IB Diploma Programme

Chuyên luyện thi IELTS/SAT → AP / IB / A-levels

8020 ENGLISH

IB Diploma Programme 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.

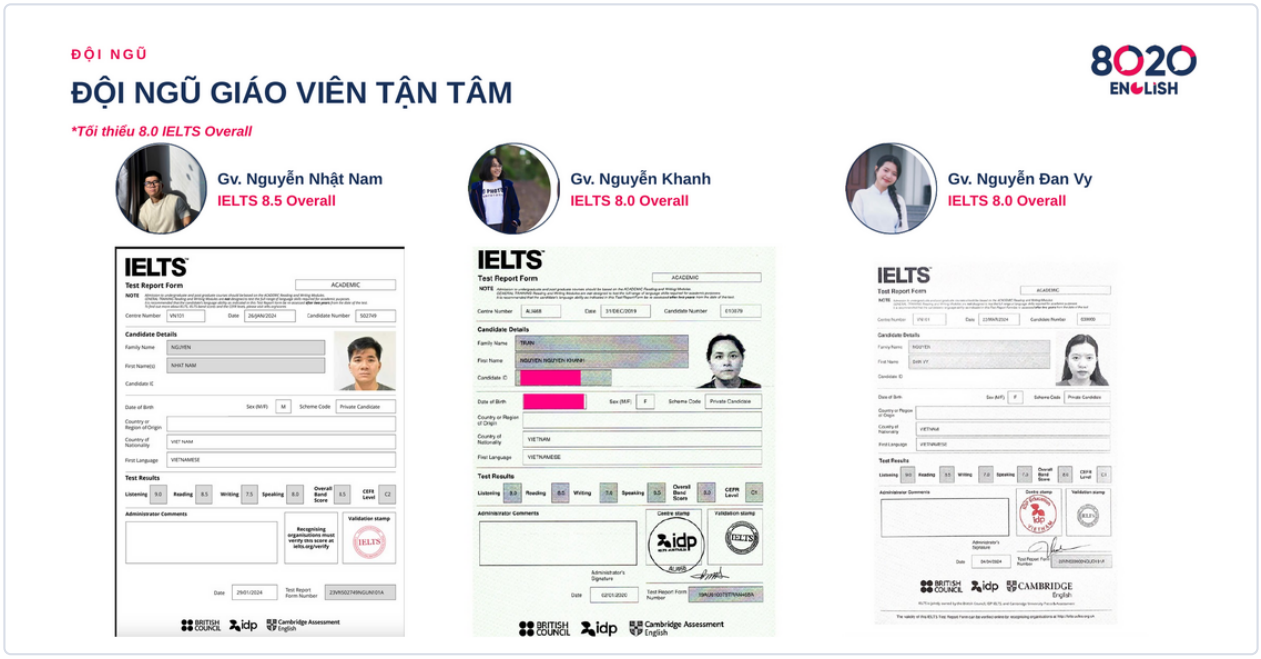
Kết quả học viên — điểm thi thật: IELTS 8.0–9.0 · SAT 1550 / 1570 / 1590 · AP 5/5 (Calculus BC, Microeconomics) · IB 90/100 (Economics) · Duolingo 110 · PTE 90 · TOEFL 120. **Bảng vàng SAT:** Khánh Đăng 1510 · Thảo Nguyên 1520 · Tâm Anh 1530.

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

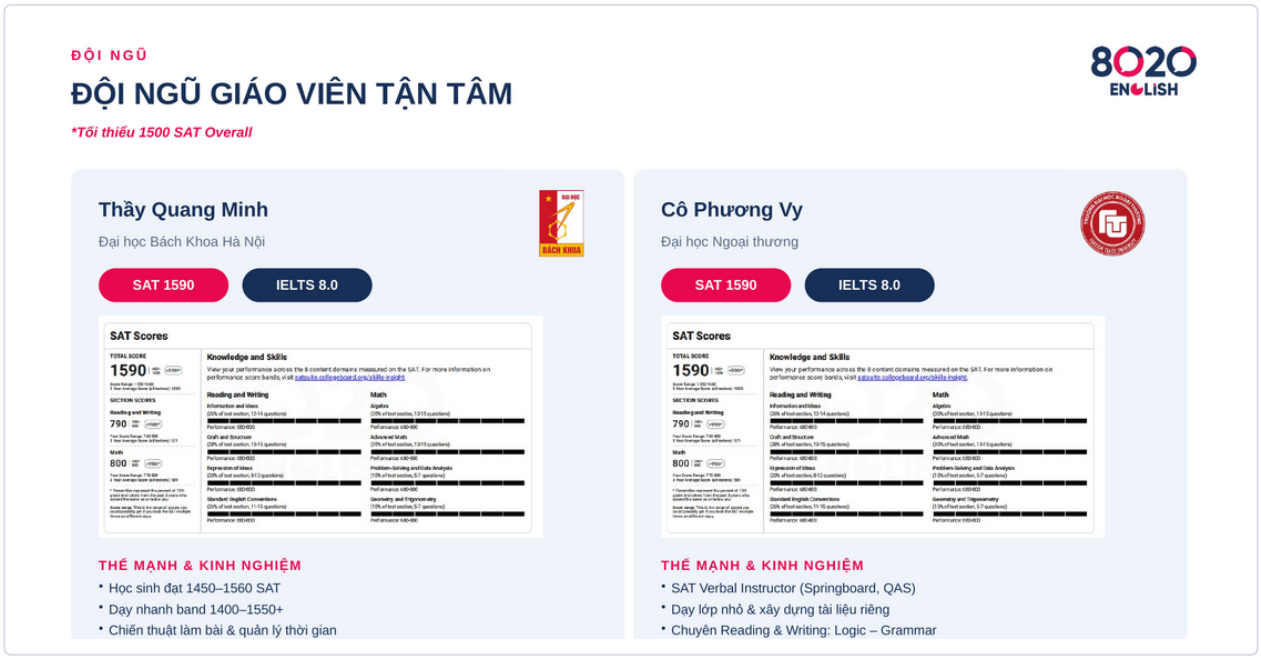
Cách dùng sách hiệu quả: mỗi Unit gồm (1) **Lý thuyết trọng tâm** tiếng Anh kèm **giải thích tiếng Việt**; (2) **Ví dụ mẫu** có lời giải; (3) **Hệ thống bài tập** kèm **lời giải chi tiết**. Hãy tự làm bài trước khi xem lời giải để đạt hiệu quả tối đa.

THÀNH TÍCH THỰC TẾ · 8020 ENGLISH

Điểm thi thật · Bằng & bảng điểm thật của giảng viên và học viên 8020 English — **Điểm thật · Thầy thật · Kết quả thật**



Đội ngũ giảng viên — IELTS 8.5 & 8.0 Overall (British Council · IDP · Cambridge)



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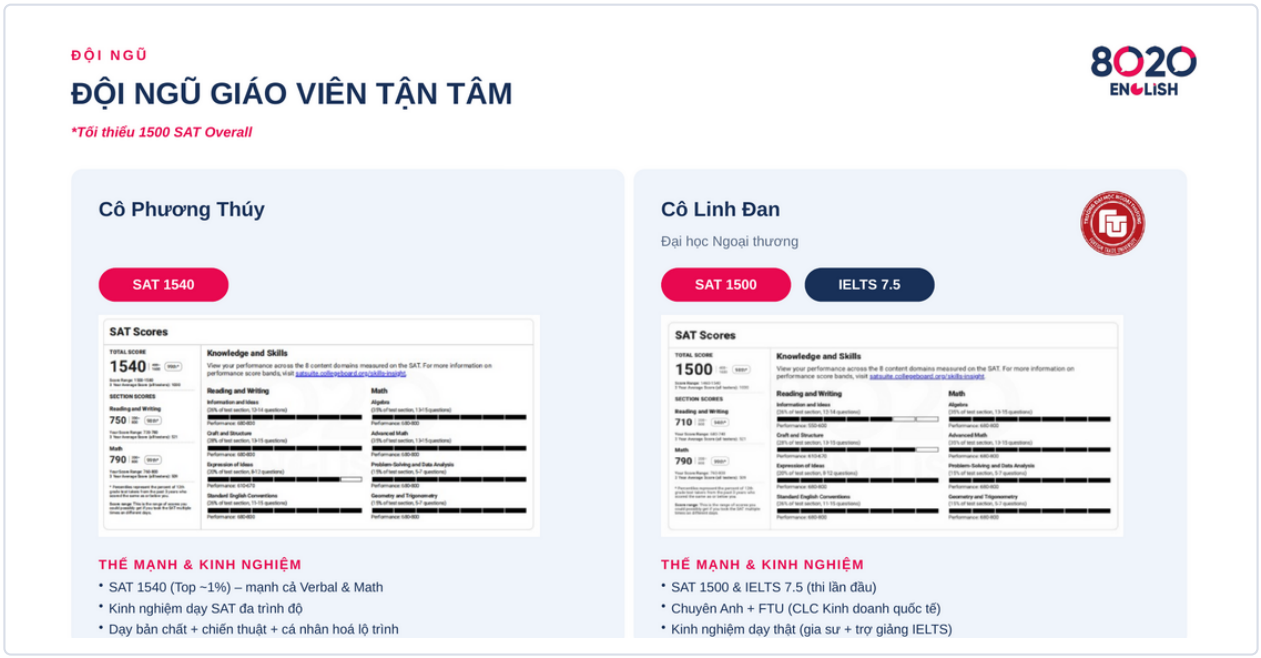

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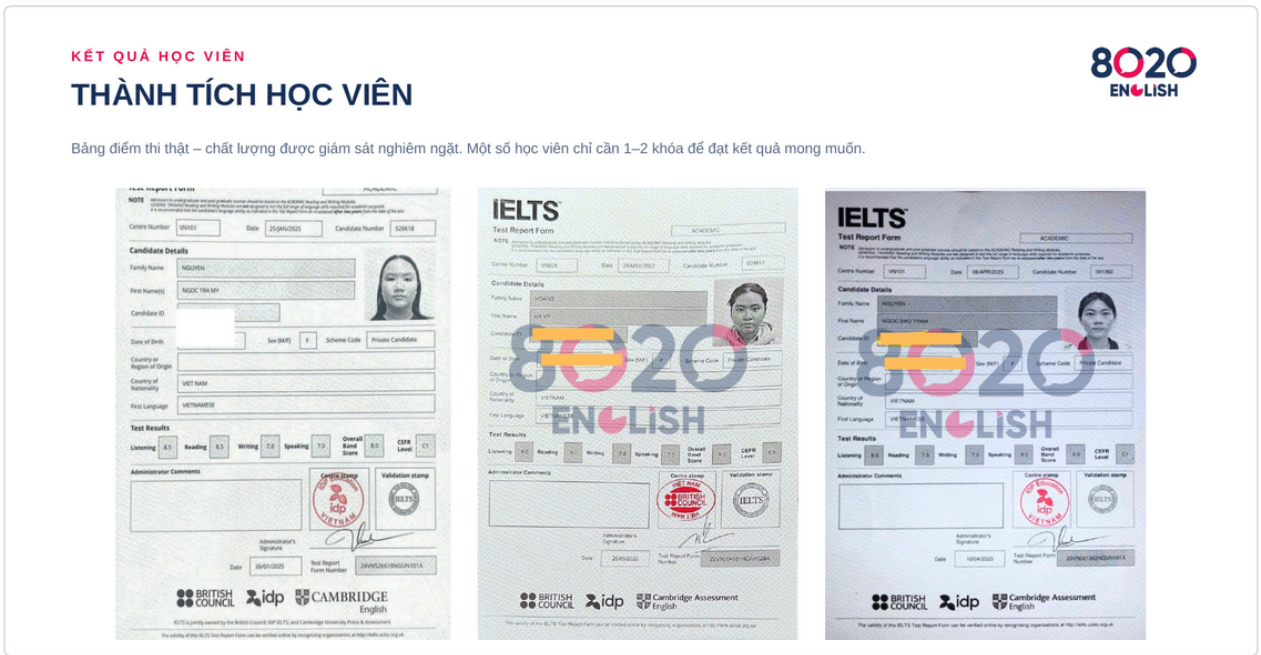

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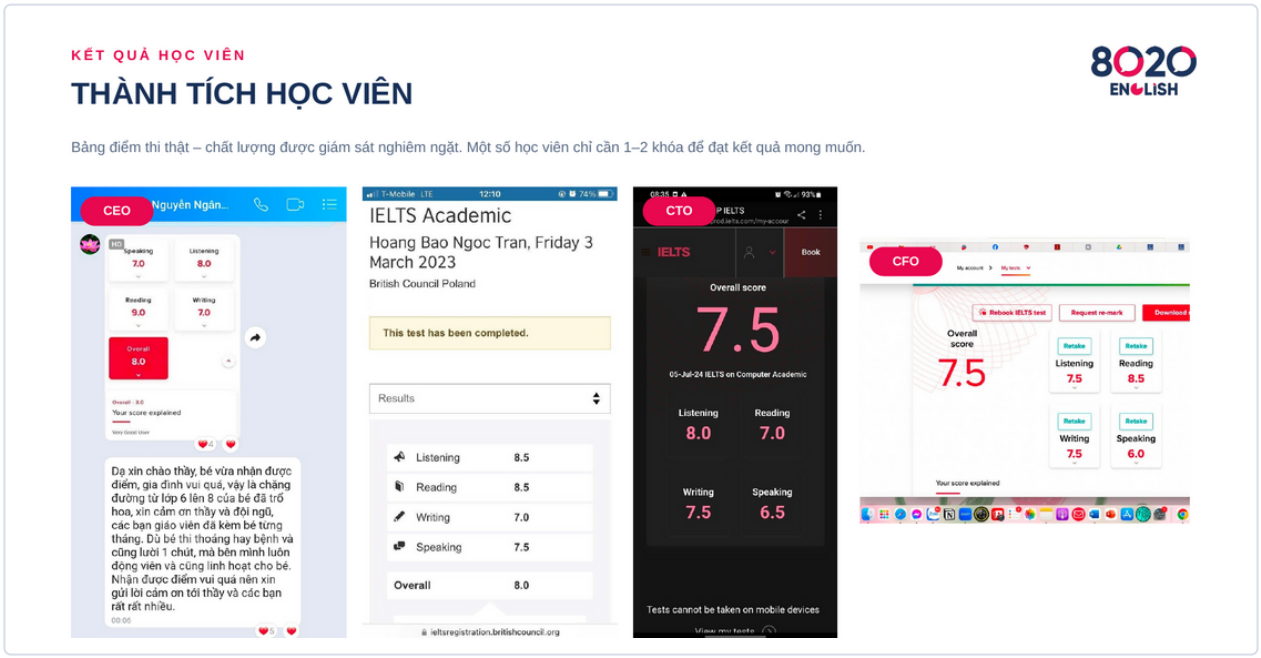
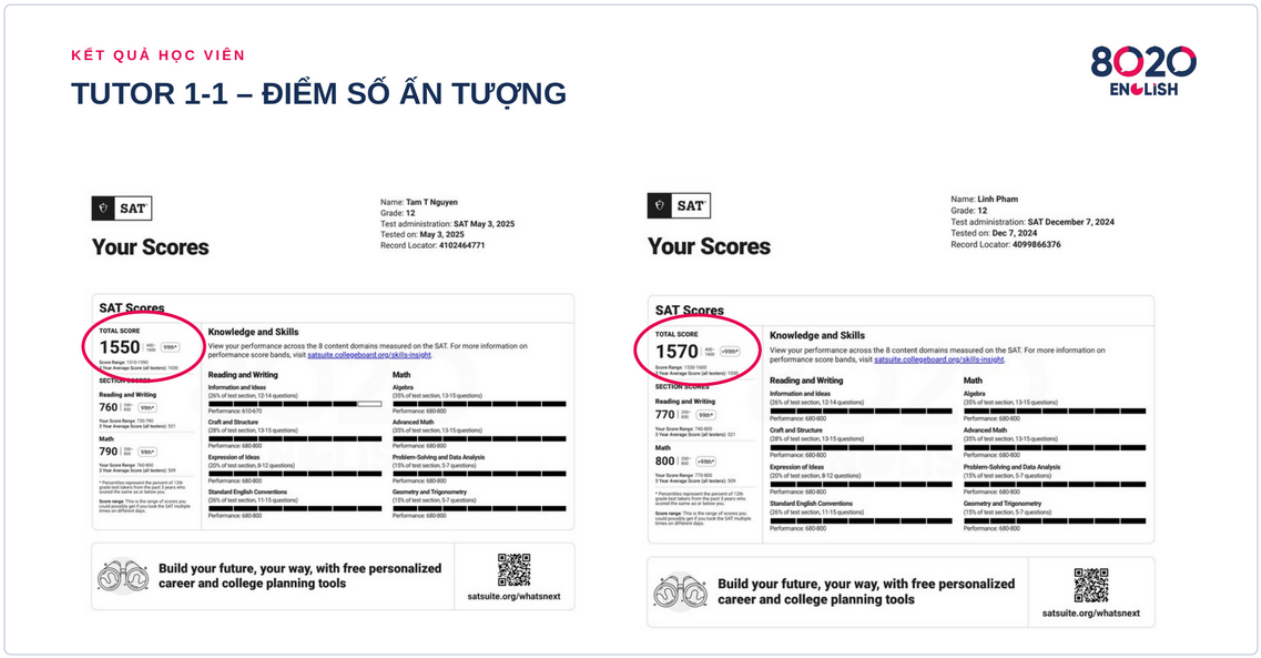


Học viên 8020 — IELTS 8.0 / 7.5 / 8.5 (báo điểm thật)

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



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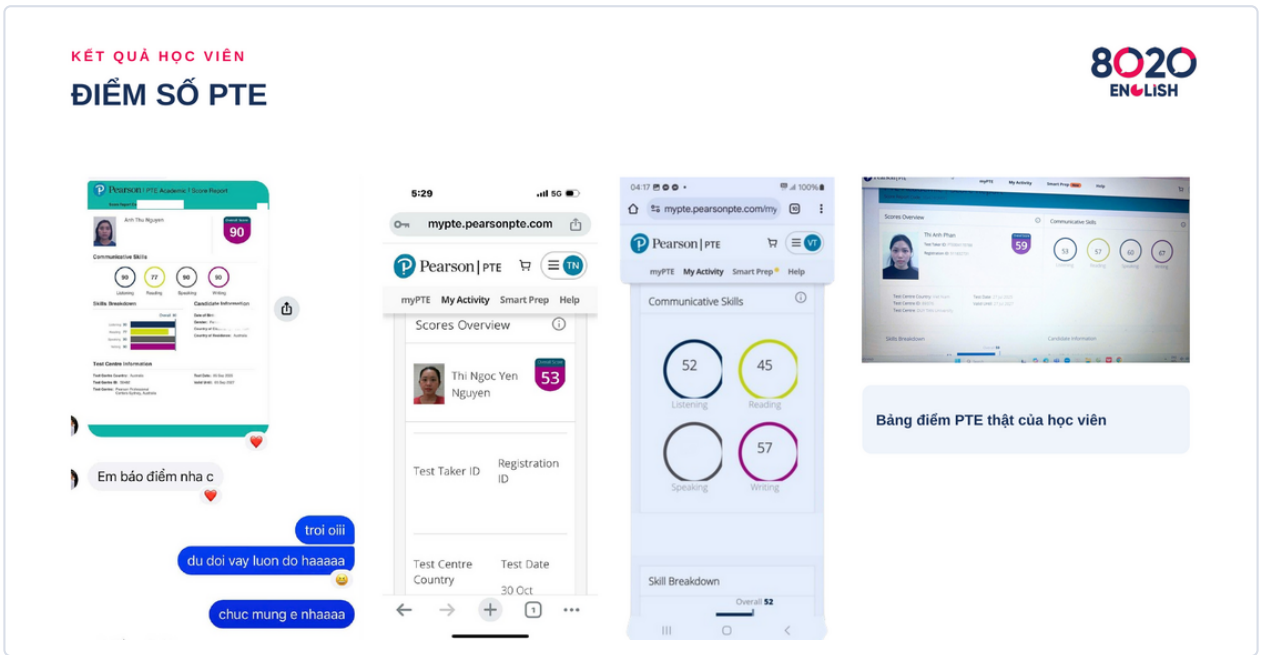
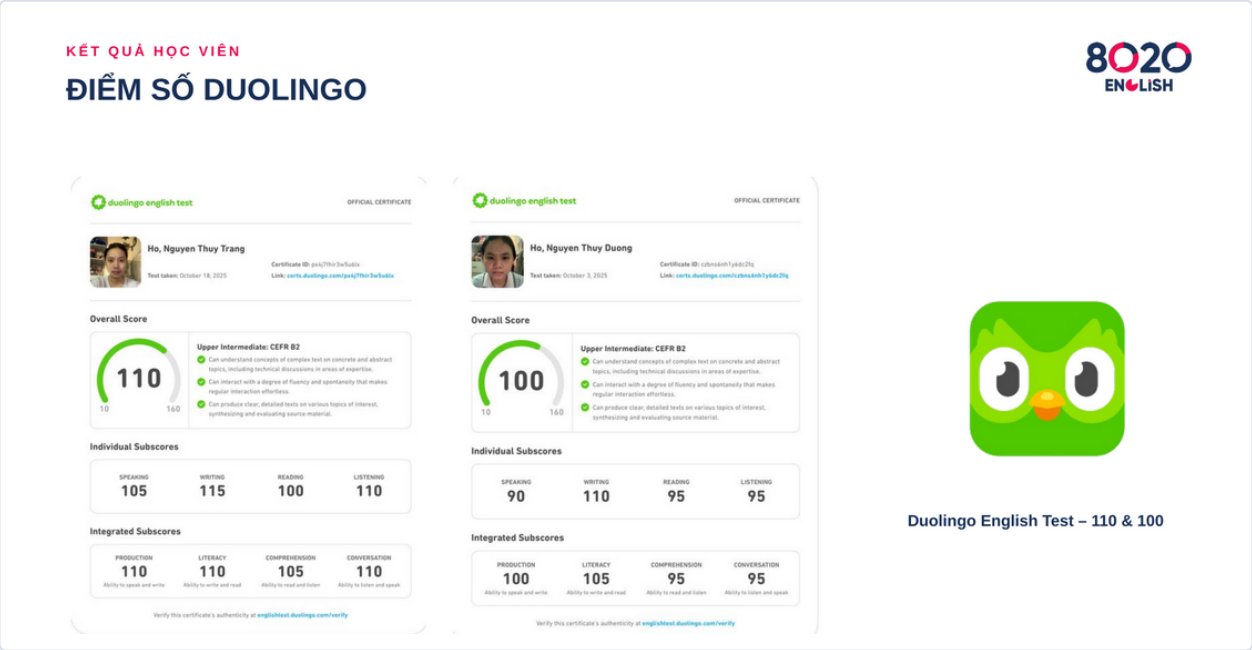


Học viên 8020 — PTE Academic 90



Học viên 8020 — Duolingo English Test 110 & 100

Mục lục · Contents

Structure 1 --- Models of the Particulate Nature of Matter

Mục tiêu Unit: Sau chương này, học sinh có thể: mô tả ba trạng thái vật chất và thuyết động học phân tử, bao gồm đường cong đun nóng/làm lạnh, phân biệt hỗn hợp đồng nhất và không đồng nhất, và giải thích hiện tượng khuếch tán; trình bày cấu tạo nguyên tử, khái niệm đồng vị và nguyên lý hoạt động của khối phổ kế thời gian bay (TOF) để tính khối lượng nguyên tử tương đối; viết cấu hình electron đầy đủ tới $Z \approx 36$ (kể cả các trường hợp bất thường Cr, Cu), đọc quang phổ phát xạ nguyên tử và năng lượng ion hoá liên tiếp để suy ra nhóm nguyên tố; thực hiện các phép tính về mol, khối lượng mol, phần trăm khối lượng, nước kết tinh (hydrate), nồng độ mol và pha loãng, và xác định công thức đơn giản nhất cũng như công thức phân tử; áp dụng phương trình khí lý tưởng $PV = nRT$, định luật Avogadro và định luật khuếch tán Graham ở cấp độ AHL.

1.1 States of matter and the kinetic molecular theory

Matter exists as **solid**, **liquid**, or **gas**, distinguished by the arrangement, spacing, and motion of the particles that compose it. The **kinetic molecular theory (KMT)** models every particle (atom, ion, or molecule) as a constantly-moving point possessing kinetic energy proportional to the absolute temperature of the sample. A phase change occurs when particles gain or lose enough energy to overcome (or fall back into) the attractive forces holding them together; no particles are created or destroyed during a phase change, only their spacing, order, and motion change.

Khái niệm cốt lõi

Solid: particles vibrate about fixed lattice positions; strong attractive forces; fixed volume and fixed shape. **Liquid**: particles move past one another while remaining close together; fixed volume, no fixed shape (takes the shape of its container). **Gas**: particles move independently with large separations between them; attractive forces are negligible; no fixed volume or shape. **Temperature** is a measure of the *average* kinetic energy of the particles, not the total energy of the sample; **pressure** arises from the frequency and force of particle collisions with the walls of a container.

VN **GIẢI THÍCH TIẾNG VIỆT**

Ba trạng thái của vật chất khác nhau chủ yếu ở **khoảng cách** và **lực tương tác** giữa các hạt: rắn (các hạt sát nhau, lực hút mạnh, chỉ dao động tại chỗ) → lỏng (hạt trượt qua nhau, lực yếu hơn, vẫn ở gần nhau) → khí (hạt tách xa nhau, lực không đáng kể, chuyển động tự do độc lập). Nhiệt độ là thước đo **động năng trung bình** của các hạt, KHÔNG phải tổng năng lượng của toàn bộ hệ — một bể bơi lạnh có tổng động năng lớn hơn một tách trà nóng dù nhiệt độ thấp hơn nhiều, đơn giản vì có quá nhiều hạt nước hơn.

1.1.1 Postulates of the kinetic molecular theory

The behaviour of an idealised gas is captured by five postulates:

1. A gas consists of a very large number of particles in continuous, random, straight-line motion.

2. The particles are separated by distances that are large compared with their own size, so the volume occupied by the particles themselves is negligible compared with the total volume of the gas.
3. Collisions between particles, and between particles and the walls of the container, are perfectly elastic — no net kinetic energy is lost overall.
4. There are no attractive or repulsive forces between particles, except during the instant of a collision.
5. The average kinetic energy of the particles is proportional to the absolute (kelvin) temperature, and is the same for all gases at a given temperature.

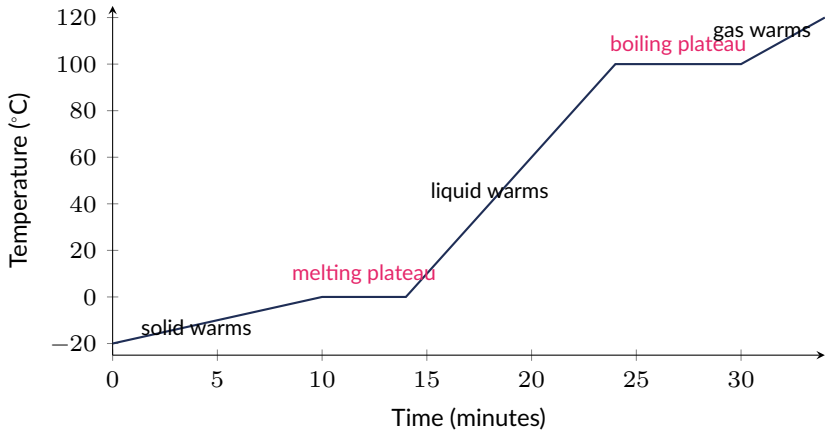
These postulates define an **ideal gas**. They also explain, at the particle level, why gases are readily compressible (mostly empty space) and expand to fill any container available to them (particles move independently, with no attractive forces confining them). Section 1.5 (AHL) returns to this model quantitatively and examines why real gases deviate from it.

VN **GIẢI THÍCH TIẾNG VIỆT**

Năm định đề của thuyết động học phân tử mô tả một **khí lý tưởng**: các hạt chuyển động hỗn loạn liên tục theo đường thẳng; thể tích riêng của hạt không đáng kể so với thể tích bình chứa; va chạm hoàn toàn đàn hồi (không mất động năng); không có lực hút/đẩy giữa các hạt (trừ lúc va chạm); và động năng trung bình tỉ lệ thuận với nhiệt độ tuyệt đối (Kelvin), giống nhau cho mọi loại khí. Đây chính là nền tảng để phần AHL (mục 1.5) xây dựng phương trình khí lý tưởng.

1.1.2 Heating and cooling curves

When a pure solid is heated at a constant rate under constant pressure, its temperature does not rise smoothly the whole time. While the sample is a single phase (all solid, all liquid, or all gas), added energy increases the average kinetic energy of the particles, so temperature rises steadily. However, exactly at the melting point or boiling point, the temperature remains **constant** for as long as both phases coexist: every joule of energy supplied is being used to overcome intermolecular or lattice forces (increasing potential energy, not kinetic energy) as particles rearrange from the more ordered to the less ordered phase. Cooling curves show the mirror-image behaviour, with plateaus as energy is released while particles come together into a more ordered phase.



A heating curve for a pure substance at constant pressure. Temperature stays constant on each plateau while the sample absorbs the enthalpy of fusion or vaporisation and changes phase; between plateaus, absorbed energy raises the average kinetic energy (and hence the temperature) of a single phase.

VN **GIẢI THÍCH TIẾNG VIỆT**
Trên đồ thị đun nóng, nhiệt độ đứng yên (plateau) tại điểm nóng chảy và điểm sôi vì toàn bộ năng lượng cấp vào lúc đó được dùng để **phá vỡ lực liên kết/lực mạng tinh thể** giữa các hạt (làm tăng thế năng), chứ không làm tăng động năng trung bình — do đó nhiệt độ không đổi cho đến khi toàn bộ mẫu chuyển pha xong.

(!) Lỗi thường gặp: "No temperature change" during a plateau does NOT mean "no energy change" — energy is still flowing into (or out of) the sample the entire time; it is simply being converted into potential energy that overcomes intermolecular/lattice forces, not into kinetic energy. Do not assume a flat region on a heating curve means heating has stopped.

1.1.3 Pure substances and mixtures

A **pure substance** is a single element or a single compound with a fixed, unvarying composition; it has a sharp, reproducible melting point and boiling point. A **mixture** contains two or more substances physically combined (not chemically bonded) in a composition that can vary continuously. Mixtures are further classified as:

- **Homogeneous**: uniform composition and properties throughout, a single visible phase (e.g. air, brass, salt water, any true solution).
- **Heterogeneous**: non-uniform composition, with visibly distinct regions or phases (e.g. sand in water, oil and water, granite, a mixture of iron filings and sulfur powder).

Melting/boiling behaviour distinguishes pure substances from mixtures: a **pure substance** melts/boils at a single, sharp temperature; a **mixture** typically melts/boils over a **range** of temperatures, and its melting point is usually depressed below that of the pure major component. This is a standard practical test for purity.

VN **GIẢI THÍCH TIẾNG VIỆT**
Chất tinh khiết (một nguyên tố hoặc một hợp chất đơn lẻ) có điểm nóng chảy/sôi **xác định, sắc nét**. Hỗn hợp nóng chảy/sôi trong một **khoảng nhiệt độ**, và điểm nóng chảy thường bị hạ thấp hơn so với chất tinh khiết — đây là cách thực nghiệm thường dùng để kiểm tra độ tinh khiết của một mẫu chất.

1.1.4 Diffusion

Diffusion is the net movement of particles from a region of higher concentration to a region of lower concentration, driven purely by the random, continuous motion of particles described by the KMT — it requires no stirring or external force. Diffusion occurs in gases, liquids, and (extremely slowly) in solids; it is fastest in gases, because gas particles move fastest, are separated by the largest distances, and experience negligible intermolecular forces resisting their motion. Different gases diffuse at different rates depending on their particle mass; section 1.5 (AHL) quantifies this relationship as **Graham's law**.

VN **GIẢI THÍCH TIẾNG VIỆT**
Khuếch tán là sự lan toả tự nhiên của các hạt từ nơi nồng độ cao đến nơi nồng độ thấp, chỉ nhờ chuyển động hỗn loạn ngẫu nhiên (không cần khuấy trộn). Khuếch tán xảy ra nhanh nhất ở thể khí vì hạt khí chuyển động nhanh, cách xa nhau, và gần như không có lực hút giữa các hạt. Tốc độ khuếch tán của các khí khác nhau phụ thuộc khối lượng mol — nội dung này được định lượng ở phần AHL bằng **định luật Graham**.

Bài tập luyện tập

Which of the following is a **homogeneous** mixture?

(A) Brass (an alloy of copper and zinc)
(B) Sand stirred into water
(C) Oil floating on water
(D) Iron filings mixed with sulfur powder

Lời giải chi tiết

A homogeneous mixture has uniform composition and a single visible phase throughout. Brass is a solid solution of Cu and Zn atoms distributed uniformly through the metal lattice — homogeneous. The other three all show visibly distinct regions or phases (heterogeneous). **(A)**.

Bài tập luyện tập

By what factor does the average kinetic energy of gas particles change when the temperature rises from 300 K to 600 K? If instead the Celsius temperature is doubled from 27°C to 54°C, by what factor does the average kinetic energy change?

Lời giải chi tiết

Average kinetic energy is proportional to **absolute** (kelvin) temperature. From 300 K to 600 K: factor $= \dfrac{600}{300} = 2.00$ — the average kinetic energy exactly doubles.

$27^{\circ}\text{C} = 300$ K and $54^{\circ}\text{C} = 327$ K (NOT 600 K). Factor $= \dfrac{327}{300} = 1.09$ — the average kinetic energy increases by only about 9%, not double, because kinetic energy scales with the *kelvin* temperature, not the Celsius reading.

Bài tập luyện tập

A pure solid is heated at a constant rate from -20°C to 120°C and its temperature is recorded every minute. Two flat regions (plateaus) are observed in the temperature–time graph: one at 0°C and one at 100°C. (a) Identify what each plateau represents. (b) Explain, using the kinetic molecular theory, why the temperature does not rise during either plateau even though heating continues.

Lời giải chi tiết

(a) The plateau at 0°C is the **melting point** (solid and liquid coexist); the plateau at 100°C is the **boiling point** (liquid and gas coexist) — the data matches water.

(b) During a phase change, all of the energy supplied is used to overcome the intermolecular (or lattice) forces holding particles in the more ordered phase, increasing the particles' **potential** energy as they separate or rearrange. Since temperature depends only on **average kinetic energy**, and kinetic energy is not increasing during this stage, temperature stays constant until every particle has completed the phase change; only then does further heating raise the kinetic energy (and temperature) of the new, single phase again.

1.2 The nuclear atom: isotopes and mass spectrometry

1.2.1 Isotopes and relative atomic mass

An atom has a tiny, dense, positively-charged **nucleus** (containing protons and neutrons) surrounded by electrons occupying the much larger remaining volume. The **atomic number** Z is the number of protons (it defines the element); the **mass number** A is the total number of protons and neutrons. **Isotopes** are atoms of the same element (same Z) with different numbers of neutrons (different A); they have identical chemical properties (determined by electron configuration) but slightly different physical properties (e.g. density, rate of diffusion) because of the mass difference.

A **mass spectrometer** ionises a sample, accelerates the ions, separates them according to their mass-to-charge ratio, and detects them, yielding the exact mass and relative abundance of each isotope present. The **relative atomic mass** A_r of an element is the abundance-weighted mean of the masses of all its naturally-occurring isotopes, measured relative to $\frac{1}{12}$ the mass of a ^{12}C atom:

$$A_r = \sum_i (\text{fractional abundance}_i \times \text{isotopic mass}_i).$$

Ví dụ mẫu · Weighted mean from two isotopes

Copper has two isotopes: ^{63}Cu (mass 62.9296, abundance 69.15%) and ^{65}Cu (mass 64.9278, abundance 30.85%). Find $A_r(\text{Cu})$.

$$A_r = (0.6915)(62.9296) + (0.3085)(64.9278) = 43.52 + 20.03 = 63.55.$$

This matches the periodic-table value for copper, 63.55.

VN **GIẢI THÍCH TIẾNG VIỆT**

A_r trên bảng tuần hoàn là **trung bình có trọng số** theo phần trăm số lượng (abundance) của từng đồng vị — KHÔNG phải trung bình cộng đơn giản của các khối lượng đồng vị. Đồng vị phổ biến hơn sẽ kéo giá trị trung bình lại gần khối lượng của chính nó hơn.

Ví dụ mẫu · Three-isotope weighted mean

Magnesium has three isotopes: ^{24}Mg (78.99%, mass 23.985), ^{25}Mg (10.00%, mass 24.986), ^{26}Mg (11.01%, mass 25.983). Find $A_r(\text{Mg})$.

$$A_r = (0.7899)(23.985) + (0.1000)(24.986) + (0.1101)(25.983) = 18.946 + 2.499 + 2.861 = 24.31.$$

The method is identical for any number of isotopes: convert each percentage abundance to a decimal fraction, multiply by its isotopic mass, and sum all the terms. This matches the periodic-table value, 24.31.

VN **GIẢI THÍCH TIẾNG VIỆT**

Phương pháp tính hoàn toàn giống nhau dù nguyên tố có 2, 3 hay nhiều đồng vị hơn: đổi phần trăm sang số thập phân, nhân với khối lượng từng đồng vị, rồi **cộng tất cả lại**. Đừng bỏ sót đồng vị nào trong phép tính.

Ví dụ mẫu · Atoms, moles, and mass via N_A

A sample contains 1.204×10^{24} atoms of aluminium ($A_r(\text{Al}) = 26.98$). Find (a) the amount in moles, (b) the mass of the sample.

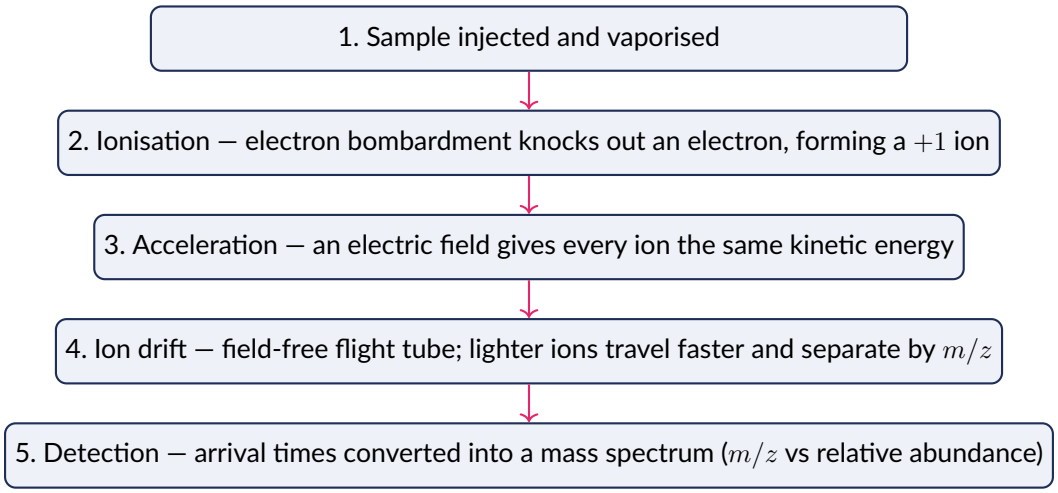
(a) $n = \dfrac{N}{N_A} = \dfrac{1.204 \times 10^{24}}{6.02 \times 10^{23}} = 2.00$ mol.
(b) $m = n \times A_r = 2.00 \times 26.98 = 53.96$ g.

VN **GIẢI THÍCH TIẾNG VIỆT**
Ba đại lượng số hạt (N), số mol (n) và khối lượng (m) luôn liên hệ qua hằng số Avogadro N_A và khối lượng mol M: $n = \dfrac{N}{N_A}$ rồi $m = n \times M$. Đây là công thức nền tảng sẽ được dùng xuyên suốt phần mol (mục 1.4).

(!) Lỗi thường gặp: Percentage abundances must be converted to **decimal fractions** (divide by 100) before multiplying by isotopic mass — forgetting this step, or accidentally using a simple (unweighted) average of the isotopic masses instead of the abundance-weighted mean, are the two most common errors in this calculation.

1.2.2 Time-of-flight mass spectrometry

A time-of-flight (TOF) mass spectrometer separates ions by the time they take to travel a fixed distance, which depends on their mass-to-charge ratio (m/z). The process proceeds through five sequential stages:



Stages of a time-of-flight (TOF) mass spectrometer, in sequence.

In more detail: electron bombardment knocks one or more electrons out of each particle, forming positive ions (most commonly $+1$); every ion is then accelerated through the same electric potential difference, so every ion, regardless of mass, gains the same kinetic energy, $E_k = zeV$. Since $E_k = \frac{1}{2}mv^2$, a lighter ion must acquire a *higher* velocity than a heavier ion to have the same kinetic energy; in the field-free drift region this means lighter ions arrive at the detector sooner. The detector records the arrival time (converted into m/z) and the size of the induced current (proportional to relative abundance), producing the mass spectrum: a plot of relative abundance against m/z.

VN **GIẢI THÍCH TIẾNG VIỆT**
Các giai đoạn của khối phổ kế TOF: mẫu được hoá hơi và bơm vào → ion hoá (thường bằng bắn phá electron, tạo ion dương) → tăng tốc bằng điện trường (mọi ion nhận cùng động năng) → trôi dạt trong ống chân không (ion nhẹ hơn di chuyển nhanh hơn vì cùng động năng nhưng khối lượng nhỏ hơn) → phát hiện, cho ra phổ khối (m/z so với độ phổ biến tương đối). Ion

càng nặng (hoặc m/z càng lớn) thì thời gian bay càng **lâu**.

Bài tập luyện tập

Boron has two isotopes: ^{10}B (mass 10.0129, abundance 19.9%) and ^{11}B (mass 11.0093, abundance 80.1%). $A_r(\text{B}) =$

(A) 10.81
(C) 11.01
(B) 10.50
(D) 10.01

Lời giải chi tiết

$A_r = (0.199)(10.0129) + (0.801)(11.0093) = 1.993 + 8.818 = 10.81$. **(A)**.

Bài tập luyện tập

Silicon has three isotopes: ^{28}Si (92.23%, mass 27.977), ^{29}Si (4.68%, mass 28.976), ^{30}Si (3.09%, mass 29.974). Calculate $A_r(\text{Si})$ to 4 significant figures.

Lời giải chi tiết

$$A_r = (0.9223)(27.977) + (0.0468)(28.976) + (0.0309)(29.974) = 25.80 + 1.356 + 0.926 = 28.09.$$

This matches the accepted relative atomic mass of silicon, 28.09.

Bài tập luyện tập

The five stages of a TOF mass spectrometer are listed below out of order. (a) Place them in the correct sequence. (b) Explain why an ion with a larger mass-to-charge ratio takes *longer* to reach the detector.

Detection; Ionisation; Acceleration; Sample injected and vaporised; Ion drift (velocity separation).

Lời giải chi tiết

(a) Correct order: **Sample injected and vaporised** → **Ionisation** → **Acceleration** → **Ion drift (velocity separation)** → **Detection**.

(b) Every ion is accelerated through the same electric potential difference and so gains the same kinetic energy, $E_k = zeV$. Since $E_k = \frac{1}{2}mv^2$, an ion with a larger mass (larger m/z, taking $z = 1$) must have a **smaller** velocity v to have the same E_k. A slower ion takes longer to cross the fixed length of the field-free drift tube, so it reaches the detector later — time of flight increases with m/z.

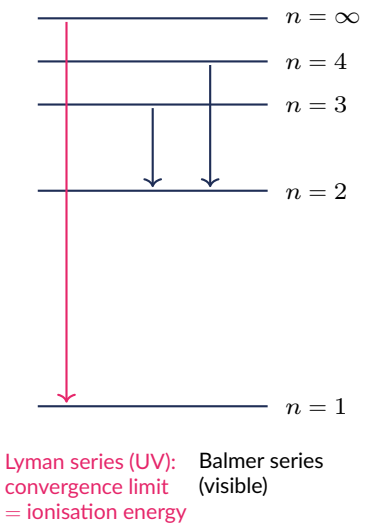
1.3 Electron configuration and atomic emission spectra

1.3.1 Energy levels, subshells, and filling principles

Electrons occupy quantised energy levels called **shells** ($n = 1, 2, 3, \ldots$), each of which splits into **subshells** labelled s, p, d, f of increasing energy and size. Subshells are built from **orbitals**, each of which can hold a maximum of two electrons. Three principles govern how electrons fill these orbitals in the ground state:

- **Aufbau principle**: electrons fill the lowest-energy available subshell first.
- **Pauli exclusion principle**: each orbital holds at most two electrons, and they must have opposite spin.
- **Hund's rule**: within a set of degenerate (equal-energy) orbitals, electrons occupy separate orbitals singly, with parallel spins, before any pairing occurs.

When an electron absorbs energy it can jump to a higher (excited) level; when an electron in an excited atom falls back to a lower level it emits a photon of energy equal to the difference between the two levels, $\Delta E = hf = \dfrac{hc}{\lambda}$. Because atoms have discrete energy levels (not a continuum), the emitted light forms a **line emission spectrum** rather than a continuous rainbow. As $n \to \infty$ the energy gaps between successive levels shrink towards zero, so the spectral lines of a series converge; the **convergence limit** corresponds to the electron being completely removed from the atom, i.e. **ionisation**.



Simplified energy-level diagram for the hydrogen atom (not to scale). Lines converge as $n \to \infty$; the Lyman-series convergence limit gives the first ionisation energy of hydrogen.

Ví dụ mẫu · Worked example

The Lyman series convergence limit for hydrogen occurs at $\lambda = 91.2$ nm. Estimate the ionisation energy of hydrogen (in kJ mol^{-1}).

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34})(3.00 \times 10^{8})}{91.2 \times 10^{-9}} = 2.18 \times 10^{-18}\ \text{J}.$$

$$IE_1 = E_{\text{photon}} \times N_A = (2.18 \times 10^{-18})(6.02 \times 10^{23}) = 1.31 \times 10^{6}\ \text{J mol}^{-1} = 1310\ \text{kJ mol}^{-1}.$$

This is close to the accepted value, $IE_1(\text{H}) = 1312$ kJ mol^{-1}.

Subshell capacities: s holds 2 electrons (1 orbital), p holds 6 (3 orbitals), d holds 10 (5 orbitals), f holds 14 (7 orbitals). Filling order up to krypton ($Z = 36$): $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p$ (running electron totals: $2, 4, 10, 12, 18, 20, 30, 36$).

VN **GIẢI THÍCH TIẾNG VIỆT**

Vạch quang phổ hội tụ dần khi n tăng vì khoảng cách năng lượng giữa các mức giảm dần. **Giới**

hạn hội tụ (convergence limit) của dãy Lyman ($n \to 1$) tương ứng với năng lượng cần để bứt hẳn electron ra khỏi nguyên tử ở trạng thái cơ bản — tức là **năng lượng ion hoá thứ nhất**.

1.3.2 Writing full electron configurations

Using the Aufbau filling order above, ground-state electron configurations can be written for any element up to $Z = 36$. Electrons fill $4s$ before $3d$ (it is lower in energy while both are empty), but by **convention** a finished configuration is written with subshells grouped in order of increasing principal quantum number n — so $3d$ is written before $4s$ even though $4s$ filled first.

Ví dụ mẫu · Full configuration of iron

Write the ground-state electron configuration of Fe ($Z = 26$).
Filling order: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^6$ (running total: $2, 4, 10, 12, 18, 20, 26$ — correct).
Conventional written form: $[\text{Ar}]3d^6 4s^2$, where $[\text{Ar}] = 1s^2 2s^2 2p^6 3s^2 3p^6$ (18 electrons).

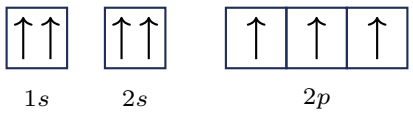
Ví dụ mẫu · Anomalous configurations: Cr and Cu

The Aufbau principle predicts Cr ($Z = 24$) to be $[\text{Ar}]3d^4 4s^2$ and Cu ($Z = 29$) to be $[\text{Ar}]3d^9 4s^2$. Experimentally, both are exceptions:

$$\text{Cr}: \; [\text{Ar}]3d^5 4s^1 \;\; (18 + 5 + 1 = 24) \;\; \text{not } [\text{Ar}]3d^4 4s^2.$$

$$\text{Cu}: \; [\text{Ar}]3d^{10} 4s^1 \;\; (18 + 10 + 1 = 29) \;\; \text{not } [\text{Ar}]3d^9 4s^2.$$

A half-filled (d^5) or completely-filled (d^{10}) d subshell is unusually stable (extra exchange stabilisation from the maximum number of electrons with parallel spin, plus reduced electron–electron repulsion in the symmetric, singly-occupied set), so one $4s$ electron is promoted into $3d$ to reach it.



Ground-state orbital diagram for nitrogen ($1s^2 2s^2 2p^3$). Hund's rule: the three degenerate $2p$ orbitals are each occupied singly (parallel spins) before any pairing occurs, minimising electron–electron repulsion.

VN **GIẢI THÍCH TIẾNG VIỆT**

Quy ước viết cấu hình electron: liệt kê các phân lớp theo thứ tự **số lượng tử chính** n **tăng dần** (nên $3d$ viết trước $4s$), dù thứ tự **điền electron** thực tế là $4s$ trước $3d$. Hai trường hợp ngoại lệ kinh điển cần nhớ: Cr và Cu "mượn" một electron từ $4s$ để đạt cấu hình $3d^5$ (bán bão hoà) hoặc $3d^{10}$ (bão hoà) bền vững hơn.

(!) Lỗi thường gặp: Two different orders are easy to confuse: the **filling order** ($4s$ before $3d$, used only while building up the configuration step by step) versus the **writing convention** (subshells grouped by increasing n, so $3d$ appears before $4s$ in the final answer). A related and very common exam error: when a transition-metal atom forms a cation, the $4s$ electrons are always removed **first**, before any $3d$ electrons — e.g. Fe is $[\text{Ar}]3d^6 4s^2$ but Fe^{2+} is $[\text{Ar}]3d^6$ (not $[\text{Ar}]3d^4 4s^2$).

1.3.3 Successive ionisation energies

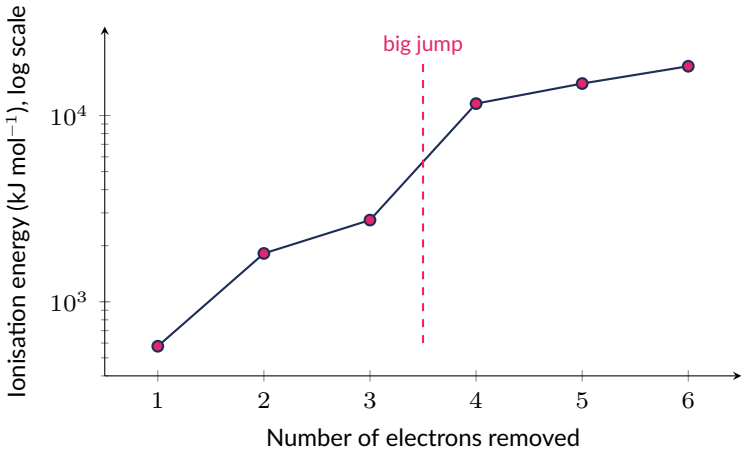
The n-th **successive ionisation energy**, IE_n, is the energy required to remove one electron from a gaseous ion of charge $(n-1)+$, forming a gaseous ion of charge $n+$:

$$M^{(n-1)+}(g) \;\rightarrow\; M^{n+}(g) + e^{-}.$$

Successive ionisation energies always **increase** (each electron is removed from an increasingly positive ion, held more tightly by the same nuclear charge), but the increase is small within a shell and **jumps sharply** whenever the next electron must come from a shell closer to the nucleus, where it experiences less shielding and stronger nuclear attraction. The position of a large jump reveals how many electrons are in the outermost (valence) shell, and hence the **group number** of the element.

Electron removed	1st	2nd	3rd	4th	5th	6th
IE (kJ mol^{-1}) of Al	577	1817	2745	11577	14842	18379

Successive ionisation energies of aluminium ($Z = 13$).



Successive ionisation energies of aluminium. The large jump between the 3rd and 4th electrons removed shows the first three electrons come from the outer (valence) shell, while the 4th comes from a much more tightly-held inner shell — confirming aluminium has 3 valence electrons (Group 13).

Ví dụ mẫu · Deducing a group from successive ionisation energies

An element Q has successive ionisation energies (kJ mol^{-1}): $1012,\ 1907,\ 2914,\ 4964,\ 6274,\ 21267,\ 25431$. Deduce the group of Q.

The ratio between consecutive values stays modest (roughly 1.3–$1.9\times$) up to the 5th electron, then jumps sharply between the 5th (6274) and 6th (21267) — a factor of about 3.4. This means the first **5** electrons come from the outer (valence) shell and the 6th comes from a much more tightly bound inner shell. Q therefore has 5 valence electrons and belongs to **Group 15** (this dataset in fact matches phosphorus).

VN **GIẢI THÍCH TIẾNG VIỆT**

Một bước nhảy lớn giữa IE_n và IE_{n+1} đánh dấu ranh giới giữa hai lớp electron (shell). **Đếm số electron bị tách ra TRƯỚC bước nhảy** chính là số electron hoá trị, và số đó bằng số nhóm (đối với các nguyên tố nhóm chính). Không nên chỉ nhìn độ lớn của IE_1 một mình để kết luận về nhóm.

Bài tập luyện tập

The ground-state electron configuration of Fe^{3+} ($Z = 26$) is:

(A) $[Ar]3d^5$
(C) $[Ar]4s^23d^3$
(B) $[Ar]3d^6$
(D) $[Ar]3d^44s^1$

Lời giải chi tiết

Fe: $[Ar]3d^64s^2$. Cations lose $4s$ electrons first: removing 3 electrons removes both $4s$ electrons and one $3d$ electron, leaving $[Ar]3d^5$. **(A).**

Bài tập luyện tập

The Lyman-series convergence limit of hydrogen ($\lambda = 91.2$ nm) corresponds to an ionisation energy closest to:

(A) 1310 kJ mol^{-1}
(C) 131 kJ mol^{-1}
(B) 656 kJ mol^{-1}
(D) 2620 kJ mol^{-1}

Lời giải chi tiết

$E_{\text{photon}} = \dfrac{hc}{\lambda} = \dfrac{(6.63 \times 10^{-34})(3.00 \times 10^{8})}{91.2 \times 10^{-9}} = 2.18 \times 10^{-18}$ J. Per mole: $\times 6.02 \times 10^{23} = 1.31 \times 10^{6}$ J mol$^{-1} = 1310$ kJ mol^{-1}. **(A).**

Bài tập luyện tập

An element Y has successive ionisation energies (kJ mol^{-1}): $1000,\ 2250,\ 3360,\ 4560,\ 7010,\ 8490,\ 27100$. Deduce the group of Y, showing your reasoning.

Lời giải chi tiết

Ratios between consecutive values: $2.25,\ 1.49,\ 1.36,\ 1.54,\ 1.21,\ 3.19$. All ratios stay below about 1.6 until the jump between the 6th (8490) and 7th (27100) electron, where the ratio jumps to 3.19 — far larger than any previous step. This means the first **6** electrons removed come from the outer (valence) shell, and the 7th comes from an inner shell. Y therefore has 6 valence electrons and belongs to **Group 16** (this dataset matches sulfur).

Bài tập luyện tập

The ground-state electron configuration of Zn^{2+} ($Z = 30$) is:

(A) $[Ar]3d^{10}$
(C) $[Ar]4s^23d^8$
(B) $[Ar]3d^84s^2$
(D) $[Ar]3d^94s^1$

Lời giải chi tiết

Zn: $[Ar]3d^{10}4s^2$ (30 electrons). Zn^{2+} has lost 2 electrons; as always, $4s$ electrons are removed before $3d$, leaving $[Ar]3d^{10}$ (28 electrons). **(A).**

Bài tập luyện tập

Which element has the ground-state configuration ending in … $3d^5 4s^1$ rather than the Aufbau-predicted … $3d^4 4s^2$?

(A) Chromium
(B) Manganese
(C) Iron
(D) Vanadium

Lời giải chi tiết

Chromium ($Z = 24$) is the classic exception: a half-filled $3d^5$ subshell combined with a single $4s^1$ electron is more stable than the naively-predicted $3d^4 4s^2$, because the symmetric half-filled arrangement minimises electron–electron repulsion and maximises exchange stabilisation. **(A)**.

Bài tập luyện tập

For a ground-state carbon atom ($2p^2$), which orbital diagram correctly shows Hund's rule?

(A) Both electrons in the same $2p$ orbital, opposite spins; the other two $2p$ orbitals empty.
(B) One electron in each of two different $2p$ orbitals, spins parallel (both unpaired); the third $2p$ orbital empty.
(C) One electron in each of two different $2p$ orbitals, spins paired (antiparallel); the third $2p$ orbital empty.
(D) One electron in each of the three $2p$ orbitals.

Lời giải chi tiết

Hund's rule requires electrons to occupy **separate** degenerate orbitals **singly**, with **parallel** spins, before any pairing occurs. With only 2 electrons to place among 3 degenerate $2p$ orbitals, they must go into two different orbitals with parallel (unpaired) spins. **(B)**.

Bài tập luyện tập

For the hydrogen atom, which electronic transition produces the emitted photon of **shortest** wavelength (highest energy)?

(A) $n = 2 \to n = 1$
(B) $n = 3 \to n = 2$
(C) $n = 4 \to n = 3$
(D) $n = 6 \to n = 5$

Lời giải chi tiết

Photon energy is proportional to the size of the energy gap between levels, and wavelength is inversely proportional to energy ($\lambda = hc/E$). Energy gaps are largest for transitions down to $n = 1$ (Lyman series) and shrink as n increases, so $n = 2 \to 1$ releases the most energy and hence gives the shortest wavelength among the options given. **(A)**.

Bài tập luyện tập

An electron falls from an excited state to a lower state, emitting a photon of energy $\Delta E = 3.03 \times 10^{-19}$ J. Calculate the wavelength of the emitted light and state which region of the spectrum it lies in.

Lời giải chi tiết

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34})(3.00 \times 10^{8})}{3.03 \times 10^{-19}} = 6.56 \times 10^{-7}\ \text{m} = 656\ \text{nm}.$$

This is in the **visible** region (red light) — in fact it is the wavelength of the H_α line of the hydrogen Balmer series.

Bài tập luyện tập

An element Z has successive ionisation energies (kJ mol^{-1}): $590,\ 1145,\ 4912,\ 6474,\ 8144$. Deduce the group of Z and write the general form of its ground-state electron configuration.

Lời giải chi tiết

Ratios between consecutive IEs: $\frac{1145}{590} = 1.94$, then $\frac{4912}{1145} = 4.29$ — a large jump after only 2 electrons removed. Z therefore has 2 valence electrons and belongs to **Group 2**; its configuration ends in $\ldots ns^2$ (this dataset matches calcium, $[\text{Ar}]4s^2$).

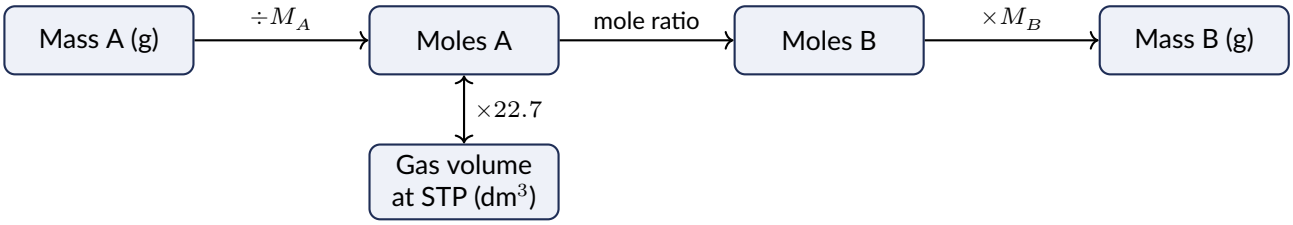
1.4 The mole, molar mass, and chemical formulas

The **mole** links the microscopic (particle count) and macroscopic (mass, volume) worlds: 1 mol $= 6.02 \times 10^{23}$ particles (**Avogadro's constant**, N_A). The key relationships are

$$n = \frac{m}{M}\ \text{(mass)}, \qquad n = \frac{N}{N_A}\ \text{(particle count)}, \qquad n = cV\ \text{(solutions)}.$$

At **standard temperature and pressure** (STP: 273 K, 100 kPa, i.e. 1.00×10^5 Pa), 1 mol of any ideal gas occupies 22.7 dm^3 (the **molar gas volume** at STP).

This book uses the current IUPAC definition, STP $= 273$ K and 100 kPa, giving molar gas volume 22.7 dm^3 mol^{-1}. Some older sources instead define STP as 273 K and 101.3 kPa (1 atm), giving 22.4 dm^3 mol^{-1} — always check which convention a question is using, and use the value it specifies.



The stoichiometry "mole bridge": always convert to moles first. At STP (273 K, 100 kPa), 1 mol of ideal gas occupies 22.7 dm^3.

Ví dụ mẫu · Empirical formula from combustion analysis

Complete combustion of 4.60 g of a compound containing C, H, O produces 8.80 g $CO_2(g)$ and 5.40 g $H_2O(l)$. Find its empirical formula.

$n(CO_2) = \frac{8.80}{44.01} = 0.2000$ mol $= n(C)$, so $m(C) = 2.402$ g. $n(H_2O) = \frac{5.40}{18.02} = 0.2997$ mol

$\Rightarrow n(\text{H}) = 0.5993$ mol, so $m(\text{H}) = 0.604$ g. $m(\text{O}) = 4.60 - 2.402 - 0.604 = 1.594$ g $\Rightarrow n(\text{O}) = \dfrac{1.594}{16.00} = 0.0997$ mol. Divide by the smallest (0.0997): C : 2.01, H : 6.01, O : 1.00 $\Rightarrow$ $\text{C}_2\text{H}_6\text{O}$ (ethanol, $M = 46.08$ g mol^{-1}).

VN **GIẢI THÍCH TIẾNG VIỆT**

Quy trình xác định công thức đơn giản nhất: đổi khối lượng mỗi nguyên tố ra **số mol**, sau đó **chia tất cả cho số mol nhỏ nhất** để ra tỉ lệ nguyên. Với dữ liệu đốt cháy hợp chất chứa C, H, O: toàn bộ C nằm trong CO_2 sinh ra, toàn bộ H nằm trong H_2O sinh ra, còn khối lượng O được suy ra bằng **bảo toàn khối lượng** (lấy khối lượng hợp chất trừ khối lượng C và H).

1.4.1 Percentage composition by mass

The percentage by mass of an element X in a compound is

$$\%X = \frac{(\text{number of } X \text{ atoms}) \times A_r(X)}{M(\text{compound})} \times 100\%.$$

Ví dụ mẫu · Worked example

Find the percentage by mass of nitrogen in ammonium nitrate, NH_4NO_3.

$M = 2(14.01) + 4(1.01) + 3(16.00) = 28.02 + 4.04 + 48.00 = 80.06$ g mol^{-1}.

$$\%N = \frac{28.02}{80.06} \times 100 = 35.0\%.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Phần trăm khối lượng của một nguyên tố = (số nguyên tử nguyên tố đó $\times$ khối lượng nguyên tử) chia cho khối lượng mol của cả hợp chất, nhân 100%. Chú ý đếm đúng số nguyên tử của nguyên tố trong công thức (ví dụ NH_4NO_3 có **2** nguyên tử N: một trong NH_4^+, một trong NO_3^-).

1.4.2 Water of crystallisation (hydrates)

Many ionic solids crystallise with a fixed number of water molecules incorporated into their lattice, called **water of crystallisation**; the general formula is written salt$\cdot x\text{H}_2\text{O}$. Heating a hydrate to constant mass drives off all the water, leaving the anhydrous salt; the mass lost equals the mass of water originally present, and comparing moles of anhydrous salt to moles of water lost gives the integer x.

Ví dụ mẫu · Finding x in a hydrate formula

A 3.13 g sample of hydrated copper(II) sulfate, $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$, is heated to constant mass, leaving 2.00 g of anhydrous CuSO_4 ($M = 159.62$ g mol^{-1}). Find x.

Mass of water lost $= 3.13 - 2.00 = 1.13$ g. $n(\text{CuSO}_4) = \dfrac{2.00}{159.62} = 0.01253$ mol. $n(\text{H}_2\text{O}) = \dfrac{1.13}{18.02} = 0.06271$ mol.

$$x = \frac{n(\text{H}_2\text{O})}{n(\text{CuSO}_4)} = \frac{0.06271}{0.01253} = 5.00.$$

The hydrate is $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (blue vitriol).

VN **GIẢI THÍCH TIẾNG VIỆT**
Bài toán ngậm nước: khối lượng mất đi khi nung chính là khối lượng nước kết tinh. Tính số mol muối khan và số mol nước, sau đó lấy **tỉ lệ mol nước : mol muối khan** để tìm x — kết quả phải làm tròn về số nguyên gần nhất.

1.4.3 Molar concentration and dilution

Molar concentration (molarity) is $c = \dfrac{n}{V}$ (mol dm^{-3}, with V in dm^3). When a solution is diluted by adding solvent, the number of moles of solute is unchanged, so

$$c_1 V_1 = c_2 V_2.$$

Ví dụ mẫu · Worked example

What volume of 2.50 mol dm^{-3} stock HCl(aq) is needed to prepare 500 cm^3 of 0.100 mol dm^{-3} HCl(aq)?

$$V_1 = \frac{c_2 V_2}{c_1} = \frac{(0.100)(500)}{2.50} = 20.0 \text{ cm}^3.$$

VN **GIẢI THÍCH TIẾNG VIỆT**
Pha loãng không làm thay đổi **số mol chất tan**, chỉ thêm dung môi làm tăng thể tích $\Rightarrow c_1 V_1 = c_2 V_2$. Đơn vị thể tích ở hai vế phải nhất quán (cùng cm^3 hoặc cùng dm^3), nhưng không bắt buộc phải đổi sang dm^3 vì tỉ lệ vẫn đúng miễn là đồng nhất.

1.4.4 Empirical versus molecular formula

The **empirical formula** gives the simplest whole-number ratio of atoms in a compound; the **molecular formula** gives the actual number of atoms in one molecule and is always a whole-number multiple of the empirical formula: molecular $= (\text{empirical})_n$, where

$$n = \frac{M(\text{molecular})}{M(\text{empirical formula unit})}.$$

Ví dụ mẫu · Worked example

A compound has empirical formula CH_2O ($M = 30.03$ g mol^{-1}) and molar mass 180.18 g mol^{-1}. Find its molecular formula.

$$n = \frac{180.18}{30.03} = 6.00 \quad \Rightarrow \quad \text{molecular formula} = C_6H_{12}O_6 \text{ (glucose)}.$$

VN **GIẢI THÍCH TIẾNG VIỆT**
Công thức phân tử luôn là **bội số nguyên** của công thức đơn giản nhất: tìm $n = \dfrac{M_{\text{phân tử}}}{M_{\text{đơn giản}}}$ (phải ra số nguyên hoặc rất gần số nguyên), rồi nhân mọi chỉ số trong công thức đơn giản với n.

(!) Lỗi thường gặp: Mole ratios rarely come out as *exact* integers because of rounding in atomic masses — round **sensibly**: a ratio of 1.98 or 2.03 should be read as 2, not truncated to 1. If a ratio is close to a simple fraction such as 1.33 ($\approx \frac{4}{3}$) or 1.50 ($\approx \frac{3}{2}$), multiply *every* ratio in the set

by the fraction's denominator instead of rounding it incorrectly on its own.

Bài tập luyện tập

How many hydrogen atoms are present in 9.01 g of water ($M = 18.02$ g mol^{-1})?

(A) 3.01×10^{23} **(C)** 1.20×10^{24}

(B) 6.02×10^{23} **(D)** 9.03×10^{23}

Lời giải chi tiết

$n(\text{H}_2\text{O}) = \dfrac{9.01}{18.02} = 0.500$ mol, containing 2 H atoms each: $n(\text{H}) = 1.00$ mol $\Rightarrow N = 1.00 \times 6.02 \times 10^{23} = 6.02 \times 10^{23}$ H atoms. **(B)**.

Bài tập luyện tập

Complete combustion of a 0.450 g sample of a hydrocarbon (C and H only) produces 1.32 g $\text{CO}_2(\text{g})$ and 0.810 g $\text{H}_2\text{O}(\text{l})$. (a) Find the empirical formula. (b) Given that its molar mass is 30.08 g mol^{-1}, find its molecular formula.

Lời giải chi tiết

(a) $n(\text{CO}_2) = \dfrac{1.32}{44.01} = 0.02999$ mol $= n(\text{C})$; $m(\text{C}) = 0.02999 \times 12.01 = 0.3602$ g. $n(\text{H}_2\text{O}) = \dfrac{0.810}{18.02} = 0.04495$ mol $\Rightarrow n(\text{H}) = 0.08990$ mol; $m(\text{H}) = 0.0908$ g. Check: $m(\text{C}) + m(\text{H}) = 0.3602 + 0.0908 = 0.451$ g ≈ 0.450 g given — confirms the compound contains only C and H. Ratio $n(\text{H}) : n(\text{C}) = \dfrac{0.08990}{0.02999} = 3.00$, so empirical formula $= \text{CH}_3$ ($M = 15.04$ g mol^{-1}).

(b) $n = \dfrac{30.08}{15.04} = 2.00 \Rightarrow$ molecular formula $= \text{C}_2\text{H}_6$ (ethane).

Bài tập luyện tập

Calculate the percentage by mass of calcium in calcium carbonate, CaCO_3 ($M = 100.09$ g mol^{-1}).

Lời giải chi tiết

$$\%\text{Ca} = \frac{40.08}{100.09} \times 100 = 40.0\%.$$

Bài tập luyện tập

A 2.46 g sample of hydrated magnesium sulfate, $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$, is heated to constant mass, leaving 1.20 g of anhydrous MgSO_4 ($M = 120.38$ g mol^{-1}). Find x.

Lời giải chi tiết

Mass of water lost $= 2.46 - 1.20 = 1.26$ g. $n(\text{MgSO}_4) = \dfrac{1.20}{120.38} = 0.009968$ mol. $n(\text{H}_2\text{O}) = \dfrac{1.26}{18.02} = 0.06992$ mol.

$$x = \frac{0.06992}{0.009968} = 7.01 \approx 7.$$

The hydrate is $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (Epsom salt).

Bài tập luyện tập

25.0 cm^3 of 0.400 mol dm^{-3} $\text{Na}_2\text{CO}_3(\text{aq})$ is diluted with water to a final volume of 200 cm^3. Calculate the new concentration.

Lời giải chi tiết

$$c_2 = \frac{c_1 V_1}{V_2} = \frac{(0.400)(25.0)}{200} = 0.0500 \text{ mol dm}^{-3}.$$

Bài tập luyện tập

Calculate the mass of NaOH ($M = 40.00$ g mol^{-1}) needed to prepare 250 cm^3 of a 0.200 mol dm^{-3} solution.

Lời giải chi tiết

$n = cV = 0.200 \times 0.250 = 0.0500$ mol.

$$m = n \times M = 0.0500 \times 40.00 = 2.00 \text{ g}.$$

Bài tập luyện tập

How many molecules of CO_2 are present in 11.0 g of $\text{CO}_2(\text{g})$?

(A) 1.50×10^{23} **(C)** 6.02×10^{23}

(B) 3.01×10^{23} **(D)** 7.53×10^{22}

Lời giải chi tiết

$M(\text{CO}_2) = 12.01 + 2(16.00) = 44.01$. $n = \dfrac{11.0}{44.01} = 0.2499$ mol. $N = 0.2499 \times 6.02 \times 10^{23} = 1.50 \times 10^{23}$ molecules. **(A)**.

Bài tập luyện tập

A sample of neon gas has isotopic composition: ^{20}Ne (90.0%, mass 19.9924), ^{21}Ne (0.30%, mass 20.9938), ^{22}Ne (9.70%, mass 21.9914). (a) Calculate $A_r(\text{Ne})$. (b) Hence find the mass of 3.01×10^{23} atoms of this neon sample.

Lời giải chi tiết

(a)

$$A_r = (0.900)(19.9924)+(0.0030)(20.9938)+(0.0970)(21.9914) = 17.993+0.063+2.133 = 20.19.$$

(b) $n = \dfrac{N}{N_A} = \dfrac{3.01 \times 10^{23}}{6.02 \times 10^{23}} = 0.500$ mol.

$$m = n \times A_r = 0.500 \times 20.19 = 10.1 \text{ g}.$$

Bài tập luyện tập

A compound containing only carbon and hydrogen has percentage composition 85.6% C and 14.4% H by mass, and molar mass 42.08 g mol^{-1}. Determine its molecular formula.

Lời giải chi tiết

Per 100 g: $n(\text{C}) = \dfrac{85.6}{12.01} = 7.127$ mol; $n(\text{H}) = \dfrac{14.4}{1.01} = 14.26$ mol. Ratio $n(\text{H}) : n(\text{C}) = \dfrac{14.26}{7.127} = 2.00 \Rightarrow$ empirical formula CH_2 ($M = 14.03$ g mol^{-1}).

$$n = \frac{42.08}{14.03} = 3.00 \Rightarrow \text{molecular formula} = \text{C}_3\text{H}_6 \text{ (propene)}.$$

1.5 Ideal gases (AHL)

1.5.1 Kinetic theory of an ideal gas and real-gas deviations (AHL)

An **ideal gas** is defined precisely by the postulates introduced in section 1.1: its particles are treated as point masses with zero volume, they exert no intermolecular forces on one another except during perfectly elastic collisions, and their average kinetic energy is directly proportional to absolute temperature. No real gas obeys this model exactly, but most gases approximate it closely under everyday conditions.

Khái niệm cốt lõi

Real gases deviate most from ideal behaviour at **high pressure** and **low temperature**:

- At high pressure, particles are forced close together, so the particles' own finite volume becomes a non-negligible fraction of the total volume — the gas is harder to compress further than the ideal model predicts (real $V >$ ideal V).
- At low temperature, particles move slowly, so intermolecular attractive forces have time to act; these forces pull particles together and reduce the force (and hence pressure) they exert on the container walls (real $P <$ ideal P), and can eventually cause condensation.

Real gases behave most nearly ideally at **low pressure and high temperature**, where particles are far apart, move fast, and interact only briefly.

VN **GIẢI THÍCH TIẾNG VIỆT**

Khí thực lệch khỏi mô hình khí lý tưởng nhiều nhất ở **áp suất cao** (thể tích riêng của hạt không còn bỏ qua được) và **nhiệt độ thấp** (lực hút giữa các hạt trở nên đáng kể, có thể dẫn đến hoá lỏng). Khí thực gần với khí lý tưởng nhất ở áp suất thấp, nhiệt độ cao.

1.5.2 The ideal gas equation and combined gas law (AHL)

The **ideal gas law** unites pressure, volume, amount, and temperature: $PV = nRT$, where $R = 8.31$ J K^{-1} mol^{-1} (equivalently 8.31 dm^3 kPa K^{-1} mol^{-1}) and T is always in kelvin. For a fixed amount of gas changing from one set of conditions to another, the **combined gas law** follows directly:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}.$$

Ví dụ mẫu · Worked example

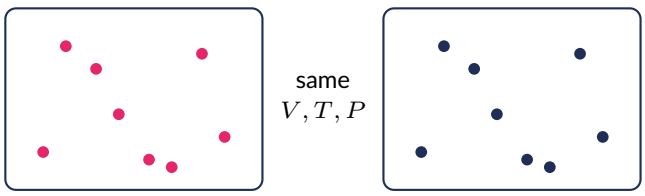
A gas sample occupies 2.00 dm^3 at 100 kPa and 293 K. Find its volume at STP (273 K, 100 kPa). Since $P_1 = P_2 = 100$ kPa, the pressures cancel:

$$V_2 = V_1 \times \frac{T_2}{T_1} = 2.00 \times \frac{273}{293} = 1.86 \text{ dm}^3.$$

(!) Lỗi thường gặp: Temperature MUST be converted to kelvin ($T(\text{K}) = T(^\circ\text{C}) + 273$) before using any gas law — using °C directly gives a wrong answer. Keep pressure/volume units consistent with the value of R used (kPa and dm^3 with $R = 8.31$ dm^3 kPa K^{-1}mol^{-1}). Also remember this book's STP is 273 K and 100 kPa (not the older 101.3 kPa convention) — always check which value a question intends.

1.5.3 Avogadro's Law (AHL)

Avogadro's Law states that equal volumes of any gases, at the same temperature and pressure, contain equal numbers of moles (and therefore equal numbers of particles) — regardless of the chemical identity of the gas. This follows directly from $PV = nRT$: at fixed T and P, $\frac{n}{V} = \frac{P}{RT}$ is a constant that does not depend on which gas is present.



Avogadro's Law: at the same temperature and pressure, equal volumes of *any* gas contain equal numbers of moles (particles) — 8 dots in each flask here, regardless of the different chemical identity or particle mass of the two gases.

