $O_3(g) + O(g) \rightarrow 2O_2(g)$. NO is consumed in step 1 but exactly regenerated in step 2, so it does not appear in the overall equation and its concentration is unchanged after the cycle — the defining feature of a catalyst.

Bài tập luyện tập

In the Haber process, the first stage of heterogeneous catalysis by iron is:

(A) Desorption of NH_3
(B) Adsorption of N_2 and H_2 onto the catalyst surface
(C) Diffusion of NH_3 away from the surface
(D) Sublimation of the iron catalyst

Lời giải chi tiết

(B). Adsorption of the reactant gases onto active sites is the first stage.

Bài tập luyện tập

Describe, in three stages, how a solid catalyst (e.g. platinum in a catalytic converter) speeds up a gas-phase reaction.

Lời giải chi tiết

(1) **Adsorption:** gas molecules (CO, NO, unburned hydrocarbons) bond to active sites on the catalyst surface. (2) **Bond weakening / surface reaction:** adsorption weakens bonds in the adsorbed molecules, lowering the activation energy for them to react on the surface (e.g. $2CO + O_2 \rightarrow 2CO_2$; $2NO + 2CO \rightarrow N_2 + 2CO_2$). (3) **Desorption:** product molecules leave the surface, freeing active sites for further reactant molecules.

Bài tập luyện tập

Which statement about catalysts is correct?

(A) A catalyst changes the value of K_c

(B) A catalyst is used up during the reaction

(C) A catalyst provides an alternative pathway of lower activation energy, without altering ΔH or K_c

(D) A catalyst only functions in heterogeneous catalysis

Lời giải chi tiết

(C). A catalyst changes neither ΔH nor the equilibrium constant, and is not consumed.

Bài tập luyện tập

Which of the following would *not* increase the rate of reaction between a solid and a gas?

(A) Increasing the gas pressure

(B) Crushing the solid into smaller pieces

(C) Increasing the temperature

(D) Using one large single lump of the solid instead of powder

Lời giải chi tiết

Using a single large lump minimises exposed surface area, which would *decrease*, not increase, the rate. **(D)**.

Bài tập luyện tập

In the acidified $MnO_4^-/C_2O_4^{2-}$ reaction, the rate is observed to increase partway through the reaction before eventually slowing down again. Explain this observation.

Lời giải chi tiết

This is **autocatalysis**: the reaction is initially slow because both MnO_4^- and $C_2O_4^{2-}$ are negatively charged, hindering their mutual approach. However, the Mn^{2+} product formed acts as a catalyst for further reaction, so as Mn^{2+} accumulates the rate increases; the rate eventually falls again as the reactant concentrations become too low, giving a characteristic rate profile that rises then falls, rather than falling monotonically from the start.

Periodicity and Group 2

Mục tiêu Unit: Xu hướng biến thiên tính chất vật lý (bán kính nguyên tử, nhiệt độ nóng chảy, độ dẫn điện) và bản chất liên kết/cấu trúc dọc theo chu kỳ 3; phản ứng của các nguyên tố chu kỳ 3 với oxi, nước và clo; tính axit–bazơ của oxit chu kỳ 3 (đặc biệt oxit lưỡng tính Al_2O_3); phản ứng của kim loại nhóm 2 với nước, độ bền nhiệt của muối cacbonat/nitrat, độ tan của hydroxit và sunfat nhóm 2; thử nghiệm màu ngọn lửa nhận biết ion nhóm 1/2 và một số ứng dụng thực tế.

9.1 Physical properties across Period 3

Atomic radius and first ionisation energy across Period 3

Going from sodium to argon, each successive element has one more proton (increasing nuclear charge) while the extra electrons are added to the *same* outer shell ($n = 3$), so inner-shell shielding stays roughly constant. The stronger, largely unshielded nuclear attraction pulls the outer electrons in more tightly, so **atomic radius decreases** and **first ionisation energy (IE_1) generally increases** across the period — with the small dips at Al (Group 13) and S (Group 16) already explained in Chapter *Atomic Structure* from the $3s/3p$ sub-shell and electron-pairing effects, and not re-derived here.

VN **GIẢI THÍCH TIẾNG VIỆT**

Dọc theo chu kỳ 3, điện tích hạt nhân tăng dần trong khi electron thêm vào vẫn ở cùng lớp vỏ ngoài cùng ($n = 3$) nên hiệu ứng chắn của các electron bên trong gần như không đổi. Do đó lực hút hạt nhân–electron ngoài cùng tăng, làm **bán kính nguyên tử giảm** và **năng lượng ion hoá thứ nhất tăng dần** (đã giải thích chi tiết phần hụt tại Al và S trong Chương Cấu tạo nguyên tử, không nhắc lại ở đây).

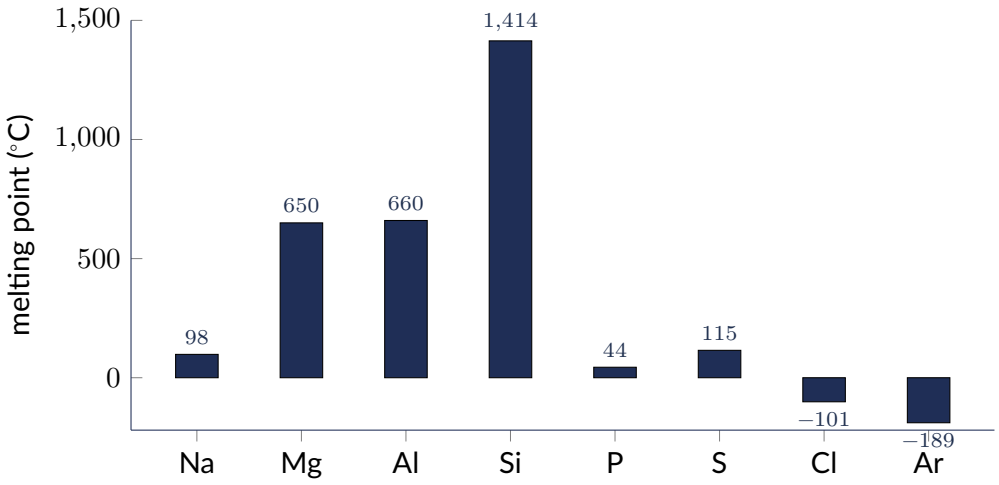


Figure 1. Melting points of the Period 3 elements (°C). The trend rises sharply from Na to a maximum at Si, then collapses abruptly for P, S, Cl_2 and Ar.

Ví dụ 1 · Explaining the melting point pattern via bonding and structure

Use Figure 1 to explain why the melting point rises steadily from Na to Si, then falls dramatically from Si to P.

Na, Mg, Al are **giant metallic** structures: a lattice of cations in a "sea" of delocalised electrons. Melting point rises Na → Mg → Al because the number of delocalised electrons per atom increases (1, 2, 3), the ionic charge increases, and ionic radius decreases, all of which strengthen the metallic bond and require more energy to melt.
Si has the highest melting point of all: it is a **giant covalent (macromolecular)** lattice in which every Si atom is bonded to four neighbours by strong covalent bonds throughout the entire crystal — an enormous number of strong bonds must be broken to melt it.
P_4, S_8, Cl_2, Ar are all **simple molecular** (or, for Ar, monatomic) substances: only **weak London (instantaneous dipole–induced dipole) forces** act *between* molecules, while the strong covalent bonds *within* each molecule are not broken on melting. Melting point therefore **collapses** at P, since only these weak intermolecular forces need to be overcome — and it rises slightly S > P > Cl_2 > Ar simply because S_8 has more electrons than P_4, which has more electrons than Cl_2, which has more than a single Ar atom, giving progressively stronger London forces.

VN **GIẢI THÍCH TIẾNG VIỆT**

Từ Na đến Al: liên kết kim loại (mạng ion dương trong biển electron tự do) mạnh dần vì điện tích ion tăng, bán kính giảm, và số electron tự do trên mỗi nguyên tử tăng. Si có nhiệt độ nóng chảy cao nhất vì là tinh thể **cộng hoá trị khổng lồ** (mỗi nguyên tử Si liên kết cộng hoá trị bền với 4 nguyên tử lân cận). Từ P trở đi là các phân tử đơn giản (P_4, S_8, Cl_2) hoặc nguyên tử đơn (Ar), chỉ có lực Van der Waals yếu giữa các phân tử nên nhiệt độ nóng chảy giảm mạnh.

Element	Na	Mg	Al	Si	P_4	S_8	Cl_2	Ar
Structure/bonding	giant metallic			giant covalent	simple molecular / monatomic			
Electrical conductivity (solid)	good	good	good	*semiconductor*	none	none	none	none

Table 1. Structure, bonding and electrical conductivity across Period 3.

Electrical conductivity across Period 3. Na, Mg and Al conduct well as solids because they have **delocalised electrons** free to move throughout the giant metallic lattice, carrying charge; conductivity increases slightly Na < Mg < Al as more delocalised electrons per atom become available. **Silicon** is a **semiconductor**: all of its outer electrons are held in localised covalent bonds, so at room temperature only a very small number of electrons have enough thermal energy to break free and conduct — conductivity is far weaker than a true metal but not exactly zero, and it *increases* with temperature (opposite to metals). **P_4, S_8, Cl_2 and Ar** do not conduct at all: there are no ions and no free (mobile) electrons — all outer electrons are either in localised covalent bonds or non-bonding pairs.

VN **GIẢI THÍCH TIẾNG VIỆT**

Na, Mg, Al dẫn điện tốt nhờ electron tự do (tăng dần theo số electron hoá trị). Si là **chất bán dẫn**: electron bị giữ trong liên kết cộng hoá trị định xứ, chỉ một số ít có đủ năng lượng để trở thành electron dẫn điện, nên độ dẫn tăng theo nhiệt độ (khác kim loại). P_4, S_8, Cl_2, Ar hoàn toàn không dẫn điện vì không có ion hay electron tự do di chuyển.

9.2 Reactions of Period 3 elements with oxygen, water and chlorine

9.2.1 Reaction with oxygen

Each Period 3 element (except Ar) burns in (or reacts directly with) oxygen to form an oxide:

$$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$$
$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$
$$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$$
$$Si(s) + O_2(g) \rightarrow SiO_2(s) \quad \text{(on strong heating)}$$
$$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s) \quad \text{(excess } O_2\text{)}$$
$$S_8(s) + 8O_2(g) \rightarrow 8SO_2(g)$$

9.2.2 Reaction with water

Na reacts **vigorously** with cold water; Mg reacts only **very slowly** with cold water but rapidly with steam:

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g) \quad \text{(vigorous, exothermic, may ignite the } H_2\text{)}$$
$$Mg(s) + 2H_2O(l) \rightarrow Mg(OH)_2(s) + H_2(g) \quad \text{(very slow — a thin, sparingly soluble } Mg(OH)_2 \text{ coating forms)}$$
$$Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g) \quad \text{(fast and vigorous, bright white flame)}$$

Al, Si, P and S do not react with cold water under normal laboratory conditions (Al is protected by a thin, tough, adherent layer of Al_2O_3 that prevents further reaction).

9.2.3 Reaction with chlorine — ionic versus covalent chlorides

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$
$$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$$
$$2Al(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s)$$
$$Si(s) + 2Cl_2(g) \rightarrow SiCl_4(l)$$
$$P_4(s) + 10Cl_2(g) \rightarrow 4PCl_5(s)$$

Ionic chlorides vs. covalent chlorides

NaCl and $MgCl_2$ are **ionic**: the electronegativity difference between the metal and chlorine is large, so electrons are essentially fully transferred. They dissolve in water simply as hydrated ions, without significant hydrolysis ($NaCl(aq)$ is neutral; $MgCl_2(aq)$ is only **weakly acidic**, pH ≈ 6, because the small, highly charged Mg^{2+} ion polarises its surrounding water molecules enough to release a small amount of H^+: $[Mg(H_2O)_6]^{2+} \rightleftharpoons [Mg(H_2O)_5OH]^+ + H^+$). $SiCl_4$ and PCl_5, by contrast, are **simple covalent molecules**: the bond has too little ionic character to be considered ionic. They react **violently** with water (**hydrolyse**), releasing **steamy, misty fumes of** HCl gas.

VN **GIẢI THÍCH TIẾNG VIỆT**

NaCl, $MgCl_2$ là hợp chất **ion** (chênh lệch độ âm điện lớn), tan trong nước chỉ tạo ion hiđrat hoá, gần như trung tính ($MgCl_2$ hơi có tính axit yếu do Mg^{2+} nhỏ, phân cực mạnh phân tử nước xung quanh). $SiCl_4$, PCl_5 là phân tử **cộng hoá trị**, thuỷ phân **rất mãnh liệt** trong nước, giải phóng khí HCl bốc khói trắng.

Ví dụ 2 · Hydrolysis of $SiCl_4$

Write a balanced equation for the reaction of liquid $SiCl_4$ with water, and explain why white, steamy fumes are observed.

$$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(g).$$

The Si − Cl bonds are polar covalent, and silicon (unlike carbon) has accessible empty $3d$ orbitals that allow a water molecule to attack the electron-deficient Si centre directly, breaking all four Si − Cl bonds rapidly. The reaction is highly exothermic and releases gaseous HCl, which reacts with moisture in the air to form a visible white mist of tiny hydrochloric acid droplets — the characteristic "steamy fumes".

VN **GIẢI THÍCH TIẾNG VIỆT**

$SiCl_4$ thuỷ phân mãnh liệt: $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$. Silic có orbital $3d$ trống nên phân tử nước dễ tấn công trực tiếp vào Si, phản ứng toả nhiệt mạnh và giải phóng khí HCl tạo khói trắng đặc trưng trong không khí ẩm. PCl_5 thuỷ phân tương tự tạo H_3PO_4 và HCl.

Chloride	Bonding	Behaviour in water	Fumes?
NaCl, $MgCl_2$	ionic	dissolve; $MgCl_2(aq)$ only weakly acidic (hydrated ion hydrolysis)	no
$AlCl_3$	mostly covalent (intermediate, exists as dimer Al_2Cl_6)	partially hydrolyses; fumes slightly in moist air	slight
$SiCl_4$, PCl_5	simple covalent	hydrolyse violently, releasing $HCl(g)$	yes, strong

Table 2. Contrast between ionic and covalent Period 3 chlorides.

9.3 Acid--base character of Period 3 oxides

Trend: basic → amphoteric → acidic

Across Period 3, the oxides change smoothly from **strongly basic** (Na_2O, MgO), through **amphoteric** (Al_2O_3), to **weakly acidic** (SiO_2) and finally **strongly acidic** (P_4O_{10}, SO_2, SO_3). This mirrors the change from ionic, metallic-oxide bonding (electron-rich oxide ion readily accepts a proton) to covalent, non-metal-oxide bonding (the oxide reacts with, rather than simply dissolving in, water to form an oxoacid).

VN **GIẢI THÍCH TIẾNG VIỆT**

Tính axit–bazơ của oxit chu kỳ 3 chuyển dần từ **bazơ mạnh** (Na_2O, MgO) sang **lưỡng tính** (Al_2O_3) rồi **axit yếu** (SiO_2) và **axit mạnh** (P_4O_{10}, SO_2, SO_3), phản ánh sự chuyển từ liên kết ion (oxit kim loại) sang liên kết cộng hoá trị (oxit phi kim).

$$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq) \quad \text{(strongly basic)}$$
$$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(s) \quad \text{(basic, but } Mg(OH)_2 \text{ only sparingly soluble)}$$
$$SiO_2(s) + 2NaOH(aq) \rightarrow Na_2SiO_3(aq) + H_2O(l) \quad \text{(weakly acidic; needs hot, concentrated alkali)}$$
$$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq) \quad \text{(strongly, vigorously acidic)}$$

Ví dụ 3 · SO_3 and the formation of a strong acid

Write the equation for the reaction of sulfur trioxide with water, and state the type of acid formed.

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq).$$

This forms **sulfuric acid**, a **strong** acid (fully ionised in water). SO_2 similarly reacts with water, $SO_2(g)+H_2O(l) \rightarrow H_2SO_3(aq)$, but sulfurous acid is a comparatively **weak** acid. Both reactions confirm sulfur's oxides are strongly acidic, consistent with sulfur's position at the acidic end of Period 3.

VN **GIẢI THÍCH TIẾNG VIỆT**

$SO_3 + H_2O \rightarrow H_2SO_4$ (axit sunfuric, axit mạnh); $SO_2 + H_2O \rightarrow H_2SO_3$ (axit sunfurơ, axit yếu hơn). Cả hai oxit của lưu huỳnh đều có tính axit, phù hợp với vị trí lưu huỳnh ở đầu axit của chu kỳ 3.

Ví dụ 4 · Al_2O_3 is amphoteric — both equations

Show, with balanced equations, that aluminium oxide is amphoteric.

Reaction with acid (Al_2O_3 behaves as a *base*):

$Al_2O_3(s)+6HCl(aq) \rightarrow 2AlCl_3(aq)+3H_2O(l)$ i.e. $Al_2O_3(s)+6H^+(aq) \rightarrow 2Al^{3+}(aq)+3H_2O(l).$

Reaction with alkali (Al_2O_3 behaves as an *acid*):

$Al_2O_3(s)+2NaOH(aq)+3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq)$ i.e. $Al_2O_3(s)+2OH^-(aq)+3H_2O(l) \rightarrow 2[Al(OH)$

Because Al_2O_3 reacts with *both* a strong acid and a strong alkali, it is **amphoteric** — it is insoluble in pure water, unlike either the strongly basic oxides (Na, Mg) or the weakly acidic SiO_2 (which reacts with alkali alone).

VN **GIẢI THÍCH TIẾNG VIỆT**

Al_2O_3 lưỡng tính: phản ứng được với **cả axit** (tạo muối nhôm và nước, đóng vai trò bazơ) **và bazơ mạnh** (tạo ion aluminat $[Al(OH)_4]^-$, đóng vai trò axit) — cần nhớ cả hai phương trình.

Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10} / SO_3
Character	strongly basic	basic	**amphoteric**	weakly acidic	strongly acidic

Table 3. Acid–base character of Period 3 oxides.

(!) Lỗi thường gặp: A common error is to state that an amphoteric oxide "dissolves in water". Al_2O_3 is **insoluble** in pure water (it does not react with water at all) — amphoteric means it reacts with *both* a strong acid *and* a strong base, not that it is soluble or reactive in neutral water.

VN **GIẢI THÍCH TIẾNG VIỆT**

Lưu ý: oxit lưỡng tính **không tan trong nước tinh khiết** — chỉ phản ứng được với axit mạnh và bazơ mạnh (hai phản ứng khác nhau), không phải là "hoà tan trong nước".

9.4 Group 2: the alkaline earth metals

Reactivity of Group 2 metals increases down the group

Going down Group 2 (Be, Mg, Ca, Sr, Ba), atomic radius increases while the outer two electrons are always in an ns^2 configuration, so the first and second ionisation energies **decrease** — the outer electrons are progressively easier to remove (greater distance from the nucleus, more shielding). Group 2 metals react by **losing electrons** (being oxidised to M^{2+}), so this trend makes them **more reactive down the group**.

VN **GIẢI THÍCH TIẾNG VIỆT**

Xuống nhóm 2, bán kính nguyên tử tăng, năng lượng ion hoá thứ nhất và thứ hai **giảm dần** (electron ngoài cùng ns^2 ngày càng xa hạt nhân, bị che chắn nhiều hơn). Vì kim loại nhóm 2 phản ứng bằng cách **mất electron**, tính **khử (hoạt động hoá học) tăng dần xuống nhóm**.

	Be	Mg	Ca	Sr	Ba
IE_1 / kJ mol^{-1}	899	738	590	549	503

Table 6. First ionisation energy of the Group 2 metals, decreasing down the group.

Ví dụ 5a · Reading the Group 2 ionisation energy trend

Use Table 6 to explain why barium is a stronger reducing agent than magnesium.

IE_1 falls steadily from Be to Ba as atomic radius increases and the outer electrons become more shielded and further from the nucleus. Since $IE_1(Ba) = 503$ kJ mol^{-1} is much lower than $IE_1(Mg) = 738$ kJ mol^{-1}, far less energy is needed to remove an outer electron from a Ba atom than from a Mg atom. Because reducing power depends on how readily a species gives up electrons, barium — which loses its outer electrons much more easily — is the **stronger reducing agent** of the two, consistent with its far more vigorous reaction with cold water.

VN **GIẢI THÍCH TIẾNG VIỆT**

Năng lượng ion hoá thứ nhất giảm dần từ Be đến Ba do bán kính nguyên tử tăng và hiệu ứng chắn tăng. Vì Ba dễ nhường electron ngoài cùng hơn Mg rất nhiều (503 so với 738 kJ mol^{-1}), Ba là chất khử **mạnh hơn** Mg — phù hợp với việc Ba phản ứng mãnh liệt hơn nhiều với nước lạnh.

9.4.1 Reaction with water

$$\mathrm{Mg(s) + 2H_2O(l) \rightarrow Mg(OH)_2(s) + H_2(g)} \quad \text{(very slow with } \textit{cold} \text{ water)}$$
$$\mathrm{Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g)} \quad \text{(fast with } \textit{steam}\text{)}$$
$$\mathrm{Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)} \quad \text{(steady, visible effervescence, mildly warm)}$$
$$\mathrm{Sr(s) + 2H_2O(l) \rightarrow Sr(OH)_2(aq) + H_2(g)} \quad \text{(more vigorous than Ca)}$$
$$\mathrm{Ba(s) + 2H_2O(l) \rightarrow Ba(OH)_2(aq) + H_2(g)} \quad \text{(most vigorous — reacts readily with } \textit{cold} \text{ water)}$$

Ví dụ 5 · Contrasting Mg and Ba with water

Mg reacts only very slowly with cold water, but Ba reacts readily and vigorously with cold water. Explain this difference and write balanced equations for both reactions.

$$\mathrm{Mg(s) + 2H_2O(l) \rightarrow Mg(OH)_2(s) + H_2(g)}, \qquad \mathrm{Ba(s) + 2H_2O(l) \rightarrow Ba(OH)_2(aq) + H_2(g)}.$$

Ba has a much larger atomic radius than Mg, and its outer $6s^2$ electrons are far more shielded from the nucleus by inner shells, so Ba's ionisation energies are much lower than Mg's — Ba loses its outer electrons to water far more readily. In addition, $\mathrm{Mg(OH)_2}$ is only sparingly soluble and forms a protective coating on the metal surface that further slows the reaction, whereas $\mathrm{Ba(OH)_2}$ is soluble and does not hinder continued reaction.

VN **GIẢI THÍCH TIẾNG VIỆT**

Ba có bán kính lớn hơn Mg rất nhiều, electron ngoài cùng bị chắn mạnh hơn nên năng lượng ion hoá thấp hơn nhiều → Ba nhường electron cho nước dễ dàng hơn, phản ứng mãnh liệt ngay ở nhiệt độ thường. Ngoài ra $\mathrm{Mg(OH)_2}$ ít tan tạo lớp màng bảo vệ làm chậm phản ứng thêm, còn $\mathrm{Ba(OH)_2}$ tan tốt nên không cản trở phản ứng tiếp diễn.

9.4.2 Thermal decomposition of carbonates and nitrates

Thermal stability increases down Group 2

All Group 2 carbonates and nitrates decompose on heating:

$$\mathrm{MCO_3(s) \rightarrow MO(s) + CO_2(g)}, \qquad \mathrm{2M(NO_3)_2(s) \rightarrow 2MO(s) + 4NO_2(g) + O_2(g)}.$$

As the cation $\mathrm{M^{2+}}$ gets larger down the group, its **charge density (polarising power)** decreases, so it distorts (polarises) the electron cloud of the large $\mathrm{CO_3^{2-}}$ or $\mathrm{NO_3^-}$ anion *less*. A less-distorted anion is more thermally stable, so a **higher temperature** is needed to decompose it — hence thermal stability of both the carbonates and the nitrates **increases down the group**: $\mathrm{MgCO_3}$ decomposes at a much lower temperature ($\approx 540\,^\circ\mathrm{C}$) than $\mathrm{BaCO_3}$ ($\approx 1360\,^\circ\mathrm{C}$).

VN **GIẢI THÍCH TIẾNG VIỆT**

Xuống nhóm 2, ion $\mathrm{M^{2+}}$ lớn dần nên **mật độ điện tích (khả năng phân cực)** giảm, làm biến dạng ít hơn đám mây electron của anion $\mathrm{CO_3^{2-}}$/$\mathrm{NO_3^-}$ lớn → anion bền nhiệt hơn → cần nhiệt độ cao hơn để phân huỷ. Do đó **độ bền nhiệt của muối cacbonat và nitrat nhóm 2 tăng dần xuống nhóm**.

Ví dụ 6 · Comparing decomposition of $\mathrm{MgCO_3}$ and $\mathrm{BaCO_3}$

Explain why $\mathrm{MgCO_3}$ decomposes on heating at a much lower temperature than $\mathrm{BaCO_3}$, and write the general equation for the decomposition.

$$\mathrm{MCO_3(s) \rightarrow MO(s) + CO_2(g)}.$$

$\mathrm{Mg^{2+}}$ is much smaller than $\mathrm{Ba^{2+}}$, so it has a much higher charge density and polarises the large $\mathrm{CO_3^{2-}}$ ion strongly, weakening a C — O bond within it enough that only a relatively low temperature is needed to complete the decomposition. $\mathrm{Ba^{2+}}$, being much larger, polarises $\mathrm{CO_3^{2-}}$ far less, so the carbonate ion remains largely intact and a much higher temperature is required to decompose $\mathrm{BaCO_3}$.

VN GIẢI THÍCH TIẾNG VIỆT

Mg^{2+} nhỏ, phân cực mạnh CO_3^{2-} nên $MgCO_3$ phân huỷ ở nhiệt độ thấp hơn nhiều so với $BaCO_3$ (ion Ba^{2+} lớn, phân cực yếu).

Ví dụ 7 · Volume of gas from decomposition of a Group 2 nitrate

4.10 g of solid calcium nitrate, $Ca(NO_3)_2$ ($M_r = 164$), is heated strongly until fully decomposed. Calculate the total volume of gas produced at r.t.p. ($24\,000$ cm^3 mol^{-1}).

$$2Ca(NO_3)_2(s) \rightarrow 2CaO(s) + 4NO_2(g) + O_2(g).$$

$$n(Ca(NO_3)_2) = \frac{4.10}{164} = 0.0250 \text{ mol}.$$

From the equation, 2 mol $Ca(NO_3)_2$ produces 4 mol $NO_2 + 1$ mol $O_2 = 5$ mol of gas in total, so 1 mol $Ca(NO_3)_2$ produces 2.5 mol of gas.

$$n(\text{gas}) = 0.0250 \times 2.5 = 0.0625 \text{ mol}.$$

$$V = 0.0625 \times 24\,000 = \mathbf{1500} \text{ cm}^3.$$

9.4.3 Hydroxide and sulfate solubility

Opposite solubility trends: hydroxides up, sulfates down

Group 2 **hydroxide** solubility **increases** down the group ($Mg(OH)_2$ almost insoluble; $Ba(OH)_2$ fairly soluble): the small OH^- anion means lattice enthalpy dominates the energetics, and lattice enthalpy falls faster than hydration enthalpy as the cation gets larger, favouring dissolving. Group 2 **sulfate** solubility **decreases** down the group ($MgSO_4$ very soluble; $BaSO_4$ essentially insoluble): the large SO_4^{2-} anion means lattice enthalpy changes relatively little down the group, while the (negative) hydration enthalpy of the cation becomes markedly less exothermic as the cation gets larger — so less energy is released on hydration relative to what is needed to break the lattice, and solubility falls.

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Độ tan **hydroxit nhóm 2 tăng** xuống nhóm ($Mg(OH)_2$ gần như không tan, $Ba(OH)_2$ tan khá tốt) vì anion OH^- nhỏ nên năng lượng mạng lưới chi phối, và năng lượng mạng lưới giảm nhanh hơn năng lượng hiđrat hoá khi cation lớn dần. Ngược lại, độ tan **sunfat nhóm 2 giảm** xuống nhóm ($MgSO_4$ tan tốt, $BaSO_4$ gần như không tan) vì anion SO_4^{2-} lớn nên năng lượng mạng lưới ít đổi, trong khi năng lượng hiđrat hoá giảm mạnh khi cation lớn dần, làm độ tan giảm.

	Mg	Ca	Sr	Ba
$M(OH)_2$ solubility	almost insoluble	slightly soluble	soluble	fairly soluble
MSO_4 solubility	very soluble	slightly soluble	sparingly soluble	essentially insoluble

Table 4. Opposite solubility trends of Group 2 hydroxides and sulfates.

Ví dụ 8 · Solubility of $BaSO_4$ from K_{sp}, and the "barium meal"

$K_{sp}(BaSO_4) = 1.1 \times 10^{-10}$ mol^2 dm^{-6} at 298 K. Calculate the molar solubility of $BaSO_4$ in water, and explain why an aqueous suspension of $BaSO_4$ (a "barium meal") can safely be

swallowed by a patient before an abdominal X-ray, even though soluble Ba^{2+} salts are toxic.

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq), \qquad K_{sp} = [Ba^{2+}][SO_4^{2-}] = s^2.$$

$$s = \sqrt{K_{sp}} = \sqrt{1.1 \times 10^{-10}} = \mathbf{1.05 \times 10^{-5}}\ \text{mol dm}^{-3}.$$

This is an extremely low solubility, so almost no free $Ba^{2+}(aq)$ ions enter the bloodstream — the patient is not exposed to a toxic dose of soluble barium — while the large number of electrons in Ba^{2+} and SO_4^{2-} still makes $BaSO_4$ an effective absorber of X-rays, giving good contrast on the X-ray image of the digestive tract.

VN **GIẢI THÍCH TIẾNG VIỆT**

Độ tan của $BaSO_4$ trong nước rất thấp ($s = \sqrt{K_{sp}} \approx 1.05 \times 10^{-5}$ mol dm^{-3}), nên hầu như không có ion Ba^{2+} tự do đi vào máu khi bệnh nhân uống "bữa ăn bari" trước khi chụp X-quang — an toàn dù Ba^{2+} hoà tan vốn độc, trong khi $BaSO_4$ vẫn hấp thụ tốt tia X nhờ nhiều electron, cho hình ảnh tương phản rõ ống tiêu hoá.

9.5 Flame tests and qualitative identification

A small sample of a metal salt, moistened with concentrated HCl, is held on a clean nichrome/-platinum wire loop in a roaring (non-luminous) Bunsen flame. Thermal energy excites outer electrons of the metal ion to higher energy levels; as these electrons fall back down, they emit light of characteristic wavelengths (frequencies), seen as a distinctive flame colour.

Ion	Li^+	Na^+	K^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
Flame colour	red (crimson)	persistent yellow	lilac	brick-red	crimson	apple/pale green

Table 5. Flame test colours for common Group 1 and Group 2 cations.

Ví dụ 9 · Identifying an unknown salt by flame test

An unknown white solid gives a brick-red flame test. Suggest the identity of the cation present, and describe one further simple test that would help confirm which Group 2 carbonate is present.

A **brick-red** flame indicates Ca^{2+} is present. To help confirm the compound (e.g. distinguishing $CaCO_3$ from another calcium salt), add dilute acid: effervescence with a gas that turns lime-water cloudy, $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$, confirms a carbonate is present.

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Ngọn lửa **đỏ gạch** là đặc trưng của ion Ca^{2+}. Cần lưu ý bảng màu ngọn lửa dùng để nhận biết nhanh cation nhóm 1/2 trong phân tích định tính, thường kết hợp thêm phản ứng với axit loãng (sủi bọt khí làm đục nước vôi trong) để xác nhận có mặt gốc cacbonat.

Ví dụ 10 · Combining flame test and solubility evidence

An unknown white solid gives an apple-green flame test. When dissolved in water and a few drops of dilute sulfuric acid are added, a dense white precipitate forms immediately. Identify the compound and justify your answer using the solubility trend of Group 2 sulfates.

An **apple-green** flame indicates Ba^{2+}. Since Group 2 sulfate solubility *decreases* sharply down the group, $BaSO_4$ — unlike $MgSO_4$ or $CaSO_4$, which are far more soluble — precipitates out almost completely and immediately on mixing $Ba^{2+}(aq)$ with $SO_4^{2-}(aq)$:

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s).$$

Both pieces of evidence (flame colour and the immediate, dense precipitate with sulfate ions) are consistent with a soluble **barium** salt, most likely $BaCl_2$ or $Ba(NO_3)_2$.

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Ngọn lửa **xanh lục táo (apple-green)** đặc trưng cho Ba^{2+}. Vì độ tan sunfat nhóm 2 giảm mạnh xuống nhóm, $BaSO_4$ kết tủa trắng ngay lập tức khi trộn Ba^{2+} với SO_4^{2-} — hai bằng chứng này cùng khẳng định có mặt muối bari tan (như $BaCl_2$ hoặc $Ba(NO_3)_2$).

9.6 Applications of Group 2 compounds

Magnesium hydroxide, $Mg(OH)_2$ ("milk of magnesia"), is used as an **antacid** to neutralise excess stomach acid: $Mg(OH)_2(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + 2H_2O(l)$; its very low solubility means only a small, controlled concentration of hydroxide ion is released at a time, avoiding a dangerously alkaline solution in the stomach. **Calcium carbonate**, $CaCO_3$ (limestone), is used in **construction** (as aggregate and, after heating to CaO then slaking to $Ca(OH)_2$, in cement and mortar) and in **agriculture** (crushed limestone or lime, $Ca(OH)_2$, is added to acidic soil to raise its pH). **Barium sulfate**, $BaSO_4$, is used as a **radiocontrast agent** ("barium meal") in medical X-ray imaging of the digestive tract, exploiting its extremely low solubility (Ví dụ 8).

VN **GIẢI THÍCH TIẾNG VIỆT**

$Mg(OH)_2$ dùng làm **thuốc kháng axit dạ dày**; $CaCO_3$/vôi dùng trong **xây dựng** (xi măng, vữa) và **nông nghiệp** (cải tạo đất chua); $BaSO_4$ dùng làm **chất cản quang** khi chụp X-quang đường tiêu hoá nhờ độ tan cực thấp.

Ôn tập nhanh

Ôn tập nhanh: (1) Chu kỳ 3: bán kính giảm, IE_1 tăng dần (trừ hụt Al, S — xem Chương Cấu tạo nguyên tử); liên kết đổi từ kim loại (Na, Mg, Al) sang cộng hoá trị khổng lồ (Si) sang phân tử đơn giản (P_4, S_8, Cl_2, Ar), làm nhiệt độ nóng chảy đạt đỉnh ở Si rồi sụp đổ. (2) Độ dẫn điện: kim loại tốt, Si bán dẫn, còn lại không dẫn. (3) Oxit chu kỳ 3 chuyển từ bazơ mạnh → lưỡng tính (Al_2O_3, hai phương trình với axit và bazơ) → axit yếu (SiO_2) → axit mạnh (P_4O_{10}, $SO_3 \rightarrow H_2SO_4$). (4) Clorua ion (NaCl, $MgCl_2$) tan êm, clorua cộng hoá trị ($SiCl_4$, PCl_5) thuỷ phân mãnh liệt tạo khói HCl. (5) Nhóm 2: tính khử tăng xuống nhóm (Mg phản ứng chậm với nước lạnh, nhanh với hơi nước; Ca, Sr, Ba phản ứng mạnh với nước lạnh). (6) Độ bền nhiệt cacbonat/nitrat nhóm 2 **tăng** xuống nhóm (mật độ điện tích cation giảm); độ tan hydroxit **tăng**, độ tan sunfat **giảm** xuống nhóm. (7) Bảng màu ngọn lửa: Li đỏ, Na vàng, K tím nhạt (lilac), Ca đỏ gạch, Sr đỏ thẫm, Ba xanh lục nhạt.

Practice

Bài tập luyện tập

Which row correctly describes the bonding and structure of silicon and phosphorus (as P_4) in Period 3?

(A) Both giant covalent
(B) Si giant covalent; P_4 simple molecular
(C) Both simple molecular
(D) Si simple molecular; P_4 giant covalent

Lời giải chi tiết

Silicon is a giant covalent (macromolecular) lattice; phosphorus exists as discrete P_4 molecules held together only by weak London forces. **(B)**.

Bài tập luyện tập

Explain why the melting point of sulfur ($115\,^\circ$C) is higher than that of chlorine ($-101\,^\circ$C), even though both are simple molecular substances.

Lời giải chi tiết

Both S_8 and Cl_2 are held together only by weak London (van der Waals) forces between molecules. S_8 has far more electrons per molecule than Cl_2, giving it much stronger London forces, so more energy is needed to overcome the intermolecular forces and melt it — hence sulfur's higher melting point.

Bài tập luyện tập

Which Period 3 element is classified as a semiconductor?

(A) Sodium
(B) Magnesium
(C) Silicon
(D) Phosphorus

Lời giải chi tiết

(C). Silicon's electrons are held in localised covalent bonds; only a small number gain enough energy to conduct at room temperature, and conductivity rises with temperature.

Bài tập luyện tập

Write balanced equations for the reaction of magnesium with (a) cold water and (b) steam, and state one observable difference between the two reactions.

Lời giải chi tiết

(a) $Mg(s) + 2H_2O(l) \rightarrow Mg(OH)_2(s) + H_2(g)$ — very slow, only a few bubbles over a long time.
(b) $Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g)$ — fast and vigorous, magnesium glows/burns with a bright white flame.

Bài tập luyện tập

Sodium reacts with cold water far more vigorously than magnesium does. Which statement best explains this?

(A) Sodium has a smaller atomic radius than magnesium

(B) Sodium has a lower first ionisation energy and NaOH is far more soluble than $Mg(OH)_2$, which coats and protects the magnesium

(C) Magnesium is a stronger oxidising agent

(D) Sodium forms a covalent oxide layer

Lời giải chi tiết

Sodium's single outer electron is removed more easily (lower IE_1), and NaOH is fully soluble so it never forms a protective barrier, unlike the sparingly soluble $Mg(OH)_2$ layer that slows magnesium's reaction. **(B)**.

Bài tập luyện tập

Write the equation for the reaction of aluminium oxide with hot concentrated sodium hydroxide, showing the aluminate ion product.

Lời giải chi tiết

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq).$$

Bài tập luyện tập

Which oxide of Period 3 is amphoteric?

(A) MgO

(B) Al_2O_3

(C) SiO_2

(D) P_4O_{10}

Lời giải chi tiết

(B). Al_2O_3 reacts with both strong acids and strong alkalis.

Bài tập luyện tập

Write the equation for the reaction of Al_2O_3 with dilute sulfuric acid.

Lời giải chi tiết

$$Al_2O_3(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3H_2O(l).$$

Bài tập luyện tập

Explain, in terms of bonding, why $SiCl_4$ hydrolyses violently in water while NaCl simply dissolves without reacting.

Lời giải chi tiết

NaCl is ionic; it dissolves in water as hydrated Na^+ and Cl^- ions without any chemical reaction occurring. $SiCl_4$ is a simple covalent molecule with polar Si — Cl bonds and an electron-deficient Si centre with accessible empty $3d$ orbitals; water attacks the Si atom directly, breaking all four Si — Cl bonds and releasing HCl gas: $SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(g)$.