Ví dụ mẫu · Worked example

Two identical flasks, both at the same temperature and pressure, contain $N_2(g)$ and $O_2(g)$ respectively. The nitrogen flask contains 11.2 g of N_2 ($M = 28.02$ g mol^{-1}). Find the mass of O_2 in the other flask.

$n(N_2) = \frac{11.2}{28.02} = 0.400$ mol. By Avogadro's Law, equal volume, T, $P \Rightarrow n(O_2) = 0.400$ mol also.

$$m(O_2) = 0.400 \times 32.00 = 12.8 \text{ g}.$$

VN GIẢI THÍCH TIẾNG VIỆT

Định luật Avogadro: cùng thể tích, cùng nhiệt độ, cùng áp suất ⇒ cùng số mol, **bất kể** khí đó là gì. Đây là hệ quả trực tiếp của $PV = nRT$: ở T, P cố định thì n/V là hằng số. Vì vậy hai bình khí khác nhau có thể có số mol bằng nhau dù khối lượng khác nhau hoàn toàn.

1.5.4 Determining molar mass from $PV = nRT$ (AHL)

Since $n = \dfrac{m}{M}$, substituting into the ideal gas law and rearranging gives a direct route to the molar mass of an unknown gas from a single measurement of P, V, T, and m:

$$M = \frac{mRT}{PV}.$$

Ví dụ mẫu · Worked example

A 0.250 g sample of an unknown gas occupies 100 cm^3 at 150 kPa and 100°C. Find its molar mass.

$V = 0.100$ dm^3, $T = 373$ K.

$$n = \frac{PV}{RT} = \frac{(150)(0.100)}{(8.31)(373)} = \frac{15.0}{3099.6} = 4.84 \times 10^{-3} \text{ mol}.$$

$$M = \frac{m}{n} = \frac{0.250}{4.84 \times 10^{-3}} = 51.7 \text{ g mol}^{-1}.$$

VN GIẢI THÍCH TIẾNG VIỆT

Khi biết khối lượng mẫu khí cùng P, V, T, có thể tính số mol bằng $PV = nRT$ rồi suy ra khối lượng mol $M = m/n$ — đây là cách xác định khối lượng mol của một khí chưa biết danh tính bằng thực nghiệm.

1.5.5 Graham's law of diffusion (AHL)

At a given temperature, all gases have the same average kinetic energy (postulate 5 of the kinetic theory). Since $E_k = \frac{1}{2}mv^2$, a gas made of heavier particles must have a lower average speed to have the same kinetic energy as a lighter gas. **Graham's law** states that the rate of diffusion (or effusion) of a gas is inversely proportional to the square root of its molar mass:

$$\text{rate} \propto \frac{1}{\sqrt{M}} \qquad \Longrightarrow \qquad \frac{\text{rate}_1}{\text{rate}_2} = \sqrt{\frac{M_2}{M_1}}.$$

Ví dụ mẫu · Graham's law: the ammonium chloride ring

Cotton wool soaked in concentrated $\text{NH}_3(\text{aq})$ and cotton wool soaked in concentrated $\text{HCl}(\text{aq})$ are placed simultaneously at opposite ends of a 100 cm horizontal glass tube. A white ring of $\text{NH}_4\text{Cl}(\text{s})$ forms where the two gases meet. Find the distance of the ring from the HCl end. ($M(\text{NH}_3) = 17.04$, $M(\text{HCl}) = 36.46$.)

$$\frac{\text{rate}(\text{NH}_3)}{\text{rate}(\text{HCl})} = \sqrt{\frac{36.46}{17.04}} = \sqrt{2.141} = 1.463.$$

Both gases travel for the same time, so distance is proportional to rate: $d(\text{NH}_3) = 1.463\, d(\text{HCl})$, and $d(\text{NH}_3) + d(\text{HCl}) = 100$ cm.

$$d(\text{HCl})(1 + 1.463) = 100 \;\Rightarrow\; d(\text{HCl}) = \frac{100}{2.463} = 40.6 \text{ cm}.$$

The ring forms 40.6 cm from the HCl end (equivalently 59.4 cm from the NH_3 end) — closer to the HCl end, because the lighter NH_3 molecules diffuse faster and travel farther in the same time.

VN **GIẢI THÍCH TIẾNG VIỆT**

Định luật Graham: tốc độ khuếch tán tỉ lệ nghịch với căn bậc hai khối lượng mol (rate $\propto 1/\sqrt{M}$). Trong thí nghiệm ống khuếch tán NH_3/HCl, khí nhẹ hơn (NH_3) di chuyển nhanh hơn nên vòng khói trắng NH_4Cl luôn hình thành **gần đầu ống chứa khí nặng hơn** (HCl) hơn.

Bài luyện AHL

A rigid 15.0 dm^3 container holds 2.50 mol of gas at 350 K. The pressure is:

(A) 485 kPa
(C) 727 kPa
(B) 194 kPa
(D) 97.0 kPa

Lời giải chi tiết

$P = \dfrac{nRT}{V} = \dfrac{(2.50)(8.31)(350)}{15.0} = \dfrac{7271}{15.0} = 485$ kPa. **(A)**.

Bài luyện AHL

Cotton wool soaked in concentrated HBr(aq) and cotton wool soaked in concentrated $\text{NH}_3\text{(aq)}$ are placed simultaneously at opposite ends of a 60.0 cm tube. Calculate the distance from the HBr end at which the white $\text{NH}_4\text{Br(s)}$ ring forms. ($M(\text{HBr}) = 80.91$, $M(\text{NH}_3) = 17.04$.)

Lời giải chi tiết

$$\frac{\text{rate}(\text{NH}_3)}{\text{rate}(\text{HBr})} = \sqrt{\frac{80.91}{17.04}} = \sqrt{4.748} = 2.179.$$

$d(\text{NH}_3) = 2.179\, d(\text{HBr})$ and $d(\text{NH}_3) + d(\text{HBr}) = 60.0$ cm.

$$d(\text{HBr})(1 + 2.179) = 60.0 \;\Rightarrow\; d(\text{HBr}) = \frac{60.0}{3.179} = 18.9 \text{ cm}.$$

The ring forms 18.9 cm from the HBr end.

Bài luyện AHL

A fixed mass of gas occupies 3.00 dm^3 at 150 kPa and 300 K. It is compressed to 1.00 dm^3 and heated to 400 K. The new pressure is:

(A) 600 kPa
(C) 800 kPa
(B) 450 kPa
(D) 300 kPa

Lời giải chi tiết

$P_2 = P_1 \times \dfrac{V_1}{V_2} \times \dfrac{T_2}{T_1} = 150 \times \dfrac{3.00}{1.00} \times \dfrac{400}{300} = 150 \times 3 \times 1.333 = 600$ kPa. **(A).**

Bài luyện AHL

What volume does 0.500 mol of an ideal gas occupy at 500 kPa and 250 K?

Lời giải chi tiết

$$V = \frac{nRT}{P} = \frac{(0.500)(8.31)(250)}{500} = \frac{1038.75}{500} = 2.08 \text{ dm}^3.$$

Bài luyện AHL

Two gas syringes of equal volume, both at 25°C and 1.00×10^5 Pa, contain $CH_4(g)$ and $C_3H_8(g)$ respectively. The methane syringe contains 0.0250 mol. State the number of moles of propane present, and calculate its mass ($M(C_3H_8) = 44.11$ g mol^{-1}).

Lời giải chi tiết

By Avogadro's Law, equal volumes at the same T, P contain equal moles, regardless of gas identity: $n(C_3H_8) = 0.0250$ mol.

$$m = n \times M = 0.0250 \times 44.11 = 1.10 \text{ g}.$$

Bài luyện AHL

A 0.560 g sample of an unknown gas occupies 250 cm^3 at 120 kPa and 27°C. Determine its molar mass.

Lời giải chi tiết

$V = 0.250$ dm^3, $T = 300$ K.

$$n = \frac{PV}{RT} = \frac{(120)(0.250)}{(8.31)(300)} = \frac{30.0}{2493} = 0.01203 \text{ mol}.$$

$$M = \frac{m}{n} = \frac{0.560}{0.01203} = 46.5 \text{ g mol}^{-1}.$$

Bài luyện AHL

Real gases deviate most strongly from ideal-gas behaviour under conditions of:

(A) high pressure and low temperature
(C) high pressure and high temperature
(B) low pressure and high temperature
(D) low pressure and low temperature

Lời giải chi tiết

At high pressure, particle volume becomes significant relative to the container; at low temperature, intermolecular attractions become significant because particles move slowly. Both effects cause the largest deviation from ideal behaviour when they act together. **(A)**.

Bài luyện AHL

Under the same conditions, hydrogen gas diffuses faster than oxygen gas by a factor closest to: ($M(\mathrm{H_2}) = 2.02$, $M(\mathrm{O_2}) = 32.00$.)

(A) 4.0
(C) 16
(B) 0.25
(D) 1.0

Lời giải chi tiết

$$\frac{\text{rate}(\mathrm{H_2})}{\text{rate}(\mathrm{O_2})} = \sqrt{\frac{32.00}{2.02}} = \sqrt{15.84} = 3.98 \approx 4.0.$$

(A).

Bài luyện AHL

Explain, in terms of the kinetic molecular theory, why gases are far more compressible than liquids. A fixed mass of gas at 500 kPa and volume V is compressed at constant temperature until its pressure reaches 1500 kPa. Express the new volume in terms of V.

Lời giải chi tiết

Gas particles are separated by distances very large compared with their own size, so a gas sample is mostly empty space; particles can be pushed much closer together before they begin to touch one another. In a liquid, particles are already in near-contact, so there is almost no empty space left to remove by compression.

Numerically, at constant temperature and fixed mass, Boyle's law applies: $P_1V_1 = P_2V_2$.

$$V_2 = \frac{P_1V_1}{P_2} = \frac{500\,V}{1500} = \frac{V}{3}.$$

The new volume is one-third of the original volume.

1.6 Stoichiometric calculations from balanced equations

The coefficients of a balanced chemical equation give the **mole ratio** in which reactants combine and products form. Once any quantity (mass, particle count, gas volume, or solution concentration) is converted to moles, the mole ratio from the equation converts it directly into moles of any other species in the equation; a final conversion (using M, N_A, 22.7 dm^3 mol^{-1}, or $c = n/V$) turns that back into whatever quantity is required. This "always go through moles" strategy is the single most important calculation skill in the whole IB Chemistry course, and it underlies every stoichiometry problem in later units (limiting reactant, titrations, electrolysis, equilibrium).

Ví dụ mẫu · Mass-to-mass stoichiometry

Calculate the maximum mass of iron, Fe, that can be obtained from 319.8 g of iron(III) oxide, Fe_2O_3 ($M = 159.70$ g mol^{-1}), by the thermite reaction:

$$Fe_2O_3(s) + 2Al(s) \rightarrow Al_2O_3(s) + 2Fe(s).$$

Step 1 — moles of the given species:

$$n(Fe_2O_3) = \frac{319.8}{159.70} = 2.002 \text{ mol}.$$

Step 2 — mole ratio from the equation ($1 : 2$ for $Fe_2O_3 : Fe$):

$$n(Fe) = 2 \times 2.002 = 4.003 \text{ mol}.$$

Step 3 — convert to the requested quantity ($M(Fe) = 55.85$ g mol^{-1}):

$$m(Fe) = 4.003 \times 55.85 = 223.6 \text{ g}.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Quy trình ba bước cho mọi bài toán định lượng: (1) đổi dữ kiện đã cho ra **số mol**; (2) dùng **tỉ lệ mol** lấy từ hệ số cân bằng của phương trình để chuyển sang số mol chất cần tìm; (3) đổi số mol đó sang đại lượng đề bài yêu cầu (khối lượng, thể tích khí, số hạt, hoặc nồng độ). Đây là khung tư duy dùng lại xuyên suốt toàn bộ chương trình Hoá IB, từ thuốc thử giới hạn, chuẩn độ, đến điện phân và cân bằng hoá học.

Ví dụ mẫu · Mass-to-gas-volume stoichiometry at STP

Calcium carbonate reacts with excess hydrochloric acid: $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$. Find the volume of $CO_2(g)$ produced at STP when 5.00 g of $CaCO_3$ ($M = 100.09$ g mol^{-1}) reacts completely.

$$n(CaCO_3) = \frac{5.00}{100.09} = 0.04996 \text{ mol}.$$

Mole ratio $CaCO_3 : CO_2 = 1 : 1$, so $n(CO_2) = 0.04996$ mol. At STP (273 K, 100 kPa), 1 mol of gas occupies 22.7 dm^3:

$$V(CO_2) = 0.04996 \times 22.7 = 1.13 \text{ dm}^3 \ (1130 \text{ cm}^3).$$

(!) Lỗi thường gặp: The mole ratio comes ONLY from the balanced equation's coefficients — never from the masses or volumes given in the question. Always write (or check) the balanced equation first, and double-check it really is balanced, before reading off a mole ratio; an unbalanced equation silently gives a wrong ratio and a wrong final answer even if every other step is done correctly.

VN **GIẢI THÍCH TIẾNG VIỆT**

Tỉ lệ mol luôn lấy từ **hệ số cân bằng** của phương trình phản ứng, tuyệt đối không lấy từ khối lượng hay thể tích đề cho. Trước khi giải, luôn kiểm tra lại phương trình đã được cân bằng đúng chưa — một phương trình cân bằng sai sẽ cho tỉ lệ mol sai, dẫn đến toàn bộ đáp số sai dù các bước tính toán sau đó đều đúng.

Bài tập luyện tập

Magnesium burns in oxygen: $2\text{Mg(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{MgO(s)}$. What mass of MgO ($M = 40.31$ g mol^{-1}) forms from 6.08 g of Mg ($M = 24.31$ g mol^{-1})?

(A) 10.08 g
(C) 20.16 g
(B) 5.04 g
(D) 6.08 g

Lời giải chi tiết

$n(\text{Mg}) = \dfrac{6.08}{24.31} = 0.2501$ mol. Ratio Mg : MgO $= 1 : 1$, so $n(\text{MgO}) = 0.2501$ mol. $m = 0.2501 \times 40.31 = 10.08$ g. **(A)**.

Bài tập luyện tập

Propane burns completely: $\text{C}_3\text{H}_8\text{(g)} + 5\text{O}_2\text{(g)} \rightarrow 3\text{CO}_2\text{(g)} + 4\text{H}_2\text{O(l)}$. What volume of $\text{O}_2\text{(g)}$ at STP is needed to burn 0.0200 mol of C_3H_8?

(A) 2.27 dm^3
(C) 4.54 dm^3
(B) 0.454 dm^3
(D) 1.135 dm^3

Lời giải chi tiết

Ratio $\text{C}_3\text{H}_8 : \text{O}_2 = 1 : 5$, so $n(\text{O}_2) = 0.0200 \times 5 = 0.100$ mol. $V = 0.100 \times 22.7 = 2.27$ dm^3. **(A)**.

Bài tập luyện tập

How many moles of Na_3PO_4 ($M = 163.94$ g mol^{-1}) contain the same number of sodium ions as 0.600 mol of NaCl?

(A) 0.200 mol
(C) 1.800 mol
(B) 0.600 mol
(D) 0.0667 mol

Lời giải chi tiết

Each NaCl gives 1 Na^+, so 0.600 mol NaCl contains 0.600 mol Na^+. Each Na_3PO_4 gives 3 Na^+, so $n(\text{Na}_3\text{PO}_4) = \dfrac{0.600}{3} = 0.200$ mol. **(A)**.

Bài tập luyện tập

A 25.0 cm^3 sample of $\text{Na}_2\text{CO}_3\text{(aq)}$ reacts exactly with 30.0 cm^3 of 0.150 mol dm^{-3} HCl(aq): $\text{Na}_2\text{CO}_3\text{(aq)} + 2\text{HCl(aq)} \rightarrow 2\text{NaCl(aq)} + \text{H}_2\text{O(l)} + \text{CO}_2\text{(g)}$. Find the concentration of the $\text{Na}_2\text{CO}_3\text{(aq)}$.

(A) 0.0900 mol dm^{-3}
(C) 0.0450 mol dm^{-3}
(B) 0.180 mol dm^{-3}
(D) 0.150 mol dm^{-3}

Lời giải chi tiết

$n(\text{HCl}) = 0.0300 \times 0.150 = 4.50 \times 10^{-3}$ mol. Ratio $\text{Na}_2\text{CO}_3 : \text{HCl} = 1 : 2$, so $n(\text{Na}_2\text{CO}_3) = \dfrac{4.50 \times 10^{-3}}{2} = 2.25 \times 10^{-3}$ mol. $c = \dfrac{n}{V} = \dfrac{2.25 \times 10^{-3}}{0.0250} = 0.0900$ mol dm^{-3}. **(A)**.

Bài luyện nâng cao

Ammonium nitrate decomposes on heating: $\text{NH}_4\text{NO}_3(\text{s}) \rightarrow \text{N}_2\text{O}(\text{g}) + 2\text{H}_2\text{O}(\text{g})$. A sample decomposes to give 3.41 dm^3 of $\text{N}_2\text{O}(\text{g})$, measured at STP. Calculate (a) the amount (mol) of NH_4NO_3 that decomposed, (b) the mass of NH_4NO_3 ($M = 80.06$ g mol^{-1}) originally present, and (c) the total volume of gas (N_2O+H_2O) produced at STP.

Lời giải chi tiết

(a) $n(\text{N}_2\text{O}) = \dfrac{3.41}{22.7} = 0.1502$ mol. Ratio $\text{NH}_4\text{NO}_3 : \text{N}_2\text{O} = 1 : 1$, so $n(\text{NH}_4\text{NO}_3) = 0.1502$ mol.
(b) $m = 0.1502 \times 80.06 = 12.03$ g.
(c) $n(\text{H}_2\text{O}) = 2 \times 0.1502 = 0.3004$ mol, so total gas $= 0.1502 + 0.3004 = 0.4506$ mol; $V = 0.4506 \times 22.7 = 10.23$ dm^3.

Bài tập luyện tập

A sample of pure calcium metal ($M = 40.08$ g mol^{-1}) reacts completely with excess water: $\text{Ca}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}(\text{OH})_2(\text{aq}) + \text{H}_2(\text{g})$, releasing 756 cm^3 of $\text{H}_2(\text{g})$ at STP. What mass of calcium reacted?

(A) 1.332 g
(B) 2.664 g
(C) 0.666 g
(D) 1.998 g

Lời giải chi tiết

$n(\text{H}_2) = \dfrac{0.756}{22.7} = 0.03330$ mol. Ratio $\text{Ca} : \text{H}_2 = 1 : 1$, so $n(\text{Ca}) = 0.03330$ mol. $m = 0.03330 \times 40.08 = 1.335$ g ≈ 1.332 g (rounding). **(A)**.

Bài tập luyện tập

Which set of steps correctly describes converting a given mass of reactant A into a required mass of product B using a balanced equation?

(A) mass A → moles A (using M_A) → moles B (mole ratio) → mass B (using M_B)
(B) mass A → mass B directly using the mole ratio as a mass ratio
(C) moles A → mass A → mass B → moles B
(D) mass A → moles B (using M_A) → mass B (using mole ratio)

Lời giải chi tiết

The mole ratio from a balanced equation relates *moles*, never masses directly, so mass must be converted to moles first (dividing by M_A), the mole ratio applied, and only then converted back to mass (multiplying by M_B). **(A)**.

1.7 Further quantitative skills

Section 1.4 introduced the ”always go through moles” strategy for stoichiometric calculations, applied there to reactants assumed to be present in exactly the ratio the equation requires. Real laboratory samples are rarely so convenient: the two reactants mixed together are often present in whatever ratio happens to be available, some analytes cannot be titrated directly at all, standard solutions frequently need to be diluted accurately before use, and a molecular mass spectrum must be interpreted carefully to identify which atoms are actually present. This closing section develops four further quantitative skills, every one of them built on exactly the same mole-based reasoning already established: identifying which reactant runs out first, preparing an accurate dilution series, working out an unknown quantity indirectly through back-titration, and recognising isotope patterns in a mass spectrum.

1.7.1 Limiting reagent and the reagent in excess

When two reactants are mixed in amounts that do not exactly match the mole ratio given by the balanced equation, one of them is used up completely first: this is the **limiting reagent** (or limiting reactant), and it alone determines the maximum amount of product that can form. Once the limiting reagent is exhausted, the reaction stops, even though some of the other reactant — the one **in excess** — still remains unreacted in the flask.

Khái niệm cốt lõi

To identify the limiting reagent: (1) convert the given quantity of every reactant into moles; (2) divide each reactant’s number of moles by its own coefficient in the balanced equation; (3) the reactant with the **smaller** resulting value is the limiting reagent, because it supplies the smaller ”share” of what the equation actually requires. Every later step (mass or volume of product formed, mass of the other reagent left over) must then be based on the limiting reagent, never on the reagent in excess.

VN **GIẢI THÍCH TIẾNG VIỆT**

Thuốc thử giới hạn (limiting reagent) là chất phản ứng hết **trước**, quyết định lượng sản phẩm tối đa có thể tạo ra; chất còn lại dư ra được gọi là thuốc thử dư (reagent in excess). Cách xác định: đổi lượng mỗi chất phản ứng ra **số mol**, sau đó **chia cho hệ số cân bằng** của chính chất đó trong phương trình — chất nào cho kết quả **nhỏ hơn** chính là thuốc thử giới hạn. Mọi phép tính tiếp theo (khối lượng sản phẩm, khối lượng chất dư) đều phải dựa trên thuốc thử giới hạn, không phải thuốc thử dư.

(!) Lỗi thường gặp: Comparing the **raw number of moles** of two reactants directly, without dividing by their coefficients, is the single most common error in this topic. Having more moles of reactant X than reactant Y does **not** automatically mean Y is limiting — if the equation requires, say, three moles of X for every mole of Y, X can still run out first even though it started with more moles present.

Ví dụ mẫu · Limiting reagent from two masses

A student mixes 12.0 g of silver nitrate, $AgNO_3$ ($M = 169.88$ g mol^{-1}), with 3.00 g of sodium chloride, NaCl ($M = 58.44$ g mol^{-1}):

$$AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq).$$

Find the mass of AgCl precipitate formed, and the mass of whichever reagent is left in excess.

Step 1 — moles of each reactant:

$$n(\text{AgNO}_3) = \frac{12.0}{169.88} = 0.07064 \text{ mol}, \qquad n(\text{NaCl}) = \frac{3.00}{58.44} = 0.05134 \text{ mol}.$$

Step 2 — the equation requires a $1 : 1$ ratio, so the smaller value is limiting: $n(\text{NaCl}) = 0.05134 < n(\text{AgNO}_3) = 0.07064$, so NaCl **is the limiting reagent**.

Step 3 — product, based on the limiting reagent ($1 : 1$ ratio NaCl:AgCl):

$$n(\text{AgCl}) = 0.05134 \text{ mol} \quad \Rightarrow \quad m(\text{AgCl}) = 0.05134 \times 143.32 = 7.36 \text{ g}.$$

Step 4 — excess AgNO_3 remaining: only 0.05134 mol of AgNO_3 reacts (matching the NaCl consumed, $1 : 1$), so

$$n(\text{AgNO}_3)_{\text{leftover}} = 0.07064 - 0.05134 = 0.01930 \text{ mol} \quad \Rightarrow \quad m = 0.01930 \times 169.88 = 3.28 \text{ g}.$$

Ví dụ mẫu · Limiting reagent with a mass and a gas volume

6.00 g of carbon is burned in 10.0 dm^3 of oxygen gas, measured at STP:

$$\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}.$$

Find the mass of CO_2 formed, and the mass of carbon left unburned.

$$n(\text{C}) = \frac{6.00}{12.01} = 0.4996 \text{ mol}, \qquad n(\text{O}_2) = \frac{10.0}{22.7} = 0.4405 \text{ mol}.$$

The equation requires a $1 : 1$ ratio, so the smaller value, $n(\text{O}_2) = 0.4405$ mol, is limiting: O_2 **is the limiting reagent** (there is not enough oxygen present to burn all of the carbon).

Product, based on O_2: $n(\text{CO}_2) = 0.4405$ mol, so

$$m(\text{CO}_2) = 0.4405 \times 44.01 = 19.4 \text{ g}.$$

Carbon consumed $= n(\text{O}_2) = 0.4405$ mol (matching, $1 : 1$), so mass of carbon consumed $= 0.4405 \times 12.01 = 5.29$ g, and

$$m(\text{C})_{\text{leftover}} = 6.00 - 5.29 = 0.71 \text{ g}.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Ở cả hai ví dụ trên, bước quyết định là **so sánh số mol đã chia cho hệ số** chứ không so sánh số mol thô. Với dữ kiện là thể tích khí, luôn đổi ra số mol bằng $n = V/22.7$ (ở STP) trước khi so sánh — không được so sánh trực tiếp thể tích với khối lượng hay số mol của chất khác.

Bài tập luyện tập

Nitrogen and hydrogen react to form ammonia: $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightarrow 2\text{NH}_3\text{(g)}$. A reaction vessel contains 5.00 mol N_2 and 12.0 mol H_2. What mass of NH_3 ($M = 17.04$ g mol^{-1}) is formed?

(A) 136 g

(B) 170 g

(C) 204 g

(D) 68.2 g

Lời giải chi tiết

Divide each by its coefficient: $\frac{n(\text{N}_2)}{1} = 5.00$; $\frac{n(\text{H}_2)}{3} = \frac{12.0}{3} = 4.00$. The smaller value, 4.00, corresponds to H_2, so H_2 **is limiting** (only enough for 4.00 mol of N_2 to react, leaving 1.00 mol N_2 unused).

Product, based on H_2 ($2:3$ ratio NH_3:H_2):

$$n(\text{NH}_3) = \frac{2}{3} \times 12.0 = 8.00 \text{ mol} \quad \Rightarrow \quad m = 8.00 \times 17.04 = 136 \text{ g}.$$

(A).

Bài tập luyện tập

5.00 g of barium chloride, BaCl_2 ($M = 208.23$ g mol^{-1}), is mixed with 5.00 g of sodium sulfate, Na_2SO_4 ($M = 142.05$ g mol^{-1}):

$$\text{BaCl}_2(\text{aq}) + \text{Na}_2\text{SO}_4(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + 2\text{NaCl}(\text{aq}).$$

Determine the limiting reagent, the mass of BaSO_4 precipitate formed ($M = 233.40$ g mol^{-1}), and the mass of the reagent left in excess.

Lời giải chi tiết

$$n(\text{BaCl}_2) = \frac{5.00}{208.23} = 0.02401 \text{ mol}, \qquad n(\text{Na}_2\text{SO}_4) = \frac{5.00}{142.05} = 0.03520 \text{ mol}.$$

The equation requires a $1:1$ ratio, and $n(\text{BaCl}_2) = 0.02401$ is smaller, so BaCl_2 **is the limiting reagent**.

$$n(\text{BaSO}_4) = 0.02401 \text{ mol} \quad \Rightarrow \quad m = 0.02401 \times 233.40 = 5.61 \text{ g}.$$

Na_2SO_4 consumed $= 0.02401$ mol (matching, $1:1$), so leftover $= 0.03520 - 0.02401 = 0.01119$ mol:

$$m(\text{Na}_2\text{SO}_4)_{\text{leftover}} = 0.01119 \times 142.05 = 1.59 \text{ g}.$$

Bài luyện nâng cao

Iron rusts according to $4\text{Fe}(\text{s}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{Fe}_2\text{O}_3(\text{s})$. A sample of 11.2 g of iron is exposed to 3.00 dm^3 of oxygen gas at STP. Determine the limiting reagent, the mass of Fe_2O_3 formed ($M = 159.70$ g mol^{-1}), and the mass of unreacted iron.

Lời giải chi tiết

$$n(\text{Fe}) = \frac{11.2}{55.85} = 0.2005 \text{ mol}, \qquad n(\text{O}_2) = \frac{3.00}{22.7} = 0.1322 \text{ mol}.$$

Divide by coefficients: $\frac{n(\text{Fe})}{4} = \frac{0.2005}{4} = 0.05013$; $\frac{n(\text{O}_2)}{3} = \frac{0.1322}{3} = 0.04407$. The smaller value corresponds to O_2, so O_2 **is the limiting reagent**.

Product, based on O_2 ($3:2$ ratio O_2:Fe_2O_3):

$$n(\text{Fe}_2\text{O}_3) = \frac{2}{3} \times 0.1322 = 0.08813 \text{ mol} \quad \Rightarrow \quad m = 0.08813 \times 159.70 = 14.1 \text{ g}.$$

Iron consumed ($4:3$ ratio Fe:O_2): $n(\text{Fe})_{\text{consumed}} = \frac{4}{3} \times 0.1322 = 0.1763$ mol, so mass consumed $= 0.1763 \times 55.85 = 9.85$ g, and

$$m(\text{Fe})_{\text{leftover}} = 11.2 - 9.85 = 1.35 \text{ g}.$$

1.7.2 Serial dilution and solution preparation

Many procedures — preparing a set of standards for a calibration curve in colorimetry, or diluting a concentrated stock reagent down to a usable working concentration — require a **dilution series**: a sequence of solutions, each made by diluting the previous one by the same factor. Every single step still obeys $c_1V_1 = c_2V_2$ (the number of moles of solute is conserved; only the volume of solvent changes), applied repeatedly, once per stage of the series.

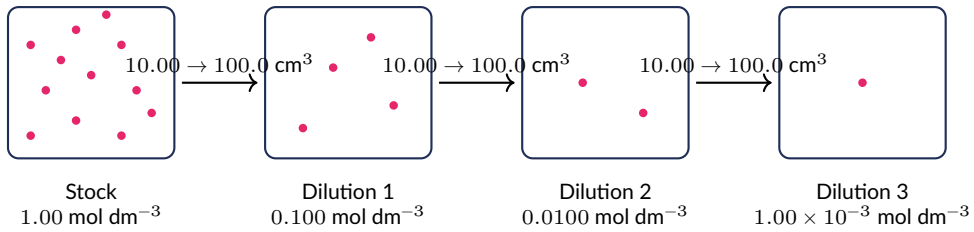
Khái niệm cốt lõi

If a fixed volume v is taken from a solution and made up to a fixed final volume V at every stage, the **dilution factor** at each stage is $f = \dfrac{V}{v}$, and the concentration falls by this same factor every time:

$$c_1 = \frac{c_{\text{stock}}}{f}, \qquad c_2 = \frac{c_1}{f} = \frac{c_{\text{stock}}}{f^2}, \qquad \dots \qquad c_n = \frac{c_{\text{stock}}}{f^n}.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Pha loãng nối tiếp (serial dilution) là lấy một thể tích cố định từ dung dịch trước, pha loãng đến một thể tích cuối cố định, rồi lặp lại nhiều lần. Nếu **hệ số pha loãng** mỗi bước là $f = V_{\text{cuối}}/v_{\text{lấy}}$, thì nồng độ giảm đi đúng f lần sau mỗi bước, và sau n bước, nồng độ chỉ còn $c_{\text{gốc}}/f^n$.



A serial dilution: at each stage, 10.00 cm^3 of the previous solution is transferred and made up to 100.0 cm^3, a 10-fold dilution factor. The number of dots (particles of solute) is illustrative only and not drawn to scale.

Ví dụ mẫu · A ten-fold serial dilution

A stock solution of $CuSO_4(aq)$ has concentration 1.00 mol dm^{-3}. A calibration series is prepared by taking 10.00 cm^3 of the stock and diluting it to 100.0 cm^3 (Dilution 1); then taking 10.00 cm^3 of Dilution 1 and diluting it to 100.0 cm^3 (Dilution 2); then repeating once more to give Dilution 3. Find the concentration of each solution in the series.

$$c_1 = c_{\text{stock}} \times \frac{V_{\text{taken}}}{V_{\text{final}}} = 1.00 \times \frac{10.00}{100.0} = 0.100 \text{ mol dm}^{-3}.$$

$$c_2 = 0.100 \times \frac{10.00}{100.0} = 0.0100 \text{ mol dm}^{-3}, \qquad c_3 = 0.0100 \times \frac{10.00}{100.0} = 1.00 \times 10^{-3} \text{ mol dm}^{-3}.$$

Since the same 10-fold dilution factor is applied at every one of the three stages, $c_3 = \dfrac{c_{\text{stock}}}{10^3} =$

$\dfrac{1.00}{1000} = 1.00 \times 10^{-3}$ mol dm^{-3}, confirming the step-by-step result.

GIẢI THÍCH TIẾNG VIỆT

VN Trong pha loãng nối tiếp, mỗi bước là một phép pha loãng độc lập tuân theo $c_1V_1 = c_2V_2$. Nếu hệ số pha loãng giống nhau ở mọi bước (ở đây là 10 lần mỗi bước), có thể tính nhanh nồng độ sau n bước bằng $c_{\text{gốc}}/10^n$ thay vì tính tuần tự từng bước — nhưng vẫn nên trình bày đầy đủ từng bước trong bài thi để giám khảo thấy rõ cách làm.

Bài tập luyện tập

A stock solution of potassium permanganate, KMnO$_4$(aq), has concentration 0.0500 mol dm^{-3}. What volume of this stock solution must be diluted to a final volume of 250 cm^3 to obtain a solution of concentration 2.00×10^{-3} mol dm^{-3}?

Lời giải chi tiết

$$V_1 = \frac{c_2V_2}{c_1} = \frac{(2.00 \times 10^{-3})(250)}{0.0500} = \frac{0.500}{0.0500} = 10.0 \text{ cm}^3.$$

10.0 cm^3 of the stock solution must be measured out and made up to 250 cm^3 with distilled water.

Bài tập luyện tập

A stock solution of glucose has concentration 0.800 mol dm^{-3}. A serial dilution is prepared by taking 10.0 cm^3 of the stock and diluting it to 50.0 cm^3 (Dilution 1), then taking 10.0 cm^3 of Dilution 1 and diluting it to 50.0 cm^3 (Dilution 2), then repeating once more to obtain Dilution 3. (a) State the dilution factor applied at each stage. (b) Calculate the concentration of Dilution 3. (c) What volume must 5.00 cm^3 of Dilution 3 be diluted to, in order to obtain a fourth solution of concentration 8.00×10^{-5} mol dm^{-3}?

Lời giải chi tiết

(a) Dilution factor $f = \dfrac{V_{\text{final}}}{v_{\text{taken}}} = \dfrac{50.0}{10.0} = 5$ at every stage.

(b)

$$c_1 = 0.800 \times \frac{10.0}{50.0} = 0.160 \text{ mol dm}^{-3}, \qquad c_2 = 0.160 \times \frac{10.0}{50.0} = 0.0320 \text{ mol dm}^{-3},$$

$$c_3 = 0.0320 \times \frac{10.0}{50.0} = 6.40 \times 10^{-3} \text{ mol dm}^{-3}.$$

(c) Using $c_3V_3 = c_4V_4$ with $V_3 = 5.00$ cm^3:

$$V_4 = \frac{c_3V_3}{c_4} = \frac{(6.40 \times 10^{-3})(5.00)}{8.00 \times 10^{-5}} = \frac{0.0320}{8.00 \times 10^{-5}} = 400 \text{ cm}^3.$$

5.00 cm^3 of Dilution 3 must be made up to 400 cm^3 to give the required concentration.

1.7.3 Back-titration (excess-and-back) calculations

A direct titration requires the analyte itself to react cleanly and quickly with a standard solution added from a burette. This is not always possible: the analyte may be an **insoluble solid** (e.g. calcium carbonate in limestone or in an antacid tablet), it may react **too slowly** to give a sharp end point, or it may be **volatile** and escape from solution before it can be titrated directly (e.g. ammonia gas). A **back-titration** solves this problem by working indirectly.

Khái niệm cốt lõi

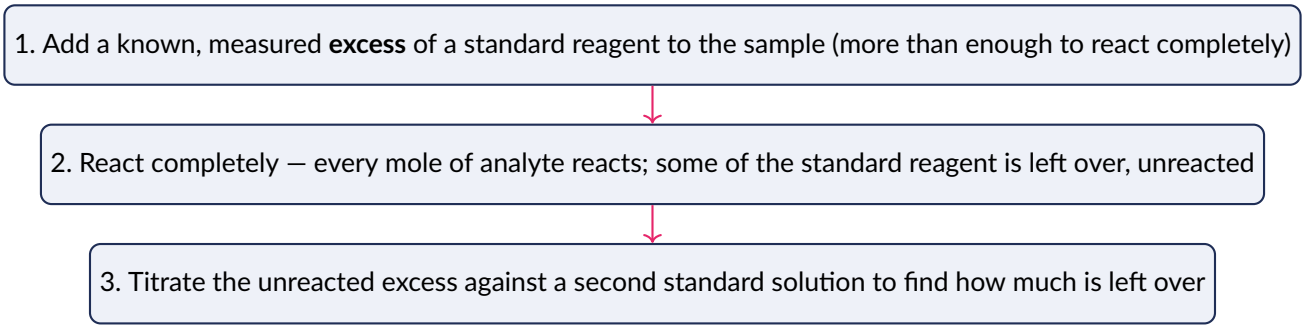
In a back-titration, a known, measured **excess** of a standard reagent is added to the sample — enough to react completely with all of the analyte, with some left over. That unreacted excess is then titrated against a **second** standard solution to find out exactly how much of the first reagent remains. The amount that reacted with the original sample is found by subtraction:

$$n(\text{reacted with sample}) = n(\text{excess reagent added}) - n(\text{excess reagent left over, found by titration}).$$

If either reaction is not a simple $1:1$ ratio, the appropriate mole ratio from each balanced equation must still be applied at the relevant step.

VN GIẢI THÍCH TIẾNG VIỆT

Chuẩn độ ngược (back-titration) được dùng khi chất cần phân tích là chất rắn không tan, phản ứng quá chậm, hoặc dễ bay hơi nên không thể chuẩn độ trực tiếp. Cách làm: thêm một lượng **dư đã biết chính xác** của thuốc thử chuẩn thứ nhất để phản ứng hết với mẫu; sau đó chuẩn độ phần thuốc thử dư **chưa phản ứng** bằng một dung dịch chuẩn thứ hai. Số mol đã phản ứng với mẫu ban đầu = số mol thuốc thử dư đã thêm vào − số mol thuốc thử dư còn lại (xác định bằng chuẩn độ).



The three stages of a back-titration. Moles reacted with the original sample = moles of excess reagent added − moles of excess reagent left over.

General back-titration recipe: total moles of reagent 1 added (from $c \times V$) − moles of reagent 1 left over (found from titrating with reagent 2, applying its own mole ratio with reagent 1 if that reaction is not $1:1$) = moles of reagent 1 that reacted with the original sample. Convert this into whatever quantity the question asks for (mass, percentage purity, concentration) using the mole ratio between reagent 1 and the sample from the *first* balanced equation.

(!) Lỗi thường gặp: The moles found directly from the second (back) titration are the moles of reagent **left over**, NOT the moles that reacted with the sample — they must be **subtracted** from the total amount of the first reagent originally added. Forgetting this subtraction, or subtracting volumes instead of moles when the two standard solutions have different concentrations,

are the two most common errors in this calculation.

Ví dụ mẫu · Purity of an impure calcium carbonate sample

A 1.250 g sample of impure chalk (containing $\mathrm{CaCO_3}$ and insoluble impurities) is added to 50.00 $\mathrm{cm^3}$ of 0.500 mol $\mathrm{dm^{-3}}$ $\mathrm{HCl(aq)}$, a known excess sufficient to dissolve all of the $\mathrm{CaCO_3}$:

$$\mathrm{CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g).}$$

The excess (unreacted) HCl remaining in the mixture is then titrated with 0.400 mol $\mathrm{dm^{-3}}$ $\mathrm{NaOH(aq)}$, requiring 21.50 $\mathrm{cm^3}$ to reach the end point:

$$\mathrm{HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l).}$$

Find the percentage by mass of $\mathrm{CaCO_3}$ in the sample ($M(\mathrm{CaCO_3}) = 100.09$ g $\mathrm{mol^{-1}}$).

Total HCl added:

$$n(\mathrm{HCl})_{\text{total}} = 0.500 \times 0.05000 = 0.02500 \text{ mol}.$$

HCl left over, found from the back-titration ($1:1$ ratio HCl:NaOH):

$$n(\mathrm{NaOH}) = 0.400 \times 0.02150 = 8.600 \times 10^{-3} \text{ mol} = n(\mathrm{HCl})_{\text{excess}}.$$

HCl that actually reacted with the $\mathrm{CaCO_3}$:

$$n(\mathrm{HCl})_{\text{reacted}} = 0.02500 - 0.008600 = 0.01640 \text{ mol}.$$

Mole ratio $\mathrm{CaCO_3} : \mathrm{HCl} = 1:2$:

$$n(\mathrm{CaCO_3}) = \frac{0.01640}{2} = 8.200\times10^{-3} \text{ mol} \quad \Rightarrow \quad m(\mathrm{CaCO_3}) = 8.200\times10^{-3}\times100.09 = 0.821 \text{ g}.$$

$$\%\mathrm{CaCO_3} = \frac{0.821}{1.250} \times 100 = 65.7\%.$$

VN GIẢI THÍCH TIẾNG VIỆT

Bốn bước của bài toán chuẩn độ ngược: (1) tính tổng số mol thuốc thử dư đã thêm vào ($n = cV$); (2) tính số mol thuốc thử dư **còn lại chưa phản ứng** từ kết quả chuẩn độ với dung dịch chuẩn thứ hai; (3) lấy hiệu (tổng − còn lại) để tìm số mol đã phản ứng với mẫu ban đầu; (4) dùng tỉ lệ mol của phương trình phản ứng với mẫu để suy ra số mol, khối lượng, hoặc phần trăm khối lượng cần tìm.

Bài tập luyện tập

A 2.00 g sample of a nitrogen-containing fertiliser is warmed with excess $\mathrm{NaOH(aq)}$, releasing ammonia gas, which is passed into 100.0 $\mathrm{cm^3}$ of 0.200 mol $\mathrm{dm^{-3}}$ $\mathrm{HCl(aq)}$ (a known excess):

$$\mathrm{NH_3(g) + HCl(aq) \rightarrow NH_4Cl(aq).}$$

The excess HCl remaining is titrated with 0.150 mol $\mathrm{dm^{-3}}$ $\mathrm{NaOH(aq)}$, requiring 30.00 $\mathrm{cm^3}$ to reach the end point. Calculate the percentage by mass of nitrogen in the fertiliser sample ($A_r(\mathrm{N}) = 14.01$).

Lời giải chi tiết

$$n(\text{HCl})_{\text{total}} = 0.200 \times 0.1000 = 0.02000 \text{ mol}.$$

$$n(\text{NaOH}) = 0.150 \times 0.03000 = 4.500 \times 10^{-3} \text{ mol} = n(\text{HCl})_{\text{excess}} \ (1:1 \text{ ratio}).$$

$$n(\text{HCl})_{\text{reacted with NH}_3} = 0.02000 - 0.004500 = 0.01550 \text{ mol}.$$

Mole ratio $\text{NH}_3 : \text{HCl} = 1:1$, so $n(\text{NH}_3) = n(\text{N}) = 0.01550$ mol:

$$m(\text{N}) = 0.01550 \times 14.01 = 0.217 \text{ g} \quad \Rightarrow \quad \%\text{N} = \frac{0.217}{2.00} \times 100 = 10.9\%.$$

Bài tập luyện tập

An indigestion tablet containing insoluble magnesium hydroxide is crushed and added to 25.00 cm^3 of 1.00 mol dm^{-3} HCl(aq), a known excess:

$$\text{Mg(OH)}_2\text{(s)} + 2\text{HCl(aq)} \rightarrow \text{MgCl}_2\text{(aq)} + 2\text{H}_2\text{O(l)}.$$

The excess HCl is titrated with 0.500 mol dm^{-3} NaOH(aq), requiring 12.00 cm^3 to reach the end point. What mass of Mg(OH)_2 ($M = 58.33$ g mol^{-1}) was present in the tablet?

(A) 0.554 g

(B) 1.108 g

(C) 0.277 g

(D) 1.900 g

Lời giải chi tiết

$$n(\text{HCl})_{\text{total}} = 1.00 \times 0.02500 = 0.02500 \text{ mol}.$$

$$n(\text{NaOH}) = 0.500 \times 0.01200 = 6.000 \times 10^{-3} \text{ mol} = n(\text{HCl})_{\text{excess}} \ (1:1 \text{ ratio}).$$

$$n(\text{HCl})_{\text{reacted with Mg(OH)}_2} = 0.02500 - 0.006000 = 0.01900 \text{ mol}.$$

Mole ratio $\text{Mg(OH)}_2 : \text{HCl} = 1:2$:

$$n(\text{Mg(OH)}_2) = \frac{0.01900}{2} = 9.500 \times 10^{-3} \text{ mol} \quad \Rightarrow \quad m = 9.500 \times 10^{-3} \times 58.33 = 0.554 \text{ g}.$$

(A).

1.7.4 Isotope patterns in molecular mass spectra

Section 1.2 introduced the mass spectrometer as a tool for measuring the relative atomic mass of an element from its isotopic composition. The same reasoning explains a distinctive feature of the mass spectra of **molecules** that contain a chlorine or a bromine atom: because these two elements each have two significant naturally-occurring isotopes of very different relative abundance, the molecular-ion region of the spectrum shows not a single peak but a small **cluster** of peaks.

Khái niệm cốt lõi

Chlorine occurs naturally as ^{35}Cl (75.77%) and ^{37}Cl (24.23%), an abundance ratio of approximately $3:1$. A molecule containing exactly **one** chlorine atom therefore shows a molecular-ion cluster of two peaks, at $m/z = M$ and $m/z = M + 2$, with heights in a ratio of approximately $3:1$.

Bromine occurs naturally as ^{79}Br (50.7%) and ^{81}Br (49.3%), an abundance ratio very close to

$1:1$. A molecule containing exactly **one** bromine atom therefore shows an M peak and an $M+2$ peak of almost **equal** height.

In both cases, the m/z values themselves are calculated using the **nominal (integer) mass** of the most abundant isotope of every atom present (e.g. C $= 12$, H $= 1$, Cl $= 35$ or 37, Br $= 79$ or 81) — NOT the abundance-weighted relative atomic mass (12.01, 35.45, 79.90, ...) used for mole calculations elsewhere in this chapter.

VN **GIẢI THÍCH TIẾNG VIỆT**

Clo tự nhiên có hai đồng vị chính ^{35}Cl (75.77%) và ^{37}Cl (24.23%), tỉ lệ xấp xỉ $3:1$; brom có ^{79}Br (50.7%) và ^{81}Br (49.3%), tỉ lệ xấp xỉ $1:1$. Một phân tử chứa đúng **một** nguyên tử Cl sẽ cho cụm peak M và $M+2$ với tỉ lệ chiều cao khoảng $3:1$; chứa đúng **một** nguyên tử Br sẽ cho hai peak M và $M+2$ cao **gần bằng nhau**. Khi tính giá trị m/z, luôn dùng **khối lượng nguyên (số nguyên)** của đồng vị phổ biến nhất, KHÔNG dùng A_r trung bình có trọng số (vốn chỉ dùng cho tính số mol).

Ví dụ mẫu · Predicting the M and M+2 peaks for chloromethane

Predict the m/z values and relative intensity ratio of the molecular-ion cluster in the mass spectrum of chloromethane, CH_3Cl.

Using nominal masses C $= 12$, H $= 1$:

M (with ^{35}Cl) : $m/z = 12+3(1)+35 = 50$. $\quad$ $M+2$ (with ^{37}Cl) : $m/z = 12+3(1)+37 = 52$.

Predicted intensity ratio = natural abundance ratio of the two chlorine isotopes:

$$\frac{^{35}\text{Cl}}{^{37}\text{Cl}} = \frac{75.77}{24.23} = 3.13.$$

The spectrum is expected to show a peak at $m/z = 50$ about 3.13 times the height of a peak at $m/z = 52$ — a ratio of approximately $3:1$, diagnostic of exactly one chlorine atom in the molecule.

Ví dụ mẫu · Predicting the M and M+2 peaks for bromoethane

Predict the m/z values and relative intensity ratio of the molecular-ion cluster in the mass spectrum of bromoethane, C_2H_5Br.

M (with ^{79}Br) : $m/z = 2(12)+5(1)+79 = 108$. $\quad$ $M+2$ (with ^{81}Br) : $m/z = 2(12)+5(1)+81 = 110$.

Predicted intensity ratio:

$$\frac{^{79}\text{Br}}{^{81}\text{Br}} = \frac{50.7}{49.3} = 1.03.$$

The peaks at $m/z = 108$ and $m/z = 110$ are expected to be of almost **equal** height (ratio $\approx 1:1$), diagnostic of exactly one bromine atom in the molecule — clearly distinguishable from the $\approx 3:1$ pattern of a chlorinated compound.

VN **GIẢI THÍCH TIẾNG VIỆT**

Cách làm nhanh cho dạng bài này: (1) viết công thức phân tử, tính m/z của peak M bằng **khối lượng nguyên** của đồng vị phổ biến nhất mỗi nguyên tố; (2) peak $M+2$ chỉ thay đổi khối lượng của **một** nguyên tử duy nhất (Cl: $35 \to 37$, hoặc Br: $79 \to 81$), nên luôn cộng thêm đúng 2 đơn

vị khối lượng vào M; (3) tỉ lệ chiều cao hai peak bằng đúng tỉ lệ phần trăm đồng vị tự nhiên của nguyên tố đó, không cần tính toán gì phức tạp hơn.

(!) Lỗi thường gặp: A small $M+1$ peak is present in the mass spectrum of *every* carbon-containing compound, due to the natural abundance of ^{13}C ($\approx 1.1\%$ per carbon atom); do not confuse this minor $M+1$ peak with the much larger, diagnostic $M+2$ peak caused by chlorine or bromine. A fragment ion formed by loss of the halogen atom itself (e.g. $CH_3Cl^+ \rightarrow CH_3^+ + Cl$) no longer contains that halogen, and so shows no $M+2$ partner peak of its own.

Bài tập luyện tập

The mass spectrum of a volatile organic compound shows a molecular-ion cluster with peaks at $m/z = 64$ and $m/z = 66$, in an intensity ratio of approximately $3:1$. (a) State what this ratio indicates about the compound's composition. (b) Given that $M_r \approx 64$ and that the compound contains only C, H, and at most one halogen atom, suggest its molecular formula.

Lời giải chi tiết

(a) An $M : M+2$ ratio of approximately $3:1$ is diagnostic of exactly **one chlorine atom** in the molecule (natural abundance ^{35}Cl :^{37} Cl $\approx 75.77\% : 24.23\% \approx 3:1$). A single bromine atom would instead give a ratio close to $1:1$, and the absence of any halogen would give only a small $M+1$ peak (from ^{13}C), with no significant $M+2$ peak at all.

(b) Removing one ^{35}Cl (mass 35) from $M_r = 64$ leaves $64 - 35 = 29$ for the rest of the molecule. Since C_2H_5 has nominal mass $2(12) + 5(1) = 29$, the molecular formula is C_2H_5Cl (chloroethane), $M = 2(12) + 5(1) + 35 = 64$, consistent with $M+2 = 66$ using ^{37}Cl.

Bài tập luyện tập

The mass spectrum of a brominated hydrocarbon of molecular formula CH_3Br shows a molecular-ion cluster of two peaks of almost equal height at m/z values of:

(A) 94 and 96

(B) 94 and 98

(C) 93 and 95

(D) 15 and 17

Lời giải chi tiết

Using nominal masses C $= 12$, H $= 1$: M (with ^{79}Br) $= 12 + 3(1) + 79 = 94$; $M+2$ (with ^{81}Br) $= 12 + 3(1) + 81 = 96$ (bromine's two isotopes differ by 2 mass units, not 4). Since ^{79}Br (50.7%) and ^{81}Br (49.3%) are almost equally abundant, the two peaks are almost equal in height. **(A)**.

Structure 2 --- Models of Bonding and Structure

Mục tiêu Unit: Sau chương này, học sinh có thể giải thích bản chất lực hút tĩnh điện trong ba mô hình liên kết (ion, cộng hoá trị, kim loại) và dự đoán xu hướng năng lượng mạng tinh thể; vẽ công thức Lewis và áp dụng thuyết VSEPR để xác định hình dạng, góc liên kết và độ phân cực phân tử; nhận biết liên kết cho–nhận (phối trí); tính điện tích hình thức, giải thích cộng hưởng và xác định lai hoá cùng số liên kết sigma/pi (chuyên đề AHL); phân biệt ba loại lực liên phân tử (lực phân tán London, lực lưỡng cực–lưỡng cực, liên kết hydrogen) và vận dụng để so sánh nhiệt độ sôi; đồng thời liên hệ các mô hình liên kết với tính chất thực tế của vật liệu như kim cương, graphite, hợp kim và polymer.

2.1 The ionic model

Ionic bonding is the electrostatic attraction between oppositely charged ions arranged in a giant three-dimensional lattice. It forms between atoms whose electronegativity difference (ΔEN) is large – conventionally $\Delta\text{EN} \gtrsim 1.8$ – so that valence electrons are effectively **transferred** from the less electronegative atom to the more electronegative one, rather than shared.

Pauling electronegativities used throughout this unit:
H 2.20 Li 0.98 Be 1.57 B 2.04 C 2.55 N 3.04 O 3.44 F 3.98
Na 0.93 Mg 1.31 Al 1.61 Si 1.90 P 2.19 S 2.58 Cl 3.16
K 0.82 Br 2.96 I 2.66

Electronegativity itself follows a periodic trend: it **increases across a period** (left to right) because nuclear charge increases while the outer shell stays the same, pulling bonding electrons in more strongly; it **decreases down a group** because each successive element adds a new outer shell, moving the bonding electrons further from the nucleus and shielding them from its full charge. Fluorine, at the top right of the periodic table (excluding noble gases), is the most electronegative element of all.

Reading electronegativity trends from data

Using the electronegativities given above, describe the trend (a) across period 2 from Li to F, and (b) down group 17 from F to I.

(a) Li $(0.98) \rightarrow$ Be $(1.57) \rightarrow$ B $(2.04) \rightarrow$ C $(2.55) \rightarrow$ N $(3.04) \rightarrow$ O $(3.44) \rightarrow$ F (3.98): electronegativity rises steadily across the period as nuclear charge increases across a constant outer shell ($n = 2$). (b) F $(3.98) \rightarrow$ Cl $(3.16) \rightarrow$ Br $(2.96) \rightarrow$ I (2.66): electronegativity falls steadily down the group as each element adds another occupied shell, increasing the distance (and shielding) between the nucleus and the bonding electrons.

VN **GIẢI THÍCH TIẾNG VIỆT**

Độ âm điện **tăng dần theo chu kỳ** (từ trái sang phải) vì điện tích hạt nhân tăng trong khi lớp electron ngoài cùng không đổi $\Rightarrow$ hạt nhân hút electron liên kết mạnh hơn. Độ âm điện **giảm dần theo nhóm** (từ trên xuống) vì mỗi nguyên tố thêm một lớp electron mới, làm tăng khoảng

cách và hiệu ứng chắn giữa hạt nhân và electron liên kết. Fluorine ở góc trên bên phải bảng tuần hoàn (không tính khí hiếm) có độ âm điện lớn nhất trong tất cả các nguyên tố.

2.1.1 Formation of ions

Metals (low electronegativity, low ionisation energy) lose their valence electrons to form **cations**, usually reaching the electron configuration of the preceding noble gas. Non-metals (high electronegativity, highly negative electron affinity) gain electrons to form **anions**, usually reaching the configuration of the *following* noble gas. The charge an atom typically adopts is closely tied to its group number.

Group	Typical ion charge	Example
1	$1+$	Na^{+}
2	$2+$	Mg^{2+}
13	$3+$	Al^{3+}
15	$3-$	N^{3-}
16	$2-$	O^{2-}
17	$1-$	Cl^{-}

The formula of an ionic compound is the simplest whole-number ratio of ions that makes the compound electrically neutral: the magnitude of one ion's charge becomes the subscript of the other.

Predicting the formula of an ionic compound

Aluminium (group 13) and oxygen (group 16) react to form an ionic compound. Predict its formula.

Aluminium forms Al^{3+} (loses 3 electrons to reach the neon configuration); oxygen forms O^{2-} (gains 2 electrons to reach the neon configuration). To balance total charge, take 2 Al^{3+} ($6+$ total) and 3 O^{2-} ($6-$ total): net charge $= 0$. Formula: Al_2O_3. (By the same cross-over method, magnesium and chlorine give $MgCl_2$.)

VN **GIẢI THÍCH TIẾNG VIỆT**

Kim loại nhóm n (nhóm 1, 2, 13) thường mất electron để đạt cấu hình khí hiếm *trước đó*, tạo cation điện tích $+n$. Phi kim nhóm m (từ 15 đến 17) thường nhận electron để đạt cấu hình khí hiếm *tiếp theo*, tạo anion điện tích $-(18-m)$. Khi lập công thức hợp chất ion, ta "bắt chéo" trị số điện tích của ion này làm chỉ số của ion kia rồi rút gọn nếu có thể: Al^{3+} và $O^{2-} \rightarrow Al_2O_3$.

Unlike the main-group metals above, most **transition metals** do not lose a fixed, predictable number of electrons: because their $(n-1)d$ and outer ns electrons are close in energy, transition metals commonly form **more than one stable cation charge** (e.g. both Fe^{2+} and Fe^{3+}; both Cu^{+} and Cu^{2+}). When naming or interpreting the formula of a transition-metal ionic compound, the metal's charge must be **deduced from the formula itself**, using the fact that the total positive and negative charge must balance to zero.

Deducing a transition-metal ion's charge from a formula

Deduce the charge on the iron ion in (a) FeO and (b) Fe_2O_3.

(a) One O^{2-} contributes $2-$; for the compound to be neutral, the single Fe ion must be Fe^{2+}.
(b) Three O^{2-} ions contribute $3 \times 2- = 6-$ total; this must be balanced by two Fe ions carrying a combined $6+$, so each Fe ion is Fe^{3+}.

VN **GIẢI THÍCH TIẾNG VIỆT**

Khác với kim loại nhóm chính, hầu hết **kim loại chuyển tiếp** không có điện tích cố định vì phân lớp $(n-1)d$ và ns có năng lượng gần nhau, dễ mất số electron khác nhau tuỳ hợp chất (ví dụ Fe^{2+} và Fe^{3+} đều tồn tại phổ biến). Muốn biết điện tích của ion kim loại chuyển tiếp, ta phải **suy ngược từ công thức**: dựa vào nguyên tắc tổng điện tích dương $=$ tổng điện tích âm để hợp chất trung hoà.

Bài tập luyện tập

Copper forms two common oxides, Cu_2O and CuO. Deduce the charge on the copper ion in each.

Lời giải chi tiết

In Cu_2O, one O^{2-} ($2-$ total) must be balanced by two Cu ions carrying a combined $2+$, so each Cu ion is Cu^{+}. In CuO, one O^{2-} ($2-$) is balanced by one Cu ion, so it must be Cu^{2+}.

2.1.2 Bond type from electronegativity difference

A useful (though approximate) rule of thumb classifies a bond using ΔEN between the two bonded atoms: below about 0.5 the bond is essentially **non-polar covalent**; between about 0.5 and 1.8 it is **polar covalent**; above about 1.8 the bond is best described as **ionic**. There is no sharp cut-off in reality – bonding is a continuum from pure covalent to pure ionic – but the rule is a reliable first classification.

Classifying bond type from ΔEN

Classify the bonding in KF, HCl, and Cl_2.

K–F: $\Delta\text{EN} = |3.98 - 0.82| = 3.16 \Rightarrow$ ionic.
H–Cl: $\Delta\text{EN} = |3.16 - 2.20| = 0.96 \Rightarrow$ polar covalent.
Cl–Cl: $\Delta\text{EN} = |3.16 - 3.16| = 0 \Rightarrow$ non-polar covalent.

VN **GIẢI THÍCH TIẾNG VIỆT**

Hiệu độ âm điện (ΔEN) càng lớn thì cặp electron liên kết càng bị lệch mạnh về nguyên tử âm điện hơn. Khi ΔEN đủ lớn (thường lấy mốc ≈ 1.8), ta xem như electron bị "chuyển hẳn" chứ không còn "dùng chung" nữa $\Rightarrow$ liên kết mang bản chất ion. Đây chỉ là quy ước gần đúng để phân loại nhanh, không phải ranh giới tuyệt đối.

Even bonds classified as "ionic" are never 100% pure electron transfer: a small cation with a very high charge density (large charge concentrated in a small volume) can pull and distort the electron cloud of a large, easily deformed (polarisable) anion enough to pull some electron density back into the region between the nuclei, giving the bond significant **covalent character**. This effect is strongest when the cation is small and highly charged, and the anion is large.

Covalent character in "ionic" compounds

Both LiI and KI are classified as ionic, yet LiI shows noticeably more covalent character than KI. Explain why.

Li^{+} is much smaller than K^{+} (fewer occupied shells), giving it a far higher charge density for the same $1+$ charge. This lets Li^{+} distort (polarise) the large, diffuse electron cloud of the shared anion I^{-} more strongly, pulling electron density back towards the region between the nuclei and giving LiI greater covalent character than KI, whose larger, lower-charge-density K^{+}

polarises I^- much less.

VN **GIẢI THÍCH TIẾNG VIỆT**

Không có liên kết ion nào "thuần khiết 100%": cation càng nhỏ và điện tích càng cao (mật độ điện tích lớn) thì càng có khả năng **phân cực hoá** (kéo méo đám mây electron của) anion lớn, dễ biến dạng, khiến liên kết mang thêm tính cộng hoá trị. Đây là lý do LiI ("ion" nhưng cation Li^+ rất nhỏ) có tính cộng hoá trị rõ rệt hơn KI (cation K^+ lớn hơn, mật độ điện tích thấp hơn), dù cả hai đều được phân loại là hợp chất ion.

2.1.3 Lattice enthalpy and Coulomb's law

The strength of an ionic lattice is measured by its **lattice enthalpy** (the energy released when gaseous ions come together to form one mole of solid lattice). By Coulomb's law, the electrostatic force between two point charges is

$$F \propto \frac{Q_1 Q_2}{r^2},$$

so lattice enthalpy **increases** with the **product of the ionic charges** and **decreases** with **increasing ionic radius** (greater separation r between the centres of the ions).

Coulomb's law and lattice strength

Two factors control lattice enthalpy magnitude: (1) **ionic charge** – doubling either ion's charge roughly quadruples the attractive force for the same separation, so $2+/2-$ lattices are dramatically stronger than $1+/1-$ lattices; (2) **ionic radius** – smaller ions can approach more closely, increasing the attraction. Charge dominates over radius when comparing lattices of different charge type.

Ranking lattice enthalpy magnitude

Rank NaCl, NaF, CaO, and MgO in order of increasing lattice enthalpy magnitude.

NaCl and NaF are both $1+/1-$ compounds sharing the cation Na^+; F^- is smaller than Cl^-, so NaF packs more closely and has the larger lattice enthalpy: NaCl $<$ NaF. CaO and MgO are both $2+/2-$ compounds – the charge product ($2 \times 2 = 4$) is four times that of the sodium halides ($1 \times 1 = 1$), so both must lie far above NaCl and NaF. Between them, Mg^{2+} is smaller than Ca^{2+}, so MgO $>$ CaO. Overall:

$$\text{NaCl}\ (787) \ < \ \text{NaF}\ (918) \ < \ \text{CaO}\ (3401) \ < \ \text{MgO}\ (3791)\ \text{kJ mol}^{-1}.$$

The measured values (kJ mol^{-1}, magnitudes) confirm the qualitative reasoning from Coulomb's law.

VN **GIẢI THÍCH TIẾNG VIỆT**

Định luật Coulomb cho thấy năng lượng mạng tinh thể phụ thuộc **tích điện tích** $Q_1 Q_2$ và **nghịch đảo bình phương khoảng cách** r^2. So sánh NaCl và MgO: điện tích ion của MgO ($2+$ và $2-$) lớn gấp đôi NaCl ($1+$ và $1-$) mỗi loại, khiến tích điện tích gấp 4 lần, đồng thời bán kính ion nhỏ hơn $\Rightarrow$ MgO có năng lượng mạng tinh thể và nhiệt độ nóng chảy (2852°C) vượt xa NaCl (801°C). Yếu tố điện tích thường lấn át yếu tố bán kính khi hai hợp chất khác loại điện tích.

The charge-product argument can be checked numerically: the charge product of MgO is 4 times that of NaCl, so Coulomb's law alone predicts a lattice enthalpy roughly 4 times larger; the measured

ratio is $3791/787 \approx 4.8$, close to the charge-only prediction, with the remaining difference coming from the smaller ionic radii in MgO. This confirms that ionic charge is the dominant factor, with ionic radius acting as a secondary correction.

2.1.4 Ionic radius trends

Ionic radius follows two related periodic trends. First, forming a **cation** always makes an atom **smaller** than the parent atom (electrons are removed, and often an entire shell is lost, while the same nuclear charge now pulls on fewer electrons); forming an **anion** always makes an atom **larger** than the parent atom (extra electrons increase electron–electron repulsion and the same nuclear charge is shared among more electrons). Second, for a series of **isoelectronic** ions (identical electron configuration, e.g. all matching neon), radius **decreases** as nuclear charge (atomic number) **increases**, because a larger nuclear charge pulls the same fixed number of electrons in more tightly.

Ranking isoelectronic ionic radii

Rank O^{2-}, F^-, Na^+, and Mg^{2+} in order of decreasing ionic radius.

All four ions have the electron configuration of neon (10 electrons: $1s^2 2s^2 2p^6$), so they are isoelectronic and radius is controlled entirely by nuclear charge (atomic number): $Z(\text{O}) = 8$, $Z(\text{F}) = 9$, $Z(\text{Na}) = 11$, $Z(\text{Mg}) = 12$. The larger the nuclear charge pulling on the same 10 electrons, the smaller the ion. Decreasing radius order:

$$O^{2-} > F^- > Na^+ > Mg^{2+}.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Với các ion **đẳng electron** (cùng số electron, cùng cấu hình electron), bán kính ion chỉ còn phụ thuộc vào **điện tích hạt nhân**: điện tích hạt nhân càng lớn thì lực hút hạt nhân lên cùng một số electron càng mạnh $\Rightarrow$ bán kính càng nhỏ. Đây là lý do dù cùng cấu hình electron neon, O^{2-} (Z$=8$) có bán kính lớn nhất còn Mg^{2+} (Z$=12$) có bán kính nhỏ nhất trong dãy $O^{2-}, F^-, Na^+, Mg^{2+}$.

Typical physical properties of ionic solids: high melting and boiling points (strong 3-D electrostatic attraction throughout the lattice); hard but brittle (a shearing force shifts a layer so like charges align and repel, shattering the crystal along a cleavage plane); do *not* conduct electricity as solids (ions are fixed in place); *do* conduct when molten or dissolved in water (ions become mobile); many dissolve in polar solvents such as water.

(!) Lỗi thường gặp: Ionic compounds do *not* conduct electricity as solids – this is one of the most commonly mixed-up facts in this topic. Conduction requires mobile charge carriers; in the solid lattice the ions are locked in fixed positions and can only vibrate. Only when the lattice is broken down (molten) or the ions are separated and surrounded by solvent (dissolved in water) can they move and carry current.

Bài tập luyện tập

Which pair of ions would be expected to form the ionic lattice with the greatest lattice enthalpy magnitude?

(A) Na^+ and Cl^-
(B) Mg^{2+} and O^{2-}
(C) K^+ and Br^-
(D) Li^+ and F^-

Lời giải chi tiết

Lattice enthalpy rises sharply with the product of ionic charges. Mg^{2+}/O^{2-} has a charge product of $2 \times 2 = 4$, four times larger than any of the $1+/1-$ pairs listed ($1 \times 1 = 1$), and both ions are also relatively small. **(B)**.

Bài tập luyện tập

Calcium (group 2) and nitrogen (group 15) form an ionic compound. Deduce its formula, showing the charges of both ions.

Lời giải chi tiết

Calcium loses 2 electrons: Ca^{2+}. Nitrogen gains 3 electrons to complete its octet: N^{3-}. To balance charge, the lowest common multiple of 2 and 3 is 6: take $3 \times (2+) = 6+$ from three Ca^{2+} and $2 \times (3-) = 6-$ from two N^{3-}. Formula: Ca_3N_2.

Bài tập luyện tập

Barium (group 2) and phosphorus (group 15) form an ionic compound. Deduce its formula.

Lời giải chi tiết

Barium loses 2 electrons: Ba^{2+}. Phosphorus gains 3 electrons to complete its octet: P^{3-}. The lowest common multiple of 2 and 3 is 6: three Ba^{2+} give $6+$, two P^{3-} give $6-$. Formula: Ba_3P_2.

Bài tập luyện tập

The melting point of MgO is $2852°$C, far above the melting point of NaCl, $801°$C. Explain this difference in terms of Coulomb's law.

Lời giải chi tiết

Melting an ionic solid means overcoming the electrostatic attraction throughout the lattice, so melting point tracks lattice enthalpy. By Coulomb's law $F \propto Q_1Q_2/r^2$: Mg^{2+} and O^{2-} each carry twice the charge magnitude of Na^+ and Cl^-, making the charge product four times larger; Mg^{2+} and O^{2-} are also smaller ions than Na^+ and Cl^-, allowing closer approach and a smaller r. Both effects increase the attractive force in MgO, giving it a much larger lattice enthalpy and hence a much higher melting point.

Bài tập luyện tập

Which of the following is *not* a typical property of an ionic compound?

(A) High melting point
(B) Brittle as a solid
(C) Conducts electricity as a solid
(D) Often soluble in water

Lời giải chi tiết

Ionic solids do not conduct electricity, because the ions are fixed in the lattice and cannot move to carry charge; conduction only occurs once the lattice breaks down (molten) or the ions are freed by a solvent (aqueous). **(C)**.

Bài tập luyện tập

Using the electronegativities given at the start of this section, classify the Al–Cl bond (as found in $AlCl_3$) and compare it with the Na–Cl bond (as found in NaCl).

Lời giải chi tiết

$\Delta\text{EN}(\text{Al–Cl}) = |3.16 - 1.61| = 1.55$, which falls in the polar-covalent range (0.5–1.8): $AlCl_3$ is best described as covalent (indeed, real $AlCl_3$ exists as a molecular/polymeric substance rather than a simple ionic lattice). $\Delta\text{EN}(\text{Na–Cl}) = |3.16 - 0.93| = 2.23$, above 1.8: NaCl is ionic. The much smaller, higher-charge-density Al^{3+} that would be needed for a purely ionic $AlCl_3$ distorts the electron cloud of Cl^- enough to pull the bonding back towards covalent character.

Bài tập luyện tập

For two ionic compounds with ions of the *same* charge type (e.g. both $1+/1-$), which change would increase the lattice enthalpy magnitude the most?

(A) Increasing the ionic radius of the cation
(B) Decreasing the ionic radius of both ions
(C) Decreasing the charge of the anion
(D) Increasing the ionic radius of both ions

Lời giải chi tiết

With charges fixed, lattice enthalpy is governed by r in the denominator of $F \propto Q_1Q_2/r^2$: smaller ions can pack closer together, increasing the attractive force. **(B)**.

Bài tập luyện tập

NaF has a lattice enthalpy of about $918\,\text{kJ mol}^{-1}$; LiCl has a lattice enthalpy of about $853\,\text{kJ mol}^{-1}$ – lower, even though Li^+ is smaller than Na^+. Explain why NaF still has the larger lattice enthalpy.

Lời giải chi tiết

Both compounds have $1+/1-$ ions, so charge product is not the deciding factor here; the separation r in Coulomb's law depends on the *sum* of both ionic radii, not on either ion alone. Although Li^+ is smaller than Na^+, Cl^- is considerably larger than F^-, and this increase outweighs the decrease from using Li^+ instead of Na^+: the combined Na^++F^- separation is smaller than the combined Li^++Cl^- separation. Because NaF has the smaller overall ionic separation, it has the stronger attraction and the larger lattice enthalpy, despite not containing the smallest individual cation.

Bài tập luyện tập

K^+, Cl^-, Ca^{2+}, and S^{2-} are all isoelectronic with argon. Rank them in order of *increasing* ionic radius, and explain your reasoning.

Lời giải chi tiết

All four ions share the argon electron configuration, so radius depends only on nuclear charge: $Z(\text{S}) = 16$, $Z(\text{Cl}) = 17$, $Z(\text{K}) = 19$, $Z(\text{Ca}) = 20$. A larger nuclear charge pulls the same 18

electrons in more tightly, giving a smaller ion. Increasing radius order (smallest to largest):

$$Ca^{2+} < K^{+} < Cl^{-} < S^{2-}.$$

2.2 The covalent model

A **covalent bond** is a shared pair of electrons between two atoms, typically formed between two non-metals (small or moderate ΔEN). **Lewis structures** represent covalent molecules by distributing all valence electrons as bonding pairs and lone pairs so that every atom (except H, which needs only 2 electrons) attains a full outer shell, usually an octet of 8 electrons.

2.2.1 Lewis structures and VSEPR geometry

A systematic method for drawing a Lewis structure: (1) count the total valence electrons available, adding one for each unit of negative charge or subtracting one for each unit of positive charge on an ion; (2) arrange the atoms with the least electronegative atom (usually) in the centre, and join every atom to the centre with a single bond; (3) complete the octet of every **terminal** atom first using lone pairs; (4) place any remaining electrons as lone pairs on the central atom; (5) if the central atom still lacks an octet, convert one or more lone pairs on a terminal atom into an extra bonding pair (a double or triple bond) with the central atom.

Drawing a Lewis structure

Draw the Lewis structure of CO_2.

Step 1: total valence electrons $= 4 + 2(6) = 16$. Step 2: place C in the centre, joined to each O by a single bond (uses 4 electrons, 12 remain). Step 3: give each terminal O three lone pairs to complete its octet (6 electrons each, 12 electrons used, 0 remain). Step 4: no electrons remain for C. Step 5: C currently has only 4 electrons around it (two single bonds) – short of an octet – so convert one lone pair on *each* oxygen into a second bonding pair, forming two C=O double bonds. Final structure: O = C = O, with 2 lone pairs remaining on each oxygen and none on carbon; every atom now has a full octet.

VN **GIẢI THÍCH TIẾNG VIỆT**

Quy trình vẽ công thức Lewis: (1) đếm tổng electron hoá trị (cộng/trừ theo điện tích ion); (2) đặt nguyên tử trung tâm (thường kém âm điện hơn) và nối đơn với các nguyên tử xung quanh; (3) hoàn thành bát tử cho nguyên tử **đầu mạch** trước; (4) electron còn dư đặt lên nguyên tử trung tâm; (5) nếu nguyên tử trung tâm vẫn thiếu bát tử, chuyển cặp electron riêng của nguyên tử đầu mạch thành liên kết đôi/ba với nguyên tử trung tâm. Với CO_2: sau bước 3 carbon chỉ có 4 electron bao quanh (thiếu bát tử) nên phải tạo 2 liên kết đôi C=O để carbon đạt đủ 8 electron.

Most atoms obey the octet rule, but there are three recognised classes of exception. **Electron-deficient** central atoms (typically Be or B) can be stable with fewer than 8 electrons around them, e.g. $BeCl_2$ (4 electrons around Be) and BF_3 (6 electrons around B). **Expanded octets** are possible for central atoms in **period 3 or below** (e.g. P, S, Cl, Br, I), which have accessible d-subshell character and can accommodate 10 or 12 electrons, e.g. PCl_5 and SF_6. **Odd-electron species** (radicals) such as NO_2 or NO have a total number of valence electrons that is odd, so at least one atom must end up with an unpaired, non-bonded electron instead of a complete lone pair.

Octet rule exceptions: electron-deficient (Be, B central atoms: $BeCl_2$, BF_3) · expanded octet (period $3+$ central atoms: PCl_5, SF_6, BrF_3, XeF_4) · odd-electron radicals (odd total valence electrons: NO_2, NO).

Valence Shell Electron Pair Repulsion (VSEPR) theory predicts the three-dimensional shape of

a molecule from the number of **electron domains** (regions of electron density: single bonds, double bonds, triple bonds, and lone pairs each count as *one* domain) around the central atom. Electron domains arrange themselves in space to minimise mutual repulsion; because a lone pair is held closer to the nucleus and spreads out more than a bonding pair, **lone pair – lone pair** repulsion $>$ **lone pair – bonding pair** repulsion $>$ **bonding pair – bonding pair** repulsion, which compresses bond angles below the "ideal" geometric values wherever lone pairs are present. Chemists often summarise a molecule's composition with **AX_mE_n notation**: A is the central atom, X is a bonded atom (m of them), and E is a lone pair (n of them) – so NH_3 is AX_3E_1 and H_2O is AX_2E_2.

VSEPR in one sentence

Count the electron domains around the central atom to get the **electron-domain geometry**; then look only at where the *atoms* are (ignoring lone pairs, though not their repulsive effect) to name the **molecular shape**.

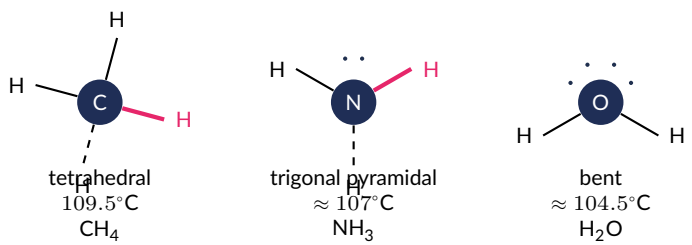
Domains	Bonding	Lone pairs	AX_mE_n	Molecular shape	Example
2	2	0	AX_2	linear ($180°$C)	CO_2
3	3	0	AX_3	trigonal planar ($120°$C)	BF_3
3	2	1	AX_2E_1	bent ($\approx 119°$C)	SO_2
4	4	0	AX_4	tetrahedral ($109.5°$C)	CH_4
4	3	1	AX_3E_1	trigonal pyramidal ($\approx 107°$C)	NH_3
4	2	2	AX_2E_2	bent ($\approx 104.5°$C)	H_2O
5	5	0	AX_5	trigonal bipyramidal ($90°$C/$120°$C)	PCl_5
5	4	1	AX_4E_1	seesaw	SF_4
5	3	2	AX_3E_2	T-shaped	BrF_3
6	6	0	AX_6	octahedral ($90°$C)	SF_6
6	4	2	AX_4E_2	square planar ($90°$C)	XeF_4

Shape and polarity of NH_3

Nitrogen has 5 valence electrons: 3 are used to form N–H bonds, leaving 1 lone pair. Electron domains $= 3$ bonding $+1$ lone pair $= 4 \Rightarrow$ tetrahedral electron-domain geometry. Because one domain is a lone pair, the molecular shape is **trigonal pyramidal**, with the H–N–H bond angle compressed from $109.5°$C to about $107°$C by the extra lone-pair repulsion. The three polar N–H bonds and the lone pair do not cancel by symmetry, so NH_3 is a **polar** molecule.

VN **GIẢI THÍCH TIẾNG VIỆT**

Phân biệt rõ **hình học electron** (đếm cả cặp electron riêng) và **hình học phân tử** (chỉ xét vị trí nguyên tử). Hai khái niệm trùng nhau khi không có cặp riêng (như CH_4: tứ diện $=$ tứ diện), nhưng khác nhau khi có cặp riêng (như NH_3: hình học electron là tứ diện, còn hình dạng phân tử là chóp tam giác). Một phân tử có các liên kết phân cực nhưng **đối xứng cao** (như CO_2 thẳng hàng, hay XeF_4 vuông phẳng) thường **không phân cực** vì các mô-men lưỡng cực liên kết triệt tiêu lẫn nhau theo mọi hướng.



Effect of lone pairs on molecular shape within (approximately) the same tetrahedral electron-domain geometry: CH_4 (0 lone pairs) → NH_3 (1 lone pair) → H_2O (2 lone pairs). Each extra lone pair compresses the bond angle further.

A further refinement of VSEPR: although a double or triple bond counts as only *one* electron domain for the purpose of counting shape, the extra electron density of a multiple bond makes that domain **slightly more repulsive** than a neighbouring single-bond domain – multiple-bond domains behave a little like a "fatter" version of a single bonding domain, compressing the angles of adjacent single bonds slightly.

Multiple-bond domains and bond-angle distortion

Phosgene, $COCl_2$, has a trigonal planar carbon centre (one C=O double bond and two C–Cl single bonds, no lone pairs). The measured O=C–Cl angle is $124.1°$C and the Cl–C–Cl angle is $111.8°$C – neither is exactly the "ideal" $120°$C predicted by simple trigonal planar VSEPR. Explain.

All three domains are bonding domains (no lone pairs to distort the shape), so the deviation must come from the *difference* between the domains themselves. The C=O double bond has a higher electron density than either C–Cl single bond, so it repels the two C–Cl domains more strongly than they repel each other, pushing the O=C–Cl angles open (above $120°$C) and squeezing the Cl–C–Cl angle closed (below $120°$C).

VN **GIẢI THÍCH TIẾNG VIỆT**

Dù một liên kết đôi/ba chỉ tính là **một** vùng electron khi đếm hình dạng phân tử, mật độ electron cao hơn của nó khiến vùng đó **đẩy mạnh hơn** một chút so với vùng liên kết đơn bên cạnh – tương tự cách cặp electron riêng đẩy mạnh hơn cặp liên kết. Trong $COCl_2$, vùng C=O "to" hơn đẩy hai vùng C–Cl ra xa nhau hơn $120°$C một chút (thành $124.1°$C), khiến góc Cl–C–Cl còn lại bị ép nhỏ hơn $120°$C (còn $111.8°$C).

Shape of BrF_3

Br has 7 valence electrons: 3 form Br–F bonds, leaving $(7-3)/1 = 4$ non-bonding electrons $= 2$ lone pairs. Electron domains $= 3$ bonding $+2$ lone pair $= 5 \Rightarrow$ trigonal bipyramidal electron-domain geometry. Placing both lone pairs in the (less crowded) equatorial positions leaves the 3 F atoms in a **T-shaped** molecular arrangement.

VN **GIẢI THÍCH TIẾNG VIỆT**

Với 5 vùng electron (hình học electron lưỡng chóp tam giác), có **hai** vị trí khác nhau: trục (axial, góc $90°$C với xích đạo) và xích đạo (equatorial, góc $120°$C với nhau). Cặp electron riêng luôn ưu tiên chiếm vị trí **xích đạo** vì ở đó chúng chỉ chịu lực đẩy từ 2 vùng ở góc $90°$C thay vì 3 vùng như ở vị trí trục – đây là lý do hình dạng T của BrF_3 (2 cặp riêng xích đạo) khác với hình yên ngựa của SF_4 (1 cặp riêng xích đạo).

Bài tập luyện tập

Determine the electron-domain geometry and molecular shape of SF_4.

(A) Tetrahedral domains, tetrahedral shape

(B) Trigonal bipyramidal domains, seesaw shape

(C) Trigonal bipyramidal domains, T-shaped

(D) Octahedral domains, square pyramidal

Lời giải chi tiết

S has 6 valence electrons: 4 form S–F bonds, leaving $(6-4)/1 = 2$ non-bonding electrons $= 1$ lone pair. Domains $= 4$ bonding $+1$ lone pair $= 5 \Rightarrow$ trigonal bipyramidal electron-domain geometry; with 1 lone pair in an equatorial position, the 4 F atoms form a **seesaw** shape. **(B)**.

Bài tập luyện tập

Deduce the electron-domain geometry and molecular shape of (a) PCl_5 and (b) ClF_3.

Lời giải chi tiết

(a) P has 5 valence electrons, all used in 5 P–Cl bonds, 0 lone pairs. Domains $= 5 \Rightarrow$ trigonal bipyramidal electron-domain geometry $=$ molecular shape (no lone pairs to hide). (b) Cl has 7 valence electrons: 3 form Cl–F bonds, leaving 4 non-bonding electrons $= 2$ lone pairs. Domains $= 3 + 2 = 5 \Rightarrow$ trigonal bipyramidal electron-domain geometry; with both lone pairs equatorial, the 3 F atoms form a **T-shape** (the same pattern as BrF_3).

Bài tập luyện tập

Which of these molecules is non-polar overall, despite containing polar bonds?

(A) $CHCl_3$
(B) NH_3
(C) XeF_4
(D) H_2O

Lời giải chi tiết

XeF_4 has 6 electron domains (4 bonding $+2$ lone pairs), giving a square-planar molecular shape. The 4 polar Xe–F bond dipoles point symmetrically outward at $90°$C intervals in one plane and cancel exactly, so the molecule has no net dipole. **(C)**.

Bài tập luyện tập

Both CO_2 and SO_2 have the central atom bonded to 2 oxygen atoms, yet CO_2 is linear and non-polar while SO_2 is bent and polar. Explain the difference.

Lời giải chi tiết

In CO_2, carbon forms 2 double bonds to oxygen and has *no* lone pairs, so there are only 2 electron domains $\Rightarrow$ linear ($180°$C); the two identical, oppositely-directed C=O dipoles cancel, so CO_2 is non-polar. In SO_2, sulfur forms one double bond and one single bond (with resonance) to oxygen *and* retains 1 lone pair, giving 3 electron domains $\Rightarrow$ bent ($\approx 119°$C); the two S–O dipoles no longer point in exactly opposite directions, so they do not cancel and SO_2 is polar. The key difference is the lone pair on the central atom in SO_2.

Bài tập luyện tập

Which bond angle is closest to the experimentally measured H–O–H angle in H_2O?

(A) $109.5°$C
(B) $107°$C
(C) $104.5°$C
(D) $120°$C

Lời giải chi tiết

Water has 4 electron domains (2 bonding $+2$ lone pairs). Two lone pairs compress the bond angle further than the single lone pair in NH_3 ($\approx 107^{\circ}$C), giving a measured angle of about 104.5°C. **(C)**.

Bài tập luyện tập

Deduce the electron-domain geometry and molecular shape of the ion ICl_2^-.

Lời giải chi tiết

Iodine contributes 7 valence electrons, plus 1 extra electron from the $1-$ charge $= 8$ electrons "owned" by I. Two of these are used (one each) to form the two I–Cl single bonds; the remaining 6 electrons form 3 lone pairs. Domains $= 2$ bonding $+3$ lone pairs $= 5 \Rightarrow$ trigonal bipyramidal electron-domain geometry. Placing all 3 lone pairs equatorially (to minimise repulsion) leaves the 2 Cl atoms axial, on opposite sides of I: the ion is **linear** (180°C), exactly analogous to I_3^-.

Bài tập luyện tập

Determine the electron-domain geometry and molecular shape of the ion ClO_3^-.

Lời giải chi tiết

Chlorine contributes 7 valence electrons, plus 1 extra electron from the $1-$ charge $= 8$ electrons "owned" by Cl. In the best Lewis structure (minimising formal charge) Cl forms 3 bonding domains to the O atoms and retains 1 lone pair. Domains $= 3$ bonding $+1$ lone pair $= 4 \Rightarrow$ tetrahedral electron-domain geometry; with 1 lone pair, the molecular shape is **trigonal pyramidal** (the same pattern as NH_3).

Bài tập luyện tập

Determine the electron-domain geometry and molecular shape of the phosphate ion, PO_4^{3-}.

Lời giải chi tiết

Phosphorus is bonded to all 4 oxygen atoms with no lone pairs remaining on P in the best Lewis structure (one P=O double bond and three P–O single bonds, or a resonance-averaged structure with equivalent P–O bonds). Domains $= 4$ bonding $+0$ lone pairs $= 4 \Rightarrow$ tetrahedral electron-domain geometry $=$ molecular shape (no lone pairs to distort it), with O–P–O bond angles of 109.5°C.

Bài tập luyện tập

Draw the Lewis structure of methanol, CH_3OH, and state the number of lone pairs on the oxygen atom.

Lời giải chi tiết

Total valence electrons $= 4(\text{C}) + 4(1)(\text{H on C, O}) + 6(\text{O}) + 1(\text{H on O})$; more directly: C is bonded to 3 H and 1 O (four single bonds, no lone pairs, obeying the octet with 4 bonding pairs); O is bonded to C and to 1 H (two single bonds), and must hold 2 lone pairs to complete

its octet (2 bonds $\times 2$ electrons $+2$ lone pairs $\times 2$ electrons $= 8$). **Oxygen has 2 lone pairs.**

Bài tập luyện tập

Which of the following species does *not* obey the octet rule for its central atom?

(A) CO_2 **(C)** CH_4

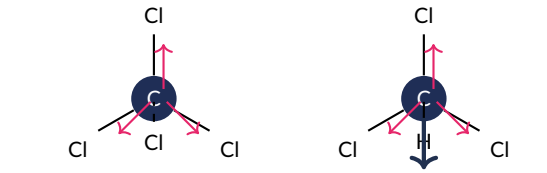
(B) BF_3 **(D)** NH_3

Lời giải chi tiết

Boron in BF_3 has only 3 bonding pairs and no lone pair, giving just 6 electrons around B – an electron-deficient exception to the octet rule. CO_2, CH_4, and NH_3 all have a full octet on the central atom. **(B)**.

2.2.2 Molecular polarity as a vector sum

Each polar bond has a **bond dipole**, a vector pointing from the less electronegative atom towards the more electronegative one. The overall polarity of a molecule is the **vector sum** of all its individual bond dipoles (and any lone-pair contribution). If the bond dipoles are arranged so that they cancel exactly – which happens only when the surrounding atoms are identical *and* arranged with sufficient symmetry (linear, trigonal planar, tetrahedral, square planar, octahedral, with every position occupied by an equivalent atom or lone pair) – the molecule is non-polar overall, even though every individual bond is polar.



CCl_4: 4 equal dipoles, symmetric tetrahedral ⇒ cancel, **non-polar**

$CHCl_3$: H replaces one Cl, net dipole remains (shown, navy), **polar**

Bond dipoles (pink arrows) as vectors. In CCl_4, four identical, symmetrically arranged C–Cl dipoles sum to zero. Replacing one Cl with the much less electronegative H (as in $CHCl_3$) removes the symmetry, leaving a net molecular dipole (navy arrow).

Predicting polarity from vector addition

BF_3 has three identical, symmetrically arranged (trigonal planar, $120°$C) polar B–F bonds. Explain why the molecule as a whole is non-polar.

Each B–F bond dipole has the same magnitude (identical bonded atoms) and the three point outward from boron at $120°$C to one another. By vector addition, three equal-magnitude vectors spaced $120°$C apart sum to exactly zero, regardless of their individual magnitude. The molecule therefore has *no* net dipole moment and is non-polar, even though every individual B–F bond is strongly polar ($\Delta\text{EN} = |3.98 - 2.04| = 1.94$).

VN **GIẢI THÍCH TIẾNG VIỆT**

Độ phân cực của cả phân tử là **tổng vector** của các mô-men lưỡng cực liên kết riêng lẻ, không phải tổng đại số. Ba vector có độ lớn bằng nhau, cách đều nhau $120°$C (như trong BF_3) sẽ triệt

tiêu hoàn toàn khi cộng vector, dù từng liên kết B–F đều rất phân cực. Chỉ cần phá vỡ tính đối xứng (thay một nguyên tử xung quanh bằng nguyên tử khác, như $CCl_4 \rightarrow CHCl_3$) là tổng vector không còn triệt tiêu, phân tử trở nên phân cực.

2.2.3 Bond order, length, and strength

The number of shared electron pairs between two bonded atoms is the **bond order**: 1 for a single bond, 2 for a double bond, 3 for a triple bond (and non-integer values, such as 1.5, are possible in a resonance hybrid, as seen for O_3 later in this section). Increasing bond order pulls the bonded nuclei closer together (shorter bond length) and increases the energy required to break the bond (greater bond enthalpy, i.e. a stronger bond).

Carbon–carbon bonds: C–C (ethane), length ≈ 154 pm, bond enthalpy ≈ 346 kJ mol^{-1} → C=C (ethene), length ≈ 134 pm, bond enthalpy ≈ 614 kJ mol^{-1} → C≡C (ethyne), length ≈ 120 pm, bond enthalpy ≈ 839 kJ mol^{-1}. As bond order rises, length falls and bond enthalpy rises – but *not* in exact proportion: a triple bond (839) is less than three times as strong as a single bond (346), since only the first bond in a multiple bond is a strong, direct σ overlap, while the additional bond(s) are weaker, sideways π overlaps.

Comparing bond order, length, and strength

Ethane (C_2H_6) has a C–C single bond, ethene (C_2H_4) has a C=C double bond, and ethyne (C_2H_2) has a C≡C triple bond. Rank their C–C bond lengths and bond strengths.

Bond order increases from ethane (1) to ethene (2) to ethyne (3). Bond length *decreases* as bond order increases (more shared electron pairs pull the nuclei closer together), while bond strength (enthalpy) *increases*:

$$\text{length: ethane} > \text{ethene} > \text{ethyne}; \qquad \text{strength: ethyne} > \text{ethene} > \text{ethane}.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Bậc liên kết (bond order) càng cao (đơn → đôi → ba) thì **độ dài liên kết càng ngắn** (hạt nhân bị kéo gần nhau hơn) và **độ bền liên kết càng lớn** (cần nhiều năng lượng hơn để phá vỡ). Tuy nhiên mối quan hệ này **không tỉ lệ thuận tuyệt đối**: liên kết ba không bền gấp 3 lần liên kết đơn, vì chỉ liên kết đầu tiên là liên kết sigma xen phủ trực tiếp mạnh, còn các liên kết pi thêm vào chỉ xen phủ ngang, yếu hơn.

Bài tập luyện tập

Hydrazine ($H_2N–NH_2$) has an N–N single bond; diazene (HN=NH) has an N=N double bond; nitrogen gas (N_2) has an N≡N triple bond. Predict how the N–N bond length and bond strength change across this series, and explain why N_2 is exceptionally unreactive.

Lời giải chi tiết

Bond order increases from hydrazine (1) to diazene (2) to N_2 (3), so bond length decreases (N_2 has the shortest N–N distance) while bond strength increases (N_2 has the strongest N–N bond). Because the N ≡ N triple bond in N_2 is exceptionally strong (one σ plus two π bonds, all needing to be broken together), an extremely large amount of energy is needed to break it, making N_2 very unreactive (kinetically inert) under ordinary conditions despite the reaction with, e.g., H_2 to form NH_3 being thermodynamically favourable.

Bài tập luyện tập

SF_4 (seesaw, 1 lone pair on S) and SF_6 (octahedral, 0 lone pairs on S) both contain only polar S–F bonds. Predict whether each molecule is polar or non-polar overall.

Lời giải chi tiết

SF_6: the 6 S–F bond dipoles point symmetrically outward along all three perpendicular axes (octahedral, every position occupied by an identical F atom), so by vector addition they cancel exactly – SF_6 is **non-polar**. SF_4: the seesaw shape is asymmetric (one equatorial position is occupied by a lone pair instead of an F atom), so the 4 S–F bond dipoles do *not* cancel; there is also a contribution from the lone pair itself. SF_4 is therefore **polar**.

2.2.4 Coordinate (dative) covalent bonding

A **coordinate (dative) covalent bond** is a covalent bond in which *both* shared electrons come from the *same* atom – one atom donates a complete lone pair into an empty orbital on the other. Once formed, a coordinate bond is indistinguishable from an ordinary covalent bond of the same type: identical in length and strength, and shown in Lewis structures with the same line (an arrow → is sometimes used only to indicate its origin).

Coordinate bond

A normal covalent bond: each atom supplies one electron. A coordinate bond: one atom (the **donor**, with a lone pair) supplies both electrons; the other (the **acceptor**) supplies an empty orbital. Common examples: NH_4^+ (N lone pair donated to H^+), H_3O^+ (O lone pair donated to H^+), and the classic Lewis acid-base adduct NH_3BF_3 (N lone pair donated into the empty p orbital on the electron-deficient B of BF_3).

Coordinate bonding in NH_4^+

NH_3 has a lone pair on N; H^+ has a completely empty $1s$ orbital. N donates its lone pair to form the fourth N–H bond, giving NH_4^+, in which all 4 N–H bonds are experimentally identical (same length and strength) even though one formed differently from the other three. Formal charge on N: valence $= 5$, non-bonding $e^- = 0$, bonding $e^- = 8$ (four bonds), so FC $= 5 - 0 - \frac{1}{2}(8) = +1$, matching the overall ion charge (each H carries FC $= 1 - 0 - 1 = 0$).

VN **GIẢI THÍCH TIẾNG VIỆT**

Liên kết cho–nhận (phối trí) khác liên kết cộng hoá trị thông thường **chỉ ở nguồn gốc electron**: cả hai electron dùng chung đều do *một* nguyên tử cung cấp (nguyên tử "cho", có cặp electron riêng), còn nguyên tử kia ("nhận") chỉ góp orbital trống. Sau khi hình thành, liên kết cho–nhận **hoàn toàn giống hệt** một liên kết cộng hoá trị thường về độ dài và độ bền – ví dụ cả 4 liên kết N–H trong NH_4^+ đều tương đương nhau, dù 1 trong số đó hình thành theo cơ chế cho–nhận.

Bài tập luyện tập

Draw the Lewis structure of H_3O^+ and calculate the formal charge on oxygen.

Lời giải chi tiết

Oxygen keeps 1 lone pair and forms 3 O–H bonds (two ordinary covalent bonds plus one coordinate bond, in which O donates a lone pair to H^+); once formed, all 3 O–H bonds are

identical. Formal charge on O: valence $= 6$, non-bonding $e^- = 2$, bonding $e^- = 6$, so FC $= 6 - 2 - \frac{1}{2}(6) = 6 - 2 - 3 = +1$, matching the overall $1+$ charge of the ion (each H: FC $= 1 - 0 - 1 = 0$).

Bài tập luyện tập

Which statement about coordinate covalent bonds is correct?

(A) They are always weaker than an ordinary covalent bond between the same two elements

(B) Once formed, they are indistinguishable in length and strength from other bonds of the same type in the molecule or ion

(C) They can only occur between two identical atoms

(D) They violate the octet rule on the donor atom

Lời giải chi tiết

Once a coordinate bond has formed, both electrons are shared exactly as in any other covalent bond – the "origin" of the electrons has no effect on the final bond, so it is identical in length and strength to any other bond of the same type in the species. **(B)**.

Coordinate bonds are also central to how **transition-metal complex ions** form: a central metal cation (an electron-poor Lewis acid, with empty low-energy orbitals) accepts lone pairs donated by several surrounding molecules or ions called **ligands** (e.g. H_2O, NH_3, Cl^-), each acting as a Lewis base. For example, in $[Cu(NH_3)_4]^{2+}$, four NH_3 ligands each donate their N lone pair into an empty orbital on Cu^{2+}, forming four coordinate bonds arranged around the central copper ion.

Bài tập luyện tập

In the complex ion $[Cu(H_2O)_6]^{2+}$, identify (a) the Lewis acid, (b) the Lewis base(s), and (c) the total number of coordinate bonds formed.

Lời giải chi tiết

(a) Cu^{2+} is the Lewis acid: it is electron-deficient (a cation with empty accessible orbitals) and accepts electron pairs. (b) Each of the 6 H_2O molecules is a Lewis base, donating a lone pair on its oxygen atom. (c) Each H_2O forms one coordinate bond to Cu^{2+}, so there are 6 coordinate bonds in total.

2.2.5 Formal charge, resonance, and hybridisation (AHL)

Formal charge is a bookkeeping tool used to choose between alternative Lewis structures for the same molecule or ion, and to identify which resonance structures contribute most to the true structure:

$$\text{FC} = (\text{valence } e^- \text{ of free atom}) - (\text{non-bonding } e^- \text{ on that atom}) - \tfrac{1}{2}(\text{bonding } e^- \text{ around that atom}).$$

The best Lewis structure keeps formal charges as close to zero as possible, and places any negative formal charge on the more electronegative atom(s).

(!) Lỗi thường gặp: Formal charge is *not* the real, physical charge on an atom – it is an accounting device assuming perfectly equal (covalent) sharing of every bonding pair, which is rarely exactly true. Do not confuse it with oxidation number (which assumes the *opposite* extreme: fully ionic, unequal sharing).

Formal charge in NO_2^-

Total valence electrons $= 5+6+6+1(\text{charge}) = 18$. The best structure has N double-bonded to one O, singly bonded to the other O, and one lone pair on N.
FC(N) $= 5 - 2 - \frac{1}{2}(6) = 5 - 2 - 3 = 0$.
FC(O$_=$) $= 6 - 4 - \frac{1}{2}(4) = 6 - 4 - 2 = 0$ (the doubly-bonded O).
FC(O$_-$) $= 6 - 6 - \frac{1}{2}(2) = 6 - 6 - 1 = -1$ (the singly-bonded O).
Sum of formal charges $= 0 + 0 - 1 = -1$, matching the charge on the ion.

Formal charge (AHL)

Draw the Lewis structure of the cyanide ion, CN^- (C triple-bonded to N, one lone pair on each atom), and confirm the formal charges sum to -1.

Lời giải chi tiết

Total valence electrons $= 4 + 5 + 1 = 10$. Structure: $:\text{C} \equiv \text{N}:^-$, with 1 lone pair on C and 1 lone pair on N.
FC(C) $= 4 - 2 - \frac{1}{2}(6) = 4 - 2 - 3 = -1$.
FC(N) $= 5 - 2 - \frac{1}{2}(6) = 5 - 2 - 3 = 0$.
Sum $= -1 + 0 = -1$, matching the charge on the ion (the negative formal charge falls on carbon, the less electronegative atom here – an unusual case that helps explain why cyanide often bonds to metal ions through carbon).

Formal charge and bond-length averaging in O_3

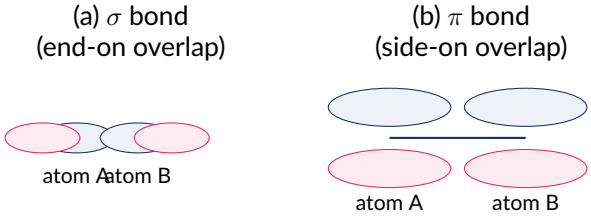
Ozone's best Lewis structure has a central O with one lone pair, one double bond to a terminal O, and one single bond to the other terminal O. Formal charges: central O, FC $= 6 - 2 - \frac{1}{2}(6) = +1$; doubly-bonded terminal O, FC $= 6 - 4 - \frac{1}{2}(4) = 0$; singly-bonded terminal O, FC $= 6 - 6 - \frac{1}{2}(2) = -1$ (sum $= 0$, correct for a neutral molecule). A second, equally valid resonance structure simply swaps which terminal O carries the double bond. **Neither** structure alone is correct: the real molecule is a **resonance hybrid**, an average of the two contributing structures. Consequently both O–O bonds are experimentally identical – each has a bond order of 1.5 (halfway between a single bond, order 1, length ≈ 148 pm, and a double bond, order 2, length ≈ 121 pm) – and both terminal oxygens carry an averaged formal charge of -0.5. The measured O–O bond length in ozone, ≈ 128 pm, sits neatly between the single- and double-bond values, confirming the resonance picture.

VN **GIẢI THÍCH TIẾNG VIỆT**

Cộng hưởng (resonance) xảy ra khi **nhiều hơn một** công thức Lewis hợp lệ có thể vẽ cho cùng một phân tử, chỉ khác nhau ở vị trí electron (không khác vị trí nguyên tử). Cấu trúc thật của phân tử không phải là *bất kỳ* công thức nào trong số đó, mà là **trung bình** (hybrid) của tất cả các công thức cộng hưởng – vì vậy trong O_3, hai liên kết O–O có độ dài **bằng nhau** và nằm giữa độ dài liên kết đơn và đôi, chứ không phải một liên kết đơn và một liên kết đôi riêng biệt như mỗi công thức Lewis đơn lẻ thể hiện.

Hybridisation mixes an atom's atomic orbitals into new, energy-degenerate hybrid orbitals used for σ bonding and holding lone pairs; the number of hybrid orbitals equals the number of electron domains (only σ-bond regions and lone pairs count – a π bond uses an unhybridised orbital, not an extra hybrid domain).

Domains → hybridisation: 2 domains → sp (linear); 3 domains → sp^2 (trigonal planar); 4 domains → sp^3 (tetrahedral). A single bond is $1\,\sigma$. A double bond is $1\,\sigma + 1\,\pi$ (sideways overlap of unhybridised p orbitals). A triple bond is $1\,\sigma + 2\,\pi$.



Orbital overlap in σ and π bonds. A σ bond forms by direct, end-on overlap along the bond axis, concentrating electron density directly between the nuclei. A π bond forms by sideways overlap of unhybridised p orbitals above and below the bond axis; the weaker, off-axis overlap makes π bonds easier to break and prevents free rotation about the bond.

Hybridisation and σ/π bonds in C_2H_4

In ethene, $H_2C = CH_2$, each carbon has 3 electron domains (2 C–H +1 C–C, no lone pairs) ⇒ sp^2 hybridised, with the 3 hybrid orbitals arranged trigonal planar (120°C) around each carbon. The unhybridised p orbital left on each carbon (perpendicular to the molecular plane) overlaps sideways with its counterpart on the other carbon to form the π bond. Totalling the whole molecule: 4 C–H σ bonds +1 C–C σ bond = $5\,\sigma$ bonds, plus $1\,\pi$ bond, making up the C=C double bond.

VN **GIẢI THÍCH TIẾNG VIỆT**

Số vùng electron dùng để xác định lai hoá **chỉ đếm** các liên kết sigma và cặp electron riêng, **không đếm** liên kết pi – vì liên kết pi dùng orbital p chưa lai hoá, xen phủ ngang chứ không tham gia tạo orbital lai. Trong C_2H_4, mỗi C có 3 vùng electron (lai hoá sp^2), nhưng tổng số liên kết sigma toàn phân tử là 5 vì còn có các liên kết C–H khác.

(!) Lỗi thường gặp: A double bond is *not* simply "twice as strong" as a single bond in the same direction – it is one strong σ bond (rotation blocked) plus one weaker, sideways-overlapping π bond. This is exactly why alkenes cannot rotate freely about the C=C axis (giving rise to E/Z isomerism), while alkanes rotate freely about their C–C σ bonds: rotating a π bond would have to break the sideways overlap.

Formal charge (AHL)

Draw the best Lewis structure of CO_3^{2-} and confirm that the formal charges sum to -2.

Lời giải chi tiết

Total valence electrons $= 4 + 3(6) + 2 = 24$. Structure: C central, one C=O double bond, two C–O single bonds, no lone pairs on C.
FC(C) $= 4 - 0 - \frac{1}{2}(8) = 4 - 0 - 4 = 0$.
FC(O$_=$) $= 6 - 4 - \frac{1}{2}(4) = 6 - 4 - 2 = 0$.
FC(O$_-$) $= 6 - 6 - \frac{1}{2}(2) = 6 - 6 - 1 = -1$ (each of the two singly-bonded O atoms).
Sum $= 0 + 0 + (-1) + (-1) = -2$, matching the ion's charge. (Three equivalent resonance structures exist, one for each possible position of the double bond, so in the real ion all three

C–O bonds are identical, each with bond order $\frac{4}{3}$.)

Hybridisation (AHL)

What is the hybridisation of the central Be atom in $BeCl_2$?

(A) sp
(B) sp^2
(C) sp^3
(D) sp^3d

Lời giải chi tiết

Be has only 2 valence electrons, forming 2 Be–Cl bonds with no lone pairs (Be is an exception to the octet rule). Domains $= 2 \Rightarrow sp$ hybridised, linear molecule. **(A)**.

Hybridisation (AHL)

Determine the hybridisation of carbon and the total number of σ and π bonds in a molecule of HCN.

Lời giải chi tiết

Carbon is bonded to 1 H (single bond) and triple-bonded to N; it has no lone pairs. Domains around C $= 2$ (1 H region $+1$ N region) $\Rightarrow sp$ hybridised, linear molecule. Bond count: the C–H bond is $1\,\sigma$; the C≡N triple bond is $1\,\sigma + 2\,\pi$. Total: $2\,\sigma$ bonds and $2\,\pi$ bonds.

Resonance (AHL)

Which statement best describes the meaning of resonance structures?

(A) The molecule physically flips back and forth between the drawn structures
(B) The real structure is a single hybrid/average of the contributing structures, not any one of them
(C) Only one resonance structure is physically real; the others are simply incorrect
(D) Resonance only occurs in ionic compounds

Lời giải chi tiết

Resonance structures are alternative electron-arrangement drawings for the *same* fixed arrangement of atoms; none of them is individually correct. The true structure is a weighted average (hybrid) of all contributing structures, with bond lengths and charges intermediate between those shown in the individual drawings. **(B)**.

Hybridisation (AHL)

Determine the hybridisation of carbon and the total σ/π bond count in ethyne, C_2H_2 (HC ≡ CH).

Lời giải chi tiết

Each carbon has 2 electron domains (1 H region $+1$ other-C region, no lone pairs) $\Rightarrow sp$ hybridised, linear about each carbon. Bond count: 2 C–H σ bonds $+1$ C–C σ bond $= 3\,\sigma$ bonds;

the triple bond additionally contributes $2\,\pi$ bonds. Total: $3\,\sigma$ and $2\,\pi$ bonds.

Hybridisation (AHL)

Methanal (formaldehyde), $H_2C{=}O$, has a central carbon bonded to 2 H atoms and double-bonded to 1 O atom. Determine the hybridisation of carbon and the total number of σ and π bonds in the molecule.

Lời giải chi tiết

Carbon has 3 electron domains (2 H regions $+1$ O region, no lone pairs on C) $\Rightarrow sp^2$ hybridised, trigonal planar around carbon. Bond count: 2 C–H σ bonds $+1$ C–O σ bond (part of the double bond) $= 3\,\sigma$ bonds; the second bond of C=O is $1\,\pi$ bond (sideways overlap of the unhybridised p orbitals on C and O). Total: $3\,\sigma$ and $1\,\pi$ bond.

Resonance (AHL)

When two or more non-equivalent resonance structures can be drawn for the same molecule, which structure contributes *most* to the true resonance hybrid?

(A) The structure with the greatest number of atoms bearing a formal charge

(B) The structure with formal charges closest to zero overall, and any negative formal charge on the most electronegative atom

(C) The structure that was drawn first

(D) All valid resonance structures contribute exactly equally, regardless of their formal charges

Lời giải chi tiết

Structures that minimise formal charge (ideally zero everywhere) and, where a formal charge cannot be avoided, place negative charge on the most electronegative atom, are lower in energy and therefore contribute more to the real structure. **(B)**.

Using formal charge to select the best Lewis structure

Two Lewis structures can be drawn for the thiocyanate ion, SCN^-: (I) $S{=}C{=}N^-$ and (II) $^-S{-}C \equiv N$. Use formal charge to decide which contributes more to the true structure.

Structure (I) has two lone pairs on S, none on C, and two lone pairs on N: FC(S) $= 6-4-\frac{1}{2}(4) = 0$; FC(C) $= 4-0-\frac{1}{2}(8) = 0$; FC(N) $= 5-4-\frac{1}{2}(4) = -1$. All formal charges are 0 or -1, and the single negative charge sits on **N** (electronegativity 3.04).

Structure (II) has three lone pairs on S, none on C, and one lone pair on N: FC(S) $= 6-6-\frac{1}{2}(2) = -1$; FC(C) $= 4-0-\frac{1}{2}(8) = 0$; FC(N) $= 5-2-\frac{1}{2}(6) = 0$. Here the single negative charge sits instead on **S** (electronegativity 2.58).

Both structures have formal charges no larger than 1 in magnitude, so the deciding factor is which atom carries the negative charge: structure (I) places it on **N** (3.04), structure (II) places it on **S** (2.58). Since N is more electronegative than S, structure (I) is preferred and contributes most to the real resonance hybrid (consistent with SCN^- coordinating to many metal ions through its N atom).

VN **GIẢI THÍCH TIẾNG VIỆT**

Khi có nhiều công thức Lewis khả dĩ khác nhau về *vị trí nguyên tử mang điện tích hình thức* (chứ

không chỉ khác vị trí electron như cộng hưởng thông thường), ta chọn công thức có điện tích hình thức âm nằm trên nguyên tử **âm điện hơn**. Với SCN^-, cấu trúc đặt điện tích âm lên N (độ âm điện 3.04) hợp lý hơn cấu trúc đặt lên S (độ âm điện 2.58), nên đóng góp chính vào cấu trúc thật của ion.

Formal charge (AHL)

Two Lewis structures are proposed for OCN^- (cyanate): (I) $O{=}C{=}N^-$ and (II) $^-O{-}C{\equiv}N$. Calculate the formal charges in each and state which structure is favoured.

Lời giải chi tiết

Structure (I) (two lone pairs on O, none on C, two lone pairs on N): FC(O) $= 6-4-\frac{1}{2}(4) = 0$; FC(C) $= 4-0-\frac{1}{2}(8) = 0$; FC(N) $= 5-4-\frac{1}{2}(4) = -1$ (negative charge on N, electronegativity 3.04). Structure (II) (three lone pairs on O, none on C, one lone pair on N): FC(O) $= 6-6-\frac{1}{2}(2) = -1$; FC(C) $= 4-0-\frac{1}{2}(8) = 0$; FC(N) $= 5-2-\frac{1}{2}(6) = 0$ (negative charge on O, electronegativity 3.44). Both structures keep formal charges within 0 to -1, so the choice again comes down to which atom holds the negative charge. Since O is *more* electronegative than N, structure (II) – with the formal negative charge on oxygen rather than nitrogen – is favoured here, in contrast to SCN^-, where N (rather than S) is the more electronegative atom and structure (I) was favoured instead.

2.2.6 Intermolecular forces

Intermolecular forces (IMFs) are the attractive forces *between* separate molecules (as opposed to the covalent bonds *within* a molecule). They are much weaker than covalent or ionic bonds, but they govern melting point, boiling point, viscosity, and solubility of molecular substances. There are three types relevant at this level, in order of typical strength.

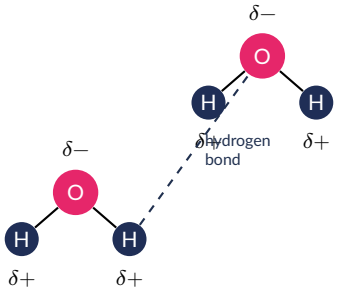
The three intermolecular forces

London (dispersion) forces – present between *every* pair of molecules or atoms, polar or non-polar, because instantaneous fluctuations in electron distribution create a temporary dipole that induces a matching dipole in a neighbour. They strengthen with more electrons and larger surface area (greater polarisability).
Permanent dipole–dipole forces – an additional attraction between polar molecules, from the permanent $\delta+$ of one molecule to the permanent $\delta-$ of another.
Hydrogen bonding – an especially strong, short-range dipole–dipole interaction that requires a hydrogen atom **covalently bonded directly to N, O, or F** (the donor) attracted to a **lone pair** on an N, O, or F atom of a neighbouring molecule (the acceptor).

VN **GIẢI THÍCH TIẾNG VIỆT**
Lực phân tán London tồn tại ở **mọi** phân tử (kể cả phân tử không phân cực) vì đám mây electron luôn dao động, tạo lưỡng cực tức thời. Lực này **mạnh lên** khi phân tử có nhiều electron hơn / diện tích bề mặt lớn hơn (dễ bị phân cực hoá hơn). Lực lưỡng cực–lưỡng cực chỉ có thêm ở phân tử phân cực. Liên kết hydrogen là trường hợp đặc biệt **mạnh nhất** trong ba loại, đòi hỏi H liên kết trực tiếp với N, O hoặc F (rất âm điện, kích thước nhỏ) và một cặp electron riêng của N/O/F ở phân tử bên cạnh.

(!) Lỗi thường gặp: Hydrogen bonding does *not* occur simply because a molecule "contains hydrogen" – CH_4 has no hydrogen bonding at all. The H must be bonded directly to N, O, or

F (small, highly electronegative atoms that pull electron density strongly away from H, leaving it with a large, concentrated $\delta+$), and there must be a lone pair on an N, O, or F atom nearby to accept it. Also remember: hydrogen bonding is an **intermolecular** force between separate molecules, not a "bond" holding one molecule together.



Hydrogen bonding between two H_2O molecules: the $\delta+$ hydrogen (bonded to the very electronegative O) is attracted to a lone pair on the $\delta-$ oxygen of a neighbouring molecule (dashed line). This intermolecular attraction is distinct from – and much weaker than – the covalent O–H bonds (solid lines) within each molecule.

The anomalous boiling point of HF

Explain the boiling-point trend of the hydrogen halides: HF (19.5°C), HCl (-85°C), HBr (-67°C), HI (-35°C).

From HCl to HI, all four molecules are polar, but going down the group the number of electrons increases sharply, strengthening **London dispersion forces** enough to outweigh the steadily *decreasing* dipole–dipole contribution (electronegativity difference falls from Cl to I): boiling point rises steadily, HCl$<$HBr$<$HI. HF breaks this pattern: fluorine is the only halogen small and electronegative enough for its H atom to form strong **hydrogen bonds** to neighbouring HF molecules. Hydrogen bonding is a much stronger force than the dipole–dipole and dispersion forces present in HCl, HBr, and HI, so despite having by far the fewest electrons, HF has the highest boiling point of the four.

Boiling points of the hydrogen halides. HF is anomalously high because of hydrogen bonding; from HCl to HI the boiling point rises steadily as the number of electrons – and hence the strength of London dispersion forces – increases.

VN **GIẢI THÍCH TIẾNG VIỆT**

Từ HCl đến HI, nhiệt độ sôi **tăng dần** vì số electron tăng ⇒ lực phân tán London mạnh lên, thắng thế so với lực lưỡng cực–lưỡng cực đang **yếu dần** (do ΔEN giảm dần từ Cl đến I). Riêng HF có liên kết hydrogen – lực liên phân tử mạnh hơn hẳn hai loại lực kia – nên dù có ít electron

nhất, HF vẫn sôi ở nhiệt độ **cao nhất** trong bốn chất, phá vỡ xu hướng đều đặn của ba chất còn lại.

London dispersion forces down group 17

Explain the steady increase in boiling point of the halogens: F_2 (-188°C), Cl_2 (-34°C), Br_2 (59°C), I_2 (184°C).

All four molecules are non-polar (identical atoms, zero ΔEN), so the *only* intermolecular force present is London dispersion. Down the group, each successive halogen has more electrons and a larger, more easily distorted electron cloud, so the instantaneous dipoles – and the induced dipoles they create in neighbouring molecules – become stronger. Stronger dispersion forces require more thermal energy to overcome, so boiling point rises steadily from F_2 (a gas at room temperature) to I_2 (a solid that sublimes).

VN **GIẢI THÍCH TIẾNG VIỆT**

Vì cả 4 phân tử halogen đều không phân cực (hai nguyên tử giống hệt nhau, $\Delta\text{EN} = 0$), lực liên phân tử duy nhất tồn tại là **lực phân tán London**. Càng xuống nhóm, số electron càng nhiều, đám mây electron càng dễ bị biến dạng (dễ phân cực hoá hơn) $\Rightarrow$ lực phân tán càng mạnh $\Rightarrow$ nhiệt độ sôi càng tăng đều đặn từ F_2 đến I_2.

Bài tập luyện tập

Which type of intermolecular force is present between *every* pair of covalent molecules, whether polar or non-polar?

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

Lời giải chi tiết

Instantaneous fluctuations in electron density occur in every molecule or atom, creating temporary dipoles that induce matching dipoles in neighbours – this dispersion force is present universally, on top of any dipole–dipole or hydrogen bonding that may also be present. **(C)**.

Bài tập luyện tập

Butane, C_4H_{10}, boils at about -1°C; propan-1-ol, C_3H_7OH, boils at 97°C, despite having a similar molar mass and fewer carbon atoms. Explain the difference.

Lời giải chi tiết

Butane is non-polar and has only London dispersion forces between its molecules. Propan-1-ol has an –OH group, so it can form **hydrogen bonds** between its O–H hydrogen and the lone pairs on a neighbouring molecule's oxygen, in addition to dispersion forces. Hydrogen bonding is much stronger than dispersion alone, so significantly more energy is needed to separate propan-1-ol molecules, giving it the far higher boiling point despite the similar molar mass.

Bài tập luyện tập

Which pair of molecules can form hydrogen bonds *with each other*?

(A) CH_4 and CH_4

(B) CH_3OH and H_2O

(C) CO_2 and CO_2

(D) Cl_2 and Cl_2

Lời giải chi tiết

Both methanol (CH_3OH) and water have an O–H bond (hydrogen-bond donor) and lone pairs on oxygen (hydrogen-bond acceptor), so they can hydrogen-bond to each other. None of the other molecules has H bonded directly to N, O, or F. **(B)**.

Bài tập luyện tập

Rank the noble gases He, Ne, Ar, and Kr in order of increasing boiling point, and explain the trend.

Lời giải chi tiết

As monatomic, non-polar species, noble gases experience only London dispersion forces, which strengthen with increasing number of electrons (greater polarisability). Increasing order: He (-269°C) < Ne (-246°C) < Ar (-186°C) < Kr (-153°C), matching the increase in atomic number (and electron count) down the group.

Bài tập luyện tập

Methanol (CH_3OH, 65°C), ethanol (C_2H_5OH, 78°C), and propan-1-ol (C_3H_7OH, 97°C) all contain a single –OH group, yet their boiling points increase steadily. Explain this trend, given that all three molecules can hydrogen-bond.

Lời giải chi tiết

All three alcohols have an –OH group and can hydrogen-bond to their neighbours in essentially the same way, so hydrogen bonding alone cannot explain the increasing trend. The distinguishing factor is chain length: methanol, ethanol, and propan-1-ol have an increasing number of carbon (and hydrogen) atoms, giving a progressively larger, more polarisable electron cloud along the hydrocarbon part of each molecule. This steadily strengthens the **London dispersion forces** between molecules on top of the (roughly constant) hydrogen bonding contribution, so the boiling point rises steadily from methanol to propan-1-ol.

Bài tập luyện tập

Which statement about hydrogen bonding is correct?

(A) It occurs whenever a molecule contains a hydrogen atom

(B) It requires H bonded directly to N, O, or F, attracted to a lone pair on an N, O, or F atom of another molecule

(C) It is stronger than a covalent bond

(D) It only occurs in liquid water

Lời giải chi tiết

Hydrogen bonding needs a small, highly electronegative atom (N, O, or F) directly bonded to H to create a strongly localised $\delta+$, and a lone pair on N, O, or F on a neighbouring molecule to accept it. It is an intermolecular force, weaker than any covalent bond, and occurs in many substances (e.g. NH_3, HF, alcohols), not only water. **(B)**.

Bài tập luyện tập

NH_3 boils at -33°C, while PH_3 (same group, same trigonal pyramidal AX_3E shape) boils at -87°C. Explain this large difference.

Lời giải chi tiết

Both molecules have an identical electron-domain arrangement (4 domains: 3 bonding $+1$ lone pair) and the same trigonal pyramidal shape, so shape alone cannot explain the gap. The key difference is intermolecular forces: N is small and highly electronegative (3.04), so N–H bonds are strongly polarised and NH_3 can hydrogen-bond extensively between molecules. Phosphorus is larger and considerably less electronegative (2.19), so the P–H bond is only weakly polar and its lone pair is more diffuse; PH_3 experiences only dispersion forces and weak dipole–dipole attraction, with no hydrogen bonding. The extra hydrogen bonding in NH_3 requires much more energy to overcome, giving it the far higher boiling point.

Bài tập luyện tập

Methanol (CH_3OH) boils at 65°C; methanethiol (CH_3SH, with S replacing O) boils at only 6°C, despite CH_3SH having more electrons (and thus stronger dispersion forces). Explain.

Lời giải chi tiết

Oxygen (3.44) is far more electronegative than sulfur (2.58) and much smaller, so the O–H bond in methanol is strongly polarised, giving methanol extensive hydrogen bonding between molecules. Sulfur's lower electronegativity and larger size make the S–H bond only weakly polar, and its lone pairs are too diffuse to accept a hydrogen bond effectively, so CH_3SH experiences only dispersion forces and weak dipole–dipole attraction, with no meaningful hydrogen bonding. Even though CH_3SH has more electrons (stronger dispersion forces alone), the loss of hydrogen bonding outweighs this, giving methanol the much higher boiling point.

Intermolecular forces also govern **solubility** and **viscosity**. The general rule "**like dissolves like**" follows directly from IMF theory: a polar or hydrogen-bonding solvent (such as water) dissolves polar or hydrogen-bonding solutes well, because new solute–solvent attractions of similar strength can replace the solute–solute and solvent–solvent attractions broken during dissolving; a non-polar solvent (such as hexane) dissolves non-polar solutes well for the same reason, but mixes poorly with water because the strong hydrogen-bonded network of water would have to be broken without a comparably strong replacement force forming with a non-polar solute. Viscosity (resistance to flow) increases with the strength of IMFs, since stronger attractions between molecules make it harder for them to slide past each other.

Solubility and "like dissolves like"

Explain why iodine, I_2, dissolves readily in non-polar hexane but only very slightly in water.

I_2 is a non-polar molecule (identical atoms, $\Delta\text{EN} = 0$) held to other I_2 molecules only by London

dispersion forces. Hexane is also non-polar, interacting with other hexane molecules (and with I_2) only through dispersion forces of comparable strength – dissolving simply exchanges one set of dispersion interactions for another of similar strength, which is energetically easy. Water, by contrast, is extensively hydrogen-bonded to itself; dissolving I_2 in water would require breaking strong O–H···O hydrogen bonds between water molecules and replacing them with only weak dispersion forces to non-polar I_2 – an energetically unfavourable exchange, so very little I_2 dissolves.

VN **GIẢI THÍCH TIẾNG VIỆT**

Quy tắc "chất tương tự hoà tan chất tương tự" (like dissolves like) xuất phát trực tiếp từ lý thuyết lực liên phân tử: dung môi và chất tan hoà tan tốt vào nhau khi lực hút mới hình thành giữa chúng có độ mạnh **tương đương** lực hút bị phá vỡ. I_2 tan tốt trong hexane (không phân cực – không phân cực, đều chỉ có lực phân tán) nhưng tan rất kém trong nước, vì hoà tan sẽ phải phá vỡ liên kết hydrogen bền vững giữa các phân tử nước mà chỉ thay bằng lực phân tán yếu với I_2 – một sự đánh đổi năng lượng bất lợi.

Relative strength of attractive forces (typical order of magnitude): ionic/covalent bonds (hundreds of kJ mol^{-1}) $\gg$ hydrogen bonding (~ 10–$40\,\text{kJ mol}^{-1}$) $>$ permanent dipole–dipole forces $>$ London dispersion forces (though dispersion forces can exceed dipole–dipole forces for large, highly polarisable molecules, as seen when comparing CCl_4 with $CHCl_3$).

Bài tập luyện tập

Ethanol, C_2H_5OH, is miscible with water in all proportions, but hexane, C_6H_{14}, is not. Explain this difference using intermolecular forces.

Lời giải chi tiết

Ethanol has an –OH group capable of hydrogen bonding to water molecules, so new ethanol–water hydrogen bonds can replace the ethanol–ethanol and water–water hydrogen bonds broken during mixing, at comparable strength – mixing is energetically easy, giving complete miscibility. Hexane is non-polar and can only offer weak dispersion forces to water molecules, which is far too weak to compensate for breaking water's extensive hydrogen-bonded network; hexane and water therefore remain separate, immiscible layers.

Bài tập luyện tập

At room temperature, ethylene glycol ($HOCH_2CH_2OH$, used in antifreeze, with an –OH group on each end of a short carbon chain) is a noticeably more viscous (syrupy) liquid than ethanol (C_2H_5OH, a single –OH group). Suggest why, in terms of intermolecular forces.

Lời giải chi tiết

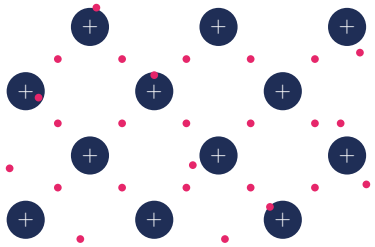
Viscosity increases with the strength (and number) of intermolecular attractions that must be continually broken and reformed as molecules slide past one another. Ethylene glycol has *two* –OH groups per molecule, capable of forming hydrogen bonds at both ends, so each molecule can hydrogen-bond to more neighbours simultaneously than ethanol (only one –OH group). This more extensive hydrogen-bonded network makes it harder for ethylene glycol molecules to move past each other, giving it the higher viscosity.

2.3 The metallic model

Metallic bonding is the electrostatic attraction between a regular lattice of metal **cations** and a "sea" of **delocalised valence electrons** that belong to the structure as a whole rather than to any individual atom. Because this attraction is **non-directional** – it does not point along fixed bond axes, unlike covalent bonds – whole layers of cations can slide past one another under stress without breaking any bonds, and the freely moving electrons can carry both charge and heat efficiently.

Metallic bonding

Cations + delocalised electron sea, held together by non-directional electrostatic attraction ⇒ **malleable** and **ductile** (layers slide without breaking bonds), **good electrical and thermal conductors** (mobile electrons), typically **lustrous** (mobile electrons reflect light).



The "sea of electrons" model of metallic bonding: a regular lattice of metal cations (navy, labelled +) is held together by its electrostatic attraction to a cloud of delocalised valence electrons (pink dots) belonging to the lattice as a whole. Because the attraction has no fixed direction, whole layers of cations can slide past one another without breaking any bond.

VN **GIẢI THÍCH TIẾNG VIỆT**

Liên kết kim loại là lực hút tĩnh điện giữa mạng ion dương (cation) và "biển electron" hoá trị di chuyển tự do khắp toàn mạng, không thuộc về một nguyên tử cụ thể nào. Vì lực hút này **không định hướng** (khác với liên kết cộng hoá trị có hướng cố định), các lớp cation có thể trượt qua nhau dưới tác dụng lực mà **không làm gãy liên kết nào** ⇒ kim loại **dẻo, dễ dát mỏng, dễ kéo sợi**. Electron tự do mang điện tích và năng lượng nhiệt di chuyển dễ dàng ⇒ kim loại **dẫn điện và dẫn nhiệt tốt**.

Unlike ionic and giant covalent lattices, metallic melting points vary widely, because the strength of the metallic bond itself varies: it increases with the **number of delocalised electrons contributed per atom** and **decreases with cation radius** (the same Coulombic reasoning as for ionic lattices, applied to cation–electron sea attraction instead of cation–anion attraction).

Why metallic melting points vary so widely

Sodium melts at only 98°C, while iron melts at 1538°C. Both are metals – explain the large difference.

Sodium (group 1) contributes only 1 delocalised electron per atom and forms a relatively large, low-charge-density Na^{+} cation, giving a comparatively weak metallic bond. Iron is a transition metal that can contribute several delocalised electrons per atom (from both its $4s$ and part of its $3d$ subshells) and forms a smaller, higher-charge-density cation. The stronger electrostatic attraction between the iron cations and their more concentrated electron sea requires far more thermal energy to overcome, giving iron a much higher melting point than sodium.

VN **GIẢI THÍCH TIẾNG VIỆT**

Độ bền liên kết kim loại (và do đó nhiệt độ nóng chảy) phụ thuộc vào **số electron giải toả trên mỗi nguyên tử** và **bán kính cation**, hoàn toàn tương tự định luật Coulomb áp dụng cho liên kết ion. Natri (nhóm 1) chỉ góp 1 electron/nguyên tử, cation lớn $\Rightarrow$ liên kết kim loại yếu, nóng chảy ở 98°C. Sắt (kim loại chuyển tiếp) góp nhiều electron hơn (từ cả phân lớp $4s$ và $3d$), cation nhỏ hơn $\Rightarrow$ liên kết kim loại bền hơn nhiều, nóng chảy ở 1538°C.

Bài tập luyện tập

The group 1 metals have the following melting points: Li (181°C), Na (98°C), K (63°C), Rb (39°C), Cs (28°C). Explain this trend using the metallic bonding model.

Lời giải chi tiết

Every group 1 metal contributes exactly 1 delocalised electron per atom, so the number of electrons per atom is constant down the group – charge is not the varying factor here. Instead, atomic (and cation) radius **increases** steadily down the group as successive shells are added, increasing the distance between each cation and the delocalised electron sea. By the same Coulombic reasoning used for ionic lattices, a larger separation weakens the electrostatic attraction, so the strength of the metallic bond – and hence the melting point – decreases steadily from Li to Cs.

2.3.1 Alloys

An **alloy** is a mixture of a metal with one or more other elements (metallic or non-metallic) that disrupts the regular, single-sized-atom lattice of the pure metal. Two common types: **substitutional** alloys, where atoms of a similar-sized different element replace some host atoms in the lattice (e.g. brass, Cu substituted by Zn); and **interstitial** alloys, where much smaller atoms squeeze into the gaps between the host lattice atoms (e.g. steel, small C atoms sitting between Fe atoms).

Why steel is harder than pure iron

Pure iron has a regular lattice of identically sized Fe atoms; its layers can slide past each other relatively easily under stress, so pure iron is comparatively soft and very malleable. In steel, a small percentage of much smaller carbon atoms occupies interstitial gaps within the iron lattice, distorting the regular arrangement and creating local irregular strain around each carbon atom. This distortion **pins** the layers of iron cations in place, making it much harder for them to slide past one another. The result: steel is significantly harder and stronger than pure iron, at some cost to malleability and ductility.

VN **GIẢI THÍCH TIẾNG VIỆT**

Hợp kim làm gián đoạn mạng tinh thể đều đặn của kim loại nguyên chất. Trong **thép** (hợp kim xen kẽ), các nguyên tử carbon nhỏ hơn nhiều chen vào khoảng trống giữa các nguyên tử sắt, làm biến dạng cục bộ mạng tinh thể $\Rightarrow$ các lớp ion sắt **khó trượt qua nhau hơn** $\Rightarrow$ thép cứng và bền hơn sắt nguyên chất, dù kém dẻo hơn một chút. Cơ chế tương tự (nhưng thay thế thay vì xen kẽ) xảy ra ở **đồng thau** (brass), hợp kim của đồng và kẽm.

The same lattice-disruption principle explains many familiar alloys: **stainless steel** adds chromium and nickel to iron, both disrupting the lattice (increasing hardness) and forming a thin, adherent, chemically resistant chromium oxide layer that protects against corrosion; **duralumin** (aluminium alloyed with a small amount of copper) is substantially stronger than pure aluminium while remaining much lighter than steel, making it useful in aircraft construction; **solder** alloys (historically tin–lead,

now often tin–copper or tin–silver) are formulated to melt at a much lower temperature than either pure metal, because disrupting the regular lattice with a second metal also lowers the melting point in many alloy systems, alongside increasing hardness.

Bài tập luyện tập

Which explanation correctly accounts for the malleability and ductility of metals?

(A) Strong, fixed-direction covalent bonds between neighbouring atoms

(B) Non-directional attraction between cations and the delocalised electron sea allows layers to slide past each other without breaking bonds

(C) Only weak London dispersion forces hold metal atoms together

(D) The ionic lattice cleaves cleanly along fixed planes

Lời giải chi tiết

Because the attractive force between cations and the delocalised electrons does not point in any fixed direction, one layer of cations can slide over another under stress and still remain fully surrounded by (and attracted to) the electron sea – no bond is broken in the process. **(B)**.

Bài tập luyện tập

Explain, in terms of the metallic bonding model, why the electrical conductivity of a pure metal decreases slightly as its temperature increases.

Lời giải chi tiết

Electrical conduction in a metal depends on delocalised electrons moving relatively freely through the lattice. As temperature rises, the cations vibrate about their lattice positions with greater amplitude. These larger vibrations scatter the moving electrons more frequently, impeding their net flow through the lattice, so the metal's electrical conductivity falls (equivalently, its resistance rises) as temperature increases.

Bài tập luyện tập

Brass (an alloy of copper and zinc) is harder than pure copper. Explain why, using the metallic bonding model.

Lời giải chi tiết

Pure copper has a regular lattice of identically sized Cu atoms whose layers can slide past each other fairly easily. In brass, Zn atoms (a different size from Cu) substitute for some Cu atoms in the lattice, disrupting its regular layered structure. This irregularity makes it harder for layers to slide smoothly past one another, so more force is needed to deform the alloy: brass is harder (though less malleable) than pure copper.

Bài tập luyện tập

Which statement about alloys is correct?

(A) Alloys are always weaker than the pure parent metal

(B) Alloys disrupt the regular metallic lattice, typically increasing hardness and strength at some cost to malleability

(C) Alloys always conduct electricity better than the pure metal

(D) Alloys are ionic compounds formed between two metals

Lời giải chi tiết

Introducing atoms of a different size (substitutional or interstitial) distorts the regular lattice of the host metal, making it harder for layers of cations to slide past each other; this generally increases hardness and strength, usually with some reduction in malleability/ductility. **(B)**.

Bài tập luyện tập

A manufacturer wants a metal component that is both very strong (resists deformation) and highly electrically conductive. Explain why alloying, which increases strength, typically *reduces* electrical conductivity compared with the pure parent metal.

Lời giải chi tiết

Alloying strengthens a metal by distorting its regular cation lattice with atoms of a different size, which pins dislocations and makes it harder for layers to slide past one another under mechanical stress. However, the same lattice distortion also disrupts the smooth, regular path that delocalised electrons would otherwise follow: the irregular arrangement of differently sized atoms scatters moving electrons more frequently than a perfectly regular lattice would, impeding their net flow. The same structural change (irregularity) that increases mechanical strength therefore also tends to decrease electrical conductivity – engineers must balance the two properties when choosing a pure metal or a specific alloy for a given application.

2.4 From models to materials

Real materials can be classified by which bonding model dominates their structure, and this classification predicts their bulk physical properties directly.

Structure	Melting point	Electrical conductivity	Example
Ionic	High	Only when molten or dissolved	NaCl
Metallic	Variable, often high	Always good (solid and liquid)	Fe, Cu
Giant covalent (network)	Very high	Usually poor (graphite: good within layers)	diamond, SiO_2, graphite
Simple molecular	Low	Poor (no ions or free electrons)	I_2, H_2O(s), CO_2

Ranking melting points across all four structure types

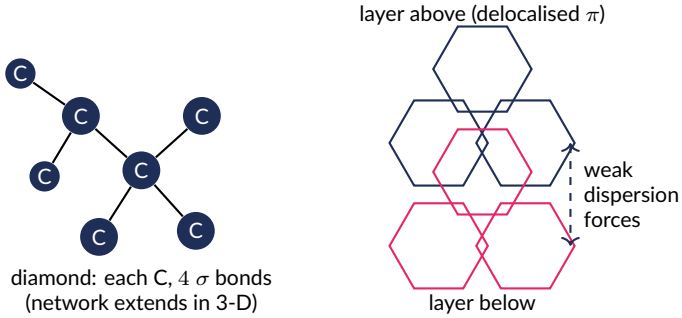
Rank ice (0°C), NaCl (801°C), iron (1538°C), and diamond ($> 3500^\circ$C) in order of increasing melting point, and explain the order using structure and bonding.

Ice is simple molecular: melting only needs to disrupt the hydrogen bonds *between* H_2O molecules (the strongest common intermolecular force, but still far weaker than a covalent or ionic bond), so it melts at the lowest temperature. NaCl is ionic: melting must overcome the strong electrostatic attraction of a $1+/1-$ lattice throughout the crystal, requiring far more energy than breaking hydrogen bonds. **Iron** is metallic, with a comparatively strong metallic bond (several delocalised electrons per atom, small cation), requiring even more energy to overcome than the NaCl lattice. **Diamond** is a giant covalent network: melting would require breaking an extensive lattice of strong, directional C–C σ bonds throughout the entire crystal, needing by far the most energy of the four. Overall: ice $<$ NaCl $<$ Fe $<$ diamond.

VN **GIẢI THÍCH TIẾNG VIỆT**

Xếp hạng nhiệt độ nóng chảy giữa bốn loại cấu trúc minh hoạ rõ độ bền tương đối của các loại liên kết: lực liên phân tử (dù là liên kết hydrogen, như trong đá) luôn yếu hơn hẳn liên kết ion, liên kết kim loại, và đặc biệt là mạng lưới cộng hoá trị khổng lồ (bền nhất, vì phải phá vỡ vô số liên kết cộng hoá trị định hướng trải khắp tinh thể). Lưu ý nhiệt độ nóng chảy kim loại rất **biến thiên** (như Na chỉ 98°C) nên thứ tự này chỉ đúng với các chất cụ thể được nêu, không phải quy luật tuyệt đối cho mọi chất cùng loại cấu trúc.

Giant covalent (network) structures, such as diamond (C, each atom sp^3-bonded to 4 neighbours in a rigid 3-D network) and SiO_2 (quartz, each Si tetrahedrally bonded to 4 bridging O atoms), have extremely high melting points because melting requires breaking a vast, interconnected network of strong covalent bonds; both are electrical insulators because every valence electron is localised in a σ bond, with none free to move. **Graphite** is also a giant covalent structure but with a different geometry: each C is sp^2-bonded to only 3 neighbours within a flat hexagonal sheet, leaving one electron per carbon in an unhybridised p orbital that overlaps with those of every other carbon in the sheet, forming a **delocalised π system** spread over the whole layer. This makes graphite an excellent conductor *within* each layer (though a poor conductor perpendicular to the layers). The layers themselves are held together only by weak London dispersion forces, so they slide over one another easily – graphite is soft and slippery, useful as a solid lubricant, even though breaking the strong covalent bonds *within* a layer still requires an extremely high temperature.



Left: diamond, a giant covalent network of sp^3 carbon atoms extending rigidly in three dimensions (insulator, extremely high melting point). Right: graphite, stacked hexagonal sp^2 layers with a delocalised π system within each layer (conducts along the layer) held to neighbouring layers only by weak dispersion forces (dashed double arrow), allowing layers to slide – hence graphite's softness and lubricating properties despite its very high melting point.

Diamond versus graphite

Both diamond and graphite are pure carbon, both are giant covalent structures with extremely high melting/sublimation points (breaking a network of strong C–C σ bonds requires enormous energy either way), yet diamond is an electrical insulator and one of the hardest known materials, while graphite conducts electricity and is soft enough to leave a mark on paper. The difference is purely structural: in diamond, all 4 valence electrons of each carbon are used in 4 strong, rigid σ bonds (sp^3), leaving none delocalised and no planes along which the structure can easily slide. In graphite, each carbon uses only 3 valence electrons for σ bonds within its layer (sp^2), leaving the 4th delocalised over the whole layer (enabling conduction) and leaving only weak forces *between* layers (enabling sliding).

VN **GIẢI THÍCH TIẾNG VIỆT**

Kim cương và graphite đều là carbon nguyên chất nhưng có cấu trúc khác nhau: kim cương – mỗi C lai hoá sp^3, tạo 4 liên kết sigma cứng chắc theo mọi hướng $\Rightarrow$ mạng lưới cứng, cách điện. Graphite – mỗi C lai hoá sp^2, chỉ tạo 3 liên kết sigma trong một lớp phẳng, electron thứ 4 giải toả (delocalised) khắp lớp đó $\Rightarrow$ **dẫn điện** trong lớp; các lớp chỉ liên kết với nhau bằng lực phân tán London yếu $\Rightarrow$ dễ trượt, mềm, dùng làm chất bôi trơn rắn – dù nhiệt độ nóng chảy/thăng hoa vẫn cực cao vì liên kết cộng hoá trị *trong* lớp rất bền.

(!) Lỗi thường gặp: Not every giant covalent (network) structure is an electrical insulator – graphite is the classic exception. Whether a covalent network conducts depends on whether it has delocalised electrons available to move (graphite, because each C is only 3-bonded, leaving a free p electron per atom) or not (diamond and SiO_2, where all valence electrons are tied up in σ bonds).

Silicon, directly below carbon in group 14, forms the same diamond-like giant covalent structure (every Si atom sp^3-bonded to 4 neighbours), yet pure silicon is neither a good insulator like diamond nor a good conductor like a metal – it is a **semiconductor**, with an electrical conductivity that lies between the two and that *increases* (unlike a metal) as temperature rises, since more electrons gain enough energy to break free of their localised σ bonds and move through the structure. Deliberately introducing tiny amounts of a different element into the silicon lattice (**doping**) can add extra mobile electrons or "holes", tuning the conductivity precisely – the basis of the semiconductor devices that make modern electronics possible.

Bài tập luyện tập

Diamond is an electrical insulator, silicon is a semiconductor, and graphite conducts well within its layers, yet all three are giant covalent structures built from group 14 elements (or, for graphite, a different bonding arrangement of the same element as diamond). Explain this spectrum of conductivity in terms of the availability of mobile electrons.

Lời giải chi tiết

Conductivity in a covalent solid depends on how easily electrons can move through the structure. In diamond, every valence electron of every sp^3 carbon is tightly localised in a σ bond, with no easy pathway to become mobile, so diamond is an insulator. In graphite, each sp^2 carbon leaves one electron per atom delocalised across an entire hexagonal layer, giving abundant mobile charge carriers and good conductivity within the layer. Silicon sits between these extremes: its diamond-like sp^3 structure normally localises all valence electrons in σ bonds (like diamond), but the Si–Si bonds are weaker and the electrons less tightly held than in diamond,

so a small but significant number of electrons gain enough thermal energy to break free and move through the lattice, giving intermediate (semiconducting) conductivity.

Carbon exists in still more structural forms (**allotropes**) beyond diamond and graphite. **Fullerenes** (e.g. C_60, "buckminsterfullerene") are discrete, hollow, roughly spherical cage molecules of sp^2 carbon – because they are individual molecules rather than an infinite network, they are held to *each other* only by London dispersion forces, giving fullerene solids a far lower melting point and greater solubility in non-polar solvents than diamond or graphite. **Graphene** is essentially a single isolated layer of graphite – one atom thick, with the same delocalised π system giving excellent electrical conductivity *within* the sheet, but (having no neighbouring layers) no weak interlayer forces to provide the lubricating property of bulk graphite. These allotropes illustrate the same underlying principle as diamond and graphite: identical atoms (carbon) can give dramatically different bulk properties depending purely on how they are connected.

Ceramics (e.g. aluminium oxide, silicon carbide, and traditional clay-based pottery) are typically giant structures with strong ionic and/or covalent bonding throughout, giving them the family of properties expected from that model: very high melting points, high hardness and stiffness, but brittleness (like ionic solids, an applied stress can easily propagate a crack through a structure with no ability to deform by sliding, unlike a metal) and electrical insulation. **Composite materials** (e.g. fibreglass, carbon-fibre-reinforced polymer) deliberately combine two structure types – a strong, stiff giant-covalent-like reinforcing fibre embedded in a tougher polymer matrix – to gain the strength of the network material and the toughness/formability of the polymer simultaneously.

Bài tập luyện tập

A ceramic material has an extremely high melting point, is very hard, is an electrical insulator, but shatters rather than bends under a sharp impact. Explain this combination of properties in terms of bonding.

Lời giải chi tiết

The very high melting point, hardness, and electrical insulation are consistent with strong ionic and/or covalent bonding extending throughout a giant structure – breaking the structure apart (melting) or moving charge through it (conducting) both require overcoming this strong, extensive bonding. The brittleness arises because, unlike a metal's non-directional cation–electron-sea attraction, ionic and covalent bonds are highly directional and localised: a sudden impact cannot be absorbed by layers sliding past each other (as in a metal), so any local stress instead propagates rapidly as a crack through the rigid, ordered structure, causing it to shatter.

2.4.1 Polymers: structure and intermolecular forces

Polymers are very long molecules built from repeating covalently-bonded units (monomers). Within a single polymer chain the atoms are held together by strong covalent bonds, but the *bulk* physical properties of a polymer – its melting/softening point, rigidity, and strength – are controlled largely by the **intermolecular forces between neighbouring chains**, exactly as for any other simple molecular substance, just on a much longer molecule.

Intermolecular forces and polymer properties

Low-density polyethylene (LDPE), a long hydrocarbon chain with no polar groups, softens/melts at around 115°C; its chains attract one another only through London dispersion forces. Nylon-6,6, a polyamide of comparable chain length, melts at a much higher $\approx 265^\circ$C; its chains contain N–H and C=O groups that form extensive **hydrogen bonds** between neighbouring

chains, in addition to dispersion forces. Because hydrogen bonding is far stronger than dispersion forces alone, substantially more thermal energy is required to separate nylon chains than polyethylene chains, giving nylon the much higher melting point and greater mechanical strength – even though the covalent backbone of both polymers is comparably strong.

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Trong một chuỗi polymer, các nguyên tử liên kết với nhau bằng liên kết cộng hoá trị bền vững, nhưng **tính chất khối** (nhiệt độ nóng chảy, độ cứng, độ bền) của vật liệu polymer lại phụ thuộc chủ yếu vào **lực liên phân tử giữa các chuỗi** – giống hệt nguyên lý áp dụng cho các phân tử nhỏ, chỉ khác là "phân tử" ở đây rất dài. Polyethylene chỉ có lực phân tán London giữa các chuỗi (nhiệt độ nóng chảy thấp), trong khi nylon có thêm liên kết hydrogen giữa các nhóm N–H/C=O của chuỗi lân cận (nhiệt độ nóng chảy cao hơn nhiều).

Beyond intermolecular forces between otherwise separate chains, some polymers form actual **covalent cross-links** directly between chains. **Thermoplastic** polymers (e.g. polyethylene, nylon) consist of individual chains held to their neighbours only by intermolecular forces; heating provides enough energy to overcome these (much weaker) forces without breaking the covalent backbone, so thermoplastics soften and can be remoulded repeatedly. **Thermosetting** polymers (e.g. vulcanised rubber, epoxy resins) additionally have covalent cross-links directly bonding neighbouring chains into one enormous three-dimensional network – much like a giant covalent structure. Because breaking a thermoset apart would mean breaking strong covalent bonds (not just weak intermolecular forces), thermosets do not melt on heating; they remain rigid until they char or decompose.

Thermoplastic versus thermosetting polymers

Explain why a thermoplastic polymer such as polyethylene can be melted and remoulded repeatedly, while a thermosetting polymer such as vulcanised rubber cannot be melted at all.

In polyethylene (thermoplastic), separate chains are held to one another only by London dispersion forces; heating the solid supplies enough thermal energy to overcome these relatively weak intermolecular forces, allowing the chains to move past one another (melting), while the strong covalent bonds *within* each chain remain intact. Cooling allows the chains to solidify again in a new shape, so the process can be repeated. In vulcanised rubber (thermoset), sulfur cross-links form strong covalent bonds directly *between* neighbouring polymer chains, converting the whole sample into one continuous covalently-bonded network, much like a giant covalent structure. Melting would require breaking these strong covalent cross-links throughout the material, which needs far more energy than is available before the polymer instead chars and decomposes – so thermosets cannot be melted and reshaped.

VN **GIẢI THÍCH TIẾNG VIỆT**

Polymer nhiệt dẻo (thermoplastic, như polyethylene) chỉ có lực liên phân tử **yếu** giữa các chuỗi riêng biệt ⇒ đun nóng đủ làm các chuỗi trượt qua nhau (nóng chảy) mà không phá vỡ liên kết cộng hoá trị trong mạch ⇒ có thể nung chảy và tạo hình lại nhiều lần. Polymer nhiệt rắn (thermoset, như cao su lưu hoá) có thêm **liên kết cộng hoá trị ngang** (cross-link) nối trực tiếp các chuỗi lại thành một mạng lưới khổng lồ giống cấu trúc cộng hoá trị khổng lồ ⇒ không thể nung chảy lại (chỉ cháy/phân huỷ) vì phải phá vỡ liên kết cộng hoá trị bền chứ không chỉ lực liên phân tử.

Bài tập luyện tập

A rigid plastic component made from a thermosetting polymer cracks when overheated in an oven, rather than melting and dripping like a thermoplastic container would. Explain this difference in behaviour.

Lời giải chi tiết

A thermosetting polymer's chains are joined by covalent cross-links into one continuous three-dimensional network, so there are no separate chains free to slide past one another and flow, however much intermolecular energy is supplied – the whole sample behaves as a single giant covalent-like structure. As the temperature keeps rising, the polymer cannot melt (there is no weak intermolecular force alone to overcome); instead, the covalent bonds themselves eventually begin to break in an uncontrolled way (decomposition/charring), which shows up macroscopically as cracking and degradation rather than a smooth transition to a flowing liquid, as would occur when a thermoplastic's much weaker interchain forces are overcome.

Deducing bonding type from property data

Four unknown solids, A–D, were tested and gave the following results.

Solid	Melting point	Conducts as solid?	Conducts molten/aq.?	Solubility in water
A	801°C	No	Yes	Soluble
B	1538°C	Yes	Yes	Insoluble
C	1710°C	No	No	Insoluble
D	sublimes at -78°C	No	No	Insoluble

Deduce the bonding/structure type of each.

A: high melting point, insulator as a solid but conducts once molten, soluble in water $\Rightarrow$ **ionic** (consistent with NaCl). **B**: high melting point, conducts in *both* the solid and molten state $\Rightarrow$ **metallic** (consistent with Fe: mobile delocalised electrons conduct regardless of physical state). **C**: extremely high melting point, insulator in every state, insoluble $\Rightarrow$ **giant covalent network** (consistent with SiO_2: an extensive network of strong covalent bonds, no ions or delocalised electrons). **D**: very low melting/sublimation point, insulator, insoluble in water $\Rightarrow$ **simple molecular** (consistent with CO_2: only weak dispersion forces between discrete non-polar molecules need to be overcome).

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Bốn "manh mối" – nhiệt độ nóng chảy, khả năng dẫn điện ở trạng thái rắn, khả năng dẫn điện khi nóng chảy/hoà tan, và độ tan trong nước – kết hợp lại cho phép xác định **duy nhất** một loại cấu trúc. Quy tắc suy luận nhanh: dẫn điện *cả rắn lẫn lỏng* $\Rightarrow$ kim loại; dẫn điện *chỉ khi* nóng chảy/hoà tan $\Rightarrow$ ion; không dẫn điện ở bất kỳ trạng thái nào kèm nhiệt độ nóng chảy **rất cao** $\Rightarrow$ mạng lưới cộng hoá trị khổng lồ; không dẫn điện kèm nhiệt độ nóng chảy **thấp** $\Rightarrow$ phân tử đơn giản.