Bài tập luyện tập

A few drops of water are added to solid PCl_5. Which observation is expected?

(A) No visible change

(B) A slow colour change only

(C) Vigorous reaction with steamy white fumes of HCl

(D) Formation of a yellow precipitate

Lời giải chi tiết

(C). PCl_5 hydrolyses violently: $PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(g)$, giving steamy HCl fumes.

Bài tập luyện tập

Write the equation for the reaction of sulfur trioxide with water and name the acid formed.

Lời giải chi tiết

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq) \quad \text{(sulfuric acid)}.$$

Bài tập luyện tập

Which best explains why the reactivity of Group 2 metals increases down the group?

(A) Atomic radius decreases, so ionisation energy increases down the group

(B) Atomic radius increases and shielding increases, so ionisation energy decreases, making electron loss easier

(C) The metals become less dense down the group

(D) Nuclear charge decreases down the group

Lời giải chi tiết

Down the group, atomic radius and shielding increase, lowering ionisation energy, so the outer ns^2 electrons are lost more easily. **(B)**.

Bài tập luyện tập

Write balanced equations for the reactions of (a) calcium and (b) barium with cold water.

Lời giải chi tiết

(a) $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$. (b) $Ba(s) + 2H_2O(l) \rightarrow Ba(OH)_2(aq) + H_2(g)$; the barium reaction is more vigorous than the calcium reaction.

Bài tập luyện tập

Explain why $MgCO_3$ decomposes at a much lower temperature than $BaCO_3$ on strong heating.

Lời giải chi tiết

Mg^{2+} is much smaller than Ba^{2+}, giving it a much higher charge density (polarising power). It distorts the large CO_3^{2-} ion strongly, weakening a C – O bond and allowing decomposition at a relatively low temperature. Ba^{2+}, being large, polarises CO_3^{2-} much less, so the carbonate remains stable to a much higher temperature.

Bài tập luyện tập

Which of the following Group 2 carbonates is expected to be the most thermally stable?

(A) $MgCO_3$ **(C)** $SrCO_3$

(B) $CaCO_3$ **(D)** $BaCO_3$

Lời giải chi tiết

(D). Thermal stability of Group 2 carbonates increases down the group, so $BaCO_3$ (largest cation, lowest charge density) is the most stable.

Bài tập luyện tập

Write the general equation for the thermal decomposition of a Group 2 nitrate, $M(NO_3)_2$.

Lời giải chi tiết

$$2M(NO_3)_2(s) \rightarrow 2MO(s) + 4NO_2(g) + O_2(g).$$

Bài tập luyện tập

3.28 g of $Mg(NO_3)_2$ ($M_r = 148$) is heated strongly until completely decomposed. Calculate the total volume of gas produced at r.t.p. ($24\,000$ cm^3 mol^{-1}).

Lời giải chi tiết

$$2Mg(NO_3)_2(s) \rightarrow 2MgO(s) + 4NO_2(g) + O_2(g).$$

$$n(Mg(NO_3)_2) = \frac{3.28}{148} = 0.02216 \text{ mol}.$$

Total gas per mole of $Mg(NO_3)_2 = \dfrac{4+1}{2} = 2.5$ mol gas per mol nitrate.

$$n(\text{gas}) = 0.02216 \times 2.5 = 0.0554 \text{ mol}, \qquad V = 0.0554 \times 24\,000 = \mathbf{1330} \text{ cm}^3 \text{ (3 s.f.)}.$$

Bài tập luyện tập

Which Group 2 hydroxide is the most soluble in water?

(A) $Mg(OH)_2$
(B) $Ca(OH)_2$
(C) $Sr(OH)_2$
(D) $Ba(OH)_2$

Lời giải chi tiết

(D). Group 2 hydroxide solubility increases down the group; $Ba(OH)_2$ is the most soluble.

Bài tập luyện tập

Which Group 2 sulfate is the most soluble in water?

(A) $MgSO_4$
(B) $CaSO_4$
(C) $SrSO_4$
(D) $BaSO_4$

Lời giải chi tiết

(A). Group 2 sulfate solubility decreases down the group; $MgSO_4$ is the most soluble.

Bài tập luyện tập

$K_{sp}(SrSO_4) = 3.2 \times 10^{-7}$ mol^2 dm^{-6}. Calculate the molar solubility of $SrSO_4$ in water.

Lời giải chi tiết

$$K_{sp} = s^2 \implies s = \sqrt{3.2 \times 10^{-7}} = \mathbf{5.66 \times 10^{-4}} \text{ mol dm}^{-3}.$$

Bài tập luyện tập

Explain why Group 2 hydroxide solubility *increases* down the group while Group 2 sulfate solubility *decreases* down the group.

Lời giải chi tiết

For the small OH^- anion, lattice enthalpy dominates the energetics and falls off faster than hydration enthalpy as the cation grows down the group, so the hydroxides become progressively more soluble. For the large SO_4^{2-} anion, lattice enthalpy changes comparatively little down the group, while the (negative) hydration enthalpy of the cation becomes markedly less exothermic as the cation gets larger; less energy is released on hydration relative to the energy needed to break the lattice, so the sulfates become progressively less soluble.

Bài tập luyện tập

Which cation gives a lilac flame colour?

(A) Na^+
(B) K^+
(C) Ca^{2+}
(D) Ba^{2+}

Lời giải chi tiết

(B). Potassium gives a lilac flame.

Bài tập luyện tập

A solid gives a crimson (deep red) flame test and, when heated strongly, releases a gas that relights a glowing splint together with brown fumes. Identify the cation present and the anion group most consistent with these observations.

Lời giải chi tiết

Crimson flame $\Rightarrow$ Sr^{2+}. Brown fumes (NO_2) plus a gas that relights a glowing splint (O_2) on strong heating are consistent with thermal decomposition of a **nitrate**: $2Sr(NO_3)_2(s) \rightarrow 2SrO(s) + 4NO_2(g) + O_2(g)$.

Bài tập luyện tập

State the flame colour used to identify each of the following ions: (a) Li^+, (b) Na^+, (c) Ba^{2+}.

Lời giải chi tiết

(a) Red (crimson). (b) Persistent yellow. (c) Apple-green (pale green).

Bài tập luyện tập

Explain why $Mg(OH)_2$ is a suitable ingredient for an antacid medicine despite being classified as an insoluble/sparingly soluble base.

Lời giải chi tiết

Because $Mg(OH)_2$ is only sparingly soluble, it releases OH^- ions slowly and in a controlled, low concentration as it reacts with stomach acid, $Mg(OH)_2(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + 2H_2O(l)$, neutralising excess acid gently without making the stomach contents dangerously (strongly) alkaline, which a highly soluble hydroxide would risk doing.

Bài tập luyện tập

State one use each of (a) $CaCO_3$, (b) $BaSO_4$ in industry or medicine.

Lời giải chi tiết

(a) $CaCO_3$ (limestone) is used in construction (aggregate, and as a raw material for cement/-mortar via CaO and $Ca(OH)_2$) and in agriculture to neutralise acidic soil. (b) $BaSO_4$ is used as a radiocontrast ("barium meal") agent for X-ray imaging of the digestive tract, since its extremely low solubility prevents toxic Ba^{2+} from entering the bloodstream while its heavy atoms still absorb X-rays well.

Bài tập luyện tập

Which statement about Period 3 electrical conductivity is correct?

(A) Chlorine conducts well because it is a diatomic gas

(B) Silicon's conductivity decreases with increasing temperature, like a metal

(C) Sodium, magnesium and aluminium all conduct due to delocalised electrons in a giant metallic lattice

(D) Argon conducts moderately due to its large atomic radius

Lời giải chi tiết

(C). Na, Mg and Al are giant metallic structures with mobile delocalised electrons; silicon's conductivity actually *increases* with temperature (opposite to a metal), and Cl_2 and Ar do not conduct at all.

Bài tập luyện tập

0.500 g of magnesium ribbon reacts completely with excess steam. Calculate the volume of hydrogen gas produced at r.t.p. ($24\,000$ cm^3 mol^{-1}; $A_r(\text{Mg}) = 24.3$).

Lời giải chi tiết

$$\text{Mg(s)} + \text{H}_2\text{O(g)} \rightarrow \text{MgO(s)} + \text{H}_2\text{(g)}.$$

$$n(\text{Mg}) = \frac{0.500}{24.3} = 0.02058 \text{ mol} = n(\text{H}_2).$$

$$V = 0.02058 \times 24\,000 = \textbf{494 cm}^3 \text{ (3 s.f.)}.$$

Bài tập luyện tập

Explain, in terms of bonding and structure, why the electrical conductivity of the Period 3 elements falls sharply between aluminium and silicon.

Lời giải chi tiết

Aluminium is a giant metallic structure with delocalised electrons free to move throughout the lattice, giving good conductivity. Silicon is a giant *covalent* structure in which every outer electron is held in a localised covalent bond between two atoms; there are no delocalised or mobile electrons available at room temperature except the very small number that gain enough thermal energy to escape their bonds, so silicon conducts only weakly (as a semiconductor), far less well than aluminium.

Bài tập luyện tập

Which of the following correctly ranks the reactivity of Ca, Sr and Ba with cold water, from least to most vigorous?

(A) Ba $<$ Sr $<$ Ca

(B) Ca $<$ Sr $<$ Ba

(C) Sr $<$ Ca $<$ Ba

(D) Ca $<$ Ba $<$ Sr

Lời giải chi tiết

Reactivity increases down Group 2, so Ca is least vigorous and Ba is most vigorous. **(B)**.

Group 17 and Transition Elements

Mục tiêu Unit: Tính chất vật lý và hoá học của các halogen (nhóm 17): xu hướng tính oxi hoá, phản ứng đẩy halogen, phản ứng với hiđro và kim loại, nhận biết ion halogenua, phản ứng dị li hoá (disproportionation) của clo; định nghĩa, cấu hình electron, trạng thái oxi hoá thay đổi, màu sắc và tính xúc tác của nguyên tố chuyển tiếp (A2); hình dạng và số phối trí của phức chất; phản ứng thế phối tử (ligand exchange); các phép chuẩn độ oxi hoá–khử (Fe^{2+}/MnO_4^- và I_2/thiosunfat).

10.1 Physical properties of the halogens

	F_2	Cl_2	Br_2	I_2
State at room temperature	gas	gas	liquid	solid
Colour	pale yellow	pale green	red-brown	grey-black (purple vapour on subliming)
Boiling point /°C	−188	−34	59	184

Table 1. Physical properties of the Group 17 elements (as diatomic molecules X_2).

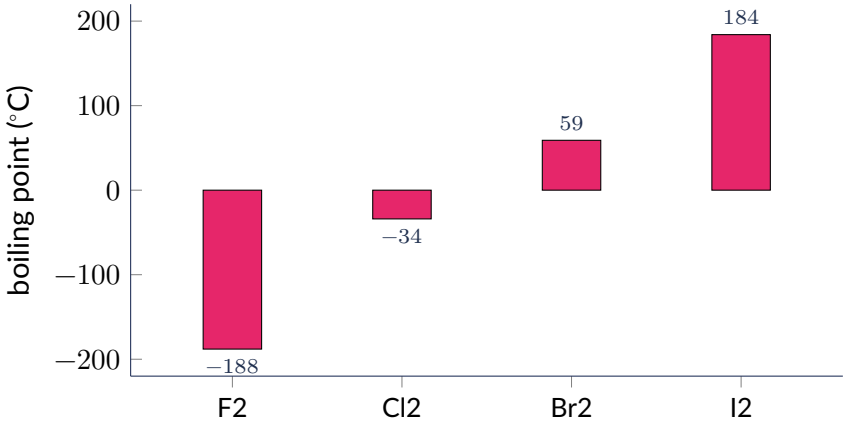

Figure 1. Boiling points of the halogens increase steadily down the group.

Trend in boiling point down Group 17

All halogens exist as simple diatomic molecules held together *between* molecules only by weak **London (instantaneous dipole–induced dipole) forces.** Down the group, each successive halogen molecule has **more electrons**, so the instantaneous dipoles are larger and the London forces stronger — more energy is needed to separate the molecules, so boiling point (and melting point) **increases** steadily from F_2 to I_2.

VN **GIẢI THÍCH TIẾNG VIỆT**

Halogen tồn tại dạng phân tử hai nguyên tử đơn giản, chỉ có lực Van der Waals (London) yếu **giữa** các phân tử. Xuống nhóm, số electron mỗi phân tử tăng → lực London mạnh dần → nhiệt độ sôi/nóng chảy **tăng dần** từ F_2 đến I_2.

10.2 Oxidising power and displacement reactions

Oxidising power decreases down Group 17

Oxidising power (ability to gain an electron, being reduced to X^-) **decreases** down the group: $F_2 > Cl_2 > Br_2 > I_2$. As atomic radius increases down the group, the incoming electron is added to a shell progressively further from (and more shielded from) the nucleus, so it is attracted less strongly, and oxidising power falls. A more oxidising halogen can therefore **displace** a less oxidising halide ion from solution.

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Tính oxi hoá halogen **giảm dần** xuống nhóm ($F_2 > Cl_2 > Br_2 > I_2$) vì bán kính nguyên tử tăng, electron thêm vào ở lớp vỏ xa hạt nhân và bị chắn nhiều hơn. Halogen có tính oxi hoá mạnh hơn sẽ **đẩy** được halogenua có tính oxi hoá yếu hơn ra khỏi dung dịch muối của nó.

Ví dụ 1 · Halogen displacement reactions

Chlorine water is added separately to aqueous potassium bromide and aqueous potassium iodide. Predict the observations and write balanced equations.

$$Cl_2(aq) + 2KBr(aq) \rightarrow 2KCl(aq) + Br_2(aq) \qquad (\text{colourless} \rightarrow \text{orange}),$$

$$Cl_2(aq) + 2KI(aq) \rightarrow 2KCl(aq) + I_2(aq) \qquad (\text{colourless} \rightarrow \text{brown}).$$

In both cases, Cl_2 (a stronger oxidising agent than Br_2 or I_2) is reduced to Cl^-, while Br^-/I^- is oxidised to the free halogen. By contrast, adding iodine water to potassium bromide or potassium chloride solution produces **no reaction**, because I_2 is the weakest oxidising agent of the three and cannot oxidise Br^- or Cl^-.

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Cl_2 đẩy được cả Br^- và I^- ra khỏi dung dịch (do tính oxi hoá mạnh hơn), nhưng I_2 không đẩy được Br^- hay Cl^- (tính oxi hoá yếu nhất trong ba halogen này).

10.2.1 Reaction with hydrogen

	F_2	Cl_2	Br_2
Reaction with H_2	explosive, even cold/dark	explosive in sunlight; slow in the dark	needs heat + catalyst; reaches equ

Table 2. Reactivity of the halogens with hydrogen gas, $X_2(g) + H_2(g) \rightleftharpoons 2HX(g)$, decreases down the group.

Ví dụ 2 · Halogen + metal — Fe with Cl_2 versus I_2

Explain, with equations, why heating iron in chlorine gas gives iron(III) chloride, whereas heating iron with iodine gives only iron(II) iodide.

$$2Fe(s) + 3Cl_2(g) \rightarrow 2FeCl_3(s), \qquad Fe(s) + I_2(s) \rightarrow FeI_2(s).$$

Cl_2 is a strong enough oxidising agent to oxidise iron all the way to its higher oxidation state, Fe^{3+}. I_2 is a much weaker oxidising agent (lowest in the group) and can only oxidise iron as far as Fe^{2+} — it is not strong enough to remove a third electron from iron to form Fe^{3+}.

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Cl_2 có tính oxi hoá đủ mạnh để oxi hoá Fe lên Fe^{3+} (tạo $FeCl_3$), trong khi I_2 yếu hơn nhiều, chỉ oxi hoá được Fe đến Fe^{2+} (tạo FeI_2).

10.3 Tests for halide ions

Silver nitrate / ammonia test

Aqueous $AgNO_3$ (acidified with dilute HNO_3 to prevent interference from carbonate or hydroxide ions) is added to a solution suspected of containing a halide ion. The precipitate colour identifies which halide is present; adding aqueous ammonia (dilute, then concentrated) distinguishes them further by **solubility of the silver halide in ammonia**, which depends on the strength of the Ag — X ionic/covalent-character bond (decreasing solubility as X^- becomes larger and more polarisable, down the group).

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Thêm $AgNO_3(aq)$ (đã axit hoá bằng HNO_3 loãng) vào dung dịch nghi ngờ chứa ion halogenua; màu kết tủa cho biết loại halogenua, còn amoniac loãng rồi đặc giúp phân biệt thêm dựa vào độ tan của muối bạc halogenua trong amoniac.

Halide	Precipitate with $AgNO_3(aq)$	Dilute $NH_3(aq)$	Concentrated $NH_3(aq)$
Cl^-	white	dissolves	dissolves
Br^-	cream	insoluble	dissolves
I^-	yellow	insoluble	insoluble

Table 3. The silver nitrate / ammonia test for halide ions.

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)\downarrow, \qquad AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Cl^-(aq).$$

Ví dụ 3 · Identifying an unknown halide

A colourless solution gives a cream precipitate with acidified $AgNO_3(aq)$. The precipitate does not dissolve in dilute ammonia but does dissolve in concentrated ammonia. Identify the halide ion present.

A **cream** precipitate that is insoluble in dilute NH_3 but soluble in concentrated NH_3 is the diagnostic result for AgBr — the halide present is **bromide**, Br^-.

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Kết tủa **màu kem**, không tan trong NH_3 loãng nhưng tan trong NH_3 đặc — đây là dấu hiệu đặc trưng của AgBr, tức ion halogenua có mặt là **bromua**.

10.3.1 The concentrated sulfuric acid reducing-power test

Reducing power of halide ions increases down the group

Adding concentrated H_2SO_4 to a solid sodium halide first produces steamy fumes of the hydrogen halide, $NaX(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HX(g)$. Whether *further* redox reaction occurs depends on whether X^- is a strong enough **reducing agent** to reduce the sulfur in H_2SO_4 (S oxidation number $+6$) to a lower oxidation state. Reducing power of the halide ions increases down the group ($Cl^- < Br^- < I^-$), since larger, more easily polarised (more loosely held outer-electron) halide ions give up an electron more readily.

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Tính khử của ion halogenua **tăng dần** xuống nhóm ($Cl^- < Br^- < I^-$) vì ion càng lớn càng dễ bị phân cực, electron ngoài cùng càng lỏng lẻo, càng dễ nhường electron (bị oxi hoá).

Halide	Observations with concentrated H_2SO_4
Cl^-	steamy white fumes of HCl only — Cl^- is too weak a reducing agent to reduce H_2SO_4 further
Br^-	steamy fumes of HBr, *plus* orange/brown fumes of Br_2 and choking, pungent SO_2 gas (S: $+6 \rightarrow +4$)
I^-	steamy fumes of HI, *plus* a black solid/purple vapour of I_2, a smell of rotten eggs (H_2S, S: $+6 \rightarrow -2$), and some yellow solid sulfur

Table 4. Reducing-power test: solid sodium halide + concentrated H_2SO_4.

Ví dụ 4 · Oxidation-number bookkeeping — reduction of H_2SO_4 by iodide

Solid NaI is warmed with concentrated H_2SO_4. Iodide reduces sulfur all the way from H_2SO_4 to H_2S. Deduce the oxidation number change of sulfur, the oxidation number change of iodine, and construct the balanced overall equation.

Oxidation number of S: in H_2SO_4, S $= +6$; in H_2S, S $= -2$. This is a change of 8 units — sulfur **gains 8 electrons** (reduced).
Oxidation number of I: in I^-, I $= -1$; in I_2, I $= 0$. Each iodide ion **loses 1 electron** (oxidised), so $8I^-$ are required to supply the 8 electrons needed by one S atom.
Balanced equation:

$$8HI + H_2SO_4 \rightarrow 4I_2 + H_2S + 4H_2O.$$

Check: H: $8 + 2 = 10$ (left) $= 4(H_2S) + 4 \times 2(H_2O) = 2 + 8 = 10$ (right) ☑. I: 8 (left) $= 4 \times 2 = 8$ (right) ☑. S: $1 = 1$ ☑. O: $4 = 4$ ☑.

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S trong H_2SO_4 có số oxi hoá $+6$, giảm xuống -2 trong H_2S (nhận 8 electron). Mỗi ion I^- (-1) bị oxi hoá thành I_2 (0), nhường 1 electron, nên cần 8 ion I^- để cân bằng electron với 1 nguyên tử S: $8HI + H_2SO_4 \rightarrow 4I_2 + H_2S + 4H_2O$.

(!) Lỗi thường gặp: Cl^- produces **only** steamy HCl fumes with concentrated H_2SO_4 — no further redox occurs, because Cl^- is not a strong enough reducing agent to reduce sulfur below $+6$. Do not expect SO_2 or S/H_2S to form from a chloride; these extra reduction products are seen only with the more easily oxidised Br^- and (especially) I^-.

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Lưu ý: Cl^- chỉ tạo khí HCl bốc khói, **không** có phản ứng oxi hoá–khử thêm vì tính khử của Cl^- quá yếu để khử lưu huỳnh xuống dưới $+6$ — chỉ Br^- và đặc biệt I^- mới đủ mạnh để tạo thêm SO_2/H_2S/S.

10.4 Disproportionation of chlorine and uses of chlorine

Disproportionation

Disproportionation is a redox reaction in which the *same* element is *simultaneously* oxidised and reduced. With **cold, dilute** sodium hydroxide, chlorine disproportionates to form the basis of household bleach:

$$Cl_2(g) + 2NaOH(aq) \rightarrow NaCl(aq) + NaOCl(aq) + H_2O(l).$$

Oxidation number of Cl_2 is 0; it is simultaneously **reduced** to Cl^- (-1, in NaCl) and **oxidised** to OCl^- ($+1$, sodium chlorate(I)/hypochlorite, in NaOCl, the active ingredient of bleach). With **hot, concentrated** NaOH, chlorine disproportionates further, to Cl^- (-1) and ClO_3^- ($+5$): $3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$.

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Dị li hoá (disproportionation): cùng một nguyên tố vừa bị oxi hoá vừa bị khử trong cùng một phản ứng. Clo phản ứng với NaOH lạnh, loãng tạo nước Javel (thành phần chính chất tẩy): $Cl_2 + 2NaOH \rightarrow NaCl + NaOCl + H_2O$, trong đó Cl_2 (số oxi hoá 0) vừa bị khử thành Cl^- (-1) vừa bị oxi hoá thành OCl^- ($+1$).

Uses of chlorine: (1) **water treatment** — small amounts of Cl_2 dissolved in water form the weak acid HOCl ($Cl_2(g) + H_2O(l) \rightleftharpoons HOCl(aq) + HCl(aq)$), which kills disease-causing bacteria in drinking-water supplies and swimming pools; (2) **manufacture of bleach** (sodium chlorate(I) solution) via the cold, dilute disproportionation reaction above; (3) **manufacture of PVC** (poly(chloroethene)) and other chlorinated organic chemicals, using chlorine as a key industrial feedstock.

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Ứng dụng của clo: **xử lý nước** (diệt khuẩn qua HOCl), **sản xuất chất tẩy trắng** (nước Javel), và **sản xuất PVC** cùng nhiều hoá chất hữu cơ chứa clo khác.

10.5 Transition elements: definition and electronic configuration (A2)

Definition of a transition element

A **transition element** is a d-block element that forms **at least one stable ion with a partially filled (incomplete) d subshell**. By this definition, **scandium** and **zinc** are d-block elements but are **not** classed as transition elements: Sc ($[Ar]3d^14s^2$) forms only the Sc^{3+} ion, which has configuration $[Ar]$ — an **empty** (d^0) d subshell; Zn ($[Ar]3d^{10}4s^2$) forms only the Zn^{2+} ion, which has configuration $[Ar]3d^{10}$ — a **completely full** d^{10} subshell. Neither ion ever has a *partially* filled d subshell.

GIẢI THÍCH TIẾNG VIỆT VN

Nguyên tố chuyển tiếp là nguyên tố khối d tạo được ít nhất một ion bền có phân lớp d **chưa lấp đầy hoàn toàn**. Sc chỉ tạo Sc^{3+} (d^0, phân lớp d rỗng hoàn toàn) và Zn chỉ tạo Zn^{2+} (d^{10}, phân lớp d đầy hoàn toàn) — cả hai đều **không bao giờ** có phân lớp d bán lấp đầy nên **không** được xem là nguyên tố chuyển tiếp, dù nằm trong khối d.

Ví dụ 5 · Why Sc and Zn are excluded from the transition series

Explain, using electron configurations, why scandium and zinc are not classified as transition elements even though they lie within the d-block.

Scandium's only common ion is Sc^{3+}: Sc has configuration $[Ar]3d^14s^2$, and forming Sc^{3+} removes all three outer electrons (the $4s^2$ and the single $3d^1$), leaving $[Ar]$ — no d electrons remain at all (d^0). Zinc's only common ion is Zn^{2+}: Zn has configuration $[Ar]3d^{10}4s^2$, and forming Zn^{2+} removes only the two $4s$ electrons, leaving $[Ar]3d^{10}$ — the d subshell is completely full. Since neither ion has a *partially* filled d subshell (one is empty, the other full), neither Sc nor Zn shows the characteristic properties (variable oxidation state, coloured ions, catalytic behaviour via partially-filled d orbitals) that define a true transition element.

GIẢI THÍCH TIẾNG VIỆT VN

Sc^{3+} có cấu hình $[Ar]$ (d^0, mất hết electron d), còn Zn^{2+} có cấu hình $[Ar]3d^{10}$ (phân lớp d đầy đủ) — cả hai đều không có phân lớp d bán lấp đầy nên không có các tính chất đặc trưng của nguyên tố chuyển tiếp (số oxi hoá thay đổi, ion có màu, tính xúc tác).

10.5.1 Variable oxidation states and colour of aqueous ions (A2)

Element	Common oxidation states	Typical colour of aqueous ion
Ti	$+3$, $+4$	Ti^{3+} purple; Ti^{4+}/TiO^{2+} colourless
V	$+2$, $+3$, $+4$, $+5$	V^{2+} violet; V^{3+} green; VO^{2+} blue; VO_2^+ yellow
Cr	$+2$, $+3$, $+6$	Cr^{2+} blue; Cr^{3+} green; CrO_4^{2-} yellow / $Cr_2O_7^{2-}$ orange
Mn	$+2$, $+4$, $+7$	Mn^{2+} very pale pink; MnO_2 black solid; MnO_4^- deep purple
Fe	$+2$, $+3$	Fe^{2+} pale green; Fe^{3+} yellow-brown
Cu	$+1$, $+2$	Cu^+ (unstable in water, disproportionates); Cu^{2+} blue

Table 5. Common oxidation states and characteristic colours for selected transition elements.

Origin of colour: d–d electron transitions

In a free (gaseous) transition-metal ion, all five d orbitals have the same energy (are **degenerate**). When **ligands** bond to the metal ion, their electron lone pairs repel the d electrons unevenly, **splitting** the d orbitals into two (or more) slightly different energy levels. If the d subshell is *partially* filled, an electron can absorb a photon of visible light and jump from the lower to the higher d level (a **d–d transition**); the *complementary* colour of the light *not* absorbed is what we observe as the colour of the ion. Ions with an *empty* (d^0, e.g. Sc^{3+}) or *completely full* (d^{10}, e.g. Zn^{2+}) d subshell cannot undergo a d–d transition (there is no different-energy d orbital to promote an electron into, or no vacancy to receive it), so their compounds are **colourless (white)**.

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Trong ion tự do, 5 orbital d có cùng năng lượng. Khi phối tử liên kết, chúng đẩy electron d không đều, làm **tách mức năng lượng** các orbital d. Nếu phân lớp d **bán lấp đầy**, electron có

thể hấp thụ ánh sáng khả kiến để nhảy lên mức năng lượng d cao hơn (chuyển mức d–d); màu ta thấy là màu **bù** của ánh sáng bị hấp thụ. Ion có d^0 (Sc^{3+}) hay d^{10} (Zn^{2+}) không thể có chuyển mức d–d nên hợp chất của chúng **không màu**.

Ví dụ 6 · The vanadium "traffic lights" — oxidation state and colour together

An acidified solution of ammonium vanadate(V), containing yellow VO_2^+, is reduced by excess zinc metal. Describe the sequence of colour changes observed and relate each colour to the oxidation state of vanadium.

Zinc progressively reduces vanadium through each accessible oxidation state:

$$VO_2^+\ (+5,\ \text{yellow}) \xrightarrow{Zn} VO^{2+}\ (+4,\ \text{blue}) \xrightarrow{Zn} V^{3+}\ (+3,\ \text{green}) \xrightarrow{Zn} V^{2+}\ (+2,\ \text{violet}).$$

Each step is a one-electron reduction (Zn supplying the electrons, being oxidised to Zn^{2+}); the colour changes because both the oxidation state *and* the identity/geometry of ligands around vanadium change, altering the d-orbital splitting and hence which wavelengths of visible light are absorbed.

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Kẽm khử dần vanadi qua các mức oxi hoá: VO_2^+ ($+5$, vàng) → VO^{2+} ($+4$, xanh dương) → V^{3+} ($+3$, xanh lục) → V^{2+} ($+2$, tím) — mỗi bước là một phản ứng khử 1 electron, minh hoạ rõ tính chất "nhiều trạng thái oxi hoá, mỗi trạng thái một màu" của nguyên tố chuyển tiếp.

10.5.2 Catalysis by transition metals and their compounds (A2)

Transition metals and their compounds are effective catalysts because their **variable oxidation states** allow them to be oxidised and reduced reversibly, providing an alternative, lower-activation-energy reaction pathway (**homogeneous** catalysis), or because their **partially filled** d **orbitals** allow reactant molecules to bond (adsorb) to the metal's surface, weakening bonds within them (**heterogeneous** catalysis).

Ví dụ 7 · V_2O_5 in the Contact process (heterogeneous, variable oxidation state)

In the Contact process for manufacturing sulfuric acid, V_2O_5 catalyses the oxidation of SO_2 to SO_3. Show, with equations, how vanadium's variable oxidation state allows this catalytic cycle to work.

$$SO_2(g) + V_2O_5(s) \rightarrow SO_3(g) + V_2O_4(s) \qquad (V:\ +5 \rightarrow +4,\ V_2O_5 \text{ reduced}),$$

$$V_2O_4(s) + \tfrac{1}{2}O_2(g) \rightarrow V_2O_5(s) \qquad (V:\ +4 \rightarrow +5,\ \text{catalyst regenerated}).$$

Overall:

$$2SO_2(g) + O_2(g) \xrightarrow[\text{catalyst}]{V_2O_5,\ \sim 450^\circ C} 2SO_3(g).$$

Vanadium cycles between $+5$ and $+4$, first being reduced as it oxidises SO_2, then being reoxidised by O_2 back to its original state — so it is regenerated, unchanged overall, exactly as a catalyst must be.

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V_2O_5 xúc tác oxi hoá $SO_2 \rightarrow SO_3$ trong quá trình Contact nhờ vanadi chuyển đổi thuận nghịch giữa số oxi hoá $+5$ và $+4$: bị khử khi oxi hoá SO_2, rồi được oxi hoá trở lại bởi O_2 để tái sinh xúc tác — không đổi về bản chất sau cả chu trình.

Ví dụ 8 · Nickel-catalysed hydrogenation of alkenes (heterogeneous, surface adsorption)

Margarine manufacture converts liquid unsaturated vegetable oils into solid saturated fats by catalytic hydrogenation. Write a general equation and explain the role of the nickel catalyst.

$$CH_2=CH_2 \xrightarrow[\text{Ni catalyst}]{150^\circ C} CH_3CH_3$$

(shown for ethene as a simple model of a C = C double bond in an unsaturated fat). Solid nickel provides a surface onto which both H_2 and the alkene **adsorb**; adsorption weakens the H — H bond and the π bond of C = C, allowing hydrogen atoms to add across the double bond on the metal surface at a much lower temperature than would otherwise be needed, after which the saturated product **desorbs**, freeing the surface for further reaction. Unlike V_2O_5 above, this is a **heterogeneous** catalytic mechanism based on surface adsorption rather than a change in the metal's own oxidation state.

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Ni xúc tác hiđro hoá liên kết đôi C = C trong dầu thực vật không no thành chất béo no (sản xuất bơ thực vật): H_2 và anken hấp phụ lên bề mặt Ni, làm yếu liên kết H — H và liên kết π để phản ứng cộng H_2 dễ xảy ra hơn ở nhiệt độ thấp hơn — đây là cơ chế xúc tác dị thể qua hấp phụ bề mặt, khác với cơ chế đổi số oxi hoá của V_2O_5.

Autocatalysis is also seen with transition metal ions: in the reaction of acidified MnO_4^- with $C_2O_4^{2-}$ (ethanedioate/oxalate) — $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$ — the initial rate is slow (both reactant ions are negatively charged, hindering their mutual approach), but the Mn^{2+} *product* itself catalyses further reaction, so the rate visibly speeds up partway through before eventually slowing again as reactants are consumed.

10.6 Shapes and coordination numbers of complex ions (A2)

Complex ions, ligands and coordination number

A **complex ion** consists of a central transition-metal ion surrounded by a number of **ligands** — ions or molecules with at least one **lone pair of electrons** — bonded to the metal through **dative (coordinate) covalent bonds**. The **coordination number** is the number of dative bonds (points of attachment) to the central ion, and it depends strongly on the **size** of the ligand: small ligands such as H_2O and NH_3 typically give **6-coordinate, octahedral** complexes, whereas the larger Cl^- ion typically gives only **4-coordinate, tetrahedral** complexes (fewer, larger ligands can pack around the metal ion before they begin to repel each other too strongly). A small number of complexes (e.g. some Pt^{2+} and Ni^{2+} complexes, including the anticancer drug cis-platin, $[PtCl_2(NH_3)_2]$) are instead **4-coordinate but square planar**.

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Phức chất gồm ion kim loại chuyển tiếp trung tâm liên kết với các **phối tử** (có cặp electron

chưa liên kết) qua liên kết **cho–nhận (phối trí)**. **Số phối trí** phụ thuộc kích thước phối tử: phối tử nhỏ (H_2O, NH_3) thường cho phức **8 mặt (octahedral), số phối trí 6**; phối tử lớn hơn (Cl^-) thường chỉ cho phức **tứ diện (tetrahedral), số phối trí 4** do không gian hạn chế. Một số ít phức (VD Pt^{2+}, Ni^{2+}, như thuốc cisplatin) có dạng **vuông phẳng (square planar)**, cũng số phối trí 4 nhưng hình dạng khác tứ diện.

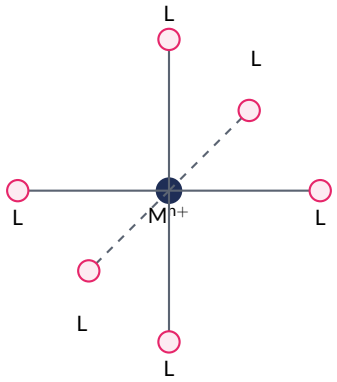

Figure 2. Schematic octahedral complex ion: six ligands (L = H_2O or NH_3) arranged symmetrically around the central metal ion M^{n+}, giving coordination number 6.

Ví dụ 9 · Predicting coordination number and shape from ligand size

$Co^{2+}(aq)$ forms a pink, 6-coordinate complex with water, $[Co(H_2O)_6]^{2+}$, but on adding concentrated hydrochloric acid it forms a blue, 4-coordinate complex, $[CoCl_4]^{2-}$. Explain this change in coordination number and shape.

H_2O is a small ligand, so six can pack around the Co^{2+} ion, giving an **octahedral**, 6-coordinate complex. Cl^- is a considerably **larger** ion; only four Cl^- ligands can fit around Co^{2+} before they begin to repel one another too strongly, so the complex formed is **tetrahedral**, 4-coordinate.

VN **GIẢI THÍCH TIẾNG VIỆT**

H_2O nhỏ nên 6 phân tử xếp quanh Co^{2+} tạo phức bát diện; Cl^- lớn hơn nhiều nên chỉ 4 ion xếp được quanh tâm kim loại trước khi đẩy nhau quá mạnh, tạo phức tứ diện.

10.7 Ligand exchange and variable oxidation state (A2)

Ligand substitution/exchange reactions

In a **ligand exchange (substitution)** reaction, one type of ligand in a complex ion is replaced by another, often with a visible **colour change** and sometimes a change in **coordination number and shape**, because the new ligand has different electron-donating ability (different d-orbital splitting) and/or a different size.

VN **GIẢI THÍCH TIẾNG VIỆT**

Phản ứng **thế phối tử** thay một loại phối tử trong phức bằng loại khác, thường kèm theo **đổi màu** và có thể **đổi cả số phối trí, hình dạng** vì phối tử mới có khả năng cho electron khác (tách mức d khác) và/hoặc kích thước khác.

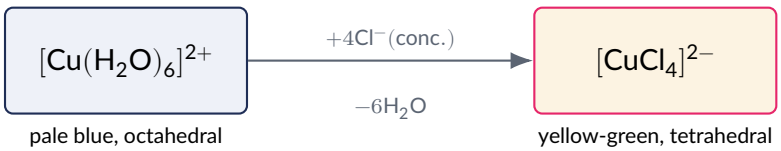

Figure 3. Ligand exchange: excess concentrated Cl^- displaces H_2O from the octahedral copper(II) complex, forming a tetrahedral complex with a marked colour change.

Ví dụ 10 · Ligand exchange: hexaaquacopper(II) with excess concentrated chloride

Write the equation for the reaction of aqueous copper(II) sulfate with excess concentrated hydrochloric acid, and describe the observed colour and shape change.

$$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq) + 6H_2O(l).$$

The pale blue, **octahedral** aqua-complex is converted to a yellow-green, **tetrahedral** chloro-complex. The coordination number falls from 6 to 4 because Cl^- is a much larger ligand than H_2O, so fewer can coordinate around the Cu^{2+} centre; the colour changes because the different ligand and different geometry alter the splitting of the d orbitals, changing which wavelengths of visible light are absorbed.

VN **GIẢI THÍCH TIẾNG VIỆT**

$[Cu(H_2O)_6]^{2+}$ (xanh nhạt, bát diện) chuyển thành $[CuCl_4]^{2-}$ (vàng-lục, tứ diện) khi thêm dư Cl^- đặc — số phối trí giảm từ 6 xuống 4 vì Cl^- lớn hơn H_2O nhiều, và màu đổi vì mức tách năng lượng d thay đổi theo phối tử và hình dạng mới.

Ví dụ 11 · Partial ligand substitution — hexaaquacopper(II) with aqueous ammonia

Aqueous ammonia is added dropwise, then in excess, to aqueous copper(II) sulfate. Describe what is observed at each stage and write equations.