Bài tập luyện tập

An unknown solid F conducts electricity in the solid state, has a very high melting/sublimation point ($\approx 3600^\circ$C), is soft and slippery to the touch, and is insoluble in water. Deduce its structure type, and explain why it is *not* simply classified as metallic despite conducting electricity

as a solid.

Lời giải chi tiết

Solid F is **giant covalent**, specifically graphite. Conducting as a solid might initially suggest a metal, but the combination of an extremely high melting point (consistent with breaking a network of strong covalent bonds, far higher than typical metals) together with softness and slipperiness (consistent with weak forces *between* layers, not typical of a metallic lattice) points instead to a layered covalent network. Graphite conducts because each carbon retains one delocalised electron per atom within its hexagonal layers (from sp^2 bonding), even though the structure as a whole is held together by strong, directional covalent bonds rather than a non-directional metallic "sea" of electrons.

Bài tập luyện tập

Which single substance below would you expect to be an electrical insulator, have a very high melting point, and be extremely hard?

(A) NaCl(s)
(B) Fe(s)
(C) SiO_2(s)
(D) I_2(s)

Lời giải chi tiết

Fe(s) conducts electricity (metallic), so it is excluded. I_2(s) has a low melting point and is soft (simple molecular), so it is excluded. NaCl(s) is an insulator but its melting point (801°C) is far lower than a giant covalent network, and it is not classed as "extremely hard". SiO_2(s) (quartz) is an electrical insulator, has a very high melting point ($\approx 1710^\circ$C), and is extremely hard, consistent with its giant covalent network structure. **(C)**.

Bài tập luyện tập

Low-density polyethylene (chains of $-CH_2-CH_2-$, no polar groups) softens at around 115°C. Poly(vinyl alcohol) (chains with regularly spaced –OH groups along the backbone) melts at around 230°C. Explain the difference in terms of intermolecular forces between the polymer chains.

Lời giải chi tiết

Polyethylene chains have no polar groups, so neighbouring chains attract one another only through London dispersion forces – relatively weak, so the chains separate (and the solid softens) at a comparatively low temperature. Poly(vinyl alcohol) chains carry –OH groups that can form **hydrogen bonds** to the –OH groups of neighbouring chains, in addition to dispersion forces. Because hydrogen bonds are considerably stronger than dispersion forces, substantially more thermal energy is needed to pull poly(vinyl alcohol) chains apart, giving it the much higher melting point.

Bài tập luyện tập

CCl_4 (a symmetric, non-polar tetrahedral molecule) boils at 77°C; $CHCl_3$ (chloroform, also roughly tetrahedral but with one Cl replaced by H, giving it a permanent dipole) boils at 61°C – *lower* than the non-polar CCl_4. Explain why the polar molecule has the lower boiling point.

Lời giải chi tiết

$CHCl_3$ is indeed polar (it has an AX_4-type tetrahedral shape, but the different substituents – 3 Cl and 1 H – mean the individual bond dipoles do not cancel), so it experiences dipole–dipole forces in addition to dispersion forces, while CCl_4 is symmetric and non-polar, experiencing only dispersion forces. However, CCl_4 has *four* chlorine atoms (each with many electrons) compared with $CHCl_3$'s three chlorines and one hydrogen, giving CCl_4 a substantially larger, more polarisable electron cloud. The resulting increase in **London dispersion forces** for CCl_4 outweighs the modest dipole–dipole contribution present in $CHCl_3$, so CCl_4 has the higher boiling point overall. This shows that dispersion forces, not polarity alone, often dominate the intermolecular attraction between moderately sized molecules.

Bài tập luyện tập

A student claims: "Since diamond and NaCl are both very hard, high-melting-point solids, they must have the same type of bonding." Evaluate this claim, and describe one experiment that would distinguish between the two structure types.

Lời giải chi tiết

The claim is incorrect: diamond is a giant **covalent** network (directional sp^3 σ bonds throughout a 3-D lattice of carbon atoms) with no ions present, while NaCl is an **ionic** lattice (electrostatic attraction between discrete Na^+ and Cl^- ions). Both being hard and high-melting only shows that both involve strong, extensive bonding throughout the structure – it does not identify the *type* of bonding. A simple distinguishing test: melt a small sample of each (or dissolve in water) and test electrical conductivity. Molten (or dissolved) NaCl conducts electricity well, because it contains mobile Na^+ and Cl^- ions; diamond does not melt under normal laboratory conditions and, even if it could be melted, would still not conduct, because it contains no ions and no delocalised electrons – all four valence electrons of every carbon atom are localised in σ bonds.

Bài tập luyện tập

Summarise, in one sentence each, the source of the attractive force in the ionic, covalent, and metallic models of bonding.

Lời giải chi tiết

Ionic: electrostatic attraction between oppositely charged ions (cations and anions) throughout a giant lattice, formed by electron transfer. **Covalent:** attraction between two positively charged nuclei and a shared pair (or pairs) of electrons concentrated between them, formed by electron sharing. **Metallic:** electrostatic attraction between a lattice of metal cations and a delocalised "sea" of valence electrons belonging to the structure as a whole, formed when metal atoms release their outer electrons into a shared, mobile pool.

Bài tập luyện tập

An unknown solid G has a low melting point, does not conduct electricity in any physical state, is insoluble in water, but dissolves readily in a non-polar organic solvent. A second unknown solid H has an extremely high melting point, does not conduct electricity in any state, and is insoluble in both water and non-polar solvents. Identify the structure type of G and H, and explain how their solubility patterns support your answer.

Lời giải chi tiết

Solid G is **simple molecular**: a low melting point and lack of conductivity in any state both indicate that only weak intermolecular forces (not ions, delocalised electrons, or a covalent network) hold the structure together, consistent with the "like dissolves like" principle – G dissolves in a non-polar solvent because it is itself a non-polar (or weakly polar) molecular substance interacting through comparable dispersion forces, but cannot replace the strong hydrogen-bonded network of water with anything comparably strong. Solid H is **giant covalent**: the extremely high melting point indicates an extensive network of strong covalent bonds must be broken to melt it, and the lack of conductivity in any state shows there are no ions or freely delocalised electrons available. Being insoluble in *both* water and non-polar solvents is also consistent with a giant covalent network: dissolving would require breaking apart the covalent network entirely, which no ordinary solvent (polar or non-polar) can supply enough energy to do.

Bài tập luyện tập

Explain, using ideas from across this unit, why $MgCl_2$ has a much higher melting point (714°C) than CCl_4 (-23°C), even though both compounds contain chlorine bonded to a group 2 or 14 element in a similar $1{:}4$ or $1{:}2$ ratio of central atom to Cl.

Lời giải chi tiết

The key difference is the *type* of bonding, driven by electronegativity difference: $\Delta\text{EN}(\text{Mg–Cl}) = |3.16 - 1.31| = 1.85$, above the ionic threshold, so $MgCl_2$ is an **ionic** lattice in which melting requires overcoming strong electrostatic attraction between Mg^{2+} and Cl^- ions throughout the giant structure. Carbon and chlorine, by contrast, have a much smaller electronegativity difference ($\Delta\text{EN} = |3.16 - 2.55| = 0.61$), placing C–Cl bonds firmly in the polar-covalent range: CCl_4 is a **simple molecular** substance, and melting (or boiling) it only requires overcoming the comparatively weak London dispersion forces *between* separate CCl_4 molecules, not breaking any covalent or ionic bond. The far smaller energy needed to overcome intermolecular forces compared with a giant ionic lattice explains the huge gap between the two melting points.

Bài tập luyện tập

A pure metal is melted and allowed to cool slowly under the presence of dissolved carbon and chromium, forming a new alloy. Using ideas of lattice regularity, predict how the new alloy's (a) hardness, (b) electrical conductivity, and (c) melting behaviour compare with those of the original pure metal.

Lời giải chi tiết

(a) **Hardness increases**: the dissolved carbon and chromium atoms (differing in size from the host metal atoms) disrupt the regular cation lattice, pinning dislocations and making it harder for layers to slide past one another under stress. (b) **Electrical conductivity decreases**: the same lattice irregularity that increases hardness also scatters the delocalised electrons more frequently as they move through the structure, impeding their net flow. (c) **Melting point/behaviour becomes less sharp**: unlike a pure metal (or any single pure substance), which has one fixed melting point, an alloy typically melts over a *range* of temperatures, because its lattice is no longer a single, perfectly regular repeating structure – different local regions (with slightly different local compositions) can begin to break down at slightly different temperatures.

Bài tập luyện tập

State whether each bond is best described as ionic, polar covalent, or non-polar covalent, using the electronegativities given at the start of this unit: (a) Mg–O; (b) Si–Cl; (c) Br–Br.

Lời giải chi tiết

(a) $\Delta\text{EN}(\text{Mg–O}) = |3.44 - 1.31| = 2.13 > 1.8 \Rightarrow$ **ionic**. (b) $\Delta\text{EN}(\text{Si–Cl}) = |3.16 - 1.90| = 1.26$, between 0.5 and $1.8 \Rightarrow$ **polar covalent**. (c) $\Delta\text{EN}(\text{Br–Br}) = |2.96 - 2.96| = 0 \Rightarrow$ **non-polar covalent** (identical atoms can never differ in electronegativity).

Structure 3 --- Classification of Matter

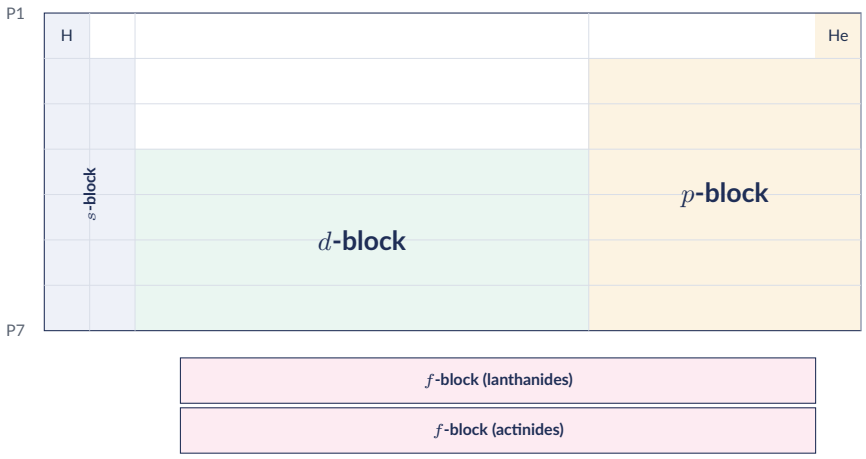
Mục tiêu Unit: Phân loại vật chất trong hoá học: cấu trúc bảng tuần hoàn theo chu kỳ, nhóm và khối nguyên tố (s, p, d, f); giải thích các xu hướng tuần hoàn (bán kính nguyên tử, năng lượng ion hoá, độ âm điện, ái lực electron, nhiệt độ nóng chảy) kèm các bất thường (dip) ở nhóm 13 và nhóm 16; phân loại tính kim loại/phi kim/lưỡng tính (metalloid); nắm vững đặc điểm nguyên tố chuyển tiếp (AHL): trạng thái oxi hoá biến đổi, màu sắc do chuyển mức năng lượng d–d, và vai trò xúc tác; phân loại hợp chất hữu cơ theo nhóm chức và dãy đồng đẳng, áp dụng quy tắc IUPAC để gọi tên hệ thống; phân biệt đồng phân cấu tạo (mạch, vị trí, nhóm chức) và đồng phân lập thể (E/Z và quang học – AHL); mô tả mô hình electron π giải toả của benzene (AHL) và giải thích vì sao benzene ưu tiên phản ứng thế hơn phản ứng cộng.

3.1 The Periodic Table: Groups, Blocks and Periodic Trends

Chemists organise the known elements, in order of increasing atomic number, into the **periodic table** so that elements with similar chemical behaviour fall into the same column. Two structural facts underlie almost every trend in this section: elements in the same **period** (horizontal row) have the same number of occupied electron shells, while elements in the same **group** (vertical column) have the same number of valence electrons and therefore similar chemical behaviour. Nearly every periodic trend can be traced back to a single idea: the **effective nuclear charge**, $Z_{\text{eff}} \approx Z - (\text{shielding electrons})$, the net positive pull felt by an outer (valence) electron once the repulsion of inner-shell electrons is accounted for.

3.1.1 Periods, groups and blocks

The table is also divided into four **blocks**, according to which subshell holds the last electron added in the building-up (Aufbau) order: the s-block (Groups 1–2), the p-block (Groups 13–18), the d-block (Groups 3–12, the transition metals and their neighbours), and the f-block (the lanthanides and actinides, usually detached below the main body of the table for space). Elements are further classified as **metals** (left and centre of the table: shiny, malleable, good conductors, tend to lose electrons), **non-metals** (upper right: poor conductors, tend to gain electrons), and **metalloids** (a narrow diagonal staircase between the two – boron, silicon, germanium, arsenic, antimony and tellurium – with intermediate physical and chemical properties, e.g. silicon and germanium are semiconductors).



The shape of the periodic table by block. Helium sits in Group 18 by chemical position (it is an unreactive noble gas), even though its electron configuration, $1s^2$, is that of an s-block atom – a well-known placement anomaly.

Assigning block from electron configuration

Identify the block of (a) calcium ($[\text{Ar}]4s^2$), (b) chlorine ($[\text{Ne}]3s^2 3p^5$), (c) iron ($[\text{Ar}]3d^6 4s^2$).

(a) The last (highest-energy) subshell being filled is $4s$, so calcium is an s**-block** element (Group 2).
(b) The last subshell filled is $3p$, so chlorine is a p**-block** element (Group 17).
(c) The last subshell filled is $3d$ (even though $4s$ fills first and empties first on ionisation), so iron is a d**-block** element.

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Bảng tuần hoàn được chia thành 4 khối s, p, d, f theo phân lớp electron cuối cùng được điền vào theo thứ tự Aufbau. Nguyên tố kim loại nằm bên trái/giữa bảng (dễ mất electron), phi kim nằm phía trên bên phải (dễ nhận electron), và metalloid (lưỡng tính về tính chất) nằm trên đường chéo hẹp giữa hai vùng này (B, Si, Ge, As, Sb, Te) với tính chất trung gian, ví dụ Si và Ge là chất bán dẫn.

A further, well-known periodic curiosity is the **diagonal relationship**: certain Period 2 elements resemble the Period 3 element diagonally below and to the right more closely than they resemble other members of their own group. Li (Group 1) behaves more like Mg (Group 2) than like Na (e.g. both Li_2CO_3 and $MgCO_3$ decompose on heating, unlike the far more thermally stable Na_2CO_3); Be (Group 2) behaves more like Al (Group 13) than like Mg (both BeO and Al_2O_3 are amphoteric, unlike the basic MgO); and B (Group 13) behaves more like Si (Group 14) than like Al (both form acidic, covalent, network-forming oxides, and both are metalloids/semiconducting in character). The diagonal relationship arises because moving one step right (increasing Z_{eff}, decreasing radius) and one step down (adding a shell, increasing radius) partially cancel, leaving diagonal neighbours with similar charge density and hence similar chemical behaviour.

3.1.2 Periodic trends across a period and down a group

Property	Across a period (left→right)	Down a group
Atomic radius	decreases (Z_{eff} ↑, same shell pulled in tighter)	increases (new outer shell added)
Ionisation energy	increases (harder to remove an electron)	decreases (outer electron farther from nucleus, more shielded)
Electronegativity	increases (stronger pull on shared electrons)	decreases
Melting point (Period 3)	rises then falls: metallic (Na, Mg, Al) → giant covalent (Si, highest) → simple molecular/atomic (P_4, S_8, Cl_2, Ar, low)	varies with bonding type of the group

The melting-point pattern deserves special attention because it is not monotonic: Na (98°C), Mg (650°C) and Al (660°C) are metals with increasingly strong metallic bonding; Si (1414°C) is a giant covalent (macromolecular) network held together by strong covalent bonds throughout, giving by far the highest melting point in the period; then P_4, S_8, Cl_2 and Ar are simple molecular or monatomic substances held together only by weak London (van der Waals) forces between molecules, so their melting points fall sharply. Notably, **electronegativity increases smoothly** across Period 3 with no dips of the kind seen in ionisation energy (Section 3.1.5) – electronegativity is a comparative, bonding-context property rather than a directly measured energy, so it does not show the same fine-structure anomalies.

VN GIẢI THÍCH TIẾNG VIỆT

Z_{eff} tăng dần trong một chu kỳ làm bán kính nguyên tử giảm, năng lượng ion hoá và độ âm điện tăng. Xuống một nhóm, lớp vỏ electron mới xuất hiện làm bán kính tăng mạnh, lấn át hiệu ứng Z_{eff} nên năng lượng ion hoá và độ âm điện giảm. Nhiệt độ nóng chảy ở chu kỳ 3 tăng rồi giảm mạnh vì kiểu liên kết đổi từ kim loại → cộng hoá trị mạng lưới khổng lồ (Si, cao nhất) → phân tử đơn giản (thấp).

3.1.3 Electronegativity and bond polarity

Electronegativity is a relative measure of an atom's ability to attract the shared pair of electrons in a covalent bond toward itself; unlike ionisation energy or electron affinity, it is not measured directly but assigned on a relative scale, most commonly the **Pauling scale**, running from about 0.7 (caesium) to 4.0 (fluorine, the most electronegative element). Electronegativity increases across a period (higher Z_{eff} pulls bonding electrons in more strongly) and decreases down a group (bonding electrons are farther from the nucleus and more shielded) – the same underlying cause as the atomic-radius and ionisation-energy trends above.

The *difference* in electronegativity between two bonded atoms, ΔEN, is used to classify the character of the bond formed between them.

Bond polarity from ΔEN (Pauling scale): $\Delta EN < 0.4$: essentially **non-polar covalent** (electrons shared almost equally, e.g. C—H, $\Delta EN \approx 0.4$, or Cl—Cl, $\Delta EN = 0$). $0.4 \leq \Delta EN \leq 1.8$: **polar covalent** (electrons shared unequally, giving partial charges $\delta+/\delta-$, e.g. H—Cl, $\Delta EN \approx 0.9$). $\Delta EN > 1.8$: predominantly **ionic** (electron(s) effectively transferred rather than shared, e.g. Na—Cl, $\Delta EN \approx 2.1$). These boundaries are guidelines, not sharp cut-offs: bonding is a continuum from purely covalent to purely ionic, not three separate categories.

Classifying bond type from electronegativity difference

Using Pauling electronegativities H $= 2.20$, C $= 2.55$, O $= 3.44$, Na $= 0.93$, Cl $= 3.16$, classify the bonds in (a) C–H, (b) C–O, (c) Na–Cl.

(a) $\Delta EN = |2.55 - 2.20| = 0.35 < 0.4 \implies$ essentially **non-polar covalent**.
(b) $\Delta EN = |3.44 - 2.55| = 0.89$, between 0.4 and $1.8 \implies$ **polar covalent** (oxygen carries the partial negative charge, $\delta-$).
(c) $\Delta EN = |3.16 - 0.93| = 2.23 > 1.8 \implies$ predominantly **ionic**.

VN **GIẢI THÍCH TIẾNG VIỆT**
Độ âm điện đo khả năng một nguyên tử hút cặp electron dùng chung về phía mình, tăng dần qua một chu kỳ và giảm dần xuống một nhóm (cùng nguyên nhân Z_{eff} như các xu hướng khác), nhưng tăng **trơn tru**, không có "dip" bất thường như năng lượng ion hoá. Hiệu độ âm điện ΔEN giữa hai nguyên tử quyết định loại liên kết: $\Delta EN < 0.4$ là cộng hoá trị không phân cực, 0.4–1.8 là cộng hoá trị phân cực, và > 1.8 chủ yếu mang tính ion.

3.1.4 Isoelectronic species and ionic radius

Forming an ion changes atomic radius dramatically. A **cation** (formed by losing electrons) is always smaller than its parent atom – it may lose an entire outer shell, and the remaining electrons experience less mutual repulsion while the same nuclear charge now acts on fewer electrons. An **anion** (formed by gaining electrons) is always larger than its parent atom – the added electron(s) increase electron-electron repulsion with no corresponding increase in nuclear charge to pull the cloud back in.

A precise way to compare ionic radii is to examine an **isoelectronic series**: a set of atoms/ions that all have the *same number of electrons* (and hence the same electron configuration and essentially the same shielding) but *different* nuclear charges. Because the number of occupied shells is fixed across such a series, the species with the **largest** nuclear charge pulls those electrons in most tightly and therefore has the **smallest** radius.

Ranking isoelectronic ionic radii

N^{3-}, O^{2-}, F^-, Na^+, Mg^{2+} and Al^{3+} are all isoelectronic with neon (each has 10 electrons, configuration $1s^2 2s^2 2p^6$). Rank them from largest to smallest radius.

All six species share the identical electron configuration, so the deciding factor is nuclear charge Z: N ($Z = 7$) < O ($Z = 8$) < F ($Z = 9$) < Na ($Z = 11$) < Mg ($Z = 12$) < Al ($Z = 13$). The larger the nuclear charge pulling on the same 10 electrons, the smaller the ion, so radius *decreases* in this order:

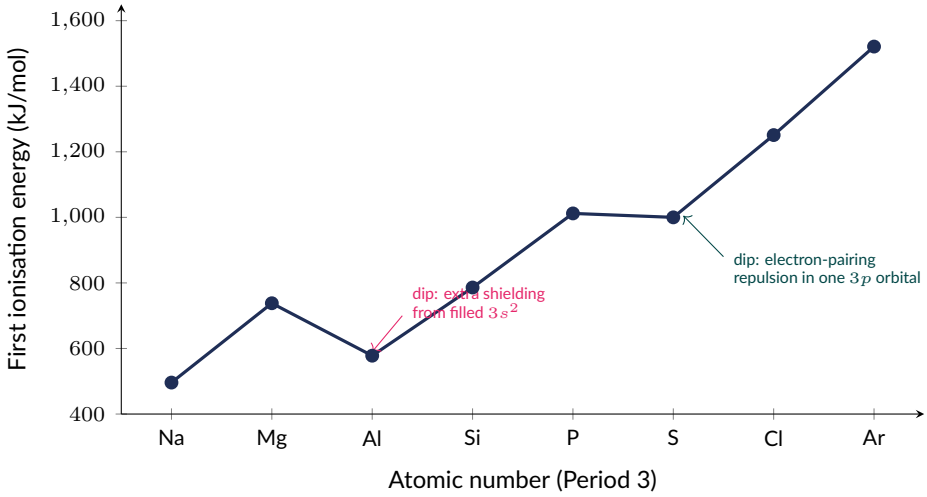
$$N^{3-} > O^{2-} > F^- > Na^+ > Mg^{2+} > Al^{3+}.$$

VN **GIẢI THÍCH TIẾNG VIỆT**
Cation luôn nhỏ hơn nguyên tử gốc (mất electron, đôi khi mất cả một lớp vỏ), còn anion luôn lớn hơn nguyên tử gốc (thêm electron gây lực đẩy electron-electron mà không tăng điện tích hạt nhân). Với các ion **đẳng electron** (isoelectronic, cùng số electron và cấu hình), ion nào có điện tích hạt nhân Z lớn hơn sẽ hút electron mạnh hơn nên có bán kính **nhỏ hơn**.

3.1.5 Ionisation energy trend and its anomalies

The **first ionisation energy** (IE_1) is the energy required to remove one electron from a mole of gaseous atoms in their ground state, $X(g) \rightarrow X^+(g) + e^-$. Across a period IE_1 generally increases

because Z_{eff} increases while the electron remains in the same shell, but the increase is not perfectly smooth: two genuine anomalies interrupt the trend, and both are frequently examined.



First ionisation energies across Period 3. The overall trend rises, but Al $<$ Mg and S $<$ P, breaking the smooth increase at Groups 13 and 16.

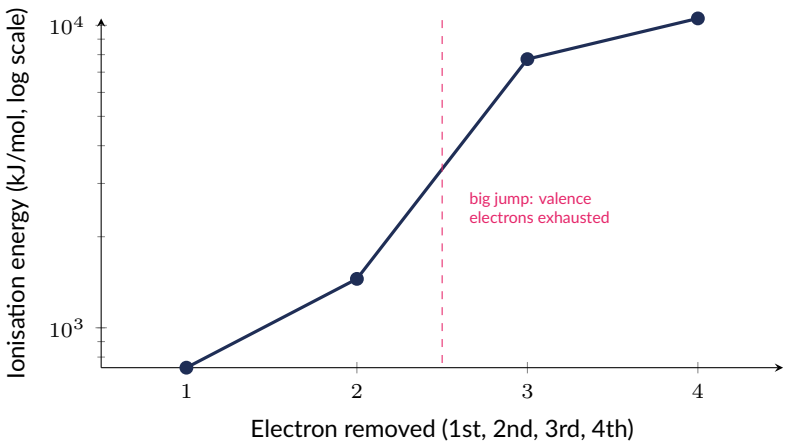
Explaining the Group 13 and Group 16 ionisation-energy dips

Explain why $IE_1(\text{Al}) = 578$ kJ/mol is *lower* than $IE_1(\text{Mg}) = 738$ kJ/mol, and why $IE_1(\text{S}) = 1000$ kJ/mol is *lower* than $IE_1(\text{P}) = 1012$ kJ/mol, even though nuclear charge increases in both cases.

Mg → Al (Group 2 → 13): Mg is $[\text{Ne}]3s^2$; its outermost electron is removed from a full, low-energy $3s$ subshell. Al is $[\text{Ne}]3s^2 3p^1$; its outermost electron sits in the higher-energy $3p$ subshell, and that $3p$ electron is additionally **shielded** by the filled, more penetrating $3s^2$ pair beneath it. Both effects (higher starting energy, extra shielding) make the single $3p$ electron easier to remove than a $3s$ electron, despite aluminium's larger nuclear charge.

P → S (Group 15 → 16): P is $[\text{Ne}]3s^2 3p^3$, with *one* electron in each of the three $3p$ orbitals (all unpaired, by Hund's rule) – a relatively low-repulsion, stable arrangement. S is $[\text{Ne}]3s^2 3p^4$, which forces a fourth electron to **pair up** in an already-occupied $3p$ orbital. The extra electron-electron repulsion between this paired-up electron and its orbital partner makes it easier to remove than would otherwise be expected, outweighing sulfur's larger nuclear charge.

Successive ionisation energies of a single element ($IE_1 < IE_2 < IE_3 < \ldots$) always increase, because each electron is removed from an increasingly positively charged ion. They increase *sharply* (jump by a factor of several) at the point where the next electron must come from a full, lower-energy inner shell rather than the (partially emptied) valence shell. Locating this jump reveals the number of valence electrons, and hence the group number, directly from data – e.g. aluminium's successive IE values $577,\ 1817,\ 2745,\ 11\,577$ kJ/mol jump sharply between the 3rd and 4th values, confirming 3 valence electrons and Group 13.



Successive ionisation energies of magnesium ($IE_1 = 738$, $IE_2 = 1451$, $IE_3 = 7733$, $IE_4 = 10\,540$ kJ/mol, log scale). The sharp jump between the 2nd and 3rd electrons (removing an electron from the full $2p^6$ core rather than the $3s^2$ valence shell) confirms magnesium has 2 valence electrons and belongs to Group 2.

GIẢI THÍCH TIẾNG VIỆT VN

Năng lượng ion hoá thứ nhất tăng dần trong một chu kỳ nhưng có hai chỗ "lõm" (dip) cần nhớ: (1) từ nhóm 2 sang nhóm 13 (ví dụ Mg→Al) – electron $3p$ duy nhất bị chắn thêm bởi phân lớp $3s^2$ đã đầy nên dễ bị lấy đi hơn; (2) từ nhóm 15 sang nhóm 16 (ví dụ P→S) – electron thứ tư phải ghép đôi trong một orbital $3p$ đã có electron, gây lực đẩy electron-electron làm electron đó dễ bị lấy đi hơn. Năng lượng ion hoá liên tiếp của một nguyên tố tăng dần và nhảy vọt mạnh khi electron kế tiếp phải lấy từ lớp vỏ trong đã đầy – vị trí bước nhảy cho biết số electron hoá trị (và do đó số nhóm).

(!) Lỗi thường gặp: Do not assume ionisation energy increases *strictly* monotonically across every period – the Group 13 dip (extra shielding from a filled s subshell) and the Group 16 dip (electron-pairing repulsion) are genuine, examinable exceptions, not errors in the data. The same two anomalies recur identically in Period 2 (Be → B and N → O).

3.1.6 Electron affinity

The (first) **electron affinity** is the energy change when one mole of gaseous atoms each gain one electron to form a mole of gaseous $1-$ ions, $X(g) + e^- \rightarrow X^-(g)$. Most non-metals release energy in this process (exothermic, negative electron affinity), because the incoming electron experiences a net attraction to the nucleus. Across a period, electron affinity generally becomes *more* exothermic (more negative) left to right, as Z_{eff} increases and pulls the incoming electron in more strongly; down a group it generally becomes *less* exothermic, as atomic radius increases and the incoming electron is added farther from the nucleus. Two genuine anomalies are worth knowing: nitrogen's electron affinity ($+7$ kJ/mol, actually endothermic) is *less* exothermic than both carbon's (-122 kJ/mol) and oxygen's (-141 kJ/mol) around it, because nitrogen's stable, half-filled $2p^3$ configuration resists accepting an extra electron, which would have to pair up and disturb that stability; and fluorine's electron affinity (-328 kJ/mol) is *less* exothermic than chlorine's (-349 kJ/mol), even though fluorine is smaller and more electronegative, because the incoming electron is forced into fluorine's very compact, already electron-dense $2p$ subshell, and the resulting electron-electron repulsion partly cancels the energy released.

Explaining the nitrogen electron-affinity anomaly

Explain why the electron affinity of nitrogen ($+7$ kJ/mol) is less exothermic than that of both its period-2 neighbours, carbon (-122 kJ/mol) and oxygen (-141 kJ/mol).

Nitrogen's configuration is $[\text{He}]2s^2 2p^3$, with one electron in each of the three $2p$ orbitals – a symmetric, half-filled, comparatively low-repulsion, stable arrangement. Adding one more electron would force it to pair up in an already-occupied $2p$ orbital, and the resulting electron-electron repulsion (combined with the loss of the stable half-filled configuration) makes the process only barely favourable to slightly unfavourable overall, unlike carbon (which still has an empty $2p$ orbital available with no pairing penalty) or oxygen (whose fourth $2p$ electron pairs up but is compensated by a considerably higher nuclear charge).

VN **GIẢI THÍCH TIẾNG VIỆT**

Ái lực electron là năng lượng giải phóng khi một nguyên tử ở thể khí nhận thêm một electron. Nhìn chung ái lực electron trở nên âm hơn (toả nhiều năng lượng hơn) khi đi qua một chu kỳ và kém âm hơn khi xuống một nhóm, tương tự như xu hướng năng lượng ion hoá nhưng đo một quá trình ngược lại. Hai bất thường cần nhớ: Nitơ có ái lực electron kém âm hơn hẳn C và O lân cận (do cấu hình $2p^3$ bán bão hoà bền vững), và Fluorine có ái lực electron kém âm hơn Chlorine (do lực đẩy electron-electron trong orbital $2p$ nhỏ và dày đặc của F).

3.1.7 Metallic and non-metallic character

Metallic character – the tendency to lose electrons and form positive ions, associated with metallic bonding, electrical conductivity, malleability and basic oxides – decreases across a period (as Z_{eff} and electronegativity increase, holding valence electrons more tightly) and increases down a group (as atomic radius increases and IE_1 falls, making the outer electron(s) easier to remove). **Non-metallic character** is essentially the reverse trend. Elements along the metal/non-metal boundary (the metalloids, Section 3.1.1) show intermediate, sometimes amphoteric behaviour – for example, Al_2O_3 and $Al(OH)_3$ can react with both acids and bases.

Classifying elements by metallic character

Classify Na, Si, Cl, and Ar as a metal, metalloid, non-metal, or noble gas, and justify each briefly from periodic position.

Na (Group 1, far left): a reactive **metal** – one loosely-held valence electron, very low IE_1, forms Na^+ readily.
Si (Group 14, on the diagonal staircase): a **metalloid** – intermediate properties, a semiconductor, forms a giant covalent lattice rather than a metallic or simple molecular one.
Cl (Group 17, upper right): a reactive **non-metal** – high Z_{eff}, high electronegativity, readily gains one electron to form Cl^-.
Ar (Group 18): a **noble gas** – a complete valence shell ($3s^2 3p^6$) gives an extremely high IE_1 and essentially no tendency to gain or lose electrons under normal conditions.

VN **GIẢI THÍCH TIẾNG VIỆT**

Tính kim loại (dễ mất electron, tạo liên kết kim loại, dẫn điện, oxide có tính base) giảm dần khi đi qua một chu kỳ và tăng dần khi xuống một nhóm – ngược lại hoàn toàn với tính phi kim. Các nguyên tố nằm trên đường biên metal/non-metal (metalloid) có tính chất trung gian, đôi khi lưỡng tính (ví dụ Al_2O_3 phản ứng được với cả acid và base).

Metallic character also predicts observable physical behaviour directly, independent of any reaction: metals conduct electricity well in the solid state (delocalised "sea" of electrons free to move),

are malleable and ductile (layers of positive ions can slide past one another without breaking the non-directional metallic bond), and are lustrous; non-metals in the solid state are typically brittle or powdery insulators (or, if covalent network solids like Si, semiconductors at best); and physical properties trend smoothly from one extreme to the other across a period or down a group, in step with the trends already described.

Predicting physical properties from metallic character

Astatine (At, Group 17, Period 6) is the heaviest common halogen. Based on the trend that metallic character increases down a group, predict whether At is likely to show more metallic physical character than the lighter halogens, and justify briefly.

Yes. Metallic character increases down a group as atomic radius increases and IE_1 falls, making valence electrons progressively easier to delocalise. Astatine, at the bottom of Group 17, is expected to show markedly more metallic character than F, Cl, Br or I – consistent with astatine being described as having a distinctly more metallic appearance and lower electronegativity than its lighter Group 17 relatives, even though it remains formally classified as a non-metal/metalloid.

VN **GIẢI THÍCH TIẾNG VIỆT**

Tính kim loại còn dự đoán được tính chất vật lý: kim loại dẫn điện tốt (electron tự do di chuyển), dễ dát mỏng/kéo sợi (các lớp ion dương trượt lên nhau mà không phá vỡ liên kết), có ánh kim; phi kim ở thể rắn thường giòn hoặc là chất cách điện. Xuống nhóm 17, At (astatine) có tính kim loại rõ rệt hơn hẳn so với F, Cl, Br, I do bán kính lớn hơn và năng lượng ion hoá thấp hơn.

3.1.8 Oxides across Period 3: acid–base character

Metallic and non-metallic character (Section 3.1.7) can be observed directly in how each element's oxide behaves toward water, acids and bases. **Metal oxides** are generally **basic**: they contain the O^{2-} ion, which reacts with water to give OH^-, and they react directly with acids to form a salt and water. **Non-metal oxides** are generally **acidic**: they react with water to form an oxoacid, or react directly with bases to form a salt and water. Oxides of elements close to the metal/non-metal boundary are often **amphoteric**, reacting with both acids and bases.

Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
Character	basic	basic	**amphoteric**	weakly acidic	acidic	acidic	strongly acidic

Predicting oxide acid–base behaviour

Predict whether MgO and SO_3 will react with dilute hydrochloric acid, with aqueous sodium hydroxide, or both, and write one equation for whichever reaction(s) occur.

Mg is a metal (Group 2), so MgO is **basic**: it reacts with the acid but not with the base.

$$MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l).$$

S is a non-metal (Group 16), so SO_3 is **acidic**: it reacts with the base but not with the acid.

$$SO_3(g) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + H_2O(l).$$

VN GIẢI THÍCH TIẾNG VIỆT

Oxide kim loại (bên trái bảng tuần hoàn) thường có tính **base** (phản ứng với acid), oxide phi kim (bên phải) thường có tính **acid** (phản ứng với base), còn oxide của nguyên tố gần biên metal/non-metal (như Al_2O_3) có tính **lưỡng tính** (phản ứng được với cả acid lẫn base). Xu hướng này là hệ quả trực tiếp của xu hướng tính kim loại/phi kim đã học ở mục 3.1.7.

3.1.9 Transition elements (AHL)

The d-block spans Groups 3–12, but a slightly narrower term, **transition element**, is reserved for a d-block element that forms *at least one stable ion with a partially filled d subshell*. By this precise definition, **scandium** and **zinc** are d-block elements but are *not* classified as transition elements: scandium forms only Sc^{3+}, which is $[Ar]3d^0$ (empty d subshell), and zinc forms only Zn^{2+}, which is $[Ar]3d^{10}$ (completely full d subshell) – neither has any *partially* filled d subshell available. The elements titanium through copper, by contrast, all form at least one ion with a partially filled d subshell and are true transition elements.

(!) Lỗi thường gặp: "d-block" and "transition element" are *not* synonyms. Every transition element is a d-block element, but Sc and Zn are d-block elements that are *not* transition elements, precisely because none of their common ions has a partially filled d subshell.

Two d-block elements have famously **anomalous ground-state electron configurations** that deviate from the pattern predicted by simply filling $4s$ before $3d$. **Chromium** is $[Ar]3d^5 4s^1$, not the "expected" $[Ar]3d^4 4s^2$; and **copper** is $[Ar]3d^{10}4s^1$, not the "expected" $[Ar]3d^9 4s^2$. Both anomalies arise for the same reason: a half-filled (d^5) or completely filled (d^{10}) d subshell is an unusually low-energy, stable arrangement (each orbital singly or fully occupied minimises electron-electron repulsion and, for the half-filled case, maximises exchange stabilisation between parallel-spin electrons), stable enough that promoting one $4s$ electron into the $3d$ subshell to reach that special configuration lowers the atom's overall energy, even though it leaves only one $4s$ electron rather than two.

VN GIẢI THÍCH TIẾNG VIỆT

Hai trường hợp cấu hình electron bất thường cần nhớ ở khối d: Chromium là $[Ar]3d^5 4s^1$ (không phải $3d^4 4s^2$ như dự đoán) và Copper là $[Ar]3d^{10}4s^1$ (không phải $3d^9 4s^2$). Cả hai đều do phân lớp d **bán bão hoà** (d^5) hoặc **bão hoà hoàn toàn** (d^{10}) có năng lượng thấp bất thường (giảm lực đẩy electron-electron, tăng ổn định trao đổi electron cùng spin), đủ lợi để một electron $4s$ "nhảy" sang $3d$ nhằm đạt cấu hình đặc biệt này.

Two defining chemical features of transition elements follow directly from the availability of low-energy $3d$ (or $4d$, $5d$) electrons close in energy to the outer s electrons: **variable oxidation states** and, when combined with ligands, **coloured compounds**.

Variable oxidation states

Determine the oxidation state of iron in (a) FeO and (b) Fe_2O_3; and of manganese in (c) MnO_4^-.

(a) Oxygen is virtually always -2; for the neutral compound FeO: $x + (-2) = 0 \implies x = +2$. Iron is $+2$.
(b) For neutral Fe_2O_3: $2x + 3(-2) = 0 \implies 2x = 6 \implies x = +3$. Iron is $+3$.
(c) For the ion MnO_4^- (overall charge -1): $x + 4(-2) = -1 \implies x - 8 = -1 \implies x = +7$. Manganese is $+7$ (permanganate).

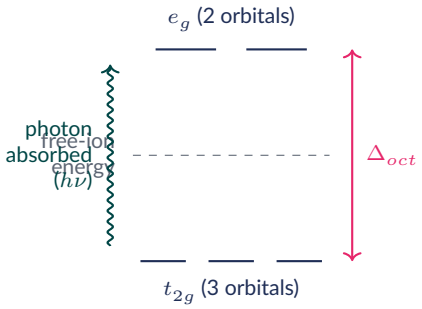
The same element, iron, exists in two different everyday oxides with two different oxidation states – exactly the "variable oxidation state" behaviour that distinguishes transition elements from most main-group metals (which almost always show one fixed ionic charge, e.g. Na is always $+1$).

GIẢI THÍCH TIẾNG VIỆT VN

Nguyên tố chuyển tiếp là nguyên tố khối d tạo được **ít nhất một ion** có phân lớp d **chưa đầy hoàn toàn** (partially filled). Theo định nghĩa này, Sc (chỉ tạo Sc^{3+}, $3d^0$) và Zn (chỉ tạo Zn^{2+}, $3d^{10}$) thuộc khối d nhưng **không** phải nguyên tố chuyển tiếp thật sự. Đặc trưng hoá học quan trọng nhất của nguyên tố chuyển tiếp là **trạng thái oxi hoá biến đổi** (ví dụ Fe có thể là $+2$ trong FeO hoặc $+3$ trong Fe_2O_3), khác với hầu hết kim loại nhóm chính chỉ có một điện tích ion cố định.

A transition-metal ion in solution is virtually never "bare" – it is surrounded by a fixed number of **ligands** (molecules or ions with a lone pair available to donate into an empty orbital on the metal, e.g. H_2O, NH_3, Cl^-, CN^-), forming a **complex ion**. The number of coordinate (dative covalent) bonds from ligands to the central metal ion is the **coordination number**; the two most common values are 6 (an **octahedral** arrangement of six ligands, e.g. $Cu(H_2O)_6^{2+}$) and 4 (either **tetrahedral** or, for some d^8 ions, **square planar**, e.g. $CoCl_4^{2-}$).

Transition-metal ions and complexes are frequently **coloured** in aqueous solution, whereas main-group ions are almost always colourless. The explanation is the **splitting of the five degenerate d orbitals** by the electric field of the surrounding ligands. In a typical octahedral complex, the five d orbitals split into a lower-energy set of three (t_{2g}) and a higher-energy set of two (e_g), separated by an energy gap Δ_{oct}; the size of this gap depends on both the identity of the ligand and the coordination number/geometry, which is why changing either one (Example below) can change the observed colour even though the metal's own d-electron count is unchanged.



Ligand-field (d-orbital) splitting in an octahedral transition-metal complex. If Δ_{oct} matches the energy of a visible-light photon, an electron can absorb it and jump $t_{2g} \rightarrow e_g$ (a d–d transition); the wavelength(s) absorbed are removed from white light, and the *complementary* colour of the remaining, transmitted light is what is observed.

Predicting colour from d-electron count

$Cu(H_2O)_6^{2+}$ is pale blue, while $Sc^{3+}(aq)$ and $Zn^{2+}(aq)$ are colourless. Explain the difference in terms of d-electron configuration.

Cu^{2+} is $[Ar]3d^9$ – a *partially* filled d subshell, so a d–d electron transition ($t_{2g} \rightarrow e_g$) is possible: $Cu(H_2O)_6^{2+}$ absorbs orange/red light (≈ 600–700 nm) and the complementary blue light is transmitted, giving the observed pale blue colour. Sc^{3+} is $[Ar]3d^0$ (no d electrons at all) and Zn^{2+} is $[Ar]3d^{10}$ (a completely full d subshell) – in both cases there is no partially filled d subshell, so no d–d transition is possible, no visible light is absorbed, and both ions are **colourless**.

GIẢI THÍCH TIẾNG VIỆT VN

Phức chất kim loại chuyển tiếp có màu vì ligand xung quanh làm 5 orbital d suy biến bị tách thành hai mức năng lượng khác nhau (t_{2g} thấp, e_g cao). Nếu khoảng cách năng lượng Δ_{oct} trùng với năng lượng một photon ánh sáng khả kiến, electron có thể nhảy mức (d–d transition), ánh sáng đó bị hấp thụ và màu bù (complementary) của nó được truyền qua/phản xạ, tạo ra màu quan sát được. Ion không có phân lớp d nào chưa đầy (Sc^{3+}: d^0; Zn^{2+}: d^{10}) thì không thể có

chuyển mức d–d nên không màu.

Ligand substitution and colour change

When excess concentrated ammonia is added to a pale blue aqueous solution of $Cu(H_2O)_6^{2+}$, the solution turns a much deeper, royal blue as the complex $Cu(NH_3)_4(H_2O)_2^{2+}$ forms. Explain this colour change.

Replacing four water ligands with four ammonia ligands is a **ligand substitution** reaction. Different ligands create electric fields of different strength around the central Cu^{2+} ion, which changes the size of the d-orbital splitting energy, Δ_{oct}. Ammonia is a stronger-field ligand than water, so $Cu(NH_3)_4(H_2O)_2^{2+}$ has a *larger* Δ_{oct} than $Cu(H_2O)_6^{2+}$: a higher-energy (shorter-wavelength) photon is now needed for the d–d transition, so a different wavelength of visible light is absorbed, and the complementary colour transmitted is a deeper blue.

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Khi thay ligand xung quanh ion kim loại chuyển tiếp (ví dụ H_2O bị thay bằng NH_3 dư), độ tách năng lượng Δ_{oct} giữa hai mức d thay đổi theo "độ mạnh trường ligand" của phối tử mới, làm bước sóng ánh sáng hấp thụ thay đổi – do đó màu quan sát được cũng thay đổi theo, dù ion trung tâm vẫn giữ nguyên số electron d.

Transition metals and their compounds are also widely used as **catalysts**, usually because of their variable oxidation states (allowing them to provide an alternative, lower-activation-energy reaction pathway via intermediate species) and/or their ability to adsorb reactant molecules onto their surface, weakening bonds within the adsorbed molecules.

Catalysis by transition metals: two real examples

Give one example of a transition metal acting as a heterogeneous catalyst, and one example of a transition-metal ion acting as a homogeneous catalyst via a change in oxidation state.

Heterogeneous: finely divided **iron** catalyses the Haber process, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. The gases adsorb onto active sites on the solid iron surface, weakening the very strong $N \equiv N$ and $H-H$ bonds and providing a lower-energy pathway to product; the iron itself is not consumed.

Homogeneous: Fe^{2+} catalyses the reaction between iodide and peroxodisulfate(VI) ions, $S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$, which is otherwise slow because two negatively charged ions strongly repel each other. Iron avoids this by reacting with each ion in a separate step, cycling between oxidation states: $2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$, then $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$; iron is regenerated at the end, so the overall (uncatalysed) equation is unchanged.

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Kim loại chuyển tiếp thường làm chất xúc tác nhờ hai lý do: (1) khả năng **hấp phụ** phân tử phản ứng lên bề mặt (xúc tác dị thể/heterogeneous, ví dụ Fe trong tổng hợp Haber), làm yếu liên kết trong phân tử hấp phụ; (2) khả năng **thay đổi trạng thái oxi hoá** linh hoạt (xúc tác đồng thể/homogeneous, ví dụ Fe^{2+}/Fe^{3+} xúc tác phản ứng giữa I^- và $S_2O_8^{2-}$ bằng cách tránh va chạm trực tiếp giữa hai ion âm), giúp phản ứng đi theo con đường có năng lượng hoạt hoá thấp hơn.

3.2 Organic Classification: Functional Groups and Nomenclature

Organic chemistry is organised around the **functional group**: a specific atom or group of atoms within a molecule that is primarily responsible for its characteristic chemical reactions. Classifying an organic compound by functional group, rather than simply by molecular formula, makes it possible to predict its reactivity from a relatively small number of general reaction patterns.

3.2.1 Functional groups and homologous series

A **homologous series** is a family of compounds that share the same functional group and the same general formula, with each successive member differing from the last by one CH_2 unit. Members of a homologous series show a gradual, predictable trend in physical properties (e.g. boiling point rises smoothly with chain length, because London forces strengthen with increasing molecular surface area) but identical general chemical behaviour, because that behaviour is governed by the shared functional group.

Series	General formula	Suffix	Example
Alkane	C_nH_{2n+2}	–ane	$CH_3CH_2CH_3$ (propane)
Alkene	C_nH_{2n}	–ene	$CH_2{=}CHCH_3$ (propene)
Alcohol	$C_nH_{2n+1}OH$	–ol	CH_3CH_2OH (ethanol)
Halogenoalkane	$C_nH_{2n+1}X$	(halo)- prefix	CH_3CH_2Br (bromoethane)
Carboxylic acid	$C_nH_{2n+1}COOH$	–oic acid	CH_3COOH (ethanoic acid)

Identifying functional group and homologous series

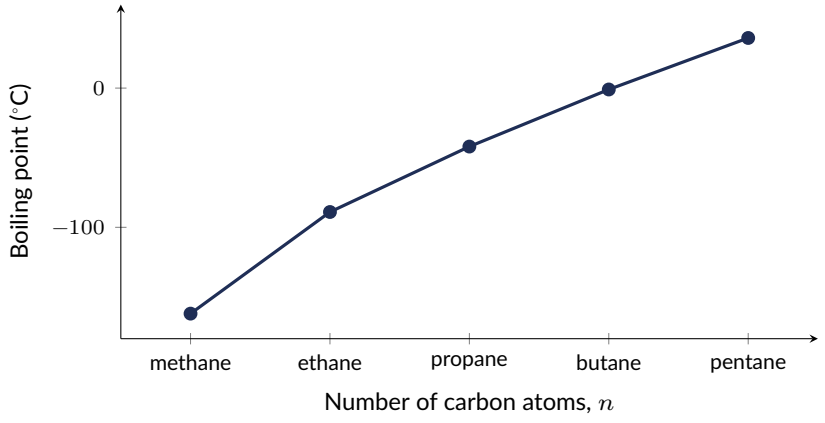
Identify the functional group and homologous series of CH_3CH_2COOH.

The –COOH group identifies this as a **carboxylic acid** (propanoic acid), belonging to the homologous series with general formula $C_nH_{2n+1}COOH$.

VN **GIẢI THÍCH TIẾNG VIỆT**

Nhóm chức quyết định **tính chất hoá học đặc trưng** của một hợp chất hữu cơ, còn độ dài mạch carbon chủ yếu ảnh hưởng **tính chất vật lý** (nhiệt độ sôi, độ tan). Các chất trong cùng một dãy đồng đẳng có công thức tổng quát giống nhau, hơn kém nhau đúng một nhóm CH_2, và có tính chất hoá học tương tự nhau.

The "gradual trend in physical properties" within a homologous series is most clearly seen in **boiling point**. Each additional CH_2 unit increases the number of electrons and the surface area of the molecule, strengthening the (instantaneous dipole-induced dipole) **London dispersion forces** between molecules, so boiling point rises steadily with chain length.



Boiling points of the first five unbranched alkanes. Each additional CH_2 unit adds electrons and surface area, strengthening London forces between molecules and steadily raising the boiling point – the smooth physical-property trend expected within a homologous series.

Branching, by contrast, *lowers* boiling point relative to an unbranched isomer of the same molecular formula, because a more compact, spherical branched molecule has less surface area available for neighbouring molecules to make contact with, weakening the London forces between them.

Chain length and branching effects on boiling point

Pentane, $CH_3CH_2CH_2CH_2CH_3$, boils at 36°C; its structural isomer 2,2-dimethylpropane, $C(CH_3)_4$, boils at only 9.5°C. Explain this difference.

Both compounds are C_5H_{12} and have identical functional groups (none – both are alkanes), so both are held together only by London dispersion forces of similar total strength (same number of electrons). However, pentane is a long, thin, unbranched chain that can make extended side-by-side contact with neighbouring molecules, while 2,2-dimethylpropane is compact and nearly spherical, with much less surface area in contact with its neighbours at any instant. Less intermolecular contact means weaker net London forces, so the more highly branched isomer has the **lower** boiling point.

VN **GIẢI THÍCH TIẾNG VIỆT**

Trong một dãy đồng đẳng, nhiệt độ sôi tăng dần đều theo chiều dài mạch carbon vì mỗi nhóm CH_2 thêm vào làm tăng số electron và diện tích bề mặt phân tử, làm lực London (lực phân tán) giữa các phân tử mạnh hơn. Ngược lại, phân tử càng **phân nhánh** thì càng gọn/cầu hơn, diện tích tiếp xúc giữa các phân tử giảm, lực London yếu hơn, nên nhiệt độ sôi thấp hơn so với đồng phân mạch thẳng cùng công thức phân tử (ví dụ 2,2-dimethylpropane sôi ở 9.5°C, thấp hơn nhiều so với pentane ở 36°C).

3.2.2 IUPAC nomenclature

The International Union of Pure and Applied Chemistry (**IUPAC**) system gives every organic compound a unique, unambiguous name built from a small set of rules:

1. Identify the **longest continuous carbon chain** (the parent chain) that includes the principal characteristic group, if one is present; its length gives the stem of the name (meth-, eth-, prop-, but-, pent-, …).
2. Identify the **principal characteristic group** (the highest-priority functional group present, e.g. carboxylic acid > ester > amide > aldehyde > ketone > alcohol > amine); this determines the name's **suffix**. Halogen substituents are *never* given a suffix – they are always named as prefixes (chloro-, bromo-, …), regardless of priority.
3. **Number the chain** to give the principal characteristic group the *lowest possible locant* first; if there is a tie (or no principal group), give the lowest locants to the substituents as a set.
4. Name every **substituent** (alkyl branches, halogens) as a prefix with its locant, listed in **alphabetical order**, using di-, tri-, tetra- for repeated identical substituents (these multiplying prefixes are not counted in the alphabetisation).
5. Assemble the full name: (locants + alphabetised prefixes) + parent chain stem + (locant +) suffix.

Naming a branched alkane

Name the alkane $CH_3{-}CH(CH_3){-}CH(CH_3){-}CH_2{-}CH_3$.

Step 1 (parent chain): the longest continuous chain has 5 carbons $\Longrightarrow$ pentane.
Step 2 (substituents): there are two methyl branches, one on each of the two internal CH carbons.
Step 3 (numbering): numbering from the left gives the methyls locants 2 and 3; numbering from the right gives locants 3 and 4. The set $\{2, 3\}$ is lower, so number from the left.
Step 4–5 (assemble): two identical substituents (methyl) at positions 2 and 3 $\Longrightarrow$ **2,3-dimethylpentane**.

Naming a compound with a functional-group suffix and a halogen prefix

Name the compound $CH_3{-}CO{-}CHCl{-}CH_2{-}CH_3$.

Step 1 (parent chain): 5 carbons in the main chain $\Longrightarrow$ pentane skeleton.
Step 2 (principal group): the C=O is a ketone – the highest-priority group present (chlorine is always a prefix, never a suffix) $\Longrightarrow$ suffix –one.
Step 3 (numbering): the ketone carbon must get the lowest possible locant. Numbering from the left: carbonyl at C2, chlorine at C3 $\Longrightarrow$ locant set for the principal group is $\{2\}$. Numbering from the right would put the carbonyl at C4 – higher, so numbering from the left is correct.
Step 4–5 (assemble): chloro- prefix at C3, -one suffix at C2, pentane stem $\Longrightarrow$ **3-chloropentan-2-one**.

For an alkene, the position of the C=C double bond itself is treated as the principal characteristic group locant (the "-ene" suffix), so Step 3 requires giving the *double bond* the lowest possible locant *before* considering any substituents – even if that choice happens to give a substituent a higher locant than the alternative numbering would.

Locant priority: the double bond outranks substituents

Name the alkene $CH_3{-}CH{=}CH{-}CH(CH_3){-}CH_3$.

Step 1: the longest chain containing the double bond has 5 carbons $\Longrightarrow$ pentene.
Step 2: numbering from the left gives the double bond locant 2 (between C2–C3) and the methyl substituent locant 4. Numbering from the right gives the double bond locant 3 (between C3–C4 in that direction) and the methyl substituent locant 2.
Step 3 (decide): the double bond, as the principal characteristic group, must receive the lowest locant *first* – locant 2 (from the left) beats locant 3 (from the right) – so numbering from the left is correct, *even though* this gives the substituent the higher locant (4 instead of 2).
Step 4–5: methyl at C4, double bond at C2, pentene stem $\Longrightarrow$ **4-methylpent-2-ene**.

VN **GIẢI THÍCH TIẾNG VIỆT**

Với anken, vị trí liên kết đôi C=C (đuôi -ene) được coi là nhóm chức chính và **luôn được đánh số nhỏ nhất trước tiên**, kể cả khi điều đó khiến nhóm thế có vị trí lớn hơn so với cách đánh số khác. Ví dụ $CH_3CH{=}CHCH(CH_3)CH_3$ phải đánh số từ trái (liên kết đôi ở vị trí 2) dù cách đánh số từ phải cho nhóm methyl vị trí nhỏ hơn (2 thay vì 4), vì liên kết đôi có độ ưu tiên cao hơn nhóm thế.

VN **GIẢI THÍCH TIẾNG VIỆT**

Quy tắc gọi tên IUPAC theo 5 bước: (1) tìm mạch carbon dài nhất chứa nhóm chức chính; (2) xác định nhóm chức có độ ưu tiên cao nhất hiện diện (quyết định đuôi -suffix; halogen luôn là

tiền tố, không bao giờ là đuôi); (3) đánh số mạch để nhóm chức chính có vị trí (locant) nhỏ nhất; (4) đặt tên các nhóm thế theo thứ tự chữ cái kèm vị trí, dùng di-/tri-/tetra- nếu lặp lại; (5) ghép lại thành tên đầy đủ. Ví dụ 2,3-dimethylpentane (ankan phân nhánh) và 3-chloropentan-2-one (có cả nhóm chức và halogen) minh hoạ đầy đủ 5 bước này.

3.2.3 Further functional groups

Beyond the alkane/alkene/alcohol/halogenoalkane/carboxylic-acid families already listed, IB Chemistry requires recognising several further functional groups by their identifying group and the naming pattern they take.

Group	Identifying feature	Suffix/prefix	Example
Aldehyde	—CHO, carbonyl at the *end* of the chain	—al	CH_3CHO (ethanal)
Ketone	C=O, carbonyl *within* the chain	—one	CH_3COCH_3 (propanone)
Ester	—COO—	—oate	$CH_3COOCH_2CH_3$ (ethyl ethanoate)
Amine	—NH_2	—amine / amino-	$CH_3CH_2NH_2$ (ethanamine)
Ether	—O— (between two carbon chains)	alkoxy- prefix	CH_3OCH_3 (methoxymethane)

Both aldehydes and ketones contain the carbonyl group C=O (with two lone pairs on oxygen). The carbonyl carbon of an aldehyde is always terminal (bonded to at least one H); the carbonyl carbon of a ketone is always internal (bonded to two carbon-containing groups), so a ketone's carbonyl carbon can never be C1 or the last carbon of the chain.

Identifying further functional groups

Identify the functional group present in each of (a) $CH_3COOCH_2CH_3$, (b) $CH_3CH_2CH_2NH_2$, (c) CH_3OCH_3.

(a) The —COO— linkage identifies an **ester** (ethyl ethanoate).
(b) The terminal —NH_2 identifies an **amine** (propan-1-amine).
(c) The —O— linking two separate carbon chains, with no carbonyl present, identifies an **ether** (methoxymethane, common name dimethyl ether).

VN **GIẢI THÍCH TIẾNG VIỆT**

Ngoài các nhóm chức cơ bản (ankan, anken, alcohol, halogenoalkane, carboxylic acid), cần nhận biết thêm: aldehyde (—CHO, carbonyl ở đầu mạch, đuôi -al), ketone (C=O trong mạch, đuôi -one), ester (—COO—, đuôi -oate), amine (—NH_2, đuôi -amine), và ether (—O— nối hai mạch carbon, không có đuôi riêng mà gọi theo tiền tố alkoxy-). Vị trí carbonyl (đầu mạch hay giữa mạch) là cách nhanh nhất để phân biệt aldehyde với ketone.

Two further groups complete the standard IB list: the **amide**, —$CONH_2$ (a carbonyl bonded directly to nitrogen, suffix —amide, e.g. CH_3CONH_2, ethanamide), and the **nitrile**, —C≡N (a carbon triple-bonded to nitrogen, suffix —nitrile, e.g. CH_3CH_2CN, propanenitrile – note that the nitrile carbon itself is always counted as part of the main chain, unlike a halogen or amine substituent).

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Hai nhóm chức bổ sung: amide ($-CONH_2$, carbonyl gắn trực tiếp với nitrogen, đuôi -amide) và nitrile ($-C{\equiv}N$, carbon liên kết ba với nitrogen, đuôi -nitrile). Lưu ý carbon của nhóm nitrile luôn được tính là một carbon của mạch chính khi đếm số carbon để đặt tên.

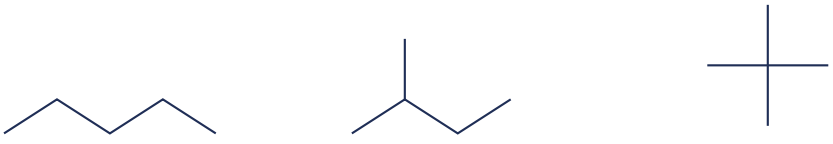
3.3 Structural and Stereoisomerism

Isomers are compounds that share the same molecular formula but differ in structure. IB Chemistry distinguishes two broad categories: **structural (constitutional) isomers**, which differ in how the atoms are *connected*, and **stereoisomers**, which have *identical* connectivity but differ in the spatial arrangement of atoms in three dimensions. The table below previews all five isomer types covered in this section, before each is developed in full with worked examples.

Isomer type	Connectivity	Defining requirement	Example pair
Chain	different	different carbon-skeleton branching pattern	pentane / 2-methylbutane
Positional	different	same functional group, different position on the chain	propan-1-ol / propan-2-ol
Functional group	different	entirely different functional groups	propanal / propanone
E/Z (AHL)	identical	each C=C carbon bears two different groups	E- / Z-but-2-ene
Optical (AHL)	identical	a carbon bonded to four different groups (chiral centre)	the two enantiomers of 2-bromobutane

3.3.1 Structural (constitutional) isomerism

Structural isomers fall into three recognised types: **chain isomers** (different patterns of branching in the carbon skeleton), **positional isomers** (the same functional group attached at a different position on an otherwise identical skeleton), and **functional group isomers** (the same molecular formula but entirely different functional groups, e.g. an alcohol and an ether, or an aldehyde and a ketone).



pentane 2-methylbutane 2,2-dimethylpropane

The three chain isomers of C_5H_{12}. Each line endpoint/vertex is a carbon atom (with enough hydrogens to complete four bonds); all three share the molecular formula C_5H_{12} but differ in carbon-skeleton branching.

Counting structural isomers

How many structural isomers does C_4H_{10} have?

Butane, $CH_3CH_2CH_2CH_3$ (unbranched), and 2-methylpropane, $(CH_3)_3CH$ (branched) – **2** isomers in total. (No positional or functional-group isomers are possible here, since a saturated C_4H_{10} alkane has no functional group to reposition.)

VN **GIẢI THÍCH TIẾNG VIỆT**

Đồng phân cấu tạo (structural isomer) khác nhau về **cách liên kết** giữa các nguyên tử, gồm 3 loại: đồng phân mạch (branching khác nhau), đồng phân vị trí (nhóm chức ở vị trí khác nhau

trên cùng một mạch), và đồng phân nhóm chức (nhóm chức hoàn toàn khác nhau, ví dụ alcohol và ether). C_4H_{10} có đúng 2 đồng phân mạch: butane và 2-methylpropane.

3.3.2 Stereoisomerism: E/Z isomerism (AHL)

Stereoisomers share identical atomic connectivity but differ in spatial arrangement. E/Z **isomerism** arises about a C=C double bond because rotation around that bond is restricted (rotating would require temporarily breaking the π bond); it occurs whenever *each* carbon of the double bond carries two *different* substituents. If either carbon carries two identical substituents, E/Z isomerism is impossible for that double bond.

Identifying E/Z isomerism

Does but-2-ene, $CH_3CH{=}CHCH_3$, show E/Z isomerism? Does 2-methylpropene, $CH_2{=}C(CH_3)_2$, show E/Z isomerism?

In but-2-ene, each double-bond carbon carries CH_3 and H – two *different* groups on *each* carbon $\implies$ **yes**, E/Z isomerism exists. *Z*-but-2-ene has both CH_3 groups on the same side of the double bond; *E*-but-2-ene has them on opposite sides.

In 2-methylpropene, one carbon of the double bond carries *two identical* CH_3 groups $\implies$ **no** E/Z isomerism, regardless of what the other carbon carries.

(!) Lỗi thường gặp: A common error is assuming that *any* alkene bearing a halogen or other substituent automatically shows E/Z isomerism. Check *both* carbons of the double bond individually: chloroethene, $CH_2{=}CHCl$, has *no* E/Z isomerism, because its terminal carbon carries two identical H atoms, even though the other carbon carries two different groups (Cl, H).

VN **GIẢI THÍCH TIẾNG VIỆT**

Đồng phân E/Z xuất hiện ở liên kết đôi C=C (không quay tự do được) **khi và chỉ khi** mỗi carbon của liên kết đôi mang hai nhóm **khác nhau**. But-2-ene có E/Z (mỗi C mang CH_3 và H, khác nhau); 2-methylpropene thì không (một C mang hai CH_3 giống nhau). Lỗi thường gặp: không phải mọi anken có nhóm thế đều có E/Z – phải kiểm tra **cả hai** carbon của liên kết đôi.

When the two substituents on a double-bond carbon are not a simple symmetric pair, the descriptors E and Z are assigned formally using the **Cahn–Ingold–Prelog (CIP) priority rules** rather than the everyday terms *cis*/*trans*. On each double-bond carbon, the two attached groups are ranked by priority (the group whose directly-attached atom has the higher atomic number wins; if tied, compare the next atoms outward). If the two **higher-priority** groups (one chosen from each carbon) lie on the **same** side of the double bond, the isomer is Z (German *zusammen*, "together"); if they lie on **opposite** sides, it is E (*entgegen*, "opposite").

Assigning E/Z using CIP priority

1-bromo-1-chloropropene, $CH_3CH{=}CBrCl$, has Br and Cl on one double-bond carbon and CH_3 and H on the other. Assign the descriptor for the isomer in which Br and CH_3 lie on the same side of the double bond.

On the CBrCl carbon: Br ($Z = 35$) outranks Cl ($Z = 17$), so Br is the higher-priority group on that carbon. On the $CHCH_3$ carbon: the carbon of CH_3 outranks H, so CH_3 is the higher-priority group on that carbon. If Br and CH_3 (the two higher-priority groups) are on the *same* side of the double bond, the higher-priority groups are "together" $\implies$ this is the Z-isomer,

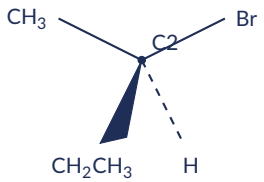
(Z)-1-bromo-1-chloropropene.

VN **GIẢI THÍCH TIẾNG VIỆT**

Khi hai nhóm thế trên mỗi carbon của liên kết đôi không đối xứng đơn giản, phải dùng quy tắc ưu tiên CIP (Cahn–Ingold–Prelog): so sánh số hiệu nguyên tử của nguyên tử gắn trực tiếp vào carbon liên kết đôi, số hiệu lớn hơn được ưu tiên cao hơn. Nếu hai nhóm ưu tiên cao nhất (mỗi carbon một nhóm) nằm **cùng phía** thì gọi là Z (zusammen), nếu nằm **khác phía** thì gọi là E (entgegen) – thay cho cách gọi cis/trans chỉ dùng được khi hai nhóm thế trên mỗi carbon giống hệt kiểu đối xứng đơn giản.

3.3.3 Stereoisomerism: optical isomerism and chirality (AHL)

Optical isomerism arises at a **chiral centre**: a carbon atom bonded to *four different* groups. A molecule with one chiral centre exists as two **enantiomers** – non-superimposable mirror images of each other, related the same way a left hand is related to a right hand. Enantiomers have identical physical and chemical properties in every respect except their interaction with other chiral objects, most notably **plane-polarised light**: one enantiomer rotates the plane of polarised light clockwise (labelled $+$ or d, dextrorotatory) and the other rotates it by the same angle counterclockwise (labelled $-$ or l, laevorotatory).



The chiral centre (C2) of 2-bromobutane, $CH_3CHBrCH_2CH_3$: two in-plane bonds, one bold wedge bond (toward the viewer), one dashed bond (away from the viewer). Because Br, H, CH_3 and CH_2CH_3 are all different, C2 is chiral, and the molecule exists as two non-superimposable enantiomers.

Identifying a chiral centre, and a non-chiral contrast

Is 2-bromobutane, $CH_3CHBrCH_2CH_3$, chiral? Is 2-bromopropane, $CH_3CHBrCH_3$, chiral?

In 2-bromobutane, carbon C2 is bonded to four groups: Br, H, CH_3 (methyl), and CH_2CH_3 (ethyl) – **all four different** $\Longrightarrow$ C2 is a **chiral centre**, and the molecule is **chiral** (exists as two enantiomers).

In 2-bromopropane, carbon C2 is bonded to Br, H, CH_3, and CH_3 – the *two methyl groups are identical*, so only three genuinely different groups are present $\Longrightarrow$ C2 is **not** a chiral centre, and 2-bromopropane is **not chiral** (it is identical to its own mirror image).

(!) Lỗi thường gặp: A chiral centre requires *four different* groups, not merely four groups or four bonds. Every sp^3 carbon has four bonds, but only a carbon whose four attached groups are all distinct from one another is a chiral centre. Always compare the full substituent (not just the first atom) – e.g. CH_3 and CH_2CH_3 both start with carbon but are different groups.

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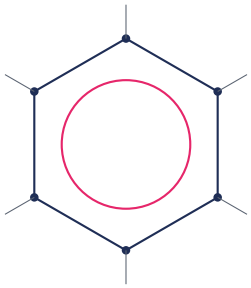
Đồng phân quang học xuất hiện tại carbon bất đối (chiral centre) – carbon gắn với **4 nhóm khác nhau**. Phân tử có 1 tâm bất đối tồn tại dưới dạng 2 enantiomer (ảnh gương không chồng khít

được), có tính chất hoá lý giống nhau hoàn toàn nhưng làm quay mặt phẳng ánh sáng phân cực theo hai chiều ngược nhau. 2-bromobutane có tâm bất đối (Br, H, CH_3, CH_2CH_3 đều khác nhau) nên là chiral; 2-bromopropane thì không (hai nhóm CH_3 giống nhau).

3.3.4 Benzene and aromatic compounds (AHL)

Benzene, C_6H_6, is the parent aromatic hydrocarbon. Early structural proposals depicted it as cyclohexatriene – a six-membered ring with alternating single and double bonds – but this model fails to explain benzene's real properties. The accepted **delocalised model** treats each of the six ring carbons as sp^2-hybridised (planar, bond angles $120°$), each contributing one electron in a p orbital oriented perpendicular to the ring plane. These six p orbitals overlap continuously around the ring, forming a single **delocalised π electron system** spread over all six carbons (above and below the ring plane) rather than three separate, localised C=C double bonds.

benzene, C_6H_6



The delocalised model of benzene: a planar hexagonal ring of sp^2 carbons (each bearing one H, short outer lines), with six π electrons delocalised into a continuous ring system (inner circle) rather than three isolated C=C double bonds.

Three pieces of experimental evidence support the delocalised model over the cyclohexatriene model: (1) all six **C–C bond lengths are equal** (about 139 pm, intermediate between a typical C–C single bond, ≈ 154 pm, and a C=C double bond, ≈ 134 pm), whereas cyclohexatriene would predict two alternating bond lengths; (2) benzene is roughly 150 kJ/mol **more stable** (lower in enthalpy) than the hypothetical, non-delocalised cyclohexatriene, an extra stabilisation called the **delocalisation (resonance) energy**; and (3) benzene's characteristic reactivity is **electrophilic substitution** (replacing a ring hydrogen while keeping the ring intact), not the electrophilic *addition* readily undergone by simple alkenes.

Why benzene resists addition reactions

Cyclohexene rapidly decolourises bromine water by an addition reaction, $C_6H_{10} + Br_2 \rightarrow C_6H_{10}Br_2$. Explain why benzene does *not* decolourise bromine water in the same way, and state what benzene does instead react to form with bromine.

Cyclohexene's C=C is a *localised*, electron-dense double bond; breaking it to add two bromine atoms is energetically favourable (exothermic addition), because two new, strong C–Br σ bonds are formed at a modest energy cost. Benzene's six π electrons, however, are **delocalised** around the whole ring, giving the ring roughly 150 kJ/mol of extra stability relative to three isolated double bonds. An addition reaction would have to break this delocalisation and force two of the six π electrons to localise into a single new bond – the energy required to destroy the delocalisation is greater than the energy released by forming new bonds, so addition is thermodynamically unfavourable and does *not* occur under normal conditions.

Instead, in the presence of a catalyst (e.g. $FeBr_3$), benzene undergoes **electrophilic substitution**: one ring hydrogen is replaced by bromine, $C_6H_6 + Br_2 \xrightarrow{FeBr_3} C_6H_5Br + HBr$, and the

stable delocalised ring is fully preserved in the product.

VN **GIẢI THÍCH TIẾNG VIỆT**

Benzene có 6 electron π giải toả (delocalised) khắp vòng thay vì 3 liên kết đôi cố định – điều này được chứng minh bởi (1) 6 liên kết C–C dài bằng nhau (≈ 139 pm, giữa liên kết đơn và đôi), (2) benzene bền hơn cyclohexatriene giả định khoảng 150 kJ/mol (năng lượng giải toả), và (3) benzene ưu tiên phản ứng **thế** (substitution) hơn phản ứng **cộng** (addition) vì phản ứng cộng sẽ phá vỡ hệ electron π giải toả bền vững đó, khiến năng lượng cần để phá vỡ lớn hơn năng lượng toả ra khi tạo liên kết mới.

Quantitative evidence for delocalisation: enthalpy of hydrogenation

The enthalpy of hydrogenation of cyclohexene (one C = C, forming cyclohexane) is -120 kJ/mol. If benzene behaved as the hypothetical cyclohexatriene (three independent, localised C = C double bonds), its enthalpy of hydrogenation to cyclohexane would be predicted to be $3 \times (-120) = -360$ kJ/mol. The *experimentally measured* enthalpy of hydrogenation of benzene is only -208 kJ/mol. Calculate benzene's delocalisation (resonance) stabilisation energy from these data.

Benzene releases *less* energy on hydrogenation than the cyclohexatriene model predicts, meaning benzene started from a *lower*, more stable energy level to begin with:

$$\text{Stabilisation energy} = E_{\text{measured}} - E_{\text{predicted}} = (-208) - (-360) = +152 \text{ kJ/mol}.$$

Benzene is 152 kJ/mol **more stable** than three isolated double bonds would predict – direct, quantitative experimental support for the delocalised π-electron model, independent of the bond-length argument above.

VN **GIẢI THÍCH TIẾNG VIỆT**

Bằng chứng định lượng: nhiệt hydro hoá của cyclohexene (1 liên kết đôi) là -120 kJ/mol, nên nếu benzene có 3 liên kết đôi độc lập (mô hình cyclohexatriene) thì nhiệt hydro hoá dự đoán sẽ là $3 \times (-120) = -360$ kJ/mol. Nhiệt hydro hoá đo được thực tế của benzene chỉ là -208 kJ/mol – ít âm hơn dự đoán 152 kJ/mol, chứng tỏ benzene bền hơn mô hình 3 liên kết đôi cố định đúng 152 kJ/mol, phù hợp với mô hình electron π giải toả.

3.4 Practice Problems

Problem 1

Rank the atomic radii of Na, Mg, Al, Si (Period 3) from *largest* to *smallest*.

(A) Na > Mg > Al > Si

(B) Si > Al > Mg > Na

(C) Mg > Na > Si > Al

(D) All approximately equal

Solution 1

Atomic radius decreases across a period as Z_{eff} increases (same shell, greater nuclear pull on the outer electrons). **(A)**.

Problem 2

Which block does an element with electron configuration $[\text{Ar}]3d^{10}4s^24p^3$ belong to?

(A) s-block
(B) p-block
(C) d-block
(D) f-block

Solution 2

The last (highest-energy) subshell being filled is $4p$, so this is a p**-block** element (this is arsenic, $Z = 33$). **(B)**.

Problem 3

Explain why the first ionisation energy of gallium ($[\text{Ar}]3d^{10}4s^24p^1$, $IE_1 = 579$ kJ/mol) is lower than that of zinc ($[\text{Ar}]3d^{10}4s^2$, $IE_1 = 906$ kJ/mol), even though gallium has one more proton.

Solution 3

This is the same Group 2 $\rightarrow$ 13 anomaly seen for Mg $\rightarrow$ Al in Period 3. Zinc's outermost electron is removed from a full $4s^2$ subshell. Gallium's outermost electron occupies the higher-energy $4p$ subshell and is additionally shielded by the full, more penetrating $4s^2$ (and $3d^{10}$) electrons beneath it, making it easier to remove despite the larger nuclear charge.

Problem 4

Which ionisation-energy dip, Mg $\rightarrow$ Al or P $\rightarrow$ S, is caused by electron-pairing repulsion within a single p orbital, rather than by extra shielding from a filled subshell?

(A) Mg $\rightarrow$ Al
(B) P $\rightarrow$ S
(C) Both, equally
(D) Neither

Solution 4

The Mg $\rightarrow$ Al dip is a shielding effect (a $3p$ electron shielded by filled $3s^2$); the P $\rightarrow$ S dip is a pairing-repulsion effect (a fourth $3p$ electron forced to pair up). **(B)**.

Problem 5

The successive ionisation energies of aluminium (kJ/mol) are $577,\ 1817,\ 2745,\ 11\,577$. Identify the group aluminium belongs to and justify your answer using this data.

Solution 5

There is a large jump in ionisation energy between the 3rd value (2745) and the 4th value ($11\,577$, more than four times larger), showing that the first three electrons come from the valence shell while the 4th must be removed from a full, much lower-energy inner shell. Three valence electrons $\Longrightarrow$ aluminium is in **Group 13**.

Problem 6

Which statement about electronegativity across Period 3 is correct?

(A) It increases smoothly from Na to Cl, without the dips seen in ionisation energy

(B) It shows the identical dips at Al and S as ionisation energy

(C) It decreases across the period

(D) It is constant across the period

Solution 6

Electronegativity is a comparative bonding property, not a directly measured ionisation energy, and increases smoothly (e.g. Na 0.93 to Cl 3.16, Pauling scale) with no analogous dips. **(A)**.

Problem 7

Explain why chlorine's electron affinity (-349 kJ/mol) is more exothermic than fluorine's (-328 kJ/mol), even though fluorine is smaller and more electronegative.

Solution 7

Fluorine's added electron enters a very small, already electron-dense $2p$ subshell, causing significant electron-electron repulsion that reduces the net energy released. Chlorine's $3p$ subshell is larger and less crowded, so the incoming electron experiences less repulsion, and more energy is released overall despite chlorine's lower electronegativity and larger atomic radius.

Problem 8

Classify germanium (Ge, Group 14) as a metal, non-metal, metalloid, or noble gas.

(A) Metal

(B) Non-metal

(C) Metalloid

(D) Noble gas

Solution 8

Germanium lies on the diagonal staircase between metals and non-metals and is a well-known semiconductor with intermediate properties. **(C)**.

Problem 9

Which best describes the melting-point pattern of Period 3 elements from Na to Ar?

(A) Rises through the metals, peaks at the giant covalent network Si, then falls sharply through the simple molecular/atomic elements

(B) Rises monotonically from Na to Ar

(C) Falls monotonically from Na to Ar

(D) Stays roughly constant throughout

Solution 9

Bonding type changes from metallic (Na, Mg, Al) to giant covalent (Si, by far the highest melting point) to simple molecular/atomic (P_4, S_8, Cl_2, Ar, held only by weak London forces). **(A)**.

Problem 10 (AHL)

Determine the oxidation state of chromium in (a) $K_2Cr_2O_7$ and of manganese in (b) K_2MnO_4.

Solution 10

(a) $K_2Cr_2O_7$ is neutral: $2(+1)+2x+7(-2)=0 \implies 2+2x-14=0 \implies x=+6$.
(b) K_2MnO_4 is neutral: $2(+1)+x+4(-2)=0 \implies 2+x-8=0 \implies x=+6$.
Both chromium and manganese reach the same $+6$ oxidation state in these two different compounds, illustrating the variable-oxidation-state behaviour of transition elements.

Problem 11 (AHL)

Which of the following aqueous ions are expected to be colourless, and which coloured: Sc^{3+}, Ti^{4+}, Fe^{2+}, Cu^{+}, Zn^{2+}?

Solution 11

Sc^{3+} ($3d^0$), Ti^{4+} ($3d^0$), Cu^{+} ($3d^{10}$) and Zn^{2+} ($3d^{10}$) have no partially filled d subshell, so no d–d transition is possible: all four are **colourless**. Fe^{2+} is $3d^6$ (partially filled), so a d–d transition is possible and Fe^{2+} is **coloured** (pale green).

Problem 12 (AHL)

Describe the role of iron in the Haber process, $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$, and state whether it is a homogeneous or heterogeneous catalyst.

(A) Heterogeneous: gases adsorb onto the solid iron surface, weakening bonds and lowering the activation energy

(B) Homogeneous: iron dissolves in the gas mixture and changes oxidation state

(C) Iron is a reactant consumed by the reaction

(D) Iron shifts the equilibrium position toward products

Solution 12

Solid iron provides a surface for N_2 and H_2 to adsorb onto, weakening their strong covalent bonds and providing a lower-energy pathway; the iron is a solid catalyst acting on gaseous reactants, so it is **heterogeneous**, and it is not consumed. **(A)**.

Problem 13 (AHL)

Outline, using two half-equations, how iron(II) ions catalyse the reaction $S_2O_8^{2-}+2I^- \rightarrow 2SO_4^{2-}+I_2$, and explain why this reaction is otherwise slow.

Solution 13

The uncatalysed reaction is slow because $S_2O_8^{2-}$ and I^- are both negatively charged and strongly repel each other. Fe^{2+} avoids this direct collision by reacting with each ion separately: (1) $2Fe^{2+}+S_2O_8^{2-} \rightarrow 2Fe^{3+}+2SO_4^{2-}$; (2) $2Fe^{3+}+2I^- \rightarrow 2Fe^{2+}+I_2$. Adding the two steps regenerates Fe^{2+} and reproduces the overall equation, confirming iron acts as a true (homogeneous) catalyst.

Problem 14 (AHL)

In the Contact process, V_2O_5 catalyses $SO_2(g)+\frac{1}{2}O_2(g) \rightarrow SO_3(g)$. Write two steps showing the vanadium oxidation-state change, and state which general property of transition metals

this illustrates.

Solution 14

Step 1: $SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4$ (vanadium reduced from $+5$ to $+4$ as it supplies an oxide ion to oxidise SO_2). Step 2: $V_2O_4 + \frac{1}{2}O_2 \rightarrow V_2O_5$ (vanadium reoxidised from $+4$ back to $+5$, regenerating the catalyst). This illustrates that transition metals can catalyse redox reactions by cycling between **variable oxidation states**.

Problem 15

C_5H_{12} has how many structural (chain) isomers?

(A) 3
(B) 2
(C) 4
(D) 5

Solution 15

Pentane, 2-methylbutane, and 2,2-dimethylpropane – **3** isomers. **(A)**.

Problem 16

The functional group present in $CH_3CH_2CH_2OH$ is:

(A) Alcohol
(B) Carboxylic acid
(C) Aldehyde
(D) Ether

Solution 16

The terminal $-OH$ bonded to a saturated carbon chain identifies an **alcohol** (propan-1-ol). **(A)**.

Problem 17 (AHL)

Which of the following alkenes exhibits E/Z isomerism?

(A) But-2-ene, $CH_3CH{=}CHCH_3$
(B) But-1-ene, $CH_2{=}CHCH_2CH_3$
(C) 2-methylpropene, $CH_2{=}C(CH_3)_2$
(D) Propene, $CH_2{=}CHCH_3$

Solution 17

Only but-2-ene has two *different* substituents (CH_3, H) on *each* double-bond carbon. The other three each have a terminal CH_2 (two identical H's) or two identical CH_3 groups on one carbon, ruling out E/Z isomerism. **(A)**.

Problem 18

A compound with molecular formula C_3H_6O could be propanal (CH_3CH_2CHO) or propanone (CH_3COCH_3). These are examples of:

(A) Functional group isomers
(B) E/Z isomers
(C) Optical isomers
(D) Positional isomers

Solution 18

Propanal (aldehyde) and propanone (ketone) share a molecular formula but have entirely different functional groups $\Longrightarrow$ **functional group isomers. (A).**

Problem 19

Name the haloalkane $CH_3{-}CH_2{-}CHCl{-}CH_2{-}CH_3$.

Solution 19

Longest chain: 5 carbons $\Longrightarrow$ pentane. The chlorine substituent sits on the middle (3rd) carbon; because the chain is symmetric, numbering from either end gives locant 3. Name: **3-chloropentane**.

Problem 20

Name the ketone $CH_3{-}CH_2{-}CO{-}CH_2{-}CH_3$.

Solution 20

Longest chain: 5 carbons $\Longrightarrow$ pentane, with a ketone (–one suffix). The carbonyl carbon is the middle (3rd) carbon of a symmetric chain, so its locant is 3 from either end. Name: **pentan-3-one** (common name diethyl ketone).

Problem 21

Name the branched alkane $(CH_3)_3C{-}CH_2{-}CH_3$.

Solution 21

Longest chain: number the four carbons of the chain $C(CH_3)_3{-}CH_2{-}CH_3$ as butane (C1 is one of the methyls attached to the quaternary carbon, extended through to C4). The quaternary carbon (C2) carries two extra methyl substituents. Numbering to give the substituents the lowest locants gives $2, 2$. Name: **2,2-dimethylbutane**.

Problem 22

Identify the functional group in ethyl ethanoate, $CH_3COOCH_2CH_3$.

(A) Ester
(B) Ether
(C) Carboxylic acid
(D) Ketone

Solution 22

The $-COO-$ linkage between two carbon groups identifies an **ester**. **(A).**

Problem 23

Identify the functional group in propan-1-amine, $CH_3CH_2CH_2NH_2$.

(A) Amine
(B) Amide
(C) Nitrile
(D) Ether

Solution 23

A terminal $-NH_2$ group bonded to a saturated carbon chain identifies an **amine**. **(A)**.

Problem 24

CH_3OCH_3 (dimethyl ether) and CH_3CH_2OH (ethanol) share the molecular formula C_2H_6O. Identify the functional group in each, and state what type of isomers they are.

Solution 24

CH_3OCH_3 contains an **ether** linkage ($-O-$ between two carbon groups, no $O-H$); CH_3CH_2OH contains an **alcohol** group ($-OH$ on carbon). Because the molecular formula is identical but the functional groups are completely different, they are **functional group isomers**.

Problem 25 (AHL)

Does chloroethene, $CH_2{=}CHCl$, show E/Z isomerism? Justify your answer.

Solution 25

No. The terminal carbon of the double bond (CH_2) carries two identical H atoms. Even though the other carbon carries two different groups (Cl, H), *both* carbons must carry two different substituents for E/Z isomerism to exist, so chloroethene shows **no** E/Z isomerism.

Problem 26 (AHL)

Does 1,2-dichloroethene, $CHCl{=}CHCl$, show E/Z isomerism? If so, describe the two forms.

Solution 26

Yes. Each carbon of the double bond carries Cl and H – two different groups on each carbon. The *cis*/Z-form has both Cl atoms on the same side of the double bond; the *trans*/E-form has the two Cl atoms on opposite sides.

Problem 27 (AHL)

(a) Identify the chiral centre in 2-chlorobutane, $CH_3CHClCH_2CH_3$, and list its four substituents.
(b) Explain why 2-chloropropane, $CH_3CHClCH_3$, is not chiral.

Solution 27

(a) C2 is the chiral centre, bonded to Cl, H, CH_3, and CH_2CH_3 – four different groups.
(b) In 2-chloropropane, C2 is bonded to Cl, H, CH_3, and CH_3 – the two methyl groups are identical, so only three distinct groups are present, and C2 is not a chiral centre.

Problem 28 (AHL)

Benzene's six C–C bond lengths are best described as:

(A) All equal, $\approx$ 139 pm, intermediate between a C–C single bond and a C=C double bond

(B) Alternating 154 pm and 134 pm, as in cyclohexatriene

(C) All equal to a pure C=C double bond, 134 pm

(D) All equal to a pure C–C single bond, 154 pm

Solution 28

Delocalisation of the six π electrons around the whole ring makes every C–C bond identical and intermediate in length between a single and a double bond. **(A)**.

Problem 29 (AHL)

Predict, with a reason, whether benzene will decolourise bromine water in the way cyclohexene does, and describe the reaction benzene undergoes with bromine instead, in the presence of a catalyst such as $FeBr_3$.

Solution 29

Benzene will **not** decolourise bromine water: its six π electrons are delocalised around the ring, giving substantial extra stability that an addition reaction would have to destroy, making addition thermodynamically unfavourable. Instead, with a catalyst such as $FeBr_3$, benzene undergoes **electrophilic substitution**: $C_6H_6 + Br_2 \xrightarrow{FeBr_3} C_6H_5Br + HBr$, replacing one ring hydrogen with bromine while keeping the stable delocalised ring intact.

Problem 30

An element Y has electron configuration $[\text{Ne}]3s^23p^4$. (a) Identify its block and group. (b) Predict whether it is a metal, metalloid, or non-metal. (c) State whether its first ionisation energy is higher or lower than phosphorus's ($[\text{Ne}]3s^23p^3$), and explain why.

Solution 30

(a) The last subshell filled is $3p$, with 6 total valence electrons ($3s^23p^4$) $\implies$ p-block, **Group 16** (Y is sulfur).
(b) A Group 16 p-block element with high Z_{eff} and high electronegativity $\implies$ **non-metal**.
(c) Lower. Sulfur's fourth $3p$ electron must pair up in an already-occupied $3p$ orbital (phosphorus's three $3p$ electrons are all unpaired), and the resulting electron-electron repulsion makes that electron easier to remove than phosphorus's greater nuclear charge alone would predict ($IE_1(\text{S}) = 1000$ kJ/mol $< IE_1(\text{P}) = 1012$ kJ/mol).

Problem 31 (AHL)

An organic compound has molecular formula C_4H_8. (a) Give the names and structures of two structural (positional) isomers with this formula that are alkenes. (b) State which of these two isomers shows E/Z isomerism, and explain why the other does not.

Solution 31

(a) But-1-ene, $CH_2{=}CHCH_2CH_3$, and but-2-ene, $CH_3CH{=}CHCH_3$ – the double bond occupies a different position on the same 4-carbon skeleton, so these are **positional isomers**.

(b) But-2-ene shows E/Z isomerism, because each double-bond carbon carries CH_3 and H (two different groups). But-1-ene does *not*, because its terminal double-bond carbon ($=CH_2$) carries two identical H atoms.

Problem 32

Using the general formula $C_nH_{2n+1}COOH$ for the carboxylic-acid homologous series, give the molecular formula and name of the member with $n = 3$.

Solution 32

With $n = 3$: C_3H_7COOH, i.e. $CH_3CH_2CH_2COOH$ – **butanoic acid** (the carboxyl carbon itself is the 4th carbon, so the full molecule is $C_4H_8O_2$; the parent chain including the $-COOH$ carbon is butane-based, hence the "but-" stem despite $n = 3$ in the C_nH_{2n+1} part of the formula).

Problem 33 (AHL)

Vanadium forms the ion VO_2^+. Determine its oxidation state, and state whether this supports vanadium being classified as a transition element.

Solution 33

For VO_2^+ (overall charge $+1$): $x + 2(-2) = +1 \implies x - 4 = +1 \implies x = +5$. Vanadium is $+5$ here, which as $[Ar]3d^0$ has no partially filled d subshell – but vanadium also forms V^{3+} ($3d^2$) and VO^{2+} ($3d^1$), which *do* have partially filled d subshells, so vanadium is still correctly classified as a transition element overall (the definition requires only *at least one* such ion).

Problem 34 (AHL)

Explain, in terms of π-electron delocalisation, why phenol (C_6H_5OH) undergoes electrophilic substitution reactions rather than the addition reactions typical of simple alcohols' carbon skeleton, and why its aromatic ring's C–C bonds remain equal in length even with the $-OH$ substituent attached.

Solution 34

Phenol's six-membered ring retains the same delocalised system of six π electrons spread continuously over all six ring carbons as in benzene itself; the $-OH$ group is simply a substituent attached to one ring carbon and does not localise the ring's π electrons into discrete double bonds. Because the ring's extra delocalisation stability (≈ 150 kJ/mol) is preserved, addition across the ring remains thermodynamically unfavourable, so phenol reacts by **electrophilic substitution** on the ring (in fact more readily than benzene, because the oxygen's lone pair feeds additional electron density into the ring), and all six ring C–C bonds remain equal in length, exactly as in unsubstituted benzene.

Problem 35

Using Pauling electronegativities H $= 2.20$ and F $= 3.98$, classify the H–F bond.

(A) Polar covalent
(B) Non-polar covalent
(C) Ionic
(D) Metallic

Solution 35

$\Delta EN = |3.98 - 2.20| = 1.78$, which is less than 1.8, so the bond is classified as **polar covalent** rather than ionic – consistent with HF being a molecular (covalent) compound, not an ionic solid. **(A)**.

Problem 36

S^{2-}, Cl^{-}, K^{+} and Ca^{2+} are all isoelectronic with argon (18 electrons each). Rank them from smallest to largest radius.

Solution 36

All four have the identical electron configuration [Ar], so radius is determined entirely by nuclear charge Z: Ca^{2+} ($Z = 20$) < K^{+} ($Z = 19$) < Cl^{-} ($Z = 17$) < S^{2-} ($Z = 16$). The larger the nuclear charge pulling on the same 18 electrons, the smaller the ion, so smallest to largest:

$$Ca^{2+} < K^{+} < Cl^{-} < S^{2-}.$$

Problem 37

Predict the acid–base character of Na_2O and P_4O_{10}, and write one balanced equation showing each oxide reacting with water.

Solution 37

Na is a Group 1 metal, so Na_2O is **basic**: $Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$. P is a Group 15 non-metal, so P_4O_{10} is **acidic**: $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$.

Problem 38 (AHL)

Adding concentrated hydrochloric acid to a pink aqueous solution of $[Co(H_2O)_6]^{2+}$ turns it blue, as $[CoCl_4]^{2-}$ forms. Explain why this colour change occurs.

Solution 38

This is a ligand-substitution reaction: the six H_2O ligands are replaced by four Cl^{-} ligands, and the coordination number changes from 6 to 4. Both the change in ligand identity (different field strength) and the change in geometry/coordination number alter the size of the d-orbital splitting energy, so a different wavelength of visible light is absorbed for the d–d transition. Since the cobalt ion's d-electron count (Co^{2+}, $3d^7$, partially filled) is unchanged, the complex remains coloured throughout, but the specific colour observed (pink → blue) changes because the absorbed wavelength has changed.

Problem 39 (AHL)

For CHF=CHCl, if the isomer has F and Cl on the same side of the double bond, is it the E or Z isomer?

Solution 39

On each carbon, the only substituents are a halogen and H, so the halogen is automatically the higher-priority group on its carbon (F, $Z = 9 > $ H, $Z = 1$; Cl, $Z = 17 > $ H, $Z = 1$). With the two higher-priority groups (F and Cl) on the *same* side, this is the Z-isomer.

Problem 40

SiO_2 does not react with dilute, cold sodium hydroxide solution, but does react (slowly) with concentrated, hot sodium hydroxide solution to form sodium silicate. Explain why SiO_2 is described as only *weakly* acidic, and write the equation for its reaction with concentrated hot NaOH.

Solution 40

SiO_2 is a **giant covalent (macromolecular)** structure in which every silicon atom is bonded to four oxygens in a continuous three-dimensional network. Breaking enough strong Si—O covalent bonds throughout this lattice to allow reaction requires far more energy than breaking apart a simple molecular or ionic oxide, so SiO_2 only reacts under forcing conditions (concentrated base, heated), unlike a typical acidic oxide such as SO_3 or P_4O_{10} that reacts readily with dilute base at room temperature. Equation: $SiO_2(s) + 2NaOH(aq) \rightarrow Na_2SiO_3(aq) + H_2O(l)$.

Problem 41

BeO reacts with both dilute acids and dilute bases, whereas MgO (the oxide of the element directly below beryllium) reacts only with acids. Explain this difference using the diagonal relationship.

Solution 41

Beryllium (Group 2, Period 2) shows a diagonal relationship to aluminium (Group 13, Period 3), because moving one group right and one period down leaves the charge density (charge/radius ratio) of the two elements similar. Since Al_2O_3 is amphoteric, BeO is also **amphoteric** by the same diagonal resemblance, reacting with acids (as a base) and with bases (as an acid). MgO, a typical Group 2 oxide, is simply and only **basic**, with no such diagonal partner among the acidic p-block oxides.

Problem 42 (AHL)

Write the full ground-state electron configuration of chromium ($Z = 24$) and of copper ($Z = 29$), and explain why each deviates from the configuration predicted by strictly following the Aufbau building-up order.

Solution 42

Chromium: $[Ar]3d^5 4s^1$ (not the "expected" $[Ar]3d^4 4s^2$). Copper: $[Ar]3d^{10} 4s^1$ (not the "expected" $[Ar]3d^9 4s^2$). In both cases, promoting one $4s$ electron into the $3d$ subshell produces a **half-filled** ($3d^5$, chromium) or **completely filled** ($3d^{10}$, copper) d subshell, which is an unusually stable, low-energy arrangement (minimised electron-electron repulsion and, for the half-filled case, maximised exchange stabilisation); this extra stability outweighs the small energy cost of leaving only one electron in the $4s$ subshell.

Problem 43 (AHL)

A complex ion has six ligands bonded to the central metal ion. Its coordination number and typical geometry are:

(A) 6, octahedral

(B) 4, tetrahedral

(C) 6, square planar

(D) 4, octahedral

Solution 43

Six ligands around a central metal ion is coordination number 6, and the six ligands typically arrange themselves as far apart as possible, giving an **octahedral** geometry. **(A)**.

Problem 44

Name the alkene $CH_2{=}CH{-}CH_2{-}CH(CH_3){-}CH_3$.

Solution 44

Longest chain containing the double bond: 5 carbons $\Longrightarrow$ pentene. Numbering from the left gives the double bond locant 1 (the lowest possible value) and the methyl substituent locant 4; since the double bond (principal characteristic group) must have the lowest locant, numbering from the left is correct regardless of the substituent's locant. Name: **4-methylpent-1-ene**.

Problem 45

Hexane, 2-methylpentane, and 2,2-dimethylbutane are all C_6H_{14}. Rank them from highest to lowest boiling point and justify your ranking.

Solution 45

All three have identical molecular formula and no functional group (all alkanes), so relative boiling point is governed entirely by the strength of London dispersion forces, which weaken as the molecule becomes more compact/branched (less surface-area contact between molecules). Hexane (unbranched) $>$ 2-methylpentane (one branch) $>$ 2,2-dimethylbutane (most compact, two branches at the same carbon):

$$\text{hexane } (69^\circ\text{C}) > \text{2-methylpentane } (60^\circ\text{C}) > \text{2,2-dimethylbutane } (50^\circ\text{C}).$$

Problem 46

But-1-ene and but-2-ene, both C_4H_8, are examples of:

(A) Positional isomers
(B) Chain isomers
(C) Functional group isomers
(D) Optical isomers

Solution 46

Both are alkenes (same functional group) with the same unbranched 4-carbon skeleton (same connectivity pattern), differing only in *where* the double bond sits on the chain $\Longrightarrow$ **positional isomers**. **(A)**.

Problem 47

Identify the functional group in $CH_3CH_2CH_2CN$.

(A) Nitrile
(B) Amine
(C) Amide
(D) Alkene

Solution 47

The $-C\equiv N$ group identifies a **nitrile** (butanenitrile, counting the nitrile carbon as part of the 4-carbon chain). **(A)**.

Problem 48

Using the diagonal relationship, predict whether Li_2O is likely to resemble Na_2O (same group) or show a more covalent, less strongly basic character resembling MgO, and explain briefly.

Solution 48

Lithium shows a diagonal relationship to magnesium (e.g. both Li_2CO_3 and $MgCO_3$ decompose on heating, unlike thermally stable Na_2CO_3), because Li^+ is unusually small and highly charge-dense for Group 1, giving it noticeably more covalent, polarising character than the larger Group 1 cations below it. Li_2O is therefore still **basic** like Na_2O (both are Group 1 oxides), but is expected to be **less strongly/purely ionic-basic** than Na_2O, with somewhat more covalent character – resembling the diagonally-related MgO more than a typical heavier Group 1 oxide would.

Problem 49

How many structural (chain) isomers does C_6H_{14} have? List their names.

Solution 49

C_6H_{14} has **5** chain isomers: hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane. (This is one more than the 3 isomers of C_5H_{12} – the number of possible chain isomers grows quickly with chain length as there are more distinct places to branch.)

Problem 50

Which has the higher first ionisation energy, Mg or Ca?

(A) Mg
(B) Ca
(C) They are equal
(D) Cannot be determined

Solution 50

Mg and Ca are both Group 2, with Mg above Ca. Ionisation energy decreases down a group (larger radius, more shielding, outer electrons farther from the nucleus), so Mg has the higher IE_1. **(A)**.

Problem 51 (AHL)

Titanium dioxide, TiO_2, containing Ti^{4+}, is used as a white pigment. Predict, with reasoning, whether TiO_2 should be coloured or white/colourless.

Solution 51

Ti^{4+} has configuration $[Ar]3d^0$ – an empty d subshell, so no d–d electron transition is possible (there is no electron to promote within the d orbitals). With no d–d transition available, TiO_2

absorbs no particular wavelength of visible light selectively, consistent with it being **white/-colourless** – exactly why it is used as a white pigment.

Problem 52

Name the aldehyde $CH_3CH_2CH_2CHO$.

Solution 52

The chain has 4 carbons including the carbonyl carbon, which (being an aldehyde) is always C1. Parent chain: butane; suffix: –al. Name: **butanal**.

Problem 53

Which oxide would you expect to form the more strongly acidic (lower pH) aqueous solution: Cl_2O_7 or Na_2O?

(A) Cl_2O_7
(B) Na_2O
(C) Both give the same pH
(D) Neither dissolves in water

Solution 53

Cl is a highly electronegative non-metal with the maximum number of oxygens bonded in this oxide, giving Cl_2O_7 strongly acidic character (it reacts with water to form the very strong acid $HClO_4$); Na_2O is a Group 1 metal oxide and is strongly basic. **(A)**.

Problem 54

Using Pauling electronegativities Ca $= 1.00$ and O $= 3.44$, classify the bond in CaO.

(A) Ionic
(B) Non-polar covalent
(C) Polar covalent
(D) Metallic

Solution 54

$\Delta EN = |3.44 - 1.00| = 2.44 > 1.8$, so the Ca–O interaction is classified as predominantly **ionic** – consistent with CaO being an ionic solid (quicklime), not a covalent molecule. **(A)**.

Problem 55

Propan-1-ol, $CH_3CH_2CH_2OH$, and propan-2-ol, $CH_3CH(OH)CH_3$, share the molecular formula C_3H_8O and the same functional group (alcohol). What type of isomers are they, and what distinguishes propan-2-ol structurally?

Solution 55

Both are alcohols with the same 3-carbon skeleton, differing only in *where* the –OH group is attached (C1 vs C2) $\Longrightarrow$ **positional isomers**. In propan-2-ol, the –OH is on the central (C2) carbon, which is bonded to two CH_3 groups, H, and OH – since two of the four groups are identical (CH_3, CH_3), C2 is *not* a chiral centre.

Problem 56 (AHL)

Explain briefly why Sc, despite being a d-block element, is not classified as a transition element, and why this matters for predicting whether its compounds are coloured.

Solution 56

Scandium forms only one common ion, Sc^{3+}, which has configuration $[Ar]3d^0$ – a completely *empty* d subshell, not a *partially* filled one, so scandium does not meet the definition of a transition element (at least one ion with a partially filled d subshell). This matters directly for colour: with $3d^0$, no d–d electron transition is possible, so Sc^{3+} compounds are colourless, just like the other non-transition d-block ion, Zn^{2+} ($3d^{10}$).

Problem 57

An unknown Period 3 element Z has successive ionisation energies (kJ/mol) of $786,\ 1577,\ 3232,\ 4356,\ 16\,091,\ 19\,805$. (a) Identify the group Z belongs to, using the position of the large jump. (b) Name the element, given it is in Period 3.

Solution 57

(a) The large jump occurs between the 4th ionisation energy (4356) and the 5th ($16\,091$, roughly a 3.7-fold increase), showing that the first four electrons come from the valence shell while the 5th comes from a full, much lower-energy inner shell. Four valence electrons $\Longrightarrow$ **Group 14**. **(b)** A Period 3, Group 14 element is **silicon**, Si (consistent with $IE_1 = 786$ kJ/mol, matching the Period 3 trend value used in Section 3.1.5).

Problem 58

Draw on your knowledge of homologous series (Section 3.2.1) to state the molecular formula of the alkene with 6 carbon atoms, and give its general class of isomerism relative to cyclohexane, C_6H_{12} (a ring-shaped, saturated hydrocarbon with the same molecular formula).

Solution 58

Using the alkene general formula C_nH_{2n} with $n = 6$: molecular formula C_6H_{12} (e.g. hex-1-ene). Since cyclohexane is also C_6H_{12} but has an entirely different structural feature (a saturated ring instead of a chain with a C=C double bond) and a different functional-group classification (cycloalkane vs. alkene), the two compounds are **functional group isomers** of one another.

Reactivity 1 --- What Drives Chemical Reactions?

Mục tiêu Unit: Hiểu động lực chi phối phản ứng hoá học: đo sự thay đổi enthalpy bằng nhiệt lượng kế ($q = mc\Delta T$); áp dụng định luật Hess và chu trình Born–Haber (AHL) để tính các enthalpy không thể đo trực tiếp; ước lượng ΔH từ năng lượng liên kết và so sánh mật độ năng lượng của các loại nhiên liệu; và (AHL) vận dụng entropy cùng năng lượng tự do Gibbs $\Delta G = \Delta H - T\Delta S$ để dự đoán chiều tự diễn ra của phản ứng theo nhiệt độ.

4.1 Measuring enthalpy changes

An **exothermic** reaction releases heat to the surroundings ($\Delta H < 0$); an **endothermic** reaction absorbs heat from the surroundings ($\Delta H > 0$). Enthalpy H is a **state function**: the enthalpy change of a reaction, $\Delta H = H_{\text{products}} - H_{\text{reactants}}$, depends only on the initial and final states, never on the pathway taken between them. This single fact underlies calorimetry, Hess's Law, and every energy cycle in this chapter.

4.1.1 Standard enthalpy changes: definitions and conventions

To compare enthalpy changes measured in different laboratories, chemists quote them under **standard conditions**: a pressure of 100 kPa, a stated temperature (usually 298 K, i.e. 25°C), and all solutions at a concentration of 1 mol dm^{-3}. An enthalpy change measured under these conditions carries the symbol ΔH°, read "delta H standard."

Key standard enthalpy definitions

- **Standard enthalpy 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. By definition, ΔH_f° of **any element in its standard state is zero**: $\Delta H_f^\circ(\text{O}_2(\text{g})) = 0$, $\Delta H_f^\circ(\text{C}(\text{s, graphite})) = 0$, $\Delta H_f^\circ(\text{Na}(\text{s})) = 0$.
- **Standard enthalpy 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.
- **Standard enthalpy of neutralisation**, $\Delta H_{\text{neut}}^\circ$: the enthalpy change when an acid and a base react in dilute aqueous solution, under standard conditions, to form **1 mole** of $\text{H}_2\text{O}(\text{l})$.

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Điều kiện chuẩn: 100 kPa, thường ở 298 K (25°C), dung dịch 1 mol dm^{-3}. Quy ước quan trọng nhất: ΔH_f° của một **nguyên tố** ở trạng thái chuẩn của nó LUÔN bằng 0 — đây là nền tảng để tính mọi enthalpy hình thành khác (xem Mục 2.2). ΔH_c° đo khi đốt cháy hoàn toàn 1 mol chất trong oxi dư; $\Delta H_{\text{neut}}^\circ$ đo khi acid và base phản ứng vừa đủ để tạo ra đúng 1 mol nước.

4.1.2 Enthalpy level diagrams

An **enthalpy level diagram** compares the relative enthalpy of reactants and products with two horizontal lines, joined by a vertical arrow labelled ΔH. Unlike the reaction pathway diagrams below, a level diagram shows *no* activation energy or transition state — it records only the initial and final enthalpy, which is exactly the information Hess's Law cycles need (Section 2).

Enthalpy level diagrams: exothermic (products lower, $\Delta H < 0$) versus endothermic (products higher, $\Delta H > 0$). The dashed line marks the reactants' enthalpy for comparison.

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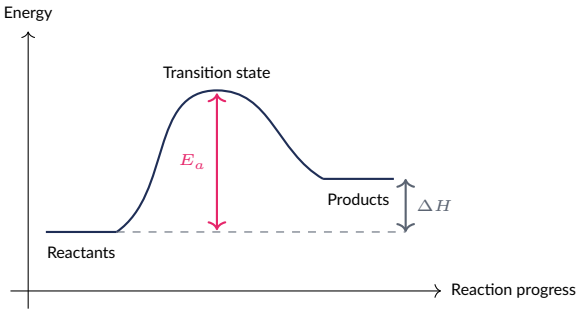
Giản đồ mức enthalpy chỉ vẽ hai đường ngang (mức năng lượng của chất phản ứng và sản phẩm) nối bằng mũi tên ΔH — KHÔNG có đường cong hay năng lượng hoạt hoá. Đây là dạng giản đồ dùng trong định luật Hess (Mục 2), khác với giản đồ đường phản ứng bên dưới (có hình "đồi").

4.1.3 Reaction pathway diagrams and activation energy

A **reaction pathway diagram** (or energy profile) plots energy against reaction progress and shows a curved hump between reactants and products, peaking at the **transition state** (activated complex). The height of this hump above the reactants is the **activation energy**, E_a: the minimum energy colliding particles must possess for a reaction to occur. Unlike ΔH, activation energy is always positive for both the forward and reverse reaction. The three quantities are linked by

$$\Delta H = E_a(\text{forward}) - E_a(\text{reverse}) \quad \Longrightarrow \quad E_a(\text{reverse}) = E_a(\text{forward}) - \Delta H.$$



Reaction pathway diagram: E_a is the energy barrier from reactants up to the transition state; ΔH is the overall energy difference between products and reactants (here exothermic, $\Delta H < 0$).

Ví dụ mẫu · Activation energy of the reverse reaction

A forward reaction has $E_a = +75$ kJ mol^{-1} and $\Delta H = -40$ kJ mol^{-1}. Find E_a for the reverse reaction.

$$E_a(\text{reverse}) = E_a(\text{forward}) - \Delta H = 75 - (-40) = 115 \text{ kJ mol}^{-1}.$$

The reverse (endothermic) reaction always has a higher activation energy than the forward (here exothermic) reaction, by exactly $|\Delta H|$.

VN GIẢI THÍCH TIẾNG VIỆT

E_a(nghịch)= E_a(thuận)$-\Delta H$. Với phản ứng toả nhiệt ($\Delta H < 0$), năng lượng hoạt hoá chiều nghịch luôn LỚN HƠN chiều thuận — vì hệ phải "leo" từ mức sản phẩm (thấp) lên đúng đỉnh của "ngọn đồi" hoạt hoá, một quãng đường dài hơn.

Bài tập luyện tập

On a reaction pathway diagram, the reactants sit at a lower energy level than the products, and the peak (transition state) lies well above both. This reaction is:

(A) exothermic, with $E_a(\text{forward}) < E_a(\text{reverse})$

(B) endothermic, with $E_a(\text{forward}) > E_a(\text{reverse})$

(C) endothermic, with $E_a(\text{forward}) < E_a(\text{reverse})$

(D) exothermic, with $E_a(\text{forward}) = E_a(\text{reverse})$

Lời giải chi tiết

Products higher than reactants means $\Delta H > 0$: endothermic. Since $\Delta H = E_a(\text{forward}) - E_a(\text{reverse})$ and $\Delta H > 0$, it follows that $E_a(\text{forward}) > E_a(\text{reverse})$ — the uphill (forward) climb from the low reactants to the peak is steeper than the downhill (reverse) climb from the already-high products to that same peak. **(B)**.

4.1.4 Calorimetry: measuring heat with $q = mc\Delta T$

A **calorimeter** measures heat transferred during a reaction by monitoring the temperature change of a known mass of water (or solution) surrounding it:

$$q = mc\Delta T,$$

where q is heat transferred (J), m is the mass of water/solution (g), c is its specific heat capacity (4.18 J g^{-1} °C^{-1} for water), and ΔT is the temperature change (°C or K, numerically identical). For a reaction carried out in solution, the molar enthalpy change is

$$\Delta H = -\frac{q}{n},$$

where n is the amount (mol) of the limiting reactant. The minus sign converts a measured, positive q (heat released *to* the surroundings, i.e. to the water) into a negative ΔH for an exothermic reaction, consistent with the sign convention in Section 1.1.

Ví dụ mẫu · Worked example

How much heat is needed to raise 200.0 g of water from 18.0°C to 82.0°C ($c = 4.18$ J g^{-1} °C^{-1})?

$$q = mc\Delta T = (200.0)(4.18)(64.0) = 53{,}504 \text{ J} = 53.5 \text{ kJ}.$$

VN GIẢI THÍCH TIẾNG VIỆT

Nhiệt lượng kế đo nhiệt trao đổi bằng $q = mc\Delta T$. Với phản ứng trong dung dịch, ΔH của phản ứng (theo mol chất phản ứng) $= -\frac{q}{n}$ — dấu trừ vì nhiệt **toả ra** từ phản ứng ($q > 0$ đo được) tương ứng $\Delta H < 0$ (phản ứng toả nhiệt).

Ví dụ mẫu · Combustion calorimetry

A 0.700 g sample of ethanol, $C_2H_5OH(l)$ ($M = 46.08$ g mol^{-1}), is burned beneath a metal can containing 200.0 g of water, raising its temperature from 20.0°C to 45.0°C. Calculate the experimental molar enthalpy of combustion of ethanol.

Step 1 — heat absorbed by the water:

$$q = mc\Delta T = (200.0)(4.18)(25.0) = 20{,}900 \text{ J} = 20.9 \text{ kJ}.$$

Step 2 — moles of ethanol burned:

$$n = \frac{0.700}{46.08} = 0.01519 \text{ mol}.$$

Step 3 — molar enthalpy of combustion:

$$\Delta H_c = -\frac{q}{n} = -\frac{20{,}900}{0.01519} \approx -1.38 \times 10^3 \text{ kJ mol}^{-1} \ (-1376 \text{ kJ mol}^{-1}).$$

This experimental value is reasonably close to the accepted literature value of -1367 kJ mol^{-1}; the small discrepancy is typical of a simple calorimetry set-up, where some heat escapes to the surroundings and the calorimeter itself, and combustion may be slightly incomplete.

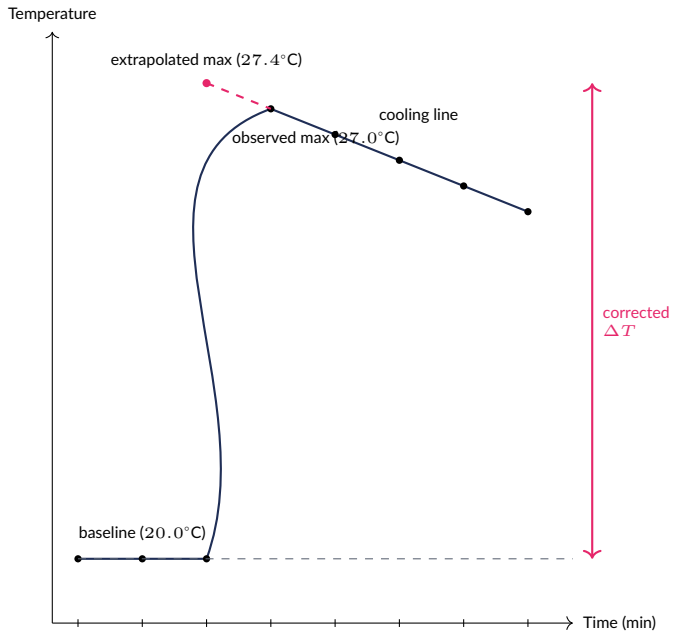
VN **GIẢI THÍCH TIẾNG VIỆT**

Nhiệt lượng kế đơn giản (đốt nhiên liệu để đun nước) là phương pháp thực nghiệm phổ biến để đo ΔH_c°. Ba bước: (1) tính q nước hấp thụ; (2) tính số mol nhiên liệu đã cháy ($n = m/M$); (3) $\Delta H_c = -q/n$. Kết quả thực nghiệm thường *kém âm hơn* giá trị lý thuyết do thất thoát nhiệt ra môi trường xung quanh và bản thân dụng cụ đo.

(!) Lỗi thường gặp: Two very common slips in calorimetry calculations: (1) mixing up units — q comes out in J, but ΔH_c° values in data tables are in kJ mol^{-1}, so remember to divide by 1000; (2) forgetting that the mass m in $q = mc\Delta T$ is the mass of the water/solution being heated, *not* the mass of the fuel or solid reactant that reacted.

4.1.5 Correcting for heat loss: the cooling-correction graph

In a real experiment, mixing is not instantaneous and heat continues to escape to the surroundings throughout the measurement, so the maximum temperature actually recorded is already somewhat lower than the true maximum the reaction would have produced with no heat loss at all. The standard correction is to record the temperature at regular time intervals both *before* and *after* the reaction, plot temperature against time, and extrapolate the steady post-reaction "cooling" trend back to the moment of mixing. The vertical gap, at that instant, between this extrapolated line and the (extrapolated) baseline gives a **corrected** ΔT that is closer to the true, heat-loss-free value than the naive difference between the observed maximum and the starting temperature.



Cooling-correction graph: the post-reaction cooling trend is extrapolated (dashed) back to the moment of mixing ($t = 0$), giving a corrected temperature rise larger than the value read directly off the observed maximum.

Ví dụ mẫu · Applying a cooling correction

Before mixing, a calorimeter reads a steady $20.0°$C. After mixing at $t = 0$, the temperature rises rapidly to an observed maximum of $27.0°$C at $t = 1.0$ min, after which it cools steadily at a constant rate of $0.4°$C per minute. Find the corrected temperature rise.

Extrapolating the cooling line back one minute, from $t = 1.0$ to $t = 0$, adds back the heat lost during that first minute:

$$T_{\text{corrected}}(t = 0) = 27.0 + (1.0)(0.4) = 27.4°\text{C}.$$

$\Delta T_{\text{corrected}} = 27.4 - 20.0 = 7.4°$C (compared with the uncorrected $\Delta T = 27.0 - 20.0 = 7.0°$C).

Using the corrected, larger ΔT in $q = mc\Delta T$ gives a larger q, and hence a more exothermic (larger-magnitude) ΔH — closer to the true literature value.

VN GIẢI THÍCH TIẾNG VIỆT

Vì phản ứng không xảy ra tức thời và nhiệt liên tục thất thoát, nhiệt độ cực đại QUAN SÁT ĐƯỢC luôn thấp hơn nhiệt độ cực đại THỰC. Cách khắc phục: vẽ đồ thị nhiệt độ theo thời gian, ngoại suy đường "nguội dần" sau phản ứng về đúng thời điểm trộn ($t = 0$) để tìm ΔT đã hiệu chỉnh — luôn LỚN HƠN ΔT chưa hiệu chỉnh, cho kết quả ΔH gần giá trị thật hơn.

Bài tập luyện tập

A calorimetry experiment has a steady baseline of $19.5°$C before mixing. The observed maximum after mixing is $24.8°$C at $t = 1.0$ min, after which the mixture cools steadily at $0.30°$C per minute. Estimate the corrected temperature rise using the extrapolation method.

Lời giải chi tiết

Extrapolating back one minute: $T_{\text{corrected}}(t=0) = 24.8 + (1.0)(0.30) = 25.1\,^{\circ}\text{C}$.

$$\Delta T_{\text{corrected}} = 25.1 - 19.5 = 5.6\,^{\circ}\text{C}.$$

4.1.6 Improving accuracy: bomb calorimetry

The simple "spirit burner" set-up above is easy to build but loses a large fraction of the heat released — to the surrounding air, to the metal can, and through incomplete combustion of the fuel — so its experimental ΔH_c° is almost always less exothermic than the accepted data-book value. A **bomb calorimeter** greatly reduces these losses: the fuel is burned electrically inside a sealed, thick-walled steel container (the "bomb") filled with an excess of pressurised oxygen, ensuring complete combustion; the bomb is immersed in a precisely measured mass of water inside a well-insulated, stirred outer jacket, so almost all the heat released is transferred to that water and none can escape as fuel vapour or smoke.

Sources of error, simple calorimeter vs. bomb calorimeter

- Simple calorimeter: heat lost to the surrounding air and to the metal can/beaker; incomplete combustion in limited, unpressurised air; some fuel may evaporate unburned before combustion is complete.
- Bomb calorimeter: combustion in excess pressurised O_2 ensures completeness; a sealed, insulated, stirred system minimises heat loss to the surroundings; results are far closer to accepted literature values, which is why data booklets are compiled from bomb calorimetry, not spirit-burner experiments.

A bomb calorimeter is often treated as a single system with a known total **heat capacity**, C_{cal} (kJ $^{\circ}\text{C}^{-1}$), covering the water, the steel bomb, and the stirrer together, so that $q = C_{\text{cal}}\Delta T$ replaces $q = mc\Delta T$.

Ví dụ mẫu · Bomb calorimeter with a known heat capacity

A bomb calorimeter has a total heat capacity $C_{\text{cal}} = 10.15$ kJ $^{\circ}\text{C}^{-1}$ (calibrated using benzoic acid, $C_7H_6O_2$, $M = 122.12$ g mol^{-1}, whose $\Delta H_c^{\circ} = -3227$ kJ mol^{-1} is known very precisely). Predict the temperature rise expected when 0.500 g of benzoic acid is burned inside it.

Step 1 — moles of benzoic acid:

$$n = \frac{0.500}{122.12} = 4.094 \times 10^{-3}\ \text{mol}.$$

Step 2 — heat released:

$$q = n \times |\Delta H_c^{\circ}| = (4.094 \times 10^{-3})(3227) = 13.21\ \text{kJ}.$$

Step 3 — temperature rise:

$$\Delta T = \frac{q}{C_{\text{cal}}} = \frac{13.21}{10.15} = 1.30\,^{\circ}\text{C}.$$

Benzoic acid is the standard substance chemists use to calibrate bomb calorimeters, precisely because its ΔH_c° is already known to high accuracy from independent measurements.

GIẢI THÍCH TIẾNG VIỆT

VN Nhiệt lượng kế bomb (bomb calorimeter) coi toàn bộ hệ (nước + vỏ thép + que khuấy) như một "nhiệt dung tổng", C_{cal} (kJ/°C), thay cho mc riêng của nước: $q = C_{\text{cal}}\Delta T$. Acid benzoic được dùng để **hiệu chuẩn** thiết bị vì ΔH_c° của nó đã biết chính xác từ trước.

Bài tập luyện tập

50.0 cm^3 of 1.00 M HCl is mixed with 50.0 cm^3 of 1.00 M NaOH; temperature rises 6.8°C. (Assume density 1.00 g cm^{-3}, $c = 4.18$ J g^{-1} °C^{-1}.) The enthalpy of neutralisation is closest to:

(A) -56.8 kJ mol^{-1}
(C) -113.6 kJ mol^{-1}
(B) -28.4 kJ mol^{-1}
(D) -6.8 kJ mol^{-1}

Lời giải chi tiết

$q = mc\Delta T = (100.0)(4.18)(6.8) = 2842$ J. $n(\text{H}_2\text{O}) = n(\text{HCl}) = 0.0500 \times 1.00 = 0.0500$ mol. $\Delta H = -\dfrac{2842}{0.0500} = -56{,}840$ J mol^{-1} $= -56.8$ kJ mol^{-1}. **(A).**

Bài tập luyện tập

150.0 g of water is heated from 22.0°C to 78.0°C ($c = 4.18$ J g^{-1} °C^{-1}). The heat absorbed is closest to:

(A) 17.6 kJ
(C) 70.2 kJ
(B) 35.1 kJ
(D) 8.77 kJ

Lời giải chi tiết

$\Delta T = 56.0$°C. $q = mc\Delta T = (150.0)(4.18)(56.0) = 35{,}112$ J $= 35.1$ kJ. **(B).**

Bài tập luyện tập

Which of the following has $\Delta H_f^\circ = 0$ by definition, under standard conditions?

(A) $\text{O}_2(\text{g})$
(C) $\text{CO}_2(\text{g})$
(B) $\text{H}_2\text{O}(\text{l})$
(D) $\text{C}(\text{s, diamond})$

Lời giải chi tiết

ΔH_f° of an element in its *standard state* is zero. Oxygen's standard state is $\text{O}_2(\text{g})$, so (A) is correct. Note that graphite, not diamond, is carbon's standard state — $\Delta H_f^\circ(\text{C, diamond})$ is a small *positive* value, not zero, which is why (D) is a trap. **(A).**

Bài tập luyện tập

A forward reaction has $E_a = +150$ kJ mol^{-1} and $\Delta H = -60$ kJ mol^{-1}. The activation energy of the reverse reaction is:

(A) 90 kJ mol^{-1}
(C) 150 kJ mol^{-1}
(B) 60 kJ mol^{-1}
(D) 210 kJ mol^{-1}

Lời giải chi tiết

$E_a(\text{reverse}) = E_a(\text{forward}) - \Delta H = 150 - (-60) = 210$ kJ mol^{-1}. **(D).**

Bài tập luyện tập

A test tube feels noticeably colder immediately after a solid dissolves in water. This process is best described as:

(A) exothermic, $\Delta H < 0$

(B) endothermic, $\Delta H > 0$

(C) exothermic, $\Delta H > 0$

(D) endothermic, $\Delta H < 0$

Lời giải chi tiết

The surroundings lose heat energy to the dissolving process (the water gets colder), meaning the system *absorbs* heat from the surroundings: endothermic, $\Delta H > 0$. **(B).**

Bài tập luyện tập

25.0 cm^3 of 2.00 M HNO_3 is mixed with 25.0 cm^3 of 2.00 M KOH; the temperature rises by 13.4°C. Assuming density 1.00 g cm^{-3} and $c = 4.18$ J g^{-1} °C^{-1}, calculate the enthalpy of neutralisation.

Lời giải chi tiết

Total mass of solution $= 50.0$ g. $q = mc\Delta T = (50.0)(4.18)(13.4) = 2800.6$ J. $n(H_2O) = n(HNO_3) = 0.0250 \times 2.00 = 0.0500$ mol (both reagents are present in exactly equal, stoichiometric amounts). $\Delta H^\circ_{\text{neut}} = -\dfrac{2800.6}{0.0500} = -56{,}012$ J mol^{-1} $= -56.0$ kJ mol^{-1}.

Bài tập luyện tập

A fixed quantity of heat, q, is released by a reaction in solution. If the mass of water used to absorb this heat is doubled (while q stays the same), what happens to the observed temperature rise, ΔT?

(A) ΔT doubles

(B) ΔT stays the same

(C) ΔT is halved

(D) ΔT is quartered

Lời giải chi tiết

Rearranging $q = mc\Delta T$ gives $\Delta T = \dfrac{q}{mc}$; with q and c fixed, ΔT is inversely proportional to m. Doubling m halves ΔT. **(C).**

Bài tập luyện tập

A 200 g block of an unknown metal absorbs 4520 J of heat and its temperature rises by 22.6°C. Its specific heat capacity is closest to:

(A) 0.500 J g^{-1} °C^{-1}

(B) 1.00 J g^{-1} °C^{-1}

(C) 2.00 J g^{-1} °C^{-1}

(D) 4.18 J g^{-1} °C^{-1}

Lời giải chi tiết

Rearranging $q = mc\Delta T$: $c = \dfrac{q}{m\Delta T} = \dfrac{4520}{(200)(22.6)} = \dfrac{4520}{4520} = 1.00$ J g^{-1} °C^{-1}. **(B)**.

Bài tập luyện tập

50.0 cm^3 of 2.00 M $CuSO_4(aq)$ reacts with excess zinc powder; the temperature rises from 21.2°C to 40.7°C. Assuming density 1.00 g cm^{-3} and $c = 4.18$ J g^{-1} °C^{-1}, calculate ΔH per mole of $CuSO_4$ reacted.

Lời giải chi tiết

$\Delta T = 19.5$°C; mass of solution $= 50.0$ g. $q = mc\Delta T = (50.0)(4.18)(19.5) = 4075.5$ J. Zinc is in excess, so $CuSO_4$ is limiting: $n = 0.0500 \times 2.00 = 0.100$ mol. $\Delta H = -\dfrac{4075.5}{0.100} = -40{,}755$ J mol^{-1} $= -40.8$ kJ mol^{-1}.

Bài tập luyện tập

A 0.485 g sample of propan-1-ol, $C_3H_7OH(l)$ ($M = 60.10$ g mol^{-1}), is burned and used to heat 150.0 g of water from 21.0°C to 46.5°C ($c = 4.18$ J g^{-1} °C^{-1}). Calculate the experimental molar enthalpy of combustion.

Lời giải chi tiết

$\Delta T = 25.5$°C. $q = mc\Delta T = (150.0)(4.18)(25.5) = 15{,}988.5$ J. $n = \dfrac{0.485}{60.10} = 8.07 \times 10^{-3}$ mol. $\Delta H_c = -\dfrac{15{,}988.5}{8.07 \times 10^{-3}} \approx -1.98 \times 10^3$ kJ mol^{-1} (-1980 kJ mol^{-1}), somewhat below the accepted magnitude of ≈ -2021 kJ mol^{-1}, consistent with typical heat losses in a simple calorimetry set-up.

Bài tập luyện tập

Compared with a simple spirit-burner calorimeter, a bomb calorimeter gives a measured ΔH_c° that is closer to the accepted (more exothermic) literature value mainly because it:

(A) records a smaller temperature rise

(B) burns the fuel in excess pressurised O_2 inside a sealed, insulated system, minimising heat loss and ensuring complete combustion

(C) uses a much larger mass of fuel

(D) is cheaper to build than a spirit burner

Lời giải chi tiết

Sealing the reaction inside an insulated bomb with excess pressurised oxygen both prevents heat escaping to the surroundings and guarantees complete combustion — the two main sources of error in a simple calorimeter. **(B)**.

Bài tập luyện tập

A bomb calorimeter with total heat capacity $C_{cal} = 8.30$ kJ °C^{-1} is used to combust 1.250 g of glucose, $C_6H_{12}O_6$ ($M = 180.16$ g mol^{-1}); the temperature rises by 2.34°C. Calculate the

experimental molar enthalpy of combustion of glucose.

Lời giải chi tiết

$q = C_{\text{cal}}\Delta T = (8.30)(2.34) = 19.42$ kJ. $n = \dfrac{1.250}{180.16} = 6.938 \times 10^{-3}$ mol. $\Delta H_c = -\dfrac{19.42}{6.938 \times 10^{-3}} \approx -2.80 \times 10^{3}$ kJ mol^{-1} (-2800 kJ mol^{-1}), in close agreement with the accepted literature value, -2803 kJ mol^{-1}.

4.2 Energy cycles: Hess's Law and the Born--Haber cycle

Hess's Law states that the enthalpy change of a reaction is independent of the pathway taken between reactants and products — a direct consequence of enthalpy being a state function. A target ΔH that cannot be measured directly can therefore be found by algebraically combining (reversing, scaling, and/or adding) the equations and enthalpy changes of other, measurable reactions. Two rules govern the combination: **reversing** an equation reverses the sign of its ΔH; **scaling** an equation's coefficients by a factor scales its ΔH by the same factor.

4.2.1 Combining thermochemical equations

A systematic method for Hess's Law problems

1. Write out the **target** equation — the one whose ΔH you are asked to find — fully balanced.
2. Label each given equation (1), (2), (3), …and note which species in each also appear in the target.
3. For each given equation, decide whether it must be **reversed** (if a species is on the "wrong" side compared with the target) and/or **scaled** (if the coefficient does not match the target).
4. Add the (possibly reversed/scaled) equations together; check that every species *not* in the target cancels exactly.
5. Add the corresponding (possibly sign-flipped/scaled) ΔH values using the same operations.

Ví dụ mẫu · Hess's Law

Given: (1) $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$, $\Delta H_1 = -393.5$ kJ; (2) $\text{H}_2\text{(g)} + \tfrac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O(l)}$, $\Delta H_2 = -285.8$ kJ; (3) $\text{CH}_3\text{OH(l)} + \tfrac{3}{2}\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 2\text{H}_2\text{O(l)}$, $\Delta H_3 = -726.0$ kJ. Find $\Delta H_f^\circ(\text{CH}_3\text{OH}, l)$.

The target equation is $\text{C(s)} + 2\text{H}_2\text{(g)} + \tfrac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CH}_3\text{OH(l)}$. Combining $(1) + 2 \times (2) - (3)$ reproduces this exactly (the CO_2 and H_2O cancel, leaving only CH_3OH as product):

$$\Delta H_f = -393.5 + 2(-285.8) - (-726.0) = -393.5 - 571.6 + 726.0 = -239.1 \text{ kJ mol}^{-1}.$$

(Close to the accepted literature value, ≈ -238.4 kJ mol^{-1}.)

VN **GIẢI THÍCH TIẾNG VIỆT**

Định luật Hess: ΔH không phụ thuộc đường đi. Kỹ thuật: viết ra phương trình **mục tiêu**, rồi cộng/trừ/nhân các phương trình đã cho sao cho các chất KHÔNG có trong mục tiêu bị triệt tiêu hai vế. Khi đảo chiều một phương trình, đổi dấu ΔH; khi nhân hệ số, nhân ΔH theo cùng hệ số đó.

Ví dụ mẫu · Hess's Law using combustion data

Given the standard enthalpies of combustion: (1) $C(s) + O_2(g) \rightarrow CO_2(g)$, $\Delta H_c^\circ = -393.5$ kJ mol^{-1}; (2) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$, $\Delta H_c^\circ = -285.8$ kJ mol^{-1}; (3) $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$, $\Delta H_c^\circ = -2220.0$ kJ mol^{-1}. Find $\Delta H_f^\circ(C_3H_8, g)$.

The target is $3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$ (formation of propane from its elements). Using combustion data, the general pattern is: combust every element on the reactant side, then *subtract* combustion of the compound itself (since the compound's combustion products must cancel with those from the elements):

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

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

(Close to the accepted literature value, ≈ -104 kJ mol^{-1}.)

VN **GIẢI THÍCH TIẾNG VIỆT**

Khi dữ liệu cho là các enthalpy **đốt cháy** (combustion) thay vì hình thành, công thức tổng quát là: $\Delta H_f^\circ(\text{hợp chất}) = \Sigma[\text{hệ số} \times \Delta H_c^\circ(\text{nguyên tố})] - \Delta H_c^\circ(\text{hợp chất})$. Đây là cách kết hợp KHÁC với ví dụ methanol ở trên (hệ số 3 và 4 thay vì 1 và 2) — luôn viết phương trình mục tiêu trước để xác định đúng hệ số nhân.

Ví dụ mẫu · Verifying a formation enthalpy from combustion data

Given: (1) $2C(s) + H_2(g) \rightarrow C_2H_2(g)$, $\Delta H_1 = ?$ (target); (2) $C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$, $\Delta H_2 = -1300$ kJ mol^{-1}; (3) $C(s) + O_2(g) \rightarrow CO_2(g)$, $\Delta H_3 = -393.5$ kJ mol^{-1}; (4) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$, $\Delta H_4 = -285.8$ kJ mol^{-1}. Find ΔH_1, the standard enthalpy of formation of ethyne (acetylene).

Following the method above: the target has $2C(s)$ and $H_2(g)$ as reactants and $C_2H_2(g)$ as the only product, so combine $2 \times (3) + (4) - (2)$ (the CO_2 and H_2O then cancel, and reversing (2) removes O_2 and C_2H_2 from the wrong sides):

$$\Delta H_1 = 2(-393.5) + (-285.8) - (-1300) = -787.0 - 285.8 + 1300 = 227.2 \text{ kJ mol}^{-1}.$$

This strongly positive value (very close to the accepted literature value, $+226.7$ kJ mol^{-1}) shows that ethyne is an unusually high-energy compound to form — which is exactly why it burns so exothermically in oxy-acetylene welding torches, releasing both the energy of combustion *and* the energy stored in its unstable triple bond.

VN **GIẢI THÍCH TIẾNG VIỆT**

Ví dụ này minh hoạ việc "xác minh" một enthalpy hình thành bằng dữ liệu đốt cháy của các chất liên quan, đồng thời cho thấy một hợp chất có ΔH_f° dương lớn (như C_2H_2, chứa liên kết ba kém bền) thường giải phóng RẤT NHIỀU năng lượng khi cháy — vừa từ phản ứng đốt cháy, vừa từ chính năng lượng "dự trữ" trong liên kết không bền của nó.

(!) Lỗi thường gặp: When reversing or scaling an equation to build a Hess cycle, students often scale the coefficients correctly but forget to scale ΔH by the same factor, or forget to flip the sign of ΔH when an equation is written in reverse. Always double-check: does your combined equation, once all repeated species cancel, exactly match the target equation — same formulas,

same states, same coefficients?

4.2.2 The ΔH_f° shortcut: $\Delta H^\circ = \Sigma\Delta H_f^\circ(\text{products}) - \Sigma\Delta H_f^\circ(\text{reactants})$

When standard enthalpies of formation are available for every reactant and product, Hess's Law reduces to a single formula, avoiding the need to hunt for a specific combination of equations:

$$\Delta H^\circ_{\text{reaction}} = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants}),$$

each term multiplied by its stoichiometric coefficient in the balanced equation. This is equivalent to a Hess cycle that decomposes every reactant into its elements and reforms those elements into every product — but it is much faster to apply directly.

Ví dụ mẫu · Enthalpy of combustion from ΔH_f° data

Given $\Delta H_f^\circ(\text{C}_2\text{H}_5\text{OH}, l) = -277.6$, $\Delta H_f^\circ(\text{CO}_2, g) = -393.5$, $\Delta H_f^\circ(\text{H}_2\text{O}, l) = -285.8$ kJ mol^{-1} (all $\Delta H_f^\circ(\text{O}_2, g) = 0$), find ΔH_c° for $\text{C}_2\text{H}_5\text{OH(l)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)} + 3\text{H}_2\text{O(l)}$.

$$\Delta H^\circ = [2(-393.5) + 3(-285.8)] - [(-277.6) + 3(0)] = (-787.0 - 857.4) - (-277.6).$$

$$\Delta H^\circ = -1644.4 + 277.6 = -1366.8 \text{ kJ mol}^{-1}.$$

This matches the calorimetry-based estimate of Section 1 ($\approx -1.38\times10^3$ kJ mol^{-1}) very closely, and is essentially identical to the accepted literature value, -1367 kJ mol^{-1}.

VN **GIẢI THÍCH TIẾNG VIỆT**

Công thức "tắt" $\Delta H^\circ = \Sigma\Delta H_f^\circ(\text{sản phẩm}) - \Sigma\Delta H_f^\circ(\text{chất phản ứng})$ rất nhanh khi có sẵn bảng ΔH_f° — không cần dò tìm cách kết hợp phương trình. Luôn nhân mỗi giá trị với đúng hệ số cân bằng trước khi cộng/trừ.

Ví dụ mẫu · Checking a calorimetry result against ΔH_f° data

By convention, the standard enthalpy of formation of the aqueous hydrogen ion, $\Delta H_f^\circ(\text{H}^+, aq)$, is defined as exactly zero, giving a reference point for tabulating ΔH_f° of every other aqueous ion. Given $\Delta H_f^\circ(\text{OH}^-, aq) = -230.0$ kJ mol^{-1} and $\Delta H_f^\circ(\text{H}_2\text{O}, l) = -285.8$ kJ mol^{-1}, verify the calorimetry-based enthalpy of neutralisation found in Section 1 (-56.8 kJ mol^{-1}) using $\text{H}^+\text{(aq)} + \text{OH}^-\text{(aq)} \rightarrow \text{H}_2\text{O(l)}$.

$$\Delta H^\circ = \Delta H_f^\circ(\text{H}_2\text{O}, l) - [\Delta H_f^\circ(\text{H}^+, aq) + \Delta H_f^\circ(\text{OH}^-, aq)] = -285.8 - [0 + (-230.0)].$$

$$\Delta H^\circ = -285.8 + 230.0 = -55.8 \text{ kJ mol}^{-1}.$$

This thermodynamic-data value (-55.8 kJ mol^{-1}) closely matches the calorimetry measurement from Section 1 (-56.8 kJ mol^{-1}) — two completely independent methods, one experimental and one from tabulated data, converging on essentially the same answer.

VN **GIẢI THÍCH TIẾNG VIỆT**

Quy ước $\Delta H_f^\circ(\text{H}^+, aq) = 0$ cho phép lập bảng ΔH_f° của MỌI ion khác trong dung dịch. Ví dụ này cho thấy hai phương pháp hoàn toàn độc lập — đo thực nghiệm bằng nhiệt lượng kế (Mục 1) và tính từ dữ liệu ΔH_f° đã lập bảng (Mục 2) — cho ra cùng một kết quả, củng cố độ tin cậy của cả hai.

4.2.3 Lattice enthalpy (AHL)

An ionic solid's **lattice enthalpy** describes the energy associated with assembling (or breaking apart) its crystal lattice from gaseous ions. IB distinguishes two directions, which are numerically equal but opposite in sign:

- **Lattice enthalpy of formation**, $\Delta H^\circ_{\text{lat.f}}$: gaseous ions come together to form 1 mole of solid ionic lattice, e.g. $\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NaCl}(\text{s})$. This is always **exothermic** (negative) — oppositely charged ions attracting and locking into an ordered lattice releases energy.
- **Lattice enthalpy of dissociation**, $\Delta H^\circ_{\text{lat.diss}}$: 1 mole of solid ionic lattice breaks apart into its gaseous ions, e.g. $\text{NaCl}(\text{s}) \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g})$. This is always **endothermic** (positive) — it is the exact reverse process, so by Hess's Law $\Delta H^\circ_{\text{lat.diss}} = -\Delta H^\circ_{\text{lat.f}}$.

Lattice enthalpy cannot be measured directly in a single experiment; it is found indirectly using a Born–Haber cycle.

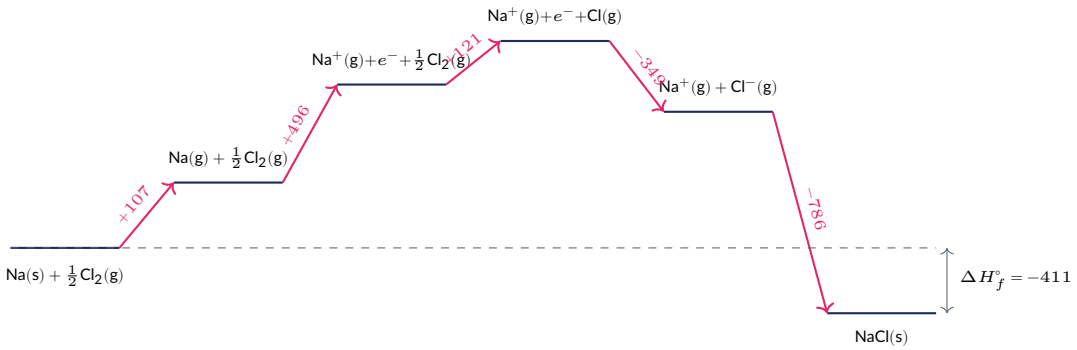
(!) Lỗi thường gặp: Always check which direction a quoted "lattice enthalpy" refers to before using it in a cycle. Data booklets and textbooks are not always consistent — some always report the (positive) dissociation value, others the (negative) formation value. In a Born–Haber cycle diagram, the arrow direction tells you unambiguously which sign to use.

VN GIẢI THÍCH TIẾNG VIỆT

Lattice enthalpy hình thành (ion khí → tinh thể rắn) LUÔN âm (toả nhiệt). Lattice enthalpy phân li (tinh thể rắn → ion khí) LUÔN dương (thu nhiệt) — hai giá trị này có cùng độ lớn, trái dấu, vì là hai chiều ngược nhau của cùng một quá trình.

4.2.4 The Born–Haber cycle (AHL)

A **Born–Haber cycle** is a specific application of Hess's Law to the formation of an ionic compound from its elements. It connects the standard enthalpy of formation, ΔH°_f, to a chain of measurable steps — atomisation, ionisation, and electron affinity — plus the one quantity that cannot be measured directly, the lattice enthalpy. Closing the cycle (all steps must sum to ΔH°_f) lets us solve for whichever single quantity is unknown.



Born–Haber cycle for NaCl (schematic, not to scale; values in kJ mol^{-1}). Atomisation of Na ($+107$), first ionisation of Na ($+496$), atomisation of Cl ($+121$), electron affinity of Cl (-349), and lattice enthalpy of formation close the cycle back to $\Delta H^\circ_f = -411$ kJ mol^{-1}.

Ví dụ mẫu · Lattice enthalpy from a Born–Haber cycle (AHL)

Using the values above ($\Delta H^\circ_f = -411$; atomisation Na $= +107$; IE_1(Na)$= +496$; atomisation Cl $= +121$; EA_1(Cl)$= -349$, all kJ mol^{-1}), find the lattice enthalpy of formation, LE.

By Hess's Law: $\Delta H_f = (\text{atomisation Na}) + IE_1 + (\text{atomisation Cl}) + EA_1 + LE$.

$$-411 = 107 + 496 + 121 - 349 + LE = 375 + LE \;\Rightarrow\; LE = -786 \text{ kJ mol}^{-1}.$$

(Matches accepted literature, ≈ -787 kJ mol^{-1}.)

VN **GIẢI THÍCH TIẾNG VIỆT**

Chu trình Born–Haber áp dụng định luật Hess để tính **năng lượng mạng tinh thể** — đại lượng không thể đo trực tiếp. Tổng các bước từ nguyên tố ở trạng thái chuẩn đến ion khí, rồi đến tinh thể rắn, phải bằng ΔH_f° của hợp chất (bảo toàn năng lượng theo định luật Hess). Cùng một chu trình có thể giải ngược để tìm BẤT KỲ đại lượng nào trong chuỗi, miễn là biết các đại lượng còn lại.

4.2.5 Trends in lattice enthalpy (AHL)

The magnitude of a lattice enthalpy depends on the strength of the electrostatic (Coulombic) attraction between the ions in the lattice, which in turn depends on two factors: the **ionic charges** and the **ionic radii**. Larger charges and smaller radii both increase the magnitude of the lattice enthalpy (make it more exothermic, for formation).

Comparing lattice enthalpies of formation (kJ mol^{-1}, accepted literature values)

- NaCl: -786 vs. NaF: -926 — same cation (Na^+); F^- is smaller than Cl^-, so ions pack closer together in NaF, giving a stronger attraction (more exothermic).
- CaO: -3414 vs. MgO: -3847 — same anion (O^{2-}); Mg^{2+} is smaller than Ca^{2+}, so MgO's lattice enthalpy is more exothermic.
- NaCl: -786 vs. MgO: -3847 — doubling both ionic charges ($1+/1- \to 2+/2-$) increases the Coulombic attraction roughly four-fold, producing a far larger magnitude.

VN **GIẢI THÍCH TIẾNG VIỆT**

Năng lượng mạng tinh thể phụ thuộc vào lực hút Coulomb giữa các ion: điện tích ion CÀNG LỚN và bán kính ion CÀNG NHỎ thì lực hút càng mạnh, lattice enthalpy càng âm (độ lớn càng cao). So sánh NaCl với NaF (cùng cation, anion khác bán kính) hoặc MgO với CaO (cùng anion, cation khác bán kính) để thấy rõ xu hướng.

AHL

Using the trends above, explain why the lattice enthalpy of formation of MgO (-3847 kJ mol^{-1}) has a far greater magnitude than that of NaCl (-786 kJ mol^{-1}).

Lời giải chi tiết

Two factors both act in the same direction. **Charge**: MgO contains Mg^{2+} and O^{2-} ($2+$ and $2-$), while NaCl contains only Na^+ and Cl^- ($1+$ and $1-$) — doubling both charges greatly increases the Coulombic attraction. **Radius**: Mg^{2+} and O^{2-} are both smaller ions than Na^+ and Cl^-, so the ions in MgO also sit closer together. Both effects strengthen the electrostatic attraction, making MgO's lattice enthalpy far more exothermic.

AHL

MgO has a far higher melting point (2852°C) than NaCl (801°C). Which best explains this difference?

(A) MgO contains metallic bonding, unlike NaCl

(B) MgO's much larger lattice enthalpy (greater ionic charge and smaller ionic radii) means far more energy is needed to break apart its lattice

(C) MgO is a covalent network solid

(D) The difference is coincidental and unrelated to bonding

Lời giải chi tiết

Melting point broadly tracks lattice enthalpy magnitude for ionic solids: a stronger lattice (larger charges, smaller ions, as in MgO) requires far more thermal energy to disrupt the ordered array of ions, hence a much higher melting point. **(B)**.

4.2.6 Enthalpy of solution: a hydration cycle (AHL)

A related Hess cycle explains why some ionic solids dissolve in water and others do not. The **enthalpy of solution**, $\Delta H^\circ_{\text{sol}}$, is the enthalpy change when 1 mole of an ionic solid dissolves completely in water to form an infinitely dilute solution. It splits into two steps: (1) breaking apart the solid lattice into gaseous ions — the **lattice enthalpy of dissociation**, $\Delta H^\circ_{\text{lat.diss}}$, always endothermic — followed by (2) surrounding those gaseous ions with water molecules, releasing the **enthalpy of hydration**, $\Delta H^\circ_{\text{hyd}}$, always exothermic (new ion–dipole attractions form). By Hess's Law,

$$\Delta H^\circ_{\text{sol}} = \Delta H^\circ_{\text{lat.diss}} + \Delta H^\circ_{\text{hyd}}(\text{cation}) + \Delta H^\circ_{\text{hyd}}(\text{anion}).$$

Ví dụ mẫu · Enthalpy of solution of NaCl (AHL)

Given $\Delta H^\circ_{\text{lat.diss}}(\text{NaCl}) = +786$ kJ mol^{-1}, $\Delta H^\circ_{\text{hyd}}(\text{Na}^+) = -406$ kJ mol^{-1}, $\Delta H^\circ_{\text{hyd}}(\text{Cl}^-) = -364$ kJ mol^{-1}, calculate $\Delta H^\circ_{\text{sol}}(\text{NaCl})$.

$$\Delta H^\circ_{\text{sol}} = 786 + (-406) + (-364) = 786 - 770 = +16 \text{ kJ mol}^{-1}.$$

This small, slightly *endothermic* value matches the well-known experimental fact that dissolving NaCl in water absorbs a small amount of heat (accepted value $\approx +3.9$ kJ mol^{-1}) — yet the process is still spontaneous at room temperature, because the large increase in entropy on dissolving ($\Delta S^\circ > 0$, Section 4) outweighs the small unfavourable ΔH°.

VN **GIẢI THÍCH TIẾNG VIỆT**

$\Delta H^\circ_{\text{sol}} = \Delta H^\circ_{\text{lat.diss}} + \Delta H^\circ_{\text{hyd}}(\text{cation}) + \Delta H^\circ_{\text{hyd}}(\text{anion})$: hoà tan = phá vỡ mạng tinh thể (thu nhiệt) + hydrat hoá các ion (toả nhiệt). NaCl tan trong nước hơi thu nhiệt một chút, nhưng vẫn tự diễn ra vì entropy tăng mạnh (Mục 4) đủ để bù lại.

AHL

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

Lời giải chi tiết

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

Like NaCl, dissolving KCl is slightly endothermic overall, yet still proceeds spontaneously in water at room temperature.

Bài tập luyện tập

Given (1) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$, $\Delta H = +180$ kJ; (2) $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$, $\Delta H = -114$ kJ. Find ΔH for $\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$.

(A) $+294$ kJ
(B) $+66$ kJ
(C) -294 kJ
(D) $+33$ kJ

Lời giải chi tiết

Target $= (1) + (2)$: $\Delta H = 180 + (-114) = +66$ kJ. **(B)**.

AHL

Given $\Delta H_f^\circ(\text{KCl}) = -436$, atomisation enthalpy of K $= +89$, atomisation enthalpy of Cl $= +121$, $EA_1(\text{Cl}) = -349$, and lattice enthalpy of KCl $= -711$ (all kJ mol^{-1}), the first ionisation energy of K is closest to:

(A) 349 kJ mol^{-1}
(B) 711 kJ mol^{-1}
(C) 414 kJ mol^{-1}
(D) 496 kJ mol^{-1}

Lời giải chi tiết

$-436 = 89 + IE_1 + 121 - 349 - 711 \Rightarrow -436 = -850 + IE_1 \Rightarrow IE_1 = 414$ kJ mol^{-1} (accepted value ≈ 419 kJ mol^{-1}). **(C)**.

AHL

For magnesium oxide, given (all kJ mol^{-1}): $\Delta H_f^\circ(\text{MgO}, s) = -602$; atomisation of Mg $= +148$; $IE_1(\text{Mg}) = +738$; $IE_2(\text{Mg}) = +1451$; atomisation of O (i.e. $\frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{O}(\text{g})$) $= +249$; $EA_1(\text{O}) = -141$; $EA_2(\text{O}) = +800$. Calculate the lattice enthalpy of formation of MgO.

Lời giải chi tiết

Hess's Law around the cycle: $\Delta H_f^\circ = (\text{atom. Mg}) + IE_1 + IE_2 + (\text{atom. O}) + EA_1 + EA_2 + LE$. Sum of known terms: $148 + 738 + 1451 + 249 - 141 + 800 = 3245$.

$$-602 = 3245 + LE \;\Rightarrow\; LE = -602 - 3245 = -3847 \text{ kJ mol}^{-1}.$$

The very large magnitude (compared with NaCl's -786 kJ mol^{-1}) reflects the $2+/2-$ ionic charges in MgO, which attract each other far more strongly than the $1+/1-$ charges in NaCl.