With a **small volume** of $NH_3(aq)$ (acting as a base), a pale blue **precipitate** of copper(II) hydroxide forms:

$$[Cu(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \rightarrow Cu(OH)_2(H_2O)_4(s) \downarrow + 2NH_4^+(aq).$$

With **excess concentrated** $NH_3(aq)$, the precipitate **redissolves** to give a deep (royal) blue solution, as four of the six water ligands are substituted by ammonia (a *partial* ligand exchange — the complex remains octahedral, still 6-coordinate):

$$Cu(OH)_2(H_2O)_4(s) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 2OH^-(aq) + 2H_2O(l).$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Thêm $NH_3(aq)$ ít vào $Cu^{2+}(aq)$ tạo kết tủa xanh nhạt $Cu(OH)_2$ (amoniac đóng vai trò bazơ); thêm dư NH_3 đặc, kết tủa tan trở lại tạo dung dịch **xanh lam đậm** do 4 trong 6 phối tử nước bị thay bằng NH_3 (thế phối tử **một phần**), phức vẫn giữ số phối trí 6, bát diện.

10.8 Redox titrations involving transition metal ions (A2)

Ví dụ 12 · Standardising an iron(II) solution against potassium manganate(VII)

25.0 cm^3 of an acidified iron(II) sulfate solution of unknown concentration requires 18.20 cm^3 of 0.0200 mol dm^{-3} $KMnO_4(aq)$ for complete oxidation (self-indicating end point: colourless to permanent very pale pink/purple). Calculate $[Fe^{2+}]$.

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l).$$

$$n(MnO_4^-) = 0.0200 \times \frac{18.20}{1000} = 3.64 \times 10^{-4} \text{ mol}.$$

Mole ratio $Fe^{2+} : MnO_4^- = 5 : 1$:

$$n(Fe^{2+}) = 5 \times 3.64 \times 10^{-4} = 1.82 \times 10^{-3} \text{ mol}.$$

$$[Fe^{2+}] = \frac{1.82 \times 10^{-3}}{25.0/1000} = \mathbf{0.0728} \text{ mol dm}^{-3}.$$

Ví dụ 13 · Iodine–thiosulfate titration

A 25.0 cm^3 sample of aqueous iodine of unknown concentration is titrated with 0.100 mol dm^{-3} $Na_2S_2O_3(aq)$, using starch indicator added near the end point (the deep blue-black starch–iodine colour disappears sharply to colourless at the end point). 21.40 cm^3 of thiosulfate solution is required. Calculate the original concentration of iodine.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq).$$

$$n(S_2O_3^{2-}) = 0.100 \times \frac{21.40}{1000} = 2.140 \times 10^{-3} \text{ mol}.$$

Mole ratio $I_2 : S_2O_3^{2-} = 1 : 2$:

$$n(I_2) = \frac{2.140 \times 10^{-3}}{2} = 1.070 \times 10^{-3} \text{ mol}.$$

$$[I_2] = \frac{1.070 \times 10^{-3}}{25.0/1000} = \mathbf{0.0428} \text{ mol dm}^{-3}.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Chuẩn độ Fe^{2+} bằng $KMnO_4$: tỉ lệ mol $Fe^{2+} : MnO_4^- = 5 : 1$, điểm dừng nhận biết bằng chính màu tím của $KMnO_4$ dư (tự chỉ thị). Chuẩn độ I_2 bằng $Na_2S_2O_3$: tỉ lệ mol $I_2 : S_2O_3^{2-} = 1 : 2$, dùng chỉ thị hồ tinh bột thêm gần điểm dừng (mất màu xanh đen đột ngột tại điểm dừng, không thêm quá sớm vì hồ tinh bột giữ I_2 chặt gây sai điểm dừng).

(!) Lỗi thường gặp: In an iodine–thiosulfate titration, starch indicator must be added **only near the end point** (when the iodine colour has already faded to pale straw-yellow), not at the start. Added too early, starch binds iodine very strongly, which can make the end point sluggish and less sharp, and can lead to an over-estimate of the volume of thiosulfate needed.

VN **GIẢI THÍCH TIẾNG VIỆT**

Hồ tinh bột chỉ thêm **gần điểm dừng** (khi màu iot đã nhạt vàng rơm), không thêm ngay từ đầu, vì tinh bột giữ iot rất chặt, làm điểm dừng kém sắc nét và có thể làm sai lệch kết quả chuẩn độ.

Ôn tập nhanh

Ôn tập nhanh: (1) Tính chất vật lý halogen: trạng thái/màu/nhiệt độ sôi tăng dần $F_2 \to I_2$ do lực London tăng theo số electron. (2) Tính oxi hoá giảm dần $F_2 > Cl_2 > Br_2 > I_2$ — halogen mạnh đẩy được halogenua yếu hơn; phản ứng với H_2 và với kim loại (Fe+$Cl_2 \to FeCl_3$ nhưng Fe+$I_2 \to FeI_2$) minh hoạ xu hướng này. (3) Nhận biết halogenua: $AgNO_3$ cho kết tủa trắng (Cl^-)/kem (Br^-)/vàng (I^-), phân biệt thêm bằng độ tan trong NH_3 loãng/đặc; thử bằng H_2SO_4 đặc cho thấy tính khử tăng dần $Cl^- < Br^- < I^-$ (chỉ I^- khử được S xuống -2 tạo H_2S). (4) Clo dị li hoá trong NaOH lạnh loãng tạo nước Javel. (5) Nguyên tố chuyển tiếp: khối d có ít nhất một ion bền d bán lấp đầy (Sc, Zn bị loại trừ); số oxi hoá thay đổi, ion có màu (chuyển mức d–d khi phối tử tách mức năng lượng d), và tính xúc tác (đổi số oxi hoá — V_2O_5; hoặc hấp phụ bề mặt — Ni) đều là hệ quả của phân lớp d bán lấp đầy. (6) Số phối trí phụ thuộc kích thước phối tử: H_2O/NH_3 nhỏ $\to$ bát diện (6); Cl^- lớn $\to$ tứ diện (4); một số phức vuông phẳng (VD cisplatin). (7) Thế phối tử đổi màu và có thể đổi hình dạng/số phối trí (VD $[Cu(H_2O)_6]^{2+} \to [CuCl_4]^{2-}$; thế một phần với NH_3). (8) Chuẩn độ oxi hoá–khử: Fe^{2+}/MnO_4^- (tỉ lệ 5:1, tự chỉ thị) và $I_2/S_2O_3^{2-}$ (tỉ lệ 1:2, chỉ thị hồ tinh bột thêm gần điểm dừng).

Practice

Bài tập luyện tập

Which of the following correctly ranks the oxidising power of the halogens, from strongest to weakest?

(A) $I_2 > Br_2 > Cl_2 > F_2$

(B) $F_2 > Cl_2 > Br_2 > I_2$

(C) $Cl_2 > F_2 > I_2 > Br_2$

(D) $Br_2 > Cl_2 > F_2 > I_2$

Lời giải chi tiết

Oxidising power decreases down the group as atomic radius increases. **(B)**.

Bài tập luyện tập

Chlorine water is added to separate samples of aqueous sodium bromide and aqueous sodium chloride. State and explain what is observed in each case.

Lời giải chi tiết

With NaBr(aq): the solution turns orange as Cl_2 (stronger oxidising agent) displaces bromine, $Cl_2(aq) + 2NaBr(aq) \to 2NaCl(aq) + Br_2(aq)$. With NaCl(aq): **no reaction** occurs, since chlorine cannot displace itself/oxidise Cl^- (already the same element).

Bài tập luyện tập

Explain why iodine water added to aqueous potassium bromide produces no visible reaction.

Lời giải chi tiết

I_2 is a weaker oxidising agent than Br_2 (oxidising power decreases down the group), so I_2 cannot oxidise Br^- to Br_2 — no displacement reaction occurs.

Bài tập luyện tập

Explain why the boiling point of the halogens increases steadily down the group, from F_2 to I_2.

Lời giải chi tiết

The halogens are simple diatomic molecules held together only by weak London (van der Waals) forces between molecules. Down the group, each molecule has progressively more electrons, giving larger instantaneous dipoles and stronger London forces between molecules, so more energy (a higher temperature) is needed to separate them and boil the substance.

Bài tập luyện tập

Which halogen reacts explosively with hydrogen even in the cold and dark?

(A) F_2
(C) Br_2
(B) Cl_2
(D) I_2

Lời giải chi tiết

(A). Fluorine is the most reactive halogen and reacts explosively with hydrogen under all conditions, including in the cold and dark.

Bài tập luyện tập

Write balanced equations for the reaction of iron with (a) chlorine gas and (b) iodine, and explain why the iron products differ.

Lời giải chi tiết

(a) $2Fe(s) + 3Cl_2(g) \rightarrow 2FeCl_3(s)$. (b) $Fe(s) + I_2(s) \rightarrow FeI_2(s)$. Chlorine is a strong enough oxidising agent to oxidise iron fully to Fe^{3+}, but iodine (the weakest oxidiser in the group) can only oxidise iron as far as Fe^{2+}.

Bài tập luyện tập

Which colour precipitate forms when aqueous silver nitrate is added to a solution containing iodide ions?

(A) White
(C) Yellow
(B) Cream
(D) No precipitate forms

Lời giải chi tiết

(C). AgI is a yellow precipitate.

Bài tập luyện tập

A white precipitate forms when acidified $AgNO_3(aq)$ is added to an unknown solution. The precipitate dissolves completely in dilute ammonia. Identify the halide ion present, and write an equation for the reaction with ammonia.

Lời giải chi tiết

White precipitate that dissolves in *dilute* ammonia $\Rightarrow Cl^-$ present (AgCl).

$$AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Cl^-(aq).$$

Bài tập luyện tập

Solid sodium chloride is warmed with concentrated sulfuric acid. Which observation is expected?

(A) Steamy white fumes of HCl only

(B) Steamy fumes plus orange Br_2 vapour

(C) Steamy fumes plus a smell of rotten eggs

(D) A black solid and purple vapour with no fumes

Lời giải chi tiết

(A). Cl^- is too weak a reducing agent to reduce sulfur further, so only HCl fumes are produced: $NaCl(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HCl(g)$.

Bài tập luyện tập

When solid NaBr is warmed with concentrated H_2SO_4, both HBr fumes and some SO_2 gas are observed. Deduce the oxidation number change of sulfur and explain why bromide (unlike chloride) can bring this about.

Lời giải chi tiết

Sulfur's oxidation number falls from $+6$ (in H_2SO_4) to $+4$ (in SO_2), a gain of 2 electrons. Br^- is a stronger reducing agent than Cl^- (larger, more easily polarised ion, more loosely held outer electrons), so it is able to reduce sulfur partially, being itself oxidised to Br_2, whereas Cl^- is not a strong enough reducing agent to do this.

Bài tập luyện tập

Deduce the change in oxidation number of sulfur when concentrated H_2SO_4 oxidises I^- all the way to H_2S, and write the balanced overall equation.

Lời giải chi tiết

Sulfur: $+6$ (in H_2SO_4) $\rightarrow -2$ (in H_2S), a change of 8 units (gains 8 electrons).

$$8HI + H_2SO_4 \rightarrow 4I_2 + H_2S + 4H_2O.$$

Bài tập luyện tập

Write the equation for the reaction of chlorine with cold, dilute sodium hydroxide, and identify which type of redox reaction this is.

Lời giải chi tiết

$$Cl_2(g) + 2NaOH(aq) \rightarrow NaCl(aq) + NaOCl(aq) + H_2O(l).$$

This is a **disproportionation** reaction: chlorine (oxidation number 0) is simultaneously reduced to Cl^- (-1) and oxidised to OCl^- ($+1$).

Bài tập luyện tập

State one use of chlorine in industry or public health.

Lời giải chi tiết

Any one of: water treatment (kills bacteria via HOCl); manufacture of bleach (sodium chlorate(I) solution); manufacture of PVC and other chlorinated organic chemicals.

Bài tập luyện tập

Which of the following ions is *not* classified as a transition element ion, and why? (A2)

(A) Fe^{2+} **(C)** Sc^{3+}

(B) Cu^{2+} **(D)** V^{3+}

Lời giải chi tiết

(C). Sc^{3+} has configuration $[Ar]$ — an empty (d^0) d subshell, never partially filled — so scandium does not meet the definition of a transition element.

Bài tập luyện tập

Explain, with reference to electron configuration, why zinc is excluded from the transition elements even though it is a d-block metal. (A2)

Lời giải chi tiết

Zinc's only common ion, Zn^{2+}, has configuration $[Ar]3d^{10}$ — a completely full d subshell. Since a transition element must form at least one ion with a *partially* filled d subshell, and zinc's d subshell is always either full (Zn, $3d^{10}4s^2$) or, in the ion, still full (Zn^{2+}, $3d^{10}$), zinc does not qualify.

Bài tập luyện tập

Explain why Cu^{2+} compounds are coloured but Zn^{2+} compounds are colourless. (A2)

Lời giải chi tiết

Cu^{2+} ($3d^9$) has a *partially* filled d subshell, so ligand bonding splits its d orbitals into two energy levels and an electron can absorb a photon of visible light to jump between them (d–d transition); the unabsorbed (complementary) light gives the observed blue colour. Zn^{2+} ($3d^{10}$) has a completely full d subshell, so no d–d transition is possible (there is no vacancy for an electron to be promoted into) and Zn^{2+} compounds are colourless.

Bài tập luyện tập

In the vanadium "traffic lights" reduction by zinc, which colour corresponds to vanadium in the $+3$ oxidation state? (A2)

(A) Yellow
(B) Blue
(C) Green
(D) Violet

Lời giải chi tiết

(C). V^{3+} is green.

Bài tập luyện tập

Explain, using changes in oxidation state, how V_2O_5 acts as a catalyst in the Contact process for the oxidation of SO_2 to SO_3. (A2)

Lời giải chi tiết

V_2O_5 first oxidises SO_2 to SO_3 while vanadium is itself reduced from $+5$ to $+4$ ($SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4$); the resulting V_2O_4 is then reoxidised back to V_2O_5 by oxygen ($V_2O_4 + \frac{1}{2}O_2 \rightarrow V_2O_5$). Vanadium cycles between $+5$ and $+4$ and is regenerated unchanged overall, providing a lower-activation-energy pathway for $2SO_2 + O_2 \rightarrow 2SO_3$.

Bài tập luyện tập

Describe, in terms of surface adsorption, how nickel catalyses the hydrogenation of alkenes in margarine manufacture. (A2)

Lời giải chi tiết

Both H_2 and the unsaturated (alkene-containing) molecule adsorb onto active sites on the nickel surface. Adsorption weakens the $H-H$ bond and the π bond of the $C=C$ double bond, allowing hydrogen atoms to add across the double bond at a lower temperature than otherwise required. The saturated product then desorbs from the surface, freeing the active site for further reaction.

Bài tập luyện tập

Which ligand would be expected to form a 4-coordinate, tetrahedral complex with a transition metal ion, rather than a 6-coordinate, octahedral one? (A2)

(A) H_2O

(B) NH_3

(C) Cl^-

(D) None of these — all give octahedral complexes

Lời giải chi tiết

(C). Cl^- is a considerably larger ligand than H_2O or NH_3, so typically only four can coordinate around the metal ion, giving a tetrahedral (rather than octahedral) complex.

Bài tập luyện tập

Write the equation for the ligand exchange reaction between $[Cu(H_2O)_6]^{2+}(aq)$ and excess concentrated hydrochloric acid, and describe the colour and shape change. (A2)

Lời giải chi tiết

$$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq) + 6H_2O(l).$$

The colour changes from pale blue (octahedral, 6-coordinate) to yellow-green (tetrahedral, 4-coordinate), because Cl^- is a much larger ligand than H_2O, so only four can coordinate, and the different ligand/geometry changes the d-orbital splitting.

Bài tập luyện tập

Describe what is observed when aqueous ammonia is added dropwise, then in large excess, to aqueous copper(II) sulfate. (A2)

Lời giải chi tiết

With a small volume of $NH_3(aq)$, a pale blue precipitate of $Cu(OH)_2$ forms (ammonia acting as a base): $[Cu(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \rightarrow Cu(OH)_2(H_2O)_4(s) + 2NH_4^+(aq)$. With excess concentrated $NH_3(aq)$, the precipitate redissolves to give a deep blue solution, as four water ligands are substituted by ammonia to form the octahedral complex $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

Bài tập luyện tập

25.0 cm^3 of acidified $FeSO_4(aq)$ requires 22.50 cm^3 of 0.0180 mol dm^{-3} $KMnO_4(aq)$ for complete oxidation. Calculate $[Fe^{2+}]$. (A2)

Lời giải chi tiết

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O.$$

$$n(MnO_4^-) = 0.0180 \times \frac{22.50}{1000} = 4.05 \times 10^{-4}\ \text{mol}, \qquad n(Fe^{2+}) = 5 \times 4.05 \times 10^{-4} = 2.025 \times 10^{-3}\ \text{mol}.$$

$$[Fe^{2+}] = \frac{2.025 \times 10^{-3}}{25.0/1000} = \mathbf{0.0810}\ \text{mol dm}^{-3}.$$

Bài tập luyện tập

In the reaction $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$, what is the change in oxidation number of manganese? (A2)

(A) $+7$ to $+2$ (gain of 5 electrons)
(C) $+2$ to $+7$ (loss of 5 electrons)
(B) $+7$ to $+4$ (gain of 3 electrons)
(D) No change

Lời giải chi tiết

(A). Mn falls from $+7$ (in MnO_4^-) to $+2$ (in Mn^{2+}), a gain of 5 electrons, oxidising 5 Fe^{2+} ions (each losing 1 electron).

Bài tập luyện tập

A 25.0 cm^3 sample of aqueous iodine requires 16.00 cm^3 of 0.0500 mol dm^{-3} $Na_2S_2O_3(aq)$ to reach the starch end point. Calculate the original concentration of I_2. (A2)

Lời giải chi tiết

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}.$$

$$n(S_2O_3^{2-}) = 0.0500 \times \frac{16.00}{1000} = 8.00 \times 10^{-4}\ \text{mol}, \qquad n(I_2) = \frac{8.00 \times 10^{-4}}{2} = 4.00 \times 10^{-4}\ \text{mol}.$$

$$[I_2] = \frac{4.00 \times 10^{-4}}{25.0/1000} = \mathbf{0.0160}\ \text{mol dm}^{-3}.$$

Bài tập luyện tập

Explain why starch indicator should be added only near the end point of an iodine–thiosulfate titration, not at the start. (A2)

Lời giải chi tiết

Starch binds iodine very strongly, forming the characteristic deep blue-black complex. If added too early (while a high concentration of iodine is still present), this strong binding can make the release of the last traces of iodine near the end point sluggish, giving a less sharp colour change and potentially requiring more titrant than is actually needed, reducing the accuracy of the titration.

Bài tập luyện tập

Which pair correctly matches a transition metal ion with its characteristic aqueous colour? (A2)

(A) Fe^{2+} — yellow-brown
(C) Cu^{2+} — blue
(B) Fe^{3+} — pale green
(D) Mn^{2+} — deep purple

Lời giải chi tiết

(C). $Cu^{2+}(aq)$ is blue; Fe^{2+} is pale green (not (A)), Fe^{3+} is yellow-brown (not (B)), and Mn^{2+} is very pale pink while MnO_4^- (not Mn^{2+}) is deep purple (not (D)).

Bài tập luyện tập

State the coordination number and shape of $[Fe(H_2O)_6]^{2+}$ and of $[CuCl_4]^{2-}$. (A2)

Lời giải chi tiết

$[Fe(H_2O)_6]^{2+}$: coordination number 6, octahedral (six small H_2O ligands). $[CuCl_4]^{2-}$: coordination number 4, tetrahedral (four larger Cl^- ligands).

Bài tập luyện tập

Which statement about catalysis by transition metals is correct? (A2)

(A) Catalysis always involves a change in the metal's oxidation state

(B) Catalysis can occur either via a change in oxidation state (homogeneous) or via surface adsorption using partially filled d orbitals (heterogeneous)

(C) Transition metal catalysts are always used up during the reaction

(D) Only d^0 ions can act as catalysts

Lời giải chi tiết

(B). Both mechanisms occur: e.g. V_2O_5 (change in oxidation state) and Ni (surface adsorption, no oxidation-state change of the metal itself in simple hydrogenation).

Nitrogen and Sulfur Chemistry

Mục tiêu Unit: Quá trình Haber sản xuất amoniac và nguyên lý thoả hiệp Le Chatelier giữa hiệu suất cân bằng và tốc độ phản ứng; các ứng dụng công nghiệp của amoniac (axit nitric, phân bón); sự hình thành oxit nitơ trong động cơ đốt trong, khói quang hoá và vai trò của bộ chuyển đổi xúc tác; mưa axit từ SO_2 và NO_x; quá trình Contact sản xuất axit sulfuric qua oleum; các phép thử định tính ion amoni, sulfat, nitrat và sulfit/SO_2; vận dụng kỹ năng tính K_p (đã học ở Chương 7) vào bối cảnh công nghiệp thực tế.

11.1 The Haber process: manufacture of ammonia

Ammonia is manufactured industrially by the direct combination of nitrogen and hydrogen gases:

$$\mathrm{N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)}, \qquad \Delta H \approx -92 \text{ kJ mol}^{-1} \text{ (exothermic)}.$$

The nitrogen is obtained from the fractional distillation of liquefied air, and the hydrogen mainly from the reaction of natural gas (methane) with steam. Because the reaction is reversible and reaches a genuine **dynamic equilibrium** (see Chapter 7), the conditions chosen for the industrial reactor are governed by Le Chatelier's principle — but, crucially, they are *not* simply the conditions that would give the theoretically highest possible % yield.

Yield versus rate: two different questions

% yield (position of equilibrium) asks: *how far* does the reaction proceed before the forward and reverse rates become equal? This is governed entirely by Le Chatelier's principle and by K_p/K_c, both of which depend only on concentration/pressure changes (shifting position, not K) and temperature (changing both position *and* K).

Rate (kinetics) asks: *how quickly* does the system reach whatever equilibrium position it is heading toward? This is governed by activation energy, temperature, and the presence of a catalyst — and is entirely independent of the equilibrium constant. A reaction can have a very favourable equilibrium position (high % yield) yet be commercially useless if it takes years to get there.

Industrial conditions are chosen to **compromise** between these two separate demands: sacrificing some theoretical % yield in exchange for a commercially viable *rate*, since a catalyst can speed up the approach to equilibrium but can never improve the equilibrium position itself.

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Cần phân biệt rõ hai khái niệm: **hiệu suất (% yield)** — vị trí cân bằng, do Le Chatelier và K_p/K_c quyết định; và **tốc độ phản ứng** — do năng lượng hoạt hoá, nhiệt độ và xúc tác quyết định, hoàn toàn độc lập với giá trị K. Điều kiện công nghiệp luôn là một **sự thoả hiệp**: chấp nhận hi sinh một phần hiệu suất lý thuyết để đổi lấy tốc độ đạt cân bằng đủ nhanh về mặt kinh tế, vì xúc tác chỉ giúp đạt cân bằng nhanh hơn chứ không bao giờ cải thiện được vị trí cân bằng.

11.1.1 Compromise conditions in the Haber process

Condition	Value used	Effect predicted by Le Chatelier alone	Practical reason for the compromise
Temperature	$\sim 450^{\circ}$C	Lower T favours the exothermic forward reaction → higher % yield	A much lower T gives an uneconomically slow rate; 450°C balances yield against a commercially viable rate
Pressure	~ 200 atm	Higher P favours the side with fewer gas moles ($4 \rightarrow 2$) → higher % yield	Pressures far higher than 200 atm require disproportionately expensive, thick-walled plant and carry safety risk
Catalyst	Fe, promoted with K_2O/Al_2O_3	No effect on position of equilibrium or K_p at all	Speeds up attainment of equilibrium at the moderate 450°C chosen, avoiding the need for an even higher (yield-reducing) temperature

Table 1. Haber process: compromise conditions, with unreacted N_2 and H_2 recycled through the reactor (rather than discarded) to raise the overall conversion beyond the modest single-pass % yield.

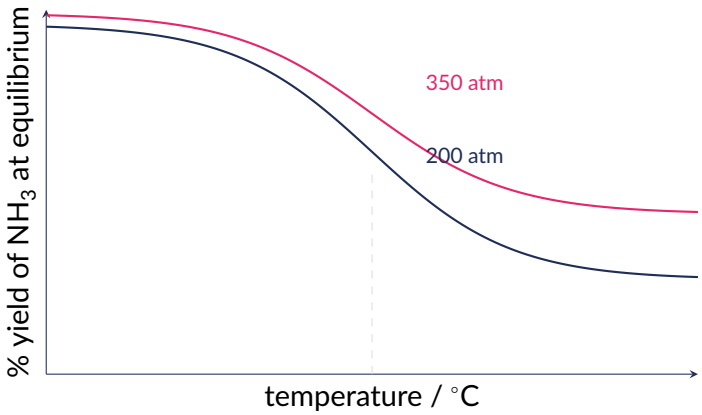

Figure 1. % yield of NH_3 at equilibrium falls steadily as temperature rises (exothermic equilibrium), at any fixed pressure; raising the pressure shifts the whole curve upward (fewer gas moles on the product side). The plant operates at the marked moderate temperature — a compromise, not the point of maximum theoretical yield.

Ví dụ 1 · Applying Le Chatelier to predict changes in % yield

Starting from the standard Haber process conditions (450°C, 200 atm, Fe catalyst), predict the effect on the equilibrium % yield of NH_3 of (a) increasing the pressure to 350 atm at constant temperature, and (b) increasing the temperature to 550°C at constant pressure.

(a) Pressure increase. The forward reaction converts 4 mol of gas into 2 mol of gas ($\Delta n = -2$). By Le Chatelier's principle, increasing the total pressure shifts the equilibrium toward the side with *fewer* gas moles — the NH_3 side. **The % yield of NH_3 increases.** (The rate of reaching this new, higher-yield equilibrium also increases, since higher pressure means more frequent molecular collisions — a bonus rather than a trade-off in this case.)

(b) Temperature increase. The forward reaction is exothermic, so by Le Chatelier's principle raising the temperature shifts the equilibrium toward the *endothermic* (reverse) direction. **The % yield of NH_3 decreases**, even though the *rate* of reaching equilibrium increases at the higher temperature. This illustrates precisely why 450°C is a compromise: a still lower temperature would raise the yield further but at an unacceptable cost in rate.

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(a) Tăng áp suất → cân bằng dịch chuyển về phía ít mol khí hơn (phía NH_3) → hiệu suất % tăng, đồng thời tốc độ đạt cân bằng cũng tăng (va chạm dày hơn) — không có sự đánh đổi ở trường hợp này. (b) Tăng nhiệt độ → phản ứng thuận toả nhiệt nên cân bằng dịch chuyển về chiều thu nhiệt (nghịch) → hiệu suất % giảm, dù tốc độ phản ứng tăng — đây chính là lý do vì sao 450°C là một sự thoả hiệp.

Ví dụ 2 · K_p for the Haber process at a stated % conversion

A stoichiometric feed of 1.00 mol N_2 and 3.00 mol H_2 reaches equilibrium at 450°C and 200 atm, with 20.0% of the N_2 converted. Calculate K_p.

Let x = mol N_2 reacted $= 0.200 \times 1.00 = 0.200$ mol.

	N_2	H_2	NH_3
Initial (mol)	1.00	3.00	0
Change (mol)	-0.200	-0.600	$+0.400$
Equilibrium (mol)	0.800	2.40	0.400

Total moles at equilibrium $= 0.800 + 2.40 + 0.400 = 3.60$ mol. Mole fractions:

$$x(N_2) = \frac{0.800}{3.60} = 0.2222, \quad x(H_2) = \frac{2.40}{3.60} = 0.6667, \quad x(NH_3) = \frac{0.400}{3.60} = 0.1111.$$

Partial pressures at $P_{\text{total}} = 200$ atm:

$$p(N_2) = 44.4 \text{ atm}, \quad p(H_2) = 133 \text{ atm}, \quad p(NH_3) = 22.2 \text{ atm}.$$

$$K_p = \frac{p(NH_3)^2}{p(N_2)\,p(H_2)^3} = \frac{22.2^2}{44.4 \times 133^3} = \frac{493}{44.4 \times 2.35 \times 10^6} = 4.7 \times 10^{-6} \text{ atm}^{-2}.$$

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Cách làm hoàn toàn giống Chương 7: lập bảng ICE theo số mol, tính tổng số mol, suy ra phân số mol, nhân với áp suất tổng để được áp suất riêng phần, rồi thay vào biểu thức K_p. Đơn vị K_p ở đây là atm^{-2} vì $\Delta n = 2 - 4 = -2$.

11.1.2 Uses of ammonia: nitric acid and fertilisers

The great majority of ammonia manufactured is converted into solid **ammonium salts** (e.g. NH_4NO_3, $(NH_4)_2SO_4$) for use as **fertilisers**, supplying nitrogen for plant growth. A significant fraction is also oxidised catalytically to make **nitric acid**, HNO_3, via the **Ostwald process**.

The Ostwald process (three catalytic/aqueous steps):

$$\text{(1)}\quad 4NH_3(g) + 5O_2(g) \xrightarrow[800^\circ C]{\text{Pt/Rh catalyst}} 4NO(g) + 6H_2O(g)$$

$$\text{(2)}\quad 2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

$$\text{(3)}\quad 3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$$

The NO regenerated in step (3) is recycled back into step (2). Ignoring this internal recycling, the three steps combine into the overall summary equation

$$NH_3(g) + 2O_2(g) \rightarrow HNO_3(aq) + H_2O(l),$$

useful for direct stoichiometric calculations.

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Quá trình Ostwald oxy hoá NH_3 qua ba bước (xúc tác Pt/Rh ở nhiệt độ cao, rồi oxy hoá tiếp NO thành NO_2, rồi NO_2 phản ứng với nước tạo HNO_3 và tái sinh một phần NO). Có thể gộp ba bước (bỏ qua phần NO tái tuần hoàn) thành một phương trình tổng quát $NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$ để tính toán khối lượng nhanh.

Ví dụ 3 · Mass of nitric acid from ammonia

Using the overall equation $NH_3(g) + 2O_2(g) \rightarrow HNO_3(aq) + H_2O(l)$, calculate the maximum mass of pure HNO_3 obtainable from 340 kg of ammonia ($M_r(NH_3) = 17.0$, $M_r(HNO_3) = 63.0$).

$$n(NH_3) = \frac{340\,000 \text{ g}}{17.0 \text{ g mol}^{-1}} = 20\,000 \text{ mol}.$$

Since the overall equation has a $1:1$ ratio between NH_3 and HNO_3, $n(HNO_3) = 20\,000$ mol.

$$m(HNO_3) = 20\,000 \times 63.0 = 1\,260\,000 \text{ g} = \mathbf{1260} \text{ kg}.$$

11.2 Nitrogen oxides and atmospheric pollution

11.2.1 Formation of NO and NO_2

Inside the cylinders of an internal combustion engine, the very high temperatures and electrical spark provide enough energy to force the otherwise highly unreactive N_2 and O_2 of the air to combine directly:

$$N_2(g) + O_2(g) \rightarrow 2NO(g), \qquad \Delta H \approx +180 \text{ kJ mol}^{-1} \text{ (endothermic)}.$$

Why NO is formed in engines but not in the open air

This reaction is strongly **endothermic** and has a very high activation energy, because it requires breaking the exceptionally strong N ≡ N triple bond. At ordinary atmospheric temperatures, an immeasurably tiny fraction of N_2/O_2 collisions carry enough energy to react, so essentially no NO forms. The much higher temperatures reached briefly during fuel combustion (and the spark itself) provide the activation energy needed, so NO is formed as an unwanted by-product of combustion rather than as the fuel's intended reaction.

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Phản ứng $N_2 + O_2 \rightarrow 2NO$ thu nhiệt mạnh và có năng lượng hoạt hoá rất cao (do phải phá vỡ liên kết ba $N \equiv N$ cực bền), nên hầu như không xảy ra ở nhiệt độ khí quyển bình thường. Nhiệt độ cực cao trong xy-lanh động cơ đốt trong cung cấp đủ năng lượng hoạt hoá, khiến NO hình thành như một sản phẩm phụ không mong muốn của quá trình đốt nhiên liệu.

Once released into the air (which contains excess O_2), NO is readily oxidised further, this time exothermically and without any special conditions:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g).$$

Ví dụ 4 · Stoichiometry of NO oxidation

Exhaust gas contains 0.0400 mol of NO. Calculate the maximum amount (in mol) of NO_2 that can form, and the minimum amount of O_2 required, assuming $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ goes to completion.

By the $2 : 1 : 2$ mole ratio: $n(NO_2) = n(NO) = 0.0400$ mol; $n(O_2)_{\text{min}} = \frac{1}{2} \times 0.0400 =$ **0.0200** mol.

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NO_2 có màu nâu đỏ đặc trưng và là chất gây ô nhiễm chính trong **khói quang hoá** (photochemical smog): dưới tác dụng ánh sáng, NO_2 phân li thành NO và nguyên tử oxy tự do, nguyên tử oxy này phản ứng với O_2 tạo ozone tầng thấp (O_3) và với hydrocarbon chưa cháy hết tạo ra các chất ô nhiễm thứ cấp gây kích ứng mắt, đường hô hấp.

Sunlight causes NO_2 to photodissociate, and the resulting reactive species combine with unburnt hydrocarbons from vehicle exhaust to generate a mixture of secondary pollutants (including ground-level ozone) known as **photochemical smog** — a significant urban air-quality problem, especially in hot, sunny, traffic-dense conditions with limited air movement.

11.2.2 Catalytic converters

Modern vehicle exhaust systems are fitted with a **catalytic converter**, a ceramic honeycomb coated with a thin layer of platinum, rhodium and palladium (Pt/Rh/Pd). As exhaust gases pass over this huge surface area, CO and NO — both toxic/polluting products of incomplete or high-temperature combustion — are converted simultaneously into harmless N_2 and CO_2:

$$2CO(g) + 2NO(g) \rightarrow N_2(g) + 2CO_2(g).$$

Ví dụ 5 · Oxidation-number analysis of the catalytic converter reaction

Verify that $2CO(g) + 2NO(g) \rightarrow N_2(g) + 2CO_2(g)$ is a redox reaction by assigning oxidation numbers, and identify the oxidising and reducing agents.

Carbon: in CO, oxygen is -2, so $C = +2$. In CO_2, $C = +4$. Carbon's oxidation number rises $+2 \rightarrow +4$: **carbon is oxidised** (each C atom loses 2 electrons).

Nitrogen: in NO, oxygen is -2, so $N = +2$. In N_2 (an element), $N = 0$. Nitrogen's oxidation number falls $+2 \rightarrow 0$: **nitrogen is reduced** (each N atom gains 2 electrons).

Electron balance check: 2 C atoms each lose 2 electrons $= 4$ electrons lost; 2 N atoms each gain 2 electrons $= 4$ electrons gained. The electrons lost and gained balance exactly, confirming the equation is correctly balanced as a redox process. **CO is the reducing agent (it is oxidised); NO is the oxidising agent (it is reduced).** The Pt/Rh/Pd catalyst does not appear in

the equation — it simply provides a lower-activation-energy surface pathway for this reaction, which is otherwise far too slow to occur to any useful extent at exhaust-pipe temperatures.

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Bộ chuyển đổi xúc tác (Pt/Rh/Pd) biến hai khí độc/gây ô nhiễm CO và NO thành N_2 và CO_2 vô hại. Đây là phản ứng oxy hoá khử: C từ $+2 \to +4$ (bị oxy hoá), N từ $+2 \to 0$ (bị khử); số electron mất và nhận bằng nhau (đều bằng 4), xác nhận phương trình cân bằng đúng.

11.2.3 Acid rain

Both SO_2 (see §11.3) and the nitrogen oxides NO/NO_2 (collectively NO_x) dissolve in atmospheric water droplets and are oxidised, forming strong or moderately strong acids that fall as **acid rain**:

$$SO_2(g) + H_2O(l) \to H_2SO_3(aq)\ \text{(sulfurous acid)}, \qquad 2H_2SO_3(aq) + O_2(g) \to 2H_2SO_4(aq)\ \text{(sulfuric acid)},$$

$$3NO_2(g) + H_2O(l) \to 2HNO_3(aq) + NO(g)\ \text{(nitric acid, as in Ostwald process step 3)}.$$

Acid rain corrodes limestone and marble buildings/statues (which are largely $CaCO_3$), lowers the pH of lakes and rivers (harming fish and other aquatic life), and can leach aluminium ions from soil into waterways, which are toxic to fish.

Ví dụ 6 · Stoichiometry of acid-rain corrosion of limestone

Acid rain reacts with marble ($CaCO_3$, $M_r = 100$) according to $CaCO_3(s) + H_2SO_4(aq) \to CaSO_4(aq) + H_2O(l) + CO_2(g)$. Calculate the mass of $CaCO_3$ that would be dissolved by 2.00 dm^3 of acid rain of concentration 1.00×10^{-4} mol dm^{-3} in H_2SO_4.

$$n(H_2SO_4) = 2.00 \times 1.00 \times 10^{-4} = 2.00 \times 10^{-4}\ \text{mol}.$$

By the $1:1$ ratio, $n(CaCO_3) = 2.00 \times 10^{-4}$ mol.

$$m(CaCO_3) = 2.00 \times 10^{-4} \times 100 = \mathbf{0.0200}\ \text{g}.$$

Although this is a very small mass per 2 dm^3 of rain, sustained acid rainfall over years causes measurable, cumulative erosion of stone buildings and monuments.

Oxide	Main source	Formation conditions	Environmental role
NO	Internal combustion engines, lightning	High T + spark; endothermic direct combination of N_2/O_2	Precursor to NO_2 and acid rain
NO_2	Rapid oxidation of NO in air	Spontaneous, exothermic, no special conditions needed	Photochemical smog; forms HNO_3 in rain
SO_2	Combustion of sulfur-containing fossil fuels; roasting sulfide ores	Combustion / roasting in air	Forms H_2SO_3/H_2SO_4 in rain; decolourises $KMnO_4$

Table 2. Sources, formation and environmental significance of the principal nitrogen and sulfur oxide pollutants.

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SO_2 và NO_x hoà tan và bị oxy hoá trong hơi nước khí quyển tạo thành axit sulfuric/sulfurơ và axit nitric — gọi chung là **mưa axit**. Tác hại: ăn mòn công trình đá vôi/đá cẩm thạch ($CaCO_3$),

làm axit hoá ao hồ gây hại sinh vật thuỷ sinh, và rửa trôi ion nhôm độc hại vào nguồn nước.

11.3 Sulfur dioxide and the Contact process

Sulfuric acid, one of the most widely manufactured industrial chemicals, is made from sulfur (or from SO_2 recovered from roasting sulfide ores) via the **Contact process**, in three stages.

Stage 1 — burn sulfur: $S(s) + O_2(g) \rightarrow SO_2(g)$

Stage 2 — catalytic oxidation (the key equilibrium):

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g), \qquad \Delta H \approx -196\,\text{kJ mol}^{-1}\,\text{(exothermic)}, \qquad V_2O_5\,\text{catalyst},\ \sim 450^\circ\text{C},\ 1\text{–}2\,\text{atm}.$

Stage 3 — conversion of SO_3 to sulfuric acid, via oleum (see below).