Bài tập luyện tập

Using $\Delta H_f^\circ(\text{CaO}, s) = -635.1$, $\Delta H_f^\circ(\text{CO}_2, g) = -393.5$, $\Delta H_f^\circ(\text{CaCO}_3, s) = -1206.9$ (all kJ mol^{-1}), calculate ΔH° for $\text{CaO(s)} + \text{CO}_2\text{(g)} \rightarrow \text{CaCO}_3\text{(s)}$.

Lời giải chi tiết

$$\Delta H^\circ = \Delta H_f^\circ(\text{CaCO}_3) - [\Delta H_f^\circ(\text{CaO}) + \Delta H_f^\circ(\text{CO}_2)] = -1206.9 - (-635.1 - 393.5).$$

$$\Delta H^\circ = -1206.9 - (-1028.6) = -1206.9 + 1028.6 = -178.3 \text{ kJ mol}^{-1}.$$

This is (as expected) essentially the exact reverse of the thermal decomposition of CaCO_3 studied later in this chapter ($\Delta H^\circ = +178$ kJ mol^{-1}).

AHL

The lattice enthalpy of *dissociation* of MgCl_2 is $+2526$ kJ mol^{-1}. Its lattice enthalpy of *formation* is:

(A) $+2526$ kJ mol^{-1}

(B) -1263 kJ mol^{-1}

(C) -2526 kJ mol^{-1}

(D) 0 kJ mol^{-1}

Lời giải chi tiết

Formation is the exact reverse of dissociation, so it has the same magnitude but opposite sign: -2526 kJ mol^{-1}. **(C)**.

AHL

For MgCl_2, given (all kJ mol^{-1}): $\Delta H_f^\circ = -641$; atomisation of Mg $= +148$; $IE_1(\text{Mg}) = +738$; $IE_2(\text{Mg}) = +1451$; atomisation of Cl $= +121$ (per mole of Cl atoms); lattice enthalpy of formation $= -2526$. Find $EA_1(\text{Cl})$. (Hint: MgCl_2 contains *two* moles of Cl, so both the atomisation and electron-affinity steps must be counted twice.)

Lời giải chi tiết

$$\Delta H_f^\circ = (\text{atom. Mg}) + IE_1 + IE_2 + 2(\text{atom. Cl}) + 2\,EA_1(\text{Cl}) + LE.$$

Sum of known terms excluding EA_1: $148 + 738 + 1451 + 2(121) + (-2526) = 148 + 738 + 1451 + 242 - 2526 = 53$.

$$-641 = 53 + 2\,EA_1(\text{Cl}) \;\Rightarrow\; 2\,EA_1(\text{Cl}) = -694 \;\Rightarrow\; EA_1(\text{Cl}) = -347 \text{ kJ mol}^{-1}.$$

This closely matches the value used for Cl in the NaCl cycle above (-349 kJ mol^{-1}), as it should — electron affinity is a property of the element, not the compound.

Bài tập luyện tập

Given $\Delta H_f^\circ(\text{Fe}_2\text{O}_3, s) = -824.2$ kJ mol^{-1} and $\Delta H_f^\circ(\text{Al}_2\text{O}_3, s) = -1675.7$ kJ mol^{-1}, find ΔH° for the thermite reaction, $2\text{Al(s)} + \text{Fe}_2\text{O}_3\text{(s)} \rightarrow \text{Al}_2\text{O}_3\text{(s)} + 2\text{Fe(s)}$.

Lời giải chi tiết

Writing (1) $2\text{Fe(s)} + \frac{3}{2}\text{O}_2\text{(g)} \rightarrow \text{Fe}_2\text{O}_3\text{(s)}$, $\Delta H_1 = -824.2$ kJ, and (2) $2\text{Al(s)} + \frac{3}{2}\text{O}_2\text{(g)} \rightarrow \text{Al}_2\text{O}_3\text{(s)}$, $\Delta H_2 = -1675.7$ kJ, the target equals (2) − (1) (the $\frac{3}{2}\text{O}_2$ cancels):

$$\Delta H^\circ = \Delta H_2 - \Delta H_1 = -1675.7 - (-824.2) = -851.5 \text{ kJ mol}^{-1}.$$

This matches the commonly cited value of approximately -850 kJ mol^{-1} for this highly exothermic reaction, used industrially in welding and in some fireworks.

Bài tập luyện tập

Given $\Delta H_c^\circ(\text{C, graphite}) = -393.5$ kJ mol^{-1} and $\Delta H_c^\circ(\text{C, diamond}) = -395.4$ kJ mol^{-1}, calculate ΔH° for $\text{C(diamond)} \rightarrow \text{C(graphite)}$, and comment on which allotrope is thermodynamically more stable.

Lời giải chi tiết

Combusting diamond to CO_2, then reversing the combustion of graphite to return from CO_2 to graphite, is equivalent to converting diamond directly into graphite:

$$\Delta H^\circ = \Delta H_c^\circ(\text{diamond}) - \Delta H_c^\circ(\text{graphite}) = -395.4 - (-393.5) = -1.9 \text{ kJ mol}^{-1}.$$

This small negative value confirms graphite is (very slightly) more thermodynamically stable than diamond — consistent with graphite, not diamond, being chosen as carbon's standard state (Section 1.1), since ΔH_f° conventions always use the most stable form of an element.

4.3 Energy from fuels

Fuels release energy by combustion, and the size of the enthalpy change can be estimated from **bond enthalpies** — the average energy needed to break one mole of a given bond in the gas phase. Breaking bonds always requires an input of energy (an endothermic contribution); forming new bonds always releases energy (an exothermic contribution). The overall enthalpy change of a reaction is the balance between the two:

$$\Delta H \approx \Sigma(\text{bonds broken}) - \Sigma(\text{bonds formed}).$$

4.3.1 Estimating enthalpy changes from bond enthalpies

Ví dụ mẫu · Worked example

Estimate ΔH for $\text{CH}_4\text{(g)} + 2\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 2\text{H}_2\text{O(g)}$ using bond enthalpies (C − H = 413, O = O = 498, C = O = 799, O − H = 463, kJ mol^{-1}).

Bonds broken: $4(413) + 2(498) = 1652 + 996 = 2648$. Bonds formed: $2(799) + 4(463) = 1598 + 1852 = 3450$.

$$\Delta H = 2648 - 3450 = -802 \text{ kJ mol}^{-1}.$$

(!) Lỗi thường gặp: Bond enthalpies are *average* values (from many different compounds), so bond-enthalpy calculations give an *estimate*, not an exact experimental ΔH. They also assume all species are gaseous — using $\text{H}_2\text{O(g)}$ instead of $\text{H}_2\text{O(l)}$ changes the answer (the true $\Delta H_{\text{combustion}}$ of methane to liquid water is more exothermic, ≈ -890 kJ mol^{-1}, because condensing water releases additional energy).

VN GIẢI THÍCH TIẾNG VIỆT

$\Delta H \approx \Sigma(\text{liên kết bị phá vỡ}) - \Sigma(\text{liên kết được tạo thành})$: phá vỡ liên kết LUÔN thu nhiệt (cần năng lượng), tạo liên kết mới LUÔN toả nhiệt. Vì năng lượng liên kết là giá trị TRUNG BÌNH, kết quả chỉ là ước lượng, không phải giá trị thực nghiệm chính xác.

Ví dụ mẫu · Solving for an unknown bond enthalpy

Given $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$, $\Delta H = -184.6$ kJ mol^{-1}, and bond enthalpies H $-$ H $= 436$, Cl $-$ Cl $= 242$ kJ mol^{-1}, find the H $-$ Cl bond enthalpy.

Let x = the H $-$ Cl bond enthalpy. Bonds broken: $436 + 242 = 678$. Bonds formed: $2x$ (two H $-$ Cl bonds per HCl molecule, two molecules).

$$\Delta H = 678 - 2x = -184.6 \;\Rightarrow\; 2x = 678 + 184.6 = 862.6 \;\Rightarrow\; x = 431.3 \text{ kJ mol}^{-1}.$$

(Close to the accepted average H $-$ Cl bond enthalpy, ≈ 432 kJ mol^{-1}.)

VN GIẢI THÍCH TIẾNG VIỆT

Nếu biết ΔH của phản ứng và tất cả năng lượng liên kết khác, có thể giải ngược phương trình $\Delta H = \Sigma(\text{phá vỡ}) - \Sigma(\text{tạo thành})$ để tìm MỘT năng lượng liên kết chưa biết — chỉ cần đặt ẩn x và giải phương trình bậc nhất.

Bài tập luyện tập

Estimate ΔH for $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ using bond enthalpies H $-$ H $= 436$, O $=$ O $= 498$, O $-$ H $= 463$ kJ mol^{-1}.

(A) -241 kJ mol^{-1} **(C)** $+482$ kJ mol^{-1}

(B) -482 kJ mol^{-1} **(D)** -964 kJ mol^{-1}

Lời giải chi tiết

Broken: $2(436) + 498 = 872 + 498 = 1370$. Formed: $4(463) = 1852$. $\Delta H = 1370 - 1852 = -482$ kJ mol^{-1}. **(B).**

Bài tập luyện tập

Given $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, $\Delta H^\circ = -92.4$ kJ mol^{-1}, and bond enthalpies N $\equiv$ N $= 945$, H $-$ H $= 436$ kJ mol^{-1}, calculate the average N $-$ H bond enthalpy.

Lời giải chi tiết

Broken: $945 + 3(436) = 945 + 1308 = 2253$. Each NH_3 has 3 N $-$ H bonds, so $2NH_3$ has 6: formed $= 6x$.

$$2253 - 6x = -92.4 \;\Rightarrow\; 6x = 2253 + 92.4 = 2345.4 \;\Rightarrow\; x = 390.9 \text{ kJ mol}^{-1}.$$

This matches the accepted average N $-$ H bond enthalpy closely (≈ 388–391 kJ mol^{-1}).

4.3.2 Comparing fuels: energy density and environmental impact

Different fuels release different amounts of energy per gram (their **energy density**) and have different environmental footprints. Energy density is calculated from the molar enthalpy of combustion and

the molar mass:

$$\text{energy per gram} = \frac{|\Delta H_c^\circ|}{M}.$$

Complete combustion of a hydrocarbon fuel in excess oxygen produces only $CO_2(g)$ and H_2O (liquid or gas), releasing the maximum possible energy per mole of fuel. In a limited supply of oxygen, **incomplete combustion** occurs instead, producing carbon monoxide, $CO(g)$, or even solid carbon (soot) alongside water; both release *less* energy per mole of fuel than complete combustion, and CO is highly toxic, since it binds to haemoglobin far more strongly than oxygen does, reducing the blood's ability to transport oxygen.

Complete versus incomplete combustion of a hydrocarbon

- **Complete** (excess O_2): products $CO_2(g) + H_2O$ — maximum energy released; no toxic products.
- **Incomplete** (limited O_2): products $CO(g) + H_2O$, or $C(s) + H_2O$ — less energy released; CO is toxic; soot pollutes.

Fuel	Type	ΔH_c° (kJ mol^{-1})	Energy density (kJ g^{-1})	Environmental notes
Coal (as carbon)	Fossil	-393.5	≈ 32	Non-renewable; high CO_2 per unit energy released; often contains sulfur impurities
Octane, C_8H_{18} (petroleum)	Fossil	-5470	47.9	Non-renewable; large total CO_2 output from vehicles
Methane, CH_4 (natural gas)	Fossil	-890	55.5	Non-renewable; lower CO_2 per unit energy than coal or petroleum
Ethanol, C_2H_5OH (bioethanol)	Biofuel	-1367	29.7	Renewable feedstock; close to carbon-neutral, since growing crops re-absorbs much of the CO_2 released
Hydrogen, H_2	—	-286	141.6	No direct CO_2 from combustion (only H_2O); overall renewability depends entirely on how the hydrogen is produced

Because burning hydrogen produces only water, its environmental impact depends almost entirely on *how* the hydrogen gas itself is manufactured:

Hydrogen production methods

- **"Grey" hydrogen**: produced from natural gas by steam methane reforming; releases substantial CO_2 during production, even though the hydrogen itself burns cleanly.
- **"Blue" hydrogen**: the same steam-reforming process, but the CO_2 by-product is captured and stored rather than released to the atmosphere, reducing (though not eliminating) net emissions.
- **"Green" hydrogen**: produced by electrolysis of water using electricity from renewable sources (solar, wind, hydroelectric); no CO_2 is released during either production or combustion.

Bài tập luyện tập

Which hydrogen production method is considered fully carbon-neutral across both production *and* combustion?

(A) Grey hydrogen
(B) Blue hydrogen
(C) Green hydrogen
(D) All three are equally clean

Lời giải chi tiết

Green hydrogen uses only renewable electricity to split water by electrolysis, releasing no CO_2 at any stage; grey hydrogen releases considerable CO_2 during production, and blue hydrogen only reduces (via carbon capture) rather than eliminates it. **(C)**.

Hydrogen's outstanding energy density *by mass* (141.6 kJ g^{-1}, more than double octane's) hides a serious practical drawback: its energy density *by volume* as an ordinary gas is extremely poor, since gases are mostly empty space. This is why hydrogen-powered vehicles must store it either highly compressed or as a cryogenic liquid, adding cost and engineering complexity that offsets some of its mass-based advantage.

Bài tập luyện tập

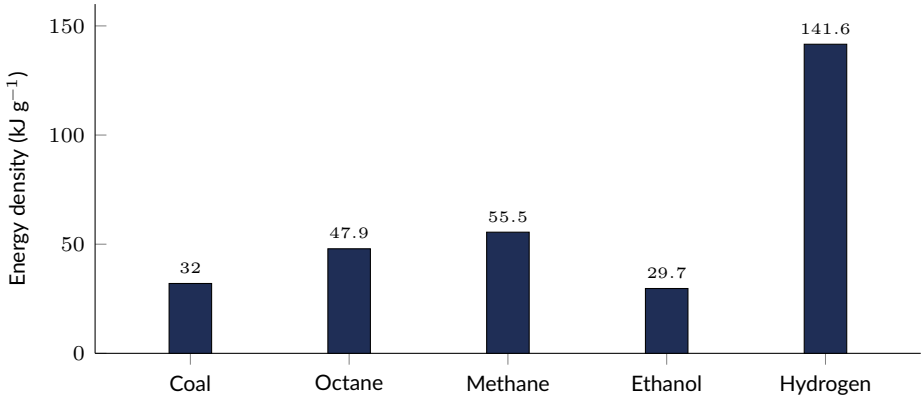
Under the standard conditions used in this book (298 K, 100 kPa), the molar volume of a gas is 24.8 dm^3 mol^{-1}, so hydrogen gas has a density of $\dfrac{2.02}{24.8} = 0.0815$ g dm^{-3}. Calculate the energy stored in 1.00 dm^3 of hydrogen gas at these conditions ($\Delta H_c^\circ(\mathrm{H_2}) = -286$ kJ mol^{-1}), and compare it with 1.00 dm^3 of liquid octane (density 0.703 g cm^{-3} $= 703$ g dm^{-3}; energy density 47.9 kJ g^{-1}, Section 3.2).

Lời giải chi tiết

Hydrogen gas: mass in 1.00 dm^3 is 0.0815 g. $n = \dfrac{0.0815}{2.02} = 0.0403$ mol. Energy $= 0.0403 \times 286 = 11.5$ kJ per dm^3.

Liquid octane: mass in 1.00 dm^3 is 703 g. Energy $= 703 \times 47.9 = 3.37 \times 10^4$ kJ per dm^3.

Liquid octane packs roughly 3000 times more energy into the same volume than hydrogen gas at ordinary pressure — the central practical challenge of using hydrogen as a transport fuel, despite its excellent energy density by mass.



Approximate energy densities (kJ per gram of fuel burned) for common fuels, calculated from $\Delta H_c^\circ / M$.

Ví dụ mẫu · Worked example

Calculate the energy released per gram of octane, $C_8H_{18}(l)$, given $\Delta H_c^\circ = -5470$ kJ mol^{-1} and $M = 114.23$ g mol^{-1}.

$$\text{energy per gram} = \frac{5470}{114.23} = 47.9 \text{ kJ g}^{-1}.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Mật độ năng lượng $= \dfrac{|\Delta H_c^\circ|}{M}$ — cho biết 1 gam nhiên liệu giải phóng bao nhiêu năng lượng, khác với ΔH_c° (tính theo mol). Nhiên liệu hoá thạch (than, dầu mỏ, khí gas) không tái tạo và thải nhiều CO_2; nhiên liệu sinh học (bioethanol) gần như trung hoà carbon; hydro không thải CO_2 trực tiếp nhưng phụ thuộc vào cách sản xuất.

Bài tập luyện tập

Given $\Delta H_c^\circ(CH_4) = -890$ kJ mol^{-1} and $M(CH_4) = 16.05$ g mol^{-1}, calculate the energy released per gram of methane burned.

Lời giải chi tiết

$$\text{energy per gram} = \frac{890}{16.05} = 55.5 \text{ kJ g}^{-1}.$$

This matches methane's well-known energy density of ≈ 55.5 MJ kg^{-1}, one reason natural gas is an efficient fuel by mass.

Bài tập luyện tập

Using $\Delta H_c^\circ(C_2H_5OH) = -1367$ kJ mol^{-1}, $M = 46.08$ g mol^{-1}, calculate ethanol's energy density and explain why it is lower than octane's (47.9 kJ g^{-1}).

Lời giải chi tiết

$$\text{energy per gram} = \frac{1367}{46.08} = 29.7 \text{ kJ g}^{-1}.$$

Ethanol already contains an oxygen atom (as an $-$OH group), so it is "partially oxidised" compared with a pure hydrocarbon like octane; less further oxidation — and hence less energy — is released per gram. The oxygen atom also adds mass without contributing combustible C $-$ H/C $-$ C bonds, further lowering the energy density.

Bài tập luyện tập

Which fuel below is generally considered closest to carbon-neutral over its full production-and-use cycle, assuming its feedstock is regrown?

(A) Coal
(B) Petroleum (octane)
(C) Bioethanol
(D) Natural gas (methane)

Lời giải chi tiết

Crops grown to make bioethanol absorb CO_2 from the atmosphere by photosynthesis as they grow, roughly offsetting the CO_2 released when the ethanol is later burned — making it close to carbon-neutral, unlike the three fossil fuels, which release CO_2 that has been locked away for millions of years. **(C)**.

Bài tập luyện tập

Combustion of hydrogen gas, $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$, produces only which product?

(A) CO_2
(B) CO
(C) Water vapour
(D) SO_2

Lời giải chi tiết

Hydrogen contains no carbon or sulfur, so its only combustion product is water: **(C)**.

Bài tập luyện tập

A fuel has an energy density of approximately 48 kJ g^{-1} and burns to give only CO_2 and H_2O. Based on the table above, which fuel is this most likely to be?

(A) Methane
(B) Octane
(C) Hydrogen
(D) Coal

Lời giải chi tiết

From the table, octane's energy density is 47.9 kJ g^{-1}, closest to the value given (methane is 55.5, hydrogen is 141.6, coal is ≈ 32). **(B)**.

Bài tập luyện tập

Based on the table in Section 3.2, which fuel combines both a very high energy density by mass and zero direct CO_2 emissions upon combustion?

(A) Coal
(B) Octane
(C) Methane
(D) Hydrogen

Lời giải chi tiết

Hydrogen has by far the highest energy density by mass in the table (141.6 kJ g^{-1}) and, containing no carbon, produces only water on combustion, with no direct CO_2 at all. **(D)**.

Bài tập luyện tập

Calculate the energy released when 5.00 g of hydrogen gas is completely combusted, given $\Delta H_c^\circ(H_2) = -286$ kJ mol^{-1} and $M(H_2) = 2.02$ g mol^{-1}.

Lời giải chi tiết

$$n = \frac{5.00}{2.02} = 2.475 \text{ mol}, \qquad E = 2.475 \times 286 = 707.7 \text{ kJ} \approx 708 \text{ kJ}.$$

Ví dụ mẫu · CO_2 emissions per gram of fuel

Calculate the mass of CO_2 produced per gram of methane burned, $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$, given $M(CH_4) = 16.05$ g mol^{-1} and $M(CO_2) = 44.01$ g mol^{-1}.

Per gram of methane: $n(CH_4) = \dfrac{1}{16.05} = 0.0623$ mol. Since the mole ratio $CH_4 : CO_2$ is $1 : 1$, $n(CO_2) = 0.0623$ mol.

$$\text{mass of } CO_2 = 0.0623 \times 44.01 = 2.74 \text{ g of } CO_2 \text{ per gram of methane burned.}$$

Combined with methane's energy density of 55.5 kJ g^{-1} (Section 1), this is equivalent to $\dfrac{2.74}{55.5} \approx 0.0494$ g of CO_2 released per kJ of energy obtained — a useful figure for comparing fuels' environmental impact *per unit of energy delivered*, not just per gram burned.

VN **GIẢI THÍCH TIẾNG VIỆT**

Để so sánh tác động môi trường công bằng, nên tính khối lượng CO_2 thải ra trên MỖI ĐƠN VỊ NĂNG LƯỢNG (g CO_2/kJ), không chỉ trên mỗi gam nhiên liệu — vì các nhiên liệu có mật độ năng lượng khác nhau.

Bài tập luyện tập

Calculate the mass of CO_2 produced per gram of carbon (representing coal) burned, $C(s) + O_2(g) \rightarrow CO_2(g)$, given $M(C) = 12.01$ g mol^{-1}, and compare with methane's value of 2.74 g CO_2 per gram of fuel (found above).

Lời giải chi tiết

$n(C) = \dfrac{1}{12.01} = 0.0833$ mol; since the ratio $C : CO_2$ is $1 : 1$, $n(CO_2) = 0.0833$ mol.

$$\text{mass of } CO_2 = 0.0833 \times 44.01 = 3.66 \text{ g of } CO_2 \text{ per gram of carbon burned.}$$

This is *more* CO_2 per gram of fuel than methane produces (3.66 vs. 2.74 g), and coal also has a lower energy density (≈ 32 vs. 55.5 kJ g^{-1}) — both factors make coal a substantially "dirtier" fossil fuel per unit of energy delivered than natural gas.

Bài tập luyện tập

Incomplete combustion of a hydrocarbon fuel in a poorly ventilated room is particularly dangerous because it produces:

(A) excess CO_2, which is denser than air

(B) carbon monoxide, which binds to haemoglobin and reduces the blood's ability to carry oxygen

(C) excess water vapour, which causes damp

(D) sulfur dioxide, which causes acid rain

Lời giải chi tiết

Limited oxygen supply favours incomplete combustion, producing toxic CO instead of CO_2; CO binds far more strongly to haemoglobin than O_2 does, starving the body of oxygen even at low concentrations. **(B)**.

Bài tập luyện tập

Given $\Delta H_f^\circ(CH_4, g) = -74.8$, $\Delta H_f^\circ(CO, g) = -110.5$, $\Delta H_f^\circ(H_2O, l) = -285.8$ kJ mol^{-1}, calculate ΔH° for the incomplete combustion $CH_4(g) + \frac{3}{2}O_2(g) \rightarrow CO(g) + 2H_2O(l)$, and compare it with methane's complete-combustion value, $\Delta H_c^\circ = -890$ kJ mol^{-1}.

Lời giải chi tiết

$$\Delta H^\circ = [(-110.5) + 2(-285.8)] - [(-74.8) + 0] = (-110.5 - 571.6) - (-74.8).$$

$$\Delta H^\circ = -682.1 + 74.8 = -607.3 \text{ kJ mol}^{-1}.$$

Incomplete combustion to CO releases noticeably less energy (-607.3 kJ mol^{-1}) than complete combustion to CO_2 (-890 kJ mol^{-1}) — confirming that incomplete combustion is both less efficient *and* more hazardous, since it also produces toxic CO.

4.4 Entropy and Gibbs free energy: $\Delta G = \Delta H - T\Delta S$ (AHL)

Not every exothermic reaction happens spontaneously, and not every endothermic process is impossible — ice melts at room temperature even though $\Delta H > 0$ for melting. A second quantity, **entropy**, together with temperature, determines whether a process is thermodynamically favourable. This entire section is AHL content.

4.4.1 Entropy and molecular disorder (AHL)

Entropy, S, is a measure of the dispersal of energy and matter within a system — loosely, the number of ways particles and their energy can be arranged. A process tends to increase entropy ($\Delta S > 0$) when:

- the number of moles of **gas** increases (gas particles have far more possible arrangements than liquids or solids);
- a substance changes from solid → liquid → gas (increasing freedom of movement);
- a solute **dissolves**, dispersing throughout the solvent;
- the number of individual particles increases (e.g. one molecule decomposing into several).

(!) Lỗi thường gặp: "Dissolving increases entropy" is a useful rule of thumb for a *solid* dissolving into solution, but it does *not* apply to a *gas* dissolving into a liquid. A gas has far greater entropy than the same substance once it is confined and surrounded by solvent molecules in solution, so a gas dissolving is typically an entropy *decrease*: for example $\Delta S^\circ < 0$ for $CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$. Always think about the actual states involved rather than applying "dissolving = more disorder" automatically.

A gas expanding spontaneously into a vacuum: removing the partition lets particles disperse through the whole volume, increasing the number of possible microscopic arrangements and hence the entropy ($\Delta S > 0$), even though $\Delta H = 0$ for expansion into a vacuum.

Ví dụ mẫu · Predicting the sign of ΔS°

Predict the sign of ΔS° for each process.

(a) $2H_2(g)+O_2(g) \rightarrow 2H_2O(l)$: gas moles fall from 3 to 0 (the only product is liquid) $\Rightarrow \Delta S^\circ < 0$.

(b) $NH_4Cl(s) \rightarrow NH_4^+(aq) + Cl^-(aq)$: an ordered solid disperses into freely-moving solvated ions in solution $\Rightarrow \Delta S^\circ > 0$.

(c) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$: gas moles fall from 4 to $2 \Rightarrow \Delta S^\circ < 0$.

VN **GIẢI THÍCH TIẾNG VIỆT**

Entropy S đo mức độ phân tán năng lượng/vật chất (số cách sắp xếp có thể có). $\Delta S > 0$ khi: số mol khí TĂNG, chất rắn → lỏng → khí, chất tan hoà tan vào dung dịch, hoặc số hạt tăng lên (một phân tử phân huỷ thành nhiều mảnh).

AHL

Predict the sign of ΔS° for $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$.

(A) Negative
(B) Positive
(C) Zero
(D) Cannot be determined

Lời giải chi tiết

A solid decomposes into a solid + a gas: moles of gas increase from 0 to 1, greatly increasing disorder $\Rightarrow \Delta S^\circ > 0$. **(B)**.

AHL

Predict the sign of ΔS° for $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$.

(A) Positive
(B) Negative
(C) Zero
(D) Cannot be determined

Lời giải chi tiết

Gas moles fall from 3 to 2, so the system becomes slightly more ordered: $\Delta S^\circ < 0$. **(B)**.

AHL

Predict the sign of ΔS° for $CO_2(g)+H_2O(l) \rightarrow H_2CO_3(aq)$ (carbon dioxide dissolving in water).

(A) Positive, since dissolving always increases entropy
(B) Negative, since a free gas becomes a confined, solvated aqueous species
(C) Zero, since no gas is produced
(D) Cannot be determined

Lời giải chi tiết

Unlike a solid dissolving, here a *gas* (very high entropy) is converted into a dissolved aqueous species (much lower entropy, since it is now surrounded and constrained by solvent molecules): $\Delta S^\circ < 0$. **(B)**.

4.4.2 Calculating ΔS° from standard entropy values (AHL)

Every substance has a standard molar entropy, S° (J K^{-1}mol^{-1}), tabulated at 298 K. Unlike ΔH_f°, S° of an element is *not* zero — entropy has an **absolute** scale, unlike enthalpy. This follows from the **Third Law of Thermodynamics**: a perfect crystal at absolute zero (0 K) has exactly one possible arrangement of its particles, so $S = 0$ at 0 K for every pure, perfectly-ordered substance. As temperature rises above 0 K, particles gain more ways to arrange their positions and energy, so S° is always a positive number for every substance — gases have the largest S° values, followed by liquids, with solids the smallest, for a given substance and a given temperature. The entropy change of a reaction is calculated the same way as with ΔH_f°:

$$\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants}).$$

Ví dụ mẫu · ΔS° from standard entropies

Given S° (J K^{-1}mol^{-1}): $CH_4(g) = 186.3$, $O_2(g) = 205.2$, $CO_2(g) = 213.8$, $H_2O(g) = 188.8$. Calculate ΔS° for $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$.

$$\Delta S^\circ = [213.8 + 2(188.8)] - [186.3 + 2(205.2)] = 591.4 - 596.7 = -5.3 \text{ J K}^{-1}\text{mol}^{-1}.$$

Note the total moles of gas are equal on both sides ($3 \rightarrow 3$), so a simple mole-counting heuristic would predict $\Delta S^\circ \approx 0$; the exact calculation reveals a small negative value, showing that mole-counting is only a rough guide.

VN **GIẢI THÍCH TIẾNG VIỆT**

$\Delta S^\circ = \Sigma S^\circ(\text{sản phẩm}) - \Sigma S^\circ(\text{chất phản ứng})$ — giống công thức ΔH_f°, nhưng LƯU Ý: S° của nguyên tố KHÔNG bằng 0 (khác với ΔH_f°), vì entropy có thang đo tuyệt đối.

For water, $\Delta S^\circ_{\text{fusion}} = +22.0$ J K^{-1}mol^{-1} (melting) is far smaller than $\Delta S^\circ_{\text{vaporisation}} = +118.8$ J K^{-1}mol^{-1} (boiling) — both used in the crossover-temperature examples of Section 4.4. This reflects how much more disorder is gained in each transition: a liquid is only slightly more disordered than a solid (molecules are still touching and constrained), whereas a gas is vastly more disordered than a liquid (molecules move almost independently through a volume roughly a thousand times larger). As a rule of thumb, $\Delta S^\circ_{\text{vaporisation}}$ is typically 4–6 times larger than $\Delta S^\circ_{\text{fusion}}$ for a given substance.

AHL

Given S° (J K^{-1}mol^{-1}): $N_2O_4(g) = 304.2$, $NO_2(g) = 240.1$. Calculate ΔS° for $N_2O_4(g) \rightleftharpoons 2NO_2(g)$.

Lời giải chi tiết

$$\Delta S^\circ = 2(240.1) - 304.2 = 480.2 - 304.2 = 176.0 \text{ J K}^{-1}\text{mol}^{-1}.$$

Strongly positive, as expected — one mole of gas splits into two, greatly increasing the number of possible particle arrangements.

AHL

Given S° (J K^{-1}mol^{-1}): $SO_2(g) = 248.2$, $O_2(g) = 205.2$, $SO_3(g) = 256.8$. Calculate ΔS° for $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$.

Lời giải chi tiết

$$\Delta S^\circ = 2(256.8) - [2(248.2) + 205.2] = 513.6 - (496.4 + 205.2).$$

$$\Delta S^\circ = 513.6 - 701.6 = -188.0 \text{ J K}^{-1}\text{mol}^{-1}.$$

This confirms the sign predicted earlier from mole-counting alone (Section 4.1): three moles of gas become two, so ΔS° is negative.

AHL

Which has the greater standard molar entropy, $H_2O(s)$ at 273 K or $H_2O(g)$ at 373 K? Explain.

(A) $H_2O(s)$, since solids are more thermodynamically stable

(B) $H_2O(g)$, since gas particles have far more freedom of motion and occupy a far larger volume, and the higher temperature adds further disorder

(C) They are equal, since both are the same substance

(D) Cannot be determined without exact values

Lời giải chi tiết

Gas particles move essentially independently through a volume thousands of times larger than the same amount of solid, giving vastly more possible arrangements of position; the higher temperature of the gas sample adds still more thermal disorder on top of this. $S^\circ(H_2O, g) \approx 189$ J K^{-1}mol^{-1} is indeed far greater than $S^\circ(H_2O, s) \approx 48$ J K^{-1}mol^{-1}. **(B)**.

4.4.3 Gibbs free energy and spontaneity: $\Delta G = \Delta H - T\Delta S$ (AHL)

Gibbs free energy, G, combines enthalpy and entropy into a single quantity that predicts whether a process is **spontaneous** (thermodynamically favourable, proceeding without continuous external energy input) at a given temperature:

$$\Delta G = \Delta H - T\Delta S, \qquad T \text{ in kelvin.}$$

A process is spontaneous when $\Delta G < 0$, non-spontaneous when $\Delta G > 0$, and at equilibrium when $\Delta G = 0$.

$\Delta H < 0,\ \Delta S > 0$: $\Delta G < 0$ always (spontaneous at all T)
$\Delta H > 0,\ \Delta S < 0$: $\Delta G > 0$ always (never spontaneous)
$\Delta H < 0,\ \Delta S < 0$: spontaneous only at *low* T (when $T < \Delta H/\Delta S$)
$\Delta H > 0,\ \Delta S > 0$: spontaneous only at *high* T (when $T > \Delta H/\Delta S$)

Ví dụ mẫu · Worked example

For $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, $\Delta H^\circ = -92.4$ kJ mol^{-1}, $\Delta S^\circ = -198.4$ J K^{-1}mol^{-1}. Find ΔG° at 298 K.

$$T\Delta S^\circ = (298)(-198.4) = -59{,}123.2 \text{ J}.$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -92{,}400 - (-59{,}123.2) = -92{,}400 + 59{,}123.2 \text{ J}.$$

$$\Delta G^\circ = -33{,}276.8 \text{ J} \approx -33.3 \text{ kJ mol}^{-1}.$$

Spontaneous at 298 K despite the unfavourable (negative) entropy change, because the large negative ΔH dominates.

VN **GIẢI THÍCH TIẾNG VIỆT**

$\Delta G = \Delta H - T\Delta S$: phản ứng tự diễn ra (spontaneous) khi $\Delta G < 0$. Khi ΔH và ΔS trái dấu thuận lợi (VD $\Delta H < 0, \Delta S > 0$), phản ứng LUÔN tự diễn ra ở mọi nhiệt độ. Khi cả hai "bất lợi một phần" (VD $\Delta H < 0$ nhưng $\Delta S < 0$ như tổng hợp NH_3), nhiệt độ quyết định — chỉ tự diễn ra khi T đủ thấp để $T\Delta S$ không "thắng" ΔH.

(!) Lỗi thường gặp: ΔH° is usually given in kJ mol^{-1} but ΔS° in J K^{-1}mol^{-1} — a factor of 1000 apart. Convert both to the *same* unit (J, or kJ) before combining them in $\Delta G = \Delta H - T\Delta S$; forgetting this conversion is one of the most common errors in AHL thermodynamics questions. Also remember T must always be in kelvin, never °C.

AHL

For $C(s) + O_2(g) \rightarrow CO_2(g)$, $\Delta H^\circ = -393.5$ kJ mol^{-1}, $\Delta S^\circ = +3.1$ J K^{-1}mol^{-1}. Calculate ΔG° at 298 K.

(A) -393.5 kJ mol^{-1}

(B) -394.4 kJ mol^{-1}

(C) $+394.4$ kJ mol^{-1}

(D) -391.6 kJ mol^{-1}

Lời giải chi tiết

$T\Delta S^\circ = (298)(3.1) = 923.8$ J $= 0.9238$ kJ. $\Delta G^\circ = -393.5 - 0.9238 = -394.4$ kJ mol^{-1}. (Choice (A) is the value you would get by forgetting the $T\Delta S^\circ$ term entirely.) **(B)**.

AHL

For a reaction with $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$, what value does ΔG° approach as $T \rightarrow 0$ K?

(A) $\Delta G^\circ \rightarrow 0$

(B) $\Delta G^\circ \rightarrow \Delta H^\circ$

(C) $\Delta G^\circ \rightarrow -\Delta H^\circ$

(D) $\Delta G^\circ \rightarrow \infty$

Lời giải chi tiết

As $T \rightarrow 0$, the term $T\Delta S^\circ \rightarrow 0$ regardless of the sign or size of ΔS°, so $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \rightarrow \Delta H^\circ$. Since $\Delta H^\circ < 0$ here, ΔG° approaches a negative value, consistent with the keyfact table: a reaction with $\Delta H^\circ < 0,\ \Delta S^\circ < 0$ is spontaneous at sufficiently low T. **(B)**.

AHL

For a reaction with $\Delta H^\circ > 0$ and $\Delta S^\circ > 0$, what happens to ΔG° as temperature increases?

(A) ΔG° increases (becomes more positive)

(B) ΔG° decreases (becomes more negative)

(C) ΔG° stays constant

(D) Cannot be determined without numerical values

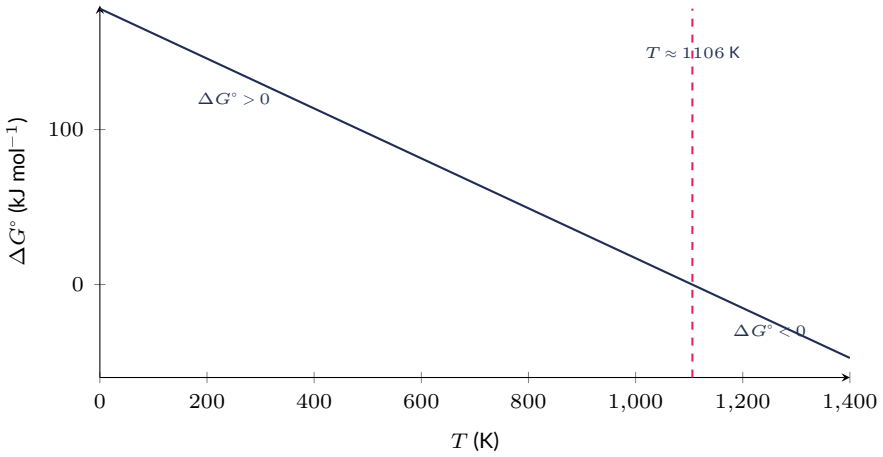
Lời giải chi tiết

In $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, with ΔH° fixed and positive and ΔS° fixed and positive, increasing T makes the $-T\Delta S^\circ$ term more negative, so ΔG° falls — eventually becoming negative (spontaneous) at high enough T, consistent with the keyfact table above. **(B)**.

4.4.4 The crossover temperature: where $\Delta G^\circ = 0$ (AHL)

When ΔH° and ΔS° have the same sign, spontaneity depends on temperature, and there is a specific **crossover temperature** at which ΔG° switches sign. Setting $\Delta G^\circ = 0$:

$$0 = \Delta H^\circ - T\Delta S^\circ \quad \Longrightarrow \quad T = \frac{\Delta H^\circ}{\Delta S^\circ}.$$



$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 178 - 0.161\,T$ (kJ mol^{-1}, T in K) for $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$. The line crosses $\Delta G^\circ = 0$ at $T \approx 1106$ K, above which decomposition becomes spontaneous.

Ví dụ mẫu · Crossover temperature for vaporisation

For the vaporisation of water, $H_2O(l) \rightarrow H_2O(g)$, $\Delta H^\circ = +44.0$ kJ mol^{-1} and $\Delta S^\circ = +118.8$ J K^{-1}mol^{-1}. Estimate the temperature at which vaporisation becomes spontaneous.

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{44{,}000}{118.8} = 370.4 \text{ K } (\approx 97^\circ\text{C}).$$

This is close to (though not exactly) water's real boiling point, 373 K (100°C); the small difference arises because ΔH° and ΔS° here are standard values at 298 K, not measured exactly at the boiling point itself.

VN **GIẢI THÍCH TIẾNG VIỆT**

Nhiệt độ chuyển tiếp (crossover temperature) là nơi $\Delta G^\circ = 0$: $T = \Delta H^\circ / \Delta S^\circ$. Trên nhiệt độ này (nếu $\Delta H^\circ, \Delta S^\circ$ cùng dương), phản ứng/quá trình trở nên tự diễn ra. Ví dụ nước hoá hơi: công thức cho $T \approx 370$ K, rất gần nhiệt độ sôi thực tế 373 K — một kiểm tra hợp lý tốt cho kết quả tính toán.

AHL

For $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$, $\Delta H^\circ = +178$ kJ mol^{-1}, $\Delta S^\circ = +161$ J K^{-1}mol^{-1}. The temperature above which this reaction becomes spontaneous is closest to:

(A) 553 K
(C) 178 K
(B) 2212 K
(D) 1106 K

Lời giải chi tiết

$T = \dfrac{\Delta H^\circ}{\Delta S^\circ} = \dfrac{178{,}000}{161} = 1106$ K. **(D).**

AHL

For the melting of ice, $H_2O(s) \rightarrow H_2O(l)$, $\Delta H^\circ = +6.01$ kJ mol^{-1}, $\Delta S^\circ = +22.0$ J K^{-1}mol^{-1}. Calculate ΔG° at (a) 263 K (-10°C) and (b) 283 K ($+10^\circ$C), and comment on whether melting is spontaneous at each temperature.

Lời giải chi tiết

(a) At $T = 263$ K: $\Delta G^\circ = 6010 - (263)(22.0) = 6010 - 5786 = +224$ J $= +0.224$ kJ mol^{-1}. Since $\Delta G^\circ > 0$, melting is *not* spontaneous at -10°C — consistent with everyday experience that ice does not melt below 0°C.

(b) At $T = 283$ K: $\Delta G^\circ = 6010 - (283)(22.0) = 6010 - 6226 = -216$ J $= -0.216$ kJ mol^{-1}. Since $\Delta G^\circ < 0$, melting *is* spontaneous at $+10^\circ$C, again matching everyday observation.

Notice the crossover temperature is $T = 6010/22.0 = 273.2$ K $= 0.0^\circ$C — exactly water's real melting point, an excellent consistency check on the given data.

AHL

Using $\Delta H^\circ = +44.0$ kJ mol^{-1} and $\Delta S^\circ = +118.8$ J K^{-1}mol^{-1} for the vaporisation of water, calculate ΔG° at 350 K and state whether vaporisation is spontaneous at this temperature.

Lời giải chi tiết

$$\Delta G^\circ = 44{,}000 - (350)(118.8) = 44{,}000 - 41{,}580 = +2420 \text{ J} = +2.42 \text{ kJ mol}^{-1}.$$

Since $\Delta G^\circ > 0$, vaporisation is *not* spontaneous at 350 K under standard conditions — consistent with 350 K lying below the crossover temperature of ≈ 370 K found earlier.

AHL

For the Haber process, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, $\Delta H^\circ = -92.4$ kJ mol^{-1}, $\Delta S^\circ = -198.4$ J K^{-1}mol^{-1} (Section 4.3). Calculate ΔG° at 700 K, and use your answer to comment on why industrial ammonia production is *not* run at very high temperatures, despite reactions generally proceeding faster at higher T.

Lời giải chi tiết

$T\Delta S^\circ = (700)(-198.4) = -138{,}880$ J.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -92{,}400 - (-138{,}880) = -92{,}400 + 138{,}880 = +46{,}480 \text{ J}.$$

$$\Delta G^\circ = +46.5 \text{ kJ mol}^{-1}.$$

At 700 K, $\Delta G^\circ > 0$: the forward reaction is no longer thermodynamically favourable, unlike at 298 K where it was strongly favourable (-33.3 kJ mol^{-1}, Section 4.3). This illustrates the trade-off behind the real Haber process's choice of operating temperature: raising T speeds up the *rate* at which equilibrium is reached (kinetics), but simultaneously pushes ΔG° — and with it the equilibrium position — away from the desired product, since the forward reaction is exothermic (thermodynamics). Industrial conditions are chosen as a compromise between these two opposing effects, together with high pressure to favour the side with fewer moles of gas.

AHL

Using the same data as above ($\Delta H^\circ = -92.4$ kJ mol^{-1}, $\Delta S^\circ = -198.4$ J K^{-1}mol^{-1}), calculate the crossover temperature for ammonia synthesis, and confirm it is consistent with $\Delta G^\circ < 0$ at 298 K and $\Delta G^\circ > 0$ at 700 K, found above.

Lời giải chi tiết

Since $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$, this reaction is only spontaneous *below* the crossover temperature (low-T case in the keyfact table, Section 4.3):

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-92{,}400}{-198.4} = 465.7 \text{ K}.$$

Both 298 K and 700 K can now be checked against this value: 298 K < 465.7 K, so $\Delta G^\circ < 0$ (spontaneous) — matching the -33.3 kJ mol^{-1} found earlier; 700 K > 465.7 K, so $\Delta G^\circ > 0$ (non-spontaneous) — matching the $+46.5$ kJ mol^{-1} found above. All three results are fully consistent.

4.5 Mixed review: drawing the chapter together

The problems below combine calorimetry, Hess's Law, Born–Haber reasoning, bond enthalpies, and Gibbs free energy in the kinds of multi-concept questions typical of a full unit assessment.

Ôn tập tổng hợp 1

A student burns 0.540 g of ethanol, $C_2H_5OH(l)$ ($M = 46.08$ g mol^{-1}), under a copper can containing 200.0 g of water. The water temperature rises from 19.5°C to 36.3°C ($c = 4.18$ J g^{-1} °C^{-1}). Calculate the experimental molar enthalpy of combustion of ethanol.

Lời giải chi tiết

$$q = mc\Delta T = (200.0)(4.18)(16.8) = 14{,}045 \text{ J}.$$

$$n(C_2H_5OH) = \frac{0.540}{46.08} = 0.01172 \text{ mol}.$$

$$\Delta H_c = -\frac{q}{n} = -\frac{14{,}045}{0.01172} = -1.198 \times 10^6 \text{ J mol}^{-1} = -1198 \text{ kJ mol}^{-1}.$$

(The literature value is ≈ -1367 kJ mol^{-1}; the experimental result is less exothermic in magnitude than this, as expected — in practice this simple setup usually *under*-estimates $|\Delta H_c|$ due to heat lost to the surroundings and incomplete combustion, so a careful student should

discuss sources of error such as incomplete combustion, heat loss to the copper can and surrounding air, and evaporation of ethanol before burning.)

Ôn tập tổng hợp 2

Given mean bond enthalpies H – H = 436, Cl – Cl = 242, H – Cl = 431 (all kJ mol^{-1}), estimate ΔH for $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$, and state whether the reaction is exothermic or endothermic.

(A) -184 kJ mol^{-1}, exothermic

(B) $+184$ kJ mol^{-1}, endothermic

(C) -862 kJ mol^{-1}, exothermic

(D) $+678$ kJ mol^{-1}, endothermic

Lời giải chi tiết

Bonds broken: $436 + 242 = 678$ kJ mol^{-1}. Bonds formed: $2 \times 431 = 862$ kJ mol^{-1}.

$$\Delta H = 678 - 862 = -184 \text{ kJ mol}^{-1}.$$

Negative ΔH means the reaction is **exothermic**. **(A)**.

Ôn tập tổng hợp 3 — AHL

For the reaction $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$, $\Delta H^\circ = -483.6$ kJ mol^{-1} and $\Delta S^\circ = -88.9$ J K^{-1}mol^{-1}. (a) Explain the sign of ΔS° in terms of moles of gas. (b) Calculate ΔG° at 298 K and comment on spontaneity.

Lời giải chi tiết

(a) There are 3 mol of gas on the reactant side ($2H_2 + 1O_2$) but only 2 mol of gas on the product side ($2H_2O$); fewer independent gas particles means fewer accessible microstates, so entropy decreases, consistent with $\Delta S^\circ < 0$.

(b)

$$\Delta G^\circ = -483{,}600 - (298)(-88.9) = -483{,}600 + 26{,}492 = -457{,}108 \text{ J} = -457.1 \text{ kJ mol}^{-1}.$$

ΔG° is very large and negative, so the reaction is strongly spontaneous at 298 K despite the unfavourable (negative) entropy change — the very large negative ΔH° completely dominates the $-T\Delta S^\circ$ term.

Ôn tập tổng hợp 4 — AHL

Using $\Delta H_f^\circ(MgO) = -602$ kJ mol^{-1}, atomisation enthalpy of Mg $= +148$ kJ mol^{-1}, first *and* second ionisation energies of Mg ($IE_1 = +738$, $IE_2 = +1451$ kJ mol^{-1}), atomisation enthalpy of O $= +249$ kJ mol^{-1}, first electron affinity of O ($EA_1 = -141$ kJ mol^{-1}), and second electron affinity of O ($EA_2 = +798$ kJ mol^{-1}, endothermic because a second electron is added to an already-negative O^- ion), calculate the lattice enthalpy of MgO.

Lời giải chi tiết

By Hess's Law, the Born–Haber cycle for MgO (formed from Mg^{2+} and O^{2-} ions) gives:

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

$$-602 = 148 + 738 + 1451 + 249 - 141 + 798 + LE = 3243 + LE.$$

$$LE = -602 - 3243 = -3845 \text{ kJ mol}^{-1}.$$

This is far more exothermic than NaCl's lattice enthalpy (≈ -786 kJ mol^{-1}), consistent with Coulomb's law: Mg^{2+} and O^{2-} carry twice the charge of Na^+/Cl^- and are also smaller ions, both of which greatly strengthen the electrostatic attraction in the lattice.

Reactivity 2 --- How Much, How Fast and How Far?

Mục tiêu Unit: Tính toán định lượng phản ứng hoá học: chất phản ứng giới hạn (limiting reactant), hiệu suất phần trăm (% yield), hiệu suất nguyên tử (atom economy), chuẩn độ và chuẩn độ ngược (back-titration), thể tích khí ở STP; tốc độ phản ứng: các yếu tố ảnh hưởng, thuyết va chạm, phân bố Maxwell–Boltzmann, phương trình tốc độ và bậc phản ứng, chu kỳ bán rã, phương trình Arrhenius, cơ chế phản ứng (HL); mức độ phản ứng: hằng số cân bằng K_c, nguyên lý Le Chatelier, thương số phản ứng Q, cân bằng dị thể, K_p và liên hệ với năng lượng tự do Gibbs chuẩn ΔG° (HL).

5.1 How much? The amount of chemical change

Stoichiometry uses the mole ratios embedded in a balanced chemical equation to relate the amounts of reactants consumed and products formed. Three quantitative ideas built on this foundation run through Reactivity 2.1: the **limiting reactant** (which reactant runs out first, capping the amount of product), the **percentage yield** (how much product is actually obtained compared with the theoretical maximum), and the **atom economy** (what fraction of the mass of the reactants ends up in the desired product – a measure of how "green" a synthetic route is).

5.1.1 Limiting reactant, percentage yield, and atom economy

Khái niệm cốt lõi

Convert every given mass, volume, or concentration into **moles** first. Compare the mole ratio actually supplied with the mole ratio required by the balanced equation: whichever reactant would run out first is the **limiting reactant**, and it alone determines the **theoretical yield** of product. Any other reactant is **in excess**.

$$\%\ \text{yield} = \frac{\text{actual amount of product obtained}}{\text{theoretical amount of product}} \times 100\%.$$

$$\text{Atom economy} = \frac{M_r(\text{desired product})}{\sum M_r(\text{all reactants})} \times 100\%.$$

Percentage yield falls below 100% because of side reactions, reversibility, or losses during separation and purification. Atom economy is a property of the reaction *route itself* – it does not depend on how efficiently a particular experiment was carried out. A reaction can have a high atom economy yet a low percentage yield in a given experiment, or vice versa.

VN **GIẢI THÍCH TIẾNG VIỆT**

Chất phản ứng giới hạn (limiting reactant) là chất hết trước, quyết định lượng sản phẩm tối đa có thể tạo ra (luôn quy đổi về **mol** trước khi so sánh tỉ lệ). **Hiệu suất phần trăm** (% yield) so sánh lượng sản phẩm thực tế thu được với lượng lý thuyết – phản ánh sự hao hụt trong thí nghiệm (phản ứng phụ, phản ứng thuận nghịch, mất mát khi tinh chế). **Hiệu suất nguyên tử**

(atom economy) gắn với bản chất phản ứng, không phụ thuộc thí nghiệm cụ thể, và là thước đo mức độ "xanh" (green chemistry) của quy trình tổng hợp.

Ví dụ mẫu · Limiting reactant, percentage yield, and atom economy

4.00 mol of aluminium is heated with 5.00 mol of chlorine gas:

$$2\text{Al(s)} + 3\text{Cl}_2\text{(g)} \rightarrow 2\text{AlCl}_3\text{(s)}$$

(a) Identify the limiting reactant. (b) Calculate the theoretical mass of AlCl_3 formed. (c) If 400.0 g of AlCl_3 is actually collected, calculate the percentage yield. (d) Calculate the atom economy.

(a) 4.00 mol Al requires $4.00 \times \dfrac{3}{2} = 6.00$ mol Cl_2, but only 5.00 mol is available $\Rightarrow$ Cl_2 **is limiting** (Al is in excess).

(b) $n(\text{AlCl}_3) = 5.00 \times \dfrac{2}{3} = 3.333$ mol. $M(\text{AlCl}_3) = 26.98 + 3(35.45) = 133.33$ g mol^{-1}.

$$m(\text{AlCl}_3)_{\text{theor}} = 3.333 \times 133.33 = 444.4 \text{ g}.$$

(c)

$$\%\text{ yield} = \frac{400.0}{444.4} \times 100 = 90.0\%.$$

(d) AlCl_3 is the only product, so all reacted mass ends up in it:

$$\text{Atom economy} = 100\%.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Cl_2 là chất giới hạn vì cần 6.00 mol nhưng chỉ có 5.00 mol. Hiệu suất nguyên tử đạt 100% vì phản ứng chỉ tạo *một* sản phẩm duy nhất (không có sản phẩm phụ) – khác biệt cốt lõi so với hiệu suất phần trăm chỉ 90.0% do hao hụt thực nghiệm.

For reactions that make one desired product alongside a **by-product**, the atom economy is normally below 100% even though mass is fully conserved – it simply ends up in a molecule other than the desired one.

Ví dụ mẫu · Atom economy with a by-product

Aspirin is manufactured from salicylic acid ($\text{C}_7\text{H}_6\text{O}_3$) and acetic anhydride ($\text{C}_4\text{H}_6\text{O}_3$):

$$\text{C}_7\text{H}_6\text{O}_3 + \text{C}_4\text{H}_6\text{O}_3 \rightarrow \text{C}_9\text{H}_8\text{O}_4 + \text{C}_2\text{H}_4\text{O}_2$$

(aspirin, $\text{C}_9\text{H}_8\text{O}_4$, is desired; acetic acid, $\text{C}_2\text{H}_4\text{O}_2$, is the by-product). Calculate the atom economy.

$M_r(\text{C}_7\text{H}_6\text{O}_3) = 7(12.01) + 6(1.01) + 3(16.00) = 138.13$. $M_r(\text{C}_4\text{H}_6\text{O}_3) = 4(12.01) + 6(1.01) + 3(16.00) = 102.10$. $M_r(\text{C}_9\text{H}_8\text{O}_4) = 9(12.01) + 8(1.01) + 4(16.00) = 180.17$.

$$\text{Atom economy} = \frac{180.17}{138.13 + 102.10} \times 100 = \frac{180.17}{240.23} \times 100 = 75.0\%.$$

Even at 100% percentage yield, at most 75.0% of the reactant mass could ever become aspirin – the rest necessarily leaves as acetic acid.

VN **GIẢI THÍCH TIẾNG VIỆT**

Khi phản ứng sinh thêm sản phẩm phụ (ở đây là axit axetic), hiệu suất nguyên tử luôn nhỏ hơn 100% dù không nguyên tử nào "biến mất" – khối lượng chỉ "đi" vào sản phẩm phụ thay vì sản phẩm mong muốn. Đây là lý do công nghiệp hoá học ưu tiên các phản ứng có hiệu suất nguyên tử cao (ít chất thải hơn).

(!) Lỗi thường gặp: Never compare the *masses* or *volumes* supplied directly to decide the limiting reactant – always convert to **moles** first and compare against the balanced-equation ratio. The reactant supplied in the larger mass is not necessarily in excess if its molar mass is much larger than the other reactant's.

Bài tập luyện tập 1 · Percentage yield vs atom economy

A synthesis has a percentage yield of 60% but an atom economy of 95%. Which statement best explains this combination?

(A) Most of the reactant mass ends up in the desired product in principle, but much of the product actually made was lost or not recovered during the experiment.

(B) The reaction mostly produces by-products, but almost all the material was collected.

(C) The rate constant for the reaction is unusually large.

(D) The equilibrium constant for the reaction is close to 1.

Lời giải chi tiết

(A). A high atom economy (95%) means the reaction *route itself* wastes little mass on by-products. A low percentage yield (60%) means that, in this particular experiment, a large fraction of the theoretically possible product was lost (incomplete reaction, side reactions, or losses during separation/purification). Options (C) and (D) refer to unrelated quantities (rate and equilibrium constants), and (B) directly contradicts a high atom economy.

Bài tập luyện tập 2 · Limiting reactant, quick check

For $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$, 3.00 mol H_2 is mixed with 3.00 mol O_2. Which is the limiting reactant?

(A) H_2

(B) O_2

(C) Both react completely, with none left over

(D) Cannot be determined without molar masses

Lời giải chi tiết

(A). 3.00 mol H_2 requires only $3.00 \times \frac{1}{2} = 1.50$ mol O_2 (mole ratio $2:1$). Since 3.00 mol O_2 is available – twice what is needed – O_2 is in large excess and H_2 is the limiting reactant. Molar mass plays no role once the calculation is done in moles.

Bài tập luyện tập 3 · Limiting reactant and percentage yield

3.00 mol N_2 reacts with 8.00 mol H_2: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$. If 72.1 g of NH_3 is actually collected, determine the limiting reactant and the percentage yield.

Lời giải chi tiết

3.00 mol N_2 requires $3.00 \times 3 = 9.00$ mol H_2, but only 8.00 mol is available $\Rightarrow$ H_2 **is limiting.**

$$n(\text{NH}_3)_{\text{theor}} = 8.00 \times \frac{2}{3} = 5.333 \text{ mol}, \qquad M(\text{NH}_3) = 14.01 + 3(1.01) = 17.04 \text{ g mol}^{-1}.$$

$$m_{\text{theor}} = 5.333 \times 17.04 = 90.9 \text{ g}, \qquad \%\text{ yield} = \frac{72.1}{90.9} \times 100 = 79.3\%.$$

Bài tập luyện tập 4 · Atom economy of a decomposition

Industrial oxygen can be produced from hydrogen peroxide: $2\text{H}_2\text{O}_2(\text{l}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$, with O_2 as the desired product. Since H_2O_2 is the only reactant, calculate the atom economy.

Lời giải chi tiết

$$M_r(\text{H}_2\text{O}_2) = 2(1.01) + 2(16.00) = 34.02, \qquad M_r(\text{O}_2) = 32.00.$$

$$\text{Atom economy} = \frac{32.00}{34.02} \times 100 = 94.1\%.$$

5.1.2 Titration calculations and solution stoichiometry

A **titration** determines the unknown concentration of one solution by reacting it, drop by drop, with a solution of precisely known concentration (the **standard solution**) until the reaction is exactly complete (the **equivalence point**, usually detected using an indicator that changes colour at the **end point**). Because concentration $c = \frac{n}{V}$, the volume of standard solution used (the **titre**), together with its concentration, gives the moles reacted – which the balanced equation then converts into moles, and hence concentration, of the unknown.

Khái niệm cốt lõi

Titration routine: (1) write the balanced equation; (2) find moles of the solution of known concentration from $n = cV$; (3) use the mole ratio from the equation to find moles of the unknown; (4) convert to concentration ($c = n/V$) or mass, as required. Always convert volumes from cm^3 to dm^3 ($\div 1000$) before using $n = cV$ with c in mol dm^{-3}.

VN **GIẢI THÍCH TIẾNG VIỆT**

Quy trình tính toán chuẩn độ: viết phương trình cân bằng → tính mol dung dịch đã biết nồng độ ($n = cV$) → dùng tỉ lệ mol trong phương trình để tìm mol chất cần tìm → đổi ra nồng độ hoặc khối lượng. Luôn đổi thể tích từ cm^3 sang dm^3 trước khi tính.

Ví dụ mẫu · Titration – finding an unknown concentration

20.0 cm^3 of a H_2SO_4 solution of unknown concentration is titrated with 0.150 mol dm^{-3} NaOH, requiring 28.4 cm^3 to reach the end point:

$$2\text{NaOH}(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$$

Find $c(H_2SO_4)$.

$$n(\text{NaOH}) = 0.0284 \text{ dm}^3 \times 0.150 \text{ mol dm}^{-3} = 0.00426 \text{ mol}.$$

Mole ratio NaOH : $H_2SO_4 = 2:1$, so

$$n(H_2SO_4) = \frac{0.00426}{2} = 0.00213 \text{ mol}, \qquad c(H_2SO_4) = \frac{0.00213}{0.0200} = 0.107 \text{ mol dm}^{-3}.$$

VN **GIẢI THÍCH TIẾNG VIỆT**
Chú ý tỉ lệ mol NaOH : $H_2SO_4 = 2:1$ (không phải $1:1$) vì H_2SO_4 là axit hai nấc (diprotic) – đây là lỗi rất thường gặp khi làm bài chuẩn độ.

(!) Lỗi thường gặp: In a titration, always identify the mole ratio from the balanced equation before dividing – it is **not** always $1:1$ (e.g. diprotic acids such as H_2SO_4 react with NaOH in a $1:2$ ratio). Forgetting this is one of the most common titration errors.

Bài tập luyện tập 5 · Simple acid–base titration

25.0 cm^3 of a NaOH solution of unknown concentration is titrated with 0.100 mol dm^{-3} HCl, requiring 22.5 cm^3 for the end point (NaOH + HCl → NaCl + H_2O). Find c(NaOH).

Lời giải chi tiết

$$n(\text{HCl}) = 0.0225 \text{ dm}^3 \times 0.100 \text{ mol dm}^{-3} = 0.00225 \text{ mol} = n(\text{NaOH}) \quad (1:1 \text{ ratio}).$$

$$c(\text{NaOH}) = \frac{0.00225}{0.0250} = 0.0900 \text{ mol dm}^{-3}.$$

5.1.3 Back-titration: finding the purity of an impure sample

A **back-titration** is used when the substance of interest cannot be titrated directly – for example, an insoluble or impure solid, or a reaction with no sharp end point. A known **excess** of a standard 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 amount from the total added gives the amount that reacted with the sample, which converts (via the mole ratio) into the amount, mass, and percentage purity of the substance of interest.

Khái niệm cốt lõi

Back-titration routine: (1) n(reagent added, total) $= cV$; (2) n(reagent left over) $=$ moles found from the second titration; (3) n(reagent reacted with sample) $=$ total $-$ left over; (4) use the mole ratio with the sample's reaction to find n(sample), then its mass and percentage purity.

VN **GIẢI THÍCH TIẾNG VIỆT**
Chuẩn độ ngược (back-titration) dùng khi không thể chuẩn độ trực tiếp chất cần xác định (ví dụ mẫu rắn không tan hoặc không tinh khiết): cho **dư** một thuốc thử đã biết nồng độ phản ứng hết với mẫu, sau đó chuẩn độ lượng thuốc thử **còn dư** bằng một dung dịch chuẩn thứ hai. Lấy tổng lượng đã thêm trừ đi lượng dư sẽ ra lượng đã phản ứng với mẫu.

Ví dụ mẫu · Back-titration – purity of impure sodium carbonate

A 2.65 g impure sample of Na_2CO_3 is reacted with 50.0 cm^3 of 1.00 mol dm^{-3} HCl (an excess):

$$Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

The excess acid requires 24.0 cm^3 of 0.500 mol dm^{-3} NaOH to reach the end point. Calculate the percentage purity of the sample (assume the impurity does not react with HCl).

$$n(\text{HCl})_{\text{total}} = 0.0500 \times 1.00 = 0.0500 \text{ mol}.$$
$$n(\text{HCl})_{\text{excess}} = n(\text{NaOH}) = 0.0240 \times 0.500 = 0.0120 \text{ mol}.$$
$$n(\text{HCl})_{\text{reacted with } Na_2CO_3} = 0.0500 - 0.0120 = 0.0380 \text{ mol}.$$

Mole ratio HCl : $Na_2CO_3 = 2 : 1$, so $n(Na_2CO_3) = \dfrac{0.0380}{2} = 0.0190$ mol. $M(Na_2CO_3) = 2(22.99) + 12.01 + 3(16.00) = 105.99$ g mol^{-1}.

$$m(Na_2CO_3) = 0.0190 \times 105.99 = 2.01 \text{ g}, \qquad \%\text{ purity} = \frac{2.01}{2.65} \times 100 = 76.0\%.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Ở bước cuối, luôn nhớ trừ lượng **dư** khỏi lượng **đã thêm** để tìm lượng thuốc thử thực sự đã phản ứng với mẫu, rồi mới áp dụng tỉ lệ mol của phản ứng chính (ở đây là HCl : $Na_2CO_3 = 2 : 1$) để tìm khối lượng và độ tinh khiết.

Bài tập luyện tập 6 · Back-titration – purity of impure sodium hydrogencarbonate

A 1.68 g impure sample of $NaHCO_3$ is added to 40.0 cm^3 of 0.500 mol dm^{-3} HCl (an excess): $NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)$. The excess acid requires 15.0 cm^3 of 0.200 mol dm^{-3} NaOH to reach the end point. Calculate the percentage purity of the sample.

Lời giải chi tiết

$$n(\text{HCl})_{\text{total}} = 0.0400 \times 0.500 = 0.0200 \text{ mol}.$$
$$n(\text{HCl})_{\text{excess}} = n(\text{NaOH}) = 0.0150 \times 0.200 = 0.00300 \text{ mol}.$$
$$n(\text{HCl})_{\text{reacted}} = 0.0200 - 0.00300 = 0.0170 \text{ mol} = n(NaHCO_3) \ \ (1:1 \text{ ratio}).$$
$$M(NaHCO_3) = 22.99 + 1.01 + 12.01 + 3(16.00) = 84.01 \text{ g mol}^{-1}.$$

$$m(NaHCO_3) = 0.0170 \times 84.01 = 1.43 \text{ g}, \qquad \%\text{ purity} = \frac{1.43}{1.68} \times 100 = 85.0\%.$$

5.1.4 Gas volume stoichiometry at STP

Because 1 mol of any ideal gas occupies the same volume at a given temperature and pressure, gas volumes can be used directly in mole-ratio stoichiometry once converted through $n = \dfrac{V}{V_m}$. At **STP** (273 K, 100 kPa, as defined in the IB data booklet), the molar volume of an ideal gas is

$$V_m = 22.7 \text{ dm}^3 \text{ mol}^{-1}.$$

Khái niệm cốt lõi

To find a gas volume from a mass of reactant (or vice versa): convert mass to moles ($n = m/M$); use the mole ratio from the balanced equation to find moles of gas; convert to volume ($V = nV_m$) at STP – or reverse the steps to go from a measured gas volume back to a mass.

VN **GIẢI THÍCH TIẾNG VIỆT**

Ở STP theo IB (273 K, 100 kPa), 1 mol khí lý tưởng bất kỳ chiếm thể tích 22.7 dm^3 – không phụ thuộc bản chất khí. Quy trình: đổi khối lượng sang mol → dùng tỉ lệ mol → đổi sang thể tích bằng $V = nV_m$.

Ví dụ mẫu · Gas volume from mass of reactant

Calculate the volume of H_2 gas produced (at STP) when 2.70 g of aluminium reacts completely with excess hydrochloric acid:

$$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$$

$$n(Al) = \frac{2.70}{26.98} = 0.100 \text{ mol}.$$

Mole ratio Al : $H_2 = 2 : 3$, so $n(H_2) = 0.100 \times \frac{3}{2} = 0.150$ mol.

$$V(H_2) = 0.150 \times 22.7 = 3.41 \text{ dm}^3.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Đây là bài toán "khối lượng chất rắn → mol → tỉ lệ mol → mol khí → thể tích khí ở STP" – luôn dùng 22.7 dm^3/mol theo quy ước STP hiện hành của IB.

(!) Lỗi thường gặp: Do not confuse the current IB definition of STP (273 K, 100 kPa, $V_m = 22.7$ dm^3 mol^{-1}) with the older STP convention (273 K, 101.3 kPa, $V_m = 22.4$ dm^3 mol^{-1}) found in some older resources – IB examinations use 22.7 dm^3 mol^{-1}.

Bài tập luyện tập 7 · Gas volume from decomposition

$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$. Calculate the volume of CO_2 gas produced at STP when 16.80 g of $NaHCO_3$ is completely decomposed.

Lời giải chi tiết

$$n(NaHCO_3) = \frac{16.80}{84.01} = 0.200 \text{ mol}.$$

Mole ratio $NaHCO_3 : CO_2 = 2 : 1$, so $n(CO_2) = 0.100$ mol.

$$V(CO_2) = 0.100 \times 22.7 = 2.27 \text{ dm}^3.$$

Bài tập luyện tập 8 · The STP molar volume

Which statement about the molar volume of an ideal gas, as used in IB Chemistry calculations, is correct?

(A) 22.7 dm^3 mol^{-1} at 273 K and 100 kPa, regardless of the identity of the gas.

(B) 22.7 dm^3 mol^{-1} at 298 K and 101.3 kPa for all gases.

(C) 24.0 dm^3 mol^{-1} at STP, but only for diatomic gases.

(D) The molar volume depends on the molar mass of the gas.

Lời giải chi tiết

(A). At STP (273 K, 100 kPa, per the IB data booklet), 1 mol of *any* ideal gas occupies 22.7 dm^3, independent of its identity or molar mass – this is the ideal-gas approximation.

5.2 How fast? The rate of chemical change

The **rate of reaction** measures how quickly reactants are consumed or products are formed, usually expressed as a change in concentration per unit time (mol dm^{-3} s^{-1}). Rate is not constant during a reaction: it is generally fastest at the start (when reactant concentrations are highest) and slows as reactants are used up.

5.2.1 Factors affecting reaction rate

- **Concentration**: a higher concentration packs more particles into the same volume, increasing collision frequency and therefore rate.
- **Surface area** (of a solid): breaking a solid into smaller pieces exposes more surface area, so more particles are accessible for collision per unit time.
- **Temperature**: raising the temperature increases both the average particle speed (slightly more frequent collisions) and, far more importantly, the *fraction* of collisions with energy $\geq E_a$ (see the Maxwell–Boltzmann distribution below).
- **Catalyst**: provides an alternative reaction pathway of lower activation energy, so a larger fraction of collisions is successful at the same temperature.
- **Pressure** (gaseous reactions): increasing pressure at constant temperature reduces the volume occupied by a fixed amount of gas – equivalent to increasing concentration – so collision frequency rises.

VN **GIẢI THÍCH TIẾNG VIỆT**

Năm yếu tố ảnh hưởng đến tốc độ phản ứng, đều giải thích qua **thuyết va chạm**: nồng độ tăng $\rightarrow$ va chạm nhiều hơn; diện tích bề mặt tăng (chất rắn) $\rightarrow$ nhiều hạt tiếp xúc hơn; nhiệt độ tăng $\rightarrow$ tăng mạnh tỉ lệ hạt có năng lượng $\geq E_a$; chất xúc tác $\rightarrow$ hạ thấp E_a qua con đường phản ứng khác; áp suất tăng (khí) $\rightarrow$ tương đương tăng nồng độ.

5.2.2 Experimental methods for measuring rate

- **Gas-volume collection**: for reactions producing a gas, the volume evolved is measured over time with a gas syringe (or by downward displacement of water), giving a direct volume–time curve.
- **Mass-loss**: if a gas escapes to the atmosphere (e.g. from an open flask on a balance), the decreasing mass of the flask and contents is recorded against time.
- **Colorimetry**: for reactions where a coloured species is consumed or formed, a colorimeter measures absorbance (proportional to concentration) as a function of time.
- **Titration (quenching)**: small samples are withdrawn at intervals, the reaction in each is "quenched" (stopped abruptly, e.g. by rapid cooling or adding a reagent that consumes a key species), and the remaining concentration of a reactant is found by titration.

- **Conductivity**: if the number or type of ions changes as the reaction proceeds, the electrical conductivity of the solution is monitored continuously as a proxy for concentration.

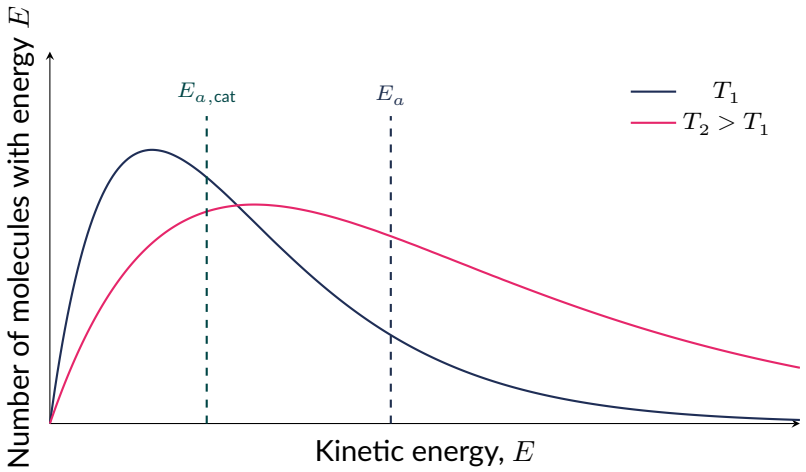
VN **GIẢI THÍCH TIẾNG VIỆT**

Các phương pháp đo tốc độ phản ứng phổ biến: thu khí bằng ống bơm khí (gas syringe), đo khối lượng giảm dần (mass-loss) nếu khí thoát ra ngoài, đo màu bằng máy so màu (colorimetry) nếu có chất màu, lấy mẫu rồi "dập tắt" phản ứng (quenching) để chuẩn độ, hoặc đo độ dẫn điện nếu số ion thay đổi.

5.2.3 Collision theory, the Maxwell–Boltzmann distribution, and catalysts

Collision theory states that a reaction between particles can only occur if they (i) collide, (ii) with energy greater than or equal to the **activation energy** E_a (the minimum energy needed to break/rearrange bonds), and (iii) with the correct relative **orientation**. Most collisions fail one of these tests, which is why reaction rates are far slower than collision frequencies alone would suggest.

At any temperature, particles in a sample have a spread of kinetic energies described by the **Maxwell–Boltzmann distribution**. The curve starts at the origin, rises to a peak (the most probable energy, which is not the same as the mean energy), and falls with a long tail toward high energy; the total area under the curve equals the total number of particles.



Maxwell–Boltzmann distribution of molecular kinetic energies at two temperatures, $T_2 > T_1$. At T_2 the peak is lower and shifted to higher E; the area under the curve to the right of E_a (the fraction of molecules with sufficient energy to react) is much larger, even though the rise in average kinetic energy itself is modest. A catalyst offers an alternative pathway with a lower activation energy $E_{a,\text{cat}} < E_a$, increasing the qualifying fraction at a *fixed* temperature.

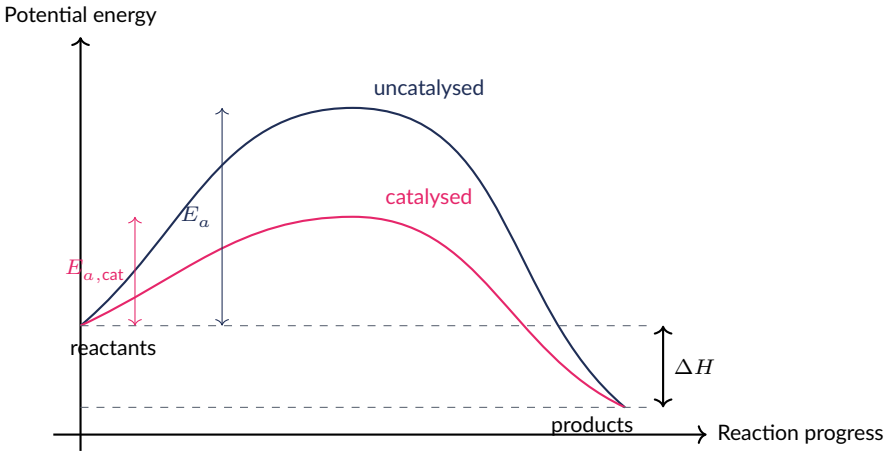
Khái niệm cốt lõi

Raising the temperature increases the rate mainly because the Maxwell–Boltzmann curve broadens and flattens: even a modest rise in average kinetic energy produces a disproportionately large increase in the (small) high-energy tail beyond E_a, since that region of the curve grows fastest as the distribution spreads out. This is why, empirically, many reaction rates roughly double for each 10 K rise near room temperature. A **catalyst** works differently: it does not change the distribution of molecular energies at all – instead it lowers E_a itself by providing an alternative reaction pathway (e.g. via adsorption on a surface, or forming a different intermediate), so a larger area of the *same* distribution now lies above the (lower) energy threshold.