Compromise conditions in the Contact process

- **Temperature $\sim 450^\circ$C:** the forward reaction is exothermic, so a lower temperature would (by Le Chatelier) give an even higher equilibrium % yield of SO_3; but the rate would be uneconomically slow. 450°C is chosen as a compromise between yield and rate, exactly as in the Haber process.
- **Pressure only 1–2 atm (*not* very high):** the forward reaction reduces gas moles ($3 \rightarrow 2$), so higher pressure would (by Le Chatelier) push the % yield even closer to 100%. However, at 450°C with the V_2O_5 catalyst, the % conversion already achieved at ordinary, only mildly elevated pressure is very high (typically $\sim$ 97–98%). Since so little further yield could be gained, the extra capital cost, energy cost and safety risk of high-pressure plant is not economically justified — unlike in the Haber process, where the uncatalysed/lower-pressure yield is far more modest and the pressure increase is worth the expense.
- V_2O_5 **catalyst:** does not shift the equilibrium position or change K_p; it simply allows the moderate 450°C chosen above to give an acceptably fast rate.

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Quá trình Contact cũng là một thoả hiệp Le Chatelier tương tự Haber: 450°C cân bằng giữa hiệu suất (phản ứng toả nhiệt, nhiệt độ thấp cho hiệu suất cao hơn) và tốc độ. Điểm khác biệt quan trọng: áp suất chỉ cần 1–2 atm (không cần cao như Haber) vì với xúc tác V_2O_5 ở 450°C, hiệu suất chuyển hoá đã đạt tới ~ 97–98% ngay ở áp suất gần khí quyển — tăng áp suất thêm sẽ tốn kém mà lợi ích hiệu suất thu được là không đáng kể.

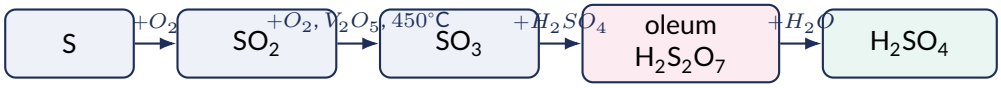

Figure 2. The Contact process route from elemental sulfur to sulfuric acid, showing the deliberate two-step absorption of SO_3 via oleum rather than direct addition of water.

(!) Lỗi thường gặp: SO_3 is **not** simply bubbled directly into water on an industrial scale, even though $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$ looks like the obvious equation. The reaction of SO_3 with water is extremely exothermic and forms a fine, dense, corrosive **acid mist/aerosol** of H_2SO_4 droplets rather than a clean liquid — this mist is very difficult and hazardous to condense and collect safely. Instead, SO_3 is dissolved in concentrated H_2SO_4 to form **oleum** (fuming sulfuric acid, $H_2S_2O_7$), which is then diluted carefully and controllably with water to regenerate

concentrated H_2SO_4:

$$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)\ \text{(oleum)}, \qquad H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l).$$

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Không cho SO_3 phản ứng trực tiếp với nước trong công nghiệp vì phản ứng toả nhiệt quá mạnh, tạo ra **sương mù axit** khó thu hồi và nguy hiểm. Thay vào đó, SO_3 được hấp thụ vào H_2SO_4 đặc tạo **oleum** ($H_2S_2O_7$), sau đó pha loãng có kiểm soát với nước để tạo lại H_2SO_4 đặc.

Ví dụ 7 · Equilibrium yield calculation for the Contact process

2.00 mol SO_2 and 1.00 mol O_2 are sealed in a vessel and allowed to reach equilibrium for $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, at which point 80.0% of the SO_2 has been converted to SO_3. The total equilibrium pressure is 2.00 atm. Calculate K_p.

Moles of SO_2 reacted $= 0.800 \times 2.00 = 1.60$ mol; moles of O_2 reacted (by the $2:1$ ratio) $= 0.800$ mol; moles of SO_3 formed $= 1.60$ mol.

	SO_2	O_2	SO_3
Initial (mol)	2.00	1.00	0
Change (mol)	-1.60	-0.800	$+1.60$
Equilibrium (mol)	0.400	0.200	1.60

Total moles $= 0.400 + 0.200 + 1.60 = 2.20$ mol. Mole fractions:

$$x(SO_2) = \tfrac{0.400}{2.20} = 0.1818, \quad x(O_2) = \tfrac{0.200}{2.20} = 0.0909, \quad x(SO_3) = \tfrac{1.60}{2.20} = 0.7273.$$

At $P_{\text{total}} = 2.00$ atm: $p(SO_2) = 0.364$ atm, $p(O_2) = 0.182$ atm, $p(SO_3) = 1.45$ atm.

$$K_p = \frac{p(SO_3)^2}{p(SO_2)^2\, p(O_2)} = \frac{1.45^2}{0.364^2 \times 0.182} = \frac{2.12}{0.0241} = \mathbf{88.0}\ \text{atm}^{-1}.$$

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Cách làm hoàn toàn giống các bài toán K_p ở Chương 7: lập ICE theo số mol, tính tổng mol tại cân bằng, suy ra phân số mol, nhân với áp suất tổng để có áp suất riêng phần, rồi thay vào biểu thức K_p. Giá trị $K_p \approx 88.0$ atm^{-1} lớn hơn 1 phản ánh đúng thực tế: cân bằng Contact process nghiêng mạnh về phía sản phẩm SO_3 ở điều kiện này.

Ví dụ 8 · Mass of sulfuric acid produced via the oleum route

Calculate the mass of pure H_2SO_4 that can ultimately be produced from 500 kg of SO_3 ($M_r(SO_3) = 80.0$, $M_r(H_2SO_4) = 98.0$), via the oleum route.

Combining $SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$ with $H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$: one of the two H_2SO_4 molecules produced in the second step is simply the H_2SO_4 that was "borrowed" to absorb the SO_3 in the first step, so the *net new* acid formed corresponds to the overall equation $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$ (1:1), even though industrially the reaction never proceeds by this direct, hazardous route.

$$n(SO_3) = \frac{500\,000\ \text{g}}{80.0\ \text{g mol}^{-1}} = 6250\ \text{mol}.$$

$$n(H_2SO_4)_{\text{net new}} = 6250\ \text{mol} \implies m(H_2SO_4) = 6250 \times 98.0 = 612\,500\ \text{g} = \mathbf{612.5}\ \text{kg}.$$

11.4 Qualitative tests for nitrogen- and sulfur-containing ions

Ion tested	Test procedure	Positive observation
NH_4^+	Warm with NaOH(aq); hold damp red litmus paper in the gas evolved	Litmus turns **blue**; pungent gas (NH_3) detected
SO_4^{2-}	Acidify with dilute HCl (or HNO_3), then add $BaCl_2$(aq)	**White precipitate** ($BaSO_4$), insoluble in the acid
NO_3^-	Add NaOH(aq), then aluminium foil/powder; warm gently; test the gas with damp red litmus	Litmus turns **blue** (NH_3 produced by reduction of NO_3^-)
SO_3^{2-}/SO_2	Add to acidified $KMnO_4$(aq) (or acidified $K_2Cr_2O_7$(aq))	$KMnO_4$: purple **decolourises**; $K_2Cr_2O_7$: orange turns **green**

Table 3. Summary of qualitative tests for the ammonium, sulfate, nitrate and sulfite ions.

VN **GIẢI THÍCH TIẾNG VIỆT**

Bốn phép thử quan trọng: (1) NH_4^+: đun với NaOH, khí thoát ra làm quỳ tím ẩm hoá xanh. (2) SO_4^{2-}: axit hoá rồi thêm $BaCl_2$, kết tủa trắng $BaSO_4$ không tan trong axit (phân biệt với CO_3^{2-}/SO_3^{2-} — các kết tủa bari của chúng tan trong axit). (3) NO_3^-: thêm NaOH rồi bột nhôm, đun nhẹ — đây là "phép thử khử", khí NH_3 sinh ra làm quỳ tím ẩm hoá xanh. (4) SO_3^{2-}/SO_2: làm mất màu tím $KMnO_4$ axit hoá (hoặc màu cam $K_2Cr_2O_7$ chuyển xanh lá) do bị oxy hoá thành sulfat.

Ví dụ 9 · Identifying an unknown ammonium salt

A white solid is warmed with NaOH(aq). A gas is evolved which turns damp red litmus paper blue and has a sharp, pungent smell. State the ion confirmed present, write an ionic equation for the reaction, and name one common salt that would give this result.

The gas is NH_3, confirming the presence of the **ammonium ion,** NH_4^+.

$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(g) + H_2O(l).$$

Any ammonium salt would give this result, e.g. **ammonium chloride,** NH_4Cl, or ammonium sulfate, $(NH_4)_2SO_4$.

Ví dụ 10 · The nitrate reduction test — verifying the balanced ionic equation

In the nitrate test, aluminium reduces NO_3^- to NH_3 in hot alkaline solution, with aluminium itself being oxidised to the aluminate ion, AlO_2^-. Verify that $3NO_3^-(aq) + 8Al(s) + 5OH^-(aq) + 2H_2O(l) \rightarrow 3NH_3(g) + 8AlO_2^-(aq)$ is correctly balanced, using oxidation numbers.

Nitrogen: in NO_3^-, N $= +5$; in NH_3, N $= -3$. Change per N atom $= 8$ electrons *gained* (reduction). For 3 N atoms: $3 \times 8 = 24$ electrons gained.

Aluminium: in Al(s), oxidation number $= 0$; in AlO_2^-, Al $= +3$. Change per Al atom $= 3$ electrons *lost* (oxidation). For 8 Al atoms: $8 \times 3 = 24$ electrons lost.

Electrons lost (24) equal electrons gained (24) ✓. Atom and charge balance can also be confirmed: N: $3 = 3$; Al: $8 = 8$; O: left $(3 \times 3) + 5 + 2 = 16$, right $8 \times 2 = 16$ ✓; H: left $5 + 4 = 9$, right $3 \times 3 = 9$ ✓; charge: left $-3 - 5 = -8$, right -8 (from AlO_2^-) ✓. **The equation is fully balanced.**

VN **GIẢI THÍCH TIẾNG VIỆT**

Ở mức AS/A2, chỉ cần mô tả quan sát (khí làm quỳ tím ẩm hoá xanh ⇒ có NO_3^-) là đủ để trả lời phép thử nitrat; phương trình ion đầy đủ ở Ví dụ 10 chỉ là phần mở rộng để luyện tập cân bằng oxy hoá khử phức tạp.

Ví dụ 11 · Redox test for SO_2/sulfite with acidified $KMnO_4$

Gaseous SO_2 is bubbled through acidified potassium manganate(VII). The purple colour is decolourised. Derive the overall balanced ionic equation from the two half-equations below, and state the oxidation number change of sulfur.

Oxidation: $SO_2(aq) + 2H_2O(l) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$
Reduction: $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

Balance electrons: multiply the oxidation half-equation by 5 and the reduction half-equation by 2 (giving $10\ e^-$ in each):

$$5SO_2 + 10H_2O + 2MnO_4^- + 16H^+ \rightarrow 5SO_4^{2-} + 20H^+ + 2Mn^{2+} + 8H_2O.$$

Cancelling $8H_2O$ and $16H^+$ common to both sides:

$$\mathbf{5SO_2(aq) + 2MnO_4^-(aq) + 2H_2O(l) \rightarrow 5SO_4^{2-}(aq) + 2Mn^{2+}(aq) + 4H^+(aq)}.$$

Sulfur's oxidation number rises from $+4$ (in SO_2) to $+6$ (in SO_4^{2-}): **sulfur is oxidised**, confirming SO_2 acts as the reducing agent that decolourises MnO_4^- (Mn: $+7 \rightarrow +2$, reduced).

VN **GIẢI THÍCH TIẾNG VIỆT**

SO_2/SO_3^{2-} bị oxy hoá thành sulfat (S : $+4 \rightarrow +6$), làm mất màu tím của $KMnO_4$ axit hoá (Mn: $+7 \rightarrow +2$) hoặc chuyển màu cam của $K_2Cr_2O_7$ sang xanh lá (Cr: $+6 \rightarrow +3$) — đây là phép thử định tính đáng tin cậy cho SO_2/sulfit.

Ví dụ 12 · Distinguishing sulfate from sulfite/carbonate

A solution gives a white precipitate with $BaCl_2(aq)$. Explain how you would determine whether the ion present is SO_4^{2-}, SO_3^{2-}, or CO_3^{2-}.

First add dilute HCl (or HNO_3) to a fresh sample of the *original* solution, *before* adding $BaCl_2$: $BaSO_3$ and $BaCO_3$ both **dissolve** in dilute acid (with effervescence of SO_2 or CO_3^{2-} releasing CO_2 gas respectively), whereas $BaSO_4$ does **not** dissolve in dilute acid. So: acidify first, then add $BaCl_2(aq)$ — a white precipitate that persists confirms SO_4^{2-} (this is the standard test, cross-referenced with the Group 2 chemistry of barium salts). If no precipitate forms until *after* acidification is skipped (i.e. only forms with neutral $BaCl_2$ and dissolves in the presence of acid), the ion was SO_3^{2-} or CO_3^{2-} instead, distinguishable further by testing the gas released on acidification (SO_2 decolourises acidified $KMnO_4$; CO_2 turns limewater milky).

VN **GIẢI THÍCH TIẾNG VIỆT**

Luôn axit hoá **trước** khi thêm $BaCl_2$: $BaSO_4$ không tan trong axit loãng (kết tủa trắng bền), còn $BaSO_3$ và $BaCO_3$ đều tan trong axit loãng (giải phóng khí). Đây là điểm mấu chốt để phân biệt sulfat với sulfit/carbonat, và liên hệ trực tiếp tới tính chất muối bari đã học ở phần hoá học Nhóm 2 (Group 2).

Ôn tập nhanh

Ôn tập nhanh: (1) Haber: $N_2 + 3H_2 \rightleftharpoons 2NH_3$, $\Delta H \approx -92$ kJ mol^{-1}; 450°C/200 atm/Fe là thoả hiệp giữa hiệu suất (Le Chatelier) và tốc độ (động học) — hai khái niệm độc lập. (2) Ostwald: $NH_3 \rightarrow NO \rightarrow NO_2 \rightarrow HNO_3$, dùng cho phân bón và axit nitric. (3) NO hình thành trong động cơ (thu nhiệt, cần T cao); NO bị oxy hoá nhanh thành NO_2 (toả nhiệt) gây khói quang hoá. (4) Bộ chuyển đổi xúc tác: $2CO + 2NO \rightarrow N_2 + 2CO_2$ (C: $+2 \rightarrow +4$; N: $+2 \rightarrow 0$). (5) Mưa axit: $SO_2/NO_x \rightarrow H_2SO_3/H_2SO_4/HNO_3$, ăn mòn đá vôi, axit hoá hồ. (6) Contact: $2SO_2 + O_2 \rightleftharpoons 2SO_3$, V_2O_5, 450°C, chỉ 1–2 atm (đã đạt hiệu suất cao, không cần áp suất lớn như Haber); SO_3 hấp thụ qua oleum, không hoà tan trực tiếp vào nước (tránh sương mù axit). (7) Bốn phép thử: NH_4^+ (NaOH, quỳ hoá xanh); SO_4^{2-} (axit hoá + $BaCl_2$, kết tủa trắng bền); NO_3^- (NaOH + Al, đun, quỳ hoá xanh); SO_3^{2-}/SO_2 (mất màu $KMnO_4/K_2Cr_2O_7$ axit hoá).

Practice

Bài tập luyện tập

For the Haber process, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H \approx -92$ kJ mol^{-1}, which change would increase the equilibrium % yield of NH_3?

(A) Increasing temperature
(B) Increasing pressure
(C) Adding an iron catalyst
(D) Removing the iron catalyst

Lời giải chi tiết

The forward reaction reduces gas moles ($4 \rightarrow 2$), so increasing pressure shifts equilibrium toward NH_3 (Le Chatelier), raising % yield. **(B)**.

Bài tập luyện tập

Explain why unreacted N_2 and H_2 are recycled through the Haber process reactor rather than discarded after a single pass.

Lời giải chi tiết

At the compromise conditions used (450°C, 200 atm), the single-pass equilibrium % yield of NH_3 is relatively modest (well below 100%), so a large proportion of the expensive feedstock gases would otherwise be wasted. Recycling the unreacted N_2/H_2 back into the reactor allows them to react further, greatly improving the overall (cumulative) conversion of feedstock into ammonia without needing more extreme (and more costly/dangerous) conditions.

Bài tập luyện tập

A stoichiometric N_2/H_2 feed reaches equilibrium with 10.0% of the N_2 converted, at a total pressure of 100 atm. Starting from 1.00 mol N_2 and 3.00 mol H_2, calculate K_p.

Lời giải chi tiết

Reacted: $N_2 = 0.100$ mol, $H_2 = 0.300$ mol, NH_3 formed $= 0.200$ mol. Equilibrium moles: $N_2 = 0.900$, $H_2 = 2.70$, $NH_3 = 0.200$; total $= 3.80$ mol. Mole fractions: $x(N_2) = 0.2368$, $x(H_2) = 0.7105$, $x(NH_3) = 0.0526$. Partial pressures at 100 atm: $p(N_2) = 23.68$, $p(H_2) = 71.05$,

$p(\text{NH}_3) = 5.26$ atm.

$$K_p = \frac{5.26^2}{23.68 \times 71.05^3} = \frac{27.7}{23.68 \times 3.59 \times 10^5} = \mathbf{3.3 \times 10^{-6}}\ \text{atm}^{-2}.$$

Bài tập luyện tập

The iron catalyst used in the Haber process:

(A) Increases the equilibrium % yield of NH_3

(B) Shifts the equilibrium position toward products

(C) Speeds up attainment of equilibrium without changing its position

(D) Increases the value of K_p

Lời giải chi tiết

A catalyst provides a lower-activation-energy pathway, speeding up both forward and reverse rates equally, so the equilibrium position and K_p are unaffected — only the time to reach equilibrium decreases. **(C)**.

Bài tập luyện tập

State two industrial uses of ammonia.

Lời giải chi tiết

(1) Manufacture of **nitrogenous fertilisers** (ammonium salts such as NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$), providing nitrogen for plant growth. (2) Manufacture of **nitric acid** via the Ostwald process (catalytic oxidation of NH_3), used both to make more ammonium fertilisers and as an industrial acid/oxidiser.

Bài tập luyện tập

Write the equation for the first step of the Ostwald process, in which ammonia is catalytically oxidised, and state the catalyst and approximate temperature used.

Lời giải chi tiết

$$4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$$

Catalyst: platinum/rhodium (Pt/Rh) gauze; approximate temperature: $\sim 800^\circ$C.

Bài tập luyện tập

Using the overall equation $\text{NH}_3(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{HNO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$, calculate the mass of HNO_3 obtainable from 85.0 kg of NH_3 ($M_r(\text{NH}_3) = 17.0$, $M_r(\text{HNO}_3) = 63.0$).

Lời giải chi tiết

$$n(\text{NH}_3) = \frac{85\,000}{17.0} = 5000\ \text{mol} \implies n(\text{HNO}_3) = 5000\ \text{mol}\ (1:1).$$

$$m(\text{HNO}_3) = 5000 \times 63.0 = 315\,000\ \text{g} = \mathbf{315}\ \text{kg}.$$

Bài tập luyện tập

Which conditions are needed for significant formation of NO directly from atmospheric N_2 and O_2?

(A) Room temperature and sunlight

(B) Very high temperature (e.g. inside an engine cylinder) or a spark

(C) Low temperature and high pressure

(D) Presence of a platinum catalyst at room temperature

Lời giải chi tiết

The reaction $N_2 + O_2 \rightarrow 2NO$ is strongly endothermic with a very high activation energy (breaking $N \equiv N$); only the very high temperatures/spark inside an internal combustion engine (or lightning) provide enough energy. **(B)**.

Bài tập luyện tập

Explain why NO does not form to any significant extent from the N_2 and O_2 of ordinary air at atmospheric temperature, even though both gases are constantly present together.

Lời giải chi tiết

The direct combination $N_2(g) + O_2(g) \rightarrow 2NO(g)$ is strongly endothermic and has a very high activation energy, because the very strong $N \equiv N$ triple bond must be broken. At ordinary atmospheric temperatures, essentially none of the colliding N_2/O_2 molecules possess enough kinetic energy to overcome this activation energy barrier, so the reaction proceeds at an immeasurably slow rate — NO only forms where a localised, much higher temperature (engine combustion, lightning) is briefly available.

Bài tập luyện tập

Write the equation for the further oxidation of NO in air, and state whether this step is exothermic or endothermic.

Lời giải chi tiết

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

This step is **exothermic** and occurs rapidly and spontaneously as soon as NO is released into air containing excess O_2, without requiring the special high-temperature conditions needed to form NO in the first place.

Bài tập luyện tập

For the catalytic converter reaction $2CO(g) + 2NO(g) \rightarrow N_2(g) + 2CO_2(g)$, state the oxidation number of carbon in CO and in CO_2, and hence state whether carbon is oxidised or reduced.

Lời giải chi tiết

In CO, carbon $= +2$; in CO_2, carbon $= +4$. Since the oxidation number increases, **carbon is oxidised** (loses electrons).

Bài tập luyện tập

In the catalytic converter reaction, nitrogen's oxidation number changes from:

(A) 0 to $+2$
(C) $+4$ to $+2$
(B) $+2$ to 0
(D) -3 to 0

Lời giải chi tiết

In NO, N $= +2$; in N_2, N $= 0$ — nitrogen is reduced. **(B)**.

Bài tập luyện tập

Which metals are typically used as the catalyst in a car's catalytic converter?

Lời giải chi tiết

Platinum, rhodium and palladium (Pt/Rh/Pd), coated as a thin layer over a ceramic honeycomb support to maximise surface area.

Bài tập luyện tập

Describe, with equations, how both SO_2 and NO_2 contribute to acid rain.

Lời giải chi tiết

SO_2 dissolves in atmospheric water to form sulfurous acid, $SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$, which is further oxidised in air to sulfuric acid, $2H_2SO_3(aq) + O_2(g) \rightarrow 2H_2SO_4(aq)$. NO_2 reacts with water to form nitric acid (with some NO regenerated), $3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$. Both H_2SO_4 and HNO_3 are strong acids that lower the pH of rainwater, causing acid rain.

Bài tập luyện tập

Acid rain reacts with limestone ($CaCO_3$, $M_r = 100$) via $CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(aq) + H_2O(l) + CO_2(g)$. Calculate the mass of $CaCO_3$ dissolved by 5.00 dm^3 of acid rain containing 2.00×10^{-4} mol dm^{-3} H_2SO_4.

Lời giải chi tiết

$$n(H_2SO_4) = 5.00 \times 2.00 \times 10^{-4} = 1.00 \times 10^{-3} \text{ mol} \implies n(CaCO_3) = 1.00 \times 10^{-3} \text{ mol } (1:1).$$

$$m(CaCO_3) = 1.00 \times 10^{-3} \times 100 = \mathbf{0.100} \text{ g}.$$

Bài tập luyện tập

For the Contact process equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, $\Delta H \approx -196$ kJ mol^{-1}, explain why the pressure used industrially is only 1–2 atm, even though higher pressure would (by Le Chatelier) increase the % yield further.

Lời giải chi tiết

Increasing pressure would indeed shift the equilibrium further toward SO_3 (fewer gas moles, $3 \to 2$), by Le Chatelier's principle. However, at 450°C with the V_2O_5 catalyst, the % conversion of SO_2 to SO_3 is already very high (~ 97–98%) even at only 1–2 atm. Since so little additional yield remains to be gained, the substantial extra capital, energy and safety cost of building and running high-pressure plant is not economically worthwhile — unlike in the Haber process, where the potential yield gain from higher pressure is much larger.

Bài tập luyện tập

Increasing the total pressure on the Contact process equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ would shift the position of equilibrium:

(A) Toward reactants, decreasing % yield of SO_3

(B) Toward products, increasing % yield of SO_3

(C) Not at all, since $\Delta n = 0$

(D) Toward products, but only if a catalyst is also added

Lời giải chi tiết

The forward reaction reduces gas moles ($3 \to 2$), so increasing pressure shifts equilibrium toward the side with fewer moles — the SO_3 side, increasing % yield. **(B)**.

Bài tập luyện tập

3.00 mol SO_2 and 2.00 mol O_2 reach equilibrium for $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, with 90.0% of the SO_2 converted, at a total pressure of 1.50 atm. Calculate K_p.

Lời giải chi tiết

SO_2 reacted $= 0.900 \times 3.00 = 2.70$ mol; O_2 reacted $= 1.35$ mol; SO_3 formed $= 2.70$ mol. Equilibrium moles: $SO_2 = 0.300$, $O_2 = 0.650$, $SO_3 = 2.70$; total $= 3.65$ mol. Mole fractions: $x(SO_2) = 0.0822$, $x(O_2) = 0.1781$, $x(SO_3) = 0.7397$. Partial pressures at 1.50 atm: $p(SO_2) = 0.123$, $p(O_2) = 0.267$, $p(SO_3) = 1.11$ atm.

$$K_p = \frac{1.11^2}{0.123^2 \times 0.267} = \frac{1.232}{0.00404} = \textbf{305}\ \text{atm}^{-1}.$$

Bài tập luyện tập

Explain why SO_3 is not simply dissolved directly in water on an industrial scale, and describe the alternative route used.

Lời giải chi tiết

Reacting SO_3 directly with water is extremely exothermic and forms a fine, dense, corrosive **acid mist** (aerosol of tiny H_2SO_4 droplets) rather than a clean liquid, which is hazardous and impractical to condense and collect. Instead, SO_3 is absorbed into concentrated H_2SO_4 to form **oleum**, $SO_3(g) + H_2SO_4(l) \to H_2S_2O_7(l)$, which is then safely and controllably diluted with water, $H_2S_2O_7(l) + H_2O(l) \to 2H_2SO_4(l)$, to regenerate concentrated sulfuric acid.

Bài tập luyện tập

Calculate the net mass of H_2SO_4 produced (via the oleum route) from 160 kg of SO_3 ($M_r(SO_3) = 80.0$, $M_r(H_2SO_4) = 98.0$).

Lời giải chi tiết

$$n(SO_3) = \frac{160\,000}{80.0} = 2000 \text{ mol} \implies n(H_2SO_4)_{\text{net}} = 2000 \text{ mol } (1:1 \text{ overall}).$$

$$m(H_2SO_4) = 2000 \times 98.0 = 196\,000 \text{ g} = \mathbf{196} \text{ kg}.$$

Bài tập luyện tập

A white solid, when warmed with NaOH(aq), releases a gas that turns damp red litmus paper blue. What ion is confirmed present, and what is the gas?

(A) NO_3^-; the gas is NO_2

(B) NH_4^+; the gas is NH_3

(C) SO_4^{2-}; the gas is SO_2

(D) CO_3^{2-}; the gas is CO_2

Lời giải chi tiết

Warming an ammonium salt with NaOH(aq) releases NH_3, an alkaline gas that turns damp red litmus blue: $NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(g) + H_2O(l)$. **(B)**.

Bài tập luyện tập

Describe the test used to confirm the presence of sulfate ions in solution, including why the sample is acidified before the key reagent is added.

Lời giải chi tiết

Add dilute HCl (or HNO_3) to the solution first, then add $BaCl_2(aq)$: a **white precipitate** of $BaSO_4$ that persists (does not dissolve) confirms SO_4^{2-}. The prior acidification is essential because it dissolves any $BaCO_3$ or $BaSO_3$ that would otherwise also precipitate with Ba^{2+} from carbonate or sulfite ions, which would give a false-positive result if the solution were not first acidified.

Bài tập luyện tập

Describe the reduction test used to confirm the presence of nitrate ions, including the expected positive observation.

Lời giải chi tiết

Add NaOH(aq) to the solution, then add aluminium foil or powder, and warm gently. If NO_3^- is present, it is reduced by aluminium (in alkaline solution) to NH_3 gas. Holding damp red litmus paper in the mouth of the tube: a colour change from red to **blue** confirms NH_3 is being evolved, and hence confirms the presence of NO_3^-.

Bài tập luyện tập

Gaseous SO_2 is bubbled through acidified $K_2Cr_2O_7(aq)$. Describe the observation and state the oxidation number change of chromium.

(A) Orange turns green; Cr goes from $+6$ to $+3$

(B) Purple decolourises; Cr goes from $+7$ to $+2$

(C) Green turns orange; Cr goes from $+3$ to $+6$

(D) No visible change; Cr is unaffected

Lời giải chi tiết

SO_2 reduces orange dichromate(VI) ions to green chromium(III) ions, while SO_2 itself is oxidised to sulfate: Cr changes from $+6$ (in $Cr_2O_7^{2-}$) to $+3$ (in Cr^{3+}). **(A)**.

Bài tập luyện tập

For $5SO_2(aq) + 2MnO_4^-(aq) + 2H_2O(l) \rightarrow 5SO_4^{2-}(aq) + 2Mn^{2+}(aq) + 4H^+(aq)$, state the oxidation number of sulfur in SO_2 and in SO_4^{2-}, and identify the reducing agent.

Lời giải chi tiết

In SO_2, S $= +4$ (O $= -2$ each, molecule neutral). In SO_4^{2-}, S $= +6$ (O $= -2$ each, four O give -8, overall charge -2, so S $= +6$). Sulfur's oxidation number rises $+4 \rightarrow +6$: sulfur is oxidised, so SO_2 **is the reducing agent**.

Bài tập luyện tập

A gas mixture from a diesel engine contains oxides of nitrogen. Explain, in terms of both formation and further reaction, why NO rather than NO_2 is the oxide formed *directly* inside the engine cylinder.

Lời giải chi tiết

Inside the cylinder, the reaction is the direct combination $N_2(g) + O_2(g) \rightarrow 2NO(g)$, which requires the very high temperatures (and spark) present during combustion to overcome its high activation energy; this reaction produces NO, not NO_2, directly. Only once the exhaust gas is released into the open air (containing excess O_2 at ordinary temperature) does the separate, much faster and exothermic reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ occur, converting the NO into NO_2.

Bài tập luyện tập

Explain briefly what is meant by "photochemical smog" and state one gas primarily responsible for triggering it.

Lời giải chi tiết

Photochemical smog is a mixture of secondary air pollutants (including ground-level ozone and other irritant compounds) formed when sunlight causes NO_2 in vehicle exhaust to photodissociate, releasing reactive oxygen species that go on to react with unburnt hydrocarbons in the exhaust. NO_2 is the gas primarily responsible for triggering this process.

Bài tập luyện tập

At equilibrium for $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, $K_p = 250$ atm^{-1}, $p(SO_2) = 0.100$ atm, $p(O_2) = 0.500$ atm. Calculate $p(SO_3)$.

Lời giải chi tiết

$$p(SO_3)^2 = K_p \times p(SO_2)^2 \times p(O_2) = 250 \times 0.100^2 \times 0.500 = 250 \times 0.00500 = 1.25.$$

$$p(SO_3) = \sqrt{1.25} = \mathbf{1.12}\ \text{atm}.$$

Introduction to Organic Chemistry and Hydrocarbons

Mục tiêu Unit: Danh pháp IUPAC cho alkane, alkene và cycloalkane; khái niệm dãy đồng đẳng và công thức tổng quát; đồng phân cấu tạo (mạch, vị trí, nhóm chức) và đồng phân lập thể (hình học E/Z, quang học) với các ví dụ đếm đồng phân đầy đủ; các loại cơ chế phản ứng hữu cơ; alkane: đốt cháy hoàn toàn/không hoàn toàn và cracking; alkene: phản ứng cộng electrophin đầy đủ (halogen, hydrogen halide theo quy tắc Markovnikov, hơi nước, hydro hoá) cùng cơ chế; polymer hoá cộng và tính trơ hoá học của polyalkene.

12.1 IUPAC nomenclature of alkanes, alkenes and cycloalkanes

Systematic (IUPAC) naming — the core rules

1. Identify the **longest continuous carbon chain** containing the maximum number of substituents (for alkanes) or the double bond (for alkenes); this chain gives the **parent name** (*meth-*, *eth-*, *prop-*, *but-*, *pent-*, *hex-*, ..., + *-ane*/*-ene*).
2. **Number the chain** from whichever end gives the **lowest possible locants** overall — for an alkene, the double bond position takes priority over substituent positions.
3. Name and locate each **substituent** (*methyl*, *ethyl*, *chloro*, ...) with a locant number; list substituents **alphabetically** in the name, using *di-*, *tri-*, *tetra-* for repeats (these multiplying prefixes are *not* counted in the alphabetical ordering).
4. For **cycloalkanes**, the prefix *cyclo-* is added to the parent name, and the ring carbons are numbered to give the lowest locants to substituents.

VN **GIẢI THÍCH TIẾNG VIỆT**

Quy tắc gọi tên IUPAC: (1) chọn mạch carbon dài nhất chứa nhiều nhánh nhất (hoặc chứa liên kết đôi với alkene); (2) đánh số sao cho tổng vị trí nhỏ nhất — với alkene, vị trí liên kết đôi được ưu tiên trước; (3) gọi tên nhóm thế theo thứ tự chữ cái, dùng di-/tri-/tetra- cho nhóm lặp lại (không tính vào thứ tự chữ cái); (4) với cycloalkane, thêm tiền tố cyclo- và đánh số vòng sao cho vị trí nhóm thế nhỏ nhất.

Ví dụ 1 · Naming a branched alkane from its structure

Name the alkane whose skeletal structure has a six-carbon main chain with a methyl group on carbon 2 and a methyl group on carbon 4, i.e. $CH_3-CH(CH_3)-CH_2-CH(CH_3)-CH_2-CH_3$.

The longest chain has 6 carbons $\rightarrow$ parent *hexane*. Numbering from the left gives substituent locants $2, 4$; numbering from the right would give $3, 5$ — the left-to-right numbering gives the

lower locant set, so it is used. Two identical methyl substituents at C2 and C4:

2,4-dimethylhexane.

Ví dụ 2 · Drawing the structure from an IUPAC name

Draw/describe the structure of **4-ethyl-2-methylhexane**.

Parent chain: hexane (6 carbons), numbered C1–C6. Substituents: an ethyl group at C4, a methyl group at C2.

$$CH_3 - CH(CH_3) - CH_2 - CH(C_2H_5) - CH_2 - CH_3$$

(C1: CH_3; C2: CH bearing a methyl branch; C3: CH_2; C4: CH bearing an ethyl branch; C5: CH_2; C6: CH_3.) Molecular formula: C_9H_{20}.

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Ví dụ 1 minh hoạ chiều "cấu trúc → tên gọi" (chọn mạch dài nhất, đánh số cho tổng vị trí nhỏ nhất); Ví dụ 2 minh hoạ chiều ngược lại "tên gọi → cấu trúc" (đọc tên để xác định mạch chính và vị trí từng nhóm thế). Luôn kiểm tra lại bằng cách đếm số carbon trong công thức phân tử cuối cùng.

Ví dụ 3 · Naming a substituted cycloalkane

Name the cycloalkane C_6H_{12} in which a cyclopentane ring bears one methyl substituent.

The ring itself (5 carbons, no substituents needing numbering priority beyond the point of attachment, taken as C1) is *cyclopentane*; the single methyl substituent needs no locant (there is only one possible position, up to symmetry, for a single substituent on an unsubstituted ring):

methylcyclopentane.

If a *second* substituent were present, the ring would then need numbering to give the lowest locant set, e.g. *1,2-dimethylcyclopentane*.

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Với cycloalkane chỉ có một nhóm thế, không cần đánh số (vị trí là duy nhất do tính đối xứng của vòng); khi có từ hai nhóm thế trở lên, phải đánh số vòng sao cho tổng vị trí nhỏ nhất, giống nguyên tắc với mạch hở.

12.2 Homologous series

A **homologous series** is a family of compounds that: (1) share the same **general formula**; (2) differ from the next member by a constant CH_2 unit; (3) show a gradual, predictable trend in physical properties (e.g. boiling point rises smoothly with chain length); and (4) share very similar **chemical properties**, since they share the same functional group.

Alkanes: C_nH_{2n+2}, **Alkenes (one C=C):** C_nH_{2n}.

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Dãy đồng đẳng là một họ hợp chất có cùng công thức tổng quát, mỗi chất hơn chất trước một nhóm CH_2, tính chất vật lý biến đổi đều đặn (ví dụ nhiệt độ sôi tăng dần), và tính chất hoá học tương tự nhau do cùng nhóm chức. Alkane: C_nH_{2n+2}; alkene (một liên kết đôi): C_nH_{2n}.

Name	Molecular formula	Structural formula	Boiling point / °C
Methane	CH_4	CH_4	-161.5
Ethane	C_2H_6	CH_3CH_3	-88.6
Propane	C_3H_8	$CH_3CH_2CH_3$	-42.1
Butane	C_4H_{10}	$CH_3(CH_2)_2CH_3$	-0.5
Pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$	36.1
Hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$	68.7

Table 1. The first six members of the alkane homologous series (C_nH_{2n+2}), with approximate normal boiling points, showing the steady rise with increasing chain length (stronger dispersion forces between longer chains).

Name	Molecular formula	Structural formula	Boiling point / °C
Ethene	C_2H_4	$CH_2=CH_2$	-103.7
Propene	C_3H_6	$CH_2=CHCH_3$	-47.6
But-1-ene	C_4H_8	$CH_2=CHCH_2CH_3$	-6.3
Pent-1-ene	C_5H_{10}	$CH_2=CH(CH_2)_2CH_3$	30.0
Hex-1-ene	C_6H_{12}	$CH_2=CH(CH_2)_3CH_3$	63.4

Table 2. The first five members of the (terminal) alkene homologous series (C_nH_{2n}), with approximate boiling points, closely paralleling the corresponding alkanes but each slightly lower-boiling.

Ví dụ 4 · Applying the general formula

(a) State the molecular formula of the alkane with 9 carbon atoms. (b) State the molecular formula of the alkene (one C = C) with 9 carbon atoms.

(a) C_nH_{2n+2} with $n=9$: C_9H_{20} (nonane).
(b) C_nH_{2n} with $n=9$: C_9H_{18} (nonene).

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Chỉ cần thay n vào công thức tổng quát: alkane C_nH_{2n+2}, alkene C_nH_{2n} — đây là cách nhanh nhất để suy ra công thức phân tử của bất kỳ thành viên nào trong dãy đồng đẳng mà không cần nhớ từng chất riêng lẻ.

12.3 Isomerism: structural and stereoisomerism

Structural (constitutional) isomers have the same molecular formula but different **connectivity** of atoms: *chain* isomers (different carbon skeleton, e.g. branched vs. straight), *positional* isomers (functional group/substituent at a different position on the same skeleton), and *functional group* isomers (a different functional group entirely, e.g. an alcohol and an ether with the same molecular formula).

Stereoisomers have the *same* connectivity but a different **spatial arrangement** of atoms: *E/Z* (geometric) isomerism arises from restricted rotation about a C = C double bond; *optical* isomerism arises from a chiral centre (a carbon bonded to four different groups), giving non-superimposable mirror-image forms (enantiomers).

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Đồng phân **cấu tạo** (structural): khác nhau về cách liên kết nguyên tử — đồng phân mạch (khung carbon khác), vị trí (nhóm chức ở vị trí khác), nhóm chức (nhóm chức khác hẳn). Đồng phân **lập thể** (stereoisomer): cùng cách liên kết nhưng khác sắp xếp không gian — hình học E/Z (do liên kết đôi C = C không quay tự do được) và quang học (do có tâm bất đối xứng, tạo ảnh gương không chồng khít).

12.3.1 Full isomer count: C_4H_8

Ví dụ 5 · Counting all the structural and geometric isomers of C_4H_8

List the open-chain (acyclic) alkene structural isomers of C_4H_8, and determine which (if any) show E/Z isomerism.

There are three open-chain structural isomers:

Name	Condensed structure	E/Z isomerism?
But-1-ene	$CH_2=CHCH_2CH_3$	No
But-2-ene	$CH_3CH=CHCH_3$	**Yes** (E and Z forms)
2-Methylprop-1-ene	$(CH_3)_2C=CH_2$	No

But-1-ene: one double-bond carbon is $=CH_2$, bearing *two identical* H atoms — since E/Z isomerism requires *each* double-bond carbon to carry two *different* substituents, having two identical groups on even one of the carbons rules it out. **No E/Z isomerism.**

2-Methylprop-1-ene: one double-bond carbon is $=CH_2$ (two identical H atoms), and the other bears *two identical* CH_3 groups. Both carbons fail the "two different substituents" test. **No E/Z isomerism.**

But-2-ene: *each* double-bond carbon bears one H and one CH_3 — two *different* groups on each carbon — so E/Z isomerism *does* exist: *(E)*-but-2-ene (the two CH_3 groups on opposite sides) and *(Z)*-but-2-ene (the two CH_3 groups on the same side).

Total count: 3 structural isomers among open-chain alkenes, but 4 isomers overall once the E/Z pair of but-2-ene is counted separately. (If cyclic structures are also permitted, *cyclobutane* and *methylcyclopropane* are two further structural isomers of C_4H_8, bringing the complete total to 6.)

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Với C_4H_8, có 3 đồng phân cấu tạo dạng alkene mạch hở: but-1-ene, but-2-ene, 2-methylprop-1-ene. Chỉ **but-2-ene** có đồng phân hình học E/Z, vì cả hai carbon của liên kết đôi đều mang hai nhóm thế **khác nhau** (H và CH_3); but-1-ene và 2-methylprop-1-ene đều có ít nhất một carbon mang hai nhóm thế **giống nhau** nên không có E/Z. Tổng cộng có 4 đồng phân alkene mạch hở (kể cả E/Z); nếu tính thêm vòng no (cyclobutane, methylcyclopropane) thì có 6 đồng phân C_4H_8.

(!) Lỗi thường gặp: A very common error is to assume *any* alkene with different substituents on *either* carbon shows E/Z isomerism. The test must be applied to **each** double-bond carbon *separately* — E/Z isomerism exists only if *both* carbons independently carry two different groups. A single carbon bearing two identical groups (e.g. a terminal $=CH_2$) rules out E/Z isomerism for the whole molecule, regardless of what is on the other carbon.

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Lỗi thường gặp: chỉ cần một carbon của liên kết đôi có hai nhóm thế khác nhau đã vội kết luận có E/Z. Thực ra phải kiểm tra **cả hai** carbon — chỉ cần một trong hai carbon mang hai nhóm giống nhau thì cả phân tử không có đồng phân hình học, bất kể carbon còn lại như thế nào.

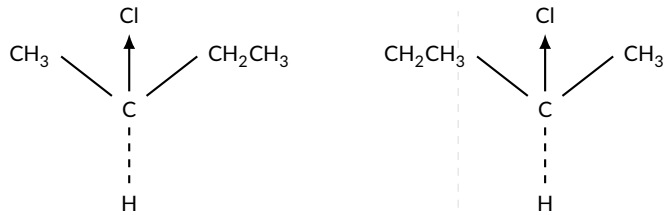
12.3.2 Optical isomerism

Ví dụ 6 · Identifying a chiral centre — 2-chlorobutane

Show that 2-chlorobutane, $CH_3CHClCH_2CH_3$, has a chiral centre, and explain what this means for the number and nature of its stereoisomers.

Consider carbon C2 (the carbon bearing Cl). Its four attached groups are: $-Cl$, $-H$, $-CH_3$, and $-CH_2CH_3$ (ethyl). All **four groups are different** from one another, so C2 is a **chiral centre** (asymmetric carbon), often marked with an asterisk: $CH_3CH^*(Cl)CH_2CH_3$.

Because C2 has four different substituents, the molecule and its mirror image cannot be superimposed on one another by any rotation — they are related as an object and its mirror image, exactly as a left hand and a right hand are non-superimposable mirror images of each other. These two non-superimposable mirror-image forms are called **enantiomers**. 2-Chlorobutane therefore exists as **exactly two** stereoisomers (a pair of enantiomers), which have identical physical properties (boiling point, density, etc.) except for their effect on plane-polarised light (one rotates it clockwise, the other anticlockwise by an equal angle) and their interactions with other chiral molecules (e.g. in biological systems).



2-chlorobutane, enantiomer 1 *2-chlorobutane, enantiomer 2 (mirror image)*

Figure 1. Schematic (simplified, not true 3-D perspective) of the two enantiomers of 2-chlorobutane, related as non-superimposable mirror images across the dashed mirror line — swapping CH_3 and CH_2CH_3 on the chiral carbon.

VN **GIẢI THÍCH TIẾNG VIỆT**

Carbon C2 của 2-chlorobutane gắn với 4 nhóm khác nhau (Cl, H, CH_3, CH_2CH_3) nên là **tâm bất đối xứng (chiral centre)**. Phân tử và ảnh gương của nó **không thể chồng khít** lên nhau (giống bàn tay trái và phải) — gọi là một cặp **đồng phân quang học (enantiomer)**. Hai enantiomer có tính chất vật lý giống hệt nhau, chỉ khác ở chiều quay mặt phẳng ánh sáng phân cực.

12.4 Alkanes: combustion and cracking

12.4.1 Complete and incomplete combustion

Ví dụ 7 · Complete versus incomplete combustion of octane

Write balanced equations for (a) the complete combustion of octane, C_8H_{18}, and (b) its incomplete combustion producing carbon monoxide as the only carbon-containing product.

(a) Complete combustion (plentiful O_2) produces only CO_2 and H_2O:

$$2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l).$$

(b) Incomplete combustion (limited O_2) produces CO instead:

$$2C_8H_{18}(l) + 17O_2(g) \rightarrow 16CO(g) + 18H_2O(l).$$

Check (b): C: $16 = 16$; H: $36 = 36$; O: left $2 \times 17 = 34$, right $16 + 18 = 34$ ✓.

(!) Lỗi thường gặp: Carbon monoxide, CO, is colourless, odourless and highly toxic — it binds irreversibly (much more strongly than O_2) to haemoglobin in red blood cells, preventing oxygen transport around the body. Poorly ventilated or faulty fuel-burning appliances (heaters, engines running in enclosed spaces) present a serious CO-poisoning risk precisely *because* incomplete combustion is undetectable by smell or sight.

VN **GIẢI THÍCH TIẾNG VIỆT**

Đốt cháy **hoàn toàn** (đủ O_2) chỉ tạo CO_2 và H_2O; đốt cháy **không hoàn toàn** (thiếu O_2) tạo thêm CO (đôi khi cả bồ hóng carbon, C). Khí CO không màu, không mùi nhưng rất độc do liên kết với hemoglobin mạnh hơn O_2 rất nhiều, ngăn cản vận chuyển oxy trong máu — đây là lý do cần thông gió tốt khi đốt nhiên liệu trong không gian kín.

12.4.2 Cracking

Cracking breaks longer-chain alkanes (obtained in excess from fractional distillation of crude oil) into shorter, more commercially useful alkanes and alkenes, driven by market demand for short-chain fuels (petrol/gasoline) and for alkenes as a feedstock for the plastics/polymer industry.

- **Thermal cracking:** high temperature (~ 700–900°C), high pressure, *no* catalyst; proceeds via a **free-radical** mechanism (homolytic C–C bond fission); tends to produce a higher proportion of alkenes.
- **Catalytic cracking:** lower temperature ($\sim 450^\circ$C), slight pressure, a **zeolite** catalyst; proceeds via a **carbocation** (ionic) mechanism; tends to produce a higher proportion of branched and aromatic hydrocarbons, useful for higher-octane petrol.

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Cracking bẻ gãy các alkane mạch dài (dư thừa sau chưng cất phân đoạn) thành alkane mạch ngắn hơn (làm nhiên liệu) và alkene (nguyên liệu sản xuất polymer). Cracking **nhiệt**: nhiệt độ rất cao, không xúc tác, cơ chế gốc tự do, tạo nhiều alkene. Cracking **xúc tác**: nhiệt độ vừa phải hơn, xúc tác zeolite, cơ chế ion carbocation, tạo nhiều sản phẩm mạch nhánh/thơm dùng làm xăng chất lượng cao.

Ví dụ 8 · Balancing a cracking equation

Decane, $C_{10}H_{22}$, is cracked to give octane, C_8H_{18}, and one other product. Identify the other product and write the balanced equation.

Cracking conserves both the number of carbon atoms and the number of hydrogen atoms

overall (it is a simple bond-breaking process, not combustion). Carbon balance: $10 - 8 = 2$ carbons remain for the second product. Hydrogen balance: $22 - 18 = 4$ hydrogens remain for the second product. A C_2H_4 fragment (ethene) fits exactly:

$$C_{10}H_{22} \rightarrow C_8H_{18} + C_2H_4.$$

Check: C: $10 = 8 + 2 = 10$ ✓; H: $22 = 18 + 4 = 22$ ✓. The second product is **ethene**, a valuable alkene monomer for polymerisation.

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Khi cracking, tổng số nguyên tử C và H phải bảo toàn (chỉ là bẻ gãy liên kết, không phải đốt cháy). Từ số nguyên tử còn thiếu ở sản phẩm đã biết, suy ra công thức sản phẩm còn lại — ở đây là C_2H_4 (ethene), một alkene quan trọng làm nguyên liệu polymer.

12.5 Alkenes: electrophilic addition reactions

The electrophilic addition mechanism — outline

The C = C double bond has a region of high electron density (the π bond) exposed above and below the plane of the molecule, making alkenes attractive to **electrophiles** (electron-deficient species). The mechanism proceeds in two steps:

1. The π electrons of the C = C bond attack the electrophile (e.g. the slightly positive end of H − Br, or Br_2 polarised by the approaching alkene), forming a new C − X bond and leaving a positively charged **carbocation intermediate** on the other former double-bond carbon.
2. A **nucleophile** (e.g. Br^-, or the halide released in step 1) then attacks the positively charged carbocation, forming the second new bond and completing the addition product.

Where two different carbocation intermediates are possible (unsymmetrical alkene + HX), the **more stable** carbocation forms preferentially and hence dominates the product distribution (Markovnikov's rule). Alkyl groups are weakly electron-donating (via the inductive effect), so they partially stabilise the adjacent positive charge: stability order is **tertiary** > **secondary** > **primary** carbocation.

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Cơ chế cộng electrophin: (1) electron π của liên kết đôi tấn công tác nhân electrophin, tạo **carbocation trung gian**; (2) tác nhân nucleophin (thường là ion halide) tấn công carbocation, hoàn tất phản ứng cộng. Khi có thể tạo hai carbocation khác nhau, carbocation **bền hơn** sẽ chiếm ưu thế (quy tắc Markovnikov) vì nhóm alkyl có hiệu ứng cảm ứng đẩy electron, ổn định điện tích dương: bậc ba > bậc hai > bậc một.

Reagent	Conditions	Product type	Example (with ethene)
X_2 (e.g. Br_2)	Room temperature; Br_2 in water (bromine water)	Dihalogenoalkane	$CH_2=CH_2+Br_2\rightarrow CH_2BrCH_2Br$
HX (e.g. HBr)	Room temperature, gas or in solution	Halogenoalkane (Markovnikov)	$CH_2=CH_2+HBr\rightarrow CH_3CH_2Br$
Steam, $H_2O(g)$	H_3PO_4 catalyst, $\sim 300^\circ$C, ~ 60–70 atm	Alcohol	$CH_2=CH_2+H_2O\rightarrow CH_3CH_2OH$
H_2	Ni catalyst, $\sim 150^\circ$C	Alkane (hydrogenation)	$CH_2=CH_2+H_2\rightarrow CH_3CH_3$

Table 3. The four classic electrophilic addition reactions of alkenes, illustrated with ethene, the simplest case (no Markovnikov selectivity issue, since both alkene carbons are equivalent).

Ví dụ 9 · Bromine water as the standard test for unsaturation

Describe the test used to distinguish an alkene from an alkane using bromine water, and write the equation for the reaction with propene.

Shake the unknown hydrocarbon with orange **bromine water**. An **alkene rapidly decolourises** the bromine water (orange $\rightarrow$ colourless), as the C = C double bond undergoes electrophilic addition with Br_2. An **alkane** shows *no* colour change under these conditions (no reaction at room temperature in the absence of light/UV).

$$CH_2=CHCH_3+Br_2\rightarrow CH_2BrCHBrCH_3 \quad \text{(1,2-dibromopropane)}.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Nước brom (màu cam) bị **mất màu nhanh** khi lắc với alkene (do cộng electrophin vào liên kết đôi), nhưng **không đổi màu** với alkane — đây là phép thử tiêu chuẩn để phân biệt alkane và alkene (kiểm tra sự không no).

Ví dụ 10 · Markovnikov addition of HBr to but-1-ene

Predict and explain the major product when but-1-ene, $CH_2=CHCH_2CH_3$, reacts with HBr.

Protonation of the C = C bond can occur at either carbon, giving two possible carbocation intermediates: adding H^+ to C1 gives a **secondary** carbocation at C2 ($CH_3-CH^+-CH_2CH_3$), while adding H^+ to C2 gives a **primary** carbocation at C1 ($^+CH_2-CH_2CH_2CH_3$). The secondary carbocation is stabilised by the inductive electron donation of *two* alkyl groups (versus only one for the primary carbocation), so it is significantly more stable and forms preferentially.

$$CH_2=CHCH_2CH_3+HBr\rightarrow CH_3CHBrCH_2CH_3 \quad \textbf{(2-bromobutane, major product)}.$$

The minor product, 1-bromobutane ($CH_3CH_2CH_2CH_2Br$), forms only in a small amount, via the less stable primary carbocation pathway.

VN **GIẢI THÍCH TIẾNG VIỆT**

Với but-1-ene + HBr: proton H^+ có thể cộng vào C1 (tạo carbocation bậc hai bền hơn ở C2) hoặc vào C2 (tạo carbocation bậc một kém bền ở C1). Vì carbocation bậc hai bền hơn (được ổn định bởi hai nhóm alkyl thay vì một), sản phẩm chính là **2-bromobutane**, sản phẩm phụ là 1-bromobutane. Đây là ví dụ thứ hai (khác propene) minh hoạ quy tắc Markovnikov.

Ví dụ 11 · Industrial hydration of ethene to ethanol

Write the equation for the industrial manufacture of ethanol from ethene, state the catalyst and conditions, and calculate the maximum mass of ethanol obtainable from 56.0 kg of ethene ($M_r(\mathrm{C_2H_4}) = 28.0$, $M_r(\mathrm{C_2H_5OH}) = 46.0$).

$$\mathrm{CH_2{=}CH_2(g) + H_2O(g) \rightarrow CH_3CH_2OH(g)}, \qquad \text{catalyst: } \mathrm{H_3PO_4},\ \sim 300^\circ\mathrm{C},\ \sim 60\text{–}70 \text{ atm}.$$

$$n(\mathrm{C_2H_4}) = \frac{56\,000}{28.0} = 2000 \text{ mol} \implies n(\mathrm{C_2H_5OH}) = 2000 \text{ mol } (1:1).$$

$$m(\mathrm{C_2H_5OH}) = 2000 \times 46.0 = 92\,000 \text{ g} = \mathbf{92.0} \text{ kg}.$$

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Sản xuất ethanol công nghiệp bằng cách hydrat hoá trực tiếp ethene với hơi nước, xúc tác $\mathrm{H_3PO_4}$, nhiệt độ $\sim 300^\circ$C, áp suất ~ 60–70 atm — tỉ lệ mol $1{:}1$ giữa ethene và ethanol giúp tính khối lượng đơn giản như một bài stoichiometry thông thường.

Ví dụ 12 · Hydrogenation of propene

Write the equation for the catalytic hydrogenation of propene, and state the catalyst used.

$$\mathrm{CH_2{=}CHCH_3(g) + H_2(g) \xrightarrow{Ni} CH_3CH_2CH_3(g)}.$$

Nickel (Ni) catalyst, typically at $\sim 150^\circ$C under moderate pressure; this addition converts the unsaturated alkene into the corresponding saturated alkane (propane), and is the industrial basis of hardening unsaturated vegetable oils into solid/semi-solid fats.

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Hydro hoá alkene (xúc tác Ni) biến alkene chưa no thành alkane no tương ứng — đây cũng là nguyên lý công nghiệp dùng để hydro hoá dầu thực vật (chứa nhiều liên kết đôi) thành chất béo rắn/bán rắn.

12.6 Addition polymerisation of alkenes

In **addition polymerisation**, many alkene **monomer** molecules join together, with the $\mathrm{C{=}C}$ π bond of each monomer opening up to form new $\mathrm{C{-}C}$ σ bonds to neighbouring monomers, building a long saturated chain (the **polymer**) with *no* atoms lost or gained. The repeating structural unit is written in square brackets with a subscript n.

VN **GIẢI THÍCH TIẾNG VIỆT**

Trong polymer hoá cộng, nhiều phân tử monomer (alkene) nối với nhau bằng cách mở liên kết π của $\mathrm{C{=}C}$ để tạo liên kết σ $\mathrm{C{-}C}$ mới, tạo thành mạch polymer no dài, không mất hay thêm nguyên tử nào. Đơn vị lặp lại được viết trong ngoặc vuông với chỉ số n.

Ví dụ 13 · Addition polymerisation of propene

Write the equation for the addition polymerisation of propene to form poly(propene), showing the repeat unit.

$$n\,CH_2=CHCH_3 \rightarrow [-CH_2-CH(CH_3)-]_n$$

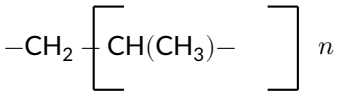

Figure 2. Repeat-unit bracket notation for poly(propene): the two open bonds on the left and right of the repeat unit represent the continuing chain connecting to further identical units.

Why poly(alkenes) are chemically inert and non-biodegradable

Poly(alkenes) such as poly(ethene) and poly(propene) consist entirely of a **saturated** $C-C/C-H$ backbone: strong, non-polar σ bonds with *no* reactive π bond remaining (unlike the monomer) and no polar functional groups for reagents (acids, bases, nucleophiles, micro-organisms' enzymes) to attack. This chemical inertness is exactly why these plastics are so useful (durable, resistant to corrosion) — but it is the very same property that makes them **non-biodegradable**, persisting in the environment for centuries rather than being broken down by natural microbial action.

VN **GIẢI THÍCH TIẾNG VIỆT**

Polyalkene (như polyethene, polypropene) chỉ gồm khung $C-C/C-H$ no, liên kết σ bền, không phân cực, không còn liên kết π hoạt động và không có nhóm chức phân cực để phản ứng — nên rất trơ về mặt hoá học. Tính trơ này vừa là ưu điểm (bền, chống ăn mòn) vừa là nhược điểm (**không phân huỷ sinh học**, tồn tại hàng trăm năm trong môi trường).

Ôn tập nhanh

Ôn tập nhanh: (1) Danh pháp IUPAC: chọn mạch dài nhất, đánh số cho tổng vị trí nhỏ nhất, gọi tên nhóm thế theo thứ tự chữ cái. (2) Dãy đồng đẳng: alkane C_nH_{2n+2}, alkene C_nH_{2n}, nhiệt độ sôi tăng đều theo mạch carbon. (3) Đồng phân cấu tạo (mạch/vị trí/nhóm chức) khác đồng phân lập thể (E/Z cần cả hai carbon của liên kết đôi mang hai nhóm khác nhau; quang học cần một carbon gắn 4 nhóm khác nhau — tâm bất đối xứng). (4) Alkane: đốt cháy hoàn toàn cho CO_2+H_2O, không hoàn toàn cho thêm CO (độc); cracking (nhiệt: gốc tự do, nhiều alkene; xúc tác: carbocation, nhiều mạch nhánh). (5) Alkene: cộng electrophin qua carbocation trung gian với X_2 (nước brom, phép thử không no), HX (Markovnikov — carbocation bền hơn ưu tiên), hơi nước (H_3PO_4, sản xuất ethanol), H_2/Ni (hydro hoá). (6) Polymer hoá cộng: mở liên kết π tạo mạch no dài; polyalkene trơ hoá học, không phân huỷ sinh học do khung $C-C/C-H$ no, không phân cực.

Practice

Bài tập luyện tập

Which IUPAC name correctly describes $CH_3CH(CH_3)CH_2CH_3$?

(A) 2-methylbutane
(C) 2-methylpropane
(B) 3-methylbutane
(D) 1,1-dimethylpropane

Lời giải chi tiết

Longest chain is 4 carbons (butane) with a methyl branch; numbering from the end nearer the branch gives locant 2 (not 3, the higher alternative). **(A)**.

Bài tập luyện tập

Name the alkane $(CH_3)_3C-CH_2-CH_3$.

Lời giải chi tiết

Longest chain: 4 carbons with three methyl groups all on C2 → **2,2-dimethylbutane**.

Bài tập luyện tập

Draw/describe the structure of 3-ethylpentane.

Lời giải chi tiết

Parent chain: pentane (5 carbons), ethyl substituent on C3: $CH_3CH_2CH(C_2H_5)CH_2CH_3$, molecular formula C_7H_{16}.

Bài tập luyện tập

Name the cycloalkane with molecular formula C_5H_{10} and no substituents.

(A) Pentane
(B) Cyclopentane
(C) Cyclopentene
(D) Pentene

Lời giải chi tiết

An unsubstituted 5-membered saturated ring, C_5H_{10}, is **cyclopentane**. **(B)**.

Bài tập luyện tập

State the molecular formula of the alkane containing 12 carbon atoms, and of the corresponding alkene (one double bond) with the same number of carbon atoms.

Lời giải chi tiết

Alkane: C_nH_{2n+2} with $n = 12$ gives $C_{12}H_{26}$ (dodecane). Alkene: C_nH_{2n} with $n = 12$ gives $C_{12}H_{24}$ (dodecene).

Bài tập luyện tập

An alkane has molecular formula C_7H_{16}. Confirm this fits the general formula for alkanes and name it (unbranched isomer).

Lời giải chi tiết

For $n = 7$: $C_nH_{2n+2} = C_7H_{16}$ ✓, confirming it is an alkane. The unbranched (straight-chain) isomer is **heptane**.

Bài tập luyện tập

Which of the following molecules shows E/Z (geometric) isomerism?

(A) $CH_2=CHCH_2CH_3$ (but-1-ene)
(B) $(CH_3)_2C=CH_2$ (2-methylprop-1-ene)
(C) $CH_3CH=CHCH_3$ (but-2-ene)
(D) $CH_2=CH_2$ (ethene)

Lời giải chi tiết

Only but-2-ene has *both* double-bond carbons bearing two different substituents (H and CH_3 on each); the others all have at least one carbon with two identical substituents. **(C)**.

Bài tập luyện tập

Explain why but-1-ene does not show E/Z isomerism, even though it is an unsymmetrical molecule overall.

Lời giải chi tiết

E/Z isomerism requires *each* carbon of the C = C double bond to bear two *different* substituents. In but-1-ene, $CH_2=CHCH_2CH_3$, the terminal double-bond carbon is $=CH_2$, bearing two identical hydrogen atoms. Since this one carbon fails the "two different groups" requirement, the whole molecule cannot show E/Z isomerism, regardless of what is attached to the other double-bond carbon.

Bài tập luyện tập

State the number of structural isomers among the open-chain (acyclic) alkenes of molecular formula C_4H_8, and the total number of isomers once stereoisomers are included.

Lời giải chi tiết

There are **3** open-chain structural isomers (but-1-ene, but-2-ene, 2-methylprop-1-ene). Including the E/Z pair of but-2-ene, the total is **4** isomers among open-chain alkenes.

Bài tập luyện tập

Identify the chiral centre in 2-bromopentane, $CH_3CHBrCH_2CH_2CH_3$, and state how many stereoisomers it has.

Lời giải chi tiết

C2 (bearing Br) is bonded to four different groups: $-Br$, $-H$, $-CH_3$, and $-CH_2CH_2CH_3$ (propyl). This is a chiral centre, so the molecule exists as **2** stereoisomers — a pair of non-superimposable mirror-image enantiomers.

Bài tập luyện tập

Which of these molecules has a chiral centre?

(A) 2-chloropropane, $CH_3CHClCH_3$
(B) 2-chlorobutane, $CH_3CHClCH_2CH_3$
(C) 2-chloro-2-methylpropane, $(CH_3)_3CCl$
(D) 1-chloropropane, $CH_3CH_2CH_2Cl$

Lời giải chi tiết

In 2-chlorobutane, C2 bears four different groups (Cl, H, CH_3, CH_2CH_3) — a chiral centre. The other three molecules each have a carbon bonded to at least two identical groups (e.g. two CH_3 groups in 2-chloropropane), so none is chiral. **(B)**.

Bài tập luyện tập

Explain the key difference between a pair of structural isomers and a pair of stereoisomers, using an example of each.

Lời giải chi tiết

Structural isomers have the *same molecular formula but different connectivity* of atoms — e.g. butane and 2-methylpropane (C_4H_{10}) have different carbon skeletons. Stereoisomers have *identical connectivity* but a different *spatial arrangement* — e.g. the two enantiomers of 2-chlorobutane are connected identically but are non-superimposable mirror images of one another.

Bài tập luyện tập

Write the balanced equation for the complete combustion of butane, C_4H_{10}.

Lời giải chi tiết

$$\mathbf{2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l).}$$

Check: C $8 = 8$; H $20 = 20$; O left 26, right $16 + 10 = 26$ ✓.

Bài tập luyện tập

Write an equation for the incomplete combustion of methane producing carbon monoxide, and explain why this is dangerous in a poorly ventilated room.

Lời giải chi tiết

$$2CH_4(g) + 3O_2(g) \rightarrow 2CO(g) + 4H_2O(l).$$

CO is colourless and odourless, so it gives no warning of its presence, yet it binds to haemoglobin far more strongly than O_2, blocking oxygen transport in the blood and potentially causing loss of consciousness or death — this is especially hazardous in a poorly ventilated room where CO concentration can build up unnoticed.

Bài tập luyện tập

Carbon monoxide is dangerous mainly because:

(A) It is highly flammable

(B) It binds strongly to haemoglobin, blocking oxygen transport

(C) It reacts explosively with water

(D) It is a strong acid

Lời giải chi tiết

CO binds to haemoglobin much more strongly than O_2, preventing oxygen from being carried around the body. **(B)**.

Bài tập luyện tập

Dodecane, $C_{12}H_{26}$, is cracked to give decane, $C_{10}H_{22}$, and one other product. Identify the missing product and write the balanced equation.

Lời giải chi tiết

Carbon balance: $12 - 10 = 2$; hydrogen balance: $26 - 22 = 4$. The missing product is C_2H_4 (ethene):

$$\mathbf{C_{12}H_{26} \rightarrow C_{10}H_{22} + C_2H_4}.$$

Bài tập luyện tập

State two differences between thermal cracking and catalytic cracking.

Lời giải chi tiết

(1) Thermal cracking uses much higher temperature (~ 700–900°C) and no catalyst; catalytic cracking uses a lower temperature ($\sim 450^\circ$C) with a zeolite catalyst. (2) Thermal cracking proceeds via a free-radical mechanism and tends to give more alkenes; catalytic cracking proceeds via a carbocation (ionic) mechanism and tends to give more branched/aromatic hydrocarbons suited to petrol.

Bài tập luyện tập

Why is cracking carried out at all, given that it consumes energy to break bonds in perfectly stable, usable alkanes?

Lời giải chi tiết

Crude oil fractional distillation yields far more long-chain alkanes (e.g. for heavy fuel oil) than the market demands, and far fewer short-chain alkanes (e.g. petrol) and alkenes than are needed. Cracking converts surplus long-chain alkanes into shorter, more valuable, more marketable alkanes (fuels) and alkenes (feedstock for the polymer/plastics industry), so the energy cost is justified by the much higher commercial value of the products obtained.

Bài tập luyện tập

State the observation when ethene gas is bubbled through bromine water, and write the equation.

Lời giải chi tiết

The orange bromine water is rapidly **decolourised**.

$$CH_2 = CH_2 + Br_2 \rightarrow CH_2BrCH_2Br \quad \text{(1,2-dibromoethane)}.$$

Bài tập luyện tập

Bromine water is used to distinguish an alkane from an alkene because:

(A) Alkanes decolourise it rapidly, alkenes do not

(B) Alkenes decolourise it rapidly (addition across C = C); alkanes show no reaction

(C) Both decolourise it equally

(D) Neither reacts with bromine water

Lời giải chi tiết

Alkenes undergo electrophilic addition with Br_2, decolourising the orange bromine water; saturated alkanes have no C = C bond to react at room temperature, so no colour change occurs. **(B)**.

Bài tập luyện tập

Predict and explain the major product when propene reacts with HBr.

Lời giải chi tiết

Protonation at C1 gives a secondary carbocation at C2 ($CH_3 - CH^+ - CH_3$), stabilised by two alkyl groups; protonation at C2 gives a less stable primary carbocation at C1. The secondary carbocation pathway dominates, so the major product is **2-bromopropane**, $CH_3CHBrCH_3$, via Markovnikov addition.

Bài tập luyện tập

Predict the major product when but-1-ene reacts with HCl, and name it.

Lời giải chi tiết

By Markovnikov's rule, H adds to the carbon already bearing more hydrogens (C1), and Cl adds to C2, via the more stable secondary carbocation intermediate. Major product: $CH_3CHClCH_2CH_3$, **2-chlorobutane**.

Bài tập luyện tập

Explain, in terms of the inductive effect, why a secondary carbocation is more stable than a primary carbocation.

Lời giải chi tiết

Alkyl groups are weakly **electron-donating** through the inductive effect (inductive donation into the electron-deficient carbon). A secondary carbocation has *two* alkyl groups directly attached to the positively charged carbon, each donating electron density toward it, whereas a primary carbocation has only *one* such alkyl group. The greater electron donation in the secondary case partially neutralises and delocalises the positive charge more effectively, making the secondary carbocation lower in energy (more stable) than the primary carbocation.

Bài tập luyện tập

Write the equation for the industrial hydration of propene to form propan-2-ol, and state the catalyst.

Lời giải chi tiết

$$CH_2=CHCH_3(g)+H_2O(g)\rightarrow CH_3CH(OH)CH_3(g), \qquad \text{catalyst: } H_3PO_4.$$

(Markovnikov addition: OH adds to the more substituted carbon, via the more stable secondary carbocation.)

Bài tập luyện tập

Calculate the mass of ethanol obtainable from 14.0 kg of ethene by steam hydration ($M_r(C_2H_4)=28.0$, $M_r(C_2H_5OH)=46.0$).

Lời giải chi tiết

$$n(C_2H_4)=\frac{14\,000}{28.0}=500\text{ mol}\implies n(C_2H_5OH)=500\text{ mol}\ (1:1).$$

$$m(C_2H_5OH)=500\times 46.0=23\,000\text{ g}=\mathbf{23.0}\text{ kg}.$$

Bài tập luyện tập

Write the equation for the hydrogenation of but-1-ene, and state the catalyst used.

Lời giải chi tiết

$$CH_2=CHCH_2CH_3+H_2\xrightarrow{\text{Ni}}CH_3CH_2CH_2CH_3.$$

Catalyst: nickel (Ni), typically $\sim 150^\circ$C.

Bài tập luyện tập

The catalyst used for the industrial hydrogenation of alkenes (e.g. in hardening vegetable oils) is:

(A) V_2O_5 **(C)** Ni

(B) Fe **(D)** Pt/Rh

Lời giải chi tiết

Nickel (Ni) is the standard catalyst for alkene hydrogenation. **(C)**.

Bài tập luyện tập

Outline, in words, the two-step mechanism by which HBr adds to an alkene.

Lời giải chi tiết

Step 1: the electron-rich π bond of the alkene attacks the slightly positive hydrogen of the polar $H-Br$ molecule, forming a new $C-H$ bond; the $Br-H$ bond breaks heterolytically, releasing Br^- and leaving a positively charged **carbocation** on the other former alkene carbon. **Step 2:** the nucleophilic Br^- ion released in step 1 attacks the electron-deficient carbocation carbon, forming the second new bond ($C-Br$) and completing the halogenoalkane product.

Bài tập luyện tập

Write the repeat unit for poly(but-1-ene), formed by addition polymerisation of but-1-ene, $CH_2=CHCH_2CH_3$.

Lời giải chi tiết

$$[-\mathbf{CH_2}-\mathbf{CH}(\mathbf{CH_2CH_3})-]_\mathbf{n}$$

Bài tập luyện tập

Explain why poly(ethene) is chemically inert and does not biodegrade readily.

Lời giải chi tiết

Poly(ethene) consists entirely of a saturated $C-C/C-H$ backbone with strong, non-polar σ bonds and no reactive π bonds or polar functional groups remaining. There is no site on the polymer chain that reagents (acids, bases, nucleophiles) or microbial enzymes can readily attack, so it resists chemical breakdown — the same property that makes it durable also makes it persist in the environment for a very long time (non-biodegradable).

Bài tập luyện tập

Which functional-group feature of an alkene is responsible for both its addition reactions *and* its ability to undergo addition polymerisation?

(A) The saturated C-C single bonds
(B) The C=C double bond (π electron density)
(C) The presence of hydrogen atoms
(D) The overall non-polarity of the molecule

Lời giải chi tiết

The $C=C$ double bond's exposed π electron density is attacked by electrophiles in addition reactions, and is exactly what opens up to form new σ bonds to neighbouring monomers in addition polymerisation. **(B)**.

Bài tập luyện tập

A hydrocarbon of molecular formula C_5H_{10} decolourises bromine water rapidly. Suggest a possible structure and name it, and explain why cyclopentane (also C_5H_{10}) would *not* give this same rapid decolourisation.

Lời giải chi tiết

A structure consistent with rapid decolourisation is **pent-1-ene**, $CH_2 = CHCH_2CH_2CH_3$ (any acyclic C_5H_{10} alkene is acceptable), which undergoes fast electrophilic addition with Br_2 due to its reactive $C = C$ double bond. Cyclopentane, although it shares the same molecular formula C_5H_{10}, is a **saturated** ring with no $C = C$ double bond, so it has no site for electrophilic addition and does *not* rapidly decolourise bromine water — illustrating that molecular formula alone does not determine reactivity; the functional group present does.

Halogen Derivatives, Hydroxy Compounds and Carbonyl Compounds

Mục tiêu Unit: Cơ chế thế nucleophin của halogenoalkan với OH^-, CN^-, NH_3; phản ứng tách loại tạo anken; so sánh tốc độ thuỷ phân theo độ bền liên kết C–X; phân loại và phản ứng oxi hoá/tách nước/este hoá của ancol; phản ứng cộng nucleophin của hợp chất carbonyl với HCN và $NaBH_4$; các phép thử phân biệt: Tollens', Fehling's, 2,4-DNPH, iodoform.

13.1 Halogenoalkanes: nucleophilic substitution

Nucleophilic substitution at a halogenoalkane

In a halogenoalkane $R-X$ ($X = Cl, Br, I$), the $C-X$ bond is polarised $C^{\delta+}-X^{\delta-}$ because the halogen is more electronegative than carbon. A **nucleophile** — a species with a lone pair of electrons that is attracted to a region of positive charge — attacks the electron-deficient carbon. The mechanism proceeds as follows:

1. The nucleophile's lone pair is attracted to, and attacks, the electron-deficient carbon bearing the halogen.
2. As the new bond forms, the $C-X$ bond breaks **heterolytically**: both electrons of the bond leave with the halogen.
3. The halide ion (X^-) leaves as the **leaving group**, and the nucleophile is now bonded to carbon in place of X.

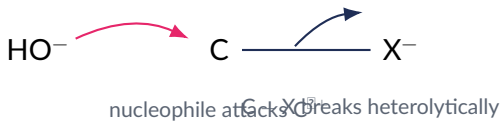

Figure 1. Mechanism outline for nucleophilic substitution of a halogenoalkane by OH^-: the nucleophile's lone pair attacks the carbon bearing the halogen while the $C-X$ bond breaks, releasing X^-.

VN **GIẢI THÍCH TIẾNG VIỆT**

Trong halogenoalkan, liên kết $C-X$ phân cực do halogen có độ âm điện lớn hơn carbon, tạo carbon mang một phần điện tích dương ($C^{\delta+}$). Một **tác nhân nucleophin** (có cặp electron chưa liên kết) tấn công vào carbon này; liên kết $C-X$ đứt theo kiểu dị li (cả hai electron đi theo halogen), và ion halogenua rời đi như một **nhóm rời**. Đây là phản ứng **thế nucleophin**.

Nucleophile	Conditions	Product
OH^- (aqueous NaOH)	warm, aqueous, reflux	alcohol: $R-X + OH^- \rightarrow R-OH + X^-$
CN^- (KCN in ethanol)	warm, ethanolic	nitrile (chain extended by one carbon): $R-X + CN^- \rightarrow R-CN + X^-$
NH_3 (excess, in ethanol)	warm, sealed tube, **excess** NH_3	primary amine: $R-X + 2NH_3 \rightarrow R-NH_2 + NH_4X$

Table 1. Three key nucleophilic substitution reactions of a halogenoalkane $R-X$.

The CN^- substitution is important synthetically because it **extends the carbon chain by one carbon** (the nitrile carbon is new), giving access to carboxylic acids (by acid hydrolysis of the nitrile) or primary amines (by reduction) with one more carbon than the starting halogenoalkane. Excess NH_3 is needed in the amine synthesis to minimise further substitution of the primary amine product (itself a nucleophile) to secondary/tertiary amines and quaternary ammonium salts.

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Phản ứng với CN^- rất quan trọng vì làm **tăng thêm một carbon** vào mạch — từ đó có thể tạo axit carboxylic (thuỷ phân nitril) hoặc amin bậc một (khử nitril), nhiều hơn một carbon so với halogenoalkan ban đầu. Cần dùng NH_3 dư khi tạo amin để hạn chế amin bậc một sinh ra tiếp tục phản ứng thế tạo amin bậc hai/ba và muối amoni bậc bốn.

Ví dụ 1 · Mechanism of 1-bromopropane + NaOH(aq)

Describe, step by step, the mechanism for the reaction of 1-bromopropane, $CH_3CH_2CH_2Br$, with warm aqueous NaOH, and give the organic product.