GIẢI THÍCH TIẾNG VIỆT

VN

Đường phân bố Maxwell–Boltzmann mô tả sự phân bố động năng của các hạt ở một nhiệt độ. Khi nhiệt độ tăng, đỉnh đường cong thấp xuống và dịch sang phải, khiến diện tích phần đuôi bên phải E_a (tỉ lệ hạt đủ năng lượng phản ứng) tăng mạnh dù động năng trung bình chỉ tăng nhẹ. Chất xúc tác KHÔNG làm thay đổi đường phân bố năng lượng, mà hạ thấp E_a bằng cách tạo con đường phản ứng khác.



Energy profile for an exothermic reaction with and without a catalyst. The catalysed pathway has a lower activation energy $E_{a,\text{cat}} < E_a$ but identical start and end energies – so ΔH is unchanged. Because the forward and reverse activation energies are both lowered by the same amount, the catalyst speeds up the forward and reverse reactions equally.

(!) Lỗi thường gặp: A catalyst provides an alternative pathway of lower activation energy and speeds up the forward *and* reverse reactions equally. It does **not** change ΔH of the reaction, and it does **not** change the position of equilibrium or the value of K – it only changes how quickly equilibrium is reached.

Bài tập luyện tập 9 · Pressure and rate

Increasing the pressure on a gaseous reaction mixture (at constant temperature) increases the rate mainly because it:

(A) increases the frequency of collisions between particles, by reducing the volume they occupy.

(B) increases the average kinetic energy of the particles.

(C) lowers the activation energy of the reaction.

(D) shifts the Maxwell–Boltzmann distribution to lower energies.

Lời giải chi tiết

(A). At constant temperature, average kinetic energy (B) and the shape of the Maxwell–Boltzmann distribution are unchanged, and pressure has no effect on activation energy (C). Increasing pressure compresses a fixed amount of gas into a smaller volume, raising its effective concentration and hence the collision frequency, which is (A).

Bài tập luyện tập 10 · Choosing a method to measure rate

A reaction between a metal carbonate and an acid produces $CO_2(g)$ as the only gaseous product; all other species remain in solution. Which experimental method is most directly suited to following this reaction's progress?

(A) Colorimetry
(B) Gas-volume collection with a gas syringe
(C) Conductivity measurement
(D) Titration with quenching

Lời giải chi tiết

(B). Since a gas is evolved and no species involved is coloured, gas-volume collection gives a direct, continuous volume–time curve with minimal disturbance to the reaction. Colorimetry (A) requires a colour change; conductivity (C) and quenched titrations (D) are better suited to reactions monitored through ionic or dissolved-species concentration changes.

Bài tập luyện tập 11 · Explaining the temperature effect

Using the Maxwell–Boltzmann distribution, explain why a 10 K rise in temperature can more than double the rate of many reactions, even though the average kinetic energy of the particles increases only slightly.

Lời giải chi tiết

A small rise in temperature broadens and flattens the Maxwell–Boltzmann distribution only slightly overall, so the *average* kinetic energy rises only a little. However, the fraction of molecules with energy at or above the (fixed) activation energy E_a corresponds to the area under the far right-hand tail of the curve. Because this tail is the most sensitive part of the distribution to a change in shape, even a small broadening produces a disproportionately large increase in that area – so the fraction of successful (sufficiently energetic) collisions, and hence the rate, can more than double for a modest temperature rise.

5.2.4 Rate expressions and orders of reaction (AHL)

Khái niệm cốt lõi

For a reaction with reactants A, B, … , the **rate expression** (rate law) has the experimentally-determined form

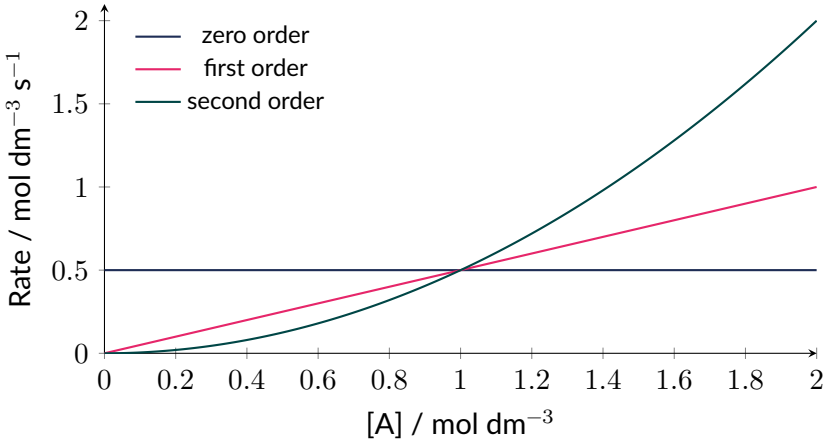
$$\text{rate} = k[\text{A}]^m[\text{B}]^n \cdots,$$

where m is the **order with respect to A**, n the order with respect to B, and $m + n + \cdots$ is the **overall order**. Orders are small numbers (usually 0, 1, or 2) determined *only by experiment* – they cannot be deduced from the balanced equation's stoichiometric coefficients. The **rate constant** k is independent of concentration and depends only on temperature (and on whether a catalyst is present); its units depend on the overall order.
The **method of initial rates** finds each order by comparing experiments in which one reactant's initial concentration is changed while the others are held fixed, and observing the resulting change in the initial rate: doubling $[\text{A}]$ with no change in rate $\Rightarrow$ order 0 in A; doubling $[\text{A}]$ doubles the rate $\Rightarrow$ order 1; doubling $[\text{A}]$ quadruples the rate $\Rightarrow$ order 2.

VN GIẢI THÍCH TIẾNG VIỆT

Bậc phản ứng (order) theo từng chất chỉ xác định được bằng **thực nghiệm**, KHÔNG được suy ra từ hệ số cân bằng của phương trình. Phương pháp tốc độ đầu (method of initial rates) so sánh các thí nghiệm thay đổi nồng độ đầu của một chất trong khi giữ nguyên các chất khác, rồi xem tốc độ đầu thay đổi ra sao.

(!) Lỗi thường gặp: The orders in a rate law are **not** the same as the stoichiometric coefficients in the balanced overall equation – they must be found experimentally (e.g. by the method of initial rates). This differs from the equilibrium-constant expression K_c, where the exponents *are* always the balancing coefficients (Section 2.3).



Shape of a rate–concentration graph for zero, first, and second order in a single reactant A: a horizontal line (rate independent of [A]), a straight line through the origin (rate directly proportional to [A]), and an upward-curving line (rate proportional to [A]^2), respectively.

Ví dụ mẫu · Method of initial rates (AHL)

For $2\text{NO(g)} + 2\text{H}_2\text{(g)} \rightarrow \text{N}_2\text{(g)} + 2\text{H}_2\text{O(g)}$, the following initial rates were measured:

Trial	[NO] / mol dm^{-3}	[H_2] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	0.10	0.10	1.20×10^{-3}
2	0.20	0.10	4.80×10^{-3}
3	0.10	0.20	2.40×10^{-3}

Determine the rate expression and the value of k.

Trials $1 \rightarrow 2$: [NO] doubles, [H_2] constant, rate increases $\dfrac{4.80}{1.20} = 4\times \Rightarrow 2^m = 4 \Rightarrow m = 2$. Trials $1 \rightarrow 3$: [H_2] doubles, [NO] constant, rate increases $\dfrac{2.40}{1.20} = 2\times \Rightarrow 2^n = 2 \Rightarrow n = 1$.

$$\text{rate} = k[\text{NO}]^2[\text{H}_2], \qquad \text{overall order} = 3.$$

Using trial 1: $k = \dfrac{1.20 \times 10^{-3}}{(0.10)^2(0.10)} = 1.20\ \text{mol}^{-2}\ \text{dm}^6\ \text{s}^{-1}$.

VN **GIẢI THÍCH TIẾNG VIỆT**

So sánh cặp thí nghiệm chỉ thay đổi **một** nồng độ tại một thời điểm: tỉ lệ tốc độ tăng bằng tỉ lệ nồng độ tăng luỹ thừa bậc phản ứng. Ở đây bậc theo NO là 2 (tốc độ tăng 4 lần khi $[\text{NO}]$ tăng gấp đôi), bậc theo H_2 là 1, bậc toàn phần $= 3$.

Bài tập luyện tập 12 · Determining a rate expression (AHL)

For A + B → products, the following initial rates were measured:

Trial	[A] / mol dm^{-3}	[B] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	0.10	0.10	1.0×10^{-3}
2	0.20	0.10	2.0×10^{-3}
3	0.10	0.20	2.0×10^{-3}

Determine the rate expression, the overall order, and the value of k (with units).

Lời giải chi tiết

Trials $1 \to 2$: [A] doubles, rate doubles $\Rightarrow$ order 1 in A. Trials $1 \to 3$: [B] doubles, rate doubles $\Rightarrow$ order 1 in B.

$$\text{rate} = k[\text{A}][\text{B}], \qquad \text{overall order} = 2.$$

$$k = \frac{1.0 \times 10^{-3}}{(0.10)(0.10)} = 0.10 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}.$$

Bài tập luyện tập 13 · Order and concentration change

A reaction is second order overall in a single reactant A (rate $= k[\text{A}]^2$). If [A] is tripled, by what factor does the rate increase?

(A) 3
(B) 6
(C) 9
(D) $1/3$

Lời giải chi tiết

(C). rate $\propto [\text{A}]^2$, so tripling [A] multiplies the rate by $3^2 = 9$.

Bài tập luyện tập 14 · Units of a rate constant

A reaction is first order overall. If rate is measured in mol dm^{-3} s^{-1} and concentration in mol dm^{-3}, what are the units of k?

Lời giải chi tiết

rate $= k[\text{A}]$, so $k = \dfrac{\text{rate}}{[\text{A}]} = \dfrac{\text{mol dm}^{-3}\text{ s}^{-1}}{\text{mol dm}^{-3}} = \text{s}^{-1}$.

5.2.5 Integrated rate law and half-life ($t_{1/2}$) for first-order reactions (AHL)

Khái niệm cốt lõi

For a reaction that is **first order overall** in a single reactant A, integrating the rate law gives

$$\ln[\mathrm{A}]_t = \ln[\mathrm{A}]_0 - kt,$$

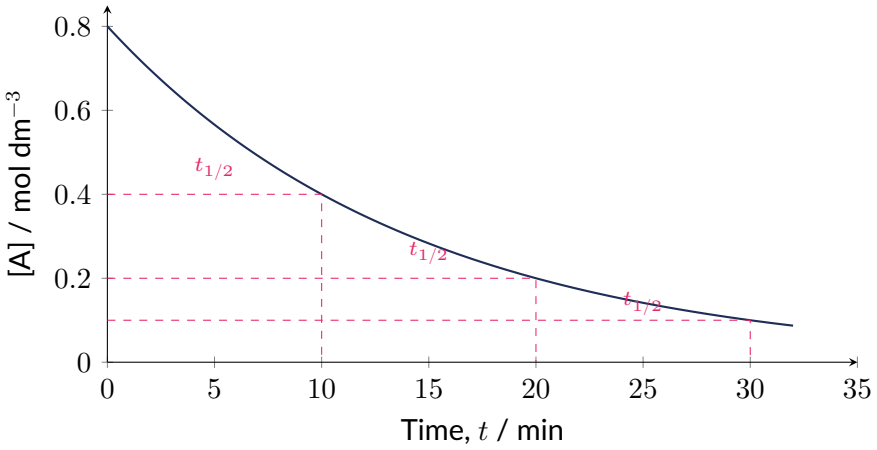
so a plot of $\ln[\mathrm{A}]$ against t is a straight line of gradient $-k$; equivalently $[\mathrm{A}]_t = [\mathrm{A}]_0 e^{-kt}$, an exponential decay. A defining feature of a first-order process is that its **half-life** $t_{1/2}$ (the time for the concentration to fall to half its value) is **constant** – independent of the starting concentration:

$$t_{1/2} = \frac{\ln 2}{k}.$$

If successive half-lives measured from a concentration–time graph or data table are equal, the reaction is first order in that species; if the half-life instead changes systematically, it is not first order.

VN **GIẢI THÍCH TIẾNG VIỆT**

Đặc điểm nhận dạng phản ứng **bậc một**: chu kỳ bán rã $t_{1/2}$ (thời gian để nồng độ giảm còn một nửa) là **không đổi**, không phụ thuộc nồng độ ban đầu. Nếu từ đồ thị hoặc bảng số liệu, các chu kỳ bán rã liên tiếp bằng nhau thì phản ứng là bậc một.



Concentration–time curve for a first-order reaction: [A] falls from 0.800 to 0.400 to 0.200 to 0.100 mol dm^{-3} in three *equal* 10-minute intervals – the constant half-life is diagnostic of first-order kinetics.

Ví dụ mẫu · Confirming first order and finding $t_{1/2}$ and k (AHL)

The concentration of reactant A was monitored over time:

t / min	0	10	20	t / min	30
[A] / mol dm^{-3}	0.800	0.400	0.200	[A] / mol dm^{-3}	0.100

Show that the reaction is first order in A and find $t_{1/2}$ and k.

Each successive 10-minute interval halves [A]: $0.800 \to 0.400$ ($0 \to 10$ min), $0.400 \to 0.200$ ($10 \to 20$ min), $0.200 \to 0.100$ ($20 \to 30$ min). Since the half-life is constant at $t_{1/2} = 10$ min

regardless of the starting concentration, the reaction is **first order** in A.

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{10} = 0.0693 \text{ min}^{-1}.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Ba khoảng 10 phút liên tiếp đều làm nồng độ giảm còn một nửa → chu kỳ bán rã không đổi → xác nhận phản ứng bậc một. Từ đó tính $k = \ln 2 / t_{1/2}$.

Bài tập luyện tập 15 · Half-life from concentration data (AHL)

The concentration of a first-order reactant falls from 0.500 mol dm^{-3} to 0.0625 mol dm^{-3} over 60 minutes. How many half-lives have elapsed? Find $t_{1/2}$ and k.

Lời giải chi tiết

$0.500 \to 0.250 \to 0.125 \to 0.0625$ mol dm^{-3}: each step is a halving, so 3 **half-lives** have elapsed in 60 minutes.

$$t_{1/2} = \frac{60}{3} = 20.0 \text{ min}, \qquad k = \frac{\ln 2}{20.0} = 0.0347 \text{ min}^{-1}.$$

5.2.6 The Arrhenius equation and the rate constant k (AHL)

Khái niệm cốt lõi

The **Arrhenius equation** relates the rate constant to temperature and activation energy:

$$k = Ae^{-E_a/RT},$$

where A is the **pre-exponential factor** (related to collision frequency and orientation, roughly constant over a modest temperature range) and E_a is the activation energy. Taking natural logs linearises this:

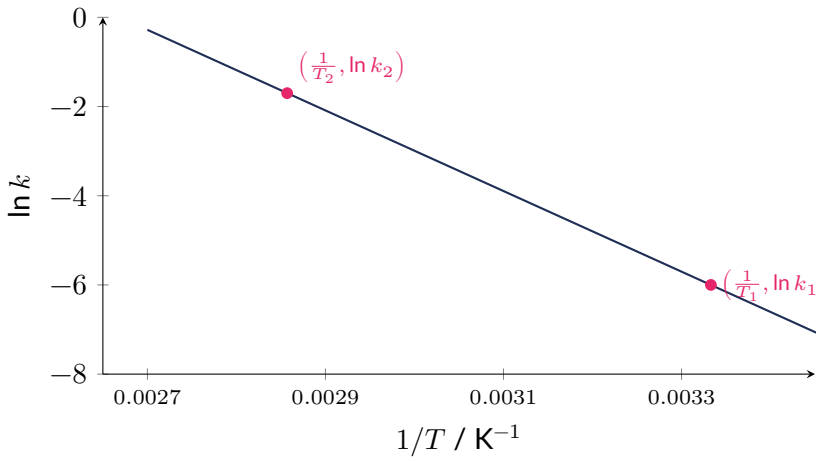
$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T},$$

so a plot of $\ln k$ (y-axis) against $1/T$ (x-axis) is a straight line of gradient $-E_a/R$ and intercept $\ln A$. Comparing the equation at two temperatures eliminates A:

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Phương trình Arrhenius liên hệ hằng số tốc độ k với nhiệt độ 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 từ số liệu thực nghiệm mà không cần biết A.



Arrhenius plot: $\ln k$ against $1/T$ is a straight line of gradient $-E_a/R$. The two marked points, at $1/T_1 = 3.333 \times 10^{-3}$ K^{-1} ($\ln k_1 = -6.00$) and $1/T_2 = 2.857 \times 10^{-3}$ K^{-1} ($\ln k_2 = -1.70$), are used in the worked example below.

Ví dụ mẫu · Predicting k at a new temperature (AHL)

A reaction has $k_1 = 2.5 \times 10^{-4}$ s^{-1} at $T_1 = 298$ K and $E_a = 65.0$ kJ mol^{-1}. Find k_2 at $T_2 = 308$ K.

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = -\left(\frac{65000}{8.31}\right)\left(\frac{1}{308} - \frac{1}{298}\right) = -(7822)(-1.090 \times 10^{-4}) = 0.852.$$

$$\frac{k_2}{k_1} = e^{0.852} = 2.34 \quad \Rightarrow \quad k_2 = (2.5 \times 10^{-4})(2.34) = 5.86 \times 10^{-4}\ \text{s}^{-1}.$$

GIẢI THÍCH TIẾNG VIỆT

VN Khi nhiệt độ tăng 10 K (từ 298K lên 308K), hằng số tốc độ tăng khoảng 2.3 lần với $E_a = 65.0$ kJ/mol – minh hoạ rõ vì sao nhiệt độ ảnh hưởng mạnh đến tốc độ phản ứng.

Ví dụ mẫu · Finding E_a from an Arrhenius plot (AHL)

Two points read from a graph of $\ln k$ against $1/T$ are $\left(3.333 \times 10^{-3}\ \text{K}^{-1},\ -6.00\right)$ and $\left(2.857 \times 10^{-3}\ \text{K}^{-1},\ -1.70\right)$. Calculate E_a.

$$\text{gradient} = \frac{-1.70 - (-6.00)}{2.857 \times 10^{-3} - 3.333 \times 10^{-3}} = \frac{4.30}{-4.76 \times 10^{-4}} = -9.03 \times 10^{3}\ \text{K}.$$

$$E_a = -\text{gradient} \times R = (9.03 \times 10^{3})(8.31) = 7.51 \times 10^{4}\ \text{J mol}^{-1} = 75.1\ \text{kJ mol}^{-1}.$$

GIẢI THÍCH TIẾNG VIỆT

VN Từ độ dốc của đồ thị Arrhenius, $E_a = -(\text{độ dốc}) \times R$ – đây là cách xác định E_a trực tiếp từ số liệu thực nghiệm mà không cần biết trước giá trị k ở bất kỳ nhiệt độ cụ thể nào ngoài các điểm đo.

Bài tập luyện tập 16 · Finding E_a from two rate constants (AHL)

A reaction has $k_1 = 3.00 \times 10^{-3}$ s^{-1} at $T_1 = 300$ K and $k_2 = 2.40 \times 10^{-2}$ s^{-1} at $T_2 = 340$ K. Calculate E_a.

Lời giải chi tiết

$$\ln\frac{k_2}{k_1} = \ln\frac{2.40\times10^{-2}}{3.00\times10^{-3}} = \ln(8.00) = 2.079.$$

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \Rightarrow E_a = \frac{R\ln(k_2/k_1)}{\frac{1}{T_1}-\frac{1}{T_2}}.$$

$$\frac{1}{300}-\frac{1}{340} = 3.922\times10^{-4}\ \text{K}^{-1}.$$

$$E_a = \frac{(8.31)(2.079)}{3.922\times10^{-4}} = 4.41\times10^{4}\ \text{J mol}^{-1} = 44.1\ \text{kJ mol}^{-1}.$$

Bài tập luyện tập 17 · Ea from an Arrhenius plot gradient (AHL)

The gradient of a graph of $\ln k$ against $1/T$ (in K^{-1}) is -8500 K. Calculate E_a in kJ mol^{-1}.

Lời giải chi tiết

$$E_a = -\text{gradient}\times R = (8500)(8.31) = 7.06\times10^{4}\ \text{J mol}^{-1} = 70.6\ \text{kJ mol}^{-1}.$$

Bài tập luyện tập 18 · The catalyst and the Arrhenius equation

Within the Arrhenius equation $k = Ae^{-E_a/RT}$, a catalyst increases the rate constant k mainly by:

(A) decreasing E_a, which increases $e^{-E_a/RT}$.

(B) increasing the temperature T of the system.

(C) increasing R, the gas constant.

(D) decreasing the pre-exponential factor A.

Lời giải chi tiết

(A). A catalyst provides an alternative pathway with a lower E_a; since E_a appears with a negative sign in the exponent, a smaller E_a makes $e^{-E_a/RT}$ larger, increasing k at the same T. A catalyst does not change T (B) or R (C, a universal constant), and its main effect is on E_a, not A (D).

5.2.7 Reaction mechanisms and the rate-determining step (AHL)

Khái niệm cốt lõi

Most reactions do not occur in a single step; they proceed through a sequence of simpler **elementary steps** called the **reaction mechanism**. The overall rate is controlled by the slowest step, the **rate-determining step (RDS)**: no product can form faster than the slowest step allows, however fast the other steps are. For an elementary step (one step of a mechanism, as opposed to the overall equation), the order with respect to each species *does* equal its stoichiometric coefficient in that step – so the experimentally-determined rate law directly reflects the species (and coefficients) appearing in the rate-determining step. A proposed mechanism is never "proved"; it is only **consistent** (or inconsistent) with the experimentally determined rate law.

VN **GIẢI THÍCH TIẾNG VIỆT**

Phương trình tốc độ thực nghiệm phản ánh **bước chậm nhất** (rate-determining step, RDS) trong cơ chế nhiều bước. Trong một bước cơ bản (elementary step), bậc phản ứng theo mỗi chất bằng đúng hệ số của chất đó trong bước đó – khác với phương trình tổng của cả phản ứng.

Ví dụ mẫu · Matching a rate law to a mechanism (AHL)

The reaction $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ has the experimentally determined rate law rate $= k[NO_2]^2$ (zero order in CO). The following two-step mechanism is proposed:

$$\text{Step 1 (slow, RDS):} \quad NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$$
$$\text{Step 2 (fast):} \quad NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$$

Show that this mechanism is consistent with the rate law, and that the two steps sum to the overall equation.

Since step 1 is the RDS and is elementary, its rate law is rate $= k[NO_2]^2$ – matching the experimental rate law exactly, including the absence of CO (which appears only in the fast step 2, after the rate is already determined). Adding the two steps: $NO_2 + NO_2 + NO_3 + CO \rightarrow NO_3 + NO + NO_2 + CO_2$; cancelling NO_3 (an intermediate) and one NO_2 from each side gives $NO_2 + CO \rightarrow NO + CO_2$, the correct overall equation.

VN **GIẢI THÍCH TIẾNG VIỆT**

NO_3 là chất trung gian (intermediate) – sinh ra ở bước 1 rồi tiêu thụ hết ở bước 2, nên không xuất hiện trong phương trình tổng và không xuất hiện trong phương trình tốc độ (vì nó không có mặt ở bước chậm, RDS).

Bài tập luyện tập 19 · Matching mechanisms to a rate law (AHL)

The experimentally determined rate law for $X + Y \rightarrow$ products is rate $= k[X][Y]$. Which of the following two proposed mechanisms is consistent with this rate law?

Mechanism (i): Step 1 (slow, RDS) $X + Y \rightarrow I$; Step 2 (fast) $I \rightarrow$ products.
Mechanism (ii): Step 1 (slow, RDS) $2X \rightarrow I$; Step 2 (fast) $I + Y \rightarrow$ products.

Lời giải chi tiết

Mechanism (i). Its RDS is elementary and involves one X and one Y, giving rate $= k[X][Y]$ directly – matching the data. Mechanism (ii)'s RDS involves two molecules of X and none of Y, which would give rate $= k[X]^2$ (second order in X, zero order in Y) – inconsistent with the experimental rate law.

Key equations – Sections 2.1 and 2.2:

- $\%$ yield $= \dfrac{\text{actual amount}}{\text{theoretical amount}} \times 100\%$; Atom economy $= \dfrac{M_r(\text{desired product})}{\sum M_r(\text{all reactants})} \times 100\%$.
- $n = cV$ (solutions, volume in dm^3); $V = nV_m$ with $V_m = 22.7$ dm^3 mol^{-1} at STP (273 K, 100 kPa).
- Rate expression: rate $= k[\text{A}]^m[\text{B}]^n$ (orders found only by experiment); overall order $= m + n + \cdots$.
- First-order integrated rate law (AHL): $\ln[\text{A}]_t = \ln[\text{A}]_0 - kt$; half-life $t_{1/2} = \dfrac{\ln 2}{k}$, constant.
- Arrhenius equation (AHL): $k = Ae^{-E_a/RT}$, so $\ln\dfrac{k_2}{k_1} = -\dfrac{E_a}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$; gradient of $\ln k$ vs $1/T$ is $-E_a/R$.

5.3 How far? The extent of chemical change

Many reactions do not go to completion: they reach a state of **dynamic equilibrium**, in which the forward and reverse reactions continue to occur but at equal rates, so the macroscopic (measurable) concentrations of reactants and products no longer change. For a general homogeneous reaction

$$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D},$$

the **equilibrium law** states that, at a fixed temperature, the ratio

$$K_c = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$$

is constant, whatever the initial concentrations used to reach that equilibrium. K_c is the **equilibrium constant**. A large K_c ($\gg 1$) means the equilibrium mixture favours products; a small K_c ($\ll 1$) means it favours reactants. Crucially, K_c changes *only* with temperature – not with initial concentrations, pressure, volume, or the presence of a catalyst.

Khái niệm cốt lõi

At dynamic equilibrium: (i) the system is closed; (ii) the forward and reverse reaction rates are equal; (iii) macroscopic properties (concentration, colour, pressure) are constant; (iv) both reactions continue at the particulate level. K_c is calculated from **equilibrium** (not initial) concentrations, each raised to the power of its coefficient in the balanced equation, products over reactants.

VN **GIẢI THÍCH TIẾNG VIỆT**

Cân bằng động (dynamic equilibrium) là trạng thái phản ứng thuận và nghịch vẫn xảy ra liên tục nhưng với **tốc độ bằng nhau**, khiến nồng độ các chất không đổi theo thời gian dù phản ứng chưa "dừng lại". K_c chỉ phụ thuộc **nhiệt độ**, không đổi khi thay đổi nồng độ ban đầu, áp suất, thể tích, hay khi thêm chất xúc tác.

Ví dụ mẫu · Kc from an ICE table

1.00 mol H_2 and 1.00 mol I_2 are placed in a 1.00 dm^3 sealed container at 698 K, where $K_c = 54.0$ for

$$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g}).$$

Find the equilibrium concentration of each species.

	$[H_2]$	$[I_2]$	$[HI]$
Initial (mol dm^{-3})	1.00	1.00	0
Change	$-x$	$-x$	$+2x$
Equilibrium	$1.00-x$	$1.00-x$	$2x$

$$K_c=\frac{(2x)^2}{(1.00-x)^2}=54.0 \quad\Rightarrow\quad \frac{2x}{1.00-x}=\sqrt{54.0}=7.35.$$

$$2x=7.35(1.00-x) \quad\Rightarrow\quad 9.35x=7.35 \quad\Rightarrow\quad x=0.786.$$

$$[H_2]=[I_2]=1.00-0.786=0.214 \text{ mol dm}^{-3}, \qquad [HI]=2(0.786)=1.57 \text{ mol dm}^{-3}.$$

Check: $\dfrac{(1.57)^2}{(0.214)^2}=54.0$ (matches K_c).

VN **GIẢI THÍCH TIẾNG VIỆT**

Bảng ICE (Initial–Change–Equilibrium) là công cụ chuẩn để giải bài toán cân bằng: đặt ẩn x cho lượng phản ứng, biểu diễn nồng độ lúc cân bằng theo x, thay vào biểu thức K_c rồi giải phương trình (thường là phương trình bậc hai hoặc có thể lấy căn bậc hai như ở đây do hai vế đều là bình phương).

(!) Lỗi thường gặp: Do not confuse the exponents in K_c with the orders in a rate law: in the **equilibrium expression**, the exponents are always the coefficients of the balanced overall equation (a thermodynamic statement about the equilibrium state). In a **rate law**, the orders must be found experimentally and often do *not* match the coefficients (a kinetic statement about the mechanism, Section 2.2).

Bài tập luyện tập 20 · Kc from an ICE table

0.500 mol of PCl_5 is introduced into a 1.00 dm^3 sealed container. At equilibrium, $PCl_5(g) \rightleftharpoons PCl_3(g)+Cl_2(g)$, and the equilibrium concentration of Cl_2 is 0.188 mol dm^{-3}. Calculate K_c (with units).

Lời giải chi tiết

	$[PCl_5]$	$[PCl_3]$	$[Cl_2]$
Initial	0.500	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.500-x$	x	x

Given $x=[Cl_2]=0.188$: $[PCl_5]=0.500-0.188=0.312$ mol dm^{-3}, $[PCl_3]=0.188$ mol dm^{-3}.

$$K_c=\frac{[PCl_3][Cl_2]}{[PCl_5]}=\frac{(0.188)(0.188)}{0.312}=0.113 \text{ mol dm}^{-3}.$$

5.3.1 Le Chatelier's principle

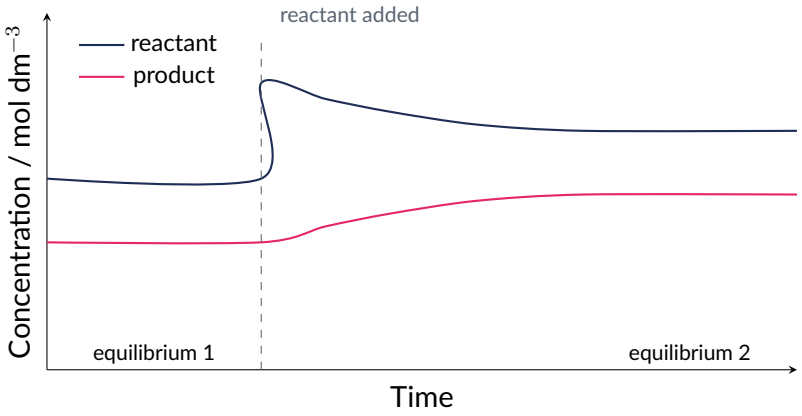
Le Chatelier's principle states that if a system at equilibrium is subjected to a change (a "stress"), the position of equilibrium shifts in the direction that partially opposes the change, until a new

equilibrium is established.

Change	Position of equilibrium shifts	Effect on K_c
Increase concentration of a reactant	toward products (right)	no change
Increase concentration of a product	toward reactants (left)	no change
Increase pressure (gaseous system)	toward the side with fewer gas moles	no change
Decrease pressure (gaseous system)	toward the side with more gas moles	no change
Increase temperature	toward the endothermic direction	changes
Decrease temperature	toward the exothermic direction	changes (opposite)
Add a catalyst	no shift; equilibrium reached faster	no change

VN GIẢI THÍCH TIẾNG VIỆT

Nguyên lý Le Chatelier: khi hệ cân bằng chịu một tác động (thay đổi nồng độ, áp suất, nhiệt độ), cân bằng sẽ dịch chuyển theo hướng **chống lại một phần** tác động đó. Chỉ có **nhiệt độ** mới làm thay đổi giá trị K_c – thay đổi nồng độ, áp suất hay thêm xúc tác chỉ làm dịch chuyển vị trí cân bằng, KHÔNG đổi K_c.



Effect of a disturbance on a system at equilibrium: extra reactant added at $t = 10$ instantly raises [reactant]; the equilibrium then shifts toward products (Le Chatelier), consuming some of the added reactant and forming more product, until a new equilibrium is reached with both concentrations constant again.

Bài tập luyện tập 21 · Le Chatelier and pressure

For $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, predict the effect of increasing the total pressure (at constant temperature) on the position of equilibrium and on K_c.

Lời giải chi tiết

There are 4 mol of gas on the reactant side and 2 mol on the product side. Increasing pressure shifts the equilibrium toward the side with **fewer** gas moles – i.e. toward products, increasing the yield of NH_3. K_c itself is **unchanged**, since temperature has not changed.

Bài tập luyện tập 22 · Le Chatelier and product removal

$CH_3COOH(aq) + C_2H_5OH(aq) \rightleftharpoons CH_3COOC_2H_5(aq) + H_2O(l)$ is at equilibrium. If the ester product is continuously removed as it forms, what happens to the position of equilibrium?

(A) It shifts toward the products, to replace the removed ester.

(B) It shifts toward the reactants.

(C) It does not shift, since K_c is fixed.

(D) It shifts, but the direction cannot be predicted.

Lời giải chi tiết

(A). Removing a product decreases its concentration below the equilibrium value, so $Q < K_c$ momentarily; the equilibrium shifts toward products (forward direction) to replace some of what was removed and restore $Q = K_c$. This principle is exploited industrially to push a reaction further toward completion than the equilibrium position would otherwise allow.

Bài tập luyện tập 23 · Le Chatelier and temperature

The synthesis of ammonia, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, is exothermic in the forward direction. Explain what happens to K_c and to the equilibrium yield of NH_3 when the temperature is raised from 400°C to 500°C.

Lời giải chi tiết

Since the forward reaction is exothermic, the reverse reaction is endothermic. Raising the temperature shifts the equilibrium in the endothermic direction (Le Chatelier) – i.e. toward the **reactants** – to absorb some of the added energy. Both K_c and the equilibrium yield of NH_3 therefore **decrease** as temperature rises from 400°C to 500°C. (This is why industrial ammonia synthesis uses a compromise temperature, balancing a reasonable equilibrium yield against an acceptable rate.)

5.3.2 The reaction quotient Q and the equilibrium constant K

Khái niệm cốt lõi

The **reaction quotient** Q has exactly the same algebraic form as K_c, but is evaluated using the concentrations present *at any instant* (not necessarily at equilibrium):

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \text{(concentrations at the instant considered).}$$

Comparing Q with K_c predicts which way the reaction will shift to reach equilibrium: if $Q < K_c$, there is "too little product" relative to equilibrium, so the reaction proceeds **forward**; if $Q > K_c$, there is "too much product," so the reaction proceeds in **reverse**; if $Q = K_c$, the system is already at equilibrium.

VN **GIẢI THÍCH TIẾNG VIỆT**

Thương số phản ứng Q có cùng công thức với K_c nhưng tính từ nồng độ tại **bất kỳ thời điểm nào**, không nhất thiết ở cân bằng. So sánh Q với K_c: $Q < K_c \rightarrow$ phản ứng dịch chuyển **thuận**; $Q > K_c \rightarrow$ dịch chuyển **nghịch**; $Q = K_c \rightarrow$ đã ở cân bằng.

Ví dụ mẫu · Predicting the direction of shift using Q

For $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $K_c = 0.500$ at a given temperature. At a certain instant, $[N_2] = 0.60$, $[H_2] = 0.30$, $[NH_3] = 0.20$ mol dm^{-3}. In which direction will the reaction proceed to reach equilibrium?

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.20)^2}{(0.60)(0.30)^3} = \frac{0.0400}{0.0162} = 2.47.$$

Since $Q(2.47) > K_c(0.500)$, the reaction proceeds in **reverse** (toward reactants) until Q falls back to 0.500.

VN **GIẢI THÍCH TIẾNG VIỆT**

$Q = 2.47$ lớn hơn $K_c = 0.500$ rất nhiều, nghĩa là hệ hiện có "quá nhiều" NH_3 so với lúc cân bằng → phản ứng phải dịch chuyển **nghịch** (tiêu thụ bớt NH_3, tạo lại N_2 và H_2) để Q giảm về đúng K_c.

Bài tập luyện tập 24 · Q versus K

A reaction has $K_c = 25$ at a given temperature. A reaction mixture at a certain instant gives $Q = 5$. In which direction will the reaction shift to reach equilibrium?

Lời giải chi tiết

Since $Q(5) < K_c(25)$, the reaction proceeds in the **forward** direction (toward products), increasing [products] and decreasing [reactants] until Q rises to equal $K_c = 25$.

5.3.3 Magnitude of the equilibrium constant K

The size of K indicates, qualitatively, how far a reaction proceeds before reaching equilibrium.

Magnitude of K	Interpretation	Example
$K \gg 1$ (e.g. $> 10^{10}$)	reaction essentially complete; equilibrium mixture almost all product	$2H_2 + O_2 \rightleftharpoons 2H_2O$ $K \approx 3 \times 10^{81}$ at 298 K
$K \approx 1$ (roughly 10^{-3}–10^{3})	significant amounts of both reactants and products at equilibrium	$H_2 + I_2 \rightleftharpoons 2HI$ $K_c = 54.0$ at 698 K
$K \ll 1$ (e.g. $< 10^{-10}$)	reaction barely proceeds; equilibrium mixture almost all reactant	$N_2 + O_2 \rightleftharpoons 2NO$ $K \approx 1 \times 10^{-30}$ at 298 K

VN **GIẢI THÍCH TIẾNG VIỆT**

Độ lớn của K cho biết mức độ phản ứng xảy ra: $K \gg 1$ (phản ứng gần như hoàn toàn), $K \approx 1$ (cả chất phản ứng và sản phẩm cùng tồn tại với lượng đáng kể), $K \ll 1$ (phản ứng gần như không xảy ra). Lưu ý K không cho biết **tốc độ** đạt đến cân bằng nhanh hay chậm – đó là vấn đề động học (Section 2.2), hoàn toàn tách biệt với nhiệt động học của cân bằng.

Bài tập luyện tập 25 · Interpreting a very small K

A reaction has $K = 4.0 \times 10^{-25}$ at 298 K. Which statement is correct?

(A) At equilibrium, the reactants overwhelmingly predominate; the reaction does not proceed to a measurable extent.

(B) At equilibrium, the products overwhelmingly predominate.

(C) The reaction reaches equilibrium very quickly.

(D) The reaction is exothermic in the forward direction.

Lời giải chi tiết

(A). $K \ll 1$ means the equilibrium mixture consists almost entirely of reactants – the forward reaction essentially does not proceed. K says nothing about the *rate* of reaching equilibrium (C) nor directly about the sign of ΔH (D, which is a separate thermodynamic quantity related to how K itself *changes* with temperature, not to its magnitude at a single temperature).

5.3.4 Heterogeneous equilibria

An equilibrium is **heterogeneous** when it involves species in more than one phase (e.g. a solid together with gases, or a solid with an aqueous solution). Because the concentration of a pure solid or pure liquid is an intrinsic, unchanging property (moles per unit volume of the solid/liquid *itself*, not of the reaction vessel), it does not vary and is **omitted** from the K_c (or K_p) expression – only species that can actually change concentration (gases, dissolved species) are included.

Ví dụ mẫu · Writing a Kc expression for a heterogeneous equilibrium

Write the K_c expression for the thermal decomposition of calcium carbonate:

$$\mathrm{CaCO_3(s)} \rightleftharpoons \mathrm{CaO(s)} + \mathrm{CO_2(g)}.$$

Both $\mathrm{CaCO_3}$ and CaO are pure solids, so they are omitted:

$$K_c = [\mathrm{CO_2}].$$

At a given temperature, this equilibrium has a single, fixed equilibrium concentration (or partial pressure) of $\mathrm{CO_2}$, independent of how much solid $\mathrm{CaCO_3}$ or CaO is present.

VN **GIẢI THÍCH TIẾNG VIỆT**

Trong cân bằng dị thể (heterogeneous equilibrium), chất rắn nguyên chất hoặc chất lỏng nguyên chất KHÔNG xuất hiện trong biểu thức K_c (vì "nồng độ" của chúng không đổi, là hằng số nội tại). Chỉ các chất khí hoặc chất tan mới xuất hiện trong biểu thức.

(!) Lỗi thường gặp: Omit pure solids and pure liquids from K_c/K_p expressions – but **never** omit gases or aqueous (dissolved) species, and never omit a solvent that is also a reactant/product in a different physical state from bulk solvent. A common error is omitting a species simply because its state symbol looks unfamiliar rather than checking whether it is genuinely a pure solid or pure liquid.

Bài tập luyện tập 26 · Kc for a heterogeneous (water-gas) equilibrium

For $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$, at equilibrium $[H_2O] = 0.20$, $[CO] = 0.15$, $[H_2] = 0.15$ mol dm^{-3} (with solid carbon present in excess). Write the K_c expression and calculate its value.

Lời giải chi tiết

Carbon is a pure solid and is omitted:

$$K_c = \frac{[CO][H_2]}{[H_2O]} = \frac{(0.15)(0.15)}{0.20} = 0.113 \text{ mol dm}^{-3}.$$

Bài tập luyện tập 27 · Kc for solid ammonium chloride decomposition

Solid ammonium chloride decomposes: $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$. At equilibrium in a sealed 2.00 dm^3 flask (with excess solid NH_4Cl present), 0.0400 mol of NH_3 and 0.0400 mol of HCl are present. Calculate K_c (with units).

Lời giải chi tiết

NH_4Cl is a pure solid and is omitted.

$$[NH_3] = [HCl] = \frac{0.0400}{2.00} = 0.0200 \text{ mol dm}^{-3}.$$

$$K_c = [NH_3][HCl] = (0.0200)(0.0200) = 4.00 \times 10^{-4} \text{ mol}^2 \text{ dm}^{-6}.$$

5.3.5 K_p and the link to ΔG° (AHL)

Khái niệm cốt lõi

For gas-phase equilibria, K_p is defined analogously to K_c but uses **equilibrium partial pressures**, each raised to its coefficient:

$$K_p = \frac{p_C^c \, p_D^d}{p_A^a \, p_B^b}.$$

The partial pressure $p_i = x_i P_{\text{total}}$, where x_i is the mole fraction of gas i. Like K_c, K_p changes only with temperature. The units of K_p (and K_c) depend on Δn_{gas} (moles of gaseous product minus moles of gaseous reactant) in the balanced equation; when $\Delta n_{\text{gas}} = 0$, both are dimensionless.

VN **GIẢI THÍCH TIẾNG VIỆT**

K_p định nghĩa tương tự K_c nhưng dùng **áp suất riêng phần** (partial pressure) tại cân bằng thay vì nồng độ. Đơn vị của K_p phụ thuộc vào $\Delta n_{\text{khí}}$ (số mol khí sản phẩm trừ số mol khí chất phản ứng) trong phương trình cân bằng.

Ví dụ mẫu · Calculating Kp (AHL)

At equilibrium in $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, the partial pressures are $p(SO_2) = 0.20$ atm, $p(O_2) = 0.30$ atm, $p(SO_3) = 0.50$ atm. Calculate K_p.

$$K_p = \frac{p(\mathrm{SO_3})^2}{p(\mathrm{SO_2})^2\,p(\mathrm{O_2})} = \frac{(0.50)^2}{(0.20)^2(0.30)} = \frac{0.25}{0.012} = 20.8\ \text{atm}^{-1}.$$

($\Delta n_{\text{gas}} = 2 - (2+1) = -1$, so K_p carries units of atm^{-1}.)

VN **GIẢI THÍCH TIẾNG VIỆT**

Cách tính K_p hoàn toàn tương tự K_c, chỉ thay nồng độ bằng áp suất riêng phần. Đơn vị atm^{-1} xuất phát từ $\Delta n_{\text{khí}} = -1$ của phản ứng này.

Khái niệm cốt lõi

The standard Gibbs free energy change of reaction is linked to the equilibrium constant by

$$\Delta G^\circ = -RT \ln K,$$

with $R = 8.31$ J K^{-1} mol^{-1}, T in kelvin, and K the equilibrium constant at that temperature. A large K (> 1) gives $\Delta G^\circ < 0$ (products favoured); a small K (< 1) gives $\Delta G^\circ > 0$ (reactants favoured); $K = 1$ gives $\Delta G^\circ = 0$.

VN **GIẢI THÍCH TIẾNG VIỆT**

Công thức $\Delta G^\circ = -RT \ln K$ liên hệ trực tiếp năng lượng tự do Gibbs chuẩn với hằng số cân bằng: $K > 1 \to \Delta G^\circ < 0$ (sản phẩm chiếm ưu thế), $K < 1 \to \Delta G^\circ > 0$ (chất phản ứng chiếm ưu thế).

Ví dụ mẫu · ΔG° from Kc (AHL)

For $\mathrm{H_2(g) + I_2(g) \rightleftharpoons 2HI(g)}$, $K_c = 54.0$ at $T = 698$ K. Calculate ΔG°.

$$\begin{aligned}\Delta G^\circ &= -RT \ln K_c = -(8.31)(698)\ln(54.0)\\ &= -(5800)(3.989) = -23140\ \text{J mol}^{-1} = -23.1\ \text{kJ mol}^{-1}.\end{aligned}$$

The negative value confirms that products are favoured, consistent with $K_c = 54.0 > 1$.

VN **GIẢI THÍCH TIẾNG VIỆT**

ΔG° âm (-23.1 kJ/mol) khớp với $K_c = 54.0 > 1$ (sản phẩm chiếm ưu thế) – hai cách diễn đạt cùng một sự thật nhiệt động học, chỉ khác đơn vị/thang đo.

(!) Lỗi thường gặp: In $\Delta G^\circ = -RT \ln K$, always use $R = 8.31$ J K^{-1} mol^{-1} (not kJ) and convert the final answer from J mol^{-1} to kJ mol^{-1} by dividing by 1000. Also, do not confuse ΔG° (standard conditions, linked directly to K) with the reaction quotient comparison Q versus K from earlier in this section – both predict "direction," but ΔG° vs K is a single fixed thermodynamic statement about the standard state, while Q vs K tracks a system's real-time approach to equilibrium.

Bài tập luyện tập 28 · Kp from an ICE table in pressure (AHL)

1.50 atm of pure $N_2O_4(g)$ is introduced into a rigid flask and allowed to reach equilibrium: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, with $K_p = 1.07$ atm at this temperature. Calculate the equilibrium partial pressures of N_2O_4 and NO_2.

Lời giải chi tiết

Let y = decrease in $p(N_2O_4)$: $p(N_2O_4) = 1.50 - y$, $p(NO_2) = 2y$.

$$K_p = \frac{(2y)^2}{1.50 - y} = 1.07 \quad \Rightarrow \quad 4y^2 + 1.07y - 1.605 = 0.$$

Solving the quadratic ($a = 4$, $b = 1.07$, $c = -1.605$):

$$y = \frac{-1.07 + \sqrt{(1.07)^2 + 4(4)(1.605)}}{2(4)} = \frac{-1.07 + 5.18}{8} = 0.514.$$

$$p(N_2O_4) = 1.50 - 0.514 = 0.986 \text{ atm}, \qquad p(NO_2) = 2(0.514) = 1.03 \text{ atm}.$$

Check: $\dfrac{(1.03)^2}{0.986} = 1.07$ atm (matches K_p).

Bài tập luyện tập 29 · ΔG° from Kc, reactants favoured (AHL)

For $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, $K_c = 0.113$ at $T = 500$ K. Calculate ΔG° and comment on its sign.

Lời giải chi tiết

$$\begin{aligned}\Delta G^\circ &= -RT \ln K_c = -(8.31)(500)\ln(0.113) \\ &= -(4155)(-2.180) = +9060 \text{ J mol}^{-1} = +9.06 \text{ kJ mol}^{-1}.\end{aligned}$$

The **positive** sign is consistent with $K_c = 0.113 < 1$: at this temperature, the equilibrium mixture favours the reactant, PCl_5.

Bài tập luyện tập 30 · Sign of ΔG° and K (AHL)

If ΔG° for a reaction is positive at a given temperature, what can be concluded about K at that temperature?

(A) $K < 1$
(B) $K > 1$
(C) $K = 1$
(D) No conclusion is possible

Lời giải chi tiết

(A). Since $\Delta G^\circ = -RT \ln K$ and $R, T > 0$, a positive ΔG° requires $\ln K < 0$, which means $K < 1$.

Bài tập luyện tập 31 · Units of Kc

Write the units of K_c for $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$.

Lời giải chi tiết

$$K_c = \frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3}, \qquad \Delta n_{\text{gas}} = 2 - (1+3) = -2.$$

Units $= (\text{mol dm}^{-3})^{\Delta n} = (\text{mol dm}^{-3})^{-2} = \text{mol}^{-2}\ \text{dm}^{6}$.

To close, a comprehensive problem that draws together the amount of chemical change from the start of this chapter with the gas-volume stoichiometry seen earlier:

Bài tập luyện tập 32 · Mixed stoichiometry review

Butane burns in oxygen: $2\mathrm{C_4H_{10}(g)} + 13\mathrm{O_2(g)} \rightarrow 8\mathrm{CO_2(g)} + 10\mathrm{H_2O(g)}$. If 2.00 mol $\mathrm{C_4H_{10}}$ is mixed with 10.0 mol $\mathrm{O_2}$, determine the limiting reactant and calculate the volume of $\mathrm{CO_2}$ produced at STP.

Lời giải chi tiết

2.00 mol $\mathrm{C_4H_{10}}$ requires $2.00 \times \dfrac{13}{2} = 13.0$ mol $\mathrm{O_2}$, but only 10.0 mol is available $\Rightarrow$ $\mathrm{O_2}$ **is limiting**.

$$n(\mathrm{CO_2}) = 10.0 \times \frac{8}{13} = 6.15 \text{ mol}.$$

$$V(\mathrm{CO_2}) = 6.15 \times 22.7 = 140 \text{ dm}^3.$$

Bài tập luyện tập 33 · Limiting reactant from masses directly

$4\mathrm{Al(s)} + 3\mathrm{O_2(g)} \rightarrow 2\mathrm{Al_2O_3(s)}$. 10.0 g of Al is heated with 10.0 g of $\mathrm{O_2}$. Determine the limiting reactant and the theoretical mass of $\mathrm{Al_2O_3}$ formed.

Lời giải chi tiết

$$n(\mathrm{Al}) = \frac{10.0}{26.98} = 0.371 \text{ mol}, \qquad n(\mathrm{O_2}) = \frac{10.0}{32.00} = 0.313 \text{ mol}.$$

0.371 mol Al requires $0.371 \times \dfrac{3}{4} = 0.278$ mol $\mathrm{O_2}$, and 0.313 mol is available (more than enough) $\Rightarrow$ Al **is limiting** ($\mathrm{O_2}$ is in excess).

$$n(\mathrm{Al_2O_3}) = 0.371 \times \frac{2}{4} = 0.185 \text{ mol}, \qquad M(\mathrm{Al_2O_3}) = 2(26.98) + 3(16.00) = 101.96 \text{ g mol}^{-1}.$$

$$m(\mathrm{Al_2O_3}) = 0.185 \times 101.96 = 18.9 \text{ g}.$$

Bài tập luyện tập 34 · Synthesis: rate versus equilibrium

A reversible, exothermic reaction is at equilibrium. A catalyst is then added at constant temperature. Which statement correctly describes the result?

(A) The equilibrium yield of product increases, and equilibrium is reached faster.

(B) The equilibrium yield of product is unchanged, but equilibrium is reached faster.

(C) K_c increases, so more product forms at equilibrium.

(D) The reaction shifts toward products, increasing K_c.

Lời giải chi tiết

(B). A catalyst lowers E_a for the forward and reverse reactions *equally*, so both rates increase by the same factor; the system reaches the *same* equilibrium position sooner, but the equilibrium yield and K_c (which depends only on temperature) are completely unchanged. This is the key distinction running through this chapter: **how fast** a system reaches equilibrium (kinetics, Section 2.2) is entirely independent of **how far** that equilibrium lies toward products (thermodynamics, Section 2.3).

5.3.6 Adding an inert gas to a gas-phase equilibrium

A subtlety of Le Chatelier's principle concerns adding an unreactive ("inert") gas, such as argon, to a gas-phase equilibrium. The outcome depends entirely on whether the container is held at **constant volume** or **constant pressure**.

Inert gas: constant volume vs constant pressure

Constant volume: adding inert gas raises the total pressure, but the *partial pressure* (and concentration) of every reacting species is unchanged, since neither their moles nor the volume they occupy has changed. Q is unaffected, so there is **no shift**.

Constant pressure: to keep total pressure constant while adding inert gas, the container volume must expand. This dilutes every reacting species, lowering their partial pressures/concentrations. The equilibrium then shifts towards the side with **more moles of gas** (to partially oppose the drop in concentration), exactly as if the pressure on the reacting mixture itself had been decreased.

Ví dụ mẫu · Inert gas at constant pressure

The equilibrium $\mathrm{N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)}$ is established in a cylinder fitted with a movable piston held at constant external pressure. Argon gas is then injected into the cylinder at constant temperature. Predict the effect on the position of equilibrium and on K_c.

Injecting Ar at constant pressure forces the piston out, increasing the total volume; this lowers the partial pressures (concentrations) of $\mathrm{N_2}$, $\mathrm{H_2}$, and $\mathrm{NH_3}$ by the same dilution factor. There are 4 mol of gas on the reactant side and 2 mol on the product side, so the equilibrium shifts towards the side with *more* moles of gas to counteract the dilution — i.e. it shifts towards the **reactants** ($\mathrm{NH_3}$ yield decreases). K_c itself is unchanged, since temperature has not changed.

GIẢI THÍCH TIẾNG VIỆT

VN Thêm khí trơ (như Ar) vào hệ cân bằng khí: nếu thể tích **không đổi**, áp suất riêng phần của các chất phản ứng không đổi $\Rightarrow$ **không dịch chuyển**. Nếu áp suất **không đổi** (bình có pittông di chuyển được), thể tích phải giãn ra để bù, làm loãng nồng độ mọi chất $\Rightarrow$ cân bằng dịch chuyển về phía có **nhiều mol khí hơn**. Trong cả hai trường hợp, K_c không đổi vì nhiệt độ không đổi.

Bài tập luyện tập 35 · Inert gas at constant volume

The equilibrium $\mathrm{2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)}$ is at equilibrium in a sealed, rigid (fixed-volume) steel vessel. Helium gas is injected at constant temperature. State and explain the effect on the equilibrium position and on K_c.

Lời giải chi tiết

Because the vessel is rigid, the volume cannot change, so the partial pressures (concentrations) of SO_2, O_2, and SO_3 are completely unaffected by the helium — helium simply adds to the total pressure without diluting the reacting species. Since Q does not change, there is **no shift** in the equilibrium position, and K_c is unchanged (temperature is constant).

Bài tập luyện tập 36 · Comprehensive gas equilibrium and rate synthesis

For the exothermic equilibrium $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$, state and explain the separate effects on (a) the initial rate of the forward reaction and (b) the equilibrium yield of NO_2, of: (i) increasing the total pressure by decreasing the container volume, (ii) adding a catalyst, (iii) increasing the temperature.

(A) (i) rate up, yield up; (ii) rate up, yield unchanged; (iii) rate up, yield down

(B) (i) rate down, yield down; (ii) rate unchanged, yield up; (iii) rate up, yield up

(C) (i) rate up, yield down; (ii) rate up, yield up; (iii) rate down, yield down

(D) (i) rate unchanged, yield up; (ii) rate up, yield unchanged; (iii) rate up, yield down

Lời giải chi tiết

(A). (i) Decreasing volume raises all concentrations, increasing collision frequency (rate up); with fewer moles of gas on the product side (2 vs 3), the equilibrium shifts towards products (yield up). (ii) A catalyst speeds up both the forward and reverse rates equally (rate up), reaching the same equilibrium position faster, so the equilibrium yield is unchanged. (iii) Raising T increases the rate (more particles exceed E_a), but since the forward reaction is exothermic, equilibrium shifts towards the endothermic (reverse) direction, decreasing the yield of NO_2 and decreasing K_c.

Bài tập luyện tập 37 · Percentage purity from a gas-evolution reaction

An impure sample of calcium carbonate, mass 5.20 g, is reacted with excess dilute hydrochloric acid: $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$. The $CO_2(g)$ produced, measured at STP, has a volume of 1.045 dm^3. Assuming the impurities do not react with the acid or produce any gas, calculate the percentage purity of the calcium carbonate sample ($M(CaCO_3) = 100.09$ g mol^{-1}).

Lời giải chi tiết

$$n(CO_2) = \frac{1.045}{22.7} = 0.04604 \text{ mol}.$$

Mole ratio $CaCO_3 : CO_2 = 1 : 1$, so $n(CaCO_3) = 0.04604$ mol reacted.

$$m(CaCO_3) = 0.04604 \times 100.09 = 4.608 \text{ g}.$$

$$\%\text{purity} = \frac{4.608}{5.20} \times 100 = 88.6\%.$$

Reactivity 3 --- What Are the Mechanisms of Chemical Change?

Mục tiêu Unit: Cơ chế của biến đổi hoá học: phản ứng chuyển proton (thuyết Bronsted–Lowry, pH, K_a/K_b, đường chuẩn độ, chất chỉ thị, thuỷ phân muối – HL, dung dịch đệm – HL), phản ứng chuyển electron (pin điện hoá, thế điện cực chuẩn, phương trình Nernst – HL, điện phân, định luật Faraday – HL, pin nhiên liệu), phản ứng chia sẻ electron (cơ chế gốc tự do, cộng electrophin vào anken), và phản ứng chia sẻ cặp electron (S_N1/S_N2, phản ứng tách, cộng nucleophin vào carbonyl, thế electrophin vào vòng benzene – HL).

6.1 Proton transfer reactions

A **Brønsted–Lowry acid** is a proton (H^+) donor; a **Brønsted–Lowry base** is a proton acceptor. Every acid–base reaction generates a **conjugate acid–base pair**: when an acid HA donates H^+ it becomes its conjugate base A^-, and when a base B accepts H^+ it becomes its conjugate acid BH^+. **Strong** acids/bases dissociate (essentially) completely in water; **weak** acids/bases dissociate only partially, reaching an equilibrium described by an acid dissociation constant K_a (or base constant K_b) — the larger K_a, the stronger the acid. Water self-ionises, $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$, giving the ion product $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ at 298 K. Taking $-\log_{10}$ throughout, $pH + pOH = 14.00$ at 298 K, where $pH = -\log_{10}[H^+]$ and $pOH = -\log_{10}[OH^-]$.

Brønsted–Lowry acids and bases

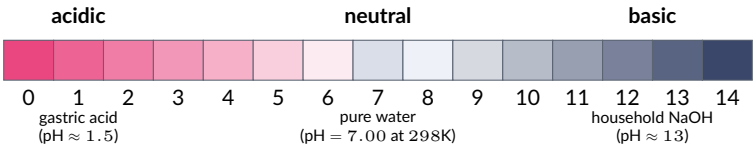
An acid–base reaction is always a **proton-transfer** reaction. For $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$: CH_3COOH (acid) and CH_3COO^- (its conjugate base) form one pair; H_2O (base) and H_3O^+ (its conjugate acid) form the other. Water is **amphiprotic** — it can act as either acid or base depending on what it reacts with.

VN **GIẢI THÍCH TIẾNG VIỆT**

Thuyết Bronsted–Lowry định nghĩa acid là chất **cho proton** (H^+), bazơ là chất **nhận proton**. Mỗi phản ứng acid–bazơ luôn sinh ra một **cặp acid–bazơ liên hợp**: acid cho proton biến thành bazơ liên hợp, bazơ nhận proton biến thành acid liên hợp. Nước có tính **lưỡng tính** (amphiprotic) — vừa có thể cho vừa có thể nhận proton tuỳ chất phản ứng cùng.

6.1.1 Acids, bases and the pH scale

The **pH scale** is a compressed, logarithmic way of expressing $[H^+]$, which in aqueous solutions typically spans many orders of magnitude (from around 10 M down to 10^{-14} M). Because pH is a $\log_{10}$ scale, each whole-number step corresponds to a **ten-fold** change in $[H^+]$ — a solution of pH 3 has 100 times the $[H^+]$ of a solution of pH 5, not merely $2/3$ or $5/3$ of it.



The pH scale, 0–14 at 298 K: lower pH = higher $[H^+]$ (more acidic); pH 7 is neutral; higher pH = higher $[OH^-]$ (more basic/alkaline). Because the scale is logarithmic, a change of one pH unit means a ten-fold change in $[H^+]$.

For a strong acid/base, dissociation is complete, so $[H^+]$ or $[OH^-]$ can be read directly from the stated concentration — taking care with formula stoichiometry, since each mole of $Ba(OH)_2$ releases *two* moles of OH^-. For a weak monoprotic acid HA at initial concentration C, the equilibrium $HA \rightleftharpoons H^+ + A^-$ gives $K_a = \dfrac{[H^+][A^-]}{[HA]}$; provided dissociation is small ($C/K_a \gtrsim 100$, so the autoionisation of water is negligible), $[H^+] \approx [A^-]$ and $[HA] \approx C$, giving the useful approximation

$$[H^+] \approx \sqrt{K_a C}.$$

The same logic, mirrored, gives $[OH^-] \approx \sqrt{K_b C}$ for a weak base B reacting as $B + H_2O \rightleftharpoons BH^+ + OH^-$. Some acids are **polyprotic**, donating more than one proton in successive equilibria with successively smaller dissociation constants (e.g. H_2SO_4, H_3PO_4) — the first dissociation is always much more extensive than the second, and so on, because removing a proton from an already-negatively-charged species is electrostatically much harder.

Ví dụ mẫu · Worked example

Find the pH of 0.0200 M $NaOH(aq)$.
NaOH is a strong base, so it dissociates completely: $[OH^-] = 0.0200$ M.

$$\text{pOH} = -\log_{10}(0.0200) = 1.70, \qquad \text{pH} = 14.00 - 1.70 = 12.30.$$

VN **GIẢI THÍCH TIẾNG VIỆT**
Với acid/bazơ **mạnh**, nồng độ ion H^+ hoặc OH^- bằng đúng nồng độ chất tan ban đầu (nhân thêm hệ số nếu công thức có nhiều nhóm OH^-, ví dụ $Ba(OH)_2$ cho $2\times$ nồng độ). Đây là điểm khác biệt then chốt so với acid/bazơ **yếu**, nơi ta phải dùng K_a/K_b vì chỉ một phần nhỏ phân li.

Ví dụ mẫu · Worked example

Find the pH of 0.0500 M CH_3COOH ($K_a = 1.8 \times 10^{-5}$).
For a weak acid, $[H^+] \approx \sqrt{K_a C} = \sqrt{(1.8 \times 10^{-5})(0.0500)} = \sqrt{9.0 \times 10^{-7}} = 9.49 \times 10^{-4}$ M.

$$\text{pH} = -\log(9.49 \times 10^{-4}) = 3.02.$$

VN **GIẢI THÍCH TIẾNG VIỆT**
Công thức gần đúng $[H^+] \approx \sqrt{K_a C}$ chỉ đáng tin cậy khi tỉ lệ C/K_a đủ lớn (thường $\gtrsim 100$) — ở ví dụ trên, $C/K_a = 0.0500/1.8 \times 10^{-5} \approx 2780$, rất lớn nên phép gần đúng hợp lệ. Nếu K_a tương đối lớn so với C, cần giải phương trình bậc hai đầy đủ thay vì dùng công thức rút gọn này.

The same approximation can be run in reverse: given the measured pH of a weak acid of known concentration, K_a can be calculated.

Ví dụ mẫu · Finding K_a from a measured pH

A 0.100 M solution of a weak monoprotic acid HA has a measured pH of 2.90. Find K_a.

$$[\mathrm{H^+}] = 10^{-2.90} = 1.26 \times 10^{-3}\ \mathrm{M}.$$

Since $[\mathrm{H^+}] \approx [\mathrm{A^-}]$ and $[\mathrm{HA}] \approx C = 0.100$ M,

$$K_a \approx \frac{[\mathrm{H^+}]^2}{C} = \frac{(1.26 \times 10^{-3})^2}{0.100} = \frac{1.59 \times 10^{-6}}{0.100} = 1.59 \times 10^{-5}.$$

(This value is close to that of a typical weak carboxylic acid, e.g. CH_3COOH, $K_a = 1.8 \times 10^{-5}$.)

VN **GIẢI THÍCH TIẾNG VIỆT**

Có thể tính ngược K_a từ pH đo được bằng thực nghiệm: đổi pH sang $[\mathrm{H^+}] = 10^{-\mathrm{pH}}$, rồi thay vào $K_a \approx \dfrac{[\mathrm{H^+}]^2}{C}$ (suy ra trực tiếp từ công thức $[\mathrm{H^+}] \approx \sqrt{K_a C}$ bằng cách bình phương hai vế).

(!) Lỗi thường gặp: Never treat a weak acid/base as if $[\mathrm{H^+}]$ or $[\mathrm{OH^-}]$ equalled the stated concentration directly — only strong acids/bases dissociate completely. Conversely, do not apply the K_a/K_b equilibrium approximation to a strong acid/base, since there is no meaningful equilibrium to describe (dissociation is essentially total).

Ví dụ mẫu · pH after mixing a strong acid and a strong base

40.0 cm^3 of 0.100 M HCl is mixed with 25.0 cm^3 of 0.150 M NaOH. Find the pH of the resulting solution.

$n(\mathrm{HCl}) = 0.100 \times 0.0400 = 0.00400$ mol. $\quad n(\mathrm{NaOH}) = 0.150 \times 0.0250 = 0.00375$ mol.

$\mathrm{HCl} + \mathrm{NaOH} \rightarrow \mathrm{NaCl} + \mathrm{H_2O}$ consumes them in a $1:1$ ratio, so HCl is in **excess**:

$$n(\mathrm{HCl})_{\text{excess}} = 0.00400 - 0.00375 = 0.000250\ \text{mol}.$$

Total volume $= 40.0 + 25.0 = 65.0$ cm^3 $= 0.0650$ dm^3:

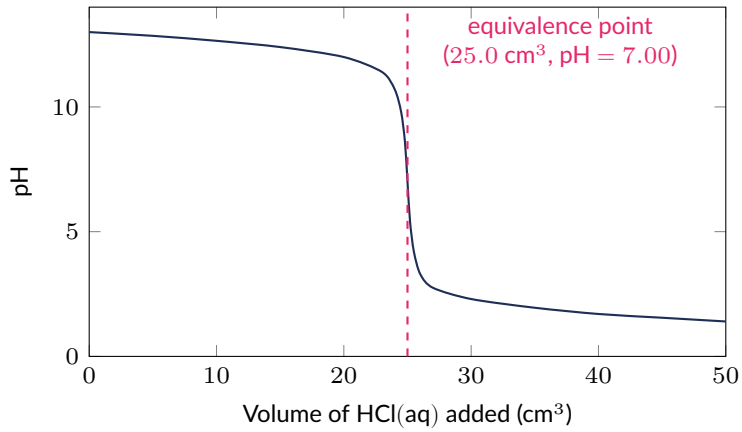
$$[\mathrm{H^+}] = \frac{0.000250}{0.0650} = 3.85 \times 10^{-3}\ \mathrm{M}, \qquad \mathrm{pH} = -\log(3.85 \times 10^{-3}) = 2.41.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Khi trộn acid mạnh với bazơ mạnh không theo đúng tỉ lệ hoá học, cần: (1) tính số mol mỗi chất; (2) trừ đi phần phản ứng vừa đủ để tìm chất còn **dư**; (3) chia số mol dư cho **tổng thể tích** dung dịch (không phải thể tích ban đầu của riêng chất đó) để ra nồng độ, rồi tính pH như bình thường.

6.1.2 Titrating a strong acid with a strong base

During a titration, pH is monitored continuously as titrant is added from a burette. For a **strong acid–strong base** titration, pH changes only gradually until very close to the **equivalence point** (where moles of acid exactly equal moles of base), then jumps sharply through pH 7 over a tiny volume of titrant, before levelling off again.



Titration curve: 25.0 cm^3 of 0.100 M NaOH(aq) titrated with 0.100 M HCl(aq) (strong acid–strong base). The steep, near-vertical jump through pH 7 at the equivalence point is characteristic of a strong–strong titration.

Besides sketching pH curves, titration data is very commonly used the other way round: to find an **unknown concentration**, using the volume of titrant needed to reach the equivalence point (the **titre**) together with the balanced equation's mole ratio.

Ví dụ mẫu · Finding an unknown concentration from titration data

25.0 cm^3 of NaOH(aq) of unknown concentration is titrated with 0.100 M HCl(aq); the equivalence point is reached after 18.40 cm^3 of acid has been added. Find the concentration of the NaOH(aq).

HCl + NaOH → NaCl + H_2O is $1:1$, so at equivalence $n(\text{HCl}) = n(\text{NaOH})$.

$$n(\text{HCl}) = 0.100 \times \frac{18.40}{1000} = 1.840 \times 10^{-3}\ \text{mol} = n(\text{NaOH}).$$

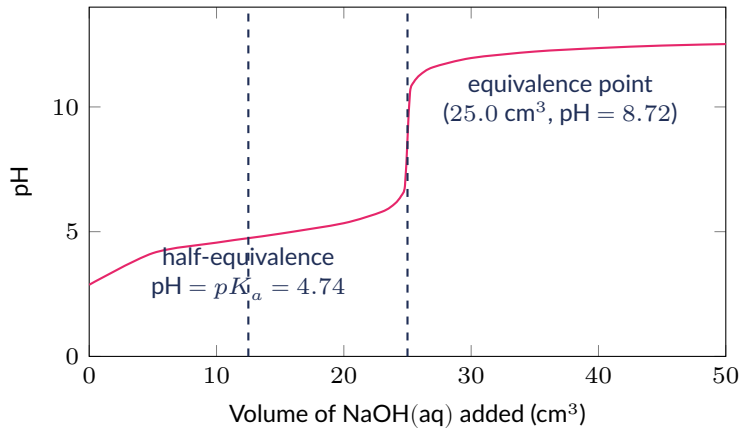
$$C(\text{NaOH}) = \frac{1.840 \times 10^{-3}}{25.0/1000} = \frac{1.840 \times 10^{-3}}{0.0250} = 0.0736\ \text{M}.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Bài toán chuẩn độ ngược lại (tìm nồng độ chưa biết) dùng đúng 3 bước quen thuộc: (1) tính số mol chất đã biết nồng độ từ thể tích chuẩn độ (titre); (2) dùng **tỉ lệ mol** trong phương trình cân bằng để suy ra số mol chất cần tìm; (3) chia cho thể tích ban đầu của chất đó để ra nồng độ.

6.1.3 Titrating a weak acid with a strong base (AHL)

When the acid is **weak**, the curve looks qualitatively different in three ways: (1) the starting pH is higher (a weak acid is only partly dissociated); (2) before the equivalence point, added base converts some HA into A^-, creating a mixture of a weak acid and its conjugate base — a **buffer** — so pH rises only slowly over a wide, gently-sloping **buffer plateau**; (3) the equivalence point itself lies **above** pH 7, because the salt formed (containing A^-, the conjugate base of a weak acid) hydrolyses to give a basic solution.



Titration curve: 25.0 cm^3 of 0.100 M $CH_3COOH(aq)$ ($K_a = 1.8 \times 10^{-5}$) titrated with 0.100 M $NaOH(aq)$. Contrast with the strong–strong curve: a gently-sloping buffer plateau before equivalence, a smaller (though still sharp) jump, and an equivalence point above pH 7.

Ví dụ mẫu · Weak-acid/strong-base titration (AHL)

For the titration above (25.0 cm^3 of 0.100 M CH_3COOH, $K_a = 1.8 \times 10^{-5}$, $pK_a = 4.74$, titrated with 0.100 M NaOH), find the pH after (a) 12.5 cm^3 and (b) 25.0 cm^3 of NaOH have been added.

(a) Half-equivalence (12.5 cm^3): exactly half the acid has been converted to its conjugate base, so $[CH_3COO^-] = [CH_3COOH]$ and, by Henderson–Hasselbalch,

$$\text{pH} = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]} = 4.74 + \log(1) = 4.74.$$

(b) Equivalence (25.0 cm^3): all the acid has become CH_3COO^-; total moles $= 2.50$ mmol in a total volume of 50.0 cm^3, so $[CH_3COO^-] = 0.0500$ M. The acetate ion hydrolyses: $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$, with $K_b = \dfrac{K_w}{K_a} = \dfrac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$.

$$[OH^-] \approx \sqrt{K_b C} = \sqrt{(5.56 \times 10^{-10})(0.0500)} = 5.27 \times 10^{-6}\ \text{M}.$$

$$\text{pOH} = 5.28, \qquad \text{pH} = 14.00 - 5.28 = 8.72.$$

The equivalence point is basic, confirming the general rule for a weak-acid/strong-base titration.

VN **GIẢI THÍCH TIẾNG VIỆT**

So sánh hai đường chuẩn độ: acid mạnh–bazơ mạnh có điểm tương đương đúng bằng pH 7 và bước nhảy rất dốc; acid yếu–bazơ mạnh có một đoạn **cao nguyên đệm** (buffer plateau) thoải trước điểm tương đương — tại đúng **nửa thể tích tương đương**, pH $= pK_a$ (đây là cách thực nghiệm xác định pK_a!) — và điểm tương đương nằm **trên** pH 7 vì ion A^- (bazơ liên hợp của acid yếu) bị thuỷ phân tạo môi trường bazơ.

6.1.4 Acid-base indicators

An **indicator** is itself a weak acid (or weak base), HInd, whose protonated form HInd and deprotonated form Ind^- have visibly different colours: $HInd \rightleftharpoons H^+ + Ind^-$. Near its own pK_a (the indicator's **transition range**, roughly $pK_a \pm 1$), both forms are present in comparable amounts and the solution shows an intermediate/changing colour. To choose a suitable indicator for a titration, its transition range must fall within the **steep, near-vertical** part of the titration curve — where a single drop of

titrant swings the pH by several units — so that the colour change occurs essentially exactly at the equivalence point.

Indicator	pK_a (range)	Colour: acid → base
Methyl orange	3.7 $(3.1–4.4)$	red → yellow
Bromothymol blue	7.0 $(6.0–7.6)$	yellow → blue
Phenolphthalein	9.3 $(8.2–10.0)$	colourless → pink

Ví dụ mẫu · Worked example

Which indicator(s) from the table are suitable for (a) the strong acid–strong base titration above, and (b) the weak-acid/strong-base titration above?

(a) The steep region spans roughly pH 4 to pH 10 (a huge jump). **All three** indicators fall within this range, so any could be used — methyl orange and phenolphthalein are the traditional choices.

(b) The steep region here runs from roughly pH 7 to pH 11 (a smaller jump, positioned higher up the scale). **Phenolphthalein** $(8.2–10.0)$ falls entirely within this steep region and is suitable. **Methyl orange** $(3.1–4.4)$ would change colour far too early, well within the gentle buffer plateau, giving a badly inaccurate endpoint.

VN **GIẢI THÍCH TIẾNG VIỆT**

Chất chỉ thị là một acid yếu (hoặc bazơ yếu) có màu sắc khác nhau giữa dạng HInd và dạng Ind^-. Nguyên tắc chọn chỉ thị: khoảng đổi màu ($pK_a \pm 1$) của chỉ thị phải nằm **trong đoạn dốc đứng** của đường chuẩn độ, KHÔNG nhất thiết phải đúng pH $= 7$. Đó là lý do phenolphthalein phù hợp cho chuẩn độ acid yếu–bazơ mạnh (điểm tương đương nằm trên pH 7) trong khi methyl orange thì không.

(!) Lỗi thường gặp: Choosing an indicator by looking only at "which one changes near pH 7" is unreliable — what matters is whether the indicator's transition range lies inside the titration curve's *steep* region, which is not centred on pH 7 for a weak-acid/strong-base or weak-base/strong-acid titration.

A **universal indicator** (a mixture of several single indicators) changes colour gradually and continuously across the whole pH range, useful for *estimating* an unknown pH by comparison with a colour chart — but it is unsuitable for locating a sharp titration endpoint, since it never gives one single, clean colour change. For titrations, a **single** indicator with a narrow, well-defined transition range (as in the table above) is always preferred.

6.1.5 Salt hydrolysis (AHL)

Dissolving a salt in water does not always give a neutral solution: if either ion is the conjugate acid/base of a *weak* acid/base, it reacts with water (**hydrolyses**), shifting the pH. NH_4Cl is **acidic**: NH_4^+ is the conjugate acid of the weak base NH_3, so it partially donates a proton, $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$. CH_3COONa is **basic**: CH_3COO^- is the conjugate base of the weak acid CH_3COOH, so it partially accepts a proton from water, $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$. A salt of a *strong* acid and *strong* base (e.g. NaCl) is neutral — neither ion hydrolyses.

Ví dụ mẫu · pH of a hydrolysing salt (AHL)

Find the pH of 0.100 M $NH_4Cl(aq)$, given $K_b(NH_3) = 1.8 \times 10^{-5}$.

NH_4^+ is a weak acid with $K_a = \dfrac{K_w}{K_b} = \dfrac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$.

$$[H^+] \approx \sqrt{K_a C} = \sqrt{(5.56 \times 10^{-10})(0.100)} = 7.45 \times 10^{-6}\ \text{M}.$$

$$\text{pH} = -\log(7.45 \times 10^{-6}) = 5.13.$$

This is below 7, confirming $NH_4Cl(aq)$ is acidic, as expected for the salt of a weak base and a strong acid.