Step 1: the hydroxide ion, OH^-, is a nucleophile (it has three lone pairs on oxygen); it is attracted to, and attacks, the electron-deficient carbon (C1) that bears the bromine, since that carbon carries a partial positive charge ($C^{\delta+} - Br^{\delta-}$).
Step 2: as the new $O-C$ bond forms, the $C-Br$ bond breaks heterolytically — both bonding electrons leave with the bromine.
Step 3: Br^- departs as the leaving group, leaving OH bonded to C1 in its place.

$$CH_3CH_2CH_2Br + NaOH \rightarrow CH_3CH_2CH_2OH + NaBr$$

Organic product: **propan-1-ol**.

VN **GIẢI THÍCH TIẾNG VIỆT**

Với 1-bromopropan, OH^- tấn công carbon số 1 (mang Br), liên kết $C-Br$ đứt dị li, Br^- rời đi — tạo propan-1-ol. Đây là ví dụ cụ thể áp dụng cơ chế thế nucleophin tổng quát ở trên.

13.1.1 Relative rates of hydrolysis: C–I, C–Br, C–Cl

Hydrolysis rate and bond enthalpy

The rate of nucleophilic substitution (hydrolysis) of halogenoalkanes with the same carbon skeleton follows the order

$$R-I > R-Br > R-Cl$$

This order is controlled by **bond enthalpy**, not bond polarity: the $C-I$ bond (mean bond

enthalpy $\approx$ 238 kJ mol^{-1}) is the **weakest** of the three (C – Br$\approx$ 276 kJ mol^{-1}, C – Cl$\approx$ 338 kJ mol^{-1}), because iodine's larger atomic radius gives poorer orbital overlap with carbon. A weaker bond is broken more easily (lower activation energy for its heterolytic fission), so C – I hydrolyses fastest even though C – Cl is the *most polar* bond of the three.

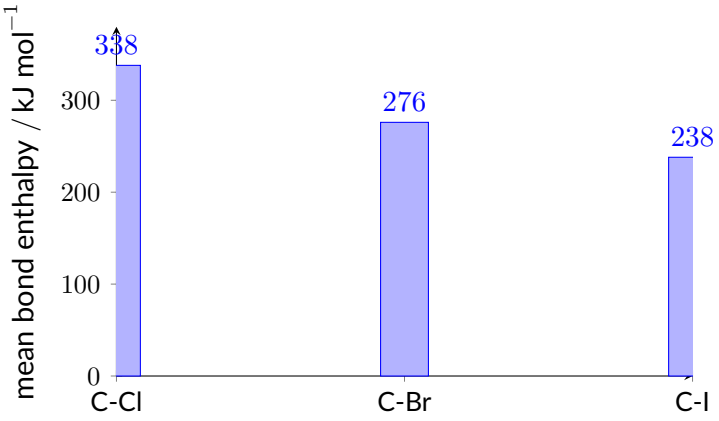

Figure 2. Mean C – X bond enthalpies. The weakest bond, C – I, breaks most easily, so iodoalkanes hydrolyse fastest — even though C – Cl is the most polar bond of the three.

VN **GIẢI THÍCH TIẾNG VIỆT**

Tốc độ thuỷ phân halogenoalkan (cùng mạch carbon) theo thứ tự R – I > R – Br > R – Cl, được quyết định bởi **độ bền liên kết** chứ không phải độ phân cực: liên kết C – I yếu nhất (do bán kính nguyên tử iot lớn, xen phủ orbital với carbon kém), nên dễ bị phá vỡ nhất, dù C – Cl mới là liên kết phân cực nhất trong ba liên kết.

Ví dụ 2 · Ranking hydrolysis rate from a precipitation-time experiment

Three test tubes each contain a few drops of 1-chlorobutane, 1-bromobutane and 1-iodobutane respectively, together with ethanol (a common solvent for the organic liquid and aqueous $AgNO_3$) and a few drops of aqueous $AgNO_3$. All tubes are placed in a water bath at the same temperature. A cream precipitate (AgBr) appears in the bromobutane tube after 40 s, a pale yellow precipitate (AgI) appears in the iodobutane tube after 15 s, and a white precipitate (AgCl) appears in the chlorobutane tube after 110 s. Rank the three halogenoalkanes by rate of hydrolysis and justify whether this order is chemically expected.

Step 1 — the halide ion released is detected as a silver halide precipitate. The halogenoalkane first undergoes (slow) hydrolysis with water/ethanol, releasing the halide ion as X^-; $Ag^+(aq)$ then immediately precipitates that halide ion: $Ag^+(aq) + X^-(aq) \rightarrow AgX(s)$. The *rate-determining* step is the slow hydrolysis of the C – X bond, not the fast precipitation, so the **time to first appearance of precipitate** is a direct measure of the rate of hydrolysis: a shorter time means faster hydrolysis.

Step 2 — rank by time. Iodobutane precipitates fastest (15 s), then bromobutane (40 s), then chlorobutane slowest (110 s), so the order of hydrolysis rate is

$$\text{1-iodobutane} > \text{1-bromobutane} > \text{1-chlorobutane}$$

Step 3 — is this expected? Yes. The order matches C – I<C – Br<C – Cl in bond enthalpy (C – I weakest, easiest to break), so C – I bonds break fastest under identical conditions, giving the fastest appearance of precipitate for iodobutane and the slowest for chlorobutane. **The**

observed order (I > Br > Cl, fastest to slowest) is chemically correct, confirming that bond enthalpy — not bond polarity — controls the relative hydrolysis rate.

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Thời gian xuất hiện kết tủa AgX phản ánh trực tiếp tốc độ thuỷ phân halogenoalkan (bước quyết định tốc độ), vì bước kết tủa với Ag^+ xảy ra gần như tức thời. Thứ tự quan sát được (iotbutan nhanh nhất, clobutan chậm nhất) khớp với thứ tự độ bền liên kết C – X, xác nhận C – I là liên kết yếu nhất.

13.1.2 Elimination: substitution vs. elimination conditions (A2)

Elimination with hot ethanolic hydroxide

When OH^- acts as a **base** rather than a nucleophile, it removes a hydrogen atom from a carbon adjacent to the carbon bearing the halogen; the electron pair from that C – H bond forms a new C = C π bond, and the halide ion leaves simultaneously from the neighbouring carbon. The overall result is **elimination** of HX to form an alkene:

$$CH_3CH_2CH_2Br + KOH \xrightarrow[\text{ethanol}]{\text{heat}} CH_3CH=CH_2 + KBr + H_2O$$

Reagent/solvent	Conditions	Outcome
NaOH or KOH, **aqueous**	warm	**substitution** — OH^- acts as nucleophile → alcohol
NaOH or KOH, **ethanolic** (dissolved in ethanol, no water)	**concentrated, heated under reflux**	**elimination** — OH^- acts as base → alkene $+H_2O$

Table 2. Summary: aqueous/warm hydroxide favours substitution; concentrated ethanolic/hot hydroxide favours elimination.

VN **GIẢI THÍCH TIẾNG VIỆT**

OH^- có thể đóng hai vai trò khác nhau: là **nucleophin** trong dung môi nước (tấn công carbon, thế X) hoặc là **bazơ** trong dung môi etanol đặc, nóng (tách H từ carbon liền kề, tạo liên kết đôi C = C, đồng thời X^- rời khỏi carbon bên cạnh) — đây là phản ứng **tách loại**, tạo anken. Điều kiện quyết định là dung môi (nước → thế; etanol đặc, nóng → tách).

Ví dụ 3 · Predicting the major product under stated conditions

2-bromopropane, $CH_3CHBrCH_3$, is separately treated with (a) aqueous NaOH, warmed, and (b) concentrated NaOH dissolved in ethanol, heated under reflux. Give the structure and name of the major organic product in each case.

(a) Aqueous NaOH**, warm:** OH^- acts as a nucleophile, substituting Br directly:

$$CH_3CHBrCH_3 + NaOH \rightarrow CH_3CH(OH)CH_3 + NaBr$$

Product: **propan-2-ol**.

(b) Concentrated ethanolic NaOH**, heat under reflux:** OH^- acts as a base, removing an H from

a carbon adjacent to C − Br and eliminating HBr:

$$CH_3CHBrCH_3 \xrightarrow[\text{ethanol}]{\text{conc. NaOH, heat}} CH_3CH=CH_2 + NaBr + H_2O$$

Product: **propene**. (2-bromopropane is symmetric about C2, so only one alkene, propene, can form.)

VN **GIẢI THÍCH TIẾNG VIỆT**

Cùng một halogenoalkan (2-bromopropan) cho hai sản phẩm hoàn toàn khác nhau tuỳ điều kiện: NaOH nước, ấm → propan-2-ol (thế); NaOH đặc trong etanol, đun hồi lưu → propen (tách). Đây là ví dụ kinh điển cho thấy điều kiện phản ứng quyết định sản phẩm.

13.2 Alcohols: classification and oxidation

Classifying alcohols

An alcohol is classified by the number of carbon atoms directly bonded to the carbon bearing the −OH group:

- **Primary (1°)**: the −OH carbon is bonded to **one** other carbon (or none, as in methanol) — general form RCH_2OH.
- **Secondary (2°)**: the −OH carbon is bonded to **two** other carbons — general form R_2CHOH.
- **Tertiary (3°)**: the −OH carbon is bonded to **three** other carbons — general form R_3COH.

VN **GIẢI THÍCH TIẾNG VIỆT**

Ancol được phân loại theo số nguyên tử carbon gắn trực tiếp vào carbon mang nhóm −OH: **bậc một** (1 carbon khác gắn vào), **bậc hai** (2 carbon), **bậc ba** (3 carbon). Bậc ancol quyết định sản phẩm oxi hoá.

Alcohol class	Oxidising agent / conditions	Product	Observation with acidified $K_2Cr_2O_7$
Primary	acidified $K_2Cr_2O_7$, **gentle heat, distil** product off as it forms	aldehyde (RCHO)	orange → green
Primary	acidified $K_2Cr_2O_7$, **excess, heat under reflux**	carboxylic acid (RCOOH)	orange → green
Secondary	acidified $K_2Cr_2O_7$, heat under reflux	ketone (R_2CO)	orange → green
Tertiary	acidified $K_2Cr_2O_7$, heat under reflux	**no reaction**	stays orange

Table 3. Oxidation of alcohols by acidified potassium dichromate(VI), $Cr_2O_7^{2-}$ (orange, Cr in $+6$) being reduced to Cr^{3+} (green, Cr in $+3$).

A tertiary alcohol has **no hydrogen atom on the** –OH **carbon**, so it cannot be oxidised by acidified $K_2Cr_2O_7$ (oxidation of an alcohol requires removal of a hydrogen from that carbon); the orange dichromate colour therefore does not change. Distilling the product off immediately in the primary case prevents **further** oxidation of the aldehyde to the carboxylic acid; refluxing (continuous heating with a condenser returning vapour to the flask) keeps the aldehyde in contact with excess oxidant, driving oxidation through to the acid.

VN **GIẢI THÍCH TIẾNG VIỆT**

Ancol bậc ba không có nguyên tử H trên carbon mang –OH nên **không bị oxi hoá** bởi $K_2Cr_2O_7/H^+$ — màu cam không đổi. Với ancol bậc một: chưng cất ngay sản phẩm ra khỏi hỗn hợp phản ứng dừng ở giai đoạn andehit; đun hồi lưu (giữ hơi quay lại bình) cho phép oxi hoá tiếp tục thành axit carboxylic.

Ví dụ 4 · Classifying three alcohols and predicting oxidation outcomes

Classify each alcohol as primary, secondary or tertiary, and state what would be observed (colour change, if any) and the organic product formed if each is heated under reflux with excess acidified $K_2Cr_2O_7$: (a) $CH_3CH_2CH_2OH$ (propan-1-ol); (b) $CH_3CH(OH)CH_3$ (propan-2-ol); (c) $(CH_3)_3COH$ (2-methylpropan-2-ol).

(a) Propan-1-ol: the –OH carbon (C1) is bonded to only one other carbon (C2) → **primary**. Under reflux with excess oxidant: orange → green; product is **propanoic acid**, CH_3CH_2COOH (oxidised fully, via the aldehyde intermediate propanal, since the aldehyde is not distilled off).

(b) Propan-2-ol: the –OH carbon (C2) is bonded to two other carbons (C1 and C3) → **secondary**. Orange → green; product is **propanone**, CH_3COCH_3 (a ketone — oxidation stops here, as ketones resist further oxidation by $K_2Cr_2O_7$).

(c) 2-methylpropan-2-ol: the –OH carbon is bonded to three methyl carbons → **tertiary**. **No reaction**; the dichromate stays orange, since there is no hydrogen on the –OH carbon for the oxidant to remove.

VN **GIẢI THÍCH TIẾNG VIỆT**

Ba ancol propan-1-ol, propan-2-ol, 2-metylpropan-2-ol lần lượt là bậc một, bậc hai, bậc ba — tương ứng cho axit carboxylic (qua trung gian andehit), xeton, và không phản ứng. Đây là bài toán phân loại-dự đoán kinh điển trong đề thi.

13.2.1 Esterification of alcohols

Esterification

An alcohol reacts with a carboxylic acid, heated under reflux with a few drops of concentrated H_2SO_4 as catalyst, to form an **ester** and water:

$$R-COOH + R'-OH \xrightarrow{\text{conc. } H_2SO_4} R-COO-R' + H_2O$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Ancol phản ứng với axit carboxylic (xúc tác H_2SO_4 đặc, đun hồi lưu) tạo este và nước — phản ứng este hoá. (Bản chất cân bằng của phản ứng này và cách kéo hiệu suất được trình bày chi tiết ở chương sau.)

Ví dụ 5 · Multi-step synthesis of propyl propanoate from propan-1-ol only

Starting only from propan-1-ol, $CH_3CH_2CH_2OH$, and any inorganic reagents, outline a route (equations + conditions) to propyl propanoate, $CH_3CH_2COOCH_2CH_2CH_3$.

Step 1 — oxidise part of the propan-1-ol fully to propanoic acid using **excess acidified $K_2Cr_2O_7$, heated under reflux** (no distillation, so oxidation proceeds past the aldehyde stage):

$$CH_3CH_2CH_2OH + 2[O] \xrightarrow[\text{reflux}]{\text{excess } K_2Cr_2O_7/H^+} CH_3CH_2COOH + H_2O$$

Step 2 — esterify the propanoic acid formed with the remaining (unreacted) propan-1-ol, heated under reflux with a few drops of concentrated H_2SO_4 as catalyst:

$$CH_3CH_2COOH + CH_3CH_2CH_2OH \xrightarrow{\text{conc. } H_2SO_4} CH_3CH_2COOCH_2CH_2CH_3 + H_2O$$

This route needs only propan-1-ol as the organic starting material (one portion is oxidised to the acid; the other portion supplies the alcohol for esterification), plus $K_2Cr_2O_7/H_2SO_4$ as inorganic reagents.

VN **GIẢI THÍCH TIẾNG VIỆT**

Chỉ dùng propan-1-ol làm nguyên liệu hữu cơ duy nhất: một phần bị oxi hoá hoàn toàn (hồi lưu, dư chất oxi hoá) thành axit propanoic; phần còn lại đóng vai trò ancol trong phản ứng este hoá với chính axit propanoic vừa tạo ra — thu được propyl propanoat.

13.2.2 Dehydration of alcohols (A2)

Acid-catalysed dehydration

Heating an alcohol with a concentrated non-oxidising acid catalyst — concentrated H_2SO_4 or concentrated H_3PO_4 — eliminates a molecule of water to form an **alkene**. Where more than one β-hydrogen environment is available, a **mixture of positional isomers** can form.

$$CH_3CH_2CH(OH)CH_3 \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4 \text{ or } H_3PO_4} CH_3CH_2CH=CH_2 + CH_3CH=CHCH_3 + H_2O$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Đun ancol với xúc tác axit đặc không có tính oxi hoá (H_2SO_4 đặc hoặc H_3PO_4 đặc) tách loại một phân tử nước, tạo anken. Butan-2-ol có H ở cả hai carbon liền kề C − OH, nên tạo hỗn hợp but-1-en và but-2-en.

Ví dụ 6 · Dehydration of butan-2-ol

Butan-2-ol, $CH_3CH_2CH(OH)CH_3$, is heated with concentrated H_3PO_4. Explain why a mixture of alkenes is obtained and identify them.

The −OH is on C2. Water can be eliminated by removing a hydrogen from **either** C1 **or** C3 (both are adjacent, "β", carbons bearing hydrogens):

- removing an H from C1 gives $CH_3CH_2CH=CH_2$ (**but-1-ene**);
- removing an H from C3 gives $CH_3CH=CHCH_3$ (**but-2-ene**, as a mixture of *cis*/*trans* isomers).

Both eliminations are accessible, so the product is a **mixture of but-1-ene and but-2-ene**.

VN **GIẢI THÍCH TIẾNG VIỆT**
Vì butan-2-ol có nguyên tử H khả dụng ở cả hai carbon liền kề nhóm –OH (C1 và C3), phản ứng tách nước cho hỗn hợp đồng phân vị trí but-1-en và but-2-en, không phải một sản phẩm duy nhất.

13.2.3 The iodoform (triiodomethane) test

Iodoform test

Warming a compound with iodine, I_2, and aqueous sodium hydroxide gives a **pale yellow precipitate** of triiodomethane, CHI_3 (a distinctive, faint "antiseptic" smell), **only** if the compound contains either the group CH_3CO- (a methyl ketone, or ethanal) **or** the group $CH_3CH(OH)-$ (which $NaOH/I_2$ first oxidises in situ to CH_3CO-).

$$CH_3COR + 3I_2 + 4NaOH \rightarrow CHI_3 \downarrow + RCOONa + 3NaI + 3H_2O$$

VN **GIẢI THÍCH TIẾNG VIỆT**
Thử nghiệm iodoform: đun nóng với I_2/NaOH cho kết tủa vàng nhạt CHI_3 **chỉ khi** hợp chất có nhóm CH_3CO- (xeton metyl hoặc etanal) hoặc nhóm $CH_3CH(OH)-$ (bị oxi hoá tại chỗ thành CH_3CO- trước khi phản ứng tạo kết tủa).

Ví dụ 7 · Distinguishing ethanol from methanol and propan-1-ol

A student has three unlabelled bottles containing methanol, ethanol and propan-1-ol. Describe and explain the result of adding I_2 and warm aqueous NaOH to each.

Ethanol, CH_3CH_2OH, contains the group $CH_3CH(OH)-$. $NaOH/I_2$ first oxidises it to ethanal, CH_3CHO, which *does* contain CH_3CO-, so the iodoform reaction proceeds: a **pale yellow precipitate of** CHI_3 forms — **positive**.

Methanol, CH_3OH, has only one carbon, so it cannot contain the CH_3CO- or $CH_3CH(OH)-$ fragment — **negative**, no precipitate.

Propan-1-ol, $CH_3CH_2CH_2OH$, has the –OH on a carbon bonded to a CH_2 group, not a CH_3 group directly — oxidation gives propanal, CH_3CH_2CHO, which does *not* contain CH_3CO- — **negative**, no precipitate.

Conclusion: only the bottle giving a pale yellow precipitate is **ethanol**.

VN **GIẢI THÍCH TIẾNG VIỆT**
Etanol có nhóm $CH_3CH(OH)-$ nên cho phản ứng iodoform dương tính (kết tủa vàng nhạt CHI_3); metanol (chỉ 1 carbon) và propan-1-ol (nhóm –OH trên carbon gắn CH_2, không phải CH_3) đều âm tính. Đây là cách phân biệt etanol với các ancol bậc một khác bằng thực nghiệm đơn giản.

13.3 Carbonyl compounds: nucleophilic addition and reduction

The carbonyl group and nucleophilic addition

The carbonyl group, C = O, is polarised $C^{\delta+} = O^{\delta-}$ (oxygen is more electronegative). Nucleophiles are therefore attracted to, and attack, the carbonyl carbon, adding across the double bond — **nucleophilic addition**. With hydrogen cyanide (generated in situ from KCN + dilute acid, providing both CN^- and H^+):

1. The cyanide ion, CN^- (the nucleophile, attacking through carbon), attacks the electrophilic carbonyl carbon.
2. The C = O π bond breaks heterolytically, with both electrons moving onto the oxygen, forming a negatively charged **alkoxide intermediate**.
3. The alkoxide oxygen is then protonated (by HCN or H^+ in solution), giving a **hydroxynitrile** product.

$$R_2C=O + HCN \rightarrow R_2C(OH)CN$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Nhóm carbonyl C = O phân cực, carbon mang một phần điện tích dương. Tác nhân nucleophin CN^- tấn công carbon này, liên kết π C = O đứt (electron chuyển về oxi tạo ion alkoxide trung gian), sau đó oxi bị proton hoá — tạo sản phẩm hydroxynitril. Đây là phản ứng **cộng nucleophin**, khác với phản ứng thế nucleophin ở halogenoalkan.

Ví dụ 8 · Addition of HCN to propanone

Propanone, CH_3COCH_3, reacts with HCN (generated from KCN/dilute H_2SO_4). Give the mechanism outline and the structure/name of the organic product.

CN^- attacks the electrophilic carbonyl carbon of propanone; the C = O π bond breaks, electrons moving to oxygen to give the alkoxide intermediate $(CH_3)_2C(O^-)CN$; protonation of the oxygen (by HCN or H_3O^+) gives the neutral product:

$$(CH_3)_2C=O + HCN \rightarrow (CH_3)_2C(OH)CN$$

Product: **2-hydroxy-2-methylpropanenitrile**, $(CH_3)_2C(OH)CN$ — a chain-extended hydroxynitrile (one carbon longer than propanone), useful because the nitrile group can subsequently be hydrolysed to a carboxylic acid or reduced to an amine.

VN **GIẢI THÍCH TIẾNG VIỆT**

Propanon cộng HCN tạo 2-hydroxy-2-metylpropanenitril — sản phẩm có thêm một carbon so với xeton ban đầu (nhờ carbon của nhóm −CN), mở đường tạo axit carboxylic hoặc amin mạch dài hơn.

13.3.1 Reduction of carbonyl compounds (A2)

Reduction with $NaBH_4$

Sodium tetrahydridoborate(III), $NaBH_4$, in aqueous or alcoholic solution, acts as a source of hydride ion, H^- — another nucleophile — which adds to the carbonyl carbon, followed by protonation of the resulting alkoxide. Aldehydes are reduced to **primary alcohols**; ketones are

reduced to **secondary alcohols**:

$$CH_3CH_2CHO + 2[H] \xrightarrow{NaBH_4} CH_3CH_2CH_2OH$$

VN **GIẢI THÍCH TIẾNG VIỆT**

$NaBH_4$ cung cấp ion hydride H^- (một nucleophin) cộng vào carbon carbonyl, sau đó proton hoá — quá trình khử ngược với oxi hoá ancol: andehit → ancol bậc một; xeton → ancol bậc hai.

Ví dụ 9 · Reduction of butanone with $NaBH_4$

Butanone, $CH_3COCH_2CH_3$, is treated with $NaBH_4$ in aqueous solution. Give the equation for the reaction and name the product.

Hydride ion, H^-, adds to the electrophilic carbonyl carbon of butanone; the resulting alkoxide is protonated by water:

$$CH_3COCH_2CH_3 + 2[H] \xrightarrow{NaBH_4} CH_3CH(OH)CH_2CH_3$$

Product: **butan-2-ol** — a secondary alcohol, since butanone is a ketone.

VN **GIẢI THÍCH TIẾNG VIỆT**

Butanon (xeton) bị khử bởi $NaBH_4$ thành butan-2-ol (ancol bậc hai) — phù hợp quy tắc: xeton khử thành ancol bậc hai, andehit khử thành ancol bậc một.

13.3.2 Distinguishing tests for carbonyl compounds

Reagent	Positive result	What it detects
2,4-dinitrophenylhydrazine (2,4-DNPH)	orange/yellow **precipitate**	confirms *any* carbonyl group, C = O (aldehyde **or** ketone) — does not distinguish between them
Tollens' reagent, $[Ag(NH_3)_2]^+$, warmed	**silver mirror** forms on the tube wall	aldehyde only (Ag^+ reduced to $Ag(s)$); ketones give no reaction
Fehling's solution (blue Cu^{2+} complex), warmed	blue solution → **brick-red precipitate** (Cu_2O)	aldehyde only (Cu^{2+} reduced to Cu^+); ketones give no reaction

Table 4. Chemical tests distinguishing aldehydes from ketones; 2,4-DNPH confirms a carbonyl group is present at all (of either type).

VN **GIẢI THÍCH TIẾNG VIỆT**

2,4-DNPH chỉ xác nhận *có* nhóm carbonyl (không phân biệt andehit/xeton, cho kết tủa cam/vàng với cả hai). Để phân biệt andehit và xeton, dùng thuốc thử Tollens' (gương bạc) hoặc Fehling's (kết tủa đỏ gạch Cu_2O) — cả hai chỉ dương tính với **andehit**, vì andehit dễ bị oxi hoá còn xeton thì không.

Ví dụ 10 · Distinguishing butanal from butanone

Describe a chemical test, with observations, to distinguish butanal, $CH_3CH_2CH_2CHO$, from butanone, $CH_3CH_2COCH_3$.

Warm each with **Tollens' reagent** (or Fehling's solution) in a water bath.
Butanal (an aldehyde) is readily oxidised by the mild oxidising agent $[Ag(NH_3)_2]^+$, itself being oxidised to butanoic acid while Ag^+ is reduced to metallic silver: a **silver mirror** forms on the inside of the test tube.
Butanone (a ketone) has no hydrogen on the carbonyl carbon and cannot be oxidised in the same way: **no silver mirror forms** (no reaction).
2,4-DNPH would *not* distinguish them — both give an orange precipitate since both contain $C=O$.

VN **GIẢI THÍCH TIẾNG VIỆT**
Butanal (andehit) cho gương bạc dương tính với Tollens'; butanon (xeton) không phản ứng. 2,4-DNPH không dùng để phân biệt hai chất này vì cả hai đều có nhóm carbonyl.

Test	Positive result	Confirms
Bromine water	orange/brown → colourless (rapid, cold)	$C=C$ unsaturation (alkene)
2,4-DNPH	orange/yellow precipitate	carbonyl, $C=O$ (aldehyde *or* ketone)
Tollens' / Fehling's, warmed	silver mirror / brick-red precipitate	aldehyde specifically (not ketone)
I_2/NaOH, warmed (iodoform)	pale yellow precipitate of CHI_3	CH_3CO- or $CH_3CH(OH)-$ group

Table 5. Consolidated summary of confirmatory tests introduced in this chapter.

Ví dụ 11 · Combined test-based identification

Three unlabelled colourless liquids are pent-1-ene, pentan-1-ol and pentanal. Describe how a combination of tests from Table 5 would identify each.

Test 1 — bromine water (cold): only **pent-1-ene** rapidly decolourises orange bromine water, since it is the only one of the three with a $C=C$ double bond available for electrophilic addition. Pentan-1-ol and pentanal do not decolourise bromine water under these conditions.

Test 2 — 2,4-DNPH, then Tollens' reagent, on the two remaining liquids: pentanal contains a carbonyl group, so it gives an orange precipitate with 2,4-DNPH and, being an aldehyde, also gives a **silver mirror** with warm Tollens' reagent.
Pentan-1-ol has no carbonyl group, so it gives *no* precipitate with 2,4-DNPH and *no* silver mirror with Tollens' reagent.

Conclusion: decolourises bromine water → pent-1-ene; positive 2,4-DNPH and Tollens' → pentanal; negative to both → pentan-1-ol.

VN **GIẢI THÍCH TIẾNG VIỆT**
Kết hợp các phép thử: nước brom phân biệt anken (mất màu nhanh) với hai chất còn lại; 2,4-DNPH và Tollens' sau đó phân biệt pentanal (có nhóm carbonyl, cho gương bạc) với pentan-1-ol (không phản ứng với cả hai). Đây là kỹ năng suy luận tổng hợp thường gặp trong đề thi.

Ví dụ 12 · Quantitative synthesis: mass of hydroxynitrile from propanone + HCN

5.8 g of propanone, CH_3COCH_3 ($M_r = 58$), is reacted with excess HCN. Calculate the maximum theoretical mass of 2-hydroxy-2-methylpropanenitrile, $(CH_3)_2C(OH)CN$, that could be obtained.

Step 1 — moles of propanone:

$$n(CH_3COCH_3) = \frac{5.8}{58} = 0.100 \text{ mol}$$

Step 2 — mole ratio. The equation $(CH_3)_2C=O + HCN \rightarrow (CH_3)_2C(OH)CN$ is $1:1:1$, so $n(\text{hydroxynitrile}) = 0.100$ mol (since HCN is in excess, propanone is the limiting reagent).

Step 3 — M_r of the hydroxynitrile, C_4H_7NO: $4(12) + 7(1) + 14 + 16 = 48 + 7 + 14 + 16 = 85$.

Step 4 — mass:

$$\text{mass} = 0.100 \times 85 = \mathbf{8.5} \text{ g}$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Bài toán định lượng: đổi khối lượng propanon sang số mol, dùng tỉ lệ mol $1:1$ trong phương trình cộng HCN, tính khối lượng mol của sản phẩm hydroxynitril rồi suy ra khối lượng lý thuyết tối đa (giả sử HCN dư, propanon là chất hết trước).

13.4 Practice bank

Bài luyện 1

Which type of mechanism describes the reaction of bromoethane with aqueous NaOH?

(A) Electrophilic addition
(B) Nucleophilic substitution
(C) Nucleophilic addition
(D) Free-radical substitution

Lời giải chi tiết

OH^- has a lone pair (nucleophile) and attacks the electron-deficient carbon bearing Br, substituting it. **Answer: (B) Nucleophilic substitution.**

Bài luyện 2

Explain, in terms of bond enthalpy, why 1-iodopropane hydrolyses faster than 1-chloropropane under the same conditions with aqueous $AgNO_3$.

Lời giải chi tiết

The C — I bond has a lower mean bond enthalpy (≈ 238 kJ mol^{-1}) than C — Cl (≈ 338 kJ mol^{-1}), because iodine's larger atomic radius gives weaker orbital overlap with carbon. The weaker C — I bond breaks more easily (lower activation energy for the rate-determining bond-breaking step), so **1-iodopropane hydrolyses faster**, releasing I^- sooner to be precipitated by Ag^+ as pale yellow AgI.

Bài luyện 3

Give the reagents and conditions to convert 1-bromopropane into butanenitrile, $CH_3CH_2CH_2CN$.

Lời giải chi tiết

Reagents/conditions: KCN dissolved in ethanol, warmed under reflux.

$$CH_3CH_2CH_2Br + KCN \xrightarrow[\text{ethanol}]{\text{warm}} CH_3CH_2CH_2CN + KBr$$

The nucleophile CN^- substitutes Br^-, extending the chain by one carbon (from 3 to 4 carbons) to give **butanenitrile**.

Bài luyện 4

State the reagents/conditions needed to convert 1-chlorobutane into butan-1-amine using excess ammonia, and explain why excess NH_3 is used.

Lời giải chi tiết

Reagents/conditions: excess NH_3 dissolved in ethanol, heated in a sealed tube (to prevent the volatile ammonia escaping).

$$CH_3CH_2CH_2CH_2Cl + 2NH_3 \rightarrow CH_3CH_2CH_2CH_2NH_2 + NH_4Cl$$

Why excess NH_3: the primary amine product, $CH_3CH_2CH_2CH_2NH_2$, is itself a nucleophile and could react further with unreacted 1-chlorobutane to give secondary/tertiary amines or a quaternary ammonium salt. A large excess of NH_3 makes it statistically far more likely that a halogenoalkane molecule collides with an NH_3 molecule than with an amine product molecule, maximising the yield of the primary amine.

Bài luyện 5

Which set of conditions favours **elimination** rather than substitution when a halogenoalkane reacts with hydroxide ion?

(A) Dilute aqueous NaOH, warmed

(B) Concentrated ethanolic NaOH, heated under reflux

(C) Dilute aqueous NaOH, cold

(D) Aqueous $AgNO_3$, warmed

Lời giải chi tiết

Ethanolic (non-aqueous), concentrated, hot hydroxide favours OH^- acting as a base (elimination) rather than a nucleophile (substitution). **Answer: (B).**

Bài luyện 6

2-bromopentane, $CH_3CHBrCH_2CH_2CH_3$, is heated under reflux with concentrated KOH dissolved in ethanol. Identify the organic product(s) formed and explain.

Lời giải chi tiết

Concentrated ethanolic KOH, heated, makes OH^- act as a **base**, eliminating HBr. The $-Br$ is on C2; hydrogens are available on **both** adjacent carbons, C1 and C3:

- removing H from C1 gives $CH_2=CHCH_2CH_2CH_3$ (**pent-1-ene**);
- removing H from C3 gives $CH_3CH=CHCH_2CH_3$ (**pent-2-ene**).

Product: a mixture of pent-1-ene and pent-2-ene.

Bài luyện 7

Classify 2-methylbutan-2-ol, $(CH_3)_2C(OH)CH_2CH_3$, as primary, secondary or tertiary.

(A) Primary
(B) Secondary
(C) Tertiary
(D) Cannot be classified

Lời giải chi tiết

The $-OH$ carbon is bonded to *three* other carbons (two methyl groups and the CH_2CH_3 chain). **Answer: (C) Tertiary.**

Bài luyện 8

Predict what would be observed if 2-methylbutan-2-ol is heated under reflux with excess acidified $K_2Cr_2O_7$.

Lời giải chi tiết

2-methylbutan-2-ol is a **tertiary** alcohol (Bài luyện 7), with no hydrogen atom on the $-OH$ carbon. It **cannot be oxidised** by acidified $K_2Cr_2O_7$. **Observation: the mixture stays orange — no reaction.**

Bài luyện 9

Write equations, with conditions, for (a) the partial oxidation of pentan-1-ol to pentanal, and (b) the full oxidation of pentan-1-ol to pentanoic acid.

Lời giải chi tiết

(a) Partial oxidation (aldehyde), gentle heat, distil product as it forms:

$$CH_3CH_2CH_2CH_2CH_2OH + [O] \xrightarrow[\text{distil}]{K_2Cr_2O_7/H^+} CH_3CH_2CH_2CH_2CHO + H_2O$$

(b) Full oxidation (carboxylic acid), excess oxidant, heat under reflux:

$$CH_3CH_2CH_2CH_2CH_2OH + 2[O] \xrightarrow[\text{reflux}]{\text{excess } K_2Cr_2O_7/H^+} CH_3CH_2CH_2CH_2COOH + H_2O$$

Bài luyện 10

Which single reagent reliably distinguishes an aldehyde from a ketone?

(A) 2,4-dinitrophenylhydrazine
(B) Bromine water
(C) Tollens' reagent
(D) Universal indicator

Lời giải chi tiết

2,4-DNPH and bromine water do not distinguish aldehyde from ketone (2,4-DNPH reacts with both; bromine water tests for C = C, not C = O). Tollens' reagent gives a silver mirror with aldehydes only. **Answer: (C).**

Bài luyện 11

Butan-2-ol and butan-1-ol are both warmed separately with I_2/NaOH. Predict and explain the result for each.

Lời giải chi tiết

Butan-2-ol, $CH_3CH(OH)CH_2CH_3$, contains the group $CH_3CH(OH)-$; I_2/NaOH oxidises it in situ to butan-2-one, $CH_3COCH_2CH_3$, which contains CH_3CO- — **positive**: pale yellow precipitate of CHI_3 forms.
Butan-1-ol, $CH_3CH_2CH_2CH_2OH$, has its $-OH$ carbon bonded to a CH_2 group, not CH_3; oxidation gives butanal, $CH_3CH_2CH_2CHO$, which does not contain CH_3CO- — **negative**: no precipitate.

Bài luyện 12

Butan-1-ol is heated with concentrated H_2SO_4. Explain why only **one** alkene product (but-1-ene) is obtained, unlike the mixture obtained from butan-2-ol.

Lời giải chi tiết

The $-OH$ in butan-1-ol is on C1 (an end carbon). The only carbon adjacent to C1 bearing hydrogens available for elimination is C2; there is no "other side" to remove a hydrogen from (since C1 is a terminal CH_2 group with no carbon beyond it). Removing an H from C2 gives only $CH_2 = CHCH_2CH_3$ (**but-1-ene**) — a single product, because only one β-carbon environment exists.

Bài luyện 13

What would be observed when propanone is warmed with 2,4-dinitrophenylhydrazine?

(A) No reaction
(B) A silver mirror
(C) An orange/yellow precipitate
(D) Effervescence

Lời giải chi tiết

Propanone contains a carbonyl group, C = O, which reacts with 2,4-DNPH to give a characteristic derivative. **Answer: (C) An orange/yellow precipitate.**

Bài luyện 14

Butanone, $CH_3COCH_2CH_3$, is reacted with HCN. Give the mechanism outline and name the hydroxynitrile product.

Lời giải chi tiết

CN^- attacks the electrophilic carbonyl carbon; the $C=O$ π bond breaks heterolytically, electrons moving onto oxygen to form the alkoxide intermediate; the oxygen is then protonated.

$$CH_3COCH_2CH_3 + HCN \rightarrow CH_3C(OH)(CN)CH_2CH_3$$

Numbering the product chain from the nitrile carbon (C1): C1(CN) - C2(OH, CH_3) - C3H_2 - C4H_3. Name: **2-hydroxy-2-methylbutanenitrile**.

Bài luyện 15

Write the equation for the reduction of pentanal, $CH_3CH_2CH_2CH_2CHO$, by $NaBH_4$, and name the product.

Lời giải chi tiết

Hydride ion adds to the carbonyl carbon, then the alkoxide is protonated:

$$CH_3CH_2CH_2CH_2CHO + 2[H] \xrightarrow{NaBH_4} CH_3CH_2CH_2CH_2CH_2OH$$

Product: **pentan-1-ol** (a primary alcohol, since pentanal is an aldehyde).

Bài luyện 16

Which class of alcohol does **not** react with acidified $K_2Cr_2O_7$?

(A) Primary
(B) Secondary
(C) Tertiary
(D) All alcohols react

Lời giải chi tiết

A tertiary alcohol has no hydrogen on the $-OH$ carbon, so it cannot be oxidised. **Answer: (C) Tertiary.**

Bài luyện 17

Write the equation, with catalyst, for the esterification of ethanoic acid with methanol, and name the ester formed.

Lời giải chi tiết

$$CH_3COOH + CH_3OH \xrightarrow{\text{conc. } H_2SO_4} CH_3COOCH_3 + H_2O$$

The concentrated H_2SO_4 acts as a catalyst. Product: **methyl ethanoate**.

Bài luyện 18

6.0 g of ethanoic acid ($M_r = 60$) is reacted with excess ethanol and a catalytic amount of concentrated H_2SO_4. Calculate the maximum theoretical mass of ethyl ethanoate ($M_r = 88$) obtainable.

Lời giải chi tiết

Step 1: $n(CH_3COOH) = \dfrac{6.0}{60} = 0.10$ mol.
Step 2: the equation $CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$ is $1:1$, so $n(\text{ester}) = 0.10$ mol (ethanoic acid is limiting, since ethanol is in excess).
Step 3: mass $= 0.10 \times 88 =$ **8.8** g.

Bài luyện 19

A colourless liquid X rapidly decolourises bromine water but gives no reaction with either 2,4-DNPH or Tollens' reagent. Identify the class of compound X belongs to.