VN **GIẢI THÍCH TIẾNG VIỆT**

Muối của acid yếu (VD CH_3COONa) tạo dung dịch **bazơ** vì ion âm bị thuỷ phân sinh ra OH^-; muối của bazơ yếu (VD NH_4Cl) tạo dung dịch **acid** vì ion dương bị thuỷ phân sinh ra H_3O^+. Kỹ thuật tính toán giống hệt bài toán acid/bazơ yếu thông thường: chỉ cần đổi K_a và K_b cho nhau bằng công thức $K_a \times K_b = K_w$ (áp dụng cho một cặp liên hợp).

6.1.6 Buffer solutions (AHL)

A **buffer** resists pH change when small amounts of acid or base are added, made from a weak acid/base together with its conjugate salt (large reserves of both HA and A^- can absorb added H^+ or OH^- without a large pH shift). The **Henderson–Hasselbalch equation**:

$$\text{pH} = pK_a + \log \frac{[A^-]}{[HA]}.$$

Ví dụ mẫu · Worked example

Find the pH of a buffer containing 0.200 M CH_3COOH and 0.300 M CH_3COONa ($K_a = 1.8 \times 10^{-5}$, $pK_a = 4.74$).

$$\text{pH} = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]} = 4.74 + \log \frac{0.300}{0.200} = 4.74 + 0.18 = 4.92.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Phương trình Henderson–Hasselbalch cho biết pH của dung dịch đệm phụ thuộc vào pK_a của acid yếu và **tỉ lệ nồng độ** giữa dạng bazơ liên hợp và dạng acid — không phụ thuộc nồng độ tuyệt đối (pha loãng vừa phải không đổi pH đáng kể, đó là lý do dung dịch đệm "đệm" được sự thay đổi pH).

A buffer's usefulness lies in how little its pH shifts when a small amount of strong acid or base is added, because the added H^+ or OH^- is largely consumed by the buffer's reserve of A^- or HA rather than accumulating freely in solution.

Ví dụ mẫu · Buffer response to added acid (AHL)

100 cm^3 of the buffer above (0.200 M CH_3COOH, 0.300 M CH_3COONa, $pK_a = 4.74$) has 5.00 cm^3 of 1.00 M HCl added. Find the new pH, and compare with the original pH (4.92).

Initial moles: $n(CH_3COOH) = 0.200 \times 0.100 = 0.0200$ mol; $n(CH_3COO^-) = 0.300 \times 0.100 = 0.0300$ mol.

Added H^+: $n = 1.00 \times 0.00500 = 0.00500$ mol, which reacts $CH_3COO^- + H^+ \to CH_3COOH$:

$$n(CH_3COOH) = 0.0200 + 0.00500 = 0.0250 \text{ mol}.$$

$$n(CH_3COO^-) = 0.0300 - 0.00500 = 0.0250 \text{ mol}.$$

$$\text{pH} = 4.74 + \log \frac{0.0250}{0.0250} = 4.74 + 0 = 4.74.$$

The pH fell only from 4.92 to 4.74 — a modest change, even though a substantial amount of strong acid was added; an unbuffered solution of similar volume would show a much larger pH drop.

6.2 Electron transfer reactions

Redox reactions involve electron transfer, tracked via **oxidation states** (oxidation = loss of electrons/increase in oxidation state; reduction = gain of electrons/decrease in oxidation state — "OIL RIG"). In a **voltaic (galvanic) cell**, a spontaneous redox reaction is physically split into two half-cells connected by a wire (external electron flow) and a salt bridge (ion flow, maintaining electrical neutrality); electrons flow from the **anode** (oxidation, negative electrode) to the **cathode** (reduction, positive electrode).

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}.$$

To write the **overall cell equation** from two half-equations, first multiply each so that the number of electrons lost by one equals the number gained by the other, then add the two half-equations and cancel the electrons. For example, combining $Fe \to Fe^{2+} + 2e^-$ with $Ag^+ + e^- \to Ag$ (multiplied by 2 to match electrons) gives $Fe + 2Ag^+ \to Fe^{2+} + 2Ag$.

Redox vocabulary

Oxidation: loss of electrons, oxidation state increases, occurs at the **anode**. **Reduction**: gain of electrons, oxidation state decreases, occurs at the **cathode**. In a voltaic cell the anode is negative and the cathode is positive; a more positive E° means a species is more easily *reduced* (a stronger oxidising agent).

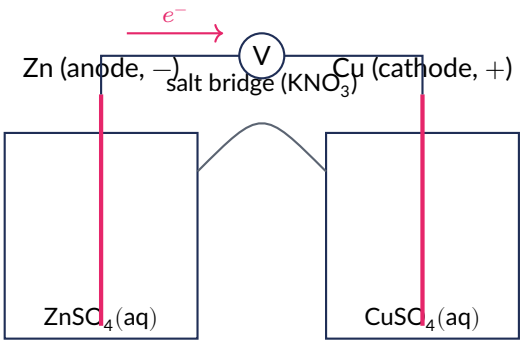
Ví dụ mẫu · Worked example

Identify the oxidising agent and reducing agent in $Zn(s) + Cu^{2+}(aq) \to Zn^{2+}(aq) + Cu(s)$.

Oxidation states: Zn goes from 0 to $+2$ (loses $2e^-$, is **oxidised**) — since it donates electrons to Cu^{2+}, Zn is the **reducing agent**. Cu goes from $+2$ to 0 (gains $2e^-$, is **reduced**) — since it accepts electrons from Zn, Cu^{2+} is the **oxidising agent**.

VN **GIẢI THÍCH TIẾNG VIỆT**

Chất **khử** (reducing agent) là chất **bị oxi hoá** (nhường electron, số oxi hoá tăng); chất **oxi hoá** (oxidising agent) là chất **bị khử** (nhận electron, số oxi hoá giảm). Dễ nhầm lẫn: tên gọi "chất khử/chất oxi hoá" mô tả **tác dụng lên chất kia**, không mô tả điều xảy ra với chính nó.



Voltaic (Daniell) cell: $\text{Zn(s)}|\text{Zn}^{2+}\text{(aq)}\,||\,\text{Cu}^{2+}\text{(aq)}|\text{Cu(s)}$. Electrons flow through the external wire from the zinc anode (oxidation, $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$) to the copper cathode (reduction, $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$); the salt bridge maintains charge balance.

This shorthand **cell notation** is a compact way to describe a voltaic cell: a single vertical line (|) marks a phase boundary (e.g. solid electrode/aqueous solution), the double vertical line (||) represents the salt bridge, and by convention the **anode** half-cell is written on the **left** and the **cathode** half-cell on the **right**.

Ví dụ mẫu · Worked example

Given $E^\circ(\text{Cu}^{2+}/\text{Cu}) = +0.34$ V and $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76$ V, find E°_{cell} for the Daniell cell.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.34 - (-0.76) = +1.10 \text{ V}.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Trong pin điện hoá (voltaic cell), phản ứng oxi hoá khử **tự xảy ra** ($\Delta G < 0$), electron di chuyển qua dây dẫn từ cực âm (anode, nơi xảy ra oxi hoá) sang cực dương (cathode, nơi xảy ra khử). $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$ càng dương thì phản ứng càng thuận lợi về nhiệt động lực học.

Electrode potentials also predict whether a **displacement reaction** will occur without needing to build a physical cell at all: treat the two half-equations as a hypothetical cell (the more positive E° as reduction/cathode, the more negative as oxidation/anode) and check the sign of E°_{cell} — positive means the reaction is thermodynamically feasible as written.

Ví dụ mẫu · Worked example

Will solid zinc displace silver from $\text{AgNO}_3\text{(aq)}$, i.e. does $\text{Zn(s)} + 2\text{Ag}^+\text{(aq)} \rightarrow \text{Zn}^{2+}\text{(aq)} + 2\text{Ag(s)}$ occur?

$E^\circ(\text{Ag}^+/\text{Ag}) = +0.80$ V (more positive, so this is the reduction/cathode half-reaction); $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76$ V (oxidation/anode).

$$E^\circ_{\text{cell}} = 0.80 - (-0.76) = +1.56 \text{ V} > 0.$$

Positive $E^\circ_{\text{cell}} \Rightarrow$ the displacement reaction **is** thermodynamically feasible, so zinc does displace silver from solution.

(!) Lỗi thường gặp: Standard electrode potentials are *intensive* quantities (per mole of electrons transferred at that electrode) — never multiply E° by the stoichiometric coefficient needed to balance the overall cell equation. For example, in $\text{Cu} + 2\text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2\text{Ag}$, use $E^\circ(\text{Ag}^+/\text{Ag}) = +0.80$ V directly (*not* 2×0.80 V) when computing E°_{cell}.

6.2.1 The Nernst equation (AHL)

Away from standard (1 M, 298 K) conditions, cell voltage depends on concentration:

$$E = E^\circ - \frac{0.0592}{n}\log Q \quad (\text{at } 298 \text{ K}),$$

where n is the moles of electrons transferred in the balanced overall equation and Q is the reaction quotient (products over reactants; pure solids/liquids omitted).

Ví dụ mẫu · Nernst equation (AHL)

For the Daniell cell ($E^\circ = 1.10$ V, $n = 2$), find E when $[\text{Zn}^{2+}] = 0.0100$ M and $[\text{Cu}^{2+}] = 1.00$ M, using $Q = \dfrac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$.

$$E = 1.10 - \frac{0.0592}{2}\log\left(\frac{0.0100}{1.00}\right) = 1.10 - (0.0296)(-2) = 1.10 + 0.0592 = 1.16 \text{ V}.$$

Diluting the product ion (Zn^{2+}) pulls the reaction further forward, *raising* the cell voltage above standard.

VN **GIẢI THÍCH TIẾNG VIỆT**

Phương trình Nernst (HL) cho biết thế điện cực thực tế thay đổi theo nồng độ ion so với điều kiện chuẩn (1 M). Pha loãng ion **sản phẩm** (bên phải phương trình) làm Q giảm, kéo phản ứng "tiến thêm" về phía sản phẩm nên E **tăng** so với E°; pha loãng ion **chất phản ứng** có tác dụng ngược lại.

A more positive E°_{cell} corresponds to a more thermodynamically favourable (spontaneous) reaction. This is formalised by

$$\Delta G^\circ = -nFE^\circ_{\text{cell}},$$

which links electrochemistry directly back to the Gibbs free energy criterion for spontaneity ($\Delta G^\circ < 0$, Reactivity 1) and to $\Delta G^\circ = -RT\ln K$ (Reactivity 2): all three expressions describe the same underlying thermodynamic quantity, ΔG°, viewed through different experimental lenses (heat/entropy, equilibrium position, and cell voltage respectively). A positive E°_{cell} always gives a negative ΔG°, confirming the reaction is spontaneous as written.

Ví dụ mẫu · ΔG° from E°_{cell} (AHL)

Find ΔG° for the Daniell cell ($E^\circ_{\text{cell}} = +1.10$ V, $n = 2$).

$$\Delta G^\circ = -nFE^\circ_{\text{cell}} = -(2)(96\,500)(1.10) = -212\,300 \text{ J} = -212 \text{ kJ mol}^{-1}.$$

The strongly negative ΔG° confirms $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$ is spontaneous, consistent with the positive E°_{cell}.

VN **GIẢI THÍCH TIẾNG VIỆT**

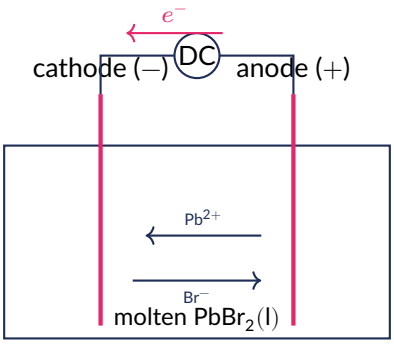
Ba công thức $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (Reactivity 1), $\Delta G^\circ = -RT\ln K$ (Reactivity 2), và $\Delta G^\circ = -nFE^\circ_{\text{cell}}$ (Reactivity 3) đều mô tả **cùng một đại lượng** ΔG° — chỉ khác cách "nhìn" (qua nhiệt/entropy, qua hằng số cân bằng, hay qua thế điện cực). E°_{cell} càng dương thì ΔG° càng âm, phản ứng càng thuận lợi về nhiệt động lực học.

(!) Lỗi thường gặp: Do not confuse a **voltaic cell** (spontaneous reaction, $\Delta G < 0$, chemical → electrical energy, cathode is +) with **electrolysis** (non-spontaneous, driven by an external power source, electrical → chemical energy, cathode is −). Reduction always occurs at the cathode in both — only the sign of the cathode and the direction of spontaneity differ.

6.2.2 Electrolysis

Electrolysis is a non-spontaneous redox reaction ($\Delta G^\circ > 0$ under standard conditions) driven forward by an external DC power supply, which forces electrons to flow against their natural direction. Two electrodes are immersed in a molten ionic compound or an electrolyte solution: the **cathode** is connected to the negative terminal and is where **reduction** occurs; the **anode** is connected to the positive terminal and is where **oxidation** occurs.

In a **molten** ionic compound, only two ions are present (the compound's own cation and anion), so the outcome is straightforward: the cation is reduced at the cathode and the anion is oxidised at the anode.



Electrolytic cell: molten $PbBr_2(l)$ decomposed by an external DC power source. Unlike a voltaic cell, the cathode here is **negative** (forced reduction, $Pb^{2+} + 2e^- \rightarrow Pb(l)$) and the anode is **positive** (forced oxidation, $2Br^- \rightarrow Br_2(g) + 2e^-$); the process is non-spontaneous and needs continuous electrical energy input.

Ví dụ mẫu · Worked example

Predict the products, and write half-equations, for the electrolysis of molten $PbBr_2(l)$ using inert electrodes.

Only Pb^{2+} and Br^- ions are present.
Cathode (reduction): $Pb^{2+}(l) + 2e^- \rightarrow Pb(l)$.
Anode (oxidation): $2Br^-(l) \rightarrow Br_2(g) + 2e^-$.
Overall: $PbBr_2(l) \rightarrow Pb(l) + Br_2(g)$.

In an **aqueous** solution, water molecules are also present and can themselves be oxidised or reduced, so each electrode is a competition between the dissolved ions and water. At the **cathode**, a metal ion is reduced only if it is easier to reduce than water; reactive metal ions (e.g. Na^+, K^+, Ca^{2+}, from groups 1–2) are *not* reduced in aqueous solution — water is reduced instead, $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$. At the **anode**, halide ions (except F^-) are oxidised preferentially over water when present at reasonably high concentration, even though the standard electrode potential for oxidising water is sometimes nominally more favourable — a kinetic (overpotential/concentration) effect not predicted by E° values alone; at low halide concentration, water oxidation, $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$, can dominate instead.

Ví dụ mẫu · Electrolysis of concentrated NaCl(aq)

Predict the products at each electrode for the electrolysis of *concentrated* NaCl(aq) (brine) using inert electrodes.

Na^+ is far too difficult to reduce in water, so water is reduced instead at the cathode:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq).$$

At high Cl^- concentration, chloride is oxidised preferentially at the anode:

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-.$$

Overall (the **chlor–alkali process**): $2NaCl(aq) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g) + Cl_2(g)$ — industrially valuable because it manufactures three useful chemicals (NaOH, H_2, Cl_2) at once. At *low* Cl^- concentration, O_2 tends to form at the anode instead.

VN **GIẢI THÍCH TIẾNG VIỆT**

Điện phân nóng chảy (chỉ có 2 loại ion của chính hợp chất) cho kết quả đơn giản: cation bị khử ở cathode, anion bị oxi hoá ở anode. Điện phân dung dịch nước phức tạp hơn vì nước cũng có thể bị điện phân: cation kim loại hoạt động mạnh (nhóm 1, 2) không bị khử — nước bị khử thay thế, sinh khí H_2; ở anode, ion halide (trừ F^-) ở nồng độ cao thường bị oxi hoá ưu tiên hơn nước dù thế điện cực chuẩn đôi khi "trên giấy" có lợi hơn cho nước — đây là hiệu ứng động học (overpotential), không chỉ đơn thuần so sánh E°.

(!) Lỗi thường gặp: Comparing standard electrode potentials alone does not always correctly predict the anode product in aqueous electrolysis. At high halide-ion concentration (e.g. concentrated NaCl(aq)), Cl_2 forms preferentially even though oxidising water is nominally more thermodynamically favourable on paper — overpotential and concentration effects matter, so simple E° comparison alone is not fully reliable for predicting aqueous electrolysis products at the anode.

Predicting electrolysis products (quick reference).

System	Cathode product	Anode product
Molten binary salt (e.g. $PbBr_2$)	cation, reduced (e.g. Pb)	anion, oxidised (e.g. Br_2)
Dilute aqueous reactive-metal halide (e.g. dilute NaCl(aq))	H_2 (water reduced)	O_2 (water oxidised)
Concentrated aqueous halide (e.g. conc. NaCl(aq))	H_2 (water reduced)	X_2 (halide oxidised)
Aqueous salt of a less-reactive metal (e.g. $CuSO_4$(aq))	metal, reduced (e.g. Cu)	O_2 (water oxidised)

6.2.3 Faraday's laws of electrolysis (AHL)

Faraday's laws quantify how much product forms during electrolysis. The charge passed is $Q = It$ (I in amperes, t in seconds, Q in coulombs). The amount (mol) of electrons transferred is

$$n(e^-) = \frac{Q}{F},$$

where $F = 96\,500$ C mol^{-1} is the Faraday constant (the charge on one mole of electrons). The relevant half-equation then gives the mole ratio between electrons and product, converting $n(e^-)$ into moles (then, via M, mass) of product.

Ví dụ mẫu · Faraday's law (AHL)

A current of 2.00 A is passed through $CuSO_4(aq)$ for 1.00 hour using inert electrodes. Find the mass of copper deposited at the cathode ($M(\text{Cu}) = 63.55$ g mol^{-1}).

$$Q = It = (2.00)(3600) = 7200 \text{ C}. \qquad n(e^-) = \frac{7200}{96\,500} = 0.0746 \text{ mol}.$$

$Cu^{2+} + 2e^- \rightarrow$ Cu needs 2 mol e^- per mol Cu:

$$n(\text{Cu}) = \frac{0.0746}{2} = 0.0373 \text{ mol}, \qquad m = 0.0373 \times 63.55 = 2.37 \text{ g}.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Quy trình tính toán định luật Faraday: (1) đổi $Q = It$; (2) đổi ra số mol electron $n(e^-) = Q/F$; (3) dùng **tỉ lệ mol** trong nửa phản ứng điện cực để đổi sang số mol sản phẩm — tỉ lệ này phụ thuộc **điện tích ion** (VD 1 mol e^- cho 1 mol Ag nhưng cần 2 mol e^- cho 1 mol Cu); (4) đổi mol sang khối lượng bằng M.

Faraday's-law calculations underpin two everyday applications: **electroplating** (depositing a thin, protective or decorative metal layer — e.g. silver-plating cutlery, where the object being plated is the cathode, a bar of pure silver is the anode, and $AgNO_3(aq)$ is the electrolyte) and **electrorefining** (purifying a metal — e.g. impure copper as the anode, a thin sheet of pure copper as the cathode, and $CuSO_4(aq)$ as the electrolyte; impurities either dissolve into solution or fall away as an anode "sludge", while pure Cu^{2+} is reduced onto the cathode).

6.2.4 Batteries and fuel cells

A **rechargeable (secondary) battery** is a voltaic cell whose product-forming reaction can be driven backwards by applying an external voltage (essentially electrolysing the cell), regenerating the original reactants so the battery can be reused many times. A **fuel cell** is different: it is continuously supplied with fuel and oxidant from outside (rather than storing a fixed amount of reactant internally) and converts chemical energy directly into electrical energy for as long as fuel keeps flowing.

Ví dụ mẫu · Worked example

Write the half-equations and overall equation for a hydrogen–oxygen fuel cell (acidic electrolyte).

Anode (oxidation): $H_2(g) \rightarrow 2H^+(aq) + 2e^-$.
Cathode (reduction): $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$.
Balancing electrons (multiply the anode equation by 2) and adding:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l).$$

The only product is water; unlike combustion, the energy is released directly as electrical work rather than heat.

VN **GIẢI THÍCH TIẾNG VIỆT**

Pin sạc lại được (rechargeable battery) thực chất là một pin điện hoá mà phản ứng có thể bị **đảo ngược** bằng dòng điện ngoài (giống điện phân) để tái tạo chất phản ứng ban đầu. Pin nhiên

liệu (fuel cell) khác pin thông thường ở chỗ nhiên liệu được **cấp liên tục từ bên ngoài**, không dự trữ sẵn bên trong — chỉ cần còn nhiên liệu là còn phát điện.

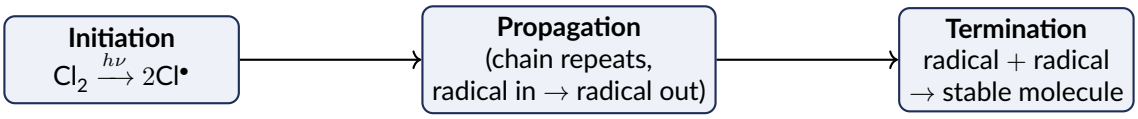
Fuel cells are, in principle, more energy-efficient than burning the same fuel in an engine (no heat-engine losses tied to the combustion/mechanical-work pathway) and produce only water when running on hydrogen, with no combustion pollutants; the practical challenges are instead infrastructure-related — storing and transporting hydrogen safely, and the cost of catalysts (often platinum) at the electrodes.

6.3 Electron-sharing reactions: radicals and electrophiles

Beyond acid–base and simple redox chemistry, many organic reactions proceed by **sharing** electrons between reacting species rather than fully transferring them. **Radicals** (species with an unpaired electron, denoted with a •) react by sharing one electron at a time in a chain process; **electrophiles** (electron-pair *acceptors*, attracted to regions of high electron density) react with electron-rich sites by forming a new covalent bond from a shared electron pair.

6.3.1 Radical substitution: halogenation of alkanes

Alkanes contain only strong, non-polar C—C and C—H σ bonds and no functional group, so they are generally unreactive towards the ionic mechanisms seen elsewhere in this chapter; UV light is needed to force reaction with halogens by supplying enough energy to start a radical chain. Alkanes undergo **radical substitution** with halogens (X_2) under UV light, replacing an H atom with a halogen atom. The mechanism has three stages: **initiation** — UV light supplies enough energy to break the halogen–halogen bond **homolytically** (each atom keeps one electron of the shared pair), generating two radicals, e.g. $Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet}$; **propagation** — a radical reacts with a stable molecule to generate a new radical, keeping the chain going (two alternating propagation steps for a simple halogenation); **termination** — two radicals combine to form a stable molecule, removing radicals from the system and ending that chain.



The radical chain: one initiation event can trigger many repeated propagation cycles (each regenerating a radical to continue the chain) before termination finally removes radicals and stops that chain.

Ví dụ mẫu · Full radical substitution mechanism

Write full mechanism steps (initiation, both propagation steps, and one termination step) for the UV-light reaction of methane with chlorine, $CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$.

Initiation: $Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet}$.
Propagation (1): $Cl^{\bullet} + CH_4 \rightarrow CH_3^{\bullet} + HCl$.
Propagation (2): $CH_3^{\bullet} + Cl_2 \rightarrow CH_3Cl + Cl^{\bullet}$ (regenerates $Cl^{\bullet}$, so steps (1) and (2) repeat as a chain).
Termination (one possibility): $CH_3^{\bullet} + Cl^{\bullet} \rightarrow CH_3Cl$ (or $2Cl^{\bullet} \rightarrow Cl_2$, or $2CH_3^{\bullet} \rightarrow C_2H_6$).

VN **GIẢI THÍCH TIẾNG VIỆT**

Cơ chế thế gốc tự do gồm 3 giai đoạn: **khơi mào** (initiation, bẻ gãy liên kết đồng li dưới tác dụng UV, sinh gốc tự do), **phát triển mạch** (propagation, gốc tự do phản ứng với phân tử bền tái sinh gốc tự do mới — lặp lại nhiều lần), **tắt mạch** (termination, hai gốc tự do kết hợp thành

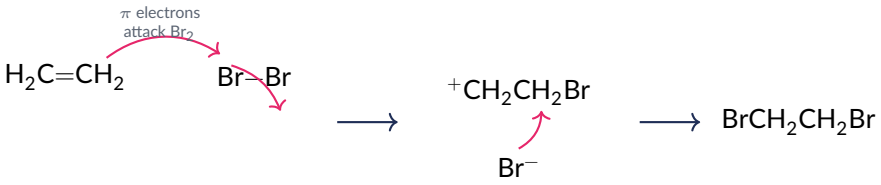
phân tử bền, chấm dứt mạch phản ứng đó).

With an **excess** of halogen, substitution does not necessarily stop after one H has been replaced: the mono-substituted product (CH_3Cl) can itself undergo further radical substitution, giving a mixture of CH_2Cl_2, $CHCl_3$, and eventually CCl_4 alongside unreacted CH_3Cl — a practical limitation that makes radical substitution a poor method for preparing a single, pure halogenoalkane in high yield.

6.3.2 Electrophilic addition to alkenes

Alkenes contain a C=C double bond: one σ bond plus one π bond formed from sideways overlap of p orbitals. The π electrons lie above and below the molecular plane, exposed and available to attack electron-poor species (**electrophiles**) such as Br_2 or HX — this is **electrophilic addition**. **Markovnikov's rule**: when HX adds across an unsymmetrical alkene, H bonds to the carbon that *already* carries more hydrogen atoms. The underlying reason is **carbocation stability**: alkyl groups are electron-donating, so a more substituted (tertiary > secondary > primary) carbocation intermediate is more stable and forms preferentially, and the nucleophile then attacks that same carbon.

For X_2 (e.g. Br_2) the mechanism proceeds in two curly-arrow steps: (1) the electron-rich π bond attacks one Br atom of Br_2, while the Br—Br σ bond breaks heterolytically (both electrons move onto the departing bromine), giving a positively-charged carbocation intermediate and a free Br^- ion; (2) the Br^- ion (now acting as a nucleophile) attacks the electron-deficient carbocation carbon, forming the second C—Br bond and completing the addition.



Simplified curly-arrow mechanism for electrophilic addition, $CH_2{=}CH_2 + Br_2 \rightarrow BrCH_2CH_2Br$: the π bond attacks Br_2, forming a carbocation intermediate and Br^-; Br^- then attacks the carbocation to give the dibromide product.

Ví dụ mẫu · Worked example

Predict the major product of $CH_3CH{=}CH_2 + HBr$.

Protonation gives the more stable secondary carbocation $CH_3\overset{+}{C}HCH_3$ (rather than the primary carbocation), so Br^- attacks there: major product is **2-bromopropane**, $CH_3CHBrCH_3$.

Ví dụ mẫu · Full electrophilic addition mechanism

Describe, with curly arrows, the mechanism for $CH_2{=}CH_2 + Br_2 \rightarrow BrCH_2CH_2Br$.

Step 1: the π electrons of C=C attack a Br atom of Br_2; simultaneously the Br—Br bond breaks heterolytically, both bonding electrons moving onto the departing bromine to give a free Br^- ion. This forms a carbocation intermediate, $^+CH_2CH_2Br$, with the positive charge on the former alkene carbon.

Step 2: the Br^- ion, acting as a nucleophile, uses a lone pair to attack the positively-charged carbon, forming the second C—Br bond and giving the saturated product $BrCH_2CH_2Br$ (1,2-dibromoethane).

Ví dụ mẫu · Worked example

Predict the major product of $CH_3CH{=}CH_2 + H_2O$ (steam, catalytic H_3PO_4).
This is another electrophilic addition, with H^+ (from H_3PO_4) as the electrophile: it adds to the terminal $=CH_2$ carbon (Markovnikov), giving the more stable secondary carbocation, which is then attacked by H_2O (loses H^+ afterwards to regenerate the catalyst). Major product: **propan-2-ol**, $CH_3CH(OH)CH_3$.

VN **GIẢI THÍCH TIẾNG VIỆT**
Anken phản ứng cộng electrophin vì liên kết π giàu electron tấn công vào chất electrophin (nghèo electron, nhận cặp electron) như Br_2 hay HX. Với Br_2: bước 1 là liên kết π tấn công Br_2 tạo carbocation trung gian $+Br^-$; bước 2 là Br^- tấn công ngược lại carbocation. Quy tắc Markovnikov (H gắn vào carbon có nhiều H sẵn hơn) xuất phát từ việc carbocation **bậc cao hơn bền hơn** (do hiệu ứng đẩy electron của nhóm alkyl).

(!) Lỗi thường gặp: Do not apply Markovnikov's rule as a memorised shortcut without understanding *why* it works — the real deciding factor is always **carbocation stability** (tertiary $>$ secondary $>$ primary). For an alkene where both possible carbocations would be equally substituted (e.g. but-2-ene), a roughly equal mixture of both addition products forms instead of one clean "major" product.

6.4 Electron-pair-sharing reactions (AHL)

Nucleophiles (electron-pair donors) attack electrophilic carbon atoms — ones bonded to an electronegative atom, or otherwise short of electron density — sharing an electron pair to form a new bond. Depending on the substrate, the attacking species, and the reaction conditions, this electron-pair sharing can result in **substitution** (a leaving group departs, taking the old bonding pair with it), **elimination** (a β-hydrogen is removed instead, forming a new double bond), or **addition** (no group leaves at all, as at a carbonyl carbon).

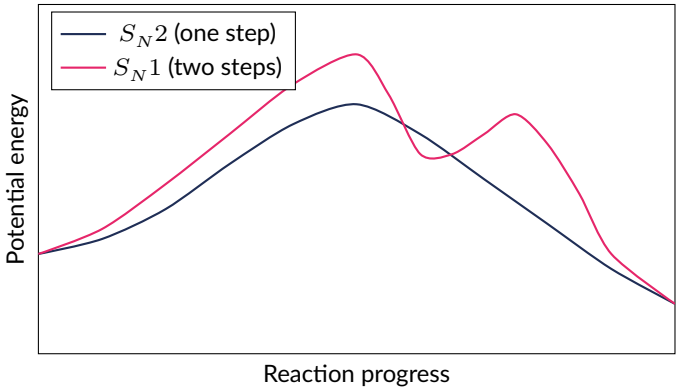
Electrophiles and nucleophiles

An **electrophile** is an electron-pair *acceptor* (*electron-loving*), attacking sites of high electron density; examples: Br_2, H^+, NO_2^+, the carbonyl carbon of C=O. A **nucleophile** is an electron-pair *donor* (*nucleus-loving*), attacking sites of low electron density/positive charge; examples: OH^-, CN^-, Br^-, H_2O, NH_3.

6.4.1 Nucleophilic substitution: S_N1 and S_N2 (AHL)

Halogenoalkanes undergo nucleophilic substitution (the halogen is replaced by a nucleophile) by one of two mechanisms, depending mainly on the substrate's structure. The *rate* of substitution also depends strongly on the identity of the halogen itself: bond enthalpy decreases down group 17 (C–F $>$ C–Cl $>$ C–Br $>$ C–I), so the carbon–halogen bond is weakest (easiest to break) in iodoalkanes, which therefore hydrolyse **fastest** — even though C–F is the most polar bond of the four. This trend can be demonstrated experimentally: treating separate samples of 1-chlorobutane, 1-bromobutane and 1-iodobutane with $AgNO_3$ dissolved in ethanol (which keeps the halogenoalkanes in solution) produces a silver halide precipitate (AgCl white, AgBr cream, AgI yellow) fastest for the iodo-compound and slowest for the chloro-compound, directly tracking C–X bond strength rather than bond polarity.

	S_N2	S_N1
Substrate	Primary halogenoalkanes	Tertiary halogenoalkanes
Mechanism	One step; nucleophile attacks as C – X breaks (backside attack)	Two steps; C – X breaks first forming a carbocation, then the nucleophile attacks
Rate law	rate $= k$[substrate][Nu]	rate $= k$[substrate]
Stereochemistry	Walden inversion (configuration inverts)	Racemisation (both faces attacked)



Schematic (not to scale) potential-energy profiles. S_N2 passes through a single transition state; S_N1 passes through two transition states separated by a lower-energy carbocation intermediate (the dip partway along the reaction).

Ví dụ mẫu · S_N1 vs S_N2 rate behaviour (AHL)

A tertiary halogenoalkane hydrolyses by S_N1 with initial rate 4.0×10^{-5} mol dm^{-3} s^{-1} at [substrate] $= 0.20$ mol dm^{-3}, [OH$^-$] $= 0.10$ mol dm^{-3}. A primary halogenoalkane hydrolyses by S_N2 with the same initial rate under the same starting concentrations. Predict the new initial rate for each if [OH$^-$] is doubled (substrate concentration unchanged).

S_N1: rate $= k$[substrate] only — independent of [OH$^-$], so the rate is **unchanged**, still 4.0×10^{-5} mol dm^{-3} s^{-1}.
S_N2: rate $= k$[substrate][OH$^-$] — doubling [OH$^-$] doubles the rate to 8.0×10^{-5} mol dm^{-3} s^{-1}.

VN **GIẢI THÍCH TIẾNG VIỆT**
Cơ chế thế thân hạch phụ thuộc bậc của halogenoalkane: bậc 1 đi theo S_N2 (một bước, nucleophile tấn công từ phía đối diện nhóm rời đi, gây **đảo cấu hình**); bậc 3 đi theo S_N1 (hai bước qua carbocation trung gian, gây **raxemic hoá** vì nucleophile có thể tấn công từ cả hai phía). Tốc độ S_N1 chỉ phụ thuộc nồng độ chất nền vì bước chậm (quyết định tốc độ) không có nucleophile tham gia — đó là lý do tăng [OH$^-$] không đổi tốc độ S_N1 nhưng làm tốc độ S_N2 tăng theo tỉ lệ thuận.

(!) Lỗi thường gặp: A tertiary halogenoalkane does not automatically react by S_N1 substitution — with a strong, bulky base under hot, non-aqueous conditions, the same substrate is more likely to undergo **elimination** instead (below), competing directly with substitution.

6.4.2 Determining mechanisms from kinetics (AHL)

A rate law is always found **experimentally** (Reactivity 2), and this experimental evidence is one of the main ways chemists distinguish between competing mechanisms that would otherwise give the same overall product. For nucleophilic substitution: if increasing [Nu$^-$] (at constant substrate concentration) increases the rate, the nucleophile must be involved in (or before) the rate-determining step

— consistent with S_N2 (rate $= k$[substrate][Nu]). If changing [Nu^-] has *no* effect on rate, the rate-determining step cannot involve the nucleophile at all — consistent with S_N1 (rate $= k$[substrate], the slow step being loss of the leaving group to form a carbocation). **Stereochemical** evidence reinforces the kinetic evidence: a single, clean inversion of configuration at an optically active substrate points to a concerted, one-step backside attack (S_N2); (near-)complete racemisation points to a planar carbocation intermediate attacked from either face with roughly equal probability (S_N1). Secondary substrates often show behaviour *between* the two extremes, because both pathways can contribute simultaneously.

Ví dụ mẫu · Using kinetic evidence to identify a mechanism (AHL)

A halogenoalkane RBr is hydrolysed by $OH^-(aq)$. Doubling [RBr] doubles the initial rate; doubling [OH^-] also doubles the initial rate. A student who starts with optically active RBr obtains an optically inactive (racemic) product. Identify the mechanism suggested by the rate data, and comment on whether the two pieces of evidence agree.

Rate depends on *both* [RBr] and [OH^-] (first order in each) $\Rightarrow$ rate $= k$[RBr][OH^-] — the rate law expected for S_N2.
However, complete racemisation is the stereochemical signature of S_N1 (attack from either face of a planar carbocation), *not* clean S_N2 inversion.
The two pieces of evidence conflict, which should prompt a chemist to investigate further — for example, checking whether the substrate is actually secondary (where *both* mechanisms can contribute at once, giving a mixed rate law and partial racemisation) rather than assuming a single, "pure" mechanism from one dataset alone.

GIẢI THÍCH TIẾNG VIỆT VN

Bằng chứng thực nghiệm (dữ liệu tốc độ, hoá học lập thể) là cách các nhà hoá học phân biệt cơ chế phản ứng khi không thể quan sát trực tiếp từng bước phản ứng. Tốc độ phụ thuộc nồng độ nucleophile $\Rightarrow$ gợi ý S_N2; tốc độ không phụ thuộc $\Rightarrow$ gợi ý S_N1. Đảo cấu hình sạch $\Rightarrow S_N2$; raxemic hoá hoàn toàn $\Rightarrow S_N1$. Chất nền bậc 2 (secondary) thường cho kết quả "pha trộn" vì cả hai cơ chế có thể cùng đóng góp đồng thời.

6.4.3 Elimination reactions: E1 and E2 (AHL)

Halogenoalkanes reacting with a base/nucleophile do not always undergo substitution: the same reagent can instead act purely as a **base**, removing a H^+ from a carbon adjacent to the one bearing the leaving group (a β-hydrogen), while the leaving group departs and a new C=C double bond forms — this is **elimination**. Elimination mirrors substitution mechanistically: **E2** is a single concerted step (the base removes H^+ as the leaving group departs simultaneously; favoured with primary/secondary substrates and a strong, often bulky, base); **E1** is two steps via a carbocation intermediate (the leaving group departs first, then a β-hydrogen is removed; favoured with tertiary substrates, competing directly with S_N1). Conditions steer the balance: **hot, concentrated** NaOH/KOH dissolved in **ethanol** (a non-aqueous solvent, where OH^- behaves mainly as a base) favours **elimination**; **dilute, aqueous** NaOH at lower temperature (where OH^- behaves mainly as a nucleophile) favours **substitution**. (For $E2$ specifically, the departing H and leaving group must be able to align **anti-periplanar** — roughly opposite each other around the C—C bond — so that the electrons released as C—H breaks can flow directly into forming the new π bond as the leaving group departs.)

Ví dụ mẫu · Substitution vs elimination (AHL)

Predict the major organic product(s) of $(CH_3)_3CBr$ reacting with (a) hot, concentrated NaOH in ethanol; (b) $NaOH(aq)$.

$(CH_3)_3CBr$ is tertiary, so it ionises readily to the stable tertiary carbocation $(CH_3)_3C^+$ in both cases (the first, shared step of $E1/S_N1$).

(a) Hot, concentrated, ethanolic conditions favour the base removing a β-hydrogen ($E1$): major product is the alkene $(CH_3)_2C{=}CH_2$ (2-methylpropene) $+H_2O + Br^-$.

(b) Aqueous conditions favour H_2O/OH^- acting as a nucleophile attacking the carbocation (S_N1): major product is the alcohol $(CH_3)_3COH$ (2-methylpropan-2-ol).

VN **GIẢI THÍCH TIẾNG VIỆT**

Phản ứng tách (elimination) cạnh tranh với phản ứng thế khi tác nhân đóng vai trò **bazơ** (lấy H^+ ở carbon bên cạnh) thay vì vai trò **nucleophile** (tấn công trực tiếp vào carbon mang nhóm rời đi). Điều kiện **nóng, đặc, trong ethanol** đẩy mạnh vai trò bazơ ⇒ ưu tiên tách; điều kiện **loãng, trong nước** đẩy mạnh vai trò nucleophile ⇒ ưu tiên thế.

(!) Lỗi thường gặp: Do not assume a given base/nucleophile always gives one single outcome — the *same* reagent (OH^-) can give substitution or elimination as the major product depending entirely on the substrate class and the solvent/temperature/concentration conditions. Always check conditions before predicting the product.

6.4.4 Nucleophilic addition to carbonyl compounds (AHL)

The carbonyl group, C=O, is strongly polarised (O far more electronegative than C), leaving the carbonyl carbon electrophilic. Because there is no leaving group attached to this carbon in a simple aldehyde/ketone, nucleophiles **add** across the double bond instead of substituting — **nucleophilic addition**. The cyanide ion, CN^- (from HCN, or generated *in situ* from KCN + dilute acid), is a good nucleophile: its lone pair attacks the carbonyl carbon while the π electrons of C=O move onto the oxygen, forming a tetrahedral **alkoxide intermediate**; this is then protonated (by HCN or H_3O^+) to give a neutral **hydroxynitrile** (cyanohydrin) product, regenerating CN^-.

Ví dụ mẫu · Nucleophilic addition to a ketone (AHL)

Deduce the mechanism and product of CH_3COCH_3 (propanone) $+HCN$.

CN^- attacks the electrophilic carbonyl carbon of propanone; the C=O π electrons move onto oxygen, giving the alkoxide intermediate $(CH_3)_2C(O^-)(CN)$. Protonation of the alkoxide oxygen (by HCN, regenerating CN^-) gives the neutral product,

$$(CH_3)_2C(OH)(CN) \quad \text{— 2-hydroxy-2-methylpropanenitrile.}$$

Other nucleophiles add to carbonyl compounds by the same general pattern: the hydride ion, H^- (delivered by a reducing agent such as $NaBH_4$ or $LiAlH_4$), attacks the carbonyl carbon and reduces an aldehyde to a primary alcohol or a ketone to a secondary alcohol, via the same two-step addition-then-protonation sequence, simply with H^- in place of CN^-.

VN **GIẢI THÍCH TIẾNG VIỆT**

Nhóm carbonyl C=O phân cực mạnh khiến carbon mang tính electrophin. Vì carbon này không có nhóm rời đi (leaving group), nucleophile (CN^-) **cộng** vào chứ không **thế**: cặp electron của CN^- tấn công carbon carbonyl, electron π của C=O chuyển hẳn sang oxy tạo ion alkoxide trung gian, sau đó proton hoá cho sản phẩm hydroxynitrile (cyanohydrin) trung hoà.

6.4.5 Electrophilic substitution in benzene (AHL)

Benzene, C_6H_6, has a ring of six delocalised π electrons spread evenly over all six carbons (not three alternating double bonds), giving it extra stability (**aromaticity**). Because addition reactions would break this delocalisation, benzene instead undergoes **electrophilic substitution**, which replaces a ring hydrogen while restoring full delocalisation once the mechanism is complete. **Nitration** is a standard example: concentrated H_2SO_4 protonates HNO_3, which loses water to generate the electrophile, the **nitronium ion** NO_2^+:

$$HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O.$$

NO_2^+ then attacks the delocalised ring, forming a positively-charged **arenium ion** intermediate in which delocalisation is broken over only part of the ring; loss of H^+ (to HSO_4^-, regenerating H_2SO_4) restores full aromatic delocalisation, giving the substituted product.

Ví dụ mẫu · Nitration of benzene (AHL)

Write the overall equation for the nitration of benzene, and identify the electrophile and catalyst.

Electrophile: NO_2^+ (nitronium ion), generated from $HNO_3 + H_2SO_4$; H_2SO_4 is the catalyst (regenerated at the end of the mechanism). Overall:

$$C_6H_6 + HNO_3 \xrightarrow{\text{conc. } H_2SO_4} C_6H_5NO_2 + H_2O.$$

Other electrophilic substitutions of benzene follow the same three-stage pattern (generate the electrophile, attack the ring to form an arenium intermediate, lose H^+ to restore aromaticity) with a different electrophile and catalyst: **halogenation** uses a halogen carrier catalyst (e.g. $FeBr_3$) to polarise Br_2 into an electrophilic Br^+-like species, giving bromobenzene; **Friedel–Crafts alkylation** uses $AlCl_3$ to polarise a haloalkane (e.g. CH_3Cl) into an electrophilic carbocation-like species, attaching an alkyl group to the ring.

VN **GIẢI THÍCH TIẾNG VIỆT**

Benzene có vòng 6 electron π giải toả đều (delocalised), bền vững hơn hẳn 3 liên kết đôi xen kẽ tưởng tượng, nên ưu tiên phản ứng **thế electrophin** (giữ lại vòng thơm) thay vì **cộng** (sẽ phá vỡ sự giải toả electron). Trong phản ứng nitro hoá, H_2SO_4 đặc tạo ra electrophile mạnh NO_2^+ từ HNO_3; sau khi NO_2^+ tấn công vòng, việc mất H^+ khôi phục lại tính thơm của vòng benzene.

Bài tập luyện tập

Which statement about water, in terms of Brønsted–Lowry theory, is correct?

(A) Water is amphiprotic — it can act as either an acid or a base

(B) Water can only ever act as an acid

(C) Water can only ever act as a base

(D) Water never participates in acid–base equilibria

Lời giải chi tiết

Water can donate a proton (e.g. to NH_3, forming $NH_4^+ + OH^-$) or accept one (e.g. from CH_3COOH, forming $H_3O^+ + CH_3COO^-$), so it is **amphiprotic**. **(A)**.

Bài tập luyện tập

Which of the following is classified as a nucleophile?

(A) CN^-
(B) Br_2
(C) NO_2^+
(D) H^+

Lời giải chi tiết

CN^- is an electron-pair donor (it has a lone pair on carbon that attacks electrophilic centres), making it a **nucleophile**; the other three are all electron-pair acceptors (electrophiles). **(A)**.

Bài tập luyện tập

The pH of 0.100 M weak acid HA ($K_a = 1.0 \times 10^{-4}$) is closest to:

(A) 2.50
(B) 4.00
(C) 1.00
(D) 3.50

Lời giải chi tiết

$[H^+] = \sqrt{K_a C} = \sqrt{(1.0 \times 10^{-4})(0.100)} = \sqrt{1.0 \times 10^{-5}} = 3.16 \times 10^{-3}$ M. pH $= -\log(3.16 \times 10^{-3}) = 2.50$. **(A)**.

Bài tập luyện tập

A weak acid HA has $K_a = 4.0 \times 10^{-6}$. Compared to CH_3COOH ($K_a = 1.8 \times 10^{-5}$) at the same concentration, HA is:

(A) A weaker acid, giving a higher pH
(B) A stronger acid, giving a lower pH
(C) Exactly as strong, giving the same pH
(D) Not comparable without knowing the volume

Lời giải chi tiết

A smaller K_a means less dissociation, so $[H^+]$ is lower and pH is higher at equal concentration — HA ($K_a = 4.0 \times 10^{-6}$) is the **weaker** acid. **(A)**.

Bài tập luyện tập

The pH of 0.0100 M $HCl(aq)$ is:

(A) 2.00
(B) 1.00
(C) 12.00
(D) 0.0100

Lời giải chi tiết

HCl is a strong acid (complete dissociation): $[H^+] = 0.0100$ M, pH $= -\log(0.0100) = 2.00$. **(A)**.

Bài tập luyện tập

The pH of 0.00500 M $Ba(OH)_2(aq)$ is closest to:

(A) 12.00
(C) 2.30
(B) 11.70
(D) 2.00

Lời giải chi tiết

Each mole of $Ba(OH)_2$ gives 2 mol OH^-: $[OH^-] = 2 \times 0.00500 = 0.0100$ M. pOH $= -\log(0.0100) = 2.00$, pH $= 14.00 - 2.00 = 12.00$. **(A).**

Bài tập luyện tập

A solution has $[OH^-] = 2.5 \times 10^{-3}$ M. Its pH is closest to:

(A) 11.40
(C) 3.40
(B) 2.60
(D) 10.60

Lời giải chi tiết

pOH $= -\log(2.5 \times 10^{-3}) = 2.60$. pH $= 14.00 - 2.60 = 11.40$. **(A).**

Bài tập luyện tập

What volume of 0.150 M NaOH(aq) is required to exactly neutralise 20.0 cm^3 of 0.100 M HCl(aq)?

(A) 13.3 cm^3
(C) 20.0 cm^3
(B) 30.0 cm^3
(D) 26.7 cm^3

Lời giải chi tiết

$n(\text{HCl}) = 0.100 \times 20.0 = 2.00$ mmol $= n(\text{NaOH})$ needed. $V = \dfrac{2.00}{0.150} = 13.3$ cm^3. **(A).**

Bài tập luyện tập

20.0 cm^3 of HCl(aq) of unknown concentration requires 32.50 cm^3 of 0.0500 M NaOH(aq) to reach the equivalence point. The concentration of the HCl(aq) is closest to:

(A) 0.0813 M
(C) 0.0308 M
(B) 0.0500 M
(D) 0.163 M

Lời giải chi tiết

$n(\text{NaOH}) = 0.0500 \times \dfrac{32.50}{1000} = 1.625 \times 10^{-3}$ mol $= n(\text{HCl})$ (1:1 ratio). $C(\text{HCl}) = \dfrac{1.625 \times 10^{-3}}{20.0/1000} = \dfrac{1.625 \times 10^{-3}}{0.0200} = 0.0813$ M. **(A).**

Bài luyện nâng cao (HL)

At the equivalence point of a weak-acid/strong-base titration, the pH is:

(A) Greater than 7 (basic)
(C) Less than 7 (acidic)
(B) Exactly 7
(D) Impossible to determine

Lời giải chi tiết

The salt formed contains the conjugate base of the weak acid, which hydrolyses to give a basic solution — e.g. pH $= 8.72$ for the CH_3COOH/NaOH titration worked above. **(A)**.

Bài luyện nâng cao (HL)

Which of the following salts, dissolved in water, gives a basic (pH > 7) solution?

(A) NaF
(C) KNO_3
(B) NH_4Br
(D) KBr

Lời giải chi tiết

F^- is the conjugate base of the weak acid HF and hydrolyses, $F^- + H_2O \rightleftharpoons HF + OH^-$, giving a basic solution. NH_4Br is acidic (NH_4^+ hydrolyses); KNO_3 and KBr are neutral (both ions come from a strong acid and a strong base). **(A)**.

Bài luyện nâng cao (HL)

A buffer contains 0.150 M NH_3 and 0.100 M NH_4Cl ($K_b = 1.8 \times 10^{-5}$, $pK_b = 4.74$). Its pH is closest to:

(A) 9.43
(C) 9.57
(B) 4.57
(D) 4.43

Lời giải chi tiết

$\text{pOH} = pK_b + \log \dfrac{[NH_4^+]}{[NH_3]} = 4.74 + \log \dfrac{0.100}{0.150} = 4.74 - 0.18 = 4.57$. $\text{pH} = 14.00 - 4.57 = 9.43$. **(A)**.

Bài luyện nâng cao (HL)

A buffer contains 0.250 M HCOOH and 0.100 M HCOONa ($K_a = 1.8 \times 10^{-4}$, $pK_a = 3.74$). Its pH is closest to:

(A) 3.35
(C) 3.74
(B) 4.13
(D) 4.35

Lời giải chi tiết

$\text{pH} = pK_a + \log \dfrac{[HCOO^-]}{[HCOOH]} = 3.74 + \log \dfrac{0.100}{0.250} = 3.74 + \log(0.400) = 3.74 - 0.40 = 3.35$. **(A)**.

Bài tập luyện tập

For titrating a weak base with a strong acid (acidic equivalence point), the most suitable indicator is:

(A) Methyl orange
(B) Phenolphthalein
(C) Both equally suitable
(D) Neither is suitable

Lời giải chi tiết

The equivalence point is acidic (well below pH 7), matching methyl orange's transition range (3.1–4.4); phenolphthalein's range (8.2–10.0) lies in the flat, already-basic region far past the steep jump. **(A)**.

Bài tập luyện tập

Given $E^\circ(\text{Ag}^+/\text{Ag}) = +0.80$ V and $E^\circ(\text{Fe}^{2+}/\text{Fe}) = -0.44$ V, the standard cell potential of $\text{Fe}|\text{Fe}^{2+}\,||\,\text{Ag}^+|\text{Ag}$ is:

(A) $+1.24$ V
(B) $+0.36$ V
(C) -1.24 V
(D) $+0.80$ V

Lời giải chi tiết

$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.80 - (-0.44) = +1.24$ V. **(A)**.

Bài luyện nâng cao (HL)

For the Daniell cell ($E^\circ = 1.10$ V, $n = 2$), if instead $[\text{Zn}^{2+}] = 1.00$ M and $[\text{Cu}^{2+}] = 0.0100$ M, the cell potential E is closest to:

(A) 1.04 V
(B) 1.16 V
(C) 1.10 V
(D) 0.94 V

Lời giải chi tiết

$Q = \dfrac{1.00}{0.0100} = 100$. $E = 1.10 - \dfrac{0.0592}{2}\log(100) = 1.10 - (0.0296)(2) = 1.10 - 0.0592 = 1.04$ V. **(A)**.

Bài tập luyện tập

Given $E^\circ(\text{Ag}^+/\text{Ag}) = +0.80$ V and $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76$ V, the standard cell potential of $\text{Zn}|\text{Zn}^{2+}\,||\,\text{Ag}^+|\text{Ag}$ is:

(A) $+1.56$ V
(B) $+0.04$ V
(C) -1.56 V
(D) $+1.06$ V

Lời giải chi tiết

$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.80 - (-0.76) = +1.56$ V. **(A)**.

Bài tập luyện tập

Given $E^\circ(\text{Ag}^+/\text{Ag}) = +0.80$ V and $E^\circ(\text{Cu}^{2+}/\text{Cu}) = +0.34$ V, the standard cell potential for $\text{Cu}|\text{Cu}^{2+}\,||\,\text{Ag}^+|\text{Ag}$ (overall equation $\text{Cu} + 2\text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2\text{Ag}$) is:

(A) $+0.46$ V
(C) $+0.23$ V
(B) $+0.92$ V
(D) $+1.14$ V

Lời giải chi tiết

$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.80 - 0.34 = +0.46$ V − E° values are *not* multiplied by the stoichiometric factor of 2 in front of Ag^+/Ag. **(A)**.

Bài tập luyện tập

Given $E^\circ(\text{Cu}^{2+}/\text{Cu}) = +0.34$ V and $E^\circ(\text{Fe}^{2+}/\text{Fe}) = -0.44$ V, will iron displace copper from $\text{CuSO}_4(\text{aq})$, i.e. is $\text{Fe(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{Cu(s)}$ feasible?

(A) Yes, since $E^\circ_{\text{cell}} = +0.78$ V > 0
(C) Yes, since $E^\circ_{\text{cell}} = -0.10$ V
(B) No, since $E^\circ_{\text{cell}} = -0.78$ V < 0
(D) Cannot be determined from E° values

Lời giải chi tiết

Treat Cu^{2+}/Cu (more positive) as reduction/cathode and Fe^{2+}/Fe as oxidation/anode: $E^\circ_{\text{cell}} = 0.34 - (-0.44) = +0.78$ V > 0, so the displacement is thermodynamically feasible. **(A)**.

Bài luyện nâng cao (HL)

For $\text{Fe} + 2\text{Ag}^+ \rightleftharpoons \text{Fe}^{2+} + 2\text{Ag}$ ($E^\circ_{\text{cell}} = +1.24$ V, $n = 2$), if $[\text{Fe}^{2+}] = 1.00$ M and $[\text{Ag}^+] = 0.0100$ M, the cell potential E is closest to:

(A) $+1.12$ V
(C) $+1.24$ V
(B) $+1.36$ V
(D) $+1.00$ V

Lời giải chi tiết

$Q = \dfrac{[\text{Fe}^{2+}]}{[\text{Ag}^+]^2} = \dfrac{1.00}{(0.0100)^2} = 1.00 \times 10^4$. $E = 1.24 - \dfrac{0.0592}{2}\log(1.00 \times 10^4) = 1.24 - (0.0296)(4.00) = 1.24 - 0.1184 = 1.12$ V. **(A)**.

Bài tập luyện tập

Electrolysis of molten Al_2O_3 (the basis of the industrial extraction of aluminium) produces at the cathode and anode respectively:

(A) Al; O_2
(C) Al; Al
(B) O_2; Al
(D) O_2; O_2

Lời giải chi tiết

Cathode (reduction): $\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$. Anode (oxidation): $2\text{O}^{2-} \rightarrow \text{O}_2 + 4e^-$. **(A)**.

Bài tập luyện tập

Electrolysis of dilute $H_2SO_4(aq)$ with inert electrodes produces at the cathode and anode respectively:

(A) H_2; O_2
(B) O_2; H_2
(C) H_2; SO_2
(D) S; O_2

Lời giải chi tiết

SO_4^{2-} is very difficult to oxidise, so effectively water is electrolysed: cathode $2H^+ + 2e^- \rightarrow H_2$; anode $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$. **(A)**.

Bài luyện nâng cao (HL)

A current of 3.00 A is passed through $AgNO_3(aq)$ for 1000 s using inert electrodes. The mass of silver deposited ($M(\text{Ag}) = 107.9$ g mol^{-1}) is closest to:

(A) 3.35 g
(B) 1.68 g
(C) 6.70 g
(D) 0.335 g

Lời giải chi tiết

$Q = It = 3.00 \times 1000 = 3000$ C. $n(e^-) = \dfrac{3000}{96\,500} = 0.0311$ mol. $Ag^+ + e^- \rightarrow Ag$ (1 electron per Ag), so $n(\text{Ag}) = 0.0311$ mol, $m = 0.0311 \times 107.9 = 3.35$ g. **(A)**.

Bài luyện nâng cao (HL)

How long (to the nearest 10 s) must a current of 1.50 A flow through $CuSO_4(aq)$ to deposit 1.00 g of copper ($M(\text{Cu}) = 63.55$ g mol^{-1})?

(A) 2020 s
(B) 1010 s
(C) 4040 s
(D) 505 s

Lời giải chi tiết

$n(\text{Cu}) = \dfrac{1.00}{63.55} = 0.01574$ mol. $Cu^{2+} + 2e^- \rightarrow Cu$, so $n(e^-) = 2 \times 0.01574 = 0.03147$ mol. $Q = n(e^-) \times F = 0.03147 \times 96\,500 = 3037$ C. $t = \dfrac{Q}{I} = \dfrac{3037}{1.50} = 2025$ s ≈ 2020 s. **(A)**.

Bài tập luyện tập

In electrolysis (as opposed to a voltaic cell), the cathode is connected to the ___ terminal of the external power supply and is the site of ___.

(A) negative; reduction
(B) positive; reduction
(C) negative; oxidation
(D) positive; oxidation

Lời giải chi tiết

The external supply forces electrons onto the cathode (negative terminal), where reduction occurs — opposite polarity to a voltaic cell's cathode, but reduction always occurs there in both. **(A)**.

Bài tập luyện tập

In a hydrogen–oxygen fuel cell, the species oxidised at the anode is:

(A) H_2
(B) O_2
(C) H^+
(D) H_2O

Lời giải chi tiết

$H_2(g) \rightarrow 2H^+(aq) + 2e^-$: hydrogen loses electrons (oxidation number rises from 0 to $+1$), so it is oxidised at the anode. **(A)**.

Bài tập luyện tập

In the radical substitution of methane with chlorine ($CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$), the homolytic fission $Cl_2 \rightarrow 2Cl^\bullet$ under UV light is which step?

(A) Initiation
(B) Propagation
(C) Termination
(D) Substitution

Lời giải chi tiết

Breaking the $Cl-Cl$ bond to generate the first radicals, before any product forms, defines **initiation**. **(A)**.

Bài tập luyện tập

In the mechanism for $CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$, the step $CH_3^\bullet + Cl_2 \rightarrow CH_3Cl + Cl^\bullet$ is:

(A) Propagation
(B) Initiation
(C) Termination
(D) Hydrolysis

Lời giải chi tiết

A radical reacts with a stable molecule to regenerate a new radical ($Cl^\bullet$), continuing the chain — this defines **propagation**. **(A)**.

Bài tập luyện tập

The step $2CH_3^\bullet \rightarrow C_2H_6$ in a radical substitution mechanism is an example of:

(A) Termination
(B) Initiation
(C) Propagation
(D) Substitution

Lời giải chi tiết

Two radicals combine to form a stable molecule with no radical product — this is **termination**, which removes reactive radicals from the system. **(A)**.

Bài tập luyện tập

Predict the major product of $(CH_3)_2C{=}CH_2$ (2-methylpropene) $+HCl$.

(A) $(CH_3)_3CCl$

(B) $(CH_3)_2CHCH_2Cl$

(C) A mixture of equal amounts of both

(D) No reaction occurs

Lời giải chi tiết

H^+ adds to the $=CH_2$ carbon (which already carries more H), generating the more stable tertiary carbocation $(CH_3)_3C^+$; Cl^- then attacks this carbon, giving $(CH_3)_3CCl$. **(A)**.

Bài tập luyện tập

The addition of Br_2 to an alkene proceeds via which type of reactive intermediate?

(A) A carbocation (with Br^- released)

(B) A free radical

(C) A carbanion

(D) A stable neutral molecule (no intermediate)

Lời giải chi tiết

The π electrons attack Br_2, breaking the Br—Br bond heterolytically and forming a positively-charged carbocation intermediate plus a free Br^- ion, which then attacks the carbocation. **(A)**.

Bài tập luyện tập

In the reaction of ethene with bromine water, which species acts as the electrophile attacked by the alkene's π electrons?

(A) Br_2

(B) H_2O

(C) OH^-

(D) Br^-

Lời giải chi tiết

The electron-rich π bond attacks the electron-poor, electron-pair-accepting Br_2 molecule, which is therefore the electrophile. **(A)**.

Bài luyện nâng cao (HL)

$(CH_3)_3CBr$ reacting with OH^- in aqueous solution proceeds mainly via:

(A) S_N1

(B) S_N2

(C) $E2$ only

(D) No reaction

Lời giải chi tiết

A tertiary substrate cannot easily be attacked from the back (steric hindrance blocks S_N2) but readily forms a stable tertiary carbocation, so it reacts via the two-step S_N1 pathway. **(A)**.

Bài luyện nâng cao (HL)

Substitution at a chiral carbon by the S_N2 mechanism results in:

(A) Inversion of configuration (Walden inversion)
(B) Retention of configuration
(C) Complete racemisation
(D) Formation of a new chiral centre only

Lời giải chi tiết

The nucleophile attacks from the face opposite the leaving group (backside attack) in a single step, flipping the configuration at that carbon — **inversion**. **(A)**.

Bài luyện nâng cao (HL)

Which condition most favours **elimination** over substitution for a tertiary halogenoalkane?

(A) Hot, concentrated NaOH dissolved in ethanol
(B) Cold, dilute $\mathrm{NaOH(aq)}$
(C) Aqueous NaOH at room temperature
(D) Neutral water alone

Lời giải chi tiết

Hot, concentrated, ethanolic (non-aqueous) hydroxide favours $\mathrm{OH^-}$ acting as a base (removing a β-hydrogen, $E1$) rather than as a nucleophile, especially for a tertiary substrate. **(A)**.

Bài luyện nâng cao (HL)

The product of $\mathrm{CH_3CHO}$ (ethanal) $+\mathrm{HCN}$ is:

(A) $\mathrm{CH_3CH(OH)CN}$
(B) $\mathrm{CH_3CH_2CN}$
(C) $\mathrm{CH_3COOH}$
(D) $\mathrm{CH_3CH_2OH}$

Lời giải chi tiết

$\mathrm{CN^-}$ adds to the electrophilic carbonyl carbon, the π electrons move onto oxygen, and protonation of the resulting alkoxide gives the hydroxynitrile $\mathrm{CH_3CH(OH)CN}$ (2-hydroxypropanenitrile). **(A)**.

Bài luyện nâng cao (HL)

The electrophile that attacks the benzene ring during nitration is:

(A) $\mathrm{NO_2^+}$
(B) $\mathrm{NO_3^-}$
(C) $\mathrm{HNO_3}$
(D) $\mathrm{SO_3}$

Lời giải chi tiết

Concentrated H_2SO_4 protonates HNO_3, which loses H_2O to generate the nitronium ion, NO_2^+ — the electrophile that attacks the delocalised ring. **(A)**.

Bài tập luyện tập

Bromination of ethane ($C_2H_6 + Br_2 \xrightarrow{h\nu} C_2H_5Br + HBr$) proceeds by which general mechanism?

(A) Radical substitution
(B) Electrophilic addition
(C) Nucleophilic substitution
(D) Electrophilic substitution

Lời giải chi tiết

An alkane reacting with a halogen under UV light always proceeds via homolytic fission and a radical chain — **radical substitution**. **(A)**.

Bài tập luyện tập

A solution has pH 3. Compared to a solution of pH 5, its $[H^+]$ is:

(A) 100 times greater
(B) 2 times greater
(C) 100 times smaller
(D) 10 times greater

Lời giải chi tiết

The pH scale is logarithmic (base 10): a difference of 2 pH units corresponds to a factor of $10^2 = 100$ in $[H^+]$; lower pH means *greater* $[H^+]$. **(A)**.

Bài luyện nâng cao (HL)

50.0 cm^3 of a buffer containing 0.400 M CH_3COOH and 0.400 M CH_3COONa ($pK_a = 4.74$) has 10.0 cm^3 of 0.500 M NaOH added. The new pH is closest to:

(A) 4.96
(B) 4.74
(C) 4.52
(D) 5.20

Lời giải chi tiết

Initial: $n(CH_3COOH) = n(CH_3COO^-) = 0.400 \times 0.0500 = 0.0200$ mol. Added OH^-: $n = 0.500 \times 0.0100 = 0.00500$ mol, reacting $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$. New $n(CH_3COOH) = 0.0200 - 0.00500 = 0.0150$ mol; new $n(CH_3COO^-) = 0.0200 + 0.00500 = 0.0250$ mol. $\text{pH} = 4.74 + \log\dfrac{0.0250}{0.0150} = 4.74 + 0.22 = 4.96$. **(A)**.

Bài tập luyện tập

Which best describes the role of the salt bridge in a voltaic cell?

(A) Maintains electrical neutrality by allowing ion flow between the half-cells

(B) Provides the electrons that flow through the external circuit

(C) Increases the standard cell potential

(D) Prevents any reaction from occurring

Lời giải chi tiết

As electrons flow externally from anode to cathode, charge would build up in each half-cell without a compensating ion flow; the salt bridge allows ions to migrate between half-cells, maintaining overall electrical neutrality so the cell keeps working. **(A)**.

Bài tập luyện tập

Electrolysis of concentrated $CuCl_2(aq)$ using inert electrodes produces at the cathode and anode respectively:

(A) Cu; Cl_2

(B) H_2; Cl_2

(C) Cu; O_2

(D) H_2; O_2

Lời giải chi tiết

Cu^{2+} is a far less reactive metal ion than Na^+/K^+ and is reduced in preference to water: cathode $Cu^{2+} + 2e^- \rightarrow Cu$. At high Cl^- concentration, chloride is oxidised preferentially at the anode: $2Cl^- \rightarrow Cl_2 + 2e^-$. **(A)**.

Bài luyện nâng cao (HL)

A nucleophilic substitution reaction's rate is unaffected by changing $[Nu^-]$, but doubles when [substrate] doubles. This kinetic behaviour is consistent with:

(A) S_N1

(B) S_N2

(C) Both mechanisms equally

(D) Neither mechanism

Lời giải chi tiết

Rate depends only on [substrate], matching rate $= k$[substrate] — the S_N1 rate law, where the rate-determining step (loss of the leaving group) does not involve the nucleophile. **(A)**.

Bài luyện nâng cao (HL)

Which observation would you expect from a clean, single-mechanism S_N2 reaction at a chiral carbon?

(A) Complete inversion of configuration

(B) Complete racemisation

(C) No stereochemical change at all

(D) Formation of a diastereomer

Lời giải chi tiết

S_N2 is a single concerted step with backside attack: the nucleophile always approaches from the face opposite the leaving group, giving **complete inversion** of configuration at that carbon (Walden inversion). **(A)**.

Bài tập luyện tập

In $\mathrm{Fe} + 2\mathrm{Ag}^{+} \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{Ag}$, the reducing agent and oxidising agent are respectively:

(A) Fe; Ag^{+}
(B) Ag^{+}; Fe
(C) Fe^{2+}; Ag
(D) Fe; Fe^{2+}

Lời giải chi tiết

Fe ($0 \rightarrow +2$) loses electrons — it is oxidised, so it is the **reducing agent**. Ag^{+} ($+1 \rightarrow 0$) gains electrons — it is reduced, so it is the **oxidising agent**. **(A)**.

Bài luyện nâng cao (HL)

Using $\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$, find ΔG° for $\mathrm{Fe} + 2\mathrm{Ag}^{+} \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{Ag}$ ($E^{\circ}_{\text{cell}} = +1.24$ V, $n = 2$).

(A) -239 kJ mol^{-1}
(B) $+239$ kJ mol^{-1}
(C) -120 kJ mol^{-1}
(D) -478 kJ mol^{-1}

Lời giải chi tiết

$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}} = -(2)(96\,500)(1.24) = -239\,320$ J $= -239$ kJ mol^{-1}. **(A)**.

Bài tập luyện tập

30.0 cm^3 of 0.200 M HCl is mixed with 50.0 cm^3 of 0.150 M NaOH. The pH of the resulting solution is closest to:

(A) 12.27
(B) 1.73
(C) 12.00
(D) 13.00

Lời giải chi tiết

$n(\mathrm{HCl}) = 0.200 \times 0.0300 = 0.00600$ mol; $n(\mathrm{NaOH}) = 0.150 \times 0.0500 = 0.00750$ mol. NaOH is in excess: $n(\mathrm{OH}^{-})_{\text{excess}} = 0.00750 - 0.00600 = 0.00150$ mol. Total volume $= 0.0800$ dm^3: $[\mathrm{OH}^{-}] = \dfrac{0.00150}{0.0800} = 0.01875$ M. pOH $= 1.73$, pH $= 14.00 - 1.73 = 12.27$. **(A)**.

Bài tập luyện tập

Methane reacts with an **excess** of Cl_2 under UV light. Besides $\mathrm{CH_3Cl}$, which further product(s) may also form?

(A) $\mathrm{CH_2Cl_2}$, $\mathrm{CHCl_3}$, and $\mathrm{CCl_4}$
(B) Only $\mathrm{C_2H_6}$
(C) Only HCl, no carbon-containing by-products
(D) No further reaction is possible once $\mathrm{CH_3Cl}$ forms

Lời giải chi tiết

$\mathrm{CH_3Cl}$ still has C–H bonds and can itself undergo further radical substitution with more Cl_2, giving a mixture of increasingly chlorinated products up to $\mathrm{CCl_4}$. **(A)**.

Bài tập luyện tập

In the cell notation $Zn(s)|Zn^{2+}(aq)\,||\,Cu^{2+}(aq)|Cu(s)$, the electrode written on the right-hand side is the:

(A) Cathode
(B) Anode
(C) Salt bridge
(D) Reference electrode

Lời giải chi tiết

By convention, the anode (oxidation) half-cell is written on the left and the cathode (reduction) half-cell on the right, separated by the salt bridge symbol $||$. **(A)**.

Bài tập luyện tập

Why is universal indicator unsuitable for locating the endpoint of an acid–base titration?

(A) It changes colour gradually across the whole pH range, with no single sharp colour change
(B) It only works with strong acids
(C) It reacts irreversibly with the titrant
(D) It is more expensive than single indicators

Lời giải chi tiết

Universal indicator is a mixture of several indicators, giving a continuous colour gradient across the pH scale rather than one sharp, easily-judged colour change at a single pH — useful for estimating pH, but not for pinpointing a titration endpoint. **(A)**.

Bài tập luyện tập

A 0.200 M solution of a weak monoprotic acid has pH $= 3.00$. K_a is closest to:

(A) 5.0×10^{-6}
(B) 1.0×10^{-3}
(C) 2.0×10^{-6}
(D) 5.0×10^{-3}

Lời giải chi tiết

$[H^+] = 10^{-3.00} = 1.0 \times 10^{-3}$ M. $K_a \approx \dfrac{[H^+]^2}{C} = \dfrac{(1.0 \times 10^{-3})^2}{0.200} = \dfrac{1.0 \times 10^{-6}}{0.200} = 5.0 \times 10^{-6}$. **(A)**.

Bài tập luyện tập

Predict the major product of $(CH_3)_2C{=}CH_2 + H_2O$ (steam, catalytic H_3PO_4).

(A) $(CH_3)_3COH$
(B) $(CH_3)_2CHCH_2OH$
(C) $(CH_3)_2CHCH_3$
(D) No reaction occurs

Lời giải chi tiết

H^+ adds to the $=CH_2$ carbon, generating the more stable tertiary carbocation $(CH_3)_3C^+$; H_2O then attacks this carbon and loses H^+, giving the tertiary alcohol $(CH_3)_3COH$. **(A)**.

Bài tập luyện tập

1-chlorobutane, 1-bromobutane and 1-iodobutane are each treated with $AgNO_3$ in ethanol. A precipitate forms fastest for:

(A) 1-iodobutane
(B) 1-chlorobutane
(C) 1-bromobutane
(D) All three at the same rate

Lời giải chi tiết

C—I is the weakest of the three carbon–halogen bonds (bond enthalpy decreases down group 17), so it breaks fastest, giving the quickest precipitate (AgI) despite C—Cl being the most polar bond. **(A)**.

Bài tập luyện tập

50.0 cm^3 of 0.100 M HCl is mixed with 50.0 cm^3 of 0.0500 M HCl. The pH of the resulting mixture is closest to:

(A) 1.12
(B) 1.00
(C) 1.30
(D) 0.88

Lời giải chi tiết

Total $n(\text{HCl}) = (0.100 \times 0.0500) + (0.0500 \times 0.0500) = 0.00500 + 0.00250 = 0.00750$ mol. Total volume $= 0.100$ dm^3, so $[\text{H}^+] = \dfrac{0.00750}{0.100} = 0.0750$ M. pH $= -\log(0.0750) = 1.12$. **(A)**.

Bài luyện nâng cao (HL)

$CH_3CH_2CHBrCH_3$ (a secondary halogenoalkane) is heated with concentrated KOH in ethanol. The major organic product is best described as forming by:

(A) Elimination ($E2$), giving predominantly but-2-ene
(B) Substitution (S_N2), giving predominantly butan-2-ol
(C) No reaction, since secondary substrates are unreactive
(D) Radical substitution, giving a mixture of dibromides

Lời giải chi tiết

Hot, concentrated, ethanolic (non-aqueous) hydroxide strongly favours OH^- acting as a base rather than a nucleophile, favouring **elimination**; a secondary substrate under these forcing conditions predominantly undergoes $E2$, removing a β-hydrogen to give the alkene but-2-ene. **(A)**.

Bài luyện nâng cao (HL)

Reduction of CH_3CHO (ethanal) by $NaBH_4$ produces:

(A) CH_3CH_2OH
(B) CH_3COOH
(C) $CH_2{=}CHOH$
(D) $CH_3CH_2CH_2OH$

Lời giải chi tiết

H^- (from $NaBH_4$) adds to the electrophilic carbonyl carbon in the same way CN^- does, and protonation of the resulting alkoxide gives the primary alcohol CH_3CH_2OH (ethanol). **(A)**.

Bài luyện nâng cao (HL)

In the Friedel–Crafts alkylation of benzene with CH_3Cl, the role of the catalyst $AlCl_3$ is to:

(A) Polarise CH_3Cl to generate an electrophilic species that attacks the ring

(B) Act as a nucleophile that attacks the ring directly

(C) Reduce the benzene ring before substitution

(D) Remove H^+ from the arenium intermediate

Lời giải chi tiết

$AlCl_3$ is a Lewis acid that polarises the C—Cl bond of CH_3Cl, generating an electrophilic carbocation-like species that then attacks the delocalised ring — exactly analogous to H_2SO_4 generating NO_2^+ in nitration. **(A)**.

Ôn tập nhanh:

- pH $= -\log_{10}[H^+]$, pOH $= -\log_{10}[OH^-]$, pH + pOH $= 14.00$ ở 298K.
- Acid/bazơ mạnh: phân li hoàn toàn, dùng trực tiếp nồng độ (nhớ hệ số, VD $Ba(OH)_2$ cho $2\times[OH^-]$). Acid/bazơ yếu: $[H^+]\approx\sqrt{K_aC}$.
- Đệm (HL): pH $= pK_a + \log\dfrac{[\text{bazơ liên hợp}]}{[\text{acid}]}$ — phụ thuộc tỉ lệ, không phụ thuộc nồng độ tuyệt đối; tại nửa điểm tương đương, pH $= pK_a$.
- Chuẩn độ acid mạnh–bazơ mạnh: điểm tương đương pH $= 7$. Acid yếu–bazơ mạnh: điểm tương đương pH > 7 (muối thuỷ phân cho môi trường bazơ). Chọn chất chỉ thị có khoảng đổi màu (pK_a) nằm trong đoạn dốc đứng của đường chuẩn độ.
- $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$ — KHÔNG nhân theo hệ số cân bằng phương trình. Pin điện hoá: electron chạy từ anode (−, oxi hoá) sang cathode (+, khử). Nernst (HL): $E = E^\circ - \dfrac{0.0592}{n}\log Q$ ở 298K.
- Điện phân: phản ứng không tự xảy ra, cần nguồn điện ngoài; cathode (−) luôn xảy ra khử, anode (+) luôn xảy ra oxi hoá (ngược cực so với pin điện hoá). Định luật Faraday (HL): $Q = It$, $n(e^-) = Q/F$ với $F = 96\,500$ C mol^{-1}.
- Cơ chế hữu cơ: gốc tự do (khơi mào–phát triển–tắt mạch) cho ankan + halogen/UV; cộng electrophin (theo Markovnikov, qua carbocation bền nhất) cho anken + HX/X_2; thế thân hạch S_N2 (một bước, đảo cấu hình, bậc 1) và S_N1 (hai bước qua carbocation, raxemic hoá, bậc 3) (HL); phản ứng tách $E1/E2$ cạnh tranh với thế (HL); cộng nucleophin vào carbonyl (VD CN^-, HL); thế electrophin vào vòng benzene (VD NO_2^+, HL).

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