Lời giải chi tiết

Decolourising bromine water indicates a $C=C$ double bond (electrophilic addition of Br_2 across the alkene). No reaction with 2,4-DNPH (no carbonyl group) rules out an aldehyde or ketone. **X is an alkene.**

Bài luyện 20

Which halogenoalkane reacts fastest by nucleophilic substitution with aqueous NaOH, all else being equal?

(A) 1-chlorobutane
(B) 1-bromobutane
(C) 1-iodobutane
(D) They all react at the same rate

Lời giải chi tiết

The $C-I$ bond is weakest (lowest mean bond enthalpy), so it breaks fastest. **Answer: (C) 1-iodobutane.**

Bài luyện 21

Butanenitrile, $CH_3CH_2CH_2CN$, is heated under reflux with dilute hydrochloric acid. Write the equation and name the organic product.

Lời giải chi tiết

Acid hydrolysis of a nitrile gives a carboxylic acid and an ammonium salt:

$$CH_3CH_2CH_2CN + 2H_2O + HCl \xrightarrow{\text{reflux}} CH_3CH_2CH_2COOH + NH_4Cl$$

Organic product: **butanoic acid**.

Bài luyện 22

The addition of HCN to a carbonyl compound is best classified as:

(A) Electrophilic addition
(B) Nucleophilic addition
(C) Nucleophilic substitution
(D) Elimination

Lời giải chi tiết

CN^- is a nucleophile that adds across the polarised $C=O$ double bond. **Answer: (B) Nucleophilic addition.**

Bài luyện 23

Explain why the nucleophile CN^- attacks the carbon of the carbonyl group and not the oxygen.

Lời giải chi tiết

The carbonyl group is polarised $C^{\delta+}=O^{\delta-}$: oxygen, being more electronegative, pulls the bonding electron density towards itself, leaving the carbon electron-deficient ($C^{\delta+}$). A nucleophile is attracted to regions of positive charge, so **it attacks the electron-deficient carbon**, not the already electron-rich oxygen.

Bài luyện 24

Pentan-2-ol, $CH_3CH(OH)CH_2CH_2CH_3$, is heated under reflux with excess acidified $K_2Cr_2O_7$. Classify the alcohol and give the product.

Lời giải chi tiết

The $-OH$ carbon (C2) is bonded to two other carbons (C1 and C3) → **secondary alcohol**. Oxidation gives a ketone:

$$CH_3CH(OH)CH_2CH_2CH_3 + [O] \rightarrow CH_3COCH_2CH_2CH_3 + H_2O$$

Product: **pentan-2-one**; observation: orange → green.

Bài luyện 25

Compound Y, on warming with excess acidified $K_2Cr_2O_7$ under reflux, gives a product that turns Tollens' reagent into a silver mirror but does *not* give a positive iodoform test. Suggest the class of alcohol Y belongs to and one specific example.

Lời giải chi tiết

A silver-mirror-positive oxidation product must be an **aldehyde**, so Y must be a **primary alcohol** (secondary alcohols give ketones, which are Tollens'-negative). Since the product (and hence Y) does *not* give a positive iodoform test, Y cannot contain the $CH_3CH(OH)-$ group — so Y is *not* ethanol. **Example: propan-1-ol**, $CH_3CH_2CH_2OH$, which oxidises to propanal (Tollens'-positive) but contains no $CH_3CH(OH)-$ group (iodoform-negative).

Bài luyện 26

Which reagent converts a ketone directly into a secondary alcohol?

(A) $NaBH_4$
(B) Acidified $K_2Cr_2O_7$
(C) 2,4-DNPH
(D) Tollens' reagent

Lời giải chi tiết

$NaBH_4$ supplies hydride ion, which adds to the carbonyl carbon of a ketone to give a secondary alcohol after protonation. **Answer: (A).**

Bài luyện 27

Outline a synthetic route (equations + conditions), starting only from ethanol, to propanoic acid, CH_3CH_2COOH.

Lời giải chi tiết

Step 1 — convert the alcohol to a halogenoalkane, e.g. with concentrated HBr, heated under reflux:

$$CH_3CH_2OH + HBr \xrightarrow{\text{heat}} CH_3CH_2Br + H_2O$$

Step 2 — chain-extend by nucleophilic substitution with KCN (ethanolic, warm):

$$CH_3CH_2Br + KCN \xrightarrow[\text{ethanol}]{\text{warm}} CH_3CH_2CN + KBr$$

Step 3 — acid hydrolysis of the nitrile (reflux with dilute HCl):

$$CH_3CH_2CN + 2H_2O + HCl \xrightarrow{\text{reflux}} CH_3CH_2COOH + NH_4Cl$$

Overall, the 2-carbon ethanol is converted, via bromoethane and propanenitrile, into the 3-carbon product **propanoic acid** — the CN^- substitution step is what extends the chain.

Bài luyện nâng cao (A2)

A student proposes that 2-bromo-2-methylpropane, $(CH_3)_3CBr$, could be converted directly into 2-methylpropan-2-ol using concentrated ethanolic NaOH under reflux. Comment on whether this choice of conditions is appropriate, and suggest better conditions.

Lời giải chi tiết

Concentrated ethanolic NaOH, heated under reflux, favours OH^- acting as a **base** (elimination), giving the alkene 2-methylpropene as the major product, *not* the alcohol. To obtain 2-methylpropan-2-ol by substitution, **dilute/aqueous** NaOH**, warmed** should be used instead, so that OH^- acts predominantly as a **nucleophile**:

$$(CH_3)_3CBr + NaOH \xrightarrow{\text{aq., warm}} (CH_3)_3COH + NaBr$$

Carboxylic Acids, Nitrogen Compounds, Polymers and Analytical Techniques

Mục tiêu Unit: So sánh tính axit axit carboxylic/phenol/ancol; phản ứng của axit carboxylic và dẫn xuất acyl chloride; tính bazơ của amin béo/thơm; muối diazoni và phản ứng ghép đôi tạo phẩm nhuộm azo (A2); axit amin, zwitterion và peptit; polime cộng và polime ngưng tụ; benzen và thế electrophin; sắc ký; phổ khối lượng; phổ hồng ngoại; phổ cộng hưởng từ hạt nhân proton và ^{13}C; kết hợp M_r, IR, NMR để xác định cấu trúc.

14.1 Carboxylic acids and acyl chlorides

Acidity: carboxylic acid > phenol > alcohol

All three classes can, in principle, lose the proton from an $-OH$ group, but they differ hugely in acid strength because of how well the resulting anion (conjugate base) is stabilised by **delocalisation (resonance)** of the negative charge:

- In a **carboxylate ion**, $RCOO^-$, the negative charge is delocalised equally over *two* oxygen atoms (both $C-O$ bonds become equivalent, of intermediate bond order) — strong stabilisation, so carboxylic acids are the most acidic of the three.
- In a **phenoxide ion**, $C_6H_5O^-$, the negative charge on oxygen can delocalise, to a lesser extent, into the benzene ring's π system — some stabilisation, but weaker than in a carboxylate (only one oxygen carries the charge, and delocalisation into the ring is less effective than symmetric delocalisation over two electronegative oxygens).
- In an **alkoxide ion**, RO^- (from an alcohol), there is **no** delocalisation available — the negative charge stays localised on one oxygen, so it is the least stable anion, and alcohols are the weakest acids of the three (essentially neutral in aqueous solution).

Order of acid strength: **carboxylic acid** > **phenol** > **alcohol**.

VN **GIẢI THÍCH TIẾNG VIỆT**

Cả ba loại hợp chất đều có thể mất proton từ nhóm $-OH$, nhưng độ bền của anion tạo thành (nhờ giải toả điện tích âm) quyết định độ mạnh axit: ion carboxylat giải toả điện tích đều trên hai nguyên tử oxi (bền nhất); ion phenoxit giải toả một phần vào vòng benzen (bền vừa); ion ancolat không giải toả được (kém bền nhất). Do đó: **axit carboxylic** > **phenol** > **ancol** về độ mạnh axit.

Reactions of carboxylic acids

Carboxylic acids, RCOOH, show typical acid reactions and are converted to acyl chlorides by two key reagents:

- with carbonates/hydrogencarbonates: $2RCOOH + Na_2CO_3 \rightarrow 2RCOONa + H_2O + CO_2$

(effervescence — a useful confirmatory test for a carboxylic acid);

- with an alcohol (conc. H_2SO_4 catalyst, reflux): esterification, $RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$;
- with PCl_5 or $SOCl_2$: converted to the corresponding **acyl chloride**, $RCOOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$ (or $RCOOH + SOCl_2 \rightarrow RCOCl + SO_2 + HCl$), both giving observable steamy/acidic fumes of HCl.

VN **GIẢI THÍCH TIẾNG VIỆT**

Axit carboxylic phản ứng với muối carbonat (sủi bọt khí CO_2 — phép thử nhận biết), với ancol (xúc tác H_2SO_4 đặc, tạo este), và với PCl_5/$SOCl_2$ để chuyển thành **acyl chloride** (kèm khí HCl có khói trắng).

14.1.1 Esterification as a reversible reaction, and driving the equilibrium

Esterification is an equilibrium

Esterification is a **reversible** reaction that reaches **dynamic equilibrium**, catalysed by concentrated H_2SO_4:

$$RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$$

By Le Chatelier's principle (Chapter 7), the position of equilibrium — and hence the **yield** of ester — can be increased by:

- using an **excess** of one reactant (usually the cheaper alcohol or acid), which shifts the equilibrium towards the products to partially consume the excess; or
- **removing product** as it forms — e.g. distilling off the low-boiling ester as it is produced, or adding concentrated H_2SO_4 in excess (which also absorbs water, removing it from the equilibrium mixture) — shifting the equilibrium further to the right.

The catalyst (conc. H_2SO_4) speeds up the attainment of equilibrium but does **not** change its position or the equilibrium yield.

VN **GIẢI THÍCH TIẾNG VIỆT**

Este hoá là phản ứng **thuận nghịch**, đạt trạng thái cân bằng động. Theo nguyên lý Le Chatelier (Chương 7), có thể tăng hiệu suất este bằng cách dùng **dư** một chất phản ứng hoặc **loại bỏ sản phẩm** (chưng cất este, hoặc dùng H_2SO_4 đặc dư để hút nước). Xúc tác chỉ làm cân bằng đạt nhanh hơn, **không** làm thay đổi vị trí cân bằng hay hiệu suất cân bằng.

Ví dụ 1 · Driving esterification to higher yield

Ethanoic acid is reacted with ethanol, catalysed by concentrated H_2SO_4, to form ethyl ethanoate: $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$. Suggest **two** distinct practical changes that would increase the yield of ester, explaining each using Le Chatelier's principle.

Change 1 — use a large excess of ethanol. Adding excess C_2H_5OH increases the concentration of one reactant; by Le Chatelier's principle the equilibrium position shifts to the **right** (towards products) to partially oppose this increase, converting more ethanoic acid into ester and increasing the yield based on the acid.

Change 2 — continuously remove the ester (or water) as it forms, e.g. by distilling off the ester (which typically has a lower boiling point than the acid/alcohol) as soon as it forms. Removing

a product decreases its concentration, so by Le Chatelier's principle the equilibrium shifts to the **right** to replace the removed ester, again increasing the overall yield.

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Hai cách tăng hiệu suất este: (1) dùng dư một chất phản ứng (đẩy cân bằng sang phải theo Le Chatelier); (2) loại bỏ sản phẩm liên tục (chưng cất este hoặc hút nước bằng H_2SO_4 đặc dư), cũng đẩy cân bằng sang phải.

14.1.2 Acyl chlorides: reactivity contrasted with carboxylic acids (A2)

Acyl chlorides are far more reactive than the parent acid

An acyl chloride, RCOCl, reacts with water, alcohols and amines via **nucleophilic addition-elimination**: the nucleophile's lone pair attacks the electrophilic carbonyl carbon (made even more electrophilic than in the acid because Cl is strongly electron-withdrawing and is also a good leaving group), forming a tetrahedral intermediate, which then collapses, expelling Cl^- (as HCl).

$CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$ $CH_3COCl + C_2H_5OH \rightarrow CH_3COOC_2H_5 + HCl$ $CH_3COCl + 2$

Reaction with	Acyl chloride, RCOCl	Carboxylic acid, RCOOH
Water	fast, vigorous, exothermic; visible steamy/acidic HCl fumes; complete in seconds	no vigorous reaction — carboxylic acids are already stable in water
Alcohol	fast, exothermic, goes to completion (no catalyst, no reflux needed) — direct addition-elimination	slow, reversible **equilibrium**; needs conc. H_2SO_4 catalyst and heating under reflux (Section above)
Amine	fast, vigorous, exothermic; gives an amide directly	carboxylic acids react with amines only as an acid-base neutralisation (forming an ammonium carboxylate salt), *not* directly to an amide

Table 1. Acyl chlorides react fast and irreversibly (addition-elimination, Cl^- a good leaving group); the corresponding acids react slowly and/or reversibly, or not at all with the same nucleophile.

VN **GIẢI THÍCH TIẾNG VIỆT**

Acyl chloride phản ứng **nhanh, mạnh, toả nhiệt** với nước/ancol/amin theo cơ chế cộng-tách nucleophin (vì Cl^- là nhóm rời tốt), tạo khói HCl rõ rệt với nước. Axit carboxylic tương ứng phản ứng **chậm hơn nhiều** hoặc ở dạng cân bằng thuận nghịch (như este hoá cần xúc tác, đun hồi lưu), và với amin chỉ cho phản ứng axit-bazơ tạo muối, không trực tiếp tạo amit.

Ví dụ 2 · Ethanoyl chloride + ethylamine forming an amide

Ethanoyl chloride, CH_3COCl, is added dropwise to excess ethylamine, $C_2H_5NH_2$. Describe the mechanism briefly and give the equation and name of the organic product.

The lone pair on the nitrogen of ethylamine (nucleophile) attacks the electrophilic carbonyl carbon of CH_3COCl; a tetrahedral intermediate forms and then collapses, expelling Cl^-, which is picked up by a second molecule of ethylamine (acting as a base) to form the ammonium salt

by-product:

$$CH_3COCl + 2C_2H_5NH_2 \rightarrow CH_3CONHC_2H_5 + C_2H_5NH_3Cl$$

Organic product: **N-ethylethanamide** (an amide), $CH_3CONHC_2H_5$. Two moles of ethylamine are needed per mole of acyl chloride: one is incorporated into the amide, the other neutralises the HCl by-product.

VN **GIẢI THÍCH TIẾNG VIỆT**

Cặp electron trên N của etylamin tấn công carbon carbonyl của CH_3COCl (cơ chế cộng-tách nucleophin), tạo amit N-etyletanamit; cần 2 mol amin — 1 mol vào sản phẩm amit, 1 mol trung hoà HCl sinh ra.

14.2 Nitrogen compounds: amines, diazonium salts, amino acids

Basicity of amines

An amine acts as a base (and a nucleophile) because the nitrogen atom has a lone pair of electrons that can accept a proton (or attack an electrophile). The base strength depends on how available that lone pair is:

- **Aliphatic amines** (e.g. ethylamine, $C_2H_5NH_2$) are **more basic than ammonia**: the alkyl group is electron-donating (positive inductive effect), pushing electron density onto nitrogen and making its lone pair *more* available to accept a proton.
- **Ammonia**, NH_3, is intermediate.
- **Aromatic amines** (e.g. phenylamine, $C_6H_5NH_2$) are **less basic than ammonia**: the nitrogen lone pair is partly delocalised into the benzene ring's π system, making it *less* available to bind a proton.

Order of base strength: **aliphatic amine** > **ammonia** > **aromatic amine**.

VN **GIẢI THÍCH TIẾNG VIỆT**

Tính bazơ của amin phụ thuộc mức độ "sẵn có" của cặp electron tự do trên N: amin béo (nhóm ankyl đẩy electron) có tính bazơ **mạnh hơn** NH_3; amin thơm (phenylamin, cặp electron N giải toả một phần vào vòng benzen) có tính bazơ **yếu hơn** NH_3. Thứ tự: **amin béo** > NH_3 > **amin thơm**.

Ví dụ 3 · Ranking base strength

Rank ethylamine, ammonia and phenylamine in order of **increasing** base strength, explaining your reasoning.

Phenylamine (weakest): the nitrogen lone pair is partly delocalised into the aromatic ring, reducing its availability to accept a proton.
Ammonia (intermediate): no substituent effects — the reference point.
Ethylamine (strongest): the ethyl group is electron-donating, increasing electron density on nitrogen and making the lone pair more available to bind H^+.

Order (increasing base strength): phenylamine < ammonia < ethylamine.

VN **GIẢI THÍCH TIẾNG VIỆT**
Phenylamin yếu nhất (cặp electron N giải toả vào vòng thơm), NH_3 trung gian, etylamin mạnh nhất (nhóm etyl đẩy electron làm tăng mật độ electron trên N).

14.2.1 Diazonium salts and azo dyes (A2)

Diazotisation and azo coupling

Phenylamine reacts with nitrous acid, HNO_2 (generated in situ from $NaNO_2$ and HCl), at **0–5** °C, to form a **diazonium salt**:

$$C_6H_5NH_2 + HNO_2 + HCl \xrightarrow{0\text{–}5\,^\circ C} C_6H_5N_2^+Cl^- + 2H_2O$$

The diazonium salt then reacts with phenol under **alkaline** conditions (phenol first converted to the more reactive phenoxide ion, $C_6H_5O^-$) in a **coupling reaction**, forming a highly coloured **azo compound** containing the $-N=N-$ (azo) linkage — the basis of many synthetic azo dyes:

$$C_6H_5N_2^+Cl^- + C_6H_5OH \xrightarrow{NaOH(aq)} C_6H_5N=NC_6H_4OH + HCl$$

(!) Lỗi thường gặp: Diazonium salts are **thermally unstable** and decompose (releasing N_2 gas) if the temperature rises much above about $5\,^\circ C$. The diazotisation step **must** therefore be carried out below $5\,^\circ C$ (typically in an ice bath, $0\text{–}5\,^\circ C$) — a very common mistake is to forget this temperature constraint and assume any acidic conditions will do.

VN **GIẢI THÍCH TIẾNG VIỆT**
Phenylamin phản ứng với HNO_2 (từ $NaNO_2$/HCl) ở **0–5** °C tạo muối diazoni $C_6H_5N_2^+Cl^-$. Muối này ghép đôi với phenol (trong môi trường kiềm, phenol chuyển thành phenoxit phản ứng mạnh hơn) tạo hợp chất azo có màu — cơ sở của thuốc nhuộm azo. **Lưu ý quan trọng:** phải giữ nhiệt độ thấp (0–5 °C) vì muối diazoni phân huỷ nhanh ở nhiệt độ cao hơn.

14.2.2 Amino acids and peptides

Zwitterions and pH

An amino acid, $H_2NCH(R)COOH$, contains both a basic amine group and an acidic carboxylic acid group. In the solid state and near neutral pH, it exists as a **zwitterion** — a dipolar ion with both a positive and a negative charge on the *same* molecule, formed by internal proton transfer from the $-COOH$ to the $-NH_2$:

$$H_2NCH(R)COOH \rightleftharpoons H_3N^+CH(R)COO^-$$

The dominant form changes with pH:

- in **strongly acidic** solution (low pH, excess H^+): the carboxylate is protonated, giving a net **cationic** species, $H_3N^+CH(R)COOH$;
- near the **isoelectric point** (neutral pH for a simple amino acid): the **zwitterion**, $H_3N^+CH(R)COO^-$, predominates (net charge zero);
- in **strongly basic** solution (high pH, excess OH^-): the ammonium group is deprotonated, giving a net **anionic** species, $H_2NCH(R)COO^-$.

VN **GIẢI THÍCH TIẾNG VIỆT**

Axit amin tồn tại dưới dạng **ion lưỡng cực (zwitterion)** gần pH trung tính, do nhóm $-COOH$ nhường proton nội phân tử cho nhóm $-NH_2$. Ở pH thấp (axit mạnh): dạng **cation**; ở pH cao (kiềm mạnh): dạng **anion**; ở điểm đẳng điện: dạng **lưỡng cực trung hoà điện**.

Ví dụ 4 · Dominant form of glycine at different pH

Glycine, H_2NCH_2COOH, is the simplest amino acid. State and explain the dominant structural form of glycine in (a) strongly acidic solution (e.g. pH 1), (b) neutral solution (pH 7, close to its isoelectric point), and (c) strongly basic solution (e.g. pH 13).

(a) Strongly acidic (pH 1): excess H^+ protonates the amine group and the carboxylate remains protonated too, giving the fully protonated **cation**, $H_3N^+CH_2COOH$.

(b) Neutral (pH 7): internal proton transfer occurs, giving the **zwitterion**, $H_3N^+CH_2COO^-$ (net charge zero — this is the dominant, and most stable, form near the isoelectric point).

(c) Strongly basic (pH 13): excess OH^- removes the proton from $-NH_3^+$, giving the fully deprotonated **anion**, $H_2NCH_2COO^-$.

VN **GIẢI THÍCH TIẾNG VIỆT**

Glyxin: pH thấp → dạng cation $H_3N^+CH_2COOH$; pH trung tính → dạng lưỡng cực $H_3N^+CH_2COO^-$; pH cao → dạng anion $H_2NCH_2COO^-$.

Peptide bond formation

Two amino acid molecules join by **condensation**: the $-COOH$ of one reacts with the $-NH_2$ of the other, releasing a molecule of water and forming an amide linkage called a **peptide bond**, $-CONH-$:

$$H_2NCH(R_1)COOH + H_2NCH(R_2)COOH \rightarrow H_2NCH(R_1)CONHCH(R_2)COOH + H_2O$$

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Hai axit amin ngưng tụ (mất một phân tử nước) tạo liên kết peptit $-CONH-$ — bản chất là một liên kết amit giữa nhóm $-COOH$ của phân tử này và $-NH_2$ của phân tử kia.

Ví dụ 5 · Alanine: a chiral centre and racemic mixtures

Alanine, $CH_3CH(NH_2)COOH$, is a simple amino acid. Identify its chiral centre and explain what is meant by a racemic mixture in this context.

The central carbon of alanine, C2, is bonded to **four different groups**: $-CH_3$, $-NH_2$, $-COOH$, and $-H$. Because all four substituents are different, this carbon is a **chiral centre** (stereocentre), and alanine exists as **two non-superimposable mirror-image forms** (enantiomers), which rotate plane-polarised light in opposite directions.

A **racemic mixture** is an equal (1:1) mixture of both enantiomers; because the optical rotations of the two enantiomers exactly cancel, a racemic mixture shows **no net optical activity** even though each pure enantiomer individually does.

VN **GIẢI THÍCH TIẾNG VIỆT**

Carbon trung tâm của alanin gắn 4 nhóm khác nhau → là tâm bất đối (chiral centre), tạo ra hai đồng phân đối quang. Hỗn hợp raxemic (tỉ lệ 1:1 hai đồng phân đối quang) không có hoạt tính

quang học ròng vì độ quay của hai đồng phân triệt tiêu lẫn nhau.

14.3 Polymers and benzene

Addition polymers vs. condensation polymers

Addition polymers (e.g. poly(ethene), poly(chloroethene)/PVC) form when monomers containing a C = C double bond join together with no other product; the resulting polymer backbone is a long chain of C – C single bonds.
Condensation polymers (e.g. polyesters such as Terylene, polyamides such as nylon-6,6) form when bifunctional monomers react with loss of a small molecule (usually H_2O or HCl) at each linkage, producing **ester** or **amide** linkages along the backbone.

VN **GIẢI THÍCH TIẾNG VIỆT**
Polime **cộng** hình thành từ monome có liên kết đôi C = C, không giải phóng sản phẩm phụ, mạch chính chỉ gồm liên kết C – C. Polime **ngưng tụ** hình thành từ monome đa chức, giải phóng phân tử nhỏ (thường là nước) ở mỗi liên kết, tạo liên kết **este** hoặc **amit** dọc mạch chính.

VN **GIẢI THÍCH TIẾNG VIỆT**
Về khả năng phân huỷ sinh học: polime cộng có mạch chính chỉ toàn liên kết C – C rất bền, **trơ** với enzyme và nước — do đó **không phân huỷ sinh học**, tồn tại rất lâu trong môi trường (như túi nilon PE). Ngược lại, polime ngưng tụ có các liên kết **este** hoặc **amit** dọc mạch chính — đây là các liên kết có thể bị **thuỷ phân** (bởi nước, axit/bazơ, hoặc enzyme), nên polime ngưng tụ nhìn chung **dễ phân huỷ sinh học hơn** polime cộng.

14.3.1 Benzene: structure and electrophilic substitution

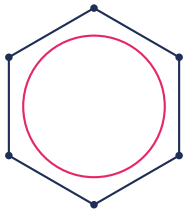

Figure 1. Benzene, C_6H_6: a planar hexagonal ring of six carbons, each bonded to one hydrogen, with the six "extra" electrons delocalised evenly above and below the ring plane (represented by the inner circle) rather than existing as three fixed, alternating C = C double bonds.

Evidence for delocalisation: enthalpy of hydrogenation

If benzene contained three *localised* C = C double bonds (the "cyclohexatriene" model), its enthalpy of hydrogenation would be expected to be about three times that of cyclohexene (-120 kJ mol^{-1} per double bond), i.e. ≈ -360 kJ mol^{-1}. The *experimental* enthalpy of hydrogenation of benzene to cyclohexane is only -208 kJ mol^{-1} — **much less exothermic** than predicted, by $360 - 208 = 152$ kJ mol^{-1}. This "missing" 152 kJ mol^{-1} is the **resonance (delocalisation) stabilisation energy**: real benzene is more stable (lower in energy) than the hypothetical localised structure, because its π electrons are delocalised over all six carbons. This is why benzene undergoes **electrophilic substitution** (which preserves the stable delocalised ring) rather than the electrophilic **addition** typical of alkenes (which would destroy the delocalisation).

VN **GIẢI THÍCH TIẾNG VIỆT**

Nếu benzen có 3 liên kết đôi C = C định xứ, nhiệt hiđro hoá dự đoán ≈ -360 kJ mol^{-1} (gấp 3 lần xiclohexen, -120 kJ mol^{-1} mỗi liên kết). Thực nghiệm chỉ đo được -208 kJ mol^{-1} — kém toả nhiệt hơn 152 kJ mol^{-1}. Chênh lệch này chính là **năng lượng bền hoá do giải toả electron**, giải thích vì sao benzen bền hơn dự đoán và ưu tiên phản ứng **thế electrophin** (giữ nguyên hệ giải toả) thay vì **cộng electrophin** (phá vỡ hệ giải toả) như anken.

14.4 Chromatography and mass spectrometry

Paper/thin-layer chromatography: R_f

In chromatography, components of a mixture separate because they distribute differently between a **stationary phase** and a **mobile phase** (solvent). The **retention factor**, R_f, is defined as:

$$R_f = \frac{\text{distance travelled by the spot (component)}}{\text{distance travelled by the solvent front}}$$

R_f is always between 0 and 1, and is characteristic of a given compound under fixed conditions (same solvent, temperature, stationary phase), allowing identification by comparison with known reference values.

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Hệ số lưu giữ R_f = quãng đường vết chất di chuyển ÷ quãng đường dung môi di chuyển, luôn nằm trong khoảng 0 đến 1 và đặc trưng cho từng chất trong điều kiện xác định — dùng để nhận dạng bằng cách so sánh với giá trị chuẩn.

Ví dụ 6 · Calculating R_f

On a chromatogram, the solvent front travels 10.0 cm from the baseline, and a particular spot travels 4.0 cm from the baseline. Calculate R_f for this spot.

$$R_f = \frac{4.0}{10.0} = \mathbf{0.40}$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Áp dụng trực tiếp công thức R_f = quãng đường vết / quãng đường dung môi = 4.0/10.0 = 0.40.

In **gas chromatography (GC)**, a gaseous mobile phase carries a vaporised sample through a long column packed with (or coated with) a stationary phase; different components travel through the column at different speeds and emerge (are "detected") at different times, called **retention times**. Under fixed, identical conditions, a compound's retention time is reproducible and can be compared against known reference compounds to help identify it.

VN **GIẢI THÍCH TIẾNG VIỆT**

Sắc ký khí (GC): pha động là khí mang mẫu hoá hơi đi qua cột chứa pha tĩnh; các thành phần khác nhau di chuyển với tốc độ khác nhau, ra khỏi cột ở các **thời gian lưu** khác nhau — đặc trưng cho từng chất trong cùng điều kiện, dùng để so sánh nhận dạng.

14.4.1 Mass spectrometry

Molecular ion and fragmentation

In a mass spectrometer, a molecule is ionised (typically by electron impact) to give a **molecular ion**, M^+, whose mass-to-charge ratio (m/z) equals the relative molecular mass, M_r, of the compound. The molecular ion can fragment into smaller charged and neutral pieces; only the *charged* fragments are detected, appearing as additional peaks at lower m/z. Characteristic mass losses from the molecular ion peak include:

Mass lost	Fragment lost	Typical structural feature indicated
15	CH_3 (methyl radical)	a methyl group attached to the rest of the molecule
17	OH	an alcohol or carboxylic acid $-$OH
29	CHO or C_2H_5	an aldehyde carbonyl fragment, or an ethyl group
45	COOH or OC_2H_5	a carboxylic acid group, or an ethoxy fragment

Table 2. Common mass losses from the molecular ion, M^+, and the structural fragments they indicate.

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Ion phân tử M^+ có m/z bằng đúng M_r của hợp chất. Các mảnh vỡ đặc trưng (mất khối lượng 15, 17, 29, 45...) giúp suy luận nhóm chức: mất 15 (CH_3), mất 17 (OH), mất 29 (CHO hoặc C_2H_5), mất 45 (COOH hoặc OC_2H_5).

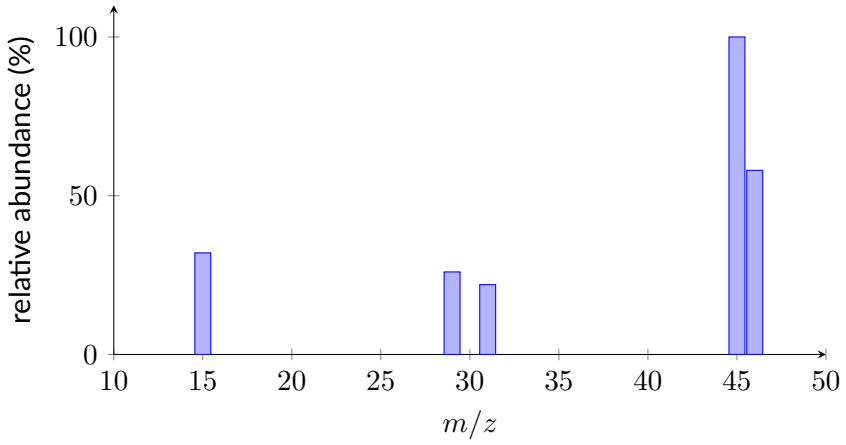


Figure 2. Simplified mass spectrum of ethanol, C_2H_5OH ($M_r = 46$). Molecular ion peak at $m/z = 46$; loss of CH_3 ($46 - 15$) gives $m/z = 31$ ($CH_2 = OH^+$); loss of H (or CHO, $46 - 29 = 17$; here shown as the $m/z = 29$ peak, $CHO^+/C_2H_5^+$); the base peak at $m/z = 45$ corresponds to loss of H (CH_3CHOH^+ or $CH_3CH_2O^+$).

Ví dụ 7 · Ethyl ethanoate: the acylium fragment at $m/z = 43$

Ethyl ethanoate, $CH_3COOC_2H_5$ ($M_r = 88$), gives a prominent fragment peak at $m/z = 43$. Suggest the identity and structure of this fragment, and explain why it is particularly stable.

Loss of the $-OC_2H_5$ group (M_r contribution $= 45$) from the molecular ion ($88 - 45 = 43$) leaves the **acylium ion**, CH_3CO^+ (M_r of fragment: $12 + 16 + 12 + 3 = 43$). This cation is relatively stable because the positive charge is delocalised through resonance between the carbon and the adjacent oxygen lone pair (i.e. a contributing structure $CH_3C \equiv O^+$), which helps explain

why it is observed as a strong peak.

VN **GIẢI THÍCH TIẾNG VIỆT**

Mảnh $m/z = 43$ từ etyl etanoat ứng với ion axyli CH_3CO^+ (mất nhóm $-OC_2H_5$, khối lượng 45, từ ion phân tử 88). Ion này bền tương đối do điện tích dương được giải toả cộng hưởng giữa carbon và oxi lân cận.

14.5 Infrared and proton NMR spectroscopy

Infrared spectroscopy: identifying bonds/functional groups

Different covalent bonds absorb infrared radiation at characteristic wavenumbers because of bond vibration (stretching/bending); comparing an unknown spectrum against reference wavenumber ranges identifies which bonds (functional groups) are present.

Bond	Wavenumber range/ cm^{-1}	Notes
O – H (alcohol)	3230–3550 (broad)	broad due to hydrogen bonding
O – H (carboxylic acid)	2500–3300 (very broad)	much broader and shifted to lower wavenumber than an alcohol O – H, due to stronger/more extensive hydrogen bonding (often overlaps C – H region)
N – H	3100–3500	amines, amides (often sharper/narrower than O – H)
C – H	2850–3100	almost all organic compounds
C ≡ N	2200–2260	nitriles
C = O	1650–1750	aldehydes, ketones, acids, esters, amides
C = C	1620–1680	alkenes (often weak)

Table 3. Characteristic infrared absorption wavenumber ranges.

(!) Lỗi thường gặp: A common error is failing to distinguish an alcohol's O – H peak (broad, but confined roughly to 3230–3550 cm^{-1}) from a carboxylic acid's O – H peak (**very broad**, extending down to about 2500 cm^{-1} and overlapping the C – H stretching region). If a spectrum shows *both* a very broad absorption starting near 2500–3300 cm^{-1} **and** a strong C = O peak near 1700 cm^{-1}, the compound is a **carboxylic acid**, not a simple alcohol.

VN **GIẢI THÍCH TIẾNG VIỆT**

Phổ IR: mỗi loại liên kết hấp thụ ở một khoảng số sóng đặc trưng. Lỗi thường gặp: nhầm O – H của ancol (rộng, khoảng 3230–3550) với O – H của axit carboxylic (rất rộng, kéo dài xuống ~2500, chồng lấn vùng C – H) — nếu thấy đỉnh rất rộng từ 2500–3300 **và** đỉnh C = O mạnh gần 1700, đó là **axit carboxylic**.

Proton (^{1}H) NMR spectroscopy

^{1}H NMR gives three key pieces of information for each signal (peak or group of peaks):

- **Chemical shift** (δ, ppm): indicates the chemical environment of the proton(s) responsible

(e.g. $-$OH, $-CH_3$ next to C $=$ O, aromatic $-$H).

- **Integration (relative peak area)**: proportional to the *number* of equivalent protons giving that signal.
- **Splitting pattern (multiplicity), the "$n+1$ rule"**: a signal is split into $n+1$ peaks by n non-equivalent protons on *adjacent* carbon(s).

Adding D_2O to the sample causes $-$OH and $-$NH protons to exchange rapidly for deuterium; their signal then **disappears** from the spectrum — a useful way to identify which peak was due to an exchangeable $-$OH/$-$NH proton.

VN **GIẢI THÍCH TIẾNG VIỆT**

Phổ NMR proton cho ba thông tin: **độ dịch chuyển hoá học** δ (môi trường hoá học), **diện tích tích phân** (tỉ lệ số proton tương đương), và **kiểu tách vân** theo quy tắc $n+1$ (n proton không tương đương ở carbon liền kề). Thêm D_2O làm tín hiệu $-$OH/$-$NH biến mất do trao đổi nhanh với đơteri — cách nhận biết proton linh động.

Ví dụ 8 · Ethanol's splitting pattern

Predict the splitting pattern (multiplicity) and relative integration of each proton environment in ethanol, CH_3CH_2OH.

$-CH_3$ **protons (3H):** adjacent to $-CH_2-$, which has 2 protons → split into $2+1=3$ peaks, a **triplet**; integration 3.
$-CH_2-$ **protons (2H):** adjacent to $-CH_3$ (3H) — normally would give a quartet, but is also adjacent to the $-$OH proton; in practice (with fast $-$OH proton exchange, as in most samples) the $-$OH coupling is not resolved, so the $-CH_2-$ signal appears as a **quartet** (split by the 3 CH_3 protons only, $3+1=4$ peaks); integration 2.
$-$OH **proton (1H):** appears as a broad singlet (not usually split, due to rapid proton exchange); integration 1; this signal **disappears** on shaking with D_2O.

VN **GIẢI THÍCH TIẾNG VIỆT**

Etanol: nhóm CH_3 tách thành vân ba (do 2H của CH_2 liền kề); nhóm CH_2 tách thành vân bốn (do 3H của CH_3 liền kề); proton OH cho vân đơn rộng, biến mất khi thêm D_2O.

14.5.1 ^{13}C NMR: number of carbon environments

^{13}C NMR — one peak per distinct carbon environment

In ^{13}C NMR, each chemically **distinct carbon environment** gives (in principle) one signal, regardless of how many carbons share that environment — unlike ^{1}H NMR, ^{13}CNMR spectra are not normally interpreted using integration or splitting, simply the **number** and **chemical shift** of the peaks. Counting the number of peaks directly tells you the number of chemically non-equivalent carbon atoms in the molecule.

Ví dụ 9 · Propanone: two carbon environments

Propanone, CH_3COCH_3, is a symmetric molecule. State the number of peaks expected in its ^{13}C NMR spectrum and identify the carbon environments.

Propanone has a plane of symmetry through the central carbonyl carbon: the **two** CH_3 **groups**

are chemically equivalent to each other (one environment), and the **carbonyl carbon** is a second, distinct environment. **Number of ^{13}C peaks: 2** — one for the (equivalent) methyl carbons, one for the carbonyl carbon — even though there are three carbon atoms in total.

VN **GIẢI THÍCH TIẾNG VIỆT**

Số vân trong phổ ^{13}C NMR bằng số môi trường carbon **khác nhau** về mặt hoá học, không phải tổng số nguyên tử carbon. Propanon có 3 carbon nhưng chỉ 2 môi trường khác nhau (2 nhóm CH_3 tương đương + 1 carbon carbonyl) → 2 vân phổ.

14.5.2 Combining M_r, IR and NMR to deduce structure

A structure-elucidation question typically combines: (1) the molecular ion peak, M^+, from mass spectrometry (gives M_r, and hence the molecular formula together with elemental composition/combustion data); (2) IR absorptions (identify functional groups present, e.g. C = O, broad O – H); (3) ^{1}H NMR chemical shifts, integration ratios and splitting patterns (assemble the carbon skeleton and pinpoint exactly which carbons bear which groups). Always cross-check that the proposed structure's M_r, all IR peaks, and the full *integration + splitting* pattern are **simultaneously** consistent — a structure that fits the NMR alone but contradicts the IR (or vice versa) must be rejected.

VN **GIẢI THÍCH TIẾNG VIỆT**

Bài tập xác định cấu trúc thường kết hợp: M_r (phổ khối) → công thức phân tử; IR → nhóm chức hiện diện; NMR (độ dịch chuyển + tích phân + tách vân) → khung carbon chi tiết. Luôn kiểm tra cấu trúc đề xuất phải khớp **đồng thời** cả ba loại dữ liệu.

Ví dụ 10 · Combined-spectra identification: ethyl ethanoate

An unknown liquid compound X has $M_r = 88$. Its IR spectrum shows a strong absorption at 1740 cm^{-1} and **no** broad absorption in the 2500–3550 cm^{-1} region. Its ^{1}H NMR spectrum shows: a triplet at $\delta 1.3$ (3H), a singlet at $\delta 2.0$ (3H), and a quartet at $\delta 4.1$ (2H). Identify X.

$M_r = 88$ is consistent with $C_4H_8O_2$ ($4 \times 12 + 8 \times 1 + 2 \times 16 = 48 + 8 + 32 = 88$).
IR: the 1740 cm^{-1} peak indicates a C = O group; the *absence* of any O – H absorption rules out a carboxylic acid or alcohol, pointing to an **ester**.
NMR: the quartet (2H) at $\delta 4.1$ (deshielded, next to the ester oxygen) coupled to the triplet (3H) at $\delta 1.3$ indicates an $-OCH_2CH_3$ (ethyl ester) fragment; the singlet (3H) at $\delta 2.0$ (no neighbouring protons to split it) indicates an isolated CH_3 attached directly to the carbonyl carbon.
Assembling: $CH_3 - CO - O - CH_2 - CH_3$ — **ethyl ethanoate**, $M_r = 88$, matching all three data sets.

VN **GIẢI THÍCH TIẾNG VIỆT**

Kết hợp $M_r = 88$ (công thức $C_4H_8O_2$), IR (C = O, không có O – H) → este, và NMR (vân bốn $\delta 4.1$ ghép vân ba $\delta 1.3$ → nhóm etyl este; vân đơn $\delta 2.0$ → CH_3 cạnh carbonyl) → xác định etyl etanoat.

Ví dụ 11 · Combined-spectra identification: propanoic acid (A2)

Compound Y has $M_r = 74$. Its IR spectrum shows a very broad absorption from about 2500–3300 cm^{-1} and a strong sharp absorption at 1715 cm^{-1}. Its ^{1}H NMR spectrum shows: a triplet at $\delta 1.1$ (3H), a quartet at $\delta 2.4$ (2H), and a singlet at $\delta 11.8$ (1H, exchanges with D_2O). Identify Y.

$M_r = 74$ fits $C_3H_6O_2$ ($3 \times 12 + 6 \times 1 + 2 \times 16 = 36 + 6 + 32 = 74$).
IR: the very broad 2500–3300 cm^{-1} absorption (overlapping the C – H region) together with the strong C = O peak at 1715 cm^{-1} is the classic signature of a **carboxylic acid** –COOH (not a simple alcohol, whose O – H would be confined to 3230–3550 cm^{-1} and would not accompany a C = O peak).
NMR: the very downfield singlet at $\delta 11.8$ (1H), which disappears with D_2O, is the acidic –COOH proton; the quartet (2H) at $\delta 2.4$ coupled to the triplet (3H) at $\delta 1.1$ indicates a $-CH_2CH_3$ (ethyl) fragment attached to the carboxyl carbon.
Assembling: $CH_3 - CH_2 - COOH$ — **propanoic acid**, $M_r = 74$, consistent with all three data sets.

VN **GIẢI THÍCH TIẾNG VIỆT**
$M_r = 74$ ($C_3H_6O_2$), IR (đỉnh rất rộng 2500–3300 kèm C = O mạnh 1715) → axit carboxylic, và NMR (vân đơn rất lệch trường $\delta 11.8$ biến mất với D_2O → proton COOH; vân bốn + vân ba → nhóm etyl) → xác định axit propanoic.

Ví dụ 12 · Combined-spectra identification: 1-chloropropane (A2)

Compound Z has $M_r = 78.5$ (consistent with one chlorine atom present) and shows **no** absorption in the C = O region (1650–1750 cm^{-1}) and no broad O – H/N – H absorption. Its ^{1}H NMR spectrum shows: a triplet at $\delta 1.0$ (3H), a sextet (six lines, from coupling to 5 neighbouring protons) at $\delta 1.8$ (2H), and a triplet at $\delta 3.5$ (2H, relatively deshielded). Identify Z.

$M_r \approx 78.5$: C_3H_7Cl has $M_r = 3(12) + 7(1) + 35.5 = 36 + 7 + 35.5 = 78.5$, consistent.
IR: the absence of C = O and O – H/N – H absorptions rules out carbonyl- or hydroxyl-/amine-containing structures, consistent with a simple **halogenoalkane**.
NMR: three proton environments (3H, 2H, 2H — total 7H, matching C_3H_7Cl) with a triplet–sextet–triplet pattern (each proton set coupled only to its immediate neighbours, consistent with an unbranched, straight chain) and the most deshielded signal ($\delta 3.5$, 2H) assigned to the $-CH_2-$ bonded directly to the electronegative Cl.
Assembling: $CH_3 - CH_2 - CH_2 - Cl$ — **1-chloropropane**, $M_r = 78.5$, consistent with all data.

VN **GIẢI THÍCH TIẾNG VIỆT**
$M_r = 78.5$ (có 1 nguyên tử Cl, ứng với C_3H_7Cl), IR không có C = O/O – H → loại trừ nhóm carbonyl/hydroxyl, và NMR ba môi trường proton (3H-2H-2H, mạch thẳng không phân nhánh) với tín hiệu lệch trường nhất ($\delta 3.5$) gắn với CH_2 cạnh Cl → xác định 1-clopropan.

14.6 Practice bank

Bài luyện 1

Which of the following correctly ranks acid strength from strongest to weakest?

(A) ethanol > phenol > ethanoic acid
(B) ethanoic acid > phenol > ethanol
(C) phenol > ethanoic acid > ethanol
(D) ethanol > ethanoic acid > phenol

Lời giải chi tiết

The carboxylate ion is the most resonance-stabilised (delocalisation over two oxygens), phenoxide less so (delocalisation into the ring only), and alkoxide not stabilised at all. **Answer: (B).**

Bài luyện 2

Describe the observation, and give the equation, when ethanoic acid is added to solid sodium carbonate.

Lời giải chi tiết

Observation: effervescence (bubbles of colourless gas, CO_2, which turns limewater milky).

$$2CH_3COOH + Na_2CO_3 \rightarrow 2CH_3COONa + H_2O + CO_2$$

Bài luyện 3

Suggest two practical ways to increase the yield of ester in the reversible reaction $CH_3CH_2COOH + CH_3OH \rightleftharpoons CH_3CH_2COOCH_3 + H_2O$.

Lời giải chi tiết

(1) Use a **large excess** of methanol (the cheaper reactant), shifting the equilibrium to the right by Le Chatelier's principle. (2) **Remove the ester** as it forms (e.g. by distillation, since it typically has a lower boiling point), or use excess concentrated H_2SO_4 to also absorb the water product — both shift the equilibrium further to the right, increasing yield.

Bài luyện 4

Explain why propanoyl chloride reacts with water far more readily than propanoic acid does.

Lời giải chi tiết

In propanoyl chloride, CH_3CH_2COCl, the Cl atom is strongly electron-withdrawing (making the carbonyl carbon highly electrophilic) and is also an excellent leaving group, so nucleophilic addition-elimination with water is fast, vigorous and irreversible (releasing HCl fumes). Propanoic acid has no such reactive leaving group on the carbonyl carbon (only $-OH$), so it does not react vigorously with water — indeed, it is already stable in aqueous solution.

Bài luyện 5

Give the equation for propanoyl chloride reacting with excess methylamine, and name the organic product.

Lời giải chi tiết

$$CH_3CH_2COCl + 2CH_3NH_2 \rightarrow CH_3CH_2CONHCH_3 + CH_3NH_3Cl$$

Organic product: **N-methylpropanamide**.

Bài luyện 6

Which statement about acyl chlorides compared to the corresponding carboxylic acid is correct?

(A) Acyl chlorides react more slowly with alcohols than the corresponding acid

(B) Acyl chlorides need a conc. H_2SO_4 catalyst to react with water

(C) Acyl chlorides react with water to release HCl fumes rapidly, without a catalyst

(D) Acyl chlorides do not react with amines

Lời giải chi tiết

Acyl chlorides react fast, exothermically, and without any catalyst with water, releasing visible HCl fumes. **Answer: (C).**

Bài luyện 7

Rank ethylamine, ammonia and phenylamine in order of **decreasing** base strength.

Lời giải chi tiết

Ethylamine $>$ **ammonia** $>$ **phenylamine.** The ethyl group donates electron density onto nitrogen (increasing basicity); the phenyl ring withdraws the nitrogen lone pair by delocalisation into the ring (decreasing basicity).

Bài luyện 8

State the conditions required for the diazotisation of phenylamine, and explain what happens if the temperature is allowed to rise above about $10\,^{\circ}\text{C}$.

Lời giải chi tiết

Conditions: $NaNO_2$ and dilute HCl, at 0–$5\,^{\circ}\text{C}$ (an ice bath). If the temperature rises significantly above $5\,^{\circ}\text{C}$, the diazonium salt is **thermally unstable** and decomposes, releasing nitrogen gas, N_2, and forming phenol as a by-product — the diazonium salt (and hence any subsequent coupling reaction) is lost.

Bài luyện 9

Describe the reaction of benzenediazonium chloride with phenol under alkaline conditions, including the type of product formed.

Lời giải chi tiết

Under alkaline conditions, phenol is converted to the more reactive phenoxide ion, $C_6H_5O^-$, which undergoes an electrophilic **coupling reaction** with the diazonium ion at the ring position para to the $-OH$:

$$C_6H_5N_2^+Cl^- + C_6H_5OH \xrightarrow{\text{NaOH(aq)}} C_6H_5N{=}NC_6H_4OH + HCl$$

This forms a highly coloured **azo compound** (containing the $-N=N-$ linkage) — the basis of azo dyes.

Bài luyện 10

Which form of glycine, H_2NCH_2COOH, predominates in strongly acidic solution?

(A) H_2NCH_2COOH (neutral)
(B) $H_3N^+CH_2COOH$ (cation)
(C) $H_3N^+CH_2COO^-$ (zwitterion)
(D) $H_2NCH_2COO^-$ (anion)

Lời giải chi tiết

Excess H^+ in strongly acidic solution protonates *both* the amine and (already protonated) carboxylic acid group, giving the fully protonated cation. **Answer: (B).**

Bài luyện 11

Explain, using structures, what is meant by the isoelectric point of an amino acid.

Lời giải chi tiết

The isoelectric point is the pH at which the amino acid exists predominantly as the electrically neutral **zwitterion**, $H_3N^+CH(R)COO^-$ — a dipolar ion with equal and opposite charges on the same molecule (a positive charge on the protonated amine and a negative charge on the deprotonated carboxylate), giving zero *net* charge, so the molecule does not migrate towards either electrode in an electric field at this pH.

Bài luyện 12

Write the equation for the condensation of two molecules of glycine, H_2NCH_2COOH, to form a dipeptide, and name the type of bond formed.

Lời giải chi tiết

$$H_2NCH_2COOH + H_2NCH_2COOH \rightarrow H_2NCH_2CONHCH_2COOH + H_2O$$

The new $-CONH-$ linkage formed is a **peptide bond** (an amide linkage).

Bài luyện 13

Explain why a racemic mixture of alanine shows no net optical activity, even though pure alanine is chiral.

Lời giải chi tiết

A racemic mixture contains the two enantiomers of alanine in equal (1:1) proportions. Each enantiomer rotates plane-polarised light by an equal amount but in **opposite** directions; in a 1:1 mixture, these equal and opposite rotations exactly **cancel out**, giving a net optical rotation of zero.

Bài luyện 14

Which type of polymer is expected to be more readily biodegradable, and why?

(A) Addition polymers, because their C–C backbone is easily hydrolysed

(B) Condensation polymers, because their ester/amide linkages can be hydrolysed

(C) Addition polymers, because they contain C=C double bonds

(D) Neither type is biodegradable

Lời giải chi tiết

Condensation polymers contain hydrolysable ester or amide linkages along the backbone, making them more susceptible to breakdown by water/enzymes; addition polymers have an inert all-carbon backbone. **Answer: (B).**

Bài luyện 15

Explain, using bond enthalpy/resonance ideas, why benzene undergoes electrophilic substitution rather than electrophilic addition.

Lời giải chi tiết

Benzene's six π electrons are delocalised evenly over all six ring carbons, giving substantial extra stability (the resonance/delocalisation energy, ≈ 152 kJ mol^{-1}, from comparing the experimental hydrogenation enthalpy, -208 kJ mol^{-1}, with the predicted value for three localised double bonds, ≈ -360 kJ mol^{-1}). Addition would use up two of these delocalised electrons to form new single bonds, destroying this stabilising delocalisation. **Substitution** instead replaces a hydrogen atom while regenerating the intact delocalised ring system afterwards, preserving the extra stability — so substitution is strongly favoured energetically over addition.

Bài luyện 16

On a chromatogram the solvent front travels 8.0 cm and a spot travels 6.0 cm. Calculate R_f.

Lời giải chi tiết

$$R_f = \frac{6.0}{8.0} = \mathbf{0.75}$$

Bài luyện 17

A compound has $M_r = 46$ and a strong IR absorption showing broad O $-$ H at 3300 cm^{-1} but **no** C $=$ O absorption. Suggest its identity.

Lời giải chi tiết

$M_r = 46$ with a broad O $-$ H but no carbonyl absorption is consistent with C_2H_6O ($2(12) + 6(1) + 16 = 24 + 6 + 16 = 46$) — **ethanol**, CH_3CH_2OH (not, for example, methanoic acid, which would show a C $=$ O peak).

Bài luyện 18

Butanone, $CH_3COCH_2CH_3$, shows a quartet in its ^{1}H NMR spectrum. Identify which protons give this signal and explain the splitting.

Lời giải chi tiết

The $-CH_2-$ protons (adjacent to the terminal $-CH_3$ of the ethyl group) give the quartet. By the $n+1$ rule, these 2 protons are split by the $n = 3$ non-equivalent protons on the neighbouring CH_3 group, giving $3 + 1 = 4$ peaks — a **quartet**, with relative integration 2 (versus a triplet, integration 3, for the CH_3 of the ethyl group, and a singlet, integration 3, for the isolated CH_3 attached directly to the carbonyl carbon).

Bài luyện 19 (A2)

Compound W has $M_r = 88$, an IR spectrum with a very broad O − H/C − H region from 2500–3300 cm^{-1} and a strong peak at 1710 cm^{-1}, and a ^{1}H NMR spectrum with a doublet at $\delta 1.2$ (6H), a septet at $\delta 2.5$ (1H), and a singlet at $\delta 12.0$ (1H, exchanges with D_2O). Identify W.

Lời giải chi tiết

$M_r = 88$ fits $C_4H_8O_2$ ($4(12) + 8(1) + 2(16) = 48 + 8 + 32 = 88$). The very broad O − H (2500–3300) plus the C = O peak at 1710 cm^{-1} indicates a **carboxylic acid**.
NMR: the doublet (6H) at $\delta 1.2$ is two equivalent CH_3 groups, each split by the 1 neighbouring CH proton ($n + 1 = 2$); the septet (1H) at $\delta 2.5$ is the single CH proton, split by the 6 equivalent protons of the two CH_3 groups ($n + 1 = 7$); the singlet at $\delta 12.0$ (1H, disappears with D_2O) is the acidic $-COOH$ proton.
Assembling: $(CH_3)_2CH - COOH$ — **2-methylpropanoic acid**, $M_r = 88$, consistent with all three data sets.

Bài luyện 20 (A2)

Explain why 1-chloropropane's most deshielded ^{1}H NMR signal (the $-CH_2-$ bonded to Cl) appears further downfield than a $-CH_2-$ bonded only to other carbons.

Lời giải chi tiết

Chlorine is highly electronegative and withdraws electron density from the adjacent C − H bonds through the C − Cl bond (an inductive effect), reducing the electron density (shielding) around those hydrogen nuclei. Less shielded protons experience a stronger effective magnetic field and resonate at a **higher chemical shift** (further downfield), so the $-CH_2-Cl$ protons appear more downfield than a $-CH_2-$ bonded only to carbon and hydrogen.

Bài luyện 21

State the number of peaks expected in the ^{13}C NMR spectrum of ethanoic acid, CH_3COOH, and identify the carbon environments.

Lời giải chi tiết

Ethanoic acid has two chemically distinct carbons: the CH_3 carbon and the COOH (carbonyl) carbon. **Number of peaks: 2.**

Bài luyện 22

Which technique would best confirm the presence of a C ≡ N (nitrile) group in an unknown compound?

(A) ^{1}H NMR
(B) Mass spectrometry only
(C) Infrared spectroscopy
(D) Chromatography

Lời giải chi tiết

Infrared spectroscopy detects the characteristic C ≡ N stretching absorption at 2200–2260 cm^{-1}. **Answer: (C).**

Bài luyện 23

Explain why the molecular ion peak, M^+, in a mass spectrum has the same m/z value as the compound's relative molecular mass, M_r.

Lời giải chi tiết

The molecular ion is formed by removing a single electron from the neutral molecule (electron impact ionisation), giving a species with essentially the **same mass** as the original molecule but a **charge of** $+1$. Since m/z is mass divided by charge, and the charge is 1, $m/z =$ mass of the ion $\approx M_r$ of the original compound (the mass of the lost electron is negligible).

Bài luyện 24

A carboxylic acid shows a fragment ion at $M-45$ in its mass spectrum. Suggest what has been lost and why this loss is common for carboxylic acids.

Lời giải chi tiết

A mass loss of 45 corresponds to loss of $-$COOH (or, viewed the other way, retention of $-$COOH while the rest of the molecule is lost, depending on which fragment is charged); loss of the whole carboxyl group, COOH ($12+16+16+1=45$), is common because the C $-$ C bond adjacent to the carbonyl is relatively easily broken during fragmentation, and the resulting acylium-type or alkyl cation can be reasonably stable.

Bài luyện 25

Describe how you would use 2,4-DNPH, Tollens' reagent and bromine water together to distinguish propanal, propanone and propene.

Lời giải chi tiết

Bromine water: only **propene** rapidly decolourises it (electrophilic addition across C = C); propanal and propanone do not react.
2,4-DNPH (on the two remaining liquids): both **propanal** and **propanone** give an orange precipitate (both contain C = O); this alone does not distinguish them.
Tollens' reagent (to distinguish the two carbonyls): **propanal** (an aldehyde) gives a **silver mirror**; **propanone** (a ketone) gives **no reaction**.

Bài luyện 26

Predict the ^{1}H NMR splitting pattern of the $-OCH_2-$ protons in ethyl ethanoate, $CH_3COOCH_2CH_3$, and state their approximate chemical shift region.

Lời giải chi tiết

The $-OCH_2-$ protons are adjacent only to the $-CH_3$ of the ethyl group (3 protons), so by the $n+1$ rule they appear as a **quartet** ($3+1=4$ peaks). Being bonded to the electronegative ester oxygen, they are strongly deshielded, appearing at a relatively downfield chemical shift, typically around $\delta 4.0$–4.3.

Bài luyện 27

A student claims that all polymers, whether addition or condensation, are equally resistant to biodegradation. Explain why this claim is incorrect.

Lời giải chi tiết

This is incorrect. **Addition polymers** have a backbone of unreactive C – C single bonds only, which are not readily attacked by water or enzymes, so they persist in the environment (not biodegradable). **Condensation polymers**, by contrast, contain **ester** or **amide** linkages in their backbone, both of which *can* be hydrolysed (broken down by water, acid/base, or microbial enzymes), making condensation polymers generally more biodegradable than addition polymers.

Bài luyện nâng cao (A2)

Outline, with equations and conditions, how phenylamine could be converted into an orange azo dye using phenol, and explain the one critical temperature condition that must be observed.

Lời giải chi tiết

Step 1 — diazotisation: phenylamine is treated with $NaNO_2$ and dilute HCl at 0–$5\,^\circ$C:

$$C_6H_5NH_2 + HNO_2 + HCl \xrightarrow{0\text{–}5\,^\circ C} C_6H_5N_2^+Cl^- + 2H_2O$$

Step 2 — coupling: the cold diazonium salt solution is added to phenol dissolved in aqueous NaOH (forming the more reactive phenoxide ion):

$$C_6H_5N_2^+Cl^- + C_6H_5OH \xrightarrow{NaOH(aq)} C_6H_5N{=}NC_6H_4OH + HCl$$

Critical condition: the temperature **must be kept at** 0–$5\,^\circ$C throughout diazotisation (and the diazonium salt kept cold until coupling), because diazonium salts **decompose** (releasing N_2 gas) at higher temperatures — if the temperature rises, the diazonium salt is destroyed before it can couple with phenol, and no azo dye is obtained.

14.7 Ôn tập nhanh

Ôn tập nhanh:

- Luôn đổi số mol sang đơn vị chuẩn và nhiệt độ sang **Kelvin** ($T/\text{K} = T/^\circ\text{C} + 273$) trước khi thay vào các công thức khí lý tưởng hay tính hằng số cân bằng.
- ΔH có thể âm hoặc dương (toả nhiệt/thu nhiệt), nhưng năng lượng hoạt hoá E_a **luôn dương**.
- Xúc tác làm giảm E_a và tăng tốc độ phản ứng nhưng **không** làm thay đổi ΔH hay hằng số cân bằng (K_c/K_p).
- K_c và K_p chỉ thay đổi khi **nhiệt độ** thay đổi — không đổi khi thay đổi nồng độ, áp suất, hay thêm xúc tác.
- Công thức tính pH: $\text{pH} = -\log_{10}[\text{H}^+]$; tại điểm nửa trung hoà (half-equivalence point) của một axit yếu, $\text{pH} = \text{p}K_a$.
- Trong pin điện hoá (galvanic cell) tự phát, electron di chuyển từ cực âm (anot, nơi xảy ra oxi hoá) qua mạch ngoài đến cực dương (catot, nơi xảy ra khử); trong điện phân, dòng điện được cấp từ bên ngoài để **cưỡng bức** phản ứng đi ngược chiều tự phát.
- Khi áp dụng thuyết VSEPR, đếm **số vùng electron** (bao gồm cả cặp electron chưa liên kết) quanh nguyên tử trung tâm để xác định hình dạng phân tử, không chỉ đếm số nguyên tử liên kết.
- Khi xác định cấu trúc hữu cơ, luôn kết hợp **cả ba** nguồn dữ liệu: M_r (phổ khối lượng) để xác định công thức phân tử, phổ hồng ngoại (IR) để xác định nhóm chức, và phổ cộng hưởng từ hạt nhân (NMR, độ dịch chuyển + tích phân + tách vân) để dựng khung carbon chi tiết — một cấu trúc đề xuất phải khớp đồng thời với toàn bộ dữ liệu.

Đồng hành cùng 8020 English

Cảm ơn bạn đã học cùng bộ giáo trình quốc tế 8020. **Điểm thật · Thầy thật · Kết quả thật** — nhiều học viên chỉ cần 1–2 khoá để đạt kết quả mong muốn.

Chương trình đào tạo tại 8020 English

IELTS Academic/General · **SAT** · PTE · Duolingo · TOEFL | **AP** (College Board) · **IB** Diploma · **Cambridge** IGCSE / A-Level | săn học bổng du học.

Vì sao chọn 8020 English?

- **100% giáo viên** đạt tối thiểu 8.0 IELTS hoặc 1500 SAT — đội ngũ Giáo sư · Tiến sĩ · Thạc sĩ tốt nghiệp trường top đầu thế giới (Carnegie Mellon — #1 Hoa Kỳ về Khoa học Máy tính).
- **Kèm 1–1** mọi độ tuổi; lớp sĩ số nhỏ 2–5 bạn (đa số dưới 10 bạn/lớp).
- Lộ trình cá nhân hoá, theo sát tiến độ từng học viên; lớp OFFLINE tại TP.HCM & ONLINE toàn quốc.

Bảng vàng học viên

AP 5/5 — Calculus AB/BC	**AP** 4–5 — Biology, Chemistry	**IB** 90/100 — Economics
SAT 1590 / 1570 / 1550	**IELTS** 8.0–9.0	**Duolingo** 110 · **PTE** 90

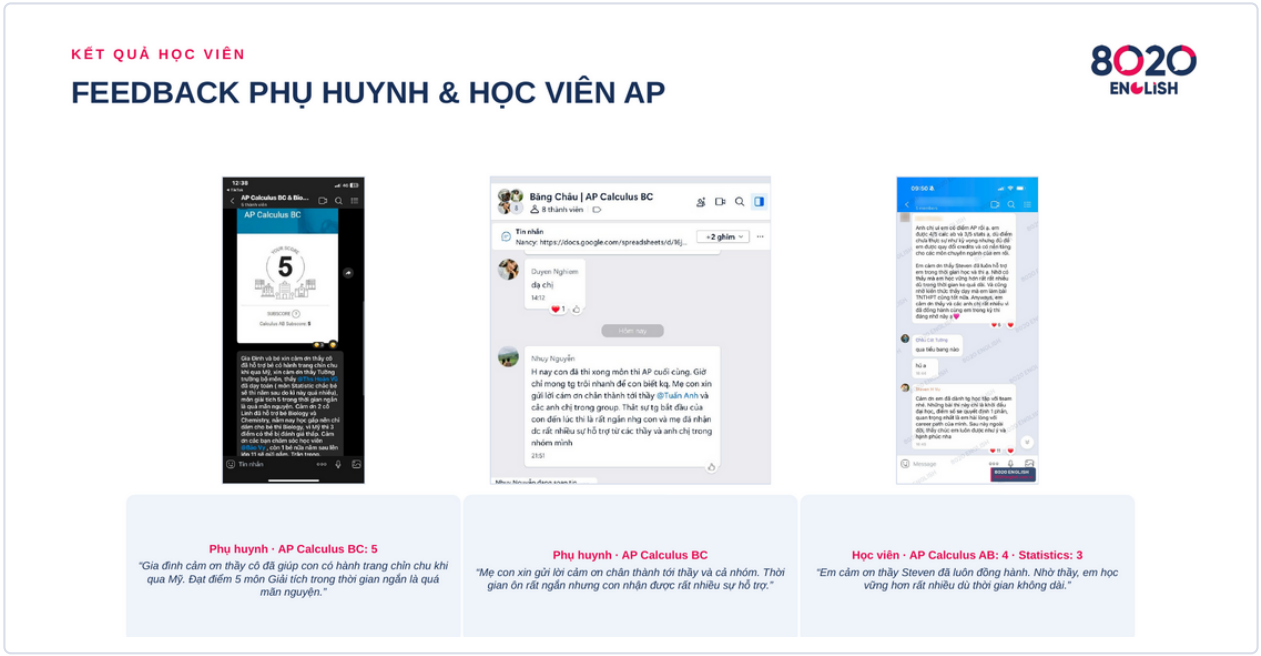
Cảm nhận học viên & phụ huynh

> *"Bạn đã cải thiện được tư duy Writing — kỹ năng từng là nỗi sợ lớn nhất — và cuối cùng đã đậu vào trường top như mong muốn. Thái độ học tập cực kỳ nghiêm túc; ngay cả khi nằm viện vẫn cố gắng học đều đặn."*
>
> — Phan Thị Thanh Hằng · IELTS Overall 8.5

> *"Cần tất cả kỹ năng trên 7.5 để xét vào trường top 1 Anh Quốc về Y học (chương trình UKFPO của NHS) — và đã đạt mục tiêu sau khi học Writing 1–1."*
>
> — Trần Hoàng Bảo Ngọc · IELTS Overall 8.0 (Writing 6.0 → 7.5)

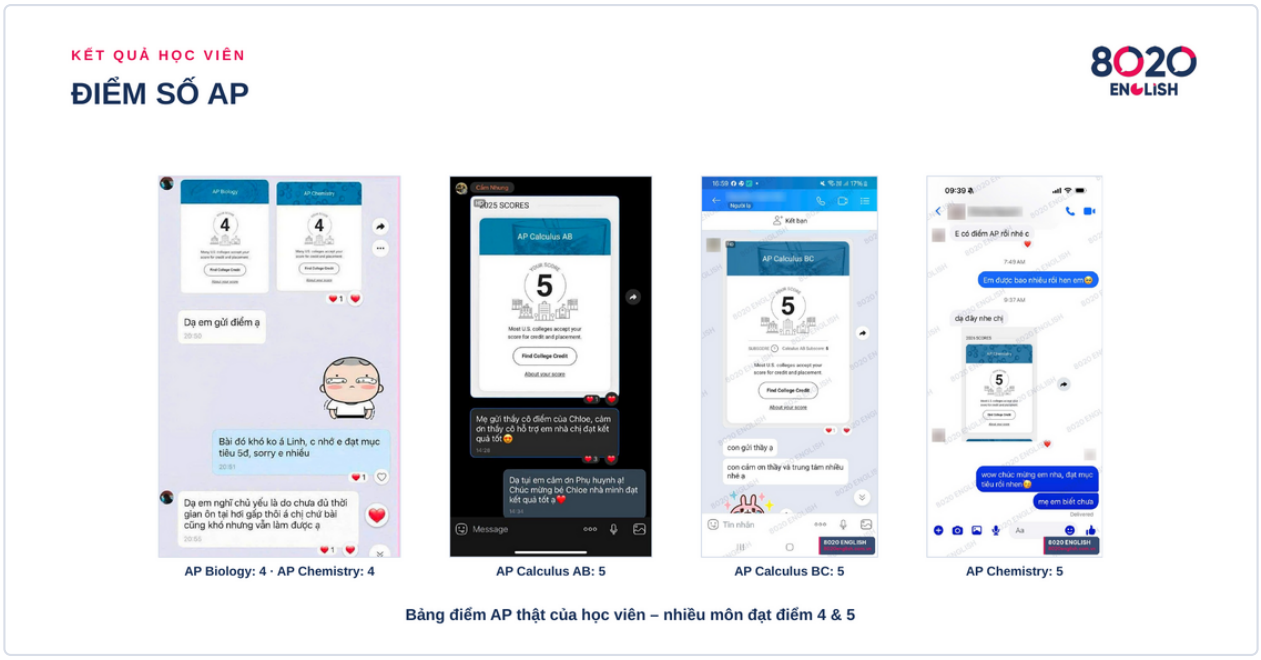
> *"Gia đình và bé xin cảm ơn thầy cô đã giúp con có hành trang chỉn chu khi qua Mỹ. Đạt điểm 5 môn Giải tích trong thời gian ngắn là quá mãn nguyện."*
>
> — Phụ huynh · AP Calculus BC 5/5

> *"Em cảm ơn thầy đã luôn đồng hành. Nhờ thầy, em học vững hơn rất nhiều dù thời gian ôn không dài."*
>
> — Học viên · AP Calculus AB 4

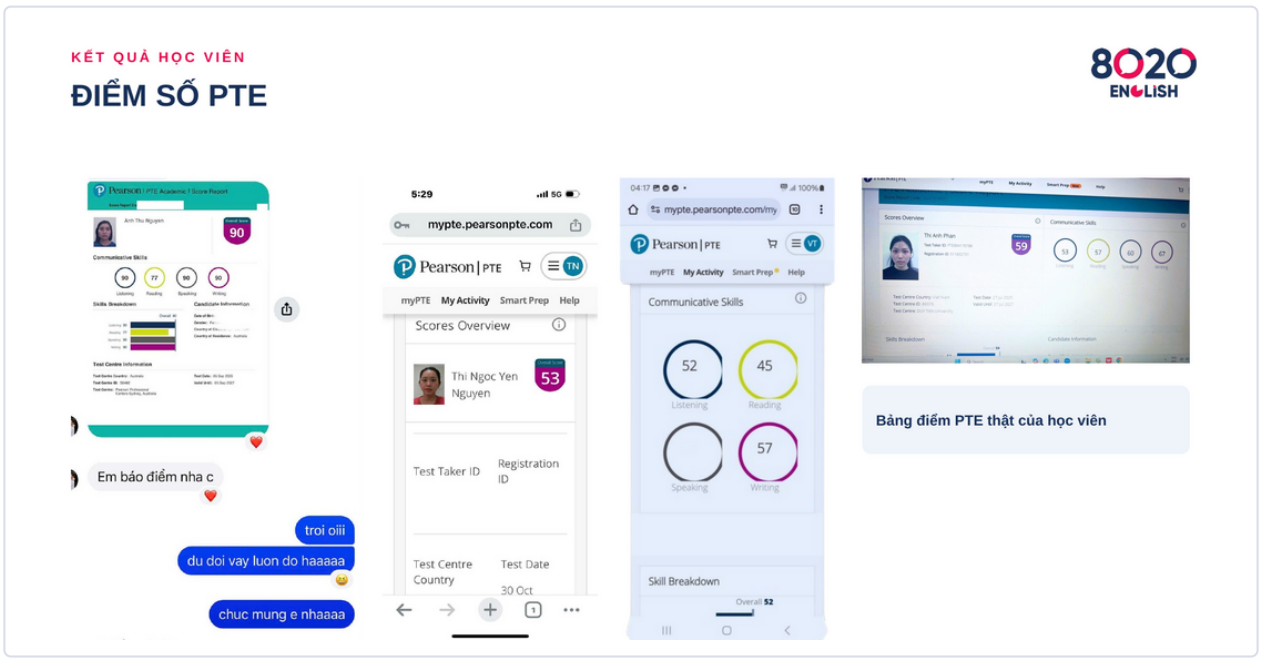


Feedback phụ huynh & học viên AP — nhiều môn đạt điểm 4 & 5

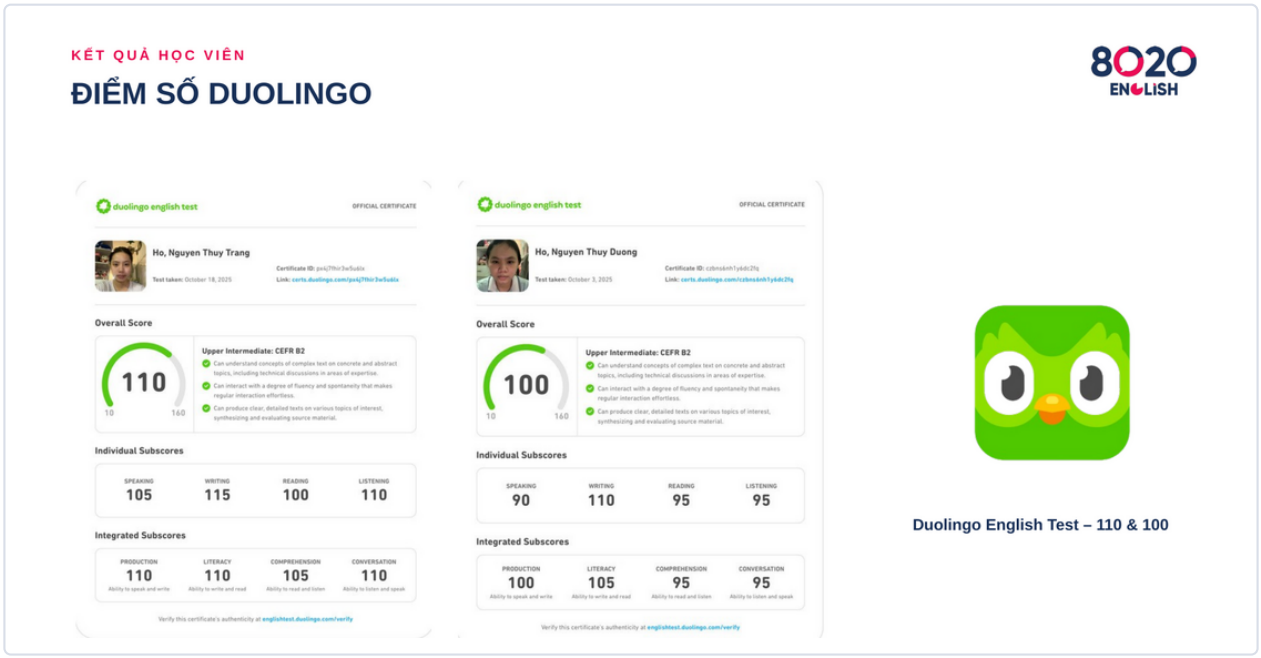
Điểm thi thật của học viên



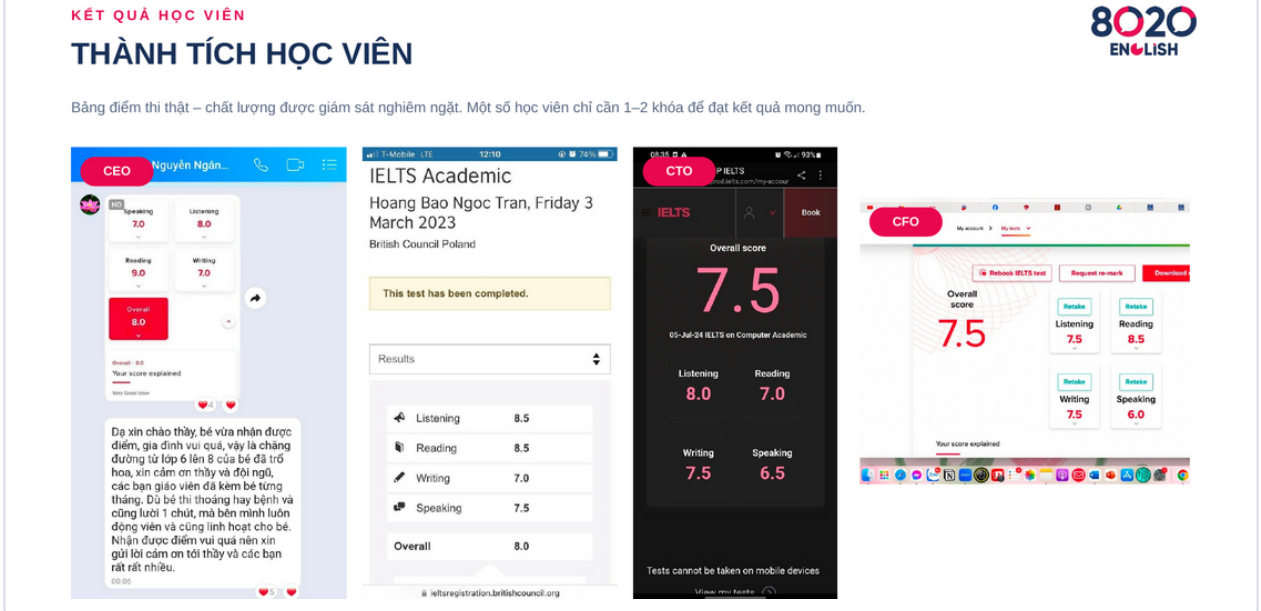
Bảng điểm AP thật — Calculus AB/BC 5/5 · Biology & Chemistry 4–5 (College Board)



Học viên 8020 — PTE Academic 90



Học viên 8020 — Duolingo English Test 110 & 100



Học viên 8020 — IELTS 8.0 / 7.5 / 8.5 (báo điểm thật